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Resource recovery from waste LCD panel by hydrothermal transformation of polarizer into organic acids

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HIGHLIGHTS

- Hydrothermal technology can effectively decompose LCD panel.
- Organic materials in LCD panel was mainly decomposed into acetic and lactic acid.
- The conversion rate of organic materials reached 71.47% under the optimized condition.
- Analysis on structural changes reveals the decomposition reaction process.

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ABSTRACT

Based on the significant advantages of hydrothermal technology, it was applied to treat polarizer from the waste LCD panel with the aim of transforming it into organic acids (mainly acetic acid and lactic acid). Investigation was done to evaluate the effects of different factors on yields of organic acids, including the reaction temperature, reaction time and H_2O_2 supply, and the degradation process of polarizer was analyzed. Liquid samples were analyzed by GC/MS and HPLC, and solid-phase products were characterized by SEM and FTIR. Results showed that at the condition of temperature 300 °C and reaction time 5 min, the organic materials reached its highest conversion rate of 71.47% by adding 0.2 mL H_2O_2 and acetic acid was dominant in the products of organic acids with the yield of 6.78%. When not adding H_2O_2 to the system, the yields of lactic and acetic acid were respectively 4.24% and 3.80% at a nearly equal degree, they are suitable for esterification to form ethyl lactate instead of separating them for this case. In the hydrothermal process, polarizer was first decomposed to monosaccharides, alkane, etc., and then furfural and acids are produced with further decomposition.

1. Introduction

In view of their distinctive advantages, liquid crystal displays (LCD) have been widely adopted in televisions, notebooks, monitors and cell phones, etc. [1]. However, due to the fast-paced innovations or built-in obsolescence [2], the typical lifespan of LCD is only 3–5 years in notebooks and only has a service life of just under two years in smartphones [3]. Subsequently the waste LCDs have become new emerging contributor to the global e-waste burden.

The LCD units mainly consist of LCD panel, thin films and backlight modules. The LCD panel, as the core components of LCDs, primarily contains two pieces of polarizer (mainly composed of cellulose triacetate (TCA) and polyvinyl alcohol (PAV)), glass etched with indium tin oxide (ITO) film and liquid crystals. Heavy metals are contained in LCD panel with indium as the most important and precious [4–6]. Indium and liquid crystals which are aromatic-based polymers are the main hazardous substances in LCDs [4,7]. If not treated properly, they would cause undesirable impacts on the environment and human health. On the other hand, these precious metals (indium), plastic and glass contained in LCDs are all valuable and can be recycled with proper methods. Especially indium is a kind of rare strategic metal and almost two-third of global indium production is applied in ITO [8–10]. Therefore the treatment of the waste LCDs has become an urgent task [11–14].

The particularity of structure and composition of materials, make the treatment of LCD panel be a concerned problem in the treating and recycling process of waste LCDs, and most of the current researches mainly focus on the recycling of indium and glass, ignoring the pretreatment of waste LCD panel [8,14,15]. For facilitating the recycling process, the primary step is to separate the

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polarizing film from the glass panel, mainly by incineration in practice [16–18]. However, certain harmful pollutants such as polycyclic aromatic hydrocarbons generated during the combustion process, inducing to serious environmental pollution [1]. In addition, organic materials which account for around 12 percent of LCD panel are wasted. Therefore, environmentally friendly technologies are urgent to be developed for treating polarizer. Hydrothermal technology, with the distinctive characteristics of water as a reaction medium at elevated temperatures and pressures, has drawn the researchers' attention in recent years. In the hydrothermal environment, organic materials can be decomposed into small molecules, monomer species, or harmless end products [19,20]. Concerning that, the hydrothermal technique has been effectively used in resource recovery and harmless treatment of organics waste [21–24]. Moreover, lactic acid and acetic acid, main intermediates of organics in hydrothermal reaction, are important and widely used chemical materials, contributing them to be the objective products for resource recovery from organic waste [25]. For example, Jin et al. [26] carried a two-step hydrothermal process to convert carbohydrates into acetic acid. Glycerin was an important by-product during the alkali biodiesel manufacturing process [27], in order to optimize the manufacture process, Kishida et al. [28] proposed to convert glycerin into lactic acid by alkaline hydrothermal reaction, and their studies showed that lactic acid yield reached its maximum yield of 90 mol.% at 300 °C with 1.25 M NaOH.

In the present work, based on the chemical constitutions of polarizer and distinctive characteristics of hydrothermal reaction, waste LCD panel was treated by hydrothermal transformation into organic acids with the aim of recycling the organic materials and facilitating the further recovery of indium and glass. In the reaction process, H^+ or OH— as a catalytic factor could affect the yield of organic acid, but the strongly acidic or alkaline environment will lead to serious corrosion of the equipment and it will be enhanced greatly by the high temperature in the hydrothermal reaction. For economic considering, the neutral hydrothermal system is recommended and used in this study for the LCD panel decomposition. In the experiments, the effects of reaction temperature, reaction time and H_2O_2 supply on yield of organic acids from waste LCD panel were evaluated. Additionally, TCA and PVA are selected as model compounds for hydrothermal decomposition to investigate the decomposition process.

2. Materials and methods

2.1. Materials and chemicals

LCD panel from computers used in this study was provided by Taicang Shun Hui-Ferrous Metals Ltd., with organic carbon content of 12.6%. Before the experiments, LCD panel was cut into small pieces approximately 1 cm × 0.5 cm.

TCA and PVA were provided by US Acros Company and Sinopharm Chemical Reagent Co., Ltd., respectively. H_2O_2 (30%) was used as oxidant. The hydrogen peroxide, TCA and PVA used in this study are all analytically reagent. Chromatographically pure acetonitrile from Fisher Scientific was used for HPLC analysis. Deionized water was used during the whole study.

2.2. Apparatus and procedure

The hydrothermal decomposition experiments were conducted with a batch reactor system that consisted of a stainless steel vessel (1 mm wall thickness, 120 mm long and inner volume of 5.7 mL) and a salt-bath.

The batch reactor was rinsed by ethanol and water sequentially before the decomposition experiment. Then 200 mg reactant and deionized water or H_2O_2–water mixture were added into the reactor which was placed horizontally into a salt bath that had been preheated to desired temperature. In the salt bath, the reactor was shaken to enhance mixing and heat transfer. When reaction reached the setting time, the reactor was taken out of the salt bath and immediately put into a cold-water bath to quench the reaction.

2.3. Analytical methods

After the reaction, solid-phase products were characterized by SEM and FTIR. Liquid samples were collected and analyzed by GC/MS and HPLC. The yields of lactic and acetic acid were defined as the percentage of lactic acid and acetic acid in relation to the initial LCD panel, and the conversion rate of organic materials in LCD panel was defined as the percentage of total acids in relation to the initial organic materials, as follows:

$$\text{Yield, wt\%} = \frac{\text{Mass of lactic and acetic acid, mg}}{\text{Mass of LCD panel, mg}} \times 100\%$$

$$\text{Conversion rate, wt\%} = \frac{\text{Mass of organic acid, mg}}{\text{Mass of initial organic materials, mg}} \times 100\%$$

2.3.1. Solid product identification

The morphology of solid-phase products were analyzed by SEM. FTIR analysis can reveal the changes on the functional group. For FTIR, the samples were firstly ground to powder, and then dried for about 30-60 s under the infrared lamp after thoroughly grinding the mixture that consisted of power and potassium bromide (KBr) at a mass ratio of 0.5–1.0%. The mixture was compressed into slices with thickness of 2 mm for further analysis. According to the absorption peak intensity, the location and shape in the infrared spectrum, the material structure can be inferred.

2.3.2. Liquid product identification

Products contained in the water phase were analyzed by the 6890A GC system with 5975 inert MSD with Triple-axis Detector. The column of HP-INNOWAX (MS) (Cross-linked, polyethylene, glycol, 30 m × 0.25 mm × 0.25 μm, film thickness) was used for substance separation. The carrier gas was helium and the flow rate was 1 mL/min. The volume of sample injection was 1 μL with the injection mode of splitless and the injector temperature was 200 °C. The profile of oven temperature was as follows: the initial temperature was 80 °C which was held for 2 min, then it increased to 180 °C at 10 °C min^{-1}; finally, it increased up to 250 °C at 2 °C min^{-1} and maintained for 10 min. The temperature of GC interface and MSD ion chamber was 280 °C.

For GC/MS analysis, samples were transferred into a glass vial. 2 mL methylene dichloride was used to rinse the empty reactor and was subsequently transferred into the same glass vial. Then a liquid–liquid extraction was performed, through which the samples were divided into two phase: methylene dichloride and water. Water would be absorbed by anhydrous sodium sulfate. Methylene dichloride was then transferred into different vial and filtered for further analysis. To ensure mass transfer, the rinsing was repeated.

2.3.3. Quantitative analysis of lactic and acetic acid

An Alliance HPLC system with Waters e2695 Separation Module and Waters 2489 UV–vis Detector was used to quantify the yields of lactic and acetic acid. System control and data acquisition were conducted by Empower version 2. Substance separation was achieved by waters Untimate AQ-C18 (5 μm, 4.6 nm × 150 nm) at 25 °C. The flow rate was 1.0 mL min^{-1} and the injection volume was 10 μL. The UV detection was set at 210 nm.

Samples were firstly collected and transferred into a 20 mL glass vial for HPLC analysis. The empty reactor would be rinsed with 2 mL