

Development on Recovery of MFB from Industrial Waste without Second Pollution

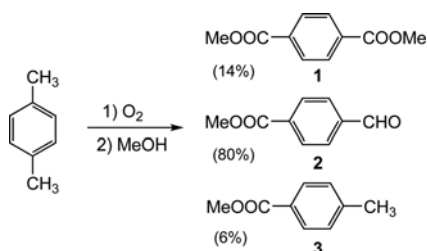
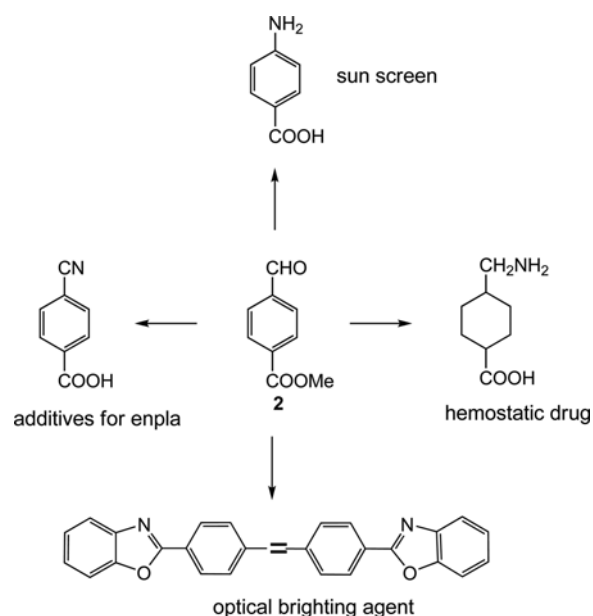
Kyung Duck Kim, Young Yu, Hyo Jin Jeong, Ham Mi Jung, Ki Lim Kim, Ah Na Kim,
Oyunerdene Dagvajantsan, Gyoo Soon Park, and Seok Chan Kim*Department of Bio & Nano Chemistry, Kookmin University, Seoul 136-702, Korea. *E-mail: skim@kookmin.ac.kr
Received August 14, 2012, Accepted October 19, 2012**Key Words :** Methyl 4-formylbenzoate (MFB), Methyl 4-((hydroxyimino)methyl)benzoate (MHB), Oxime hydrolysis, Industrial waste, Second pollution

DMT (dimethyl terephthalate, **1**) is well-defined raw material for PET production.¹ In commercial DMT **1** has been synthesized from *p*-xylene in air oxidation followed by esterification (Figure 1). In this process, partial oxidation of xylene gave rise to major by-products MFB (methyl 4-formylbenzoate, **2**) and MMB (methyl 4-methylbenzoate, **3**).

After separation of DMT **1** by distillation under reduced pressure, residues containing DMT **1**, MFB **2**, and MMB **3** with 14%, 80%, and 6%, respectively have been disposed by open burning/detonation. The use of open burning/detonation is becoming unacceptable due to public concern and environmental regulations. Therefore, the chemical conversion study of MFB **2** to higher value products would be highly desirable.² The West have used MFB **2** as a versatile starting material for the design of different types of valuable products (Figure 2).³

During our research on conversion of MFB **2** into high valuable materials, we have to develop new purification protocol of crude MFB **2** without second pollution. Herein, we would like to report recovery process of MFB **2** from residual waste.

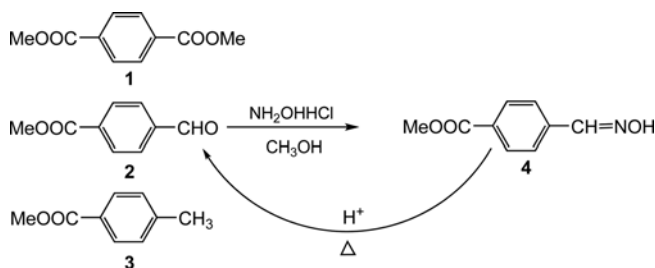
The conversion of aldehyde functional group into aldoxime group is one of the well-known operations in organic chemistry.⁴ Therefore, among DMT **1**, MFB **2**, and MMB **3** only MFB reacted with hydroxylamine in methanol and water solution to give MHB (methyl 4-((hydroxyimino)methyl)benzoate, **4**) which was easily crystallized out. These crude MHB **4** was further purified by refluxing with boiling toluene and all soluble impurities in toluene such as unreacted DMT **1** and MMB **3** were completely removed. After filtration and dry pure MHB **4** was obtained 95% yield based on original crude MFB **2** content. Toluene was recovered from mother liquor by distillation and reused.

Figure 1. The residues after DMT **1** separation from *p*-xylene.Figure 2. Various fine chemicals from MFB **2**.

The hydrolysis of aldoximes proceeds easily by heating in the presence of various inorganic acids, and the aldoximes decompose into the corresponding aldehydes, and hydroxylamine.⁵ Therefore, treatment of MHB **4** with various inorganic acids gave back to crude MFB **2**. Among them, we observed 3 equiv. of hydrochloric acid in refluxing toluene afforded best result (Figure 3).

Final purification of MFB **2** was accomplished with extraction with toluene followed by evaporation of resulting toluene layer in 98% yield.

Figure 4 shows block diagram for mass production of

Figure 3. Formation and hydrolysis of MHB **4**.

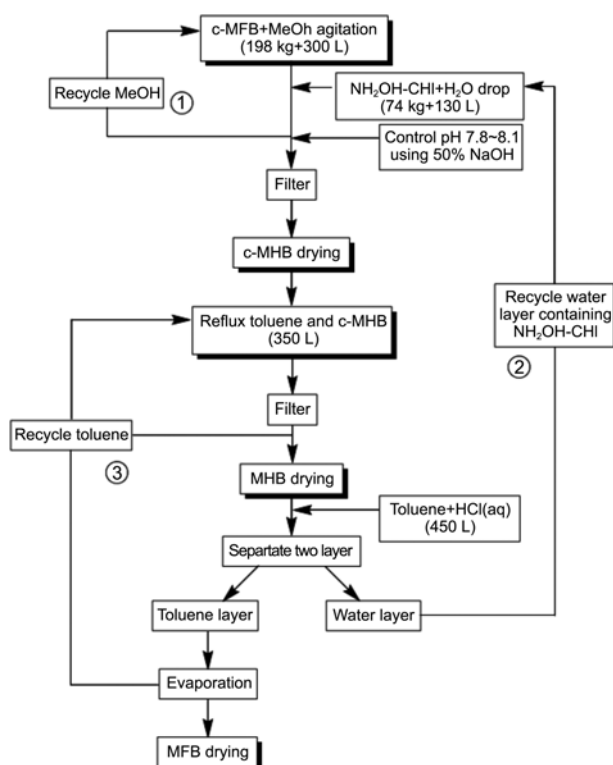


Figure 4. Block diagram for mass production of MFB 2.

MFB 2 from industrial waste through MHB 4. As shown in diagram, methanol, toluene, and water layer containing hydroxylamine hydrochloride were completely recycled without second pollution. The performances of recycled materials were tested and the results were shown in Table 1. Since utilization of all recycled materials to obtain MFB 2 through MHB 4 was successful, this process is suitable for purifying MFB 2.

In summary, we have developed MFB 2 purification process from industrial waste. Main advantage of this process is that all materials and solvents used were recycled and reused without second pollution. The future works including conversion of MFB 2 into high valuable fine chemicals are under investigation in our laboratory.

Experimental Section

Methyl 4-((hydroxyimino)methyl)benzoate (4). Crude MFB (198 kg) and methanol (300 L) was introduced in 1,000 L reactor at RT. This resulting mixture was heated to

40 °C for 1 h. Hydroxylamine hydrochloride (74 kg) in H₂O (130 L) was added over 5 h at RT. After addition, additional stirring was continued for 1 h at room temperature (the reaction progress was monitored by HPLC) and 50% aqueous NaOH solution (80.0 L) was added until pH 7.8. Methanol was recovered by distillation and resulting solid was filtered. After dry for 8 h at 60 °C, crude MHB was obtained (190 kg, 87% purity), which was dissolved in refluxing toluene (350 L) and cooled down to RT. The resulting pure solid MHB (165 kg, 95%, purity 99.5%) was filtered and toluene was collected by distillation under reduced pressure for reuse. mp 129-131 °C; ¹H NMR (300 MHz, DMSO-*d*₆) δ 11.58 (s, 1H), 8.23 (s, 1H), 7.70 (d, *J* = 6.9 Hz, 2H), 8.0 (d, *J* = 7.0 Hz, 2H), 3.86 (s, 3H); ¹³C NMR (75 MHz, DMSO-*d*₆) δ 166.4, 148.0, 138.2, 130.5, 130.2, 127.1, 52.7.

Methyl 4-Formylbenzoate (2): To a solution of MHB (150 kg) in toluene (450 L) at RT was added aqueous hydrochloric acid (220 L) over 2 h. The resulting mixture was refluxed 2 h, and then cooled down to RT. Two layers were separated. Water layer containing hydroxylamine hydrochloride was collected for reuse. Toluene layer was washed with water (120 L) and evaporation of toluene gave pure MFB (135 kg, 98%, purity 99.9%). mp 63-65 °C; ¹H NMR (300 MHz, DMSO-*d*₆) δ 10.1 (s, 1H), 8.06 (m, 4H), 3.93 (s, 3H); ¹³C NMR (75 MHz, DMSO-*d*₆) δ 193.3, 166.0, 139.6, 134.8, 130.3, 130.1, 53.0.

Acknowledgments. This research was supported by the Kookmin University Research fund and also supported by Ministry of Knowledge Economy, Republic of Korea.

References

1. Fukushima, K.; Coulembier, O.; Lecuyer, J. M.; Almegren, H. A.; Alabdulrahman, A. M.; Alsewailam, F. D.; Mcneil, M. A.; Dubois, P.; Waymouth, R. M.; Horn, H. W.; Rice, J. E.; Hedrick, J. L. *Journal of Polym. Sci., Part A: Polym. Chem.* **2011**, *49*, 1273.
2. (a) Dees, J. G.; Barts, S. *U.S. Patent*. 5,470,998. **1995**. (b) Hoarau, C.; Couture, A.; Deniau, E.; Grandclaoudon, P. *J. Am. Chem.* **2002**, *67*, 5846. (c) Yamataka, H.; Nagase, S. *J. Am. Chem. Soc.* **1998**, *120*, 7530.
3. (a) Suzuki, K.; Kuroda, H.; Nabeta, S. *U.S. Patent*. 3,875,217. **1975**. (b) Daus, D. G. *U.S. Patent*. 5,332,828. **1994**.
4. (a) Bravo, P.; Pregolato, M.; Resnati, G. *J. Org. Chem.* **1992**, *57*, 2726. (b) LaMattina, J. L.; Suleske, R. T. *Org. Synth. Coll.* **1990**, *7*, 149.
5. (a) Hartman, W. W.; Roll, L. *J. Org. Synth. Coll.* **1955**, *3*, 20. (b) Semon, W. L. *Org. Synth. Coll.* **1941**, *1*, 318.

Table 1. Recycled solvents and reagent data for MHB 4 and MFB 2

	① MeOH (L)	② NH ₂ OH·HCl/water (kg/L)	③ Toluene (L)	Yield (%) / Purity (%)	
				MHB	MFB
First	300	74/130	800	95/99.5	98/99.9
Second	249+(51)	63.6+(10.4) ^a /131	760+(40) ^a	94.2/99.5	96.3/98.3
Third	250+(50)	63.2+(10.8) ^a /131	760+(40) ^a	90/99.5	92.2/96.6

^aRecycled amount+(added amount)