

Comparative Economic and Environmental Assessments of H₂O₂-based and Tertiary Butyl Hydroperoxide-based Propylene Oxide Technologies

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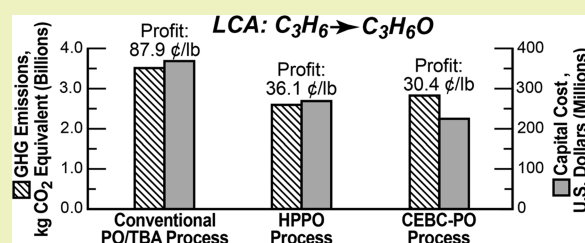
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Supporting Information

ABSTRACT: Until a decade ago, the industrial technologies for producing propylene oxide from propylene were predominantly based on variations of the venerable chlorohydrin and organic hydroperoxide processes. Within the past decade, highly selective H₂O₂-based propylene epoxidation technologies have been developed by Dow-BASF (HPPO process) and the University of Kansas Center for Environmentally Beneficial Catalysis (CEBC-PO process). We present comparative economic and environmental impact analyses based on plant scale simulations of the processes for an assumed 200,000 tonnes/yr of PO production capacity and employing relevant process data from the literature. The predicted capital costs for the CEBC-PO process (\$228 million) and HPPO process (\$275 million) are lower than the conventional PO/TBA process (\$372 million). The PO production costs *via* the conventional PO/TBA and HPPO processes are 150.4¢/lb PO (profit 87.9¢/lb, assuming a market value of 41¢/lb for the TBA co-product and 42¢/lb for the enriched propane co-product) and 107.1¢/lb PO (profit 36.1¢/lb, assuming a market value of 42¢/lb for the enriched propane co-product), respectively. For the CEBC-PO process, the production cost is 90.6¢/lb PO (profit 30.4¢/lb), assuming a life of one year for the methyltrioxorhenium catalyst and a catalyst leaching rate of 9.3×10^{-2} lb/h (or 1.6 ppm Re in the reactor effluent). The comparative economic analysis suggests that the CEBC-PO process has potential for being economically competitive and establishes quantitative catalyst performance metrics for achieving the same. Quantitative *cradle-to-gate* LCA shows that the environmental impacts of producing PO by the conventional PO/TBA, HPPO, and CEBC-PO processes are of the same order of magnitude. The lower GHG emissions predicted for the HPPO and CEBC-PO technologies, compared to the PO/TBA process, lie within the prediction uncertainty of this analysis. This comparative LCA analysis traces the adverse environmental impacts to sources outside the propylene oxide plant in all three processes: fossil fuel-based energy (natural gas, transportation fuel) utilization during raw material (*i*-butane, propylene and hydrogen peroxide) production.

The predicted capital costs for the CEBC-PO process (\$228 million) and HPPO process (\$275 million) are lower than the conventional PO/TBA process (\$372 million). The PO production costs *via* the conventional PO/TBA and HPPO processes are 150.4¢/lb PO (profit 87.9¢/lb, assuming a market value of 41¢/lb for the TBA co-product and 42¢/lb for the enriched propane co-product) and 107.1¢/lb PO (profit 36.1¢/lb, assuming a market value of 42¢/lb for the enriched propane co-product), respectively. For the CEBC-PO process, the production cost is 90.6¢/lb PO (profit 30.4¢/lb), assuming a life of one year for the methyltrioxorhenium catalyst and a catalyst leaching rate of 9.3×10^{-2} lb/h (or 1.6 ppm Re in the reactor effluent). The comparative economic analysis suggests that the CEBC-PO process has potential for being economically competitive and establishes quantitative catalyst performance metrics for achieving the same. Quantitative *cradle-to-gate* LCA shows that the environmental impacts of producing PO by the conventional PO/TBA, HPPO, and CEBC-PO processes are of the same order of magnitude. The lower GHG emissions predicted for the HPPO and CEBC-PO technologies, compared to the PO/TBA process, lie within the prediction uncertainty of this analysis. This comparative LCA analysis traces the adverse environmental impacts to sources outside the propylene oxide plant in all three processes: fossil fuel-based energy (natural gas, transportation fuel) utilization during raw material (*i*-butane, propylene and hydrogen peroxide) production.

KEYWORDS: Comparative economic analysis, Cradle-to-gate LCA, Propylene oxide production, Plant scale simulation



INTRODUCTION

Propylene oxide (PO) is the precursor of a variety of industrially important chemicals including propylene glycol and polyether polyols. The classic chlorohydrin process and variations of the organic hydroperoxide process have long been the dominant industrial technologies for PO manufacture. These commercial technologies generate significant amounts of co-products.¹ For example, in the chlorohydrin process, for every kilogram of PO produced, approximately 1.35–1.5 kg of chlorine is consumed producing significant quantities of calcium chloride co-product.^{2,3}

Four variations of hydroperoxide technology are in commercial operation: (i) the propylene oxide/*t*-butyl alcohol process (PO/TBA) using *t*-butyl hydroperoxide (practiced by LyondellBasell and Huntsman Corporation); (ii) propylene oxide/styrene monomer process (PO/SM) using ethylbenzene hydroperoxide (practiced by LyondellBasell and Shell Chemical

Company); (iii) propylene oxide formed by using cumene hydroperoxide (PO/CHP), (commercialized by Sumitomo Chemical Company), and (iv) the HPPO process (commercialized by Dow-BASF) that will serve as our example.³ In the PO/CHP process, the co-product dimethylbenzyl alcohol (DMBA) is dehydrated and later hydrogenated back to cumene for recycle, incurring additional processing costs.^{4,5}

In contrast, the demand and pricing of the co-products TBA and styrene monomer (SM) factor into the profit margins for the PO/TBA and PO/SM processes, respectively. The positive qualities of the *t*-butyl alcohol and styrene monomer system are significant, but in the past few years, the styrene monomer market has been fairly stagnant. A major use for tertiary butyl

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alcohol (TBA), a byproduct of the PO/TBA process, is as a feedstock for methyl *t*-butyl ether (MTBE).^{6,7} At the present time, the revenue stream from using MTBE as a gasoline additive is significant and continues to grow due to an increasing standard of living and affordability in Asia, making the PO/TBA process more attractive than the PO/SM process. However, MTBE is banned as a gasoline additive in the United States because of its miscibility with water and suspected carcinogenicity.⁸ While the bulk of the TBA produced in the United States is sold for MTBE in Asia, various benign alternatives to MTBE are being considered by governments across the world.⁹

In 2004, Dow and BASF jointly commercialized a new epoxidation technology, the Hydrogen Peroxide/Propylene Oxide (HPPO) process, that uses a titanium silicate-based catalyst to convert propylene to propylene oxide selectively under mild reaction conditions ($T = 40\text{ }^{\circ}\text{C}$, $P = 5\text{ MPa}$).^{10–12} In 2012, the SCG Dow Group started a second plant based on this process. Currently, the H_2O_2 oxidant utilized in this process is produced using the amylanthraquinone process developed by Solvay.¹³

In 2007, researchers at the Center for Environmentally Beneficial Catalysis (CEBC) demonstrated a new process for propylene epoxidation to propylene oxide by H_2O_2 with near complete selectivity based on converted propylene.^{14,15} The process is catalyzed by a methyltrioxorhenium (MTO) catalyst and pyridine *N*-oxide promoter in solution. The CEBC-PO process is highly versatile and can selectively epoxidize light olefins (ethylene and propylene).^{14,16,15,17,18} Propylene dissolves in the liquid phase under mild pressure (1 MPa) and temperature (20–40 $^{\circ}\text{C}$) conditions. Because the reaction conditions are near propylene's critical pressure ($P_c = 4.5\text{ MPa}$) and below its critical temperature ($T_c = 90\text{ }^{\circ}\text{C}$), a propylene-expanded liquid phase exists.¹⁹ The PO product remains dissolved in the liquid phase at the operating conditions and can be recovered by simple distillation.¹⁴ The hydrogen peroxide for this process is assumed to be procured from an external supplier.²⁰

The present work compares economic and environmental impact analyses of the CEBC-PO process with the conventional PO/TBA and a modified HPPO process. This analysis identifies the major economic drivers and establishes performance benchmarks (catalyst life, catalyst leaching rate, oxidant/catalyst ratio, etc.) for economic viability. Similarly, comparative cradle-to-gate life cycle assessment (LCA) identifies the sources that cause significant adverse environmental impacts in these three technologies. Analogous comparative analyses have been performed for ethylene epoxidation by H_2O_2 , hydroformylation, and solid-acid catalyst alkylation processes developed at the CEBC.^{21–23}

ECONOMIC ANALYSES OF PO PROCESSES: PROCESS DESCRIPTIONS AND ASSUMPTIONS

Simulation Package. Aspen HYSYS 2009.7.1 software was employed to perform process simulations. The annual PO capacity for the plant scale simulations was set at 200,000 tonnes/year.²⁴ Process information (mass and energy balances) obtained from the HYSYS simulation was utilized in the sizing of process equipment.^{25–28} The UNIQUAC model was chosen to estimate the relevant thermodynamic properties because the reaction mixture contains polar nonelectrolytes at high pressures. The UNIQUAC model was validated in previous publications by comparing the simulated vapor–liquid

equilibria data with reported experimental data for propylene + methanol, propylene + water, methanol + water, propylene oxide + methanol, propylene oxide + propylene, propylene + nitrogen binary systems.^{14,16,29–34} A good match was also obtained between the experimental and simulated (using the validated binary interaction parameters) vapor–liquid equilibrium data for the propylene + methanol + nitrogen ternary system.²⁹

The PO production technology employed at all the LyondellBasell PO/TBA plants is assumed to be similar. A similar assumption is made for the HPPO process. The electricity obtained from the United States power grid is assumed to be from a portfolio of sources, and steam is produced from natural gas (Table S1, section A, Supporting Information contains the list of specifications and assumptions). In all these processes, medium-pressure steam is employed to meet the heating requirement, and cooling water is utilized to remove the heat of reaction. Tables S2–S4 of the Supporting Information summarize the simulation parameters that are germane to the conventional PO/TBA, HPPO, and CEBC-PO processes and the literature sources from which they were obtained.

PROCESS DESCRIPTIONS

Conventional PO/TBA Process. This process may be viewed in two parts (Figure S1, Supporting Information): *i*-butane oxidation and propylene epoxidation.

***i*-Butane Oxidation Reactor (Part A).** *i*-Butane undergoes noncatalytic liquid-phase oxidation to form *t*-butyl hydroperoxide (TBHP). Typical reaction conditions are 3 MPa at 135 $^{\circ}\text{C}$ with an average residence time of 10 h. Under optimized conditions, the *i*-butane conversion is 37%, and the TBHP selectivity is 53 mol % based on *i*-butane consumption. A major co-product of this step is *t*-butyl alcohol (TBA), with a selectivity of 41 mol % (based on *i*-butane conversion).³⁵ The unreacted raw material (isobutane, butane, oxygen), inert gas (nitrogen), co-products (methanol, acetone), and product (TBHP) are separated from the reactor effluent stream in a train of distillation columns.

Propylene Epoxidation (Part B). In the second step, propylene is selectively epoxidized by TBHP in the presence of a homogeneous molybdenum-based catalyst at 121 $^{\circ}\text{C}$ and 3.5 MPa. For a residence time of 2 h, the reported TBHP conversion is 98%, and the PO selectivity is 98.4% (based on converted TBHP).^{36,37} The reactor effluent stream containing the unreacted reactants and products are recovered in a train of distillation columns (see detailed process description of the LyondellBasell PO/TBA process in Section B of the Supporting Information).

Hydrogen Peroxide/Propylene Oxide (HPPO) Process. Because of the lack of published information on the amylanthraquinone process, this analysis assumes that the oxidant (H_2O_2) is procured from an external supplier. The process flow diagram of the modified HPPO process (hereafter referred to as HPPO process) is shown in Figure S2 of the Supporting Information.

Propylene Epoxidation. A mixture of 50 wt % $\text{H}_2\text{O}_2/\text{H}_2\text{O}$, methanol, makeup reactants (propylene/propane feed ratio of 1.5:1), and recycled gases (propylene/propane) are fed into a fixed-bed catalytic reactor.^{38–40} The mass flow rates of components entering and leaving the reactor are summarized in Table S2 of the Supporting Information. A titanium silicate (often referred to as TS-1) catalyzes propylene epoxidation by H_2O_2 at 40 $^{\circ}\text{C}$ and 2 MPa (Figure S2, Supporting

Information). The activity of the TS-1 catalyst gradually declines from an initial H₂O₂ conversion of 96% to 63% after two weeks, necessitating catalyst regeneration.⁴¹ In this analysis, roughly 90% of the H₂O₂ is utilized in the reactor for epoxidation, while the remaining 10% unreacted H₂O₂ is safely decomposed. The selectivities toward PO and propylene glycol (PG) are 95.5% and 4.5%, respectively.³⁸ In addition to PG, trace quantities of acetone, acetic acid, and formaldehyde are also formed as byproducts (see detailed description of the HPPO process in section C of the Supporting Information).⁴¹

CEBC-PO Process. Similar to the HPPO process, the CEBC-PO process also occurs in the liquid phase. It is assumed that the H₂O₂ is procured from an external supplier.

Propylene Epoxidation. Fresh (99.99%) and recycled propylene, nitrogen, aqueous H₂O₂, makeup catalyst, promoter, and methanol are fed into a continuous stirred tank reactor fitted with a nanofiltration membrane.¹⁵ The assumption of a nearly pure propylene feed is based on the fact that our initial tests with the MTO/H₂O₂ system utilized pure propylene. While this assumption would appear to handicap the CEBC-PO process economics, it nevertheless helps in assessing to what extent the use of pure propylene feed affects the economics. The CSTR volume for 90% H₂O₂ conversion is estimated from reported kinetic parameters and PO selectivity (based on propylene) values of 99% (see section D of the Supporting Information for details).^{14,15} It is further assumed that the Re-based catalyst is bound to a soluble polymer support and that the activity and selectivity of the polymer-bound catalyst are similar to the unbound MTO catalyst. The size exclusivity of the nanofiltration membrane effectively retains the bulky polymer-bound catalyst in the reactor while allowing the passage of only smaller components (such as PO, unreacted propylene, unreacted H₂O₂, water, and methanol) (see detailed description of the CEBC-PO process in section D of the Supporting Information).

The CEBC-PO process qualitatively satisfies many of the principles of green chemistry and green engineering (shown below in italics) as follows. It produces PO *selectively* by using a highly active and selective catalyst that transfers oxygen to propylene and produces water as byproduct. The solvents (methanol and water) and H₂O₂ (oxidant) employed in this process are considered to be *benign*. *Process intensification* is achieved at *mild pressures and near ambient temperatures* at which H₂O₂ decomposition is avoided. The absence of O₂ in the vapor phase eliminates flammability concerns and makes the process *inherently safe*. However, quantitative environmental impact analysis, as described in this work, is essential to confirm whether or not the qualitative deductions regarding process greenness are valid. For example, H₂O₂ is considered a green oxidant, but its overall environmental impact will very much depend on the sources of both the raw materials (H₂ and O₂) and the energy needed for the synthesis (fossil fuel vs renewable). This paper performs cradle-to-gate environmental impact analysis of the CEBC-PO process to gain quantitative insights into the extent of mitigation of adverse environmental impacts.

■ CAPITAL COST CATEGORIES

Capital investments are estimated on the basis of standard methods, and costs are adjusted to 2010 dollars using the Chemical Engineering Plant Index (CEPCI).^{28,42} Direct costs are estimated as a percentage of purchased equipment costs and installation costs and include all expenses for the purchase of

pipework, painting, contingency, freight, instrumentation and control, electrical, yard improvement, buildings, and land use. Indirect costs are estimated as a percentage of direct costs and include engineering, supervision, and expenses related to construction, and legal and contractor's fees.²⁸ The costs of *offsite* equipment such as water purification systems and refrigeration units are also considered. Table S1 of section A of the Supporting Information lists the cost of utilities and the percentages utilized in the estimation of direct and indirect costs.

■ PRODUCTION COST CATEGORIES

Production costs include raw materials, labor, and utility expenses. The cost of raw material is obtained from Chemical Market Reporter.⁴³ The energy balance information obtained from Aspen HYSYS simulation serves as the basis for the estimation of utility expenses. The cost of utilities is obtained from the U.S. Department of Energy, Energy Information Administration.^{44,45} Operating labor expenses are dictated by plant capacity and principal operating steps. Average hourly wage and monthly labor indexes for both skilled and unskilled labor are obtained from the U.S. Bureau of Labor and Engineering News Record and are listed in Table S1 (Section A of the Supporting Information).^{46,47}

■ COMPARISON OF ECONOMICS FOR THE THREE PO PROCESSES

Table 1 compares the Total Capital Investment (TCI) and the expenses related to the purchase and installation of major process equipment for all the simulated PO processes.

Table 1. Comparison of Total Capital Investments for the Conventional PO/TBA, HPPO, and CEBC-PO Processes

cost item	conventional PO/ TBAProcess (\$)	HPPO process (\$)	CEBC-PO process (\$)
reactors	17,188,500	4,968,200	6,252,400
columns	4,004,500	3,228,100	2,877,600
compressors	2,232,500	936,500	936,500
heat exchangers	20,050,300	22,659,600	13,743,100
pumps	1,854,900	1,506,000	1,506,000
vessels and tanks	3,439,700	2,199,400	2,199,400
direct installation costs	134,707,000	99,820,600	77,306,800
indirect costs	99,683,200	73,867,200	68,803,100
auxiliaries	89,195,700	65,893,600	54,692,000
total fixed capital investment	372,356,300	275,079,200	228,588,500

Total Capital Investments. The estimated total capital investments for the conventional PO/TBA, HPPO, and CEBC-PO processes (Table 1) are approximately \$372 million, \$275 million, and \$228 million, respectively. The higher capital cost for the PO/TBA process is because of the fact that this process includes both *t*-butyl hydroperoxide (TBHP oxidant) production and PO synthesis sections. Hence, the direct costs (\$134 million) and indirect costs (\$99 million) for the conventional PO/TBA process are higher than the HPPO process (\$99 million and \$73 million, respectively) and the CEBC-PO process (\$77 million and \$68 million, respectively). The major differences between the processes are associated with reactor and heat exchanger costs.

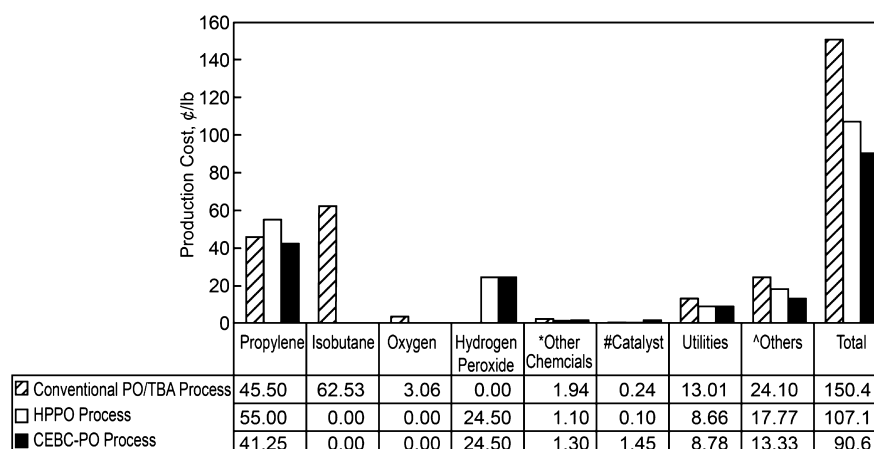


Figure 1. Contributing costs to produce 1 lb of PO in the conventional PO/TBA, HPPO, and CEBC-PO processes. Catalyst life and leaching rate are assumed to be 1 year and 0.018 lbs MTO/year. *Other includes costs for research, plant overhead, materials, supplies for operation and maintenance, and labor. #Other Chemicals includes oxalic acid, caustic soda, Amberlyst, potassium hydroxide, magnesium oxide (conventional PO/TBA process), and methanol (CEBC-PO and HPPO processes).

Table 2. Costs of Various Raw Materials and Values of Products^{43,48}

commodity	price (\$/lb)
hydrogen peroxide	0.24
<i>i</i> -butane	0.30
methanol	0.35
methyltrioxorhenium	5000
molybdenum	450
nitrogen	0.033
oxygen	0.033
propane	0.42
propylene (pure)	0.55
propylene oxide	1.21
pyridine- <i>N</i> -oxide	1.35
<i>t</i> -butyl alcohol	0.41
titanium metal	4.8
steam	7\$/1000 lbs
cooling water	10¢/1000 gal
electricity	6.55¢/KWH

Reactor. Costs for the reactor in the conventional PO/TBA process are approximately \$17 million (includes both PO and TBHP synthesis reactors) compared to \$4.9 million and \$6.2 million for the HPPO and CEBC-PO processes (PO reactors only), respectively. Reactors in the three processes are constructed using carbon steel clad with stainless steel metal (SS-304) to minimize metal catalyzed decomposition of the oxidants (TBHP and H₂O₂). The oxygen concentration in the TBHP synthesis reactor is maintained at 4–7 mol % to minimize the formation of flammable *i*-butane/oxygen mixtures. This, along with the long residence times (10 h) needed for TBHP production, result in a large reactor volume and therefore high reactor costs for TBHP synthesis.

Heat Exchanger. Costs for the heat exchanger in the conventional PO/TBA, HPPO, and CEBC-PO processes are estimated at \$20 million, \$22 million, and \$13.7 million, respectively. The higher heat exchanger cost in the PO/TBA process is attributed to the higher surface area requirement associated with the TBHP synthesis section. In contrast, the mild operating temperatures employed in the HPPO and CEBC-PO processes require lower heat transfer area in the reactor. However, these savings are offset in the HPPO process

due to the higher heat exchanger costs necessitated by the separation of propylene glycol from the reaction mixture. In contrast, no such downstream separation is required in the CEBC-PO process due to the almost total PO selectivity.

It must be noted that the heat of reaction from the higher temperature TBHP and PO reactors is captured as high-pressure steam, which partially meets the process steam requirements and thereby lowers the installation costs of auxiliary steam generation units.

Total Production Costs. Raw material and product costs are summarized in Table 2. Figure 1 provides a comparison of the contributing costs by category to produce 1 lb of PO for the conventional PO/TBA, HPPO, and CEBC-PO processes. Raw materials (*i*-butane, propylene, and hydrogen peroxide) and utilities dominate the expenses in all three processes. It is assumed that the H₂O₂ oxidant needed for propylene epoxidation for the HPPO and CEBC-PO processes is procured from equivalent sources. Further, the concentration of H₂O₂ in the reactor feed stream is similar in both technologies.

Propylene. For reasons discussed earlier, high-purity propylene (cost: 55¢/lb) is assumed as feed for the CEBC-PO process.⁴³ In the conventional process, the propylene purity in the feed stream is 89 wt %, with propane accounting for the remaining 11 wt %, whereas the propylene purity in the feed stream of the HPPO process is 60 wt %, with propane accounting for the remaining 40 wt %. Because of the lack of pricing information for the mixed propylene/propane feed stream, we assume the cost of 89 wt % pure propylene employed in LyondellBasell PO/TBA process to be 49.5¢/lb (i.e., 90% of the cost of pure propylene), and the cost of 60 wt % pure propylene employed in the modified HPPO process to be 44¢/lb (80% of the cost of pure propylene). The cost of the mixed streams is higher than the cost of propane (42¢/lb).⁴³ In the PO/TBA process, 0.92 lb of mixed feed stream, costing 45.5¢/lb, is needed for the 0.81 lb of propylene required to manufacture 1 lb PO. For the HPPO process, approximately, 1.26 lb of the mixed feed stream, costing 55¢, is needed for the 0.75 lb of propylene required to manufacture 1 lb PO. These values, obtained from HYSYS simulations, are consistent within 3% of the stoichiometric values required for the LyondellBasell PO/TBA process and HPPO process, respectively. The

relatively higher costs of feedstock in the PO/TBA and HPPO processes are significantly offset by the additional revenue generated by the sale of enriched propane co-product [0.34 lb of propane/lb of PO in the PO/TBA process generating 14¢/lb PO, and 0.53 lb of propane/lb of PO in the HPPO process generating 22.2¢/lb]. In the CEBC-PO process, 0.72 lb of pure propylene feed, costing 40¢, is required to produce 1 lb PO.

Oxidant. In the conventional PO/TBA process, the TBHP oxidant is synthesized by the liquid phase oxidation of *i*-butane. At a market price of 30¢/lb, the cost of *i*-butane is a major expense.⁴⁴ The low TBHP selectivity and yield makes the *i*-butane requirement and thus TBHP production cost high. Approximately 2.1 lbs of *i*-butane, costing 62¢, are consumed to manufacture 1.77 lb of TBHP needed for the synthesis of 1 lb of PO. For the HPPO and CEBC-PO processes, the cost of H₂O₂ procured from an external supplier is 24.5¢/lb.⁴³ To produce 1 lb of PO, 0.85 lb of H₂O₂ is needed in the HPPO and CEBC-PO processes. The overall H₂O₂ utilization is a key determinant of the PO production cost.

Utilities. The utility costs (steam, cooling water, electricity, and refrigeration) are 13.1¢/lb of PO, 8.7¢/lb of PO, and 8.8¢/lb of PO for the conventional PO/TBA, HPPO, and CEBC-PO processes, respectively, and are summarized in Table 3. The

Table 3. Cost of Utilities in Conventional PO/TBA, HPPO, and CEBC-PO Processes

utility	conventional PO/TBA process (¢/lb PO)	HPPO process (¢/lb PO)	CEBC-PO process (¢/lb PO)
steam	5.78	5.06	5.97
electricity	2.52	2.70	2.13
refrigeration	4.26	0.50	0.30
cooling water	0.48	0.40	0.38
totals	13.04	8.66	8.78

only significant difference in utility costs is that the conventional PO/TBA process uses refrigeration to cool the condensers of the propylene recovery and PO purification columns, while in the HPPO and CEBC-PO processes refrigeration is used only to cool the propylene stripper 2.

Effect of Co-Product Value on Process Profit Margins. On the basis of a co-product/product (TBA/PO) weight ratio of 2.4, the monetary return for the PO/TBA process per lb PO sold also includes the revenue generated by the sale of 2.4 lbs TBA; a declining demand for TBA (due to a potential ban on MTBE use as a gasoline additive) will lower the profit margin. For every 10¢/lb reduction in TBA market value, the profit margin is decreased by 24¢/lb of PO. For the HPPO process, the profit margin is also dependent on the sale of propane, the precursor for propylene. In contrast, the profitability of the CEBC-PO process is independent of co-product earnings.

Effect of Catalyst Life and Leaching Rate on CEBC-PO Process Economics. In the conventional PO/TBA process, the TBHP oxidant is synthesized by the noncatalytic liquid phase oxidation of *i*-butane. The costs of molybdenum (used in the conventional PO/TBA process) and titanium metals (used in the HPPO process) for propylene epoxidation are \$450/lb and \$4.8/lb, respectively. At a market price of \$3000/lb, the rhenium metal is substantially more expensive necessitating the near-quantitative recovery of the metal for economic viability.⁴⁸ Further, we assume the cost of the soluble polymer supported Re catalyst complex (assumed to be used in the continuous CEBC-PO process) to be \$5000/lb.

The 2010 market price of PO is 121¢/lb PO.⁴³ The cost to coproduce 1 lb of PO along with 2.4 lbs of TBA in the conventional PO/TBA process is 150.4¢ (Figure 1). On the basis of the current market value of 41¢/lb for TBA and 42¢/lb for propane, the PO/TBA process yields a profit margin of 87.9¢/lb of PO. As shown in Figure 1, the PO production costs by the HPPO process is 107.1¢/lb, yielding a profit margin of 36.1¢/lb, assuming a market price of 42¢/lb for the enriched propane co-product. The PO production cost for the CEBC-PO process is 90.6¢/lb, yielding a profit margin of 30.3¢/lb of PO provided the minimum catalyst life of the immobilized MTO is 1 year at a leaching rate of 9.3×10^{-2} lb MTO/h (i.e., makeup catalyst addition rate). While profitable, the CEBC-PO process has the potential to be competitive with existing processes only if these catalyst performance metrics are surpassed at a minimum. Figure 2 shows the sensitivity of the

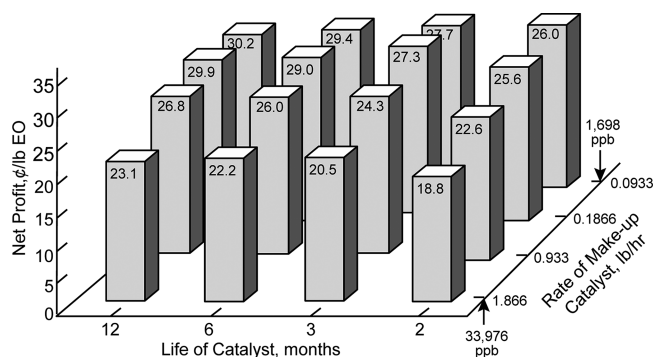


Figure 2. Effect of catalyst durability and leaching rate on the net profitability of the CEBC-PO process.

PO production cost to variations in catalyst leaching rate and catalyst life. Such an analysis helps establish quantitative catalyst performance metrics (activity, selectivity, catalyst life, and leaching rate) for the profitability of the CEBC-PO process.

ENVIRONMENTAL IMPACT ASSESSMENTS OF THE PO PROCESSES: METHODOLOGY INCLUDING LCA BOUNDARIES AND RAW MATERIAL SOURCES

GaBi 4.4 software, developed by PE solutions, is employed to perform cradle-to-gate life cycle assessments of the conventional PO/TBA, HPPO, and CEBC-PO processes. The software with its embedded United States-specific life cycle inventory (USLCI) is employed to estimate United States-specific environmental impacts.⁴⁹ The mass and energy balance information obtained from the Aspen HYSYS simulation serves as the stream inputs for the various data sets utilized in the GaBi simulation. TRACI (Tools for the Reduction and Assessment of Chemical and Other Environmental Impacts), a method developed by U.S. Environmental Protection Agency (USEPA), is employed to estimate the environmental impact of producing PO under the various categories listed in Table S5 (Section E of the Supporting Information).^{50–52} This analysis incorporates the cumulative impacts associated with raw material extraction, transport, and processing. A proportional allocation method based on the mass fraction of the products and byproducts is employed to estimate the environmental impact associated with PO production by the conventional PO/TBA process. The allocation factor is estimated as the quantity of the desired product (PO) to the total quantity of all the products produced in a process.

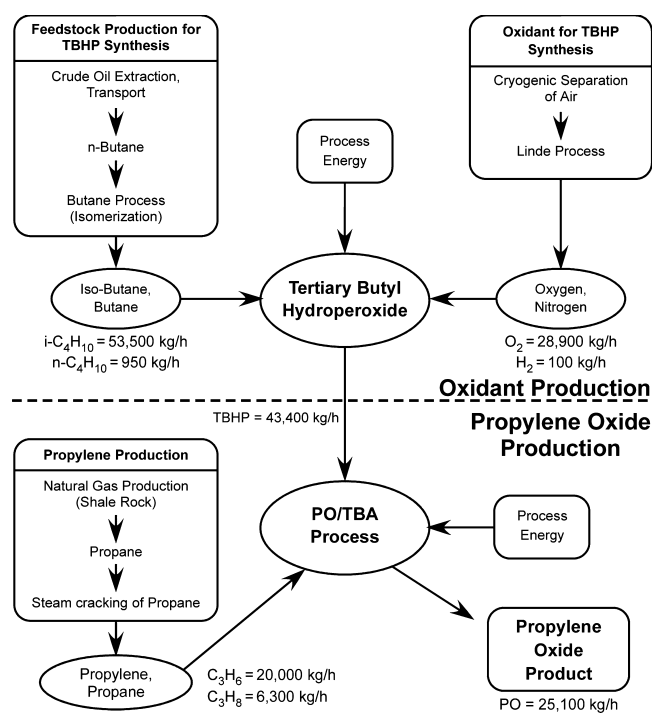


Figure 3. Boundaries of the cradle-to-gate LCA of the conventional PO/TBA process.

LCA Assumptions. A United States-specific life cycle assessment (*cradle-to-gate*) is made to quantify the environ-

mental impact of producing $\sim 200,000$ tonnes/year of PO (functional unit) by the conventional PO/TBA, HPPO, and the CEBC-PO processes. The environmental impacts due to the mining of the molybdenum, titanium, palladium, and rhenium metals are not considered in this analysis because of the lack of database information. Furthermore, the actual amounts of these catalyst metals used annually are relatively small compared to the usage of the other raw materials. In the case of the conventional PO/TBA process, in addition to TBA, acetone and methanol are also formed as byproducts. Acetone and methanol byproducts are not considered in the estimation of the allocation factor because of their low yields ($<1\%$). A factor of 0.38 (reflecting the PO/TBA weight ratio) is used in allocating the impact due to PO in the conventional PO/TBA process.

Raw Material Sourcing. The mass flow rates of raw materials consumed during the steady operation of the three PO production technologies are shown in Figures 3, 4, and 5.

The bulk of the butane and propane in the United States is sourced from natural gas and from naphtha (a fraction of crude oil). *i*-Butane is produced industrially by the isomerization of *n*-butane (Butamer process).⁵³ Propylene is produced in the United States primarily as either a byproduct of ethylene production from petroleum crackers or by propane dehydrogenation. Propane dehydrogenation is an endothermic equilibrium reaction with an overall yield of 90%.⁵⁴ Further, the energy required to produce enriched or high purity propylene is considered in this environmental assessment.⁵⁴ This analysis incorporates the impact of transporting feedstock

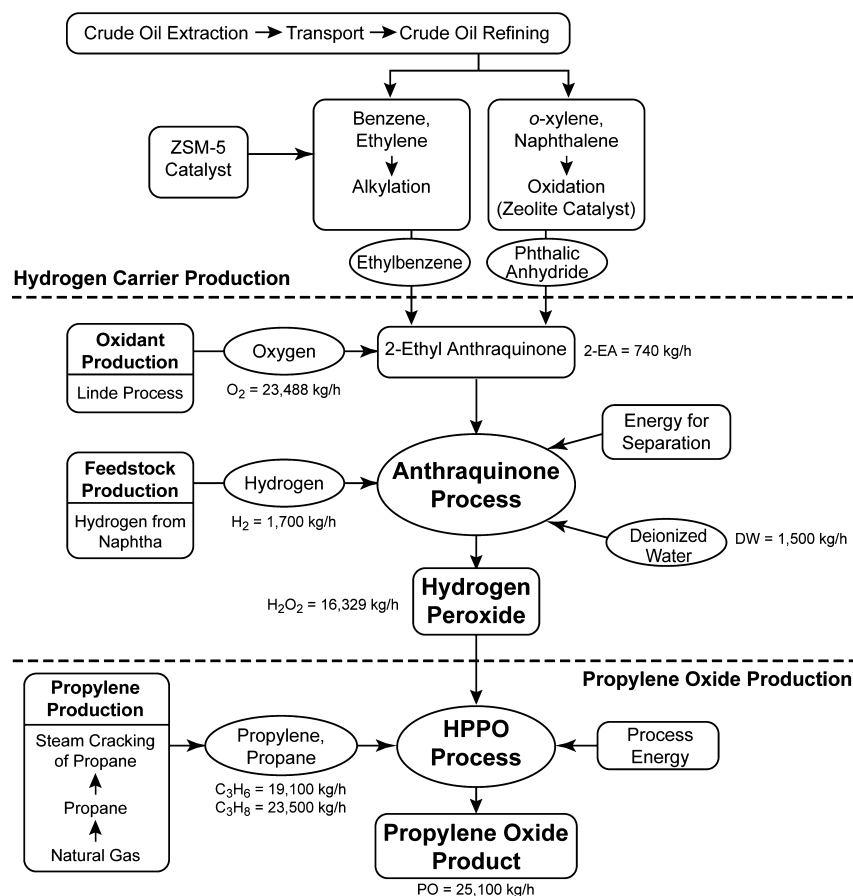


Figure 4. Boundaries of the cradle-to-gate LCA of the HPPO process.

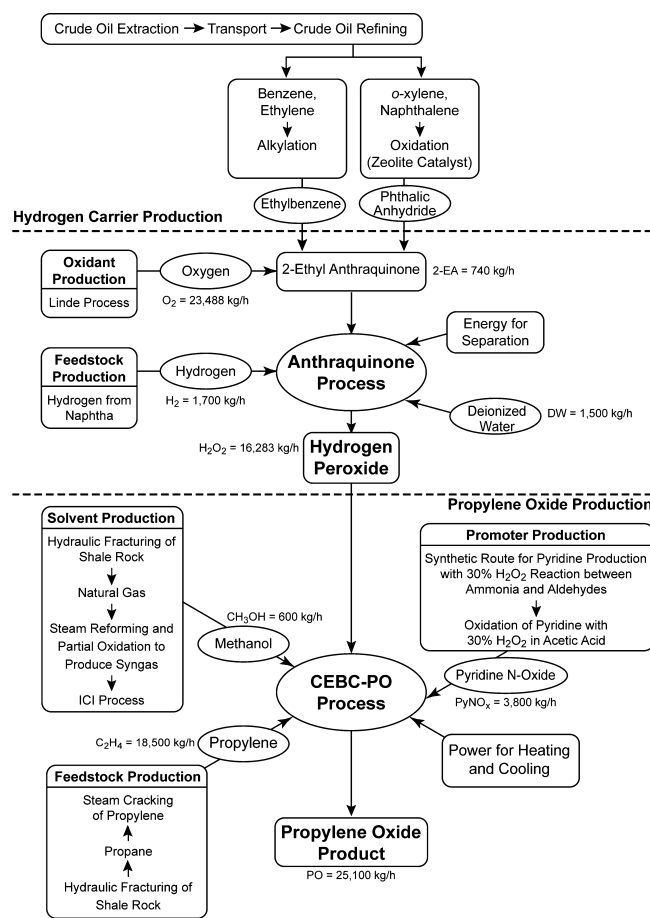


Figure 5. Boundaries of the cradle-to-gate LCA of the CEBC-PO process.

from the exporting nations to the United States. *Hydrogen peroxide* is produced by the anthraquinone process.¹² The hydrogen carrier, 2-amylanthraquinone, is prepared by the reaction of amylbenzene and phthalic anhydride.^{55,56} *Pure oxygen* is produced by the cryogenic separation of air (LINDE process).⁵⁷ *Methanol* is produced commercially by the ICI process, wherein methane is steam reformed to produce synthesis gas which is transformed to methanol.⁵⁸ *Pyridine-N-oxide* is prepared by the oxidation of pyridine with 30% H₂O₂ in acetic acid. Industrially, pyridine is produced by the reaction of acetaldehyde and formaldehyde with ammonia in the presence of solid-acid catalysts at high temperatures and space velocity.⁵⁹

ENVIRONMENTAL IMPACT ASSESSMENTS OF THE THREE PO PROCESSES

Gate-to-Gate analysis. The approach to estimate the environmental impact was first assessed by performing a *gate-to-gate* environmental impact assessment of the simulated conventional PO/TBA process and comparing the estimated emissions with those reported by LyondellBasell for their Bayport, Texas, facility (Table 4). The production capacity of this facility is 210,000 tonnes of PO/yr, which is comparable to that used in the simulation (200,000 tonnes/yr). The potential emissions are taken from the toxic release inventory data reported to the USEPA for both emitted and treated waste for this facility.⁶⁰ The environmental impacts at the plant location (*gate-to-gate*) from emissions resulting from various unit operations were estimated using empirical equations available

Table 4. Comparison of Environmental Emissions Obtained from Toxic Release Inventory Data for LyondellBasell's Bayport, Texas, Facility and Those Predicted by GaBi Software^{60a}

impact	units	LyondellBasell PO/TBA process		
		GaBi (gate-to-gate) (millions)	EPA Toxic Release Inventory (gate-to-gate) (millions)	
			total waste	released waste
acidification	[mol H ⁺ Eq.]	0	N/A	N/A
ecotoxicity water	[kg 2,4-DCP Eq.]	1.72	2.73	0.49
greenhouse gas emissions	[kg CO ₂ Eq.]	1.32 × 10 ⁻²	N/A	N/A
human health non-cancer air	[kg toluene Eq.]	0.052	0.10	0.17 × 10 ⁻²

^aOnly the major impact categories included here. For a complete list of all impacts, please refer to Table S6 of section G of the Supporting Information. DCP, dichlorophenoxyace; Eq., equivalent; N/A, data not available in the toxic release inventory.

Table 5. Predicted Cradle-to-Gate Environmental Impact for Producing Propylene Oxide by Conventional PO/TBA, HPPO, and CEBC-PO Processes^a

impact category	units	conventional PO/TBA process (millions)	HPPO process (millions)	CEBC-PO process (millions)
acidification	[mol H ⁺ Eq.]	572	465	493
ecotoxicity water	[kg 2,4-DCP Eq.]	212.6	132.9	138.2
greenhouse gas emissions	[kg CO ₂ Eq.]	3561	2598	2827
human health non-cancer air	[kg toluene Eq.]	5031	946	954

^aOnly the major impact categories are included here. For a complete list of all impacts, please refer to Table S7 of section H of the Supporting Information. DCP, dichlorophenoxyace; Eq., equivalent.

in the literature. The mass flow rates and compositions of the various process streams obtained from Aspen HYSYS simulation, equipment design information, and equipment specific fugitive emission factors (e.g., reactors, columns, and pumps) were used for estimating the environmental impacts under the various categories. TRACI, the United States-specific environmental impact estimation tool, uses this information to estimate the environmental impacts (see section G, Supporting Information, for methodology to extract environmental impact factors for TRACI from GaBi software). At present, there are no facilities in the United States that produce PO using the technology developed by the HPPO process.

As shown in Table 4, the actual emissions from the LyondellBasell PO/TBA facility are an order of magnitude lower than that of the total untreated waste. The potential emissions predicted by the GaBi software (ecotoxicity and impact on human health) are of the same order of magnitude as the total waste generated at the facility, with the predicted emissions being lower in most cases. On the basis of this *gate-to-gate* analysis, it is inferred that only the predicted environmental impacts that differ by more than an order of magnitude are reliable for making conclusions about the relative

Table 6. Major Sources of Adverse Environmental Impacts in the Conventional PO/TBA process

source of impacts	impact category	% contribution
fossil fuel-based energy (natural gas, electricity from coal, and natural gas) generation for process operations (gate-to-gate)	acidification	11.3
	greenhouse gas emissions	10.9
	human health non-cancer air	1.3
	ecotoxicity water	6.5
fossil fuel-based energy (natural gas, coal, and transportation fuel) generation for raw-material manufacture (cradle-to-gate)	acidification	88.6
	greenhouse gas emissions	89.1
	human health non-cancer air	98.7
	ecotoxicity water	93.5

Table 7. Major Sources of Adverse Environmental Impacts in HPPO and CEBC-PO Processes

sources of impacts	impact category	% contribution HPPO	% contribution CEBC-PO
fossil fuel-based energy (natural gas, electricity from coal, and natural gas) generation for process operations (gate-to-gate)	acidification	4.1	6.7
	ecotoxicity water	3.3	6.8
	greenhouse gas emissions	5.5	10.7
	human health non-cancer air	2.3	4.4
fossil fuel-based energy (natural gas, coal, and transportation fuel) production for raw material manufacture (cradle-to-gate)	acidification	95.8	93.2
	ecotoxicity water	96.6	93.1
	greenhouse gas emissions	94.4	89.2
	human health non-cancer air	97.7	95.6

impacts of the competing processes. Regardless, the quantitative data generated by the cradle-to-gate life cycle assessment is useful to identify potential sources that contribute the most to adverse environmental impacts.

Cradle-to-Gate Life Cycle Assessment. Table 5 compares the *cradle-to-gate* environmental impact of PO production for the conventional PO/TBA, HPPO, and CEBC-PO processes. The estimated cradle-to-gate environmental impacts are generally 1 to 2 orders of magnitude greater than the gate-to-gate emissions (Table 4). The overall cradle-to-gate environmental impacts of the CEBC-PO and HPPO processes are similar because of the similarity in raw material (propylene, H₂O₂, methanol) and process conditions ($T = 40$ °C and $P = 5$ MPa ranges) in these processes and are hence lumped in the discussion that follows. The predicted cradle-to-gate environmental impacts for the CEBC-PO process are of the same order of magnitude as the conventional PO/TBA process but lower in most impact categories. Tables 6 and 7 list the major environmental impacts and their percentage contributions relative to the overall impact for the conventional PO/TBA and HPPO processes. The tables clearly show that the majority (90+%) of the overall environmental impact in each of the listed categories stems from fossil fuel-based energy production for the manufacture of raw materials outside the plant and far less from fossil fuel-based energy production for process operations within the plant. Raw material production utilizes energy derived from natural gas, transportation fuel, and coal, whereas the process energy requirement for plant operations is met using steam produced from natural gas and electricity produced at coal and natural gas plants.

Potential Opportunities for Minimizing the Environmental Impact of the CEBC-PO Process. This cradle-to-gate environmental impact analysis identified raw material production (propylene and H₂O₂) as the biggest contributors to the overall environmental impact of the CEBC-PO process. Some potential opportunities and key variables that can

improve the environmental impact follow. Deployment of new highly selective H₂O₂ production technologies such as direct H₂O₂ process and the recycling of unreacted H₂O₂ (instead of decomposing it) will reduce the overall environmental impact of the CEBC-PO process. Similarly, the sourcing of propylene from cellulosic biomass or utilization of mixed propylene+propane stream will lower the overall environmental impact of the CEBC-PO process. Utilizing H₂ produced from biomass will further lower adverse environmental impact.

CONCLUSIONS

By employing Aspen HYSYS-based plant scale simulations of the conventional PO/TBA, HPPO, and CEBC-PO processes, capital costs for the HPPO (\$275 million) and CEBC-PO (\$228 million) processes are estimated to be lower than the conventional PO/TBA process (\$372 million). The cost to co-produce 1 lb of PO and 2.4 lbs of TBA by the conventional PO/TBA process is 150.4¢ yielding a profit margin of 87.9¢. Similarities in operating conditions in the HPPO and CEBC-PO processes result in comparable PO production costs: 107.1¢/lb with a profit margin of 36.1¢/lb for the HPPO process, assuming a market price of 42¢/lb for the enriched propane stream, and 90.6¢/lb with a profit margin of 30.4¢/lb for the CEBC-PO process, assuming that the MTO catalyst is active for a minimum of 1 year at a leaching rate of 9.3×10^{-2} lb/h. However, an anticipated decline in the TBA demand for MTBE (a banned fuel additive) production makes the long-term feasibility of the HPPO and CEBC-PO processes more favorable. Further, the use of a mixed feed containing propylene and propane (obviating propane separation) will make the CEBC-PO process even more competitive.

The *gate-to-gate* environmental impact of the simulated conventional PO/TBA process is of the same order of magnitude as reported by LyondellBasell to the USEPA for their Bayport, Texas, facility. The cumulative *cradle-to-gate* life cycle assessments of the PO/TBA, HPPO, and CEBC-PO

processes yield impacts that are of the same order of magnitude in all categories. The predicted emissions are highest for the conventional PO/TBA process, primarily because of the greater environmental impact from TBHP production compared to H₂O₂ production. Though the estimated reduction in GHG emissions for the H₂O₂-based processes is approximately 20%, the differences lie within the uncertainty of these predictions. Further, the major environmental impacts in all the processes mainly stem from sources outside the PO plant because of the utilization of fossil fuel-based energy for producing the raw materials (*i*-butane, propylene and hydrogen peroxide).

■ ASSOCIATED CONTENT

📄 Supporting Information

Assumptions common to all processes; detailed process description of the conventional PO/TBA process, HPPO process, and CEBC-PO process; descriptions of the various impact categories; estimations of the reactor volume for the CEBC-PO process; methodology to extract the environmental impact factors from GaBi; and the complete list of all the environmental impact categories for gate-to-gate and cradle-to-gate environmental impact assessments. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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