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Hydrothermal decomposition of liquid crystal in subcritical water

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HIGHLIGHTS

- Hydrothermal technology can effectively decompose the liquid crystal of 4-octoxy-4'-cyanobiphenyl.
- The decomposition rate reached 97.6% under the optimized condition.
- Octoxy-4'-cyanobiphenyl was mainly decomposed into simple and innocuous products.
- The mechanism analysis reveals the decomposition reaction process.

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ABSTRACT

Treatment of liquid crystal has important significance for the environment protection and human health. This study proposed a hydrothermal process to decompose the liquid crystal of 4-octoxy-4′-cyanobiphenyl. Experiments were conducted with a 5.7 mL stainless tube reactor and heated by a salt-bath. Factors affecting the decomposition rate of 4-octoxy-4′-cyanobiphenyl were evaluated with HPLC. The decomposed liquid products were characterized by GC-MS. Under optimized conditions i.e., 0.2 mL H_2O_2 supply, pH value 6, temperature 275 °C and reaction time 5 min, 97.6% of 4-octoxy-4′-cyanobiphenyl was decomposed into simple and environment-friendly products. Based on the mechanism analysis and products characterization, a possible hydrothermal decomposition pathway was proposed. The results indicate that hydrothermal technology is a promising choice for liquid crystal treatment.

1. Introduction

With the development of science and technology, the utilization of liquid crystal display (LCD) increases rapidly, and gradually replaces the cathode ray tube (CRT) used in televisions and computer monitors [1]. As statistics show that in 2011, the global output of the LCD mirrors of China was about 167 million units [2] and the global LCD TV production was about 2053 million units [3]. However, the typical lifespan of LCD is only 3–5 years in notebooks and 8–10 years in TVs [4]. Hence, the amount of discarded LCDs is huge in the following years and treatment of the waste LCDs has become an urgent task [5–9].

Liquid crystals contained in LCDs are mixture in terms of the constituents, which usually contain about 10–25 compounds. The liquid crystals are aromatic-based polymers with benzene, cyano-group, fluorine (F), bromine (Br) and chlorine (Cl), etc., which are potentially harmful to the ecosystem and human health [10]. If not treated properly, it would cause undesirable impacts on the environment and human health. Therefore, treatment of liquid crystals is a concerned problem in the treating and recycling process of waste LCDs.

By far, thermal methods have been studied and developed for liquid crystals disposing, in which liquid crystals were incinerated or pyrolysed [11–16]. However, during the combusting and pyrolysis process, certain harmful pollutant such as polycyclic aromatic hydrocarbons (PAHs) tends to occur, leading to serious environmental pollution [17,18]. Hence, other alternative technologies to treat such hazardous materials need to be developed.

Hydrothermal technology, with the distinctive characteristics of water as reaction medium, has been proven to be an

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effective method for the treatment of hazardous wastes [19–24]. In the studies of Leybros et al. [25], radioactive ion exchange resins were successfully decomposed into innoxious substances by the hydrothermal reaction and the radioactivity was eliminated. Besides, the hydrothermal technology was also used to treat the brominated wastes. For example, Yin et al. [26] applied hydrothermal technology to decompose brominated epoxy resins. Wang et al. [27], Onwudili et al. [28] and Brebu et al. [29] used hydrothermal technology to treat waste brominated flame-retarded plastics. With the element of bromine being removed or recovered, the brominated epoxy resin and brominated flame-retarded plastics were successfully decomposed into more environment-friendly compounds. In view of its successful utility in hazardous waste treatment, hydrothermal technology was introduced to decompose liquid crystal in the present work with the aim to convert it into simple and more environment-friendly products.

4-octoxy-4′-cyanobiphenyl is one of the most commonly used liquid crystals in LCDs, whose chemical structure and melting point are given in Table 1. With benzene ring and cyano-group contained in molecular structure, 4-octoxy-4′-cyanobiphenyl is potentially harmful to the ecosystem and human health. Considering with the wide use and the ecological threats, 4-octoxy-4′-cyanobiphenyl was selected as model compound for hydrothermal decomposition in this study. Effects of H_2O_2 supply, reaction temperature, reaction time, pH value, catalysts (CuO and MnO_2) on the decomposition rate of 4-octoxy-4′-cyanobiphenyl were evaluated. Decomposed liquid products and the decomposition mechanism were further analyzed. A possible hydrothermal decomposition pathway of 4-octoxy-4′-cyanobiphenyl was also proposed.

2. Materials and methods

2.1. Materials and chemicals

4-octoxy-′-cyanobiphenyl ($C_8H_{17}O(C_6H)_2CN$, 99.9%) used in this study was provided by Hebei Maison Chemical Co., Ltd. A 30% solution of hydrogen peroxide was used as an oxidant for experimental convenience. Hydrochloric acid and sodium hydroxide were used to adjust the pH value of solution. The hydrogen peroxide, hydrochloric acid, sodium hydroxide and metal oxides (CuO, MnO_2) used in this study are all analytically pure and were purchased from Sino-pharm Chemical Reagent Co., Ltd (Shanghai, China). Chromatographically pure acetonitrile from Fisher Scientific was used for HPLC analysis. Water used during the whole study was deionized.

2.2. Apparatus and procedure

The hydrothermal decomposition experiments were conducted with a batch reactor system shown in Fig. 1. The experimental equipment consists of a stainless steel vessel and a salt-bath. The reactor vessel was made of a piece of stainless steel 316 tubing (3/8 in., 1 mm wall thickness and 120 mm long) with two end fittings (Swagelok cap), providing the inner volume of 5.7 mL.

Prior the decomposition experiment, the batch reactor was rinsed by ethanol and water. Then 2 mg of 4-octoxy-4′-cyanobiphenyl and 3 mL of deionized water or H_2O_2–water mixture were added into the reactor. The liquid volume loaded in the reactor was set at 3 mL for all the experiments with H_2O_2 blend fraction 0–20 % in water.

The loaded reactor 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 finished, the reactor was taken out of the salt bath and immediately put into a cold-water bath to quench the reaction. Reaction time was defined as the time that the reactor was kept in the salt bath. Reaction pressure in the reactor can be approximately calculated based on the saturated vapor pressure of water, which is respectively about 397 kPa at 250 °C, 594 kPa at 275 °C and 858 kPa at 300 °C.

After the reaction, liquid samples were collected and analyzed by HPLC and GC/MS. For HPLC analysis, samples were firstly collected and transferred into a 20 mL glass vial. About 2 mL ethanol was used to rinse the empty reactor and was subsequently transferred into the same glass vial. The rinsing was repeated another 2 times to ensure mass transfer. The collected liquid sample was subsequently diluted to a volume of 20 mL with ethanol, and filtrated for further analysis.

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. To ensure mass transfer, the rinsing was repeated again. Then a liquid-liquid extraction was performed, through which the samples were divided into two phase: methylene dichloride and water. Each phase was then transferred into different vial and filtrated for further analysis.

In order to provide precision data, each reaction was repeated three times and the average was reported as result.

2.3. Analytical methods

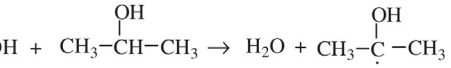
2.3.1. Quantitative analysis by HPLC

An Alliance HPLC system with waters e2695 Separation Module and Waters 2489 UV/Visible Detector was used to quantify the un-degraded 4-octoxy-4′-cyanobiphenyl. System control and data acquisition was conducted by Empower version 2. Substance separation was achieved by waters XBridge C18 column (3.5 μm, 4.6 × 150 mm, XBridge, Ireland) at 30 °C. The mobile phase contained A and B, which were respectively ultrapure water and acetonitrile. The gradient was set as follows: 90% B for 0–1 min, 100% B for 1–6.5 min and 90% B for 6.5–7.5 min. The flow rate was 1.0 mL/min and the injection volume was 2 μL. The UV detection was set at 225 nm. A series of solution with different concentration of 4-octoxy-4'-cyanobiphenyl were used as external standard for the quantification. All quantitative data reported were the average values of the analytical results of three samples with standard deviation less than 7%.

2.3.2. Liquid product identification by GC/MS

A Trace DSQ GC/MS system was used to identify the products exist in the phase of methylene dichloride. Xcalibur Roadmap was applied for data acquisition and treatment. The GC capillary column was an Agilent HP-5MS (5%-Phenyl)-methylpolysiloxane (30 m × 0.25 mm, 0.25 μm film thickness). The carrier gas was

Table 1
Chemical structure and melting point of 4-octoxy-4′-cyanobiphenyl.

Substance	Chemical structure	Melting point (°C)
4-octoxy-4′-cyanobiphenyl		51–77