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Steam gasification of printed circuit board from e-waste: Effect of coexisting nickel to hydrogen production

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ABSTRACT

Steam gasification of phenolic boards (PB) in the presence of ternary eutectic carbonates (LNK–carbonate mixture: Li_2CO_3, Na_2CO_3 and K_2CO_3) was carried out at 823–948 K under atmospheric pressure to produce clean hydrogen. Rates of hydrogen formation were accelerated in the presence of nickel metal powder in the low temperature range (823 K). The experimental results imply that unsupported nickel metal powder or small nickel pieces in molten carbonate could be used as catalyst to produce hydrogen on steam gasification of e-waste.

1. Introduction

Global production of waste electrical and electronic equipment (WEEE) amounts to around 40 million tons per year, and the fastest increment in municipal solid waste, with a rate of about three times the average [1]. In Europe, the amount of WEEE generated is 12 million tons per year, only 18% of which is treated [2]. About 100 million mobile phones and 17 million computers are estimated to be wasted annually around the world [3]. From this WEEE generated, a minimum recovery target must be achieved according to European regulations [4].

Generally, WEEE is composed of metal (40%), plastic (30%) and refractory oxides (30%) [5]. Typical metal scrap consists of copper (20%), iron (8%), tin (4%), nickel (2%), lead (2%), zinc (1%), silver (0.2%), gold (0.1%) and palladium (0.005%) [6]. Printed circuit boards (PCB) constitute about 3% of the WEEE, and they contain a variety of heavy metals and hazardous substances (lead, cadmium, mercury, PVC, halogenated flame retardants, etc.), which makes its recycling difficult [7–10].

There are two types of printed circuit boards, FR-2 and FR-4, normally used in personal computers and mobile phones. FR-2 type is a single layer of fiberglass or cellulose paper and phenolic cover, coated with copper layer. FR-4 is composed of a multilayer of epoxy resin and fiberglass, coated with a copper layer. FR-2 type is used in televisions and households appliances such as personal computers, and FR-4 is used in small devices such as mobile phones. Copper is the metal of the highest percentage in PCB due to its high conductivity [3].

Regarding the plastic fraction, there is a wide variety of polymers (more than 15 polymers), but the most common constituents in e-waste are high impact polystyrene (HIPS) (42%), acrylonitrile–butadiene–styrene copolymer (ABS) (38%) and polypropylene (PP) (10%) [11,12]. HIPS is the predominant plastic in television housings, while ABS is the most common plastic found in computers, monitors and printers. Small amounts of other plastics, such as polycarbonate (PC), polyvinyl chloride (PVC), polyamide (PA) and a blend of ABS and PC, can also be found in WEEE. Phenol and epoxy resins are important thermosetting materials widely used for PCB due to excellent thermal, mechanical and electrical properties [13,14].

Recycling of WEEE is an important subject from the point of view not only of waste treatment but also of the recovery of valuable metals [5]. Burning the electronic scrap has been demonstrated not to be a suitable process for WEEE treatment due to the formation of hazardous compounds for environment and human health [15]. Nowadays, WEEE stored in land fields [16] or uncontrolled exported to developing countries [17] are dangerous ways to treat WEEE occupying space and polluting our environment and health. Some authors studied the recovery of materials from milled PCB residues and dismantled electronic wastes [18,19]; however, mechanical recycling of WEEE is neither economically nor

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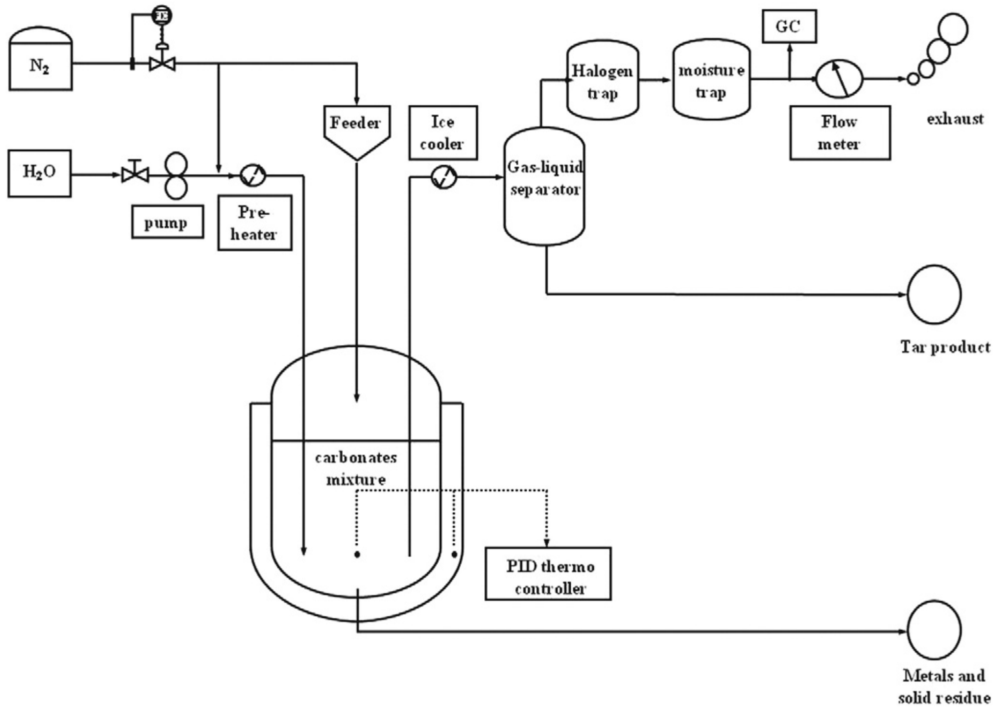

Fig. 1. Experimental diagram of the steam gasification process.

environmentally profitable [20]. Few studies have been conducted on recovering useful materials from electronic packaging residues in order to improve the process economy [21]. In some processes, the recovery of precious metals from electronic waste is carried out by high temperature processes (~1473 K), such as pyrometallurgical processing, hydrometallurgical processing and biometallurgical processing [7]. Fast pyrolysis to obtain gas, liquid and solid products and metal recovery may be a feasible and environmentally friendly technology for the treatment of WEEEs. However, many studies have shown that pyrolysis oil contains mainly aromatic compounds like benzofurans, phenols and phosphate compounds from the decomposition of flame retardants such as tetrabromobisphenol A and triphenyl phosphate [22–25]. Therefore, additional steps must be added to the process to upgrade the pyrolysis oil [26]. Some authors studied a two-step degradation process for printed circuit board wastes based on pyrolysis (573–723 K) and catalytic hydrotreatment (743 K) [27]. WEEE gasification processes for hydrogen production is a feasible technology for chemical degradation of plastic wastes [28]. Yamawaki [29] concluded that gasification of plastic WEEE at high temperature (1423 K) followed by a shock cooling step is an effective process to decompose the brominated flame retardants (BFR) to comply with the minimum regulatory values. Yang et al. [30,31] obtained similar results for the abatement of halogenated compounds by the oxidation of plastics at high temperatures (1173 K) in a molten carbonates reactor. Tongamp et al. [32,33] studied a one-step mechanochemical treatment of plastics (673–823 K) to produce hydrogen gas, using $Ni(OH)_2$ as catalyst powder and CaO or $Ca(OH)_2$ for chlorine removal. Therefore, conversion of plastics contained in WEEE to clean hydrogen by steam gasification at mild conditions contribute to use organic resources effectively and to recover useful metals easily after the process.

In our previous work, we could show that steam gasification using LNK–carbonate mixture (Li_2CO_3, Na_2CO_3 and K_2CO_3) is an effective and feasible method to recover metals contained in WEEE [34–36]. These metals have been used by many authors as catalysts for hydrocarbon chain reforming and hydrogenation processes. A great variety of metals are used in practical WEEE. In this work, steam gasification of phenol resin (PB) was carried out in the presence of LNK–carbonate mixture in order to study the effect of nickel, one of the most widely used rare metals in WEEE. However, this work is not only focused on hydrogen production from steam gasification of WEEE. The recovery of valuable metals (nickel, iron, copper, silver, gold and palladium) and rare metals (gallium, indium and tantalum) is important to reduce landfilling and is the main economic aim of the recycling of electronic waste. In this work, steam gasification of phenol resin was investigated in the presence of nickel powder in the molten LNK–carbonate mixture.

2. Experimental

2.1. Preparation and characterization of samples

PB (PL-1102, Sumitomo Bakelite Co., Ltd.) was milled (0.15 mm of particle size) by a grinder Ika Labortechnik A10 and used as samples for the steam gasification. The LNK–carbonate mixture was prepared by mixing equal weights of three carbonates (lithium, sodium and potassium carbonate, supplied by Wako Pure Chemical Industries, Ltd.). Nickel powder with 99.7% purity was provided by Alfa Aesar (−50 + 100 mesh).

Elemental analysis for the PB sample was carried out in previous work [36] and, in this work, was performed for the solid residues from steam gasification experiments of PB and PB plus nickel powder in the presence of LNK–carbonate mixture in order to determine its carbon, hydrogen, nitrogen, sulfur and oxygen concentration.

2.2. Steam gasification studies for PB

As reported in previous studies [36], hydrogen formation by steam gasification of char proceeds by means of two reactions: steam gasification (Eq. (1)) and water-gas shift (Eq. (2)):

$$C + H_2O \rightarrow CO + H_2 \quad \Delta H^0 = 131\ \text{kJ mol}^{-1} \tag{1}$$

$$CO + H_2O \rightarrow CO_2 + H_2 \quad \Delta H^0 = 41.2\ \text{kJ mol}^{-1} \tag{2}$$

2.2.1. Themogravimetric studies

Thermogravimetric studies (TG) of PB and PB (25 wt.%) plus nickel powder (75 wt.%) were carried out under nitrogen or steam atmosphere