



Inhibition of chlorinated organic compounds production by co-pyrolysis of poly (vinyl chloride) with cation exchanged coal



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HIGHLIGHTS

- Effects of pyrolysis conditions of PVC and cation exchanged coal were discussed.
- Chlorinated organic compounds were inhibited by metal dissociation in exchanged coal.
- Chlorinated organic compounds on pyrolysis of PVC and Pb exchanged coal were inhibited.
- Dissociated Pb by exchange with H⁺ in water on pyrolysis was higher than that of Cu.
- Calorific value of upgraded solid after pyrolysis was higher than that of raw coal.

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ABSTRACT

Effects of kind of heavy metal and the reaction conditions on co-pyrolysis upon inhibition of chlorinated organic compounds production during co-pyrolysis of poly (vinyl chloride) with cation exchanged coal were discussed. The remained content of chlorine using copper exchanged coal was not much higher than that using metallic copper. Formation of chlorinated organic compounds was inhibited by enhancement of dissociation of metal from the cation exchanged coal during co-pyrolysis. Production of chlorinated organic compounds after co-pyrolysis of PVC with lead exchanged coal was inhibited because the amount of lead dissociated from the exchanged coal through ion exchange with H⁺ in water solvent during co-pyrolysis was higher than that of copper exchanged coal. In comparison with the calorific value of raw coal, those of the upgraded solid fuel resulted after co-pyrolysis increased by co-pyrolysis of cation exchanged coal and PVC. Capture of chlorine from poly (vinyl chloride) was inhibited due to formation of water insoluble salt, such as Pb(OH)₂ and CuCO₃, with the increase of the amount of water solvent and holding time, respectively. Copyrolysis of poly (vinyl chloride) and lead exchanged coal with 11.1 ml of water solvent at 300 °C for 60 min is a most suitable condition in this study.

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1. Introduction

Recently, utilization of lower rank coal, such as subbituminous [1,2] and brown [3–6] coals, is discussed on a thermal power station due to a rise in price of bituminous coal. A large amount of these lower rank coals is required in order to obtain enough thermal energy for power generation because calorific values of low rank coals are lower than that of bituminous coal. Further, contents of water and oxygen atom were higher than those of

bituminous coal. Therefore, upgrading of calorific value of lower rank coal is necessary. One of the upgrading method of lower rank coal, hydrothermal treatment of lower rank coal has been discussed [7–9]. After hydrothermal treatment of Loy Yang brown coal above 300 °C, the increase in calorific value and reductions in the volatile content and self-ignition tendencies of the treated coal were observed [7].

It is known that calorific values of polyethylene, polypropylene and polystyrene are higher than that of low rank coal. In the financial year of 2012 in Japan, 80% of plastic waste was processed by means of thermal recovery and mechanical and feedstock recycling; however, 10% (0.9 Mt) of plastic waste was burnt without thermal recovery and 10% (0.9 Mt) of plastic waste was landfilled [10]. In order to prevent carbon dioxide emission and lengthen

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Nomenclature

PVC	poly (vinyl chloride)	WS	water soluble material
WI	water insoluble material (upgraded fuel)	COOH	carboxyl group

the remaining lifetime of final disposal sites, cascade utilization of plastic waste is required.

Considering the situations written above, production of the upgraded fuel with a high calorific value by co-pyrolysis of lower rank coal and plastic waste is a main object of this study. However, chlorinated organic compounds are formed from poly (vinyl chloride) (PVC) contained in plastic waste during pyrolysis. Therefore, inhibiting chlorinated organic compounds production during co-pyrolysis is indispensable for obtaining the upgraded fuel.

It is well known that the lower rank coal has ability of cation exchange through the carboxyl group in coal [11–27]. Arpa et al. utilized the cation exchange property of low rank coal for removal of heavy-metal cations in waste water from a mining industry plant [27]. It was considered that carboxylic and phenolic hydroxyl functional groups present on coal surface were the adsorption site to remove cations from the waste water via ion exchange. They concluded that the use of low rank coal was considerably effective in removing Hg, Cd and Pb cations from the waste water [27].

One of the recovery processes of chlorine in PVC, pyrolysis of PVC with metal sorbents, such as zinc oxide in tyre rubber [28], iron oxides in converter dust [29] and sodium in glass powder [30], were reported. After pyrolysis of PVC with these metal sorbents, metal chloride was formed and separated as water soluble constituent [28–30]. Cation exchanged coal is obtained by stirring the lower rank coal in an aqueous solution containing heavy metal. Therefore, the authors are investigating about removal of chlorine as metal chloride by co-pyrolysis of plastic waste and cation exchanged coal. In this study, effects of kind of heavy metal and the reaction conditions upon inhibition of chlorinated organic compounds production during co-pyrolysis are discussed from the remained contents of chlorine and metal in the resulted upgraded fuel.

2. Methods and materials

2.1. Chemicals

Upon cation exchange treatment of demineralized Morwell brown coal, copper (II) sulfate pentahydrate (CAS No. 7758-99-8; over 99.5% purity) and lead (II) nitrate (10,099-74-8; over 99.5% purity) of special grade (Japanese Industrial Standards) were used as aqueous solution without further purification. Upon pyrolysis of cation exchanged coal, poly (vinyl chloride) (9002-86-2; average Mw: less than 80,000, average Mn: less than 47,000) was added without further purification. Upon co-pyrolysis of poly (vinyl chloride) with demineralized coal, powdery copper (7440-50-8; over 99.9% purity) of special grade was added without further purification. They were commercially purchased from Wako Pure Chemical Industries, except for poly (vinyl chloride) from Sigma-Aldrich Co. LLC.

2.2. Demineralization

The experimental scheme for demineralization and cation exchange treatment of coal described below is shown in Fig. 1.

A brown coal, Morwell (Australia), was pulverized, passed through a 100 mesh screen, and dried for 3 h under vacuum at 110 °C before use. The raw coal (22 g) was magnetically stirred in

1.0 N HNO₃ aqueous solution (880 ml) at 25 °C for 24 h. After the treatment, the suspension was filtered and rinsed with deionized water until pH in filtrate became 7.0. The residual demineralized coal was dried for 10 h under vacuum at 110 °C.

2.3. Cation exchange treatments

Aqueous solutions of copper (II) sulfate (1.0 N) and lead (II) nitrate (1.0 N) were prepared. The demineralized coal (22 g) with the desired metal salt aqueous solution (880 ml) was magnetically stirred in a sealed flask at 25 °C for 24 h. The suspension was filtered and rinsed with deionized water until pH in filtrate became 7.0. After these cation exchange treatments described above were repeated, cation (copper or lead) exchanged coal was prepared by drying the residue for 10 h under vacuum at 110 °C.

2.4. Co-pyrolysis

The experimental scheme for co-pyrolysis of PVC with coal described below is summarized in Fig. 2.

Each exchanged coal (7 g) and PVC (0.4 g) with a desired amount of water as a solvent was placed in a 100 cm³ autoclave with a magnetic drive agitator. After the autoclave was sealed, the air inside was replaced with N₂ gas and the autoclave was pressurized with 2.0 MPa of nitrogen gas. The autoclave was heated to a desired temperature (200, 250, or 300 °C) in an external electric furnace and co-pyrolysis process was held at that temperature for a desired time (0, 30, or 60 min). After co-pyrolysis process was finished, the autoclave was air-cooled and the gaseous products (gas) were collected in a Tedlar bag and analyzed using GC-TCD. The products remaining in the reactor were filtered and rinsed with water. The water insoluble (WI; upgraded fuel) material was prepared by drying the residue. After water was evaporated from the filtrate, the water soluble (WS) material was obtained.

2.5. Quantification of chlorine

The remained contents of chlorine and metal in the upgraded fuel were calculated using the results of chlorine content analyzed by the high temperature combustion-ion chromatography, and ash content measured by the proximate analysis. Content of chlorine in

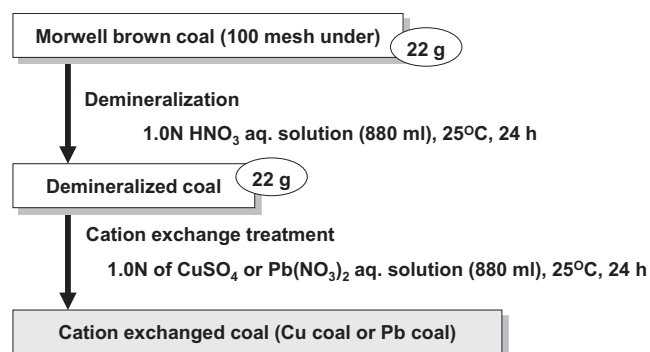


Fig. 1. Experimental scheme for demineralization and cation exchange treatment of coal.

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