Uncatalysed wet oxidation of D-glucose with hydrogen peroxide and its combination with hydrothermal electrolysis

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ABSTRACT

An increasing interest in biomass as a renewable feedstock for the chemical industry has risen over the last decades, and glucose, the monomer unit of cellulose, has been widely studied as a source material to produce value-added products such as carboxylic acids, mainly gluconic and formic. In this work, the non-catalysed wet oxidation of glucose using hydrogen peroxide has been analysed, obtaining molar yields to gluconic and formic acids up to 15% and 64%, respectively. Glucose conversion was generally between 40 and 50%, reaching over 80% under the highest temperature (200 °C). An appropriate choice of temperature can tune product distribution as well as reaction rates. The interaction of the wet oxidation with an electrolytic reaction was also analysed.

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1. Introduction

Interest in renewable feedstocks for the chemical industry has increased considerably over the last decades due to the environmental and availability problems of fossil raw materials.[1] One of the most commonly used carbohydrates is dextrose or D-glucose, obtained industrially from starch.[2] Selective oxidation of glucose yields gluconic acid, which is used as chelating agent, as additive in food and beverages and as an intermediate for pharmaceuticals.[3] It is usually produced industrially via enzymatic oxidation, but an increasing interest over heterogeneous catalysis has recently risen,[4] and the challenge is to avoid deactivation of the catalyst by oxygen poisoning. Catalysts used in this reaction are usually based on Pd or Pt supported on carbon, silica, alumina or titania.[5–7] In order to overcome the deactivation of the catalysts, they can be doped with small amounts of Bi, which improves the catalytic activity, although it can be partially leached into the reaction mixture.[8] Recently, gold has been discovered to catalyse the selective oxidation of glucose, showing a better performance with respect to Pd and Pt-based catalysts, as it does not appear to suffer oxygen poisoning.[9] The complete conversion of glucose to gluconic acid was recently reported over an Au/C catalyst,[10] and a comparative study between gold colloids and a supported Au/TiO2 catalyst has shown that, even though the activity of the supported catalyst is considerably higher, both catalysts show a very high selectivity to gluconic acid (over 99.8%).[11] The oxidant in this reaction is generally dioxygen. However, hydrogen peroxide has also been successfully employed as oxidant in the selective oxidation of D-glucose to gluconic acid over zeolite supported Ti catalysts.[6] It has the advantage that higher concentrations can be easily applied and external mass transfer limitations are excluded due to the complete water solubility.

Although most of the research on glucose oxidation is based on catalytic processes, some authors have focused on a non-catalysed approach, which avoids the issues related to the use of heterogeneous catalysts such as deactivation, catalyst recovery and possible mass transfer limitations, as well as offering a more cost-efficient alternative. Yun et al. focused on obtaining formic acid from glucose using short reaction times in hydrothermal conditions (250 °C) and a large excess of H_2O_2 as oxidant,[12] reporting up to 24% yield to formic acid. Our group first reported the retro-aldol condensation of glucose to glycolaldehyde in supercritical water[13] using a continuous flow-type micro-reactor under high temperature (350–450 °C) and pressure (250–400 bar) conditions. The main products obtained under supercritical conditions were erythrose and glycolaldehyde, although smaller amounts of fructose, glyceraldehyde, hydroxyacetone, 1,6-anhydro-β-D-glucose (1,6-AHG) and hydroxymethyl-2-furfural (5-HMF) were also found.

Later, the thermal stability of glucose under subcritical water conditions was studied using a continuous flow reactor.[14] The main products obtained were D-fructose, glyceraldehydes, 5-HMF and 2-furfural, as well as glycolic, lactic, acetic and formic acids.

According to these results, D-fructose comes from the isomerization of D-glucose, while 5-HMF is a dehydration product of D-fructose, and 2-furfural is formed from the dehydration of D-glucose. Aldehydes such as glyceraldehyde and glycolaldehyde can be obtained by retro-aldol condensation of D-glucose, as aforementioned. Further reaction of the aldehydes produces organic acids, such as formic and acetic acids.

These studies of hydrothermal degradation were later complemented with experiments of hydrothermal electrolysis of glucose to produce carboxylic acids.[15] It was found that the combination of electric current and the high ion product at hydrothermal conditions enhanced the oxidation reaction, being the possible reactions of glucose in the absence of catalysts: tautomerism to produce fructose, dehydration to 5-HMF and retro-aldol condensation to produce erythrose or glycolaldehyde (see Fig. 1). The addition of electric current to the hydrothermal atmosphere allowed that glucose or some intermediates (e.g., aldehydes) could be converted to mono- or dicarboxylic acids via partial oxidation to obtain gluconic acid with high selectivity.

Our group is focused on the development of direct and rapid production methods of value-added carboxylic acids from cellulosic biomass in aqueous systems, aiming at high product selectivity and minimum amount of additives loaded. In this work, the non-catalysed wet oxidation of D-glucose by hydrogen peroxide was studied under relatively mild conditions (120–200 °C), and the interaction of the peroxide with an electrolysis reaction was also analysed. The novelty of these results using H_2O_2 without the addition of a catalyst offers an excellent starting point for future research on this topic.

2. Experimental

2.1. Materials and methods

D-Glucose (98%) and hydrogen peroxide (30 wt %) were purchased from Wako Pure Chemicals Industries Ltd (Osaka, Japan) and used as starting materials. Phosphoric acid and KOH were also provided by Wako and used to control pH of the reaction medium.

Identification and quantitative analysis of the products were conducted using HPLC with refraction index (RI) (RI-2031 plus; Jasco Corp.) and ultraviolet–visible (970-UV; Jasco Corp.) detectors. The column used was a Sugar-SH1011 (Shodex) operating at 60 °C. Perchloric acid (3 mmol/L, 0.5 mL/min) was used as the mobile phase, and bromothymol blue (BTB) solution was used as colouring reagent, mixed with the sample immediately after the column (1.0 mL/min) to detect organic acids. The yield of each product is calculated on a carbon basis according to Eq. 1, where C_0 is the initial concentration of the D-glucose aqueous solution (mol/L), C_i is the concentration of product i in the aqueous product solution (mol/L) and n is the number of carbon atoms in a molecule of product i

$$Y_i(C\%) = \frac{C_i}{C_0} \times \frac{n}{6} \times 100. \tag{1}$$

2.2. Experimental apparatus and procedure

The oxidation of D-glucose was carried out in two different set-ups. First, wet oxidation (WO) experiments were carried out in
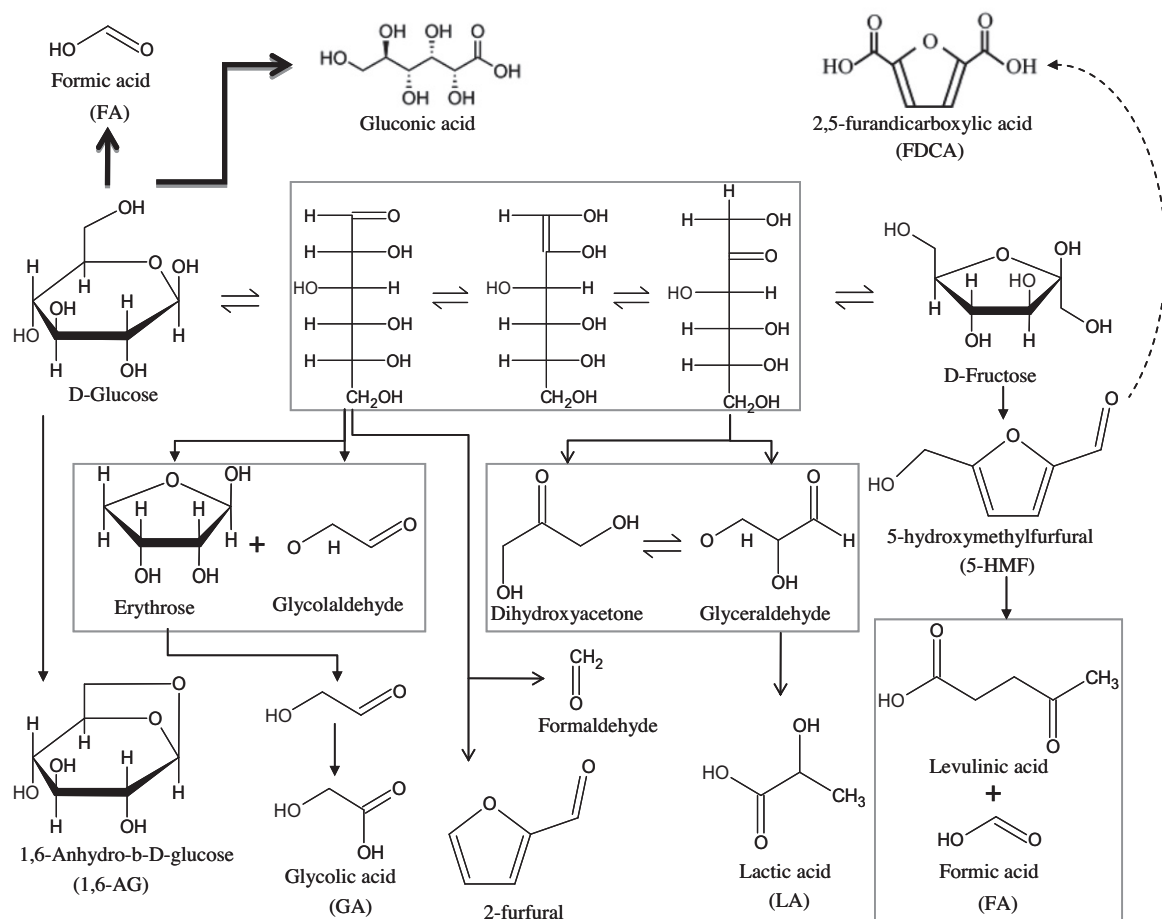

Figure 1. Proposed reaction pathway for hydrothermal electrolysis of glucose in subcritical water.[15]

8.8 mL batch tube reactors. The glucose solution (0.1 mol/L) was mixed with the appropriate amount of H_2O_2 (H_2O_2/glucose molar ratio 1:2) to a total volume of 7 mL (80% of total capacity) and the reactors were placed into an electric furnace (Akico Co. Ltd, SHS-R4-500, Japan) and quickly heated to the desired reaction temperature (120–200 °C). In most cases, there was no further acidification/alkalinization, which provided a pH of 5.4. This value, however, was modified to 2.0 or 9.0 in a few experiments, which were carried out with the addition of phosphoric acid or KOH in order to evaluate the influence of pH on the reaction. During the reaction, the reactors were shaken using a mechanical device. After a certain reaction time (15–60 min), the reactors were taken out of the furnace and quickly cooled down to stop the reaction.

The second batch of experiments combined wet oxidation and hydrothermal electrolysis (WO + HE), and were carried out in a 500 mL batch autoclave made of stainless steel. A cylindrical iridium plate electrode (23 mm diametre, 30 mm length), coaxial to the titanium beaker (74 mm internal diametre, 100 mm length), was used as an anode, and the titanium beaker was used as a cathode to promote cathodic protection of the autoclave from corrosion. Glucose aqueous solution (0.1 mol/L) was used as starting material. Phosphoric acid was used as electrolyte, and the pH of the solution was adjusted to 2.0. At the beginning of the experiment, the aqueous solution (300 mL) was loaded in a titanium beaker and placed in the autoclave. After its lid was closed tightly, the autoclave was purged twice and then pressurized with argon gas to an initial pressure of around 20 bar. At this point, the system was heated up to the desired temperature (120–160 °C) with stirring at 180 rpm. Temperature was measured with a thermocouple connected to the reactor. Reaction pressure varied between 25 and 30 bar during the reaction. A constant electric current (1–3 A) was applied to the autoclave when the whole system had reached the desired temperature, and that was considered the starting point of the reaction. Liquid samples were taken every 30 min. After 180 min the electric current was cut off and the autoclave was cooled with stirring until the temperature dropped below 40 °C. The volume of gas generated was measured using a cumulative flow metre and the liquid product was collected.

3. Results and discussion

3.1. Wet oxidation of D-glucose

Typical HPLC chromatograms obtained after the oxidation reaction of glucose are shown in Figure 2. The main products obtained were gluconic and formic acids, dihydroxyacetone and glyceraldehyde. Glycolic, acetic and glucaric acids were also obtained in smaller amounts. In the degradation experiments (i.e., without any H_2O_2), the only products obtained were glyceraldehyde, 1,6-AHG, 5-HMF and fructose. However, 1,6-AHG and 5-HMF were also found in the experiments at the highest temperature (200 °C), along with 2-furfural. Fructose was also obtained at the longest reaction times (60 min).

Table 1 summarizes the results obtained, expressed as glucose conversion and carbon-based yield for each product. The effect of reaction temperature on the oxidation reaction at a constant H_2O_2/glucose ratio of 1.5 (corresponding to 5100 ppm H_2O_2) can be observed: conversion clearly increases with temperature, reaching over 80% at 200 °C, twice as much as at 120 °C. However, at 200 °C the yield to gluconic acid is considerably lower, and dehydration products such as 5-HMF and 2-furfural appear. An acceptable balance is found at 160 °C, with 50–60% conversion and around 10% yield to gluconic acid, so for the next round of experiments the temperature was set to 160 °C and the effect of the amount of peroxide was studied. In this case, conversion increases with higher amounts of peroxide, but the effect is not as steep as with temperature, which suggests that the reaction is kinetically controlled. However, selectivity to gluconic acid increases considerably for a ratio of 2 (corresponding to 6800 ppm H_2O_2), particularly at shorter reaction times (15 min), reaching 30%. Yield of gluconic and formic acids also increase notably under these conditions, reaching 15% and 10%, respectively (note that this 10% yield to formic acid is expressed on a carbon basis and corresponds to a 60% molar yield). The higher amount of oxidant also provides a significant enhancement in the yield to glucaric acid, coming from the oxidation of gluconic acid.

In the catalytic oxidation of glucose, a slightly alkaline medium (ca. 9) is preferred in order to increase the reaction rate and to avoid deactivation of the catalyst.[16] Even though our reaction system was not catalytic, some experiments were carried out under alkaline conditions (pH 9). As observed in Table 1, significantly lower glucose conversion and yields to the products of interest were obtained when operating at high pH and the formation of dehydration products such as 1,6-AHG and 5-HMF was especially enhanced at the higher temperatures. This suggests that the alkaline medium is not particularly favourable in the absence of a suitable catalyst. However, these were only preliminary experiments that require further validation.

Alternatively, the experiments carried out with an acidified starting solution showed very similar conversions to those with the unmodified reaction medium, but generally lower yields, particularly to the product of interest, that is gluconic acid. Nonetheless, the possibility of using an acidic medium would be extremely interesting in order to develop a direct process from starch, as well as to avoid the production of gluconate instead of the free acid.

3.2. Wet oxidation + hydrothermal electrolysis of D-glucose

Since the hydrothermal electrolysis of glucose had already been studied,[15] we focused on the combination of electrolysis with a small amount of H_2O_2, and therefore the main parameters analysed were the intensity of the electric current and the amount of peroxide added to the reaction medium. Although conversion was generally lower than that in the previous wet oxidation experiments, only carboxylic acids (i.e., oxidation products) were obtained: mainly gluconic and formic acids, but also acetic, glycolic and glucaric, suggesting that the oxidation reaction is predominant. In all cases, we observed that both conversion and yield increased linearly with reaction time, unlike in some of our previous experiments. In accordance with previous results obtained by this research group, a reaction pathway was proposed (see Fig. 3).

Figure 4 shows the effect of the intensity of the current on the yield to gluconic acid, formic acid and by-products (glucaric,
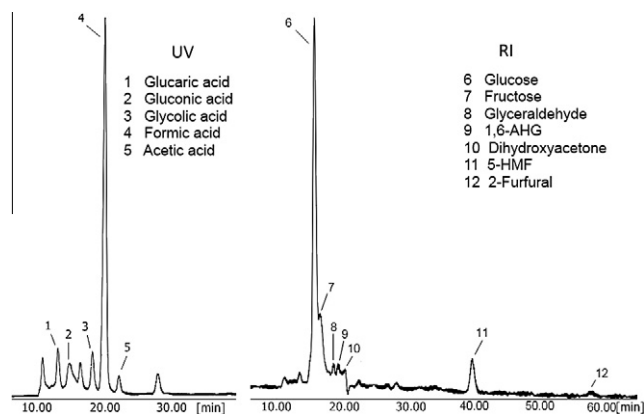

Figure 2. RI and UV chromatograms and identified peaks.

UV
1 Glucaric acid
2 Gluconic acid
3 Glycolic acid
4 Formic acid
5 Acetic acid

RI
6 Glucose
7 Fructose
8 Glyceraldehyde
9 1,6-AHG
10 Dihydroxyacetone
11 5-HMF
12 2-Furfural

Table 1
Conversion (%) and yield (C%) obtained in wet oxidation experiments

|		Ratio	Min	Conversion	Gluconic	Glucaric	Formic	Glyc.	Acetic	Dihydr.	1,6-AHG	Glycerald.	5-HMF	Fruct.	2-Furf.
Without additives	120 °C	1	15	15.52	0	0	0.18	0	0	0.55	0	0	0	0	0
(pH 5.4)			30	18.43	1.21	0	0.97	0.05	0	1.52	0	0	0	0	0
			60	44.14	9.33	0	4.34	0.15	0.16	1.05	0	0.13	0	0	0
		1.5	15	29.32	4.85	0.57	3.10	0.24	0	2.22	0	0.42	0	0	0
			30	42.96	14.01	1.14	6.72	0.97	0.09	2.96	0	0.90	0	2.13	0
			60	44.50	12.93	1.38	6.56	1.06	0	2.40	0	0.83	0	1.51	0
	160 °C	1	15	51.15	6.56	0.42	4.51	0.47	0.31	2.35	0	0.49	0	1.44	0
			30	45.02	7.69	0.68	4.92	0.46	0.35	1.59	0	0.65	0	2.71	0
			60	52.56	6.78	0.66	5.22	0.68	0.56	2.29	0	0.28	0	1.79	0
		1.5	15	49.52	10.07	1.53	6.62	1.17	0.32	2.69	0	0.90	0	0	0
			30	54.91	9.03	2.08	7.52	1.33	0.51	2.78	0	0.79	0	0	0
			60	60.07	6.37	2.22	8.60	1.49	0.96	1.64	0.26	0.65	0.45	3.18	0
		2	15	51.34	15.03	3.05	9.18	1.93	0.27	3.38	0	1.33	0	0	0
			30	59.95	9.93	3.46	10.29	1.97	0.80	1.94	0	0.88	0	0	0
			60	69.06	7.50	2.30	10.65	1.51	1.06	2.50	0.08	0.76	0	4.16	0
	200 °C	0	15	25.87	0	0	0	0	0	0	0.70	0.69	0.87	0	0
			30	31.23	0	0	0	0	0	0	0.87	0.67	1.48	0	0
			60	56.40	0	0	0.17	0.11	0.03	0	2.82	0.94	15.33	5.01	0
		1	15	43.13	11.69	0.37	4.40	1.41	0.08	0	2.52	0.47	0	0	0
			30	53.70	5.71	0.68	4.89	1.20	0.44	0	2.59	0.21	1.46	0	0
			60	88.36	2.91	0.51	5.68	1.19	0.90	0	0.39	0.18	11.55	5.66	1.31
		1.5	15	53.91	10.26	1.43	7.49	1.09	0.60	1.80	0	0.91	0	0	0
			30	72.86	5.27	1.43	7.98	1.87	0.69	1.31	0.65	0.43	4.57	0	0.85
			60	84.91	4.53	1.36	8.09	1.85	0.98	1.43	0.16	0.36	8.27	4.17	0.93
Acidic (pH 2.0)	120 °C	1.5	15	27.13	1.53	0	1.19	0.27	0	1.08	0	0	0	0	0
			30	38.37	5.50	0	3.81	0.33	0.20	0.42	1.06	0.45	0	0	0
			60	51.63	10.37	0	7.69	1.18	0.39	2.35	0	1.02	0	2.74	0
	160 °C	1.5	15	25.37	1.03	0	0.51	0.10	0	2.46	0	0	0	0	0
			30	64.38	6.74	0	8.51	1.05	1.71	1.17	0.29	0.38	0	0	0
			60	66.39	5.60	0	8.27	1.17	1.49	1.40	0.27	0.28	0.66	3.19	0
	200 °C	1.5	15	39.34	5.15	0	3.97	0.31	0.37	0.30	0.89	0.29	0	0	0
			30	79.64	2.60	0	7.66	0.97	2.00	1.20	0.54	0.34	2.49	0	0
			60	86.61	3.37	0	9.20	1.25	1.76	1.44	0.23	0.35	4.65	2.95	0.81
Alkaline (pH 9.0)	120 °C	1.5	15	11.39	0.48	0.60	0.11	0	0	0	0	0	0	0	0
			30	12.18	0.61	0.60	0.10	0	0	0	0	0	0	0	0
			60	15.78	0.41	0.75	0.11	0	0	0	0	0	0	0	0
	160 °C	1.5	15	11.49	0.12	0.05	0	0	0	0	0	0	0.44	0	0
			30	11.49	0.40	0.06	0	0	0	0	0	0	0.68	0	0
			60	17.58	0.43	0.08	0	0	0	0	0	0	1.41	0	0
	200 °C	1.5	15	39.68	4.29	0	0.38	0.23	0.06	0	6.42	0	9.66	0	0
			30	43.34	4.36	0.18	0.41	0.38	0.09	0	5.89	0	11.90	0	0
			60	51.50	3.86	0.22	0.56	0.42	0.18	0	4.76	0	22.00	0	0
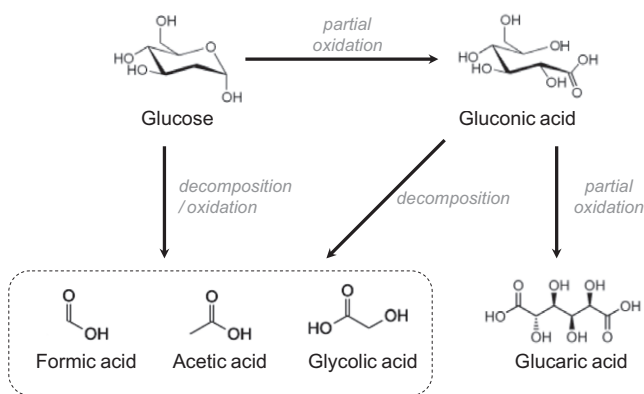
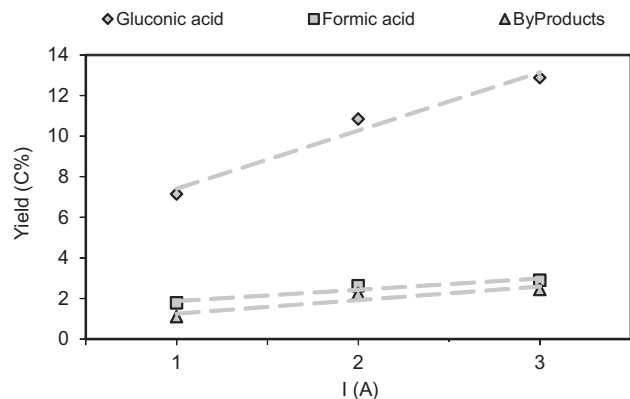**Figure 3.** Proposed reaction pathway in the WO + HE reaction of D-glucose.

Figure 4. Effect of intensity of current on the WO + HE reaction of glucose (120 °C, H_2O_2/glucose ratio = 1, reaction time 180 min).

glycolic and acetic acids). As the direct current increases, glucose conversion becomes higher, and the steepest boost in production is observed for gluconic acid, with almost 100% enhancement when raising the current from 1 to 3 A. The intensity of applied current also has a strong effect on gas formation. It has previously been reported that the main gas products obtained after hydro-thermal electrolysis of glucose are hydrogen and CO_2, and that

the amount obtained increased significantly with the intensity of applied current.[17] In our case, even though the composition of the gas phase was not analysed and we could not confirm the existence of CO_2 or H_2, there was a clear increase in total gas formation as the intensity increased (see Fig. 5), which is consistent with previous observations.[17]
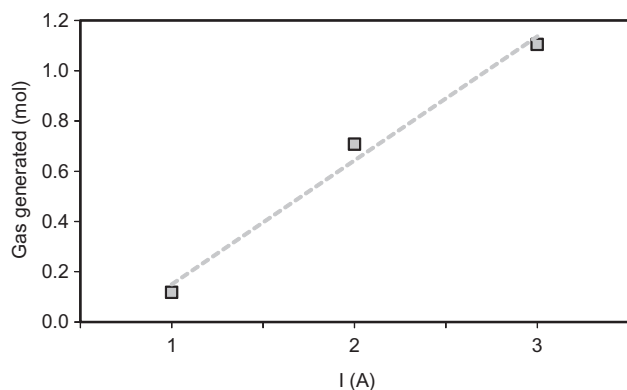
Figure 5. Effect of intensity of current on gas formation in the WO + HE reaction of glucose (120 °C, H_2O_2/glucose ratio = 1, reaction time 180 min).

Figure 7. Influence of temperature in the WO + HE reaction of glucose (1 A, H_2O_2/glucose ratio = 1, reaction time 180 min).

An opposite effect is observed when the H_2O_2/glucose ratio is increased: the production of gluconic acid is linearly diminished (see Fig. 6), indicating that the maximum yield is obtained in the absence of peroxide. We believe the excess of oxidant provided by the presence of peroxide produced further degradation of the gluconic acid formed (in fact, a slight increase in formic acid formation was observed, see Fig. 6), as well as increased oxygen production.

Finally, an additional experiment carried out at a higher temperature (160 °C) showed that the conversion increased from 38.8% to 50.5%. As shown in Figure 7, yields to formic acid as well as by-products were also increased, although there was a considerable reduction in the yield to gluconic acid, agreeing with our previous wet oxidation results (see Table 1) and suggesting that the higher temperature favours the decomposition reaction of gluconic acid to carboxylic acids through cleavage of C–C bond linkages. It seems that lower temperatures offer higher selectivities to gluconic acid by suppressing the side reactions: this parameter dropped from 27.9% to 10.2% when the temperature increased from 120 to 160 °C.

Interestingly, this run was the only one that produced coloured samples, with a dark colour increasing with reaction time (see Fig. 8), similar to those obtained in the wet oxidation reaction. This suggests the formation of some dehydration aromatic compound such as 5-HMF or 2-furfural at this temperature, and in fact a small peak at 40 min (corresponding to 5-HMF, a typical constituent of caramel colouring in the food industry) was detected in the RI chromatogram, although it was too small for quantification.
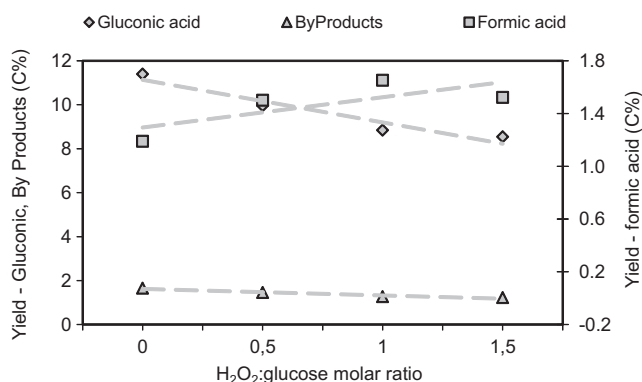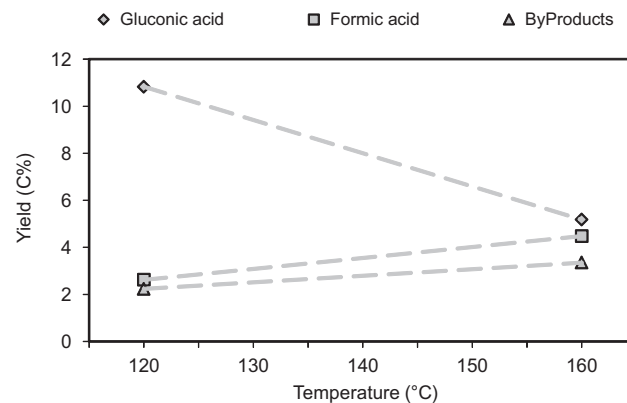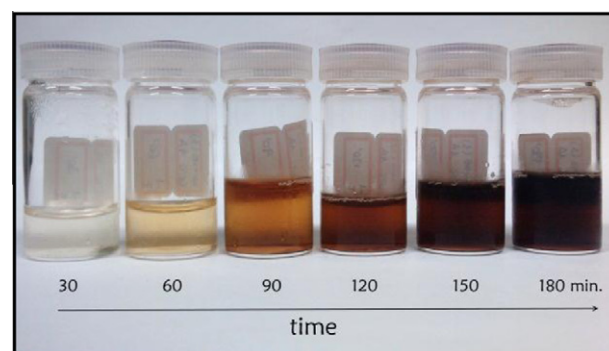

Figure 8. Samples obtained at different times in the WO + HE reaction of glucose (160 °C, 1 A, H_2O_2/glucose ratio = 1).

4. Conclusions

A novel non-catalysed wet oxidation of glucose to obtain value-added products such as gluconic and formic acids has been successfully carried out using hydrogen peroxide. When the reaction is performed in batch reactors, several by-products are formed in tautomerism, dehydration and retro-aldol condensation reactions. However, when the oxidation reaction is carried out in combination with electrolysis, the only products obtained are carboxylic acids (gluconic, formic, glucaric, glycolic and acetic acids). In both cases, lower temperatures (120 °C) favoured the production of formic acid but decreased the yield to gluconic acid, suggesting that a higher temperature favours the decomposition reaction of gluconic acid to carboxylic acids through cleavage of C–C bond linkages. In the wet oxidation experiments, we observed that higher H_2O_2/glucose ratios led to higher glucose conversions (up to 69% at 160 °C) and the highest yields to gluconic (15%) and formic acids (10% on a carbon basis, corresponding to a 60% molar yield) were obtained under these conditions at short reaction time (15 min). When the wet oxidation reaction was combined with hydrothermal electrolysis, we observed that the intensity of the current, rather than peroxide concentration, has a strong effect on glucose conversion and gas formation. The total amount of gaseous products (presumably H_2 and CO_2) generated at 3 A was 9 times higher than that generated at 1 A for the same reaction time, and the yield to gluconic acid showed almost 100% enhancement when rising the current from 1 to 3 A.

Figure 6. Effect of H_2O_2/glucose ratio in the WO + HE reaction of glucose (120 °C, 2 A, reaction time 120 min).

References

1. Lichtenthaler, F. W.; Peters, S. *C. R. Chim.* **2004**, *7*, 65–90.
2. Schenck, F. W. Glucose and Glucose-containing Syrups. In *Ullmann's Encyclopedia of Industrial Chemistry*, 7th ed.; Wiley, 2007.
3. Hustede, H.; Haberstroh, H.-J.; Schinzig, E. Gluconic Acid. In *Ullmann's Encyclopedia of Industrial Chemistry*, 7th ed.; Wiley, 2007.
4. Mäki-Arvela, P.; Holmbom, B.; Salmi, T.; Murzin, D. Y. *Cat. Rev. - Sci. Eng.* **2007**, *49*, 197–340.
5. Nikov, I.; Paev, K. *Catal. Today* **1995**, *24*, 41–47.
6. Velarde, A. M.; Bartl, P.; Nießen, T. E. W.; Hoelderich, W. F. *J. Mol. Catal. A: Chem.* **2000**, *157*, 225–236.
7. Liang, X.; Liu, C.-J.; Kuai, P. *Green Chem.* **2008**, *10*, 1318–1322.
8. Karski, S. *J. Mol. Catal. A: Chem.* **2006**, *253*, 147–154.
9. Comotti, M.; Pina, C. D.; Matarrese, R.; Rossi, M.; Siani, A. *Appl. Catal., A* **2005**, *291*, 204–209.
10. Biella, S.; Prati, L.; Rossi, M. *J. Catal.* **2002**, *206*, 242–247.
11. Mirescu, A.; Prüße, U. *Catal. Commun.* **2006**, *7*, 11–17.
12. Yun, J.; Jin, F.; Kishita, A.; Tohji, K.; Enomoto, H. *J. Phys.: Conf. Ser.* **2010**, *215*, 012126.
13. Sasaki, M.; Goto, K.; Tajima, K.; Adschiri, T.; Arai, K. *Green Chem.* **2002**, *4*, 285–287.
14. Saito, T.; Sasaki, M.; Kawanabe, H.; Yoshino, Y.; Goto, M. *Chem. Eng. Technol.* **2009**, *32*, 527–533.
15. Sasaki, M.; Oshikawa, T.; Watanabe, H.; Wahyodiono; Goto, M. *Res. Chem. Intermed.* **2011**, *37*, 457–466.
16. Abbadi, A.; van Bekkum, H. *J. Mol. Catal. A: Chem.* **1995**, *97*, 111–118.
17. Sasaki, M.; Yamamoto, K.; Goto, M. *J. Mater. Cycles Waste Manage.* **2007**, *9*, 40–46.