



Lactic acid production from rice straw in alkaline hydrothermal conditions in presence of NiO nanoplates



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ABSTRACT

The research study is based on alkaline hydrothermal liquefaction of rice straw using NiO nanoplates where temperature, reaction time and molar concentrations of alkali (NaOH) were varied to optimize lactic acid (LA) production. The highest yield of 58.81% for lactic acid was obtained at 260 °C for 2 h with 1 M NaOH and 0.052 g NiO nanoplates attributing to complete degradation of cellulosic rice straw. Influence of different morphological forms of NiO like nanoparticles, nanoplates and porous nanosheets were also investigated in this perspective where nanoplates had better catalytic activity. Lactic acid production was found to be highly dependent on and sensitive to slight changes in alkaline conditions in the existence of NiO nanoplates as catalyst.

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1. Introduction

Biomass comprising lignocellulosic materials is economically clean renewable resource with neutral carbon dioxide emissions. Lignocellulosic materials are abundantly produced as byproducts from agro-based industries [1]. Besides major contributor of bio fuel, lignocellulosic materials can be utilized for production of electricity, heat, polymeric substances and high value added products [2,3]. Usually cellulose (40–50%), hemicellulose (20–30%) and lignin (10–25%) govern chemical composition of lignocellulosic biomass [4], which laid the destiny of production of value added chemicals like phenols, ketones, organic acids and alcohols either present in combined form within bio fuel or obtained as separated product after extraction.

Cellulose has been considered as a major component for the production of various organic acids as compared to hemicellulose and lignin [5,6]. It is very abundant and highly stable polymer composed with glucose linked in linear chains up to thousands of units. The decomposition of cellulose can produce glucose, which further undergoes degradation via fermentation or chemical transformation to generate crude oil [5]. In the case of fermentation, direct

cellulose or lignocellulose biomass cannot be utilized, so other technologies have been considered to facilitate the process of chemical production [7]. On the other hand, hemicellulose is a second largest heteropolymer containing sugar monomers like xylose, mannose, galactose, rhamnose and arabinose, which break down easily and facilitate cellulose decomposition [8]. Lignin is one of the most abundant organic polymers containing phenyl-propane, methoxy groups and non-carbohydrate poly phenolic materials. Lignin is hard to be decomposed, so its application can be found more in biofuel production [1].

Cellulose degradation can be accomplished by various techniques, while hydrothermal liquefaction is becoming more favorable due to the high ion product quality [9], and its low dielectric constant which facilitates effective dissolving of non-polar biomass [10]. In hydrothermal conditions due to the high temperature, water dissociates into H⁺ and HO⁻ ions, which can behave as acid or base catalyst [9]. This property of water significantly influences cellulose degradation by favoring acid catalyzed reactions producing 5-hydroxymethyl furfural (HMF) or base catalyzed reactions producing lactic acid. Adding an acid or base catalyst can further improve the yield of these organic acids [10].

Among production of different chemicals, lactic acid (LA) has gained significant attention as it is widely utilized in production of biodegradable lactic acid polymer and poly lactic acid (PLA), biodegradable polyester used in medical materials assumed to replace plastics derived from petrochemical industry. It also serves

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as preservative in food, cosmetic and pharmaceuticals, and production of solvents in chemical industries [11]. Generally, fermentation of starch, glucose and xylose is used to produce lactic acid. But this method cannot utilize cellulosic biomass without pretreatment and also requires constant monitoring of pH and temperature for several days, whereas hydrothermal process facilitates direct use of feed stock for lactic acid production with much stable reaction conditions and relatively short time [3].

The fundamental step in production of lactic acid is the hydrolysis of non-reducing cellulose into reducing sugars like cellulobiose and glucose, which under alkaline hydrothermal conditions can be readily oxidized to carboxylic acids, including mainly lactic, formic and acetic acids [12–15]. Based on these studies, researchers have considered cellulose as a reductant which can facilitate reduction of metal oxide into its respective elemental form [16]. Alkali like NaOH, $\text{Ca}(\text{OH})_2$ and KOH have been excessively used depending on raw material being used as source of cellulose or glucose [3,16–18] to promote hydrolysis. On the other hand, some researchers have used CuO as an oxidant to decompose glucose into lactic and acetic acid in alkaline hydrothermal conditions while CuO itself is reduced to Cu_2O and Cu [7].

Due to mono-dispersion characteristic in fluid reactions, nanocatalysts have successively contributed in hydrothermal process [19]. Nano-ZnO has been reported to produce 12 times higher yield of glycolic acid as compared to nano- SnO_2 [20]. This is attributed to their better availability to oxygen atoms in ether linkages of cellulose [21]. Nickel has been well known in production of bio fuel due to its property of tar removal and increasing hydrogen gas production [22]. Ni nanocomposite has also been used for hydrocracking Jatropha oil [23], while [16] utilized cellulose to reduce NiO to Ni. Zhang et al. [24] used Zn/Ni/C to produce 42% lactic acid from cellulose.

Herein, we aimed to optimize production of lactic acid from China's most abundant agricultural waste i.e. rice straw by varying temperature, reaction time and molar concentration of NaOH used as an alkali while NiO nanoplates had been utilized as a catalyst in hydrothermal process. In addition we have further synthesized different morphologies of nano-NiO to better understand its role in this process.

2. Materials and methods

2.1. Materials

All the reagents used in this study were of analytical grade ($\geq 99\%$). Rice straw, as biomass was used in all experiments. NH_4OH , Ni $(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, urea, PEG-2000 and NaOH were obtained from Sigma-Aldrich (China).

2.2. Synthesis of nano-NiO with different morphology

NiO nanoplates were prepared by complexation-precipitation method devised by [25] while porous nanosheets and nanoparticles were synthesized by hydrothermal process used by [26]. For synthesis of NiO nanoplates, 100 ml of 2 M NH_4OH and 50 ml of 0.5 M $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ solutions were mixed and heated at 70 °C with constant stirrer. Collected nanoplates were filtered, washed and dried at 70 °C for 24 h followed by calcination at 400 °C for 2 h. For porous nanosheets, 0.68 g $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 0.96 g urea and 0.4 g PEG-2000 were dissolved in 40 ml deionized water. This solution was heated in autoclave at 85 °C for 24 h resulting in nickel carbonate. The autoclave was continued to heat at 200 °C for 24 h to produce porous sheets. After washing and drying at 70 °C, these sheets were calcined at 600 °C for 3 h. For nanoparticles, the same solution was heated at 85 °C for 24 h which was also calcined at 600 °C for 3 h.

Table 1
Chemical characterization of rice straw.

Components	wt%
Moisture	17.82
Ash	8.20
Cellulose	32.18
Hemicellulose	18.88
Lignin	24.00

The resulting nanoparticles were filtered, washed and dried and stored for future use.

2.3. Characterization of nano-NiO

Nickel oxide forms were characterized by XRD (D8 Advance Bruker Germany) and JEM-2100F TEM (Jeol, Japan) using Ni-filtered Cu $\text{K}\alpha$ radiation at an acceleration voltage of 40 kV and emission current of 40 mA. The step scan covered angles of 10–90° (2θ) at a rate of 0.0142°/s. Crystallite sizes of nano-NiO were calculated by Scherrer Equation: $D_{\text{XRD}} = K\lambda/\beta\cos\theta$ where D is mean crystallite size of powder. θ is the Bragg angle of diffraction lines, K is usually constant ($K=0.9$), λ is the wavelength of $\text{CuK}\alpha$ ($\lambda=0.15406$ nm) and β is full width at half maximum intensity of longest peak. Surface morphology was studied by Scanning electron microscope (SEM Nova Nanosem 450) and Transmission electron microscope (TEM, H-600, Hitachi).

2.4. Feed stock characterization

Rice straw was used as biomass feedstock which was supplied by Shanghai Fuhuan Bioenergy Co Ltd China with particle size ranging between 0.2–1.0 mm. Rice straw was chemically characterized by National Renewable Energy Laboratory (NREL) method as mentioned in Table 1.

2.5. Alkaline hydrothermal batch experiments

All experiments were carried out in a 100 ml GSA-0.25 type zirconic alloy cylindrical autoclave with maximum temperature range up to 300 °C and pressure up to 12.5 MPa, respectively. This equipment was heated by external furnace while a thermocouple inserted in reactor allows monitoring of operating temperatures. A water loop was also provided for rapid cooling of the reactor after completion of reaction time. For optimization of experimental conditions, set of reactions had been carried out with variation in temperature, reaction time and NiO nanoplates. For each experiment, the amounts of rice straw and deionized water were kept constant i.e. 4 g and 60 ml respectively. As a result, 260 °C with reaction time of 2 h and 0.052 mg of NiO nanoplates were considered optimum conditions for production of lactic acid. Further these conditions were used with different NaOH molar concentrations (0, 0.2, 0.5, 0.7, 1, 1.125, 1.25 and 1.375 M). For comparison, the resultant molar concentration was used with NiO nanoparticles and porous nanosheets to examine their potential in cellulose degradation.

2.6. Characterization of liquid product

Liquid samples after filtration were subjected to High Performance Liquid Chromatography (HPLC, Agilent 1200 LC) for analysis of organic acids and monosaccharides using Aminex HPX-87 column. The mobile phase was 0.005 mol/L H_2SO_4 with adjusted flow rate of 0.4 ml/min. The temperature of the column was 55 °C while the detector was refractive index detector with 50 °C thermal condition. The yield of carboxylic acids was calculated with respect to cellulose and hemicelluloses contained in the initial raw material.

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