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VARIOUS TECHNOLOGIES

A Strategy for Total Recovery of Residue from Terephthalic Acid Production Process[1]

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Abstract—Terephthalic acid is generally produced via oxidation of *p*-xylene. In this process, a large quantity of residue is produced containing cobalt, manganese, and bromine catalysts as well as by-products such as benzoic acid. Our purpose is to totally recover this residue. Extraction by water has been used as an efficient method to recover catalyst from this residue. In this study, the best condition for extraction was obtained at water/residue dilution ratio of 6 : 1, extraction temperature of 45°C and extraction time of 40 min. Efficiency of catalyst recovery was 92 wt % at these conditions. The catalyst containing extracted solution can be reused in the oxidation process after being concentrated by an evaporator. The benzoic acid content of the residue is also recovered by recrystallization. The best condition for recrystallization was achieved at water/residue dilution ratio of 4 : 1 and dissolution and crystallization temperatures of 95 and 25°C, respectively. Recovery efficiency and purity of benzoic acid were 85 and 97 wt %, respectively, at these conditions. The recovered benzoic acid can be used in many applications. Once catalysts and benzoic acid were recovered from residue, whatever remained was terephthalic acid which was recovered by up to 98 wt % with a purity of 95% and can be recycled to the purity unit.

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INTRODUCTION

Terephthalic acid (TA) is one of the raw materials used in the synthesis of polyester. Considering the increasing demand for polyester, production of TA has been studied in recent years [1]. Basically, terephthalic acid is used as a raw material for the manufacturing of polyethylene terephthalate (PET) which is used in the course of production of textiles, industrial fibers, bottles, etc. [2, 3]. Each year, several million tons of terephthalic acid are produced world wide, 70% of which is produced by a catalyst system developed by the Science Design and Amoco Company [4, 9]. In this process, terephthalic acid is produced by oxidation of *p*-xylene in the presence of acetic acid as the solvent as well as homogeneous catalysts of cobalt(II) acetate, manganese(II) acetate, and hydrogen bromide (Fig. 1).

Several by-products are formed in the Amoco oxidation process, such as *p*-toluic acid, 4-carboxybenzaldehyde (4-CBA), and benzoic acid (Fig. 1). The former two are manufactured by the step oxidation of *p*-xylene [10], while the latter is formed by decarboxylation of terephthalic acid under low pH value and high temperature condition in the oxidation reactor [11]. 4-CBA is the major impurity crystallized together with the terephthalic acid due to their similar structures. Therefore, the produced terephthalic acid is an impure compound known as raw terephthalic acid. The presence of 4-CBA, decreases the average molecular weight of polyesterand making it to appear in a yellow color. This impurity reduces polyester quality necessitating a final purification process [12]. For this purpose, a purification process was developed by Amoco Company as the provider of up to 60% of the terephthalate demand in the world [13, 14]. In this process, the aldehyde group of 4-CBA is hydrogenated

[1] The text was submitted by the authors in English.

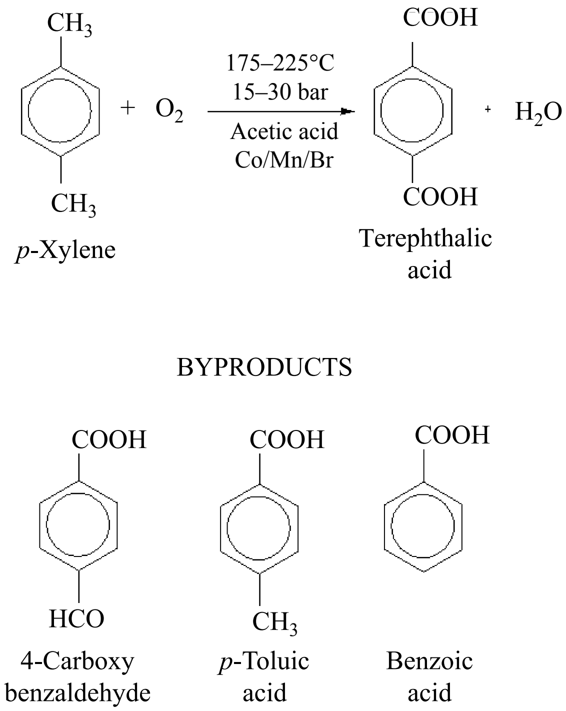

Fig. 1. Overall reaction of Amoco oxidation process and chemical structure of by-products.

in the presence of palladium catalysts and water. Under these conditions, 4-carboxybenzaldehyde converts to *p*-toluic acid which is more soluble in water and can be easily separated from the raw terephthalic acid.

Due to operating conditions in the oxidation step of the Amoco process, a large amount of residue is produced which contains cobalt, manganese, bromine, and organic compounds such as benzoic acid and terephthalic acid. These valuable compounds should be recovered by convenient methods because disposing them into the environment is dangerous. Although almost all existing methods for catalyst recovery incorporate a solvent extraction step, but purification methods are different. In the method described in [15, 16], the catalyst content of extract solution is precipitated by oxalate and carbonate. Another procedure passed the extract solution through anion-exchange resin [17]. These methods have several disadvantages such as bromide loss and column fouling, while they required too expensive equipment. Tondgouyan Petrochemical Company burns its residue in a special furnace and extracts catalysts components from ash [18]. The associated problems are loss of valuable compounds such as benzoic acid while polluting the environment via organic compounds combustion.

Several methods are proposed to recover benzoic and terephthalic acids from the residue. Some examples include distillation and solvent extraction procedures [19, 20]. These methods have several disadvantages: equipment's fouling due to benzoic acid crystallization, their need for an expensive distillation column as well as environmental pollution by organic solvents.

This study provides an economic and environment-friendly method for total recovery of residue produced in Tondgouyan Petrochemical Company. Catalysts components are recovered from residue by water extraction process. In addition, this method makes possible the recovery of valuable compounds such as benzoic and terephthalic acid. Recovered catalysts can be reused in the oxidation process. Recrystallization in water is used to recover benzoic acid from the solid residue. The recovered benzoic acid has various applications and can be used in different industries. Once the recovery of catalysts and benzoic acid from residue was accomplished, whatever remains is raw terephthalic acid that can be sent to a purification unit.

EXPERIMENTAL

Analysis

Amounts of cobalt and manganese were measured according to ASTM D-3558 and ASTM D-858 standards, respectively. For this purpose anatomic adsorption spectrophotometer was used (AA-220, made by Varian Inc. Co.). The amount of bromine was measured by a UV spectrophotometer (DR 4000, made by Hach Company) according to ASTM D-1246 standard. Organic compounds of the solid residue (benzoic acid and terephthalic acid) were analyzed by

Table 1. HPLC chromatography analysis conditions

Wavelength	Detector	Pressure	Mobile phase	Sample volume	Column temperature	Column dimension	Column type
230 nm	UV-VIS	84 bar	ACN/HOAC (1 : 1)	0.7 mL	25°C	150 mm ×4.6 mm	Agilent C18

a HPLC (Agilent Technologies, 1200 series made by Santa Clara Company) [21]. Analysis conditions of HPLC are mentioned in Table 1. It should be noted that quantity analysis was done based on the area under the peaks.

Residue Sample

After separating terephthalic acid, solvent and catalysts from the reactor output in Tondgouyan Petrochemical Company, a large amount of residue is remained. This residue is a wet yellow solid. As the analysis results show, residue sample contains various organic and inorganic compounds (Table 2).

Table 2. Chemical analysis of residue

Weight percent, wt %	Components
0.64	4-CBA
27.42	Benzoic Acid
1.00	Bromine
0.82	Cobalt
0.81	Manganese
1.00	*p*-Toluic Acid
11.10	Terephthalic Acid
57.21	Water

Schematic design. The residue produced in the oxidation process of *p*-xylene contains cobalt, manganese, bromine and organic compounds such as benzoic acid and terephthalic acid. Our proposal for the total recovery of these compounds from the residue is shown in Fig. 1. According to this technique, the catalysts were separated through water extraction. Organic compounds, mainly containing benzoic acid and terephthalic acid, were separated from the residue via recrystallization in water due to their different solubility in water at high temperatures [10, 22]. For this purpose, the solid residue was filtered after being completely mixed with water. The catalyst containing filtrate can be reused in the oxidation process once it gets concentrated. Although the concentration process can be accomplished via physical methods such as reverse osmosis (RO) and ion-exchange resins, however, these are expensive methods after which there may be an occurrence of membrane fouling. In addition, chemical methods such as precipitation can contribute to cobalt and manganese concentration only while bromine may still be wasted.

The remaining solid on the filter was mixed with hot water to separate benzoic acid and terephthalic acid from each other. Under these conditions, benzoic acid was dissolved in water while terephthalic one remained insoluble. The obtained slurry was filtered at the same temperature with the solid remaining on the filter to be terephthalic acid which can be recycledtothe purification unit. The temperature of filtrate was then reduced to crystallize the benzoic acid. Benzoic acid crystals could be separated by a filter before being used in various industries such as synthesis of phenol, Caprolactam, colors, drugs, etc. [22]. In fact, this technique divided solid residue into three categories of catalysts, benzoic acid and raw terephthalic acid, without any loss of original materials or any secondary pollution.

Solid-liquid extraction. Solid-liquid extraction method was used to recover catalysts containing cobalt, manganese, and bromine. For this purpose, solid residue was completely mixed with water at different weight ratios. The obtained slurry was filtered to separate dissolved catalyst from insoluble organic compounds. Then, catalyst containing solution was analyzed to measure the recovery efficiency of cobalt, manganese, and bromine. The insoluble organic compounds were sent to recrystallization process to recover benzoic acid.

Recrystallization. Recrystallization was used to separate benzoic acid from the solid obtained in the

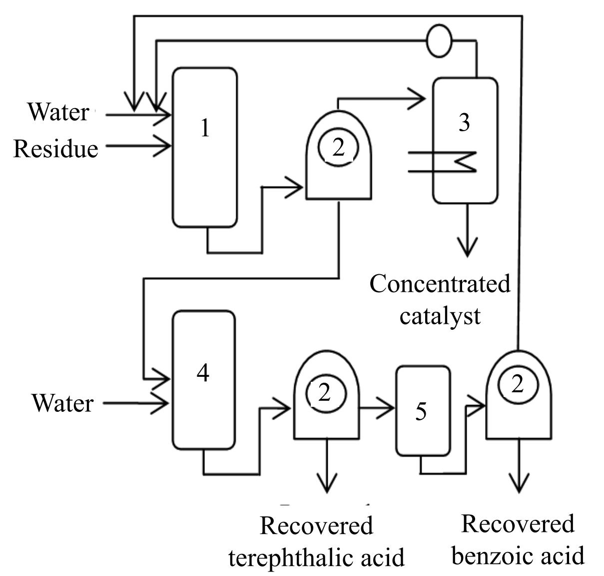

Fig. 2. The schematic of total recovery of residue. (1) Mixing tank, (2) 4 filter, (3) evaporator, (4) condensor, (5) dissolution.

Table 3. Effect of dilution ratio on catalysts recovery efficiency

Extraction efficiency, %			Dilution ratio
bromine	manganese	cobalt	
67.5	51.0	35.0	2
75.2	56.7	50.7	4
80.9	63.1	65.3	6
86.2	65.9	71.1	8
90.2	67.2	73.3	10

Table 4. Effect of extraction temperature on catalysts recovery efficiency

Extraction efficiency, %			Temperature, °C
bromine	manganese	cobalt	
80.8	62.8	64.0	25
81.7	63.3	66.5	35
83.5	64.1	69.5	50
85.8	65.6	74.6	65
87.2	68.0	83.6	80

liquid-liquid extraction process. For this purpose, the solid was completely mixed with hot water at different weight ratios before the obtained slurry was filtered at high temperature. After drying, the remaining solid on the filter was analyzed by HPLC. The filtrate temperature was reduced so as benzoic acid crystals were appeared. Once these crystals were dried, they were analyzed by HPLC to measure the recovery efficiency and purity of the obtained benzoic acid.

RESULTS AND DISCUSSIONS

Catalysts Recovery

Effect of dilution ratio. Water/residue dilution ratio is an essential factor contributing to catalyst extraction. In the present study, extraction efficiency of catalysts containing cobalt, manganese, and bromine was studied at water/residue dilution ratios of 2, 4, 6, 8, and 10. Extraction temperature and mixing time were 25°C and 10 min, respectively. As shown in Table 3, by increasing dilution ratio, the extraction efficiency exhibits an early quick raise, while it increases slightly at higher dilution ratios. In addition, increasing dilution ratio led to the need for larger equipment and higher energy consumption in the evaporator. Therefore, the dilution ratio of 6 was determined as the optimum value.

Effect of extraction temperature. In this section, recovery efficiency is studied at extraction temperatures of 25, 35, 50, 65, and 80°C with dilution ratio and extraction time of 6 and 10 min, respectively. As shown in Table 4, higher temperatures are associated with an increase in the extraction efficiency which is probably due to the increased solubility of organic compounds and release of trapped catalysts. However, increasing the solubility of organic compounds, especially benzoic acid, and recycling this compound to the oxidation reactor leads to a decrease in the oxidation efficiency of *p*-xylene. According to these results, the temperature of 45°C was determined as the optimum temperature at which the concentration of organic compounds is kept at lower values at an acceptable extraction efficiency.

Effect of extraction time. To study the effect of extraction time on recovery efficiency, the extraction was done at a dilution ratio of 6 and a temperature of 45°C for various extraction times: 10, 20, 30, 40, and 50 min. As shown in Table 5, longer extraction times led to higher efficiency in catalyst recovery. However, the long extraction times increased the total cost. Therefore, an extraction time of 40 min was determined as the optimum one considering the slight increase in the recovery efficiency for longer times.

Benzoic Acid Recovery

Effect of solubility temperature. An essential parameter in benzoic acid recrystallization is the solubility temperature. Recovery efficiency and purity of benzoic acid were studied in solubility temperatures of 70, 80, 90, and 95°C with a dilution ratio of 3 and a crystallization temperature of 20°C. Recovery efficiency of benzoic acid was increased at higher temperatures, as shown in Table 6. However, benzoic acid purity decreased at higher temperatures due to an increase in organic compounds solubility. On the other hand, the benzoic acid purity was high at lower temperatures, although low recovery efficiency was obtained. However, high temperature is desired where the recovery efficiency change is more significant than that of the purity. Since the benzoic acid is volatile in vapor state, pressure equipment should be used to prevent the water from boiling. The use of this equipment led

Table 5. Effect of extraction time on catalystsrecovery efficiency

Extraction efficiency, %			Time, min
bromine	manganese	cobalt	
87.2	74.3	76.3	10
89.3	81.0	81.8	20
90.9	86.8	86.9	30
92.5	91.9	91.2	40
93.4	92.8	92.1	50

Table 6. Effect of solubility temperature on benzoic acid recovery efficiency and purity

Purity, %	Recovery efficiency, %	Temperature, °C
98.6	16.3	70
97.5	28.8	80
97.1	51.9	90
96.8	81.3	95
94.7	65.5	100

Table 7. Effect of crystallization temperature on benzoic acid recovery efficiency and purit

Purity, %	Recovery efficiency, %	Temperature, °C
98.6	72.3	40
97.7	76.7	30
97.1	81.3	20
96.8	82.2	10
96.5	82.9	0

Table 8. Effect of dilution ratio on benzoic acidrecovery efficiency and purity

Purity, %	Recovery efficiency, %	Dilution ratio
94.1	34.2	1
95.2	59.5	2
97.1	81.3	3
97.4	85.3	4
97.2	86.0	5

to an increase in investment costs, so that the desired solubility temperature was determined at 95°C.

Effect of crystallization temperature. In this section, the effect of crystallization temperature on benzoic acid efficiency and purity was studied at 40, 30, 20, 10, and 0°C. The dilution ratio and solubility temperature were set at 3 and 95°C, respectively. As shown in Table 7, lower crystallization temperatures led to an increase in the recovery efficiency while they decreased the purity slightly. On the other hand, higher crystallization temperatures caused lower recovery efficiencies due to loss of benzoic acid. Although lower temperatures were desired, but supplying such temperatures may lead to increase in total costs. Therefore, the temperature of 25°C was chosen as the best crystallization temperature.

Effect of dilution ratio. Recovery efficiency and purity of benzoic acid were studied at water/residue dilution ratios of 1, 2, 3, 4, and 5. Solubility and crystallization temperatures were set at 95 and 25°C, respectively. Dilution ratios of less than 4 lead to lower recovery efficiencies and purity values (Table 8). However, dilution ratios of higher than 4 led to a small increase in benzoic acid recovery efficiency and purity while they were associated with a need for larger equipment, so as a dilution ratio of 4 was determined as the best dilution ratio.

Terephthalic Acid Recovery

In the recrystallization process, the solid residue was mixed with water at the dilution ratio of 4 and temperature of 95°C. Then, the obtained slurry was filtered and the remained solid on the filter was analysed by HPLC. The results showed that this solid was raw terephthalic acid with 95% purity which was recovered by up to 98%.

CONCLUSIONS

All components of the residue can be recovered economically without any secondary pollution. The extracted solution containing catalysts components can be reused in the oxidation reactor after it gets concentrated. In this way, catalyst consumption as well as environmental pollution by heavy metals is reduced. The present work not only prevented organic compounds from being burnt, but also recovered them efficiently.

The recovered benzoic acid can be used in various applications such as producing phenol, Caprolactam, color intermediates, conservators, insecticides, medications, softeners, etc. The recovered terephthalic acid can be recycled to purification unit increasing the terephthalic acid production capacity.

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