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Vacuum pyrolysis characteristics and kinetic analysis of liquid crystal from scrap liquid crystal display panels

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HIGHLIGHTS

- Pyrolysis kinetic analysis of liquid crystal is conducted under two conditions.
- Vacuum pyrolysis advantages are expounded by apparent activation energy analysis.
- Pyrolysis characteristics are conducted to better understand pyrolysis process.
- The conversion rate of liquid crystal reaches 89.10% under the optimized condition.
- Indium is able to be enriched from 7.95% to 14.18% by this technological process.

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ABSTRACT

Recycling of waste liquid crystal display (LCD) panels is an urgent task with the rapid expanding LCD market. However, as important composition of LCD panels, the treatment of liquid crystal is seldom concerned for its low concentration. In present study, a stripping product enriched liquid crystal and indium is gained by mechanical stripping process, in which liquid crystal is enriched from 0.3 wt.% to 53 wt.% and indium is enriched from 0.02 wt.% to 7.95 wt.%. For the stripping product, liquid crystal should be removed before indium recovery because (a) liquid crystal will hinder indium recycling; (b) liquid crystal is hazardous waste. Hence, an effective and green approach by vacuum pyrolysis is proposed to treat liquid crystal in the stripping product. The results are summarized as: (i) From the perspective of apparent activation energy, the advantages of vacuum pyrolysis is expounded according to kinetic analysis. (ii) 89.10 wt.% of liquid crystal is converted and the content of indium in residue reaches 14.18 wt.% under 773 K, 15 min and system pressure of 20 Pa. This study provides reliable information for further industrial application and an essential pretreatment for the next step of indium recycling.

1. Introduction

The liquid crystal display (LCD) is standing in the mainstream of the flat panel displays, which are widely used in many electronic products for the advantages of LCD of light quality, small volume, and low power consumption, instead of the old technology of cathode ray tube (CRT) [1–3]. According to *HIS Inc.*, large-area thin-film transistor (TFT) LCD shipments are forecast to decline 5% in 2016, compared with 682 million units in 2015. While the decline in unit shipments will be offset by an increase in large-area TFT-LCD shipment area, which is expected to grow 5% this year, compared with 159 million square meters in 2015 [4]. Considering the average lifespan of 3–8 years of LCD panels [5], there are enormous quantities of LCDs entering end of life in the coming years, which is a tremendous contribution to waste electric and electronic equipment (WEEE).

LCD panels mainly consist of polarizing film, glass substrate and liquid crystal, as shown in Fig. 1. A LCD panel is made of two glass substrates, between which the liquid crystal is situated. The polarizing film is attached on lateral side of both substrates. The polarizing film mainly consists of cellulose triacetate (TAC), polyving akohol (PVA) and triphenyl phosphate (TPP) [6,7]. And liquid crystal is mainly composed of rod-shaped organics with phenyl or cyclohexyl, accounted for 0.3 wt.% in LCD panels [8]. It is noteworthy that many hazardous substances used in LCD, such as Poly Brominated Diphenyl Ethers (PBDEs), toxic metals and liquid crystal materials, would have significant adverse impacts on human health and environment if improperly disposed [9–11]. On the other hand, valuable metal indium (In) and glass substrate could be recovered for secondary resource [5,12,13]. Approximately 74% consumption of indium is used for the production of LCD panels

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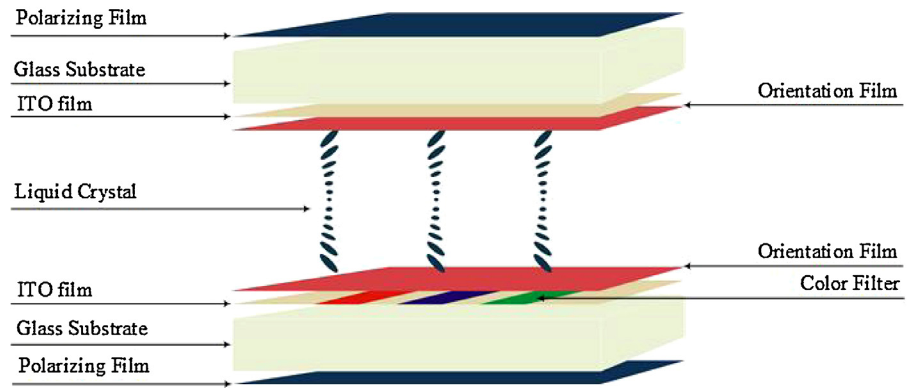

Fig. 1. Structure of LCD panels.

while the global reserve of indium is only 1/6 of gold [3,14]. However, the content of indium in LCD panels is about 0.02 wt.%, which is far more than that of in natural deposits [15]. Hence, in recent years, more attention has been paid on the recovery of indium and glass substrate from scrap LCD panels, particularly the indium-tin oxide (ITO) conductive film [14,16,17]. However, polarizing film, glass substrates with ITO film and liquid crystal are stick together, which is quite hard to separate, resulting in the complication of the recycling process of indium. Therefore, the organic parts should be removed and recovered in advance [18]. To solve the aforementioned problems, the best available technologies for treating scrap LCD panels are urgently needed.

In our previous research, efforts have been made to investigate the treatment of holistic LCD panels [1,19,20]. However, through the treatment of holistic LCD panels, the content of indium in the products obtained was still low, which would cause obstacles to the recycling of indium. Herein, a mechanical stripping process including deformation, separation, stripping, filtration and drying was adopted to treat scrap LCD panels to obtain a concentrate of liquid crystal and ITO film, realizing the enrichment of indium from 0.02 wt.% to 7.95 wt.% and liquid crystal from 0.3 wt.% to 53 wt.%. Meantime the polarizing film and glass substrate could be separated and recycled by mechanical crushing and gravity concentration [9]. In order to more effectively recover indium, the liquid crystal in the stripping product should be removed and recycled in advance. However, scant research has been done to study the reasonable treatment of liquid crystal in scrap LCD panels thus far, due to the low concentration of liquid crystal in LCD panels. The existing processes for recovering the liquid crystal in scrap LCD panels could be summarized in incineration [21], supercritical fluid extraction [22] and solvent extraction [23]. Zhu et al. studied the recycling of liquid crystal from scrap LCD panels by organic solvent extraction with ultrasonic wave and followed by membrane filtration and vacuum distillation [24]. Solvent extraction for recovering liquid crystal is feasible. However, there are still several deficiencies: (i) Solvent extraction was capable of recovering the liquid crystal of scrap LCD panels, but the recovery rate was low, approximately 50%, even with active influence of ultrasonic wave. (ii) The performance of liquid crystal recovered was inferior to the pure liquid crystal, which indicated that it was necessary for the liquid crystal recovered to conduct further purification for reuse. (3) The large number consumption of organic solvent limited the application and waste solvent might cause secondary pollution, if mishandled.

Pyrolysis has been proved to be a promising technology to effectively remove and recover organic substances for resource recovery [25–27]. Quan et al. treated waste printed circuit boards (PCBs) with pyrolysis method and obtained the oil with high concentrations of phenol and phenol derivatives as raw materials for the production of phenol-formaldehyde resin [28]. Sun et al. utilized pyrolysis method to remove the organic binders in lithium-ion batteries making cathode powder completely peeled from aluminum foils [29]. Pyrolysis technology has the advantage of high efficiency and low environment costs. It can effectively remove the organic materials and the products can be recycled as chemical materials. Meantime, due to the closed oxygen-free system, the technology could effectively avoid secondary pollution. Kinetics of scrap tyre pyrolysis under vacuum condition were investigated by Lopez et al. [30]. According to the study by Lopez, vacuum environment promoted the volatilization and internal diffusion of the products in the pyrolysis process, which attenuated the secondary reactions of repolymerization. Hence, vacuum pyrolysis might consume less energy and obtain more pure products. Moreover, through the decomposition kinetic analysis, we could get a deeper understanding of pyrolysis process.

Table 1
Composition of stripping product.

Composition	Indium	Tin	Liquid crystal	Glass powder	Others
Content/%	8	1	53	36	2

In this study, we mainly focus on the removal and recovery of liquid crystal and the enrichment of indium by an environmental friendly method. Herein, vacuum pyrolysis was proposed to treat the stripping product. The objectives in present study are: (i) to compare nitrogen pyrolysis and vacuum pyrolysis from the perspective of pyrolysis kinetics and expound the advantages of vacuum pyrolysis, (ii) to use vacuum pyrolysis method to remove liquid crystal from the stripping product obtained by a mechanical process aforementioned and (iii) to study the characteristics of vacuum pyrolysis process and optimize the parameters to prepare for the next step of recovery of indium and to guide further industrial application.

2. Experiment and method

2.1. Materials and experiment

The stripping product used in this study was from a Yangzhou company gained by a mechanical stripping process including deforming, separation of two glass substrates, stripping by several cylindrical grinding apparatuses with washing, filtration with a bag filter and drying at a low temperature. A schematic diagram of the integrated process is shown in Fig. 2. According to analysis results, the composition of the stripping product is showed in Table. 1. The content of indium reached up to about 8 wt.% while approximately 53 wt.% of the stripping product was liquid crystal. The others are mainly glass powder and trace metals.