



Full Length Article

A novel process for the production of aromatic hydrocarbons from brown coal in water medium by hydrothermal oxidation and catalytic hydrothermal decarboxylation



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ABSTRACT

With no use of hydrogen or a hydrogen donor, a novel process is proposed for the production of aromatic hydrocarbons from brown coal in water medium, which consists of hydrothermal oxidation at 240 °C and Cu_2O -catalysed hydrothermal decarboxylation at 350 °C. Using this hydrothermal oxidation and catalytic hydrothermal decarboxylation method, aromatic carboxylic acids were formed from brown coal by an oxidation process, and then decarboxylated to the corresponding aromatic hydrocarbons. The validity of the decarboxylation method was examined using several aromatic carboxylic acids as model compounds for the acid products after hydrothermal oxidation of brown coal, including *o*-phthalic acid, isophthalic acid, terephthalic acid, hemimellitic acid, trimellitic acid, trimesic acid, 1-naphthoic acid, 2-naphthoic acid, and 2,6-naphthalic acid. Use of Cu_2O catalyst increased the decarboxylation yields of all the aromatic carboxylic acids. Especially for benzene carboxylic acids, all decarboxylation yields were above 90% with 100% selectivity. The Cu_2O -catalysed hydrothermal method was proven to be effective, not only for the decarboxylation reactions from monocarboxylic acids to hydrocarbons, but also for the decarboxylation reactions from tricarboxylic acids to dicarboxylic acids and from dicarboxylic acids to monocarboxylic acids. In the presence of alkali and oxygen during the oxidation process, various valuable aromatic hydrocarbons and heterocyclic compounds, especially benzene, were obtained from Loy Yang coal using the hydrothermal oxidation and catalytic decarboxylation process. Based on analyses of aromatic carboxylic acids or ions before and after the decarboxylation process, it was found that decarboxylation reactions were the major reactions and the use of Cu_2O was effective not only for the decarboxylation from monocarboxylic acids but also from polycarboxylic acids to monocarboxylic acids, consistent with the results for the model aromatic carboxylic acids. Additionally, it was found that a Cu_2O catalyst was also effective for the conversion of 'heavy' compounds in oxidised coal to 'light' compounds.

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1. Introduction

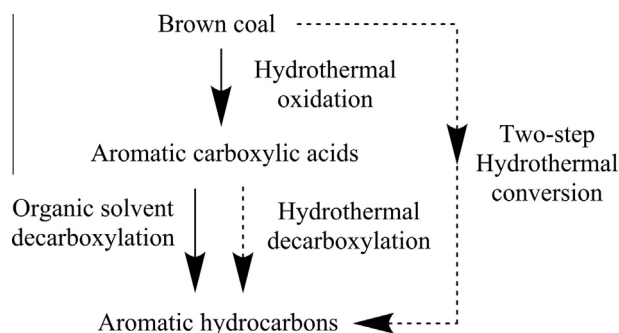
Brown coal, or lignite, is abundant worldwide at a much cheaper price than high-rank coal, and is regarded as one of the most important resources for chemicals, especially aromatic hydrocarbons, due to its rich aromatic content [1]. Despite its high moisture content, low heating value - caused by intrinsic oxygen functional groups [2] - and high spontaneous combustibility after drying, there are many methods to produce aromatic hydrocarbons from brown coal, such as pyrolysis, direct liquefaction, and indirect

liquefaction. However, the need for high energy during the drying process, high temperature, and the use of expensive hydrogen or hydrogen donors are obvious drawbacks.

A combination method of oxidation and decarboxylation is a feasible approach to convert brown coal to aromatic hydrocarbons with no use of hydrogen or hydrogen donors under mild conditions [3–8]. In the oxidation process, aromatic carboxylic acids are obtained from coal, and then during the decarboxylation process, carboxylic functional groups in aromatic carboxylic acids are removed to form aromatic hydrocarbons. Because the moisture content of brown coal is usually higher than 50% and the drying process consumes a large amount of energy, it is significant to realise both oxidation and decarboxylation processes in a water medium. Scheme 1 shows the concept of hydrothermal oxidation and

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Scheme 1. Concept of hydrothermal oxidation and hydrothermal decarboxylation process for the production of aromatic hydrocarbons from brown coal.

hydrothermal decarboxylation process for the production of aromatic hydrocarbons from brown coal. The solid and dash lines correspond to the conventional processes and our proposed processes, respectively.

Most oxidation methods for the production of aromatic carboxylic acids from coal are performed in aqueous media [9], such as the alkali-O₂ method [10–12], the H₂O₂ method [13], and the HNO₃ method [14]. However, the high stability of aromatic carboxylic acids in hot water limits their further hydrothermal decarboxylation to aromatic hydrocarbons greatly [15].

Cu-based, Ag-based, and Pd-based catalysts have been shown to be effective for the decarboxylation or protodecarboxylation of aromatic carboxylic acids, but usually organic solvents, such as quinoline, N-methylpyrrolidone, tetrahydrofuran, dimethyl sulphoxide, or toluene [16–25], are indispensable. At present, it is still rare to use a catalyst for the hydrothermal decarboxylation of aromatic carboxylic acids. In 2004, Matsubara and co-workers reported the combination of a palladium catalyst and hydrothermal water [26]. At 250 °C and 5 MPa for 14 h, 1-naphthoic acid was converted to naphthalene in 74% yield. Then, in 2015, our group realised the efficient decarboxylation of stable benzoic acid to benzene using a Cu₂O catalyst and subcritical water at 350 °C (Cu₂O-SbCW system) [27]. The conversion yields reached more than 90% in 90 min with 100% selectivity. This result was only about the reaction from benzoic acid to benzene, but it was enlightening to break through the bottleneck of the hydrothermal decarboxylation of aromatic carboxylic acids, and helpful to finally achieve the production of aromatic hydrocarbons from brown coal by hydrothermal oxidation and hydrothermal decarboxylation. Considering the various reported mono- and polycarboxylic acids obtained from the oxidation of brown coal, such as the benzene carboxylic acids [28], it is important to study the applicability of the Cu₂O-SbCW system to different carboxylic acids before examining oxidised brown coal.

Here, the decarboxylations of model aromatic carboxylic acids including *o*-phthalic acid, isophthalic acid, terephthalic acid, hemimellitic acid, trimellitic acid, trimesic acid, 1-naphthoic acid, 2-naphthoic acid, and 2,6-naphthalic acid, were performed using the Cu₂O-SbCW system. Furthermore, the Cu₂O-SbCW system was used to perform the decarboxylation of the products prepared by the hydrothermal oxidation of brown coal, with no use of hydrogen or hydrogen donors.

2. Experimental

2.1. Coal sample

Australian brown coal, Loy Yang coal (LY), was used without drying or grinding. Table 1 shows the ultimate and proximate anal-

Table 1
Ultimate and proximate analyses of LY coal.

Coal name	Ultimate analysis [wt%, daf]					Proximate analysis [wt%, db]			Moisture [wt%]
	C	H	N	S	O ^a	FC	VM	Ash	
LY	66.6	5.3	0.5	0.2	27.4	50.4	48.1	1.5	58.4

^a By difference.

yses of LY, including elemental compositions, fixed carbon (FC) and volatile matter (VM) contents, ash content, and water content (moisture). LY had a high moisture content, of 58.4%, and a high oxygen content, of 27%. The ash content of LY was only 1.5%, and the sulphur content was as low (0.2%).

2.2. Chemical reagents

The aromatic carboxylic acids included benzoic acid, *o*-phthalic acid, isophthalic acid, terephthalic acid, hemimellitic acid, trimellitic acid, trimesic acid, 1-naphthoic acid, 2-naphthoic acid, and 2,6-naphthalic acid. The information of all the model aromatic acids was shown in Table S1. Copper (I) oxide (Cu₂O, 99.5%, powder, Wako Pure Chemical Industries, Ltd.) was used as a catalyst, with no further modification. The surface area of commercial Cu₂O was 0.7 m²/g. The organic solvent dichloromethane (CH₂Cl₂, 99.5%, Wako Pure Chemical Industries, Ltd.) was used for product recovery and analyses.

2.3. Apparatus

The apparatus consisted of a cylinder-shaped autoclave with an internal volume of 50 cm³ and a rocking electric furnace [27]. The autoclave was equipped with a pressure gauge amplifier and a thermocouple to monitor the inner pressure and temperature, respectively.

2.4. Hydrothermal decarboxylation of model aromatic carboxylic acids

The experimental process followed our previous report [27]. The model carboxylic acids used here include six benzene carboxylic acids (*o*-phthalic acid, isophthalic acid, terephthalic acid, hemimellitic acid, trimellitic acid, and trimesic acid) and three naphthalene carboxylic acids (1-naphthoic acid, 2 naphthoic acid and 2,6-naphthalic acid). All relevant decarboxylation reactions were shown in Chart 1 and can be expressed by reactions (I) to (XIII).

In a typical experiment about the hydrothermal decarboxylation of *o*-phthalic acid, 1.2162 g of Cu₂O, 1.4337 g of *o*-phthalic acid, and 28.1 g of distilled water were fed into the autoclave and the interior air was replaced with nitrogen. The autoclave was inserted into the furnace, heated to the desired temperature. The temperature and pressure inside the autoclave were recorded during each reaction. The time required to reach 350 °C was ~26 min and the pressure increased from an initial pressure of 0.1 MPa to autogenous pressures. After the desired 60-min reaction time, the autoclave was removed from the furnace and allowed to cool to room temperature. The gaseous product (~99.9% of that is carbon dioxide) was collected in a gas bag by washing with nitrogen. The other products, which were the oil and water phases, and the solid catalyst, were recovered by inverting the autoclave and washing with CH₂Cl₂. After centrifugation (6000 rpm, 15 min), the solid catalyst was separated from the solution and dried at 80 °C for 24 h in a vacuum oven. The remaining solutions, composed of the oil phase fraction dissolved in CH₂Cl₂ and the H₂O phase fraction, were separated using a separating fun-

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