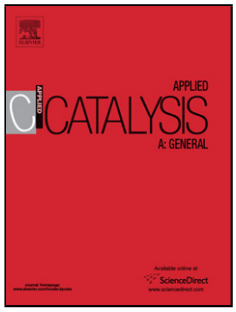

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One-pot catalytic conversion of carbohydrate biomass to lactic acid using an $ErCl_3$ catalyst

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Highlights

- Lactic acid was obtained by the conversion of various carbohydrate biomasses.
- Erbium chloride is a highly efficient catalyst.
- 91.1% lactic acid yield was obtained using cellulose feedstock.
- This catalyst could be used repeatedly.

Abstract

Cellulose was hydrothermally converted into lactic acid in the presence of an $ErCl_3$ catalyst. Lactic acid yields as high as 91.1% were obtained when reacting 0.1 g cellulose, 0.05 g catalyst and 30 mL water at 240 °C under 2 MPa N_2 for 30 min. Other carbohydrate biomass materials could also be converted into lactic acid effectively under the same reaction conditions. Materials tested included monosaccharides, disaccharides, polysaccharides, and raw biomass such as corn stalks, wheat stems and rice straw. The $ErCl_3$ catalyst could be reused at least five times without any obvious loss of activity.

Keywords: Cellulose; Lignocellulose; Carbohydrate; Lactic acid; $ErCl_3$ catalyst

1. Introduction

Lactic acid is used as a monomer for the production of biodegradable polymers and various biodegradable, nontoxic solvents and also has applications in the food, cosmetics and pharmaceutical industries [1]. Lactic acid is considered a top-twelve bio-based platform molecule and may serve as a precursor for the synthesis of a wide range of useful intermediates, such as acrylic acid, propylene glycol, 2,3-pentanedione, acetaldehyde, pyruvic acid and lactides by catalytic routes [2−4]. Currently, lactic acid itself is produced by conventional biotechnological processes involving the fermentation of carbohydrates, in which glucose and sucrose are the main raw ingredients [1]. However, low space-time yields and the difficulty in recovering lactic acid from the fermentation broth have a major impact on the production costs. Alternative catalytic processes for the production of lactic acid are highly desirable [5]. Many studies have been performed to investigate the conversion of various biomass resources such as trioses [6−11], hexoses [12−20] and even cellulose to lactic acid through catalyzed routes [21−25]. To date, however, the resulting lactic acid yields have been far from satisfactory when using cellulose or raw lignocellulosic materials, substances that represent the most abundant sources of inedible biomass on the planet.

Lignocellulosic materials such as agricultural residues (including wheat stalks, rice straw, corn stalks and peanut shells) and forest products (including poplar and platanus leaves) are renewable biomass resources that have the potential to serve as sustainable feedstocks to replace diminishing petrochemical stores in the future synthesis of biofuels and chemicals [26]. These raw materials have the added advantages of being highly abundant and generate very low net greenhouse gas emissions.

In a previous study, we found that the Lewis acid erbium triflate was able to efficiently catalyze the conversion of pure microcrystalline cellulose to lactic acid in an aqueous dispersion [27]. However, this catalyst is relatively expensive and it would be preferable to use raw

lignocellulose as the feedstock for biomass conversion, because this would represent a significant improvement in the large-scale production of bio-based products. Hence, in the present work, we employed the less expensive chemical compound $ErCl_3$ as a catalyst when transforming a variety of carbohydrate biomass materials, such as saccharides, cellulose and raw lignocellulosic substances, to lactic acid. This catalyst exhibited high catalytic activity, good recyclability and stability.

2. Experimental

2.1. Materials and characterization

D-Fructose (99%), D-glucose (99%) and sucrose (99%) were purchased from the Tianjin Chemical Reagents Co. China Microcrystalline cellulose (particles size of 20 μm) was obtained from Sigma-Aldrich, lactic acid (98%) and inulin were purchased from Alfa Aesar and D-(+)-cellobiose and mannose were obtained from the Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Starch was obtained from the Beijing Aoboxing Bio-tech Co., Ltd., while corn stalks, wheat stalks, rice straw, peanut shells, poplar leaves and platanus leaves were obtained from the ChangAn district of Xi'an. These materials were washed, milled and screened to capture particle sizes less than 200 mesh, then dried at 120 °C for 24 h before use. All other reagents were analytical grade and were used without further purification.

The various components of the raw lignocellulosic biomass (water extracts, cellulose, hemicellulose, lignin and ash) were analyzed according to the Van Soest method [28]. Fourier transform-infrared spectra were collected on a Bruker EQUINX55 FTIR spectrometer using KBr discs. The C, H and N contents of the various substrates were determined using a Vario EL III CHNS analyzer.

2.2 Reaction test and product analysis

All reactions were carried out in a 35 mL stainless steel autoclave equipped with a mechanical stirrer. In a typical experiment, 0.1 g of substrate material, 0.05 g of catalyst and 30 mL of water were added to the reactor, after which the autoclave was purged three times with N_2 and then pressurized to 2.0 MPa with N_2 at room temperature. The reaction mixture was heated to 240 °C unless otherwise stated and held at that temperature for 30 min with stirring at 600 rpm. After each reaction the reactor was quickly cooled to room temperature using an ice/water mixture and then depressurized. The post-reaction sample was diluted with mobile phase solution prior to analysis.

Sample analyses were performed on a Shimadzu LC-20AT HPLC system equipped with a RID-10A detector and a Bio-Rad Aminex HPX-87H ion exclusion column (300 × 7.8 mm), using 0.005 M H_2SO_4 as the mobile phase at a flow rate of 0.5 mL min^{-1}. The column temperature was 50 °C and the detector was set to 45 °C. The amount of product was determined using calibration curves generated with standard solutions.

2.3 The conversion of raw materials and product yield definitions

The conversion of the raw materials and the product yields were defined as follows.

Raw material conversion (wt.%):

$$X = \left(1 - \frac{mass\ of\ unconverted\ raw\ materials}{mass\ of\ initial\ raw\ materials}\right) \times 100\%$$

Product yield (C%):

$$Yi = \frac{moles\ of\ carbon\ in\ product\ i}{moles\ of\ carbon\ in\ initial\ raw\ materials} \times 100\%$$

3. Results and discussion

3.1. The conversion of various biomasses using the $ErCl_3$ catalyst

The hydrothermal conversions of various biomass materials, including monosaccharides (fructose, glucose and mannose), disaccharides (sucrose and cellobiose) and polysaccharides (starch, inulin and cellulose), were performed using the $ErCl_3$ catalyst, with the results shown in Table 1. At 240 °C, the biomass materials (the monosaccharides, disaccharides and polysaccharides) were completely converted over this catalyst. The main product was lactic acid with yields greater than 75%, together with lesser amounts of formic acid, acetic acid, levulinic acid and acetol. An 84.8% yield of lactic acid was obtained when using fructose as the substrate while glucose and mannose (a C-2 epimer of glucose) gave lactic acid yields of 76.2 and 76.7%, respectively. The distinct behaviors of these hexoses might stem from the more stable ring structures of glucose and mannose. The disaccharide sucrose, consisting of one fructose and one glucose unit, gave a moderate yield of lactic acid (82.9%), while the cellobiose, composed of two glucose molecules linked by a β(1→4) bond, produced a 75.5% yield, similar to that obtained with glucose. When using starch as the feed material, a polysaccharide consisting of a large number of glucose units joined by glycosidic bonds, a 73.7% yield of lactic acid was obtained. Inulin, a mixture of oligo and polysaccharrides composed of fructose units joined together by β linkages, gave an 83.2 % yield, which is similar to that obtained when fructose was used as the feed. Overall, these results suggest that the conversions of fructose and inulin may follow the same reaction mechanism, such that inulin may initially hydrolyze to form fructose, followed by the retro-aldol fragmentation of fructose to trioses and the subsequent conversion of these trioses to lactic acid [1]. When the substrate was cellulose, a polysaccharide consisting of a linear chain of several hundred to over ten thousand β(1→4) linked D-glucose units, the highest yield of lactic acid was obtained (91.1%). The above data clearly indicate that the highest yield of lactic acid is obtained using cellulose as the feedstock, as opposed to the use

of the corresponding monosaccharide (glucose) and cellobiose. This suggests that the catalytic conversion of cellulose may proceed *via* a different reaction route to that by which glucose and cellobiose are transformed.

Previously, Wang *et al*. found that $PbCl_2$ exhibited a remarkable promoting effect during cellulose depolymerisation [29]. A lactic acid yield of 68% was obtained following the reaction of 0.1 g ball-milled cellulose (33% crystallinity) in 20 mL water with 0.14 mmol $PbCl_2$ as the catalyst at 190 °C for 4 h under 3 MPa N_2. Wang postulated that the formation of lactic acid was preceded by a multistep cascade of reactions, including the hydrolysis of cellulose to glucose, the isomerization of glucose to fructose, the retro-aldol fragmentation of fructose to trioses and the conversion of these trioses to lactic acid. However, our present results do not fully agree with this mechanism.

At the elevated temperatures applied in our present study (above 473 K), water will generate increasing quantities of hydroxonium ions capable of promoting acid-catalyzed reactions [30,31] and this could be the driving force responsible for the depolymerisation of cellulose into soluble oligosaccharides. We propose that the Lewis acid centers produced in this reaction may function together with the hydroxonium ions present in the aqueous medium at 240 °C to convert the soluble oligosaccharides, as shown in Scheme 1 [25].

It has been demonstrated that lanthanide(III) ions can form aquated ions in water solutions. Ishida *et al.* stated that, for dehydration of hexoses, the formation of a lanthanide–saccharide complex between hydrated lanthanide ions and the hexoses is important for the dehydration step because the lanthanide(III) ions have a high affinity for oxygen-containing functional groups [32,33].

In the present case, it is very likely that the hydrated erbium ions can coordinate with the hydroxyl groups at position 2 on the cellulose rings, due to the higher electron density at these sites [34,35], resulting in easier cleavage of the protonated ether bonds between the two glucosyl

units of the soluble oligosaccharide intermediates (Scheme 1, step A) [25]. The second step could be a dehydroxylation involving C–O bond cleavage following direct coordination with the Lewis center, as presented in Scheme 1 (steps B and B'). Following this cleavage, a variety of low molecular weight carboxylic acids and similar products are produced through further C–C and C–O bonds scissions, including lactic acid, formic acid and acetol. These results suggest that lactic acid is produced by the direct transformation of the soluble oligosaccharides, without proceeding through glucose or cellobiose intermediates.

Lignocellulose is primarily composed of cellulose, hemicellulose and lignin, along with smaller amounts of pectin, protein, extractives (soluble nonstructural materials such as nonstructural sugars, nitrogenous materials, chlorophyll and waxes) and ash [36]. Among these, hemicellulose and cellulose are polymers of C_5 and C_6 sugars that intertwine within the plant cell walls. In contrast, lignin is an amorphous three-dimensional polymer containing three primary units (p-coumaryl, coniferyl and sinapyl alcohols) that embeds in and binds to the former two components. It contains a greater concentration of C–C bonds and provides rigidity to the structure that protects the lignocellulose against transformations [37]. In the conversion of lignocellulosic biomass to fuel and chemicals, the biomass generally needs to be treated so that the cellulose in the plant fibers is exposed. Pretreatment involves the use of various techniques, including ammonia fiber explosion, chemical treatment, biological treatment and steam explosion, to alter the structure of the cellulosic biomass with the goal of making the cellulose more accessible [26,38]. However, these processes are expensive and thus, to some extent, do not permit the cost effective conversion of lignocellulose. In the present work, the raw lignocellulosic biomass materials (corn stalks, rice straw, wheat stalks, peanut shells, poplar leaves and platanus leaves) were hydrothermally converted using the $ErCl_3$ catalyst under identical conditions, without applying any of the pretreatments noted above. The results of these trials are also presented in Table 1. The composition of the raw lignocellulosic biomass was

analyzed according to the Van Soest method and the results are summarized in Table 2. The data in Table 1 show again that the $ErCl_3$ catalyst is highly efficient in the conversion of raw lignocellulosic biomass materials to lactic acid. The highest yield of lactic acid (63.1%) was obtained when using wheat stalks as the feedstock, while corn stalks were converted to lactic acid with a yield of 58.6% and using rice straw and peanut shells as feedstocks gave yields of 54.8 and 45.4%, respectively. For poplar leaves and platanus leaves, the yields of lactic acid were 27.7 and 16.7%, respectively. The yields of lactic acid obtained from the conversion of these raw lignocellulosic biomass feedstocks roughly increased with increasing cellulose and hemicellulose content in the feedstocks, with the exception of the wheat stalks. The reason for this discrepancy is unclear, but it may be attributed to the presence of more soluble polysaccharides in the wheat stalk extracts.

These results demonstrate that the highest yield of lactic acid (91.1%) was obtained when using cellulose as the raw material. Hence, in the following trials, cellulose was chosen as the substrate when investigating the effects of reaction conditions on the performance of the $ErCl_3$ catalyst.

3.2. The optimization of reaction conditions

The temperature dependence of cellulose conversion when using the $ErCl_3$ catalyst was examined, with the results shown in Fig. 1. When the reaction temperature was increased from 200 to 260 °C, the conversion of cellulose was improved from 12.7 to 100%, the yield of lactic acid was enhanced from 15.2 to 91.1% and the yields of formic acid and acetol were also increased. At 240 and 260 °C, the yields of lactic acid were 91.1 and 91.7%, respectively. These results indicate that no overreaction of lactic acid took place at higher temperatures.

The influence of reaction time is summarized in Fig. 2. When the reaction was carried out at 240 °C for 0 min, the conversion of cellulose was 68.8% and the yield of lactic acid was 55.9%.

When prolonging the reaction time to 10 min, the yield of lactic acid was increased to 88.5% and, when further increasing the reaction to 30 min, the yield was slightly enhanced to 91.1%. After this point, the yield of lactic acid was essentially constant at ~90%. These results further confirm that lactic acid is stable at 240 °C in this reaction system and that overreaction of the lactic acid is negligible.

As shown in Fig. 3, with increasing amounts of cellulose the yield of lactic acid gradually decreased. When the amount of cellulose was 0.5 g, the yield of lactic acid decreased to ~26%. Under these conditions, a quantity of dark brown, insoluble matter was found in the autoclave, which could not be identified. In order to determine whether the insoluble matter was generated by the polymerization of the formed products, the reaction time was prolonged to 2 h. The results showed that the yield of lactic acid was 47.2%, while the yields of other products increased slightly. With further prolonging reaction time to 4 h, the yields of the products remained almost constant. The data suggests that some soluble oligosaccharides in the reaction system, derived from the depolymerisation of the cellulose did not convert fully due to a relatively small amount of the catalyst and a shorter reaction time when the feed of cellulose was 0.5 g, and the reaction time 30 min. Hence, the dark brown, insoluble matter was not derived from the polymerization of the formed products; we suppose that the insoluble matter was probably formed by partial carbonation of the cellulose.

The effects of the catalyst loading on the reaction are presented in Fig. 4. When the reaction was conducted in the absence of the catalyst, only 6.4% lactic acid and 9.6% HMF (5-methoxymethylfurfural) yields were obtained, while the conversion of cellulose was 45.9%. The main product in this case could be soluble oligosaccharide intermediates. In the presence of 0.01 g of the $ErCl_3$ catalyst, the cellulose was converted completely and the yield of lactic acid reached 82.3% while, with further increases in the catalyst amount, the yields of lactic acid increased and then decreased slightly. These results indicate that a small amount of the catalyst

produces low yields of lactic acid owing to the low concentration of active species available. At high catalyst concentrations, further reaction of the lactic acid to undesirable products is promoted, decreasing the yield. The highest lactic acid yield of 91.1% was obtained under the conditions of 0.1 g cellulose, 30 mL water, 0.05 g catalyst, 240 ºC, 2 MPa N_2 and 30 min reaction time. The corresponding turnover rate of lactic acid formation was 11.7 $mol \cdot mol_{Er}^{-1} \cdot h^{-1}$ and the associated lactic acid productivity was 6.4 $g \cdot L^{-1} \cdot h^{-1}$, a value that is greater than the results obtained from the conversion of glucose and sucrose by fermentation (0.3−5 $g \cdot L^{-1} \cdot h^{-1}$), heterogeneous catalysis (3.3 $g \cdot L^{-1} \cdot h^{-1}$) and homogeneous catalysis using a $PbCl_2$ catalyst [1,29].

3.2. Recycling of the catalyst

The stability and reusability of catalysts are extremely important aspects of any industrial process, since these features reduce production costs, especially in the case of metal chloride catalysts. It is known that conventional Lewis acids such as $AlCl_3$, $SnCl_4$, $CrCl_3$, $TiCl_4$ and $PbCl_2$ are decomposed or deactivated in the presence of water [39] and hence these materials cannot be recovered and reused after the reactions are complete. As an example, Peng *et al.* [40] found that chromium chloride was uniquely effective for the catalytic conversion of cellulose to levulinic acid in water, generating a yield of levulinic acid as high as 67% at 200 °C. The catalyst, however, decomposed to chromium oxide during the reaction.

The reusability of $ErCl_3$ in the conversion of cellulose to lactic acid was therefore investigated. After each trial, the water in the solution was removed by evaporation under vacuum, following which the catalyst was recovered by extracting the liquid products with diethyl ether. The recycled catalyst was then used for the next run under identical reaction conditions. Similar yields of lactic acid (~90%) were obtained during as many as five repeated reaction cycles (see Fig. 5), indicating that the $ErCl_3$ catalyst was not deactivated in the course of the catalytic runs. Moreover, the fresh catalyst had a very similar UV absorption spectrum to

that obtained from the material following its use in the water phase (Fig. S1), providing further confirmation that the active components of the catalyst were stable.

4. Conclusions

We have demonstrated that $ErCl_3$ can effectively catalyze the conversion of monosaccharides, disaccharides, polysaccharides and even raw lignocellulosic materials into lactic acid. The lignocellulosic biomass did not require pretreatment and the reaction medium was water, and so this system represents a simple, environmentally-friendly means of producing lactic acid. The almost complete transformation of lignocellulose obtained using this straightforward method is of great significance with regard to the cost-efficient production of lactic acid from biomass in large-scale applications.

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Table 1 The hydrothermal conversion of various substrates catalyzed by $ErCl_3$[a]

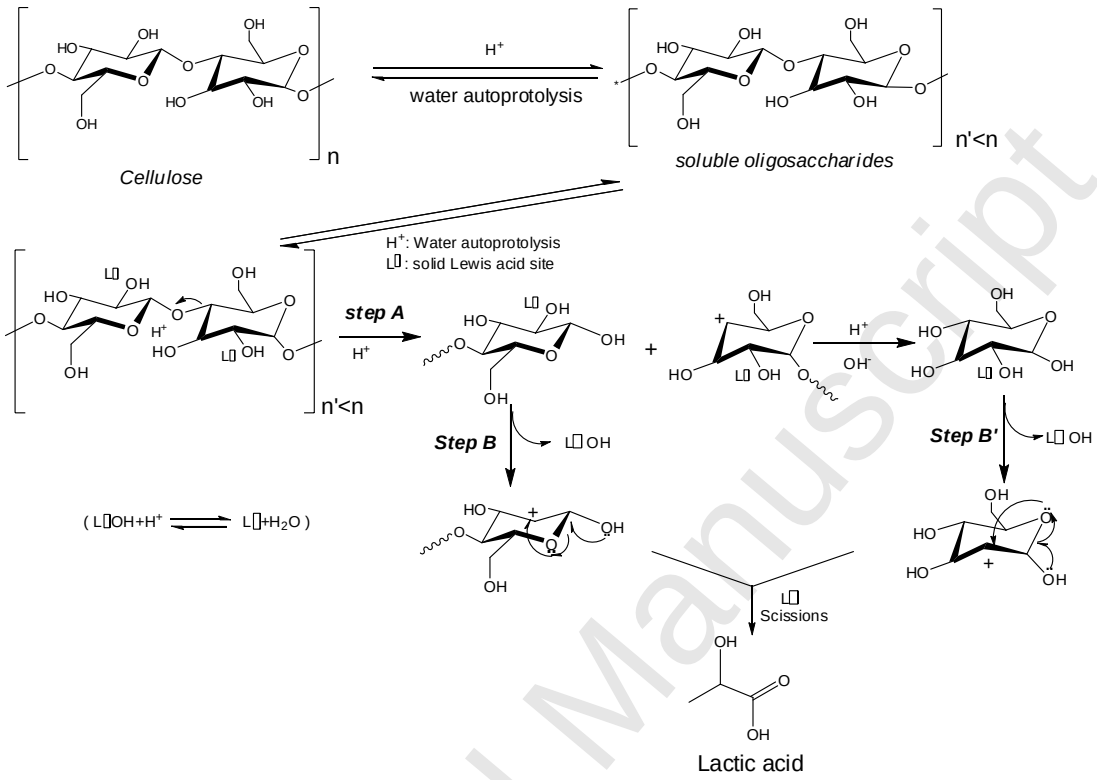
Substrates	Conversion (%)	Yield (%)				
		lactic acid	formic acid	acetic acid	levulinic acid	acetol
Fructose	100	84.8	1.2	1.0	1.3	2.6
Glucose	100	76.2	1.1	0.9	0.0	3.3
Mannose	100	76.7	2.1	1.7	1.0	4.9
Sucrose	100	82.9	1.1	0.9	0.0	3.2
Cellobiose	100	75.5	0.3	2.0	4.1	2.8
Starch	100	73.7	0.3	3.5	3.4	3.0
Inulin	100	83.2	0.4	1.5	3.8	1.5
Cellulose	100	91.1	0.4	0.1	3.3	2.1
Corn stalk	91.5	58.6	0.4	4.1	1.0	2.9
Rice straw	88.5	54.8	0.3	1.8	0.7	2.8
Wheat stalk	94.7	63.1	0.3	4.3	1.1	3.9
Peanut shell	79.5	45.4	0.4	2.8	0.3	2.7
Poplar leaves	72.8	27.7	0.4	1.3	0.3	2.9
Platanus leaves	63.8	16.7	0.4	1.6	0.3	1.1

a: Reaction conditions: substrate 0.1 g, water 30 mL, catalyst 0.05 g, 240 °C, 2 MPa N_2, 30 min.

Table 2 The composition of different biomass sources[a]

Substrates	Extraction (wt.%)	Hemicellulose (wt.%)	Cellulose (wt.%)	Lignin (wt.%)	Ash (wt.%)
Corn stalk	23.1	27.3	41.6	7.9	0.1
Rice straw	20.8	23.2	41.4	7.8	6.8
Wheat stalk	34.5	30.8	26.9	6.8	1.1
Peanut shell	15.4	12.9	40.6	31.0	0.1
Poplar leaves	63.4	6.8	18.8	9.7	1.4
Platanus orientalis leaves	53.3	1.3	18.4	26.0	1.0

a: The compositions of biomass were analyzed according to the procedures of the Van Soest method.[32]



Scheme 1 Proposed mechanism for cellulose transformation catalyzed by $ErCl_3$

Figure Captions:

Fig. 1. The effects of reaction temperature on the conversion of cellulose.

(Reaction conditions: cellulose 0.1 g, water 30 mL, catalyst 0.05 g, 2 MPa N_2, 30 min.)

Fig. 2. The effects of reaction time on the conversion of cellulose.

(Reaction conditions: cellulose 0.1 g, water 30 mL, catalyst 0.05 g, 240 °C, 2 MPa N_2.)

Fig. 3. The effects of initial cellulose amount on the conversion of cellulose.

(Reaction conditions: water 30 mL, catalyst 0.05 g, 240 °C, 2 MPa N_2, 30 min.)

Fig. 4. The effects of catalyst amount on the conversion of cellulose.

(Reaction conditions: water 30 mL, cellulose 0.1 g, 240 °C, 2 MPa N_2, 30 min.)

Fig. 5. Recycling of $ErCl_3$ during the conversion of cellulose to lactic acid.

(Reaction conditions: cellulose 0.1 g, water 30 mL, catalyst 0.05 g, 240 °C, 2 MPa N_2, 30 min.)

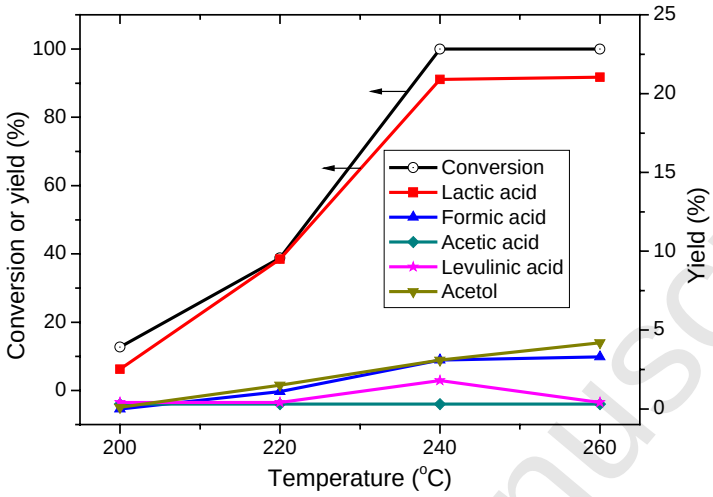


Figure 1

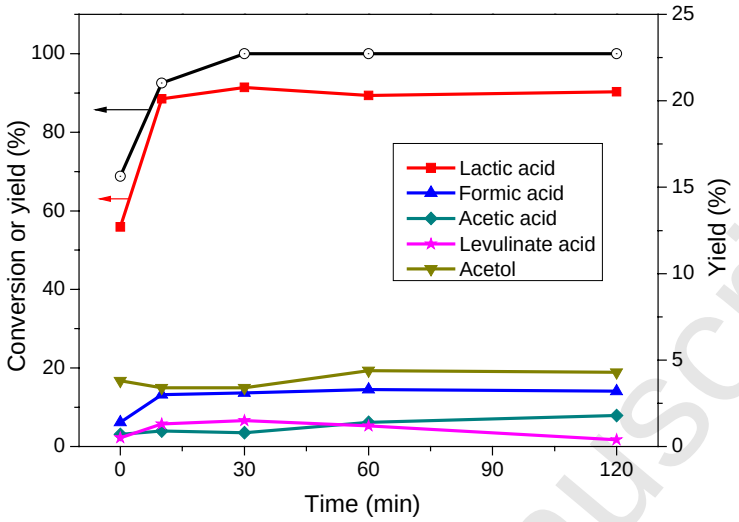


Figure 2

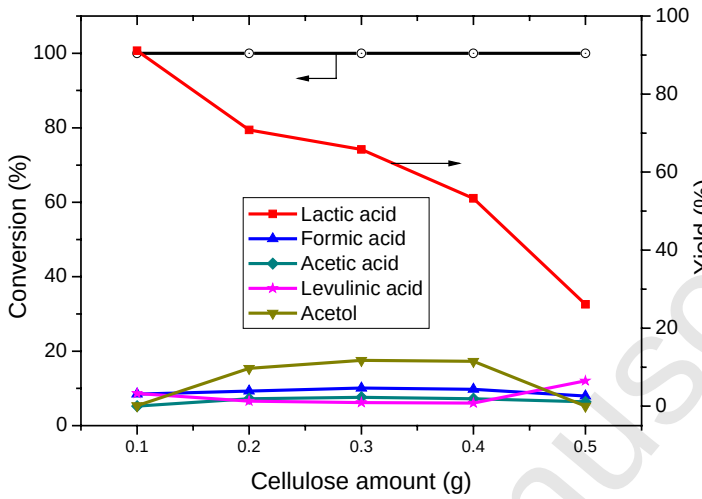


Figure 3

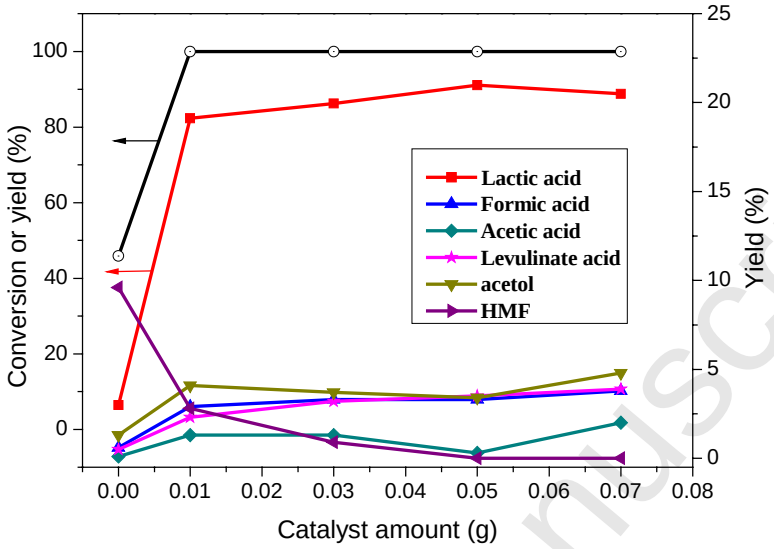


Figure 4

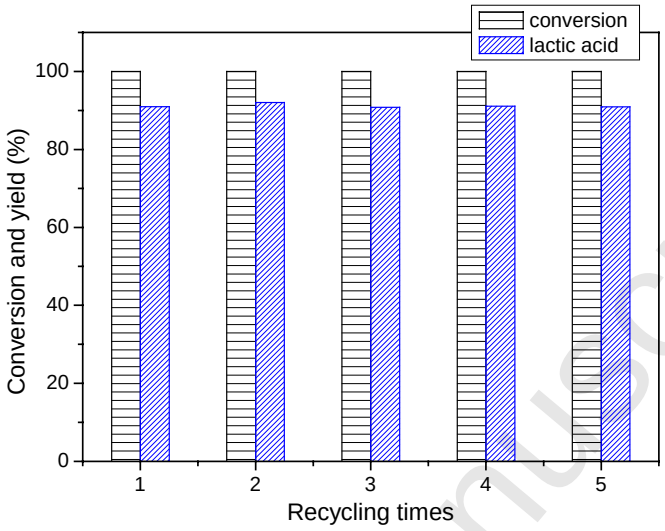


Figure 5

Graphical abstract