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Energy and valuable resource recovery from waste liquid crystal display panels by an environment-friendly technological process: Pyrolysis of liquid crystals and preparation of indium product

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ABSTRACT

The contradiction of energy, resource and environment from waste liquid crystal display (LCD) panels is becoming more and more prominent because it contain both harmful liquid crystals and valuable metal indium. However, scarce researches have considered how to separate liquid crystals and recycle indium from waste LCD panels by an environment-friendly process. In this work, an integrated technological process to recycle energy and valuable resource from LCD panels is proposed. Firstly, a stripping product enriched liquid crystals and indium is gained by a mechanical stripping separation. Then, based on a series of pyrolysis separation, vacuum chlorinated separation and substitution reaction, concentration of indium is increased to 36 wt % in final product from 0.02 wt % in waste LCD panels. Several highlights were summarized as follows: (i) Feasibility, principle and reaction mechanism was studied to understand this integrated process. (ii) For pyrolysis process, separation rate of liquid crystals approached 82.06% under optimized parameters by response surface methodology. For vacuum chlorinated process, recovery rate of indium can reach 97.16%. This technological process is quite significant in accordance with the "Reduce, Reuse and Recycle Principle" for solid waste and further provides a new opportunity for sustainable development of LCD markets.

1. Introduction

With rapid technological advances, liquid crystal display (LCD) has been completely replaced cathode ray tube (CRT) display. It has become the mainstream position of flat panel displays owing to its special merits of micron radiation, low power consumption, and multi-information display (Guan, 2015; Li et al., 2009). LCD panels are widely used in electronic devices including laptops, televisions, mobile phones and a variety of other electronics and more than 200 million laptops were produced worldwide in 2013 (Gartner, 2013; Senthilkumar et al., 2012). There is no doubt that the amount of waste LCD panels also quite vast. LCD panels mainly contain polarizing film, glass substrate, liquid crystals and ITO conductive film (Yu et al., 2016; Chen et al., 2016). On the one hand, LCD panels are valuable because of (a) resource recovery of the metallic indium and tin; (b) recycling of the glass substrates; (c) potential recycling of polymers, such as polarizing film. On the other hand, due to the lack of effective disposing technology, waste LCD panels have to be landfilled directly to the soil. A wide range of organic matter and heavy metals, such as liquid crystals, arsenic (As), lead (Pb), indium (In) and tin (Sn) has been found to release into the environment (Wang et al., 2013; Lu et al., 2012; Savvilotidou et al., 2014). Hence, the contradiction of energy, resource and environment from waste LCD panels is becoming more and more prominent.

Liquid crystals in LCD panels are mixture containing various chemical compositions, which usually have about 10–25 compounds, and consist of aromatic-based polymers with benzene, cyanogroup, fluorine, esters, cyclohexyl, etc (Gao, 2011). In worldwide, about 500 t/year liquid crystals are used in the production of LCD panels. With a surprising yield and potential toxicity, it will cause serious soil pollution and even jeopardize human health if improperly disposed. Regrettably, up to now, there have been no good methods to effectively separate and treat liquid crystals, and its relative researches are also quite scarce. Incineration still is main approach for treatment of waste liquid crystals. However, for incineration process, certain harmful pollutants such as polycyclic aromatic hydrocarbons (PAHs), dioxins (PCDD/Fs) tend to be released into atmosphere, leading to serious pollution of

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atmosphere (HussainQuasi et al., 2016; Zhuang et al., 2012).

In contrast to the harm of liquid crystals, valuable metal indium in LCD panels can be take full advantage of as renewable resources totally. Indium, as important strategic resource, has been categorized by the European commission as one of the critical resources (EC, 2010). Meanwhile, American had reserved indium as national strategy and stopped producing indium since 1990s. In worldwide, about 70% of indium was used to produce ITO thin films in LCD panels due to its merits of being transparent to visible light and electrically conductive (Dodbiba et al., 2012; Mineral Commodity S, 2014). The content of indium in LCD panels is about 200 g/t. Generally, the ores deposits containing 0.001% (namely 10 g/t) of indium possess the value of exploitation. This is surprising from the point of view that the secondary resource contains higher concentrations of indium than the primary ores. Therefore, recycling and regeneration of indium in LCD panels is a promising approach to meet market demand and avoid waste of resource.

Up to now, existing studies about recovery of indium from electronic waste mainly focused on the hydrometallurgical processes to extract indium, followed by a process to separate indium from leachates containing other elements. Technologies include acid leaching (Virolainen et al., 2011), solvent extraction (Virolainen et al., 2011; Ruan et al., 2012; Kang et al., 2013), supercritical extraction (Liu et al., 2009), selective precipitation (Jiang et al., 2011) etc. Sami Virolainen et al. (2011) proposed that three solvent systems of TBP, D2EHPA and a mixture of both were chosen to study their selectivity separate indium from tin. Indium could be selectively extracted from containing indium solution by HCl media with 1 M of TBP/0.2 M of D2EHPA, and 0.8 M of TBP. Ruan et al. (2012) leached indium from scrap TFT-LCDs by solvent extraction which was based on a system of H_2SO_4 acid leaching-D2EHPA extraction-HCl back extraction. The results showed that the final extraction efficiency of indium achieved more than 97% and other metals' leaching concentrations were relatively low under condition of H_2SO_4 solutions (1:1, v/v) with 30% D2EHPA with organic to aqueous phase (O/A) ratio of 1:5 within 5 min and 4 M HCl from D2EHPA with A/O ratio of 1:5. Kim et al. (Kang et al., 2013) studied recovery and purification of indium from waste sputtering target. The results indicated among PC88A, D2EHPA, Alamin 336 and versatic acid, PC88A was selected as the most suitable solvent and acid concentration (MH+) = 3 M, the volume ratio of organic to aqueous phase (O/A) = 3, and retention time = 10–15 min were determined as the optimal conditions to extract indium. By this method, Sn can be removed effectively and 99.9976% pure indium ingots could be obtained. Liu et al. (2009) studied supercritical CO_2 extraction method for the indium recovery from the real etching wastewater obtained from indium tin oxide (ITO) etching process. Recovery rate of indium from etching wastewater exceeded 90% when reaction condition is 80 °C, a pressure of 20.7 MPa, with 15 min static extractions followed by 15 min dynamic extraction. Jiang et al. (2011) adopted sodium tripolyphosphate to precipitate indium and extract indium. The results indicated that indium was precipitated under the conditions at pH 2.6, with a molar ratio of $Na_5P_3O_{10}$/indium 0.91, and reaction time of 1.5 h. Although these studies have focused on recycling indium resource, there are still several defects for hydrometallurgical processes. For example, large quantities of acid and extraction agent would be used in the extracting process of indium, which increases the operating risk of workers and also produces wastewater.

Currently, vacuum metallurgy is feasible method reported for recovery of metals. Its principle is that the saturation vapor pressure of metals under the vacuum condition is lower than that of under normal pressure. They can be evaporated into the gas phase, according to the principle of vacuum metallurgy (Zhang and Xu, 2016a; Dai, 2009). Vacuum technology does not need secondary off-gas or wastewater treatment and it can be considered as a complementary approach to hydrometallurgy (Chen et al., 2009; Zhan and Xu, 2014). For example, Zhang et al. (Zhang and Xu, 2016b) adopted vacuum decomposition to successfully recycle gallium from solar cell modules and gained better separation efficiency. The results indicated organic conversion rate approached 100% in the condition of 773 K, 30 min, and 0.5 L/min N_2 flow rate. Gallium can be well recycled under temperature of 1123 K, system pressure of 1 Pa and reaction time of 40 min.

In past recycling process, most of technologies adopted whole crush for waste LCD panels to treat liquid crystals and indium. But, there are still several defects: (1) capacity of treatment is vast due to using whole crush process; (2) liquid crystals and indium cannot be recycled effectively because of its low concentration which has only about 0.3–0.5 wt % liquid crystals and 200 g/t indium in a piece of LCD panel; (3) some valuable materials such as polarizing film and glass substrates are unable to realize reuse. Hence, an idea of comprehensive recycling liquid crystals and indium from waste LCD panels was presented: firstly, achieving enrichment of liquid crystals and indium, and further achieving separation of them.

This study firstly adopted a mechanical stripping process to separate glass substrates, liquid crystals and ITO conductive film. By this process, a stripping product enriched liquid crystals and indium was gained. This process not only realized enrichment of liquid crystals and indium, but also achieved capacity reduction of waste. However, before recycling indium in the stripping product, liquid crystals should be removed in advance because it is disadvantage for recycling of indium that liquid crystals with ITO film closely link together. Hence, it is necessary that separation and removing of liquid crystals should be as the first step with important significance.

Pyrolysis has been proved to be a clean thermochemical technology for recycling synthetic polymers including polymers that are mixed with glass fibers (Hall and Williams, 2006; Cunliffe et al., 2003). Several researchers have investigated the pyrolysis behavior of different components of plastics, sludge and potential secondary pollutants etc (Tian et al., 2013, 2014; Santella et al., 2016). Tian et al. (2013) investigated nitrogen conversions in relation to NH_3 and HCN during microwave pyrolysis of sewage sludge. The results indicated that the microwave pyrolysis of protein in sludge might be able to reduce the HCN and NH_3 emissions through controlling produced three intermediate compounds in pyrolysis process. Chiara Santella et al. (2016) adopted the thermal and catalytic pyrolysis to decompose plastic from e-wastes. Results showed HZSM-5 zeolites have good performances for the catalytic pyrolysis of plastics from e-wastes.

Pyrolysis with inert gas is a quite promising technology for recycling organics compared with combustion and solvent leaching (Santella et al., 2016; Alston et al., 2011; Alston and Arnold, 2011). In our previous research, pyrolysis process was used to recycle the polarizing film from waste LCD panels. The results showed acetic acid and triphenyl phosphate (TPP) are the main oil products in pyrolysis of polarizing films. 99.77% of organic matters were removed and a yield of 78.23% acetic acid was recycled (Wang and Xu, 2016). Based on the above, we put forward pyrolysis process to recycle energy from liquid crystals.

Therefore, the aims of this study are that: (1) A novel and integrated technological process to recycle energy and valuable resource from LCD panels is proposed. (2) Feasibility, principle and reaction mechanism of technological process is explored to understand this process; (3) Optimal condition of this process with purpose of fitting industrial requirements is discussed. In short, this study provides a new opportunity for sustainable development of the liquid crystal display industry from the prospect of recycling energy and resource.