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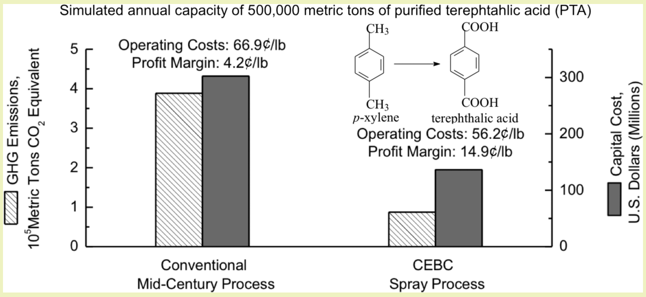
# Terephthalic Acid Production via Greener Spray Process: Comparative Economic and Environmental Impact Assessments with Mid-Century Process

Meng Li,[†,§] Thomas Ruddy,[‖] Darryl Fahey,[§] Daryle H. Busch,[‡,§] and Bala Subramaniam*[,†,§]

[†]Department of Chemical and Petroleum Engineering, [‡]Department of Chemistry, and [§]Center for Environmentally Beneficial Catalysis, University of Kansas, Lawrence, Kansas 66045, United States

[‖]River City Engineering, Lawrence, Kansas 66047, United States

Supporting Information



**ABSTRACT:** Researchers at the University of Kansas, Center for Environmentally Beneficial Catalysis (CEBC) recently reported a spray process concept as a greener alternative to the conventional Mid-Century (MC) process to produce high-purity terephthalic acid (TPA) [<25 ppm 4-carboxybenzaldehyde] in a single step at 200 °C and 15 bar pressure. Plant-scale simulations of the MC process and the spray process, which considers four cases involving different amounts of acetic acid in the feed, are performed assuming a production rate of 500,000 t/yr of high-purity TPA. Comparative economic analyses and life cycle assessments (gate-to-gate and cradle-to-gate) show that the CEBC spray process significantly reduces capital and operating costs by 55% and 16%, respectively, (when using an identical amount of acetic acid in both processes) and also lowers some (such as global warming, acidification, and human health noncancer air potential) but not all adverse environmental impacts when compared to the MC process. These benefits of the CEBC spray process are mainly derived from the avoidance of a subsequent hydrogenation step required in the conventional process for purifying the crude TPA. These results provide valuable guidance for the rational design and development of a continuous spray process that has the potential to be a greener and more sustainable process for making polymer-grade dicarboxylic acids in one step.

**KEYWORDS:** *Terephthalic acid production, Spray process, Comparative economic analysis, Life cycle assessments*

## INTRODUCTION

Terephthalic acid (TPA) is an important monomer for polyethylene terephthalate (PET), a commodity polymer that finds use in fibers, bottles, and films. The well-known Amoco Mid-Century (MC) process (acquired by BP in 1997) is currently the leading industrial technology for TPA production.[1] It involves an oxidation reactor in which air is sparged into the stirred liquid phase containing *p*-xylene (*p*X) and Co/Mn/Br-based catalyst dissolved in aqueous acetic acid, and a subsequent hydrogenation stage to remove 4-carboxybenzaldehyde (4-CBA), the main impurity stemming from incomplete oxidation.[2−4] The TPA purification by hydrogenation employs harsh reaction conditions (275−290 °C and 70−90 bar),[5,6] uses expensive metal catalysts (carbon-supported palladium catalyst), and involves a number of additional processing steps. The hydrogenation step thus accounts for a significant fraction of the capital investment and operating costs. Further, both the hydrogen feedstock as well as the energy required in the hydrogenation step are derived from fossil-based sources that increase environmental burdens. Furthermore, roughly 5% of the acetic acid is destroyed by oxidative burning per pass,[7] resulting in significant solvent loss and $CO_2$ emissions. The makeup acetic acid required to offset the acetic acid burning is one of the primary contributors to the operating cost in conventional TPA production and is therefore a significant factor in the overall economics of the MC process.[8]

The Center for Environmentally Beneficial Catalysis (CEBC) at the University of Kansas recently reported a spray process concept[9−11] that addresses some of the aforementioned sustainability challenges associated with industrial processes for TPA production. In the spray reactor, the reaction mixture is dispersed as fine droplets into a vapor phase containing stoichiometric excess of $O_2$, $CO_2$, and saturated acetic acid vapor. Besides reducing back-mixing of reactants and products, the spray reactor design also enhances the gas/liquid interfacial mass transfer area and allows facile $O_2$ saturation of the liquid phase. These spray reactor attributes promote more complete oxidation to achieve improved TPA selectivity and purity. Consequently, high-purity TPA (<25 ppm 4-CBA) was produced in one step at 200 °C and 15 bar pressure in a 700 mL

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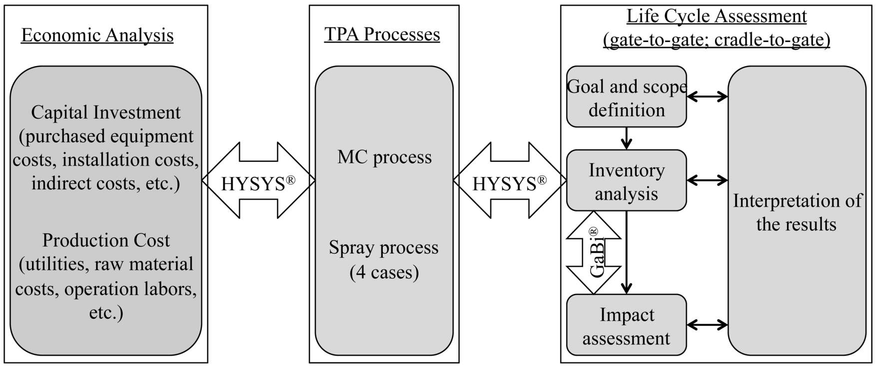

**Figure 1.** Methodological framework for economic and environmental impact assessments of the TPA processes.

semi-batch spray reactor.[11] In sharp contrast, crude TPA product from a conventional stirred reactor contains >1000 ppm 4-CBA[5] requiring further purification to obtain polymer-grade product. Further, gas-phase CO concentrations (an indicator of solvent burning reaction) in the spray reactor is roughly one-fourth of that formed in the MC process,[10] suggesting that the shorter residence times in the spray reactor could mitigate solvent burning.

The avoidance of the energy-intensive hydrogenation section in the spray reactor eliminates a number of processing steps resulting in a reduction in energy requirements as well as capital and operating costs. The lower solvent burning rate reduces not only the cost for making acetic acid but also $CO_2$ emissions. The spray process thus satisfies several principles of green chemistry and green engineering.[12] However, *quantitative sustainability assessment* is essential to not only numerically determine the economic and environmental benefits but, equally importantly, to also identify areas for further improvement in sustainability-related metrics. Such a quantitative assessment is especially insightful when process conditions are different. For example, the *p*X concentration in the demonstrated spray process is 10 times lower compared to the industrial process.[11] Consequently, the processing of larger quantities of acetic acid in the spray reactor would increase not only equipment and energy costs but also the $CO_2$ emissions associated with solvent burning. These adverse effects could either partially or totally offset the potential economic and environmental benefits anticipated by eliminating the hydrogenation step. Clearly, quantitative comparative assessment of the economics and environmental impact assessments of the two processes are essential to unambiguously address and resolve such issues.

Several reported case studies of quantitative economic and environmental impact assessments of process design alternatives provide valuable guidance for the evaluation of this particular spray process. Dunn and Savage[13,14] examined the economic feasibility and the environmental impact of a terephthalic acid process using high-temperature water (HTW) as the reaction medium. They found that a subcritical HTW-based process was equally capital intensive, less energy intensive, and more environmentally benign than the current acetic acid-based process (MC process). Similar methodology of economic and environmental impact analyses has been employed to evaluate alternative chemical processes such as the $CO_2$-based hydroformylation process,[15] solid acid-catalyzed alkylation process in supercritical $CO_2$,[16] liquid-phase $H_2O_2$-based ethylene oxide process,[17] and $H_2O_2$-based propylene oxide process.[18]

The work presented herein is a relatively thorough quantitative evaluation of the CEBC spray technology for TPA production, from both economic and environmental points of view. The conventional MC process is employed as the industrial benchmark, against which the economics and environmental impacts of four different spray reactor case studies using different amounts of acetic acid in the feed are simulated and compared. The results reveal key operating factors that affect the economics and environmental impacts, and provide valuable guidance for process design and optimization.

## ■ METHODOLOGY

Figure 1 depicts the methodological framework for economic and environmental impact assessments of the TPA processes. The methodology involves three tasks: (1) plant-scale simulations of the MC process and the CEBC spray process (four cases with various acetic acid/*p*-xylene ratios in the feed) by Aspen HYSYS software,[19] (2) comparative economic analyses by estimating capital investment and total production cost for each technology, (3) comparative gate-to-gate LCA (life cycle assessment) and cradle-to-gate LCA of both processes to evaluate the relative environmental impacts.

**Process Simulations.** Aspen HYSYS v.7.3[19] (Aspen Technology, Inc.) was employed to perform process simulations. The design basis for both the conventional MC process and the CEBC spray process is a production rate of 500,000 t/yr of purified terephthalic acid (PTA) at a 0.9 stream factor (i.e., 328 on-stream days). Plant-scale data for the simulated conventional MC process were obtained from published patent data.[20−24] Data for simulating the spray process were obtained from laboratory-scale experiments.[9−11] For estimating vapor−liquid equilibrium, the UNIQUAC model was used to simulate the liquid-phase composition, and the Peng−Robinson equation of state was used to model the vapor phase. The $CO_2$/acetic acid binary interaction coefficient[25] was set as 0.02, and other binary interaction coefficients were obtained from the HYSYS database. Process flow diagrams (PFDs), developed for both processes with various operating parameters/variables and product specifications as inputs, provide the relevant mass and energy flow rates associated with the process streams. These flow rates along with the information on stream composition are used in process equipment design and sizing and to perform the economic and environmental impact analyses presented herein.

**Economic Analysis.** The capital investment is estimated following the percentage of the purchased equipment cost method,[26] in which the cost for purchased equipment is treated as the estimation basis. Other direct and indirect costs are estimated by multiplying the purchased equipment cost with an appropriate factor (Table 3). The purchased equipment costs are estimated based on attributes such as equipment size, material of construction, weight, or surface area.[26,27] For determining production costs, the amounts of utilities and chemicals consumed are estimated from the HYSYS-estimated stream properties. The costs associated with raw materials, utilities, and labor are obtained from 2012 sources.[28−30] The uncertainty of the capital

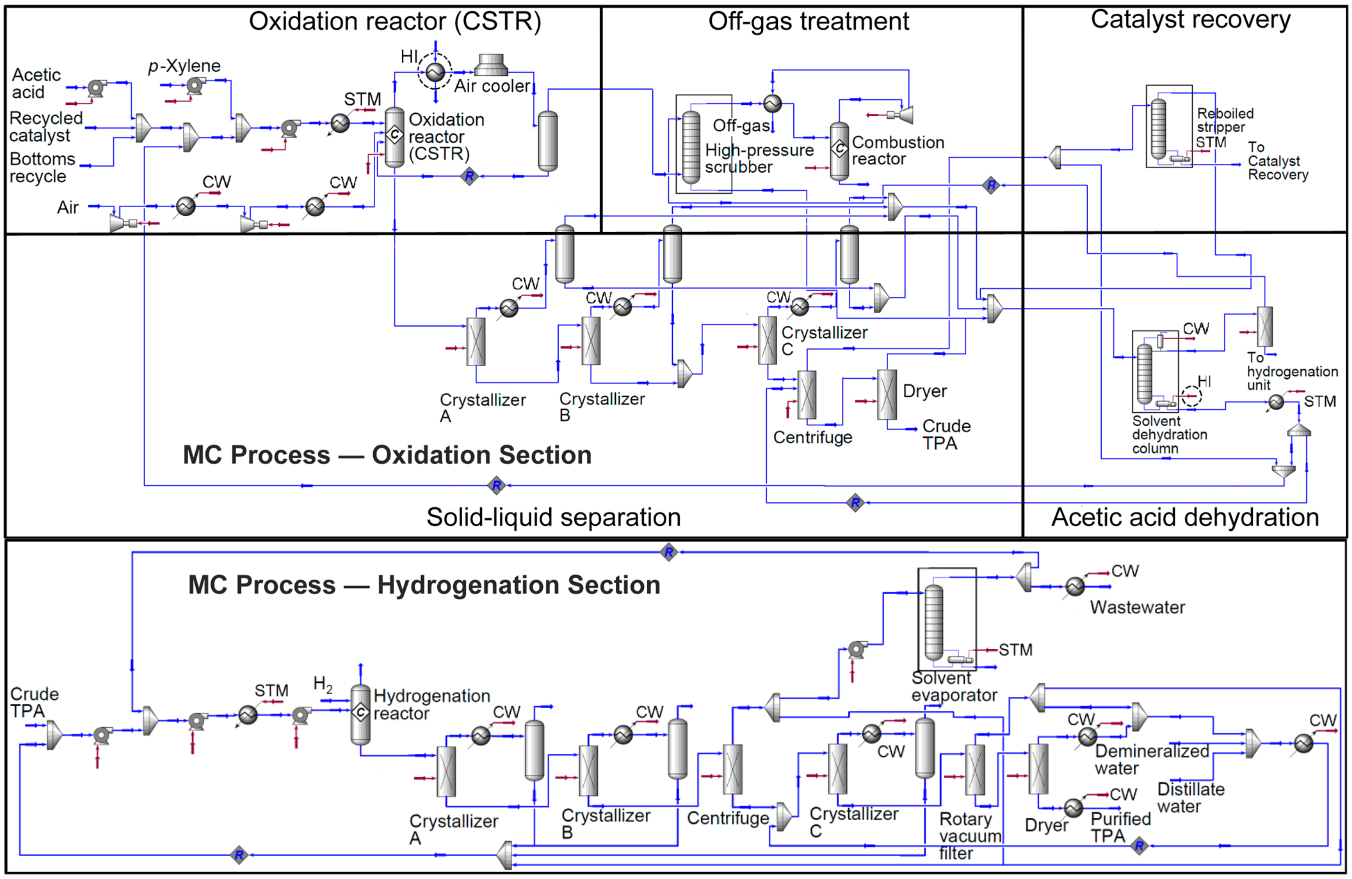

**Figure 2.** Process flow diagram for the conventional MC process (STM, steam; CW, cooling water; HI, heat integration).

and operating cost estimates using this methodology can range from 10% to 30%.[26]

**Environmental Impact Analysis.** Comparative environmental impacts of the MC and spray processes are evaluated by performing gate-to-gate LCA and cradle-to-gate LCA. The approach employed in this analysis follows the four phases (goal and scope definition, life cycle inventory, impact assessment, and interpretation) suggested by ISO (Figure 1). Life cycle inventory inputs are derived from the material and energy flows associated with the conventional and CEBC processes provided by the Aspen HYSYS simulations. The life cycle impact assessment is accomplished using GaBi 6 software[31] developed by PE International jointly with the University of Stuttgart.

GaBi is a commercial LCA software tool for product sustainability solution by creating life cycle balances. This software is accompanied by an inventory database in compliance with the ISO 14044, ISO 14064, and ISO 14025 standards. The data sets cover thousands of processes including chemicals production, power generation, and transport across the supply chain of the represented cradle-to-gate inventory. GaBi incorporates various LCA models such as TRACI, CML 2001, and Eco-indicator 99. While most of these models have been developed for use in specific country/region, particularly in Europe or Japan, TRACI was developed by the United States Environmental Production Agency (U.S. EPA) in 2002. The underlying methodologies in TRACI reflect state-of-the-art developments for LCA in the United States and employ input parameters that are specific to United States locations.[32−35] TRACI facilitates the characterization of the following environmental categories: ozone depletion, global warming, acidification, eutrophication, tropospheric ozone (smog) formation, ecotoxicity, human particulate effects, human carcinogenic effects, human noncarcinogenic effects, fossil fuel depletion, and land use effects. Depending on the category, the uncertainties in GaBi model predictions have been reported to range anywhere from 10% to 250%.[36]

## ■ PROCESS SIMULATIONS

The process flow diagrams of the conventional MC process and the CEBC spray process simulated by HYSYS are shown in Figures 2 and 3. Tables 1 and 2, respectively, summarize the key operating parameters for process simulation and the assumptions associated with acetic acid use and loss for the four cases of the CEBC spray process.

**Conventional MC Process.** The MC process includes an oxidation section that consists of five parts [oxidation reactor (CSTR), solid−liquid separation unit, catalyst recovery unit, off-gas treatment, and acetic acid dehydration] and a hydrogenation section (Figure 2). In the oxidation section, the substrate (*p*-xylene), solvent (acetic acid), and catalyst (cobalt acetate, manganese acetate, and hydrogen bromide) are mixed and pumped into the stirred tank oxidation reactor in which *p*-xylene is oxidized to TPA by the oxygen in the air. The reactor is maintained at 200 °C and 15 bar. The reactor effluent flows through three-stage crystallizers, a centrifuge, and then a dryer to yield crude TPA, which contains about 1400 ppmw 4-CBA and 600 ppmw *p*-toluic acid. A solvent dehydration column is used to separate acetic acid from water. The acetic acid is recycled back to the oxidation reactor. In the hydrogenation section, crude TPA from the oxidation section combined with recycled water is pumped to a reactor in which 4-CBA is catalytically converted to *p*-toluic acid by $H_2$. The TPA/water solution leaving the hydrogenation reactor flows through an elaborate network of multistage crystallizers, a centrifuge, a rotary vacuum filter, and finally a PTA (purified terephthalic acid) dryer. Dry PTA is composed of 7 ppmw 4-CBA and 100 ppmw *p*-toluic acid. A more detailed process

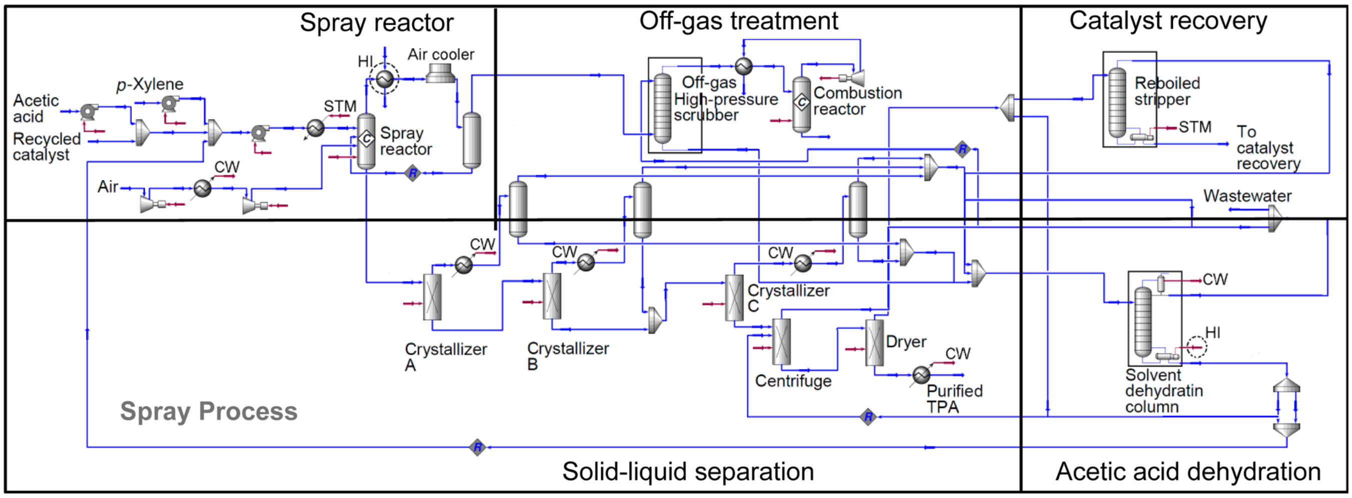

**Figure 3.** Process flow diagram for the CEBC spray process (STM, steam; CW, cooling water; HI, heat integration).

**Table 1. Key Operating Parameters for Simulation of the MC and CEBC Spray Processes**

| | MC process | spray process |
|---|---|---|
| **oxidation reactor conditions** | | |
| temperature (°C) | 195 | 200 |
| pressure (bar) | 15 | 15 |
| water concentration in reaction solvent feed (wt%) | 5 | 5 |
| *p*-xylene conversion (%) | 98.1 | 99.6 |
| *solid product quality* | | |
| 4-CBA concentration (ppmw) | 1375 | 23 |
| *p*-TA concentration (ppmw) | 608 | 2 |
| **hydrogenation reactor conditions** | | |
| temperature (°C) | 267 | —— |
| pressure (bar) | 67 | —— |
| 4-CBA conversion (%) | 90 | —— |
| *solid product quality* | | |
| 4-CBA concentration (ppmw) | 7 | —— |
| *p*-TA concentration (ppmw) | 100 | —— |
| **overall TPA yield (%)** | 95 | 97 |

**Table 2. Assumed Acetic Acid Use and Loss for the MC Process and CEBC Spray Process**

| | | spray process | | | |
|---|---|---|---|---|---|
| | MC process | case 1 | case 2 | case 3 | case 4 |
| HAc/*p*X feed ratio (w/w) | 2.3 | 20.8 | 14.4 | 8.1 | 2.3 |
| HAc loss from oxidation reactor (%) | 5.3 | 1.3 | 1.3 | 1.3 | 1.3 |

description is provided in section A of the Supporting Information.

**CEBC Spray Process.** The spray process layout looks similar to the MC process oxidation section. Instead of stirred reactor, the oxidation reaction occurs in a spray reactor in which the liquid phase containing dissolved *p*X and the catalyst (cobalt acetate, manganese acetate, and hydrogen bromide) in acetic acid is dispersed as fine droplets by a nozzle into a vapor phase containing the oxidant ($O_2$). Compressed air is used as the oxidant in the simulation of the spray process, and the $O_2$/*p*X molar feed ratio is 3.5:1. In the MC process, typical vapor phase $O_2$ partial pressure is about 0.4 bar[37] or approximately 3 vol% in the MC oxidation reactor to prevent explosions. In the HYSYS simulation of the spray reactor, $O_2$ concentration in the off-gas is also limited to 3 mol %. In addition, the acetic acid amount employed in the spray process is either equal to or greater than that in the MC process, resulting in a higher acetic acid composition in the vapor phase. Given that the composition of the vapor phase containing mostly acetic acid is above the upper flammability limit in the MC oxidation reactor, it follows that the composition of the vapor phase in the spray reactor should also be above the flammability limit.

The reaction temperature and pressure are very close to those in the MC oxidation reactor, i.e., 200 °C and 15 bar, respectively. As summarized in Table 2, four alternative spray processes using varying amounts of acetic acid in the feed are simulated with case 1 having the highest acid feed rate (10-fold more than that in the MC process) and case 4 having the least (acetic acid feed rate comparable to that in the MC process). In all cases, it is assumed that 1.3 wt % of the acetic acid fed is lost by combustion. This assumption is based on our reported experimental results showing that the CO formed is approximately one-fourth compared to the MC process.[10]

The reactor product stream flows through three-stage crystallizers, a centrifuge, and then a dryer to yield dry TPA, which is composed of 23 ppmw 4-CBA and 2 ppmw *p*-toluic acid. The purity of the solid TPA meets the polymer-grade TPA requirement, and therefore, no further purification was deemed necessary. The off-gas treatment part and the distillation part are similar to those employed in the MC process oxidation.

## ■ ECONOMIC ANALYSIS

**Capital Investment.** The estimates of purchased equipment costs are determined by equipment parameters such as equipment size, weight, surface area, and material of construction[26,27] that are in turn based on the material and energy balances obtained from HYSYS simulation. All the costs are adjusted to June 2012 figures using the Chemical Engineering Plant Cost Index (CEPCI).[38] Figure 4 shows the purchased costs of major equipment in both processes. Special equipment costs such as crystallizers, solid−liquid separation units, dryers, and storage silos account for about 40% of the costs in both processes. Miscellaneous equipment costs mainly consist of the Pd and Rh catalysts for the hydrogenation reaction in the MC process.

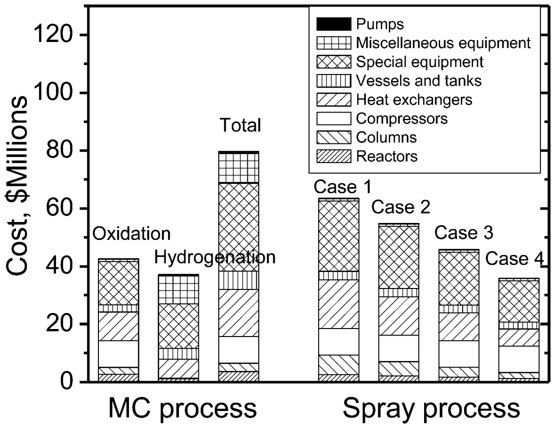

**Figure 4.** Comparison of purchased equipment costs for MC and spray processes.

The estimate of capital investment uses "purchased equipment cost" as the basis, and other costs (direct, indirect, and working capital) are estimated by multiplying the purchased equipment cost with an appropriate factor.[26] Table 3 compares the capital investments for both MC and spray processes. The estimated total capital investments of the spray process case 1 ($241 million when nearly 10 times more acetic acid is used in the feed compared to the MC process) and case 4 ($136 million when similar amounts of acetic acid feed is used as in the MC process) are approximately 80% and 45%, respectively, of those estimated for the MC process ($302 million). Thus, the capital cost benefit margin in the CEBC spray process (due to the avoidance of hydrogenation section) is progressively diminished from 55% for case 4 to 20% at the highest acetic acid throughputs of case 1. While the capital cost difference between the MC process and the CEBC process case 1 lies within the prediction uncertainty, the capital cost reductions in cases 2−4 of the CEBC process are beyond the prediction uncertainty, suggesting a clear economic advantage of the CEBC spray process.

**Total Production Cost.** The utilities and raw material costs ("variable costs") for both the MC process and spray process are summarized in Table 4. The *p*-xylene makes up the bulk of the raw material costs for both processes. Steam and electricity (used mainly in the heat exchangers and special equipment), compressors and pumps account for the large part of the utilities. Note that the estimated utility costs for the MC process (7.37¢/lb of TPA) are more compared to even case 1 of the CEBC process (6.46¢/lb of TPA), wherein maximum energy input is needed to handle the higher acetic acid throughputs (cases 1−3). Cogeneration, also known as combined heat and power (CHP), can significantly improve system efficiency and reduce utility costs. As explained in the "off-gas treatment" section of the process flow diagram (Supporting Information), the energy content of the high temperature effluent gas from the combustion reactor is used to drive one of the air compressors. The energy savings can reach approximately 25% (0.072 kW h/lb TPA), resulting in an electricity cost savings of 0.5¢/lb TPA in both processes. Also, the waste heat during electricity generation, if recovered for process heating, would further increase energy efficiency and cost savings.

Figure 5 compares the total product cost for both processes (cost details of each item are provided in Table S1 of the Supporting Information). The total cost of the polymer-grade TPA product from the MC process is estimated to be $0.67/lb. The total TPA cost from CEBC process case 1 and case 4 is estimated to be $0.635/lb and $0.56/lb, respectively. Even though the predicted TPA production costs for the CEBC process are lower than that for the MC process by 5−16%, the differences lie within the typical range of uncertainty of such predictions.

**Sensitivity Analysis.** Using lower *p*X concentration (higher acetic acid throughput) partly offsets the economic benefits accrued by the elimination of the hydrogenation step in the

**Table 3. Comparison of Capital Costs for Both MC and Spray Processes**

| | | spray process ($ million) | | | |
|---|---|---|---|---|---|
| | MC process ($ million) | case 1 | case 2 | case 3 | case 4 |
| purchased equipment costs (f.o.b.[a]) | 79.7 | 63.6 | 54.8 | 45.8 | 35.9 |
| direct installation costs (123.1% of purchased cost) | 98.1 | 78.2 | 67.4 | 56.4 | 44.2 |
| direct costs (others) (45% of purchased cost) | 35.9 | 28.6 | 24.7 | 20.6 | 16.2 |
| total direct costs | 213.8 | 170.4 | 146.9 | 122.9 | 96.3 |
| indirect costs (73% of purchased cost) | 58.2 | 46.4 | 40.0 | 33.5 | 26.2 |
| fixed capital investment (FCI) (direct + indirect) | 272.0 | 216.8 | 186.9 | 156.3 | 122.6 |
| working capital (10% of TCI) | 30.2 | 24.1 | 20.8 | 17.4 | 13.6 |
| total capital investment (TCI) (FCI + working capital) | 302.2 | 240.9 | 207.7 | 173.7 | 136.2 |

[a] f.o.b.: free on board, meaning that the purchaser pays the freight.

**Table 4. Utilities and Raw Material Costs for Both Processes**

| | | MC process | | spray process | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | case 1 | | case 2 | | case 3 | | case 4 | |
| | unit cost[a] | consumption (/lb of TPA) | cost ($/lb of TPA) | consumption (/lb of TPA) | cost ($/lb of TPA) | consumption (/lb of TPA) | cost ($/lb of TPA) | consumption (/lb of TPA) | cost ($/lb of TPA) | consumption (/lb of TPA) | cost ($/lb of TPA) |
| **utilities** | | | | | | | | | | | |
| HP steam | $0.01/lb | 5.314 lb | 0.0531 | 4.647 lb | 0.0465 | 3.562 lb | 0.0356 | 2.384 lb | 0.0238 | 1.025 lb | 0.0102 |
| electricity | $0.0655/kwh | 0.229 kwh | 0.0150 | 0.219 kwh | 0.0143 | 0.213 kwh | 0.0140 | 0.207 kwh | 0.0136 | 0.196 kwh | 0.0129 |
| cooling water | $0.0001/gal | 56.05 gal | 0.0056 | 37.66 gal | 0.0038 | 31.22 gal | 0.0031 | 23.31 gal | 0.0023 | 12.29 gal | 0.0012 |
| total utilities | | | 0.0737 | | 0.0646 | | 0.0527 | | 0.0397 | | 0.0243 |
| **raw materials** | ($/lb) | (lb) | | (lb) | | (lb) | | (lb) | | (lb) | |
| TPA (product) | 0.5849 | | | | | | | | | | |
| *p*-xylene | 0.63 | 0.6727 | 0.4238 | 0.6561 | 0.4133 | 0.6561 | 0.4133 | 0.6561 | 0.4133 | 0.6561 | 0.4133 |
| acetic acid | 0.26 | 0.0508 | 0.0132 | 0.0557 | 0.0145 | 0.0448 | 0.0116 | 0.0348 | 0.0090 | 0.0239 | 0.0062 |
| cobalt acetate | 27.11 | 0.00005 | 0.0014 | 0.00005 | 0.0014 | 0.00005 | 0.0014 | 0.00005 | 0.0014 | 0.00005 | 0.0014 |
| manganese acetate | 5.42 | 0.00015 | 0.0008 | 0.00015 | 0.0008 | 0.00015 | 0.0008 | 0.00015 | 0.0008 | 0.00015 | 0.0008 |
| HBr acid (in 48%) | 3.86 | 0.0017 | 0.0066 | 0.0017 | 0.0066 | 0.0017 | 0.0066 | 0.0017 | 0.0066 | 0.0017 | 0.0066 |
| hydrogen | 0.32 | 0.00008 | 0.000026 | | | | | | | | |
| demineralized water | $0.0257/gal | 0.0428 gal | 0.0011 | | | | | | | | |
| total chemicals | | | 0.4469 | | 0.4366 | | 0.4337 | | 0.4311 | | 0.4283 |

[a] Unit cost information is from references 28−30, 39.

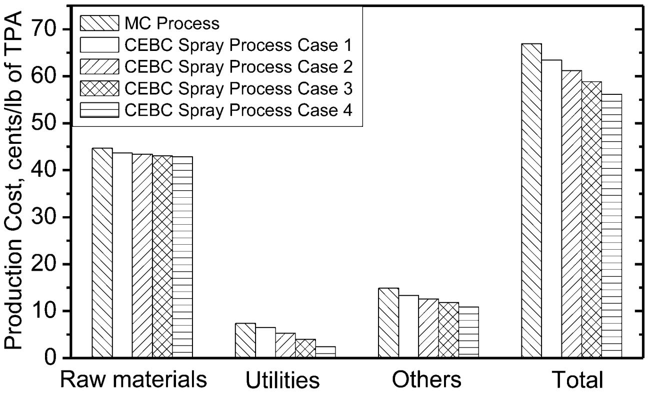

**Figure 5.** Comparison of total production costs for both processes. (Others include other direct, indirect costs, depreciation, and general expenses such as labor, research, plant overhead, operating supplies, and maintenance. Details are provided in Table S1 of the Supporting Information).

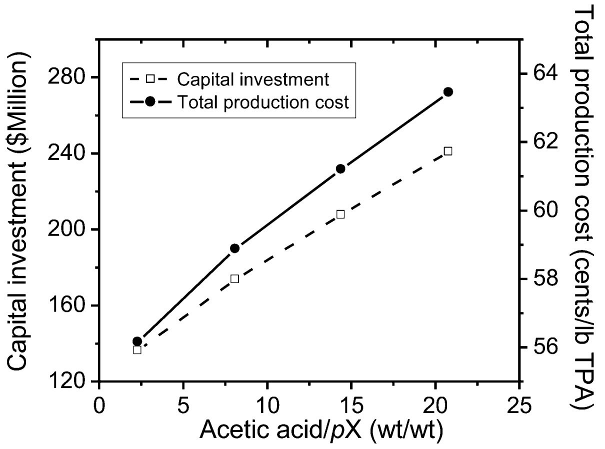

**Figure 6.** Capital and operating costs rise with acetic acid throughput in CEBC spray process.

CEBC spray process. Figure 6 plots the capital and operating costs of the CEBC process as a function of acetic acid/*p*X weight ratio. The capital investment and production cost of the spray process increase by 120% and 13%, respectively, when acetic acid amounts increase nearly 10-fold, and this change is almost linear. Clearly, as high a *p*X concentration as practically feasible should be used to maximize the savings in the CEBC spray process.

## ■ ENVIRONMENTAL IMPACT ANALYSIS

A sustainable process should demonstrate not only clear economic advantages but also superiority in terms of environmental stewardship and social progress.[40,41] Among the various environmental assessment approaches, Life cycle assessment (LCA) in conjunction with economic analysis can be valuable for guiding optimal process design and optimization. LCA can help identify the hot spots that cause the most adverse environmental impacts and thus provide decision makers with valuable information to make improvements. CEBC researchers have employed LCA methodology for performing comparative environmental impacts of novel process concepts for ethylene and propylene epoxidations with conventional processes.[17,18]

**Goal and Scope Definition.** *Goal.* The major project goal is to quantitatively benchmark the environmental impacts of TPA production by the CEBC spray process against the conventional MC process. Such a comparison should provide a clear picture of potential environmental advantages of the spray process and also identify the hot spots and opportunities for improvements.

*Scope Definition (LCA Assumptions and System Boundaries). Functional Unit.* Functional unit for this analysis is the production of 63,450 kg/h (500,000 t/year) of purified TPA (i.e., polymer-grade TPA quality specifications) by both the conventional MC process and the CEBC spray process.

*System Boundaries.* The scope of the evaluation is limited to gate-to-gate and cradle-to-gate analyses. The use and disposal phases are not considered. For gate-to-gate analysis, the system boundaries of both processes are limited to factory entry gate to exit gate (Figures 7 and 8). In other words, only the environmental impacts during TPA manufacture at the production facility stemming from emissions from unit operations, fugitive emissions, and utility emissions are considered. Electricity is assumed to be obtained from United

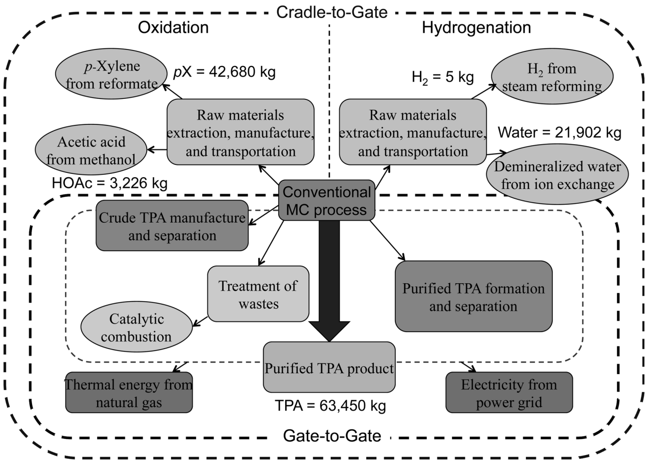

**Figure 7.** System boundaries of conventional MC process for gate-to-gate and cradle-to-gate LCA.

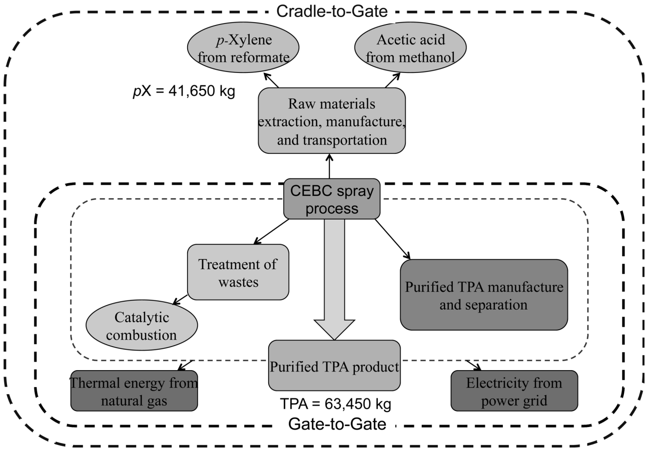

**Figure 8.** System boundaries of CEBC spray process for gate-to-gate and cradle-to-gate LCA.

States power grids from a portfolio of energy sources. Steam is assumed to be produced from natural gas. In contrast, the cradle-to-gate analysis assessment includes gate-to-gate scope and also the environmental impact from the extraction, manufacture, and transportation of the raw materials. The details of raw material sources are provided in section C of Supporting Information.

**Life Cycle Inventory.** For both the MC process and CEBC process, the inventory of the LCA system includes the inputs and outputs for the processes within the system boundaries (Figures 7 and 8), including the raw material and energy inputs, products and byproducts outputs, and generated wastes released to air, water, and soil. In this particular analysis, the inventory data associated with the material and energy balances during TPA production at the facility are the same as those used for the comparative economic analysis (obtained from Aspen HYSYS simulations, Figures 2 and 3). The background inventory data associated with raw material extraction, utility production, and transportation are obtained from GaBi U.S. professional and extension databases. Flow models for cradle-to-gate LCA, consistent with the system boundaries defined in Figures 7 and 8, are shown in Figure S1 (MC process) and Figure S2 (CEBC spray process) in section D of Supporting Information. Flow models for gate-to-gate LCA (not shown) look similar to those for cradle-to-gate LCA except that the section related to raw material extraction, manufacture, and transportation is omitted.

**Life Cycle Impact Assessment.** *Methodology Validation by Gate-to-Gate LCA of MC Process.* In order to validate the methodologies employed in the Aspen HYSYS simulations as well as in the GaBi LCA software, a gate-to-gate environmental impact assessment of the simulated conventional MC process was first performed, and the predictions were compared with the total and released chemical wastes as well as green house gas emissions from a commercial plant (BP Amoco Chemical Company, Cooper River Plant). The actual commercial plant emission data are available from public databases such as the annual toxic release inventory (TRI) data reported to the U.S. EPA[42] and EPA's facility level information on the Green House Gases Tool.[43]

Fugitive emissions (unintentional releases of process fluid from equipment and evaporation of volatile liquids from open areas) are an important aspect of environmental assessment.[44] It has been reported that 70−90% of air emissions for some plants in the United States result from the fugitive emissions.[45] Siegell[46] also claimed that in almost all cases, fugitive emissions from equipment leaks were the largest source of volatile organic compounds (VOCs) emissions in refineries, typically accounting for 40−60% of total VOC emissions. However, the GaBi software does not account for these emissions based on process flowsheets used for the LCA study. Therefore, fugitive emissions were estimated in a separate procedure based on the Environmental Fate and Risk Assessment Tool (EFRAT) developed by Shonnard and Hiew.[47] Specifically, the emission rates from process unit operations were calculated by the throughput of VOCs in each piece of equipment multiplied by the average emission factor for that particular type of chemical process unit. These emission factors are average values obtained from U.S. EPA reports based on case studies conducted on many industrial processes. Uncertainties could be up to an order of magnitude.[48] Emission sources considered in the cradle-to-gate and gate-to-gate environmental impact analysis include (a) reactors, distillation columns, and strippers; (b) fugitive emissions from valves, flanges, and pump seals, and (c) fuel combustion emissions for utility production. The estimate of utility emissions was based on the GaBi database.

*Comparison of VOC Emissions.* The gate-to-gate VOC emission rate from a unit operation is estimated as the VOC mass flow rate passing through the equipment multiplied by an average emission factor. The industry emission factors for various unit operations are obtained from the textbook by Allen and Shonnard,[48] which also provides average emission factors for estimating fugitive emissions from valves, pump seals, flanges, and other connections. The estimates of air emissions of the two reported VOCs in the TRI data, *p*-xylene and methanol (presumably generated from the hydrolysis of methyl acetate), are given in Table 5. These estimated emissions are compared with the waste quantity report of BP Amoco Chemical Company, Cooper River Plant in South Carolina with an annual production capacity of 1.345 million metric tons of purified TPA.[49] The report was obtained from EPA public database,[42] and the data therein are also included in Table 5.

As shown in Table 5, the estimated VOC emissions are approximately half of those reported by BP (total wastes). The TRI data are generally higher probably because the BP facility has two other chemical production facilities in addition to the purified TPA facility.[49] Nevertheless, the predicted and reported waste quantities are of the same order of magnitude

Table 5. Comparison of Conventional MC Process VOC Emissions Obtained from U.S. EPA Toxic Release Inventory (TRI) Data for Commercial Facility with Predicted Emissions

| | reported total and released chemical waste[b] (lb) by BP Amoco Chemical Co., 2011 | | | | |
|---|---|---|---|---|---|
| chemical | total waste | adjusted total waste[a] | released waste | adjusted released waste[a] | gate-to-gate emissions (lb), this work |
| *p*-xylene | 1,125,800 | 418,513 | 25,794 | 9,589 | 228,713 |
| methanol | 1,703,100 | 633,123 | 103,100 | 38,327 | 298,332 |
| acetic acid | NA[c] | NA | NA | NA | 11,957,586 |

[a] Adjusted wastes corresponded to the simulated annual capacity (500,000 t PTA). [b] TRI reported waste is chemical waste emissions (*p*X and methanol VOC emissions) to air. [c] NA: Not available; acetic acid emissions are not reported in the TRI data.

Table 6. Comparison of Conventional MC Process $CO_2$ Emissions Obtained from U.S. EPA GHG Data for Commercial Facility with Predicted Emissions

| reported total facility $CO_2$ emissions (in metric tons $CO_2$-equiv.), by BP Amoco Chemical Co., 2011 | | gate-to-gate $CO_2$ emissions (in metric tons $CO_2$-equiv.), this work | | |
|---|---|---|---|---|
| reported | adjusted[a] | off-gas | fuel combustion | total |
| 101,458 | 37,717 | 60,625 | 327,833 | 388,458 |

[a] Adjusted emissions corresponded to the simulated annual capacity (500,000 t purified TPA).

and consistent with reported uncertainty in VOC emission predictions,[48] implying the method used for the process simulation and gate-to-gate VOC emission estimation is generally satisfactory on this level of analysis. One can also observe from Table 5 that more than 90% of the generated wastes are treated at the facility, and the rest are released to the atmosphere. In addition, the estimated acetic acid emissions (not reported in the TRI data) are approximately 40 times greater than the methanol emissions, suggesting that the acetic acid is a large VOC emission contributor.

*Comparison of $CO_2$ Emissions.* Major sources for direct gate-to-gate $CO_2$ emissions to air are $CO_2$ generated from solvent burning in the oxidation reactor and the combustion reactor for VOCs treatment, as well as the on-site boilers for steam production by fuel combustion. Table 6 compares the GaBi-estimated $CO_2$-equiv. for the conventional MC process with the $CO_2$ emissions[43] reported by BP Amoco Chemical Company, Cooper River Plant (SC) for 2011. Clearly, less than 10% of the total $CO_2$ emission equivalent is emitted as direct $CO_2$ emissions to air at the facility. The predicted and reported $CO_2$-equiv. quantities are of the same order of magnitude, which provides a measure of the predictive ability of the TRACI tool incorporated in GaBi.

*Comparative Gate-to-Gate Life Cycle Impact Assessment.* Figure 9 compares the gate-to-gate environmental impact potentials of TPA production by the conventional MC and CEBC spray processes (only the major impact categories are shown in Figure 9). The numerical data and a complete list of all impact potentials are provided in Table S2 of the Supporting Information. The estimated environmental impact potential of direct process emissions such as off-gas, wastewater, VOCs from unit operations, and fugitive emissions (fuel combustion effect for steam production excluded) are also provided in Figure 9 (shaded regions). As expected, the adverse environmental impact potentials in the CEBC spray process decrease with a higher substrate (*p*X) concentration, i.e., when smaller amounts of acetic acid are employed.

*Comparative Cradle-to-Gate Life Cycle Impact Assessment.* The predicted cradle-to-gate environmental impact potential for both processes is shown in Figure 10. The numerical data and a complete list of all impact potentials are provided in Table S3 of the Supporting Information. The predicted cradle-to-gate environmental impacts for most of the impact categories are generally an order of magnitude greater than the predicted gate-to-gate impacts, while they are of the same order of magnitude with respect to air ecotoxicity and water ecotoxicity, the major contributors to which are VOC emissions to air and the organic solvents contained in wastewater. For both gate-to-gate and cradle-to-gate environmental impact potentials, the predicted differences between the conventional MC process and the CEBC spray process lie within the typical uncertainty ranges (1 order of magnitude) of such LCA analyses. The contributors to the various environmental impact categories are described in the following sections.

**Discussion.** *Potential Environmental Impact Contributors in the TPA Processes. Global Warming Potential.* Global warming potential arises from $CO_2$ emissions and other greenhouse gases that trap the sun's heat. As shown in Figure 9, the $CO_2$ emissions for a TPA plant that employs the MC process technology are primarily associated with the fuel combustion for steam production by on-site boilers, accounting for nearly 85% of the total $CO_2$ emissions. The hydrogenation section alone accounts for approximately 57% of the total on site $CO_2$ emissions, primarily due to the large energy input for the hydrogenation reactor. The other $CO_2$ emission sources include the oxidation reactor in which solvent burning occurs and the combustion reactor for VOCs treatment. For the gate-to-gate $CO_2$ emissions in the CEBC spray process, the fuel combustion for energy input contributes to approximately 80% of the total on site $CO_2$ emissions in each of the four cases. The global warming potential in CEBC spray process case 4 (similar acetic acid throughput to the MC process) is approximately 23% of that in the MC process. In contrast, the global warming potential in the CEBC spray process that uses 10-fold more acetic acid than the MC process (case 1) is approximately 91% of that for the MC process. The environmental benefits of avoiding the hydrogenation step in the spray process are partially offset by higher acetic acid usage, which leads to higher energy requirements for the separation columns as well as the larger off-gas $CO_2$ emissions from solvent burning and the VOCs treatment reactor.

The conventional MC process cradle-to-gate global warming potential is about 4-fold greater than that for gate-to-gate analysis (Figure 10), due primarily to $CO_2$ emissions from fossil fuel-based energy required for *p*X production. Interestingly, the impact associated with $H_2$ production from natural gas is minor because very small amounts of $H_2$ are used for the hydrogenation reaction. Given that similar amounts of *p*X are

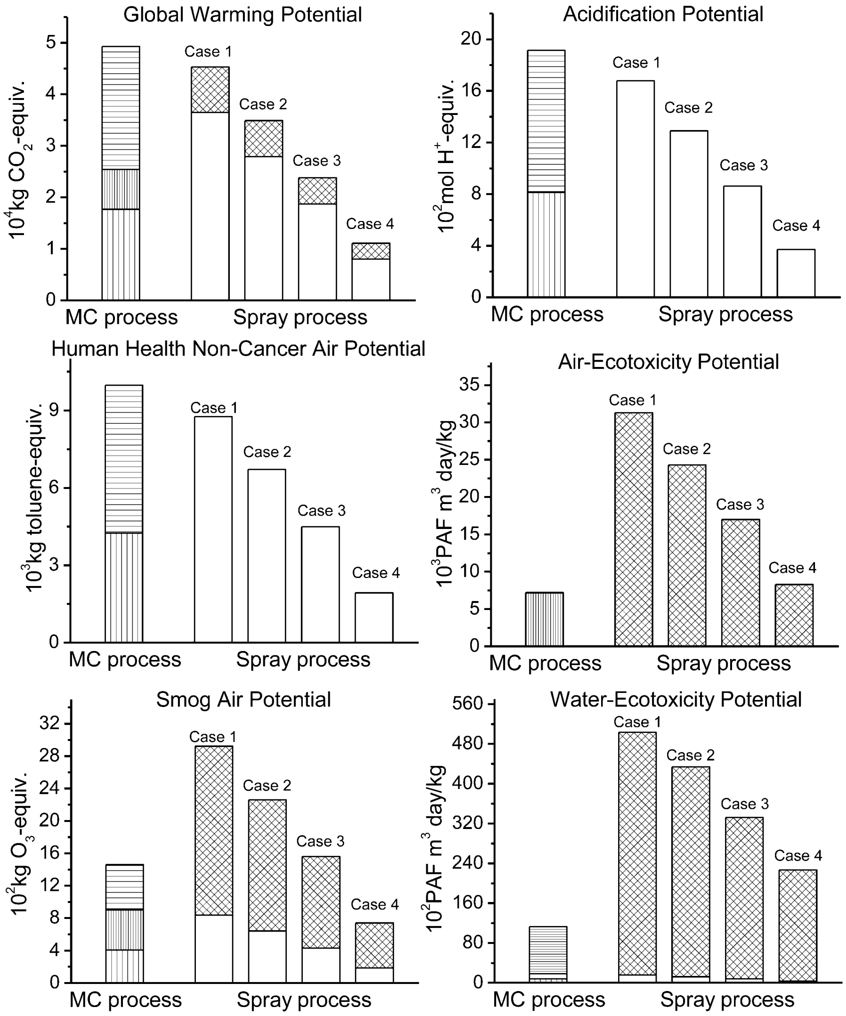

**Figure 9.** Comparison of predicted gate-to-gate environmental impact potential for both processes (Vertical line: MC process oxidation section. Horizontal line: MC process hydrogenation section. Cross-hatched: environmental impact potential of direct process emissions such as off-gas, wastewater, VOCs from unit operations, and fugitive emissions. Unshaded: fuel combustion for process steam production).

employed in the spray process, the cradle-to-gate impacts relative to gate-to-gate impacts in the spray process are about the same as those in the MC process.

*Acidification Potential.* The acidification potential is attributed to on-site SO$x$ and NO$x$ emissions from the natural gas-based energy production (Figure 9). The gate-to-gate acidification potential correlates with the steam usage in the process. When cradle-to-gate assessment is considered, the acidification potential results primarily from the coal-based electrical power generation for producing $p$X and other raw materials. Compared to the MC process, the on-site acidification potential for case 1 (10-fold more acetic acid than the MC process) and case 4 (same acetic acid usage as the MC process) of the spray process are approximately 88% and 19%, respectively, while the cradle-to-gate impacts for the two cases are approximately 96% and 85%, respectively. These results show that while acetic acid usage dictates the acidification potential from on-site emissions, coal-based power generation is a major contributor to the overall acidification potential stemming from cradle-to-gate emissions.

*Human Health Non-Cancer Air Potential.* Heavy metals (arsenic, cadmium, lead, mercury, etc.) and halogenated organic substances emitted during fossil fuel-based energy generation (electricity and steam) contribute to this category. When compared to the MC process, the human health non-cancer air potentials of the spray process (case 1 and case 4) are approximately 88% and 19%, respectively, based on on-site emissions, and 94% and 69%, respectively, when considering cradle-to-gate LCA. These comparisons again show the dominant effect of increased acetic acid usage on site and the use of coal-based power generation for producing the raw materials.

*Air Ecotoxicity Potential.* Fugitive VOC emissions and VOCs emitted from various unit operations contribute primarily to the air ecotoxicity potential. The emitted VOCs associated with the TPA processes are mainly acetic acid, methyl acetate, methanol, and $p$-xylene. Partitioning of inorganic chemicals into the air phase during fossil fuel-based energy generation has a relatively minor contribution compared to VOC emissions. As shown in Figure 9, for the MC process, the air-ecotoxicity potential based on the on-site emissions mainly stems from the fugitive acetic acid emissions from the oxidation section. The impact from the hydrogenation section, in which the relevant VOCs are mainly methanol, is relatively insignificant compared to the oxidation section (Table S2, Supporting Information). This is a reflection of the fact that the solvent used in the hydrogenation process is water. The air ecotoxicity potential of the spray process that uses 10-fold greater acetic acid (case 1) is greater (by approximately four

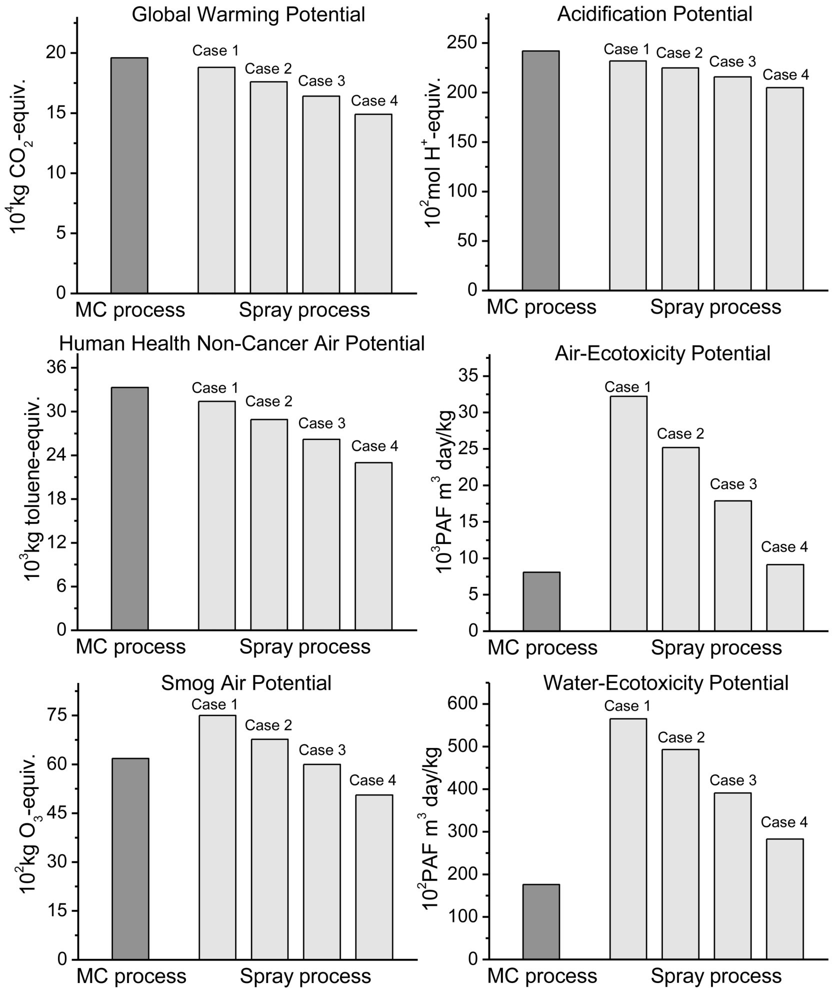

**Figure 10.** Predicted cradle-to-gate environmental impact potential for MC and spray processes.

times) based on both gate-to-gate and cradle-to-gate LCA results. These results show that the extent of acetic acid usage is by far the major contributor to the air ecotoxicity potential in both processes.

*Smog Air Potential.* Smog air potential is attributed to chemicals released to air that cause smog via photochemical reactions.[34] Both the VOC emissions during the on-site TPA processes and the inorganic chemical emissions ($NO_x$) to air during the fossil fuel-based energy generation are primary contributors to this type of air pollution. The smog air potential of the spray process case 1 is approximately 2-fold greater than that in the MC process based on the on-site emissions and 1.2 times based on cradle-to-gate LCA. This trend is consistent with the greater VOC emission potential associated with acetic acid usage (see previous section).

*Water Ecotoxicity Potential.* Organic solvents such as acetic acid, methanol, and methyl acetate, as well as trace amounts of benzoic acid contained in the wastewater released to fresh water, are the primary causes of water contamination. Partitioning of metal emissions (mercury, lead, chromium, etc.) and inorganic chemicals into the water phase during fossil fuel-based energy generation has a relatively small impact on the water ecotoxicity potential compared with the emissions/disposal of process wastewater. In the conventional MC process, the wastewater release occurs in the hydrogenation section, in which a solvent evaporator is used to concentrate the mother liquor from a centrifuge. The heavies are recycled back to the oxidation reactor, while part of the light ends containing trace amounts of acetic acid, methanol, and benzoic acid are emitted to the water phase as process wastewater. The overhead water phase from the distillation column in the oxidation section is sent to the hydrogenation reactor for use as solvent. In the spray process, however, because the hydrogenation section is eliminated, the corresponding aqueous phase from the distillation column is released as wastewater directly, resulting in significant discharge of acetic acid, methanol, and methyl acetate into the wastewater stream. This explains why the water ecotoxicity potential of the spray process is dramatically higher than that of the MC process in either gate-to-gate or cradle-to-gate LCA (Figures 9 and 10).

*Potential Opportunities for Improvements in the CEBC Spray Process. Substrate Concentration (Acetic Acid Throughput).* The use of lower substrate ($p$X) concentration in the CEBC spray process necessitates higher acetic acid throughput (e.g., nearly 10 times of acetic acid amounts in case 1 compared to the MC process). This is definitely undesirable from both economic and environmental points of view. The higher acetic acid throughput requires relatively bigger equipment and higher energy input in addition to increasing $CO_2$ emission rates, acetic acid makeup amount, and VOC emissions. The benefits of eliminating the hydrogenation step are either partially or almost totally offset (as in case 1) with respect to capital investment, operating costs, and almost all the environmental impacts except water ecotoxicity, which is primarily caused by the direct release of wastewater from the distillation column. To gain benefits in both the economic as well as environmental factors, as high a *p*X concentration as practically possible should be used for the alternative spray process. The CEBC spray process would provide significant improvements in economic and environmental performances if it is able to employ the same *p*X concentration as the conventional MC process and produce a polymer-grade TPA product in one step. This analysis also shows that the conventional MC process itself can be improved with respect to both economics and environmental performance if the acetic acid amount can be reduced at constant production capacity.

*Wastewater Treatment.* Instead of directly releasing the aqueous stream (containing mainly acetic acid, methanol and methyl acetate) from the distillation column to fresh water, the wastewater stream could be treated (using appropriate separation techniques such as adsorption, membrane separation, extraction, ion exchange, biological wastewater treatment, and the like) to selectively remove these pollutants. Adding these unit operations will place a small burden on the capital and operating costs but will play an important role in minimizing the environmental impact. As shown in Figure 11, adverse gate-to-gate water ecotoxicity effects in the spray process may be reduced when assuming a control factor of 0.35 for each of the organic compound (acetic acid, methyl acetate, methanol, and benzoic acid), implying a 65% reduction in the COD (chemical oxygen demand). As inferred from Figure 11, the extent of reduction of water ecotoxicity in the spray process (case 1) is comparable with that of the MC process without wastewater treatment.

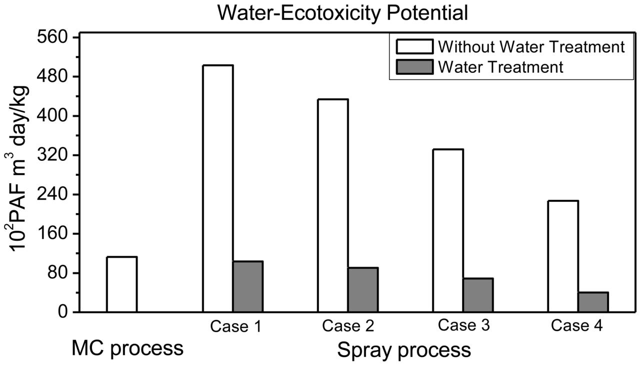

**Figure 11.** Gate-to-gate water ecotoxicity potential reduction with water treatment for the spray process (assuming a control factor of 0.35 for each of the organic compounds: acetic acid, methyl acetate, methanol, and benzoic acid).

*p-Xylene and Acetic Acid Sourcing.* Comparisons of the gate-to-gate LCA and cradle-to-gate LCA (Figures 9 and 10) indicate that the major contributors to the overall environmental impact potential stem from the fossil fuel-based energy for raw material production (primarily for *p*-xylene and acetic acid). Being able to use biosourced *p*-xylene and acetic acid as renewable feedstock (from pyrolysis/liquefaction or hydrolysis of cellulosic or woody biomass) might reduce the adverse environmental impacts of both the spray and MC processes.

## ■ CONCLUSIONS

The spray process for producing high-purity terephthalic acid (TPA) from *p*-xylene (*p*X) has the potential to provide both economic and environmental benefits when compared to the conventional MC process. Both benefits accrue mostly from the avoidance of the hydrogenation step required in the conventional process for purifying the crude TPA. The estimated capital cost of the CEBC spray process is 20% lower than that of the conventional MC process even assuming that 10-fold more acetic acid is used in the spray process to achieve the TPA production rate. In contrast, when an identical amount of acetic acid is used in both processes, the capital cost in the spray process is 55% lower than the MC process. The corresponding costs for producing polymer-grade TPA are lower than the MC process by 3.5¢/lb when using 10-fold greater acetic acid and 10.5¢/lb when using an identical amount of acetic acid as used in the MC process. The lower acetic acid usage also decreases equipment and energy costs.

The GaBi software predicts cradle-to-grave environmental impacts for both processes that are, for most of the impact categories, approximately an order of magnitude greater than the on-site (gate-to-gate) impacts. The environmental impacts are dominated by coal-based electricity generation required for producing the raw materials (*p*X, in particular). Even though acetic acid is the dominant component in the feed, >97 wt % of the acetic acid used in the process is recycled such that the net usage of acetic acid per pound of product is much less than that of *p*X. The emissions from coal-based electricity generation contribute to global warming, acidification potential, and air pollution that cause adverse but noncancerous human health hazards. With respect to both on-site emissions as well as cradle-to-gate emissions, the predicted environmental impacts for the spray process are lower than those of the MC process, even in the case where the acetic acid usage is 10-fold greater compared to the MC process. However, such acetic acid usage contributes to greater fugitive VOC emissions that result in more air toxicity (noncarcinogenic) and smog formation potential. Potential opportunities for improvements in the CEBC spray process are to lower the acetic acid throughput at a fixed TPA production rate and to treat process wastewater before discharging to fresh water. The use of biosourced *p*-xylene and acetic acid as feedstock might improve the environmental performance of both the conventional and spray processes.

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

Conventional Mid-Century (MC) process description, total production cost for the conventional MC process and CEBC spray process, description of raw material sources, flow models of conventional MC process for cradle-to-gate LCA simulated in GaBi, and predicted gate-to-gate and cradle-to-gate environmental impact potentials for conventional MC and CEBC spray processes. This material is available free of charge via the Internet at http://pubs.acs.org.

## ■ AUTHOR INFORMATION

### Corresponding Author

*Phone: 785-864-2903. Fax: 785-864-6051. E-mail: bsubramaniam@ku.edu.

### Notes

The authors declare no competing financial interest.

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## GLOSSARY OF ABBREVIATIONS

TPA: terephthalic acid
PTA: purified terephthalic acid
CTA: crude terephthalic acid
4-CBA: 4-carboxybenzaldehyde
*p*X: *p*-xylene
*p*-TA: *p*-toluic acid

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