

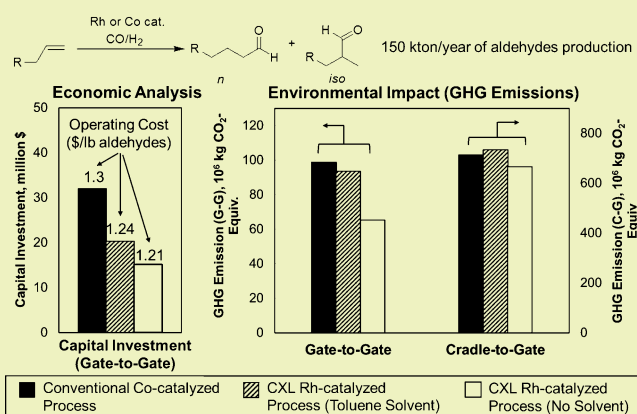
## Development of a Greener Hydroformylation Process Guided by Quantitative Sustainability Assessments

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## Supporting Information

**ABSTRACT:** Environmental impacts and economics associated with a potentially greener, Rh-catalyzed, 1-octene hydroformylation process in CO<sub>2</sub>-expanded liquid (CXL) medium are quantitatively assessed against a conventional Co-catalyzed process. The economic analysis shows a more than 30% lower capital investment for the CXL process compared to the conventional Co-catalyzed process of similar capacity. This is due to the higher reaction and catalyst recovery efficiencies at milder reaction temperature and pressures (compared to the conventional process) used in the CXL process. The total production cost (TPC) associated with the CXL process is lower than the conventional process when the Rh makeup rate is lower than 0.94% (of the total amount of Rh in the reactor) per hour at the current Rh price (\$20,800/lb). This translates to an economic viability criterion of (\$makeup Rh/\$TPC) being 0.042 or less. Life cycle analysis (LCA) was performed using GaBi software and an EIO-LCA method based on plant scale simulation of both the conventional and continuous CXL processes to produce 150 kton/year of nonanal. Gate-to-gate LCA projections show that the CXL process is environmentally friendlier than the conventional process in most impact categories such as ecotoxicity, greenhouse gas emissions, and smog formation. Predicted emissions for the conventional process are of the same order of magnitude as those reported from an actual plant of similar capacity. Cradle-to-gate environmental impacts are 1 to 2 orders of magnitude greater than the gate-to-gate impacts with energy usage for the production of raw materials being the major source of adverse environmental impacts. The EIO-LCA results agree with the GaBi analysis. Our results show that the environmental performance of the CXL process can be further improved with lower solvent usage, thus also providing valuable guidance for process optimization.

**KEYWORDS:** Olefin hydroformylation, Carbon dioxide-expanded liquids, Sustainability assessment



## INTRODUCTION

Hydroformylation of olefins with synthesis gas (hydrogen + carbon monoxide) to make aldehydes is typically accomplished by a homogeneous catalytic process. Industrial processes generally use rhodium (Rh)-based catalysts for lower olefins and cobalt (Co)-based catalysts for C<sub>5+</sub> olefins.<sup>1</sup> However, Co-based catalysts require rather harsh conditions. For example, the most common cobalt catalyst, cobalt carbonyl hydrides, requires pressures of 20–35 MPa and temperatures of 150–180 °C in order to prevent decomposition of the catalyst and avoid syngas starvation.<sup>2</sup> Recycling of the Co catalyst is usually accomplished in a series of unit operations that are not only energy intensive but also require significant amounts of acid and base resulting in sizable waste streams.<sup>3</sup> On the other hand, Rh-based catalysts are known to provide higher activity and better product selectivity toward the linear aldehydes at much milder operating conditions (40–130 °C, 1–4 MPa).<sup>4</sup> However, Rh is approximately 1000 times more expensive

than Co and a far more scarcer element. Hence, the application of Rh catalysts for higher olefin hydroformylation in practice requires strategies that provide nearly complete recovery and recycling of the Rh catalyst.

Recently, we demonstrated in a laboratory-scale stirred reactor that the use of a soluble polymer-bound Rh catalyst complex in conjunction with a size-selective nanofiltration membrane can substantially retain the bulky catalyst in solution while allowing the lighter components to pass through.<sup>5</sup> A JanaPhos-bound homogeneous Rh catalyst complex<sup>6</sup> (a polystyrene backbone-supported biphenos-type ligand) was shown to display stable activity [nearly steady turnover frequency (TOF) of ~125 h<sup>-1</sup>] and regioselectivity (*n/i* = 3.5) at 50 °C during continuous 1-octene hydroformylation

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under 3 MPa of syngas in a stirred reactor equipped with a nanofiltration membrane.<sup>5</sup> More recently, it was shown that by using only 0.6 MPa of syngas and 3.2 MPa of compressed CO<sub>2</sub> as the pressurizing gas, a CO<sub>2</sub>-expanded liquid (CXL) was created at 50 °C.<sup>7–9</sup> The CXL medium allows facile tunability of the solubilities of hydrogen and carbon monoxide. For example, it is possible to achieve molar H<sub>2</sub>/CO ratios in the CXL phase that are either comparable to or greater than those observed in conventional solvents at much lower syngas pressures, thus avoiding syngas inhibition.<sup>10</sup> Such a unique combination of H<sub>2</sub> and CO solubilities results in enhanced turnover frequency (~340 h<sup>-1</sup>), aldehydes selectivity (>90%), and regioselectivity (*n/i* ~8) at nearly steady operation for approximately 50 h. The CXL phase also has an approximate 30% lower viscosity compared to the neat solvent thereby improving the mass transfer flux across the nanofiltration membrane. Constant permeate flux was maintained during the 50 h run with Rh leakage in the effluent being less than 0.5 ppm.

Quantitative economic and environmental impact analyses at various stages of process development are essential to assess if such alternative process concepts, guided by the qualitative principles of green chemistry and green engineering, are indeed greener compared to the conventional process. Herein, we demonstrate how such analyses help identify both economic and environmental “hotspots” and provide rational guidance to the development of more sustainable process concepts. For example, based on the first demonstration of the acetylacetonatorhodium(I) dicarbonyl [Rh(CO)<sub>2</sub>(acac)]/triphenylphosphine (TPP)-catalyzed 1-octene hydroformylation process in CXL media in a batch reactor, we performed preliminary economic and environmental impact assessments employing plant-scale simulation of an envisioned CXL-based hydroformylation process. The results were compared to similar assessments of a simulated industrial Co-based hydroformylation process operating at similar production capacity.<sup>11</sup> The comparative analyses showed that the CXL process had the potential to be both economically competitive and environmentally friendlier than the conventional process subject to prescribed quantitative metrics for Rh recovery. This directly led to the development of the polymer-bound JanaPhos ligand (instead of TPP ligand) with the intention of using nanofiltration membranes to contain the bulky ligand. Such an *in situ* containment strategy obviates post-reactor catalyst separation and solvent (methanol) usage associated with the Rh/TPP catalyst.

The present work provides detailed economic and environmental impact analyses of the continuous hydroformylation process utilizing the new ligand and Rh retention strategy. The economic and environmental impact analyses were also updated and improved by including more reliable plant data for the conventional Co process and performing a cradle-to-gate life cycle analysis (LCA) (as opposed to only a gate-to-gate environmental assessment) as well as an economic input–output life cycle assessment (EIO-LCA). In addition, the sensitivity of the predictions to fluctuations in solvent usage and Rh cost are also discussed. The updated analyses provide a more reliable benchmarking of the economics and environmental impacts of the CXL process vis-à-vis the conventional Co-based process.

**Table 1. Basic Simulation Parameters for Conventional and CXL Processes**

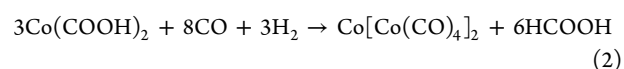
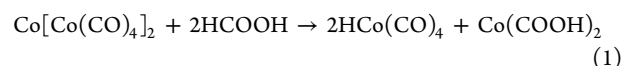
simulation parameters	units	conventional	CXL
catalyst	–	HCo(CO) <sub>4</sub>	Rh(CO) <sub>2</sub> (acac)/JanaPhos (P/Rh = 4)
catalyst concentration based on octene	wt %	0.53	0.028
catalyst recovery rate	%	98	99.8
rxn. temperature	°C	165	50
rxn. pressure	MPa	20.8	3.8 (0.6 MPa syngas + CO <sub>2</sub> )
conversion	%	94	80
selectivity to aldehydes	%	80	97
aldehyde <i>n/i</i>		4	8
syngas/olefin	mol/mol	2.02	2.02
H <sub>2</sub> :CO	mol/mol	1	1
solvent	–	none	CXL–toluene (4.5 wt % CO <sub>2</sub> , toluene = 72 wt %)

## METHODOLOGY

**Process Descriptions and Simulations.** Both the conventional and CXL processes were simulated using Aspen HYSYS. The UNIQUAC package present in Aspen HYSYS was used to predict the relevant thermodynamic properties, while the Peng–Robinson equation of state was employed for vapor phase modeling. The following assumptions were made for simulating the conventional and CXL-based processes: (1) Annual production capacity is 150 kton/year for both processes. (2) Although a mixture of different isomers of octenes is used as the raw material in industrial hydroformylation, identical feeds (1-octene and syngas with an equimolar H<sub>2</sub>/CO ratio) were used for both processes to enable a fair comparison. (3) The unit price for the raw materials, utilities, and labor was assumed to be identical for both processes. (4) The Rh catalyst remains stable for at least a year. (5) The cost of the JanaPhos polymer ligand is negligible compared to the cost of Rh. (6) The heavy byproducts (olefin tetramer, diether, and diacetal) formed in the conventional process were not subsequently cracked or recycled. Heavy products in the CXL process were assumed to be negligible based on lab-scale experimental data, wherein no such byproducts were detected.

The data for simulating the conventional process were obtained from the literature.<sup>12–18</sup> To simulate the CXL process, the data were mostly from lab-scale continuous process results. The basic parameters used in the HYSYS simulation for both processes are listed in Table 1.

The simulated processes for the conventional and CXL processes are shown in Figures 1 and 2, respectively. In the conventional process, the hydroformylation reaction is catalyzed by cobalt carbonyl at 165 °C and 20.8 MPa in three continuous stirred tank reactors (CSTR) in series. The reaction mixture (octene and cobalt catalyst) is fed into the first reactor. The effluent from the first reactor is fed to the second reactor and so on. Syngas is fed into the three reactors in parallel to maintain constant syngas pressure. The cobalt catalyst is separated from the products and recycled back to the reactors through a series of unit operations (stripper column, decanter, demetaling column, evaporator, catalyst performer, and flash column).<sup>14,15</sup> Formic acid is used to regenerate the cobalt carbonyl salt back into cobalt tetracarbonyl and cobalt formate (eq 1). The cobalt tetracarbonyl is removed via gas stripping. The cobalt formate is treated with high-pressure syngas to form cobalt salt and regenerate formic acid (eq 2).



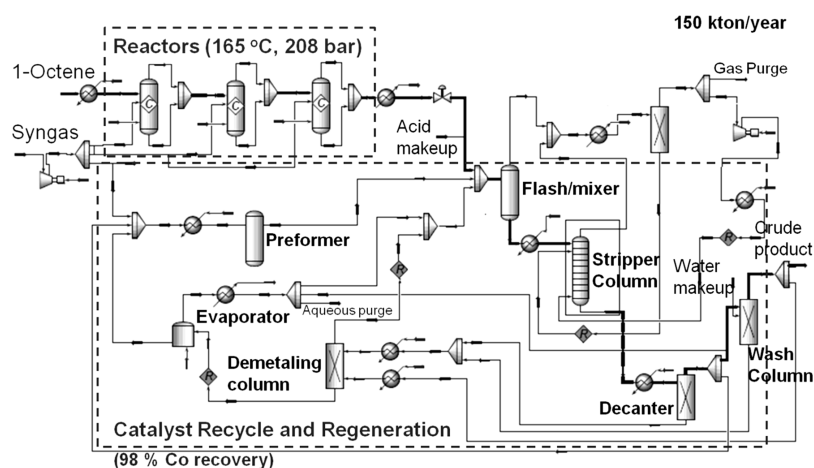


Figure 1. Process flow diagram of simulated conventional process.

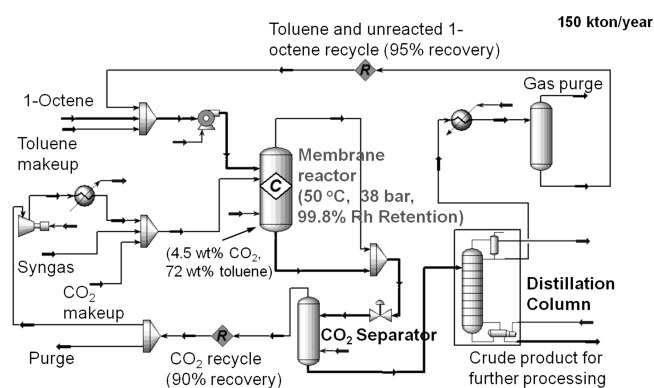


Figure 2. Process flow diagram of simulated CXL process.

In the CXL process (Figure 2), the octene hydroformylation reaction is catalyzed by the Rh/JanaPhos catalyst complex at 50 °C and 3.8 MPa in a membrane reactor, modeled as a CSTR. The total pressure is made up of 0.6 MPa syngas and CO<sub>2</sub>. The flow rate of the vapor outlet stream from the CSTR was set to zero to indicate that all reactor components exit through the membrane at the bottom of the reactor. The Rh catalyst complex is largely retained in the membrane reactor during continuous operation, with an average Rh loss in the effluent stream of approximately 0.2 wt % per hour. It is further assumed that the leached Rh in the effluent stream is not recovered. The reactor effluent stream is depressurized, causing most of the CO<sub>2</sub> to be separated from the liquid phase in a separator. The CO<sub>2</sub> is continuously recompressed and recycled back into the reactor along with other unreacted feed components. Following CO<sub>2</sub> separation, the product stream passes through a distillation column, wherein toluene is separated from unreacted 1-octene and recycled back into the reactor.

The mass and energy flows obtained from HYSYS simulations were used for performing the economic and environmental impact analyses.

**Economic Analysis.** The economic analysis was performed by calculating total capital investment (TCI) and total production cost (TPC) using the methods described in Peters et al.<sup>19</sup> All costs were adjusted for inflation to 2012 dollars using the chemical engineering plant cost index (CEPCI).<sup>20</sup> The uncertainties of the TCI and TPC values are between 10% and 30%.

Details of the prices of the raw materials, utilities, labor, and contribution of each component to the TCI and TPC are listed in Section A of the Supporting Information (SI). Further, the impact of using different Rh makeup rates on the operating costs and overall economics is analyzed through a sensitivity analysis.

**Life Cycle Analysis.** Two LCA approaches were used in parallel to identify the environmental impacts of the conventional and CXL

processes: commercial GaBi software (version 6.0, PE Solutions) and economic input–output life cycle assessment (EIO-LCA) tool.<sup>21</sup> The results of these two approaches are compared and discussed.

**GaBi.** The life cycle analysis is based on United States locations. The details of the methods applied are similar as described elsewhere.<sup>22–24</sup> The LCA process models for the conventional and CXL processes are shown in Section B of the Supporting Information. TRACI, version 2.0, (tools for the reduction and assessment of chemical and other environmental impacts)<sup>25</sup> is used as the life cycle impact assessment (LCIA) methodology. Since TRACI was developed by the U.S. Environmental Protection Agency (USEPA), it is especially well suited for impact assessment in United States locations. The annual cumulative environmental impacts from the two processes are compared under various environmental impact categories such as acidification, ecotoxicity, greenhouse gas emissions, and smog (air).

**Goal.** The goal of this LCA analysis is to quantitatively compare the environmental impacts of both the conventional and CXL processes in order to assess the environmental footprints and identify potential areas for reducing adverse environmental impacts of both processes. The scope of this LCA is as follows.

**Functional Unit.** Production of 150 kton/year of nonanals by both conventional and CXL processes.

**System Boundaries.** The boundaries of the LCA analysis for the conventional and CXL processes are shown in Figures 3 and 4,

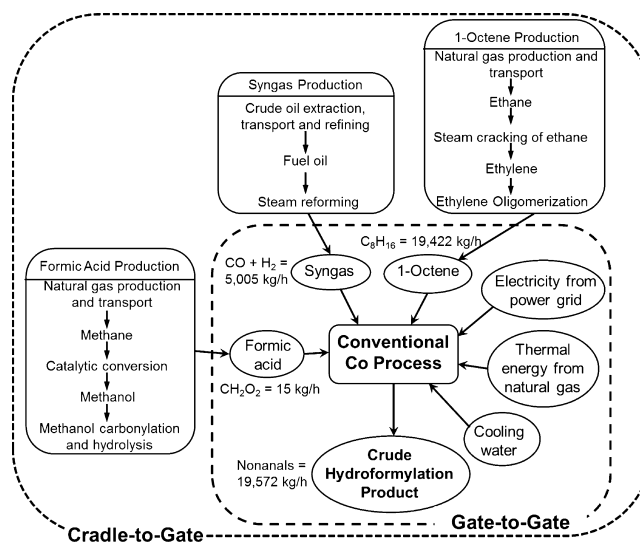
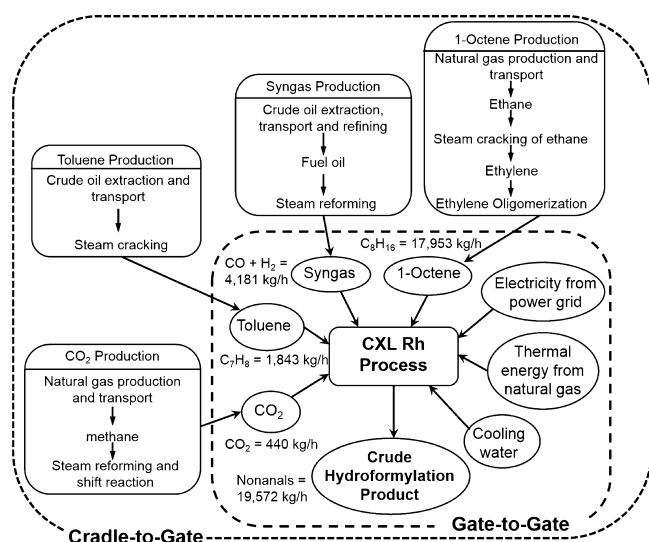


Figure 3. Boundaries of the conventional Co process considered in the cradle-to-gate life cycle analysis.



**Figure 4.** Boundaries of the CXL Rh-based process considered in the cradle-to-gate life cycle analysis.

respectively. For both processes, the cradle-to-gate analysis includes potential environmental impacts resulting from raw material extraction, transport, and processing, as well as gate-to-gate emissions and discharges inside the plant.

**Life Cycle Inventory.** The inputs and outputs of this LCA are based on the mass and energy flows in the conventional and CXL processes obtained from Aspen HYSYS simulations shown in Figures 1 and 2.

The raw material sources and production routes are as follows. 1-Octene is produced by oligomerization of ethylene via the Shell higher olefin process (SHOP).<sup>26</sup> Ethylene is produced by steam cracking of naphtha. Syngas is produced from steam reforming of fuel oil.<sup>27</sup> In the conventional process, the formic acid used for recovery and regeneration of the Co catalyst is produced by carbonylation of methanol to form methyl formate.<sup>28</sup> Hydrolysis of methyl formate provides formic acid. In the CXL process, toluene and carbon dioxide are used as reaction media. Toluene is a byproduct generated from steam cracking of crude oil.<sup>29</sup> Carbon dioxide is made as a byproduct from the water–gas shift reaction during ammonia synthesis.<sup>30</sup> In the GaBi process model, the environmental impacts stemming from the mining of the catalytic metals (cobalt and rhodium) were not considered due to a lack of information and the fact that the consumption of these catalytic metals is rather small compared to amounts of the other raw materials. Nevertheless, because the mining and refining of metals do create environmental impacts,<sup>31,32</sup> the environmental impact of the catalyst is assessed via the EIO-LCA model using the production costs of Co and Rh, the active catalytic metals.

The amount of toluene (72 wt %) used in the CXL process simulation was based on the amount used in actual lab-scale experiments, in which toluene usage was in large excess. Because the JanaPhos ligand has a relatively high solubility in toluene (60 mg/mL),<sup>6</sup> the minimum amount of toluene to completely dissolve the catalyst is 33 wt %. Hence, the amount of toluene used can be further decreased, which would reduce the environmental impacts stemming from the energy-intensive distillation step. Therefore, four different toluene amounts (72, 50, and 35 wt % and none) are used in the LCA calculations. The extent of solvent usage also affects the process economics. However, this effect is relatively small because most of the toluene is recycled back to the reactor and reused. To illustrate this, the cases where 72 wt % toluene was used in the process and one without toluene were included in the economic evaluations.

For all these sources and processes, the environmental impacts for producing the various feedstock materials and solvents are obtained from GaBi software assuming that electricity is derived from a variety of sources (coal, oil, natural gas) typical of the United States power grid, and process steam is derived from natural gas. The effects of

different energy sources (i.e., variation in grid sources) on environmental impacts have been discussed in detail in our recent work.<sup>33</sup>

**Uncertainty in GaBi Analysis.** The uncertainty of GaBi LCA is typically within an order of magnitude as shown in our previous work<sup>22–24,33</sup> where the GaBi-predicted emissions were compared with actual plant emissions. A more detailed sensitivity and uncertainty analysis is included in this work.

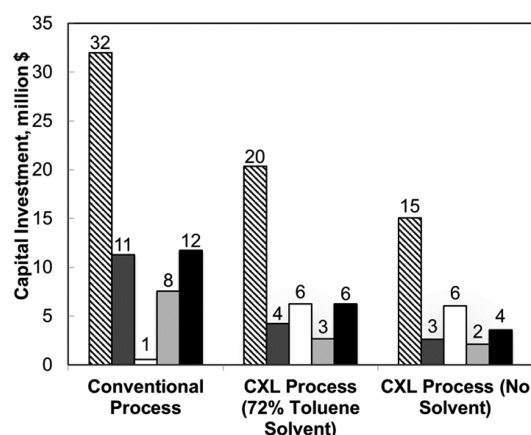
The feedstock input to the GaBi LCA are fixed numbers. The energy inputs (electricity, steam, and cooling water) are the major variables and therefore the sources of uncertainty. Because the amount of energy used is simulated by process modeling using Aspen HYSYS software, it is difficult to determine the variability of the data. A single value was used to estimate the amount of randomness of all data.<sup>34</sup> A sensitivity analysis of the energy input on the LCA output along with a stochastic Monte Carlo uncertainty analysis were performed using the built-in function in the GaBi software assuming that the relative standard deviation of the energy input is  $\pm 30\%$ . Because the majority of the environmental impacts of the cradle-to-gate analysis is from feedstock production, the sensitivity and uncertainty analysis were only carried out for gate-to-gate analysis, where the effects of the energy input variables are more significant. The sensitivity and uncertainty in estimates in the global warming impact category are shown as examples with the rest of the impact categories showing similar trends.

**EIO-LCA.** It is a life cycle assessment tool that estimates the material and energy resources required for, and associated environmental emissions resulting from, activities in our economy. The goods and services of the United States economy are divided into distinct aggregate sectors (such as petrochemical manufacturing, industrial gas manufacturing, power generation and supply, etc.).<sup>21,35</sup> The cost (purchase) of a certain product, process, or service along with the appropriate sector is used as the starting points for this model. The EIO-LCA model estimates the material and energy consumption as well as the associated environmental impacts over the entire supply chain.

In this work, the U.S. 2002 Producer model, consisting of 428 sectors, was used. The major capital investment and production costs were normalized from 2012 (used in estimating capital and operating costs) to 2002 values based on the consumer price index (CPI-U) published by the U.S. Census Bureau.<sup>36</sup> The EIO sectors used for assessing the major categories of the capital and production costs are listed in Section C of the Supporting Information. The greenhouse gas emissions and energy consumption associated with both the conventional and CXL processes are calculated and compared.

## RESULTS AND DISCUSSION

**Comparison of TCI and TPC for Both Processes.** The main cost contributors to the TCI along with the total cost are shown in Figure 5. Complete details are listed in Table 2. The estimated TCI of the conventional process is more than 50% greater than the CXL process when 72 wt % of toluene is used as solvent and more than twice as the CXL process when no added solvent is used (i.e., the reaction mixture itself acts as the solvent). The main contributors to the TCI of the conventional process are the reactor costs, heat exchangers, separators, and distillation columns. Because of the use of three high pressure reactors (20.8 MPa, 165 °C) in parallel, the reactor cost in the conventional process is almost three times greater than the CXL process, wherein only one membrane reactor that operates at much milder conditions (3.8 MPa, 50 °C) is used. The much higher reaction temperature of the conventional process results in the heat exchanger cost being more than twice that of the CXL process. The series of unit operations for Co catalyst regeneration increases the cost of separators and distillation columns in the conventional process. In the CXL process, the compressor cost is much higher than



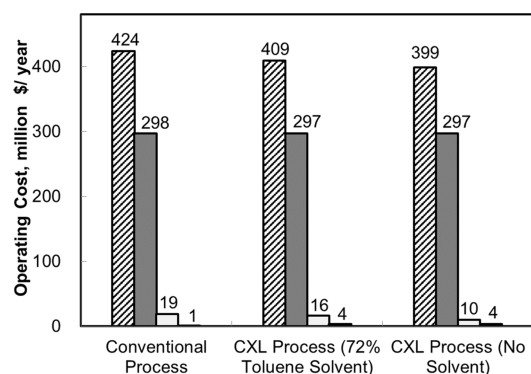
**Figure 5.** Capital investment for conventional and CXL processes (total capital investment, diagonal bar; cost of reactors, dark gray bar; cost of compressors, clear bar; cost of heat exchangers, light gray bar; cost of separators and distillation columns, black bar).

**Table 2.** Itemized Capital Investment (million \$) for Conventional and CXL Processes

category	conventional process	CXL process (72% toluene solvent)	CXL process (no solvent)
reactor(s)	11.3	4.2	2.6
heat exchangers	7.6	2.7	2.1
distillation columns	8.2	5.4	3.2
separators	3.5	0.8	0.4
pumps	0.9	0.8	0.6
compressors	0.6	6.3	6.1
filters	0.0	0.1	0.1
total	32.0	20.3	15.1

the conventional process due to the need for pumping and recycling CO<sub>2</sub>.

The annual total production cost (TPC), and the major contributors thereof, are shown in Figure 6. The details of the production cost categories are listed in Table 3. The raw material cost is approximately 70% of the total cost of both processes. At an annual production capacity of 150 kton, the nonanal product value for the conventional and CXL processes are \$1.3/lb, \$1.24/lb (72 wt % toluene), and \$1.21/lb (no



**Figure 6.** Annual production costs for the conventional and CXL processes (total annual production cost, diagonal bar; raw materials cost, gray bar; utilities cost, clear bar; and catalyst makeup cost, black bar).

**Table 3.** Itemized Annual Production Cost (million \$) for Conventional and CXL Processes<sup>a</sup>

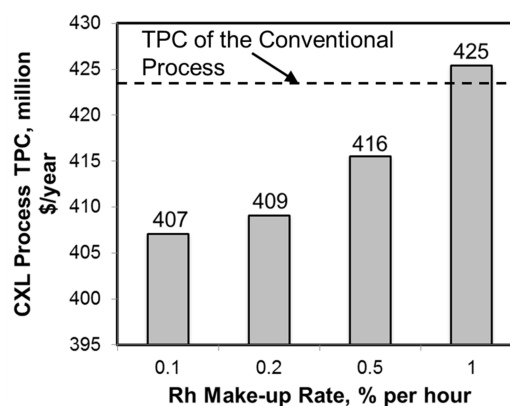
category	conventional process	CXL process (72% toluene solvent)	CXL process (no solvent)
raw materials	297.5	297.5	297.5
utilities	19.0	16.4	10.0
catalysts make-up	0.7	3.8	3.8
solvents	0.0	0.3	0.0
other variable production costs	30.3	23.3	22.4
fixed charges	3.3	2.1	1.4
plant overhead cost	6.0	3.0	3.0
general expenses	66.7	62.9	61.1
total	423.5	409.1	399.2

<sup>a</sup>Unit costs and sources are provided in Tables S3 and S4 of the Supporting Information.

solvent), respectively. Assuming a Rh makeup rate of 0.2% (of the initial Rh content in the reactor) per hour, the total production cost associated the CXL process is similar to that of the conventional process. At this Rh makeup rate, the ratio ( $r$ ) of the Rh catalyst makeup cost to TPC in the CXL process (Table 3) is 0.01. The corresponding ratio of the Co makeup (2% of total Co in the reactors) cost to TPC in the conventional process (Table 3) was approximately 0.002. Note that even though the amount of Rh makeup used for the CXL process is almost 200 times less than the amount of Co makeup used in the conventional process (Table 1), the cost of the makeup catalyst in the CXL process was more than 5-fold greater than the conventional process. This is a reflection of the fact that the average Rh metal price was approximately \$20,800/lb,<sup>37</sup> compared to Co at approximately \$14.8/lb (both year 2012 prices).<sup>38</sup>

#### Effect of Rh Makeup Ratio on TPC of the CXL Process.

A sensitivity analysis on TPC was performed with various Rh makeup rates at a Rh price of \$20,800/lb.<sup>37</sup> As shown in Figure 7, the TPC of the CXL process was lower than conventional process for the Rh makeup rates of 0.1%, 0.2%, and 0.5% of the initial Rh content in the reactor per hour at the year 2012 Rh price. The TPC of the CXL process matched the conventional process when the Rh makeup rate was around 0.94% per hour. At this rate, the ratio ( $r$ ) of the Rh makeup cost to TPC in the CXL process is 0.042.



**Figure 7.** Rh makeup rate sensitivity analysis (CXL process calculations assume 72 wt % of toluene solvent in the reaction mixture).

Lab-scale experimental results using CXL as the reaction medium show a Rh concentration of 0.5 ppm at steady state.<sup>10</sup> At this rate, the estimated  $r$  values for the lab-scale CXL process is 0.006 and substantially exceeds the economic viability criterion ( $r = 0.042$ ). It must be noted that the present simulations assume that the leached Rh is not recovered from the product stream. If the ppm levels of Rh leached in the permeate is also recovered (by suitable adsorbent/chelating agents,<sup>39–41</sup> for example) and recycled, the production cost in the CXL process will clearly be reduced even further.

**GaBi Gate-to-Gate Impacts.** To assess the reliability of the environmental impact predictions, the formic acid and CO<sub>2</sub> emissions from the conventional process simulated in this work (150 kton/year) are compared with actual emission data reported by the ExxonMobil Baton Rouge Chemical Plant in Louisiana that has a similar nonanal production capacity (100–350 kton/year). The formic acid emission predicted in this work (Table 4) is estimated as fugitive emissions using the

**Table 4. Comparison of Reported and Estimated Gate-to-Gate Emissions from Conventional Process**

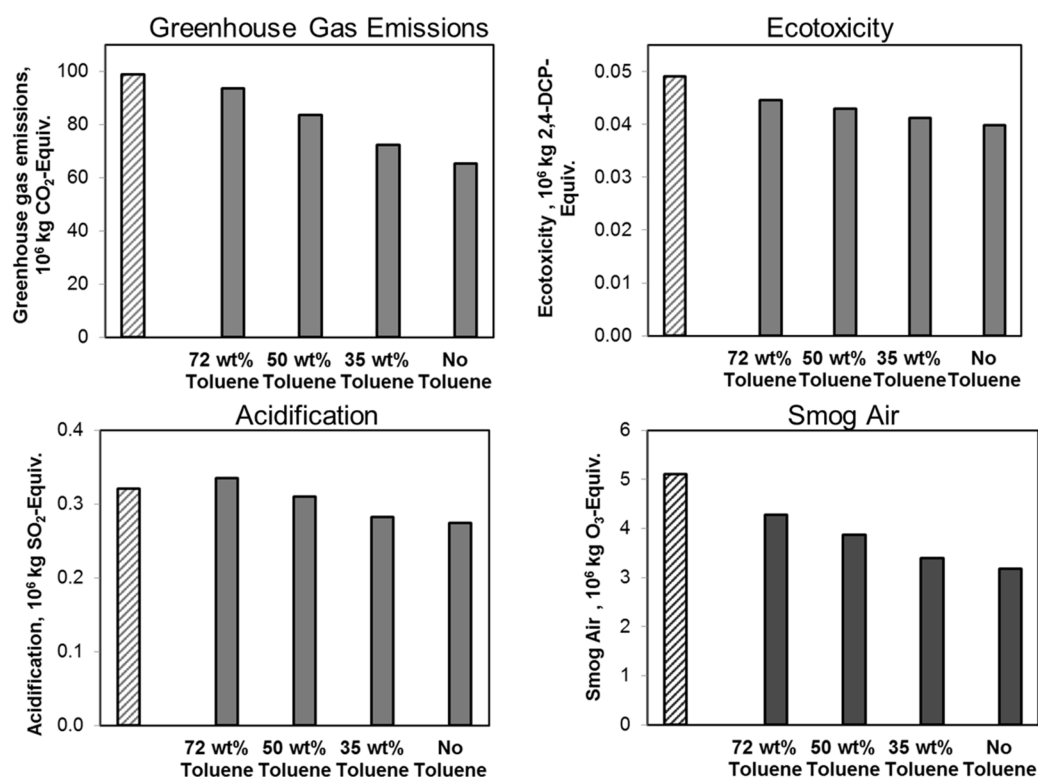
emission	reported value (ExxonMobilCorporation,2012)		predicted value (this work)
	reported	adjusted <sup>a</sup>	
fugitive formic acid (lb/year)	2212 <sup>43</sup>	948–3318	3404
CO <sub>2</sub> (ton/year)	38,494 <sup>44</sup>	16,497–57,741	98,733

<sup>a</sup>Adjusted emission value corresponds to a plant capacity of 100–350 kton/year.

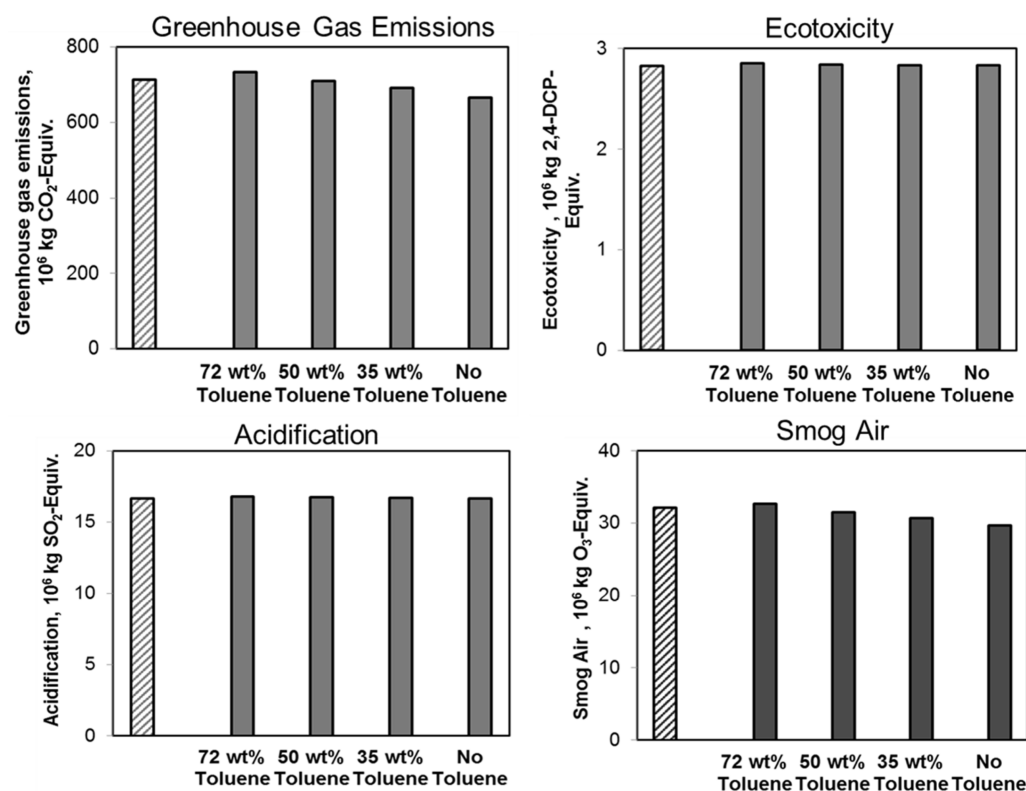
methods described by Allen and Shonnard.<sup>42</sup> The fugitive formic acid emission data from the ExxonMobil plant is obtained from the USEPA toxics release inventory (TRI).<sup>43</sup> The TRI-reported value is roughly 28–98% of the predicted formic acid emission depending on the actual plant capacity. Table 4 also compares the estimated greenhouse gas emissions (calculated as CO<sub>2</sub> equivalence by GaBi software) estimated in this work with reported values in the USEPA GHG database of the ExxonMobil Baton Rouge Chemical Plant.<sup>44</sup> The reported GHG emissions are approximately 17–59% and thus of the same order of magnitude as the predicted data.

The most significant gate-to-gate impacts predicted for the conventional and CXL processes are summarized in Figure 8. In general, the CXL process has lower environmental impacts than the conventional process, with the exception of the impact on the “acidification air” category when using 72 wt % of toluene. As the solvent amount is reduced from 72 wt % to none, the environmental impacts of the CXL process are reduced by as much as 30% (“global warming” category). The major contributions to the environmental impacts for the CXL process are from the energy usage associated with compression for CO<sub>2</sub> recycle, distillation column for toluene separation, and cooling water for the membrane reactor. In contrast, the major contributors to adverse environmental impacts for the conventional process are from energy consumption associated with reactor heating and cooling as well as Co catalyst regeneration and recycle.

**GaBi Cradle-to-Gate Impacts.** The major impact categories of the cradle-to-gate analysis are shown in Figure 9. The estimated cradle-to-gate environmental impacts are 1 to 2 orders of magnitude greater than the gate-to-gate impacts, indicating that the main sources of emissions come from the



**Figure 8.** Major predicted annual gate-to-gate environmental impacts by GaBi (conventional Co process, diagonal bar; and CXL Rh process, gray bar).



**Figure 9.** GaBi-predicted annual cradle-to-gate environmental impacts (conventional Co process, diagonal bar; and CXL Rh process, gray bar).

manufacture of raw materials outside the plants. The production of most of the raw materials (octene, toluene, and syngas) requires energy-intensive chemical processes. The production of the fossil-based energy required for these processes is the major contributor to emissions with adverse environmental impacts. When using 72 wt % of toluene in the reaction mixture, the CXL process has greater adverse environmental impacts than the conventional process, attributed mainly to the emissions from toluene production. Our analysis shows that the toluene content in the reaction mixture must be reduced to less than 50 wt % for the CXL process to have environmental benefits comparable to the conventional process. Note that the formic acid used for catalyst recovery in the conventional process is relatively small and therefore has a relatively low environmental impact.

**Sensitivity and Uncertainty of GaBi Analysis.** Table 5 shows the top three variables in the order of how sensitively

**Table 5. Top Three Variables with Highest Sensitivity on Global Warming Impact**

conventional process			CXL process		
1	evaporator cooling	±7.7%	distillation column cooling	±9.0%	
2	reactor cooling	±3.3%	distillation column heating	±3.4%	
3	evaporator heating	±3.2%	CO <sub>2</sub> pump electricity	±1.6%	

they affect the global warming impact predictions in the conventional and CXL processes. While the conventional process is most sensitive to the amount of cooling water used in the evaporator, the CXL process is most sensitive to the amount of cooling water used in the distillation column. This sensitivity is a reflection of the fact that large amounts of cooling water requiring appreciable energy input are needed in both processes.

Monte Carlo uncertainty analysis was performed for 10,000 iterations to reflect a sufficiently high number of trials. Figure 10 shows the simulation results of the probability of each deviation around the mean value for global warming impact categories in the conventional and CXL processes. The standard deviation is 9.8% for the conventional process and 13.4% for the CXL process. The smooth shapes of the distributions indicate stable predictions of the models.

**EIO-LCA.** The estimates of greenhouse gas emissions and energy consumption associated the capital investments are shown in Table 6. The most significant impacts arise from the manufacturing of the metal tanks (reactor, distillation columns, and separators) and piping. The greenhouse gas emission and energy consumption of the conventional process is more than 60% greater compared to the CXL process when 72 wt % of toluene is used as solvent and more than twice as much as the CXL process when no toluene is used. The significantly lower adverse environmental impacts associated with a CXL-based process is a reflection of its much lower material and energy consumption compared to the conventional process.

The environmental impacts associated with the production steps are listed in Table 7. The manufacture of the raw materials (octene and syngas) is the major contributor (~94%) to the environmental impacts, followed by the utilities (energy, cooling water, and steam). To evaluate the potential environmental impacts of catalyst usage (which are neglected in the GaBi analysis), the production cost of the makeup catalyst was used taking into account both the primary smelting and refining steps of the Co and Rh metal ore mining sectors (Table S6, Supporting Information). The greenhouse gas emissions attributable to the catalyst usage is approximately 0.3% for the conventional the Co-catalyzed process and approximately 1.6% for the Rh-based CXL processes. As shown in Table S6 of

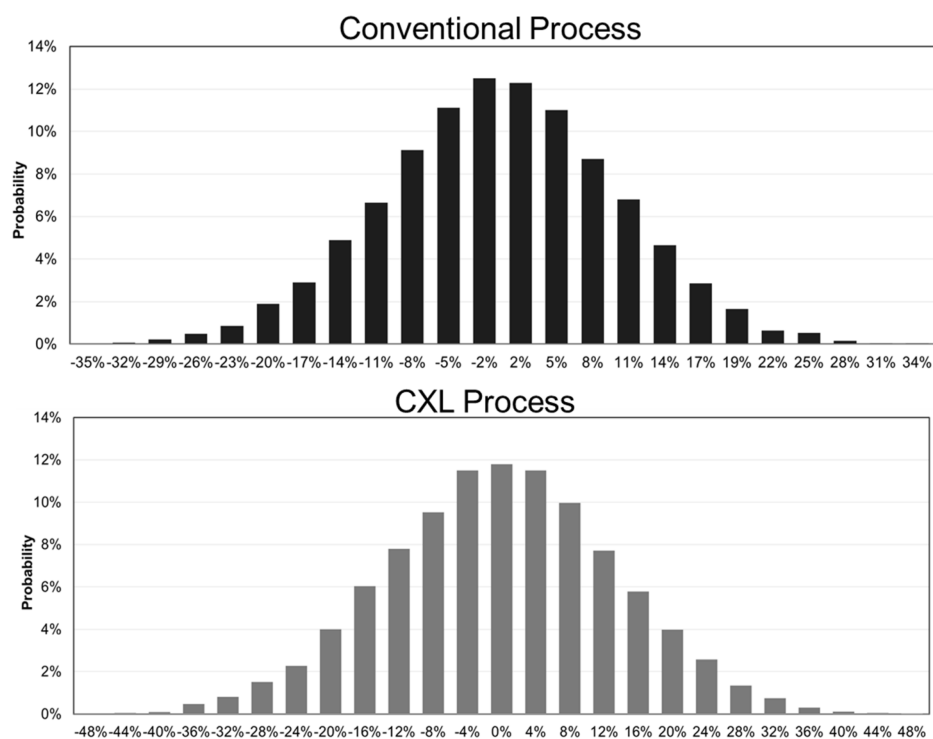


Figure 10. Monte Carlo simulations to estimate uncertainty in global warming impact results.

Table 6. EIO-LCA Estimates of Environmental Impacts Associated with Major Capital Investment Items

item	greenhouse gas emission (t CO <sub>2</sub> equivalent)			energy (TJ)		
	conventional process	CXL process		conventional Process	CXL process	
		72 wt % toluene	no solvent		72 wt % toluene	no solvent
reactors, distillation columns, separators	1980	907	487	26.5	12.1	7.2
heat exchangers	543	197	149	7.6	2.8	2.2
pump	45	39	28	0.7	0.6	0.4
compressor	28.2	321	310	0.4	4.8	4.6
equipment delivery	406	266	197	5.4	3.6	2.6
pipng	3650	2310	1728	45.4	28.7	21.5
concrete foundations	237	150	112	2.4	1.5	1.2
electrical service	65.3	42	32	1.0	0.7	0.5
building constructions	551	350	259	7.9	5.0	3.7
engineering cost	247	156	116	3.6	2.3	1.7
total	7753	4738	3417	100.9	62.0	45.6

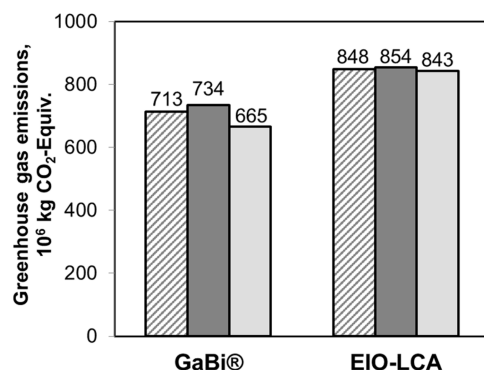
Table 7. EIO-LCA Estimates of Environmental Impacts Associated with Major Production categories

item	greenhouse gas emission (t CO <sub>2</sub> equivalent)			energy (TJ)		
	conventional process	CXL process		conventional process	CXL process	
		72 wt % toluene	no solvent		72 wt % toluene	no solvent
octene and makeup toluene	748,000	749,000	748,000	10,800	10,800	10,800
formic acid makeup	218	—	—	3.6	—	—
syngas and CO <sub>2</sub> makeup	52,500	52,800	52,600	441.0	443.0	442
catalyst makeup (Co or Rh)	2,380	13,200	13,200	29.5	163.3	163.3
electricity	4,030	8,340	6,370	47.9	99.1	76
cooling water and steam	26,400	16,800	9,940	276.0	176.0	104
direct labor	1,010	507	507	15.9	8.0	8.0
maintenance	324	205	137	4.7	3.0	2
distribution and marketing	7,070	6,790	6,600	114.0	109.0	106
research and development	6,380	6,120	5,950	90.4	86.8	84
total	848,312	853,762	843,304	11,823.0	11,888.2	11,785.3



the Supporting Information, when using 72 wt % toluene as solvent, the CXL process is predicted to emit more greenhouse gas emissions due to higher electricity usage. When toluene use is avoided in CXL process, the impacts are slightly lower than the conventional process as the utility consumption is significantly reduced.

**Comparison of GaBi Cradle-to-Gate Analysis and EIO-LCA.** The greenhouse gas emissions estimated by both methods are compared in Figure 11. The results match within



**Figure 11.** Comparison of the greenhouse gas emissions estimated by GaBi and EIO-LCA methods (conventional process, diagonal bar; CXL process with 72 wt % toluene, black bar; and CXL process without toluene, gray bar).

20%, with the GaBi predictions being lower. Considering that the impact from catalyst usage is not considered in the GaBi model, the actual difference would be even smaller. For cradle-to-gate analysis of the CXL process, GaBi predicts significant (>10%) greenhouse gas emission reduction with elimination of toluene as solvent. The differences revealed by the EIO-LCA model predictions are relatively less, reflecting the approximate nature of the model and the fact that the raw material production steps dominate the predicted emissions over the entire life cycle.

#### Potential Opportunities To Improve the CXL Process.

The polymer ligand used in this analysis requires a solvent (toluene) for dissolution. The extent of such solvent use adversely affects both the economic and environmental impacts of the CXL process. Therefore, by developing a polymer ligand that is soluble in the reaction mixture (mostly aldehydes) itself, the economic and environmental performances of the CXL process can be significantly improved. Indeed, the commercial homogeneous hydroformylation processes use the aldehyde product as solvent.<sup>45</sup> Moreover, the JanaPhos ligand is more soluble in nonanal than in 1-octene. The total elimination of the toluene solvent would reduce the unit operations associated with solvent recovery and recycle, and thereby lower both the capital and operating costs. The overall environmental impacts will also be significantly reduced as the energy usage associated with toluene production as well as toluene separation by distillation and associated environmental impacts are eliminated.

#### CONCLUSION

Comparative economic analyses, based on plant-scale simulation to produce 150 kton/year of aldehydes, shows a more than 30% lower capital investment for the CXL process compared to the conventional Co-catalyzed 1-octene hydroformylation process of similar capacity. This is due to higher

reaction and catalyst recovery efficiencies and milder operating conditions (lower reaction temperature and pressure) used in the CXL process. The total production cost associated with the CXL process is lower than the conventional process when the Rh makeup rate is less than 0.94% (of the initial Rh content in the reactor) per hour, estimated using a peak Rh price of \$20,800/lb. This translates to an economic viability criterion, defined as ( $r = \text{\$makeup Rh}/\text{\$TPC}$ ) being 0.042 or less. The demonstrated lab-scale CXL reactor exceeds this performance metric by nearly 3-fold.<sup>10</sup>

The GaBi-based gate-to-gate and cradle-to-gate LCA as well as the EIO-LCA-based results show the potential of the CXL process to be environmentally friendlier than the conventional process. In general, the CXL process generates less emissions than the conventional process within the plant. The key “hotspot” identified in the CXL process is the use of toluene as solvent. Either reducing or eliminating solvent usage not only lowers the cradle-to-gate environmental impacts compared to the conventional process but also improves the process economics.

#### ASSOCIATED CONTENT

##### Supporting Information

Details of economic analysis, process flow models for cradle-to-gate LCA calculations simulated using GaBi software, EIO sectors and costs associated with the major categories of capital investment, and production cost used in EIO-LCA for the conventional and CXL processes. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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##### Notes

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