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Resources, Conservation and Recycling 51 (2007) 294-313

Resources Conservation & Recycling

www.elsevier.com/locate/resconrec

Environmental impact assessment of different design schemes of an industrial ecosystem

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Received 5 March 2006; received in revised form 18 September 2006; accepted 16 October 2006 Available online 16 November 2006

Abstract

Industrial ecosystem is an important approach for sustainable development. In an industrial ecosystem, a group of industries are inter-connected through mass and energy exchanges for mutual benefits. However, some mass and energy exchange activities may cause unexpected environmental impacts. Therefore, it is vital to evaluate the environmental impacts of the symbiosis in order to provide a clear guidance for the decision-makers and stakeholders.

The agro-chemical complex in the Lower Mississippi River Corridor with thirteen chemical and petrochemical industries emits huge amount of carbon dioxide. A bi-level design methodology is used to reconfigure this complex for utilizing surplus carbon dioxide. By using a superstructure-based approach, a new design scheme for this industrial ecosystem is proposed. In this paper, an LCA-type environmental impact assessment of different design schemes for this complex is conducted using the software TRACI, a tool developed by the United States Environmental Protection Agency (USEPA). This analysis compares various environmental impacts of different designs and identifies the potential trade-offs in different environmental impact categories. This information provides deep insight about the environmental sustainability of industrial ecosystems and facilitates the development of the most eco-effective symbiosis for recycle, reuse and resource conservation. © 2006 Elsevier B.V. All rights reserved.

Keywords: Industrial ecosystems; Environmental impact assessment; Process design

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^{0921-3449/\$ -} see front matter © 2006 Elsevier B.V. All rights reserved. doi:10.1016/j.resconrec.2006.10.002

1. Introduction

Emission of green house gases from various domestic and industrial sources is one of the major contributors towards global warming and climatic changes. This has significant and at-times irreversible effect on the environment. Many methodologies have been developed to sequester carbon dioxide. Apart from the natural sequestration, carbon dioxide can be sequestered artificially by absorption into amine-based solvents, gas separation membranes and cryogenics as mentioned by National Energy Technology Laboratory (NETL), Department of Energy of United States (USDOE) (NETL USDOE, 2005). However, implementing these technologies may be costly. It will be most desirable if carbon dioxide, which is considered as a waste, can be used for producing products to generate revenue in a cost-effective way.

Development of industrial ecosystems is one of the most popular methods being implemented in the industrial world for recycle, reuse and resource conservation (Garner and Keoleian, 1995). In an industrial ecosystem, several industries are interconnected through mass and energy streams for mutual benefit (Ehrenfeld, 2004). It converts the industrial process from a linear process to a cyclic process where the waste generated by one industry can be used as a resource by another industry (Lou et al., 2004; Sikdar, 2003). Several such industrial ecosystems have been developed around the world. For example, the agro-chemical complex at Kalundborg, Denmark (The Kalundborg Centre for Industrial Symbiosis, 2003), Industrial Complex in the Lower Mississippi River Corridor (Indala, 2004), the Dalian Economic and Technological Development Zone, China (United Nations Environment Program, 2000) and several ecoparks in US like Cabazon Resource Recovery Park, Mecca, CA, Urban Ore Resource Recovery Park, San Leandro, CA and The Brownsville Project, Brownsville, TX (USEPA, 2006). If appropriately designed, the large amounts of carbon dioxide generated from some members of a symbiosis may be used as feedstock for some other members. However, the cost, benefit and environmental impacts of this symbiosis need to be judiciously assessed to avoid potential risks.

Life cycle analysis (LCA) is a procedure to evaluate and analyze the environmental impacts of a product or service by using the complete input and output data about the material and energy involved at various stages of the life cycle of the product or service, starting from the stage of collecting raw material from earth and ending at the stage when all this material is returned to earth. An LCA can be utilized to do a comparative analysis of various design schemes for a process or service and to isolate the process causing maximum harm to the environment in its entire life cycle.

Since an industrial ecosystem consists of various member industries producing different products, conducting an LCA for an industrial ecosystem can provide us critical quantitative data regarding the environmental impacts of each member and their products. Consequently, LCA results will provide vital information about the overall environmental sustainability of an industrial ecosystem. This information plays an instrumental role in assessing and improving the environmental sustainability of industrial processes.

In this paper, a comparative analysis has been conducted for different design schemes of an agro-chemical complex in the Lower Mississippi River Corridor to evaluate their environmental impacts. The current design of this complex is taken as the base case, which has about thirteen industries along with associated utilities for power, steam, cooling water and facilities for waste treatment. An ammonia plant in this complex emits huge amount of carbon dioxide. In order to utilize the carbon dioxide to generate useful product rather than treat it as a waste, a new design scheme is proposed to reconfigure this agro-chemical complex to maximize the consumption of pure carbon dioxide for maximal economic profit. By doing so, the amount of carbon dioxide released to the atmosphere will be minimized, thereby the green house effect will be reduced. This new design scheme has about eighteen new potential plants, some of which consume pure carbon dioxide as a raw material. These processes are selected based on the value added economic profit obtained based on the HYSYS (ASPENTECH, 2006) simulation of these new processes (Indala, 2004). An LCA-type environmental assessment for these two design schemes is conducted by using the software, Tool for Reduction and Assessment of Chemical and Other Environmental Impacts (TRACI), a tool developed by the USEPA to evaluate and compare various environmental impacts of different production processes (Bare et al., 2002).

2. Life cycle analysis (LCA)

Life cycle analysis (LCA) is a methodology used for assessing the environmental impacts of any product or service using a cradle to grave approach (Burgess and Brennan, 2001). This assessment begins at the stage of gathering raw materials from earth for production of product in concern and ends at the point when the product is decomposed and all its constituents are returned to earth. It evaluates all the stages of a product's life cycle from the perspective that they are interdependent. LCA provides an estimate of cumulative environmental impacts resulting from various stages in the life cycle of a product or service (Christen and Caspersen, 2001). This goal is accomplished by first compiling an inventory of relevant energy and material inputs and environmental releases, then evaluating their potential environmental impacts and finally interpreting these results for more informed decision-making. LCA has the following four stages: Goal and Scope Definition, Life Cycle Inventory (LCI), Life Cycle Impact Assessment (LCIA), Life Cycle Interpretation.

The International Standard on Life Cycle Assessment has been developed as part of the International Standards Organization's development of the Environmental Management Standards ISO 14000 series (Guinée, 2002). In this paper, TRACI has been used to conduct an "Entry to Exit" LCA for an agro-chemical complex in Lower Mississippi River Basin. This tool will be discussed in greater detail in the next section.

3. Tool for Reduction and Assessment of Chemical and Other Environmental Impacts (TRACI)

The software namely, Tool for Reduction and Assessment of Chemical and other environmental Impacts (TRACI) is developed by USEPA. TRACI is a modular set of LCIA methods intended to provide the most up-to-date scientifically defensible impact assessment methodologies for US that facilitates environmental comparison of product and process alternatives for internal environmental decision-making with regard to human health, environmental and resource depletion impacts (USEPA, 2004). The modular design of TRACI allows the com-

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pilation of the most sophisticated impact assessment methodologies. It also characterizes various stressors that may have potential effect on the environment. The first stage in TRACI is project description in which all the relevant details of the project are documented. After that, a list of products to be analyzed is entered and the input and output data of various phases of the life cycle of these products/services is entered into TRACI using its database. Various resources/releases can also be added using their CAS Numbers, depending upon the requirement. Once the inventory data is entered, TRACI can perform a Life Cycle Impact Assessment. During this phase, TRACI first classifies the resources and releases into various impact categories and then characterizes them based on the impact categories using their characterization value. The characterization value quantifies the extent of harm that a stressor can cause in a particular impact category (USEPA, 2004). The impact assessment methodologies in TRACI are based on "mid-point" characterization approach. Using this, the impact assessment models reflect the relative potential of the stressor at a common mid-point within the cause-effect chain. In TRACI, each impact assessment methodology is selected or developed to reflect the current state-of-the-art for each impact category, with a particular emphasis on methodologies that are relevant for the US TRACI characterizes various stressors into the following impact categories:

 Ozone depletion. This impact category accounts for the depletion of the protective ozone layer in the earth's stratosphere due to harmful emissions like chlorofluorocarbons, halons, etc. The mid-point of this category is selected on the basis of the potential of a chemical to destroy ozone based on its chemical activity and lifetime. The contribution in this impact category indicates the potential contribution to ozone depletion using

Ozone depletion index =
$$\sum_{i} e_i \times \text{ODP}_i$$

where e_i is the emission (in kilograms) of substance *i* and ODP_{*i*} is the ozone depletion potential of substance *i*. This contribution is measured in terms of CFC-11 equivalents per kilogram of emission.

 Global warming. This impact category refers to the change in earth's climate due to the build-up of chemicals that trap heat from the sunlight. TRACI uses mid-point metric for calculating the potential green house gases relative to carbon dioxide. The contribution in global warming impact category indicates the potential contribution to global warming using

Global warming index =
$$\sum_{i} e_i \times \text{GWP}_i$$

where e_i is the emission (in kilograms) of substance *i* and GWP_i is the global warming potential of substance *i*. The unit of contribution in this impact category is kilogram of CO₂ or equivalent.

3. Acidification. Acidification includes the processes that increase the acidity of water and soil systems by releasing $[H^+]$ or equivalents. The acidification model in TRACI accounts for the $[H^+]$ equivalent release in the atmosphere, water or soil by using the emission data of NO_x and SO₂. The contribution to this impact category is expressed in $[H^+]$ moles equivalent deposition per kilogram of emission. 298

- 4. Eutrophication. The characterization factor for this impact category is a product of nutrient factor and a transport factor. The nutrient factor captures the relative strength of influence on algae growth in aquatic ecosystems. The transport factor accounts for the probability that the release arrives in the aquatic environment in which it is a limiting nutrient. The contribution in this impact category is measured in terms of nitrogen equivalents released per kilogram of emission.
- 5. *Photochemical smog.* In TRACI, photochemical smog is measured by incorporating relative influence of individual VOCs on smog formation, relative influence of NO_x concentrations versus average VOC mixture on smog formation, impact of emissions upon concentration by state and methods for aggregating effects among receiving states by area. The contribution in this impact category is measured in gram of NO_x or equivalent.
- 6. Human health cancer and non-cancer. In TRACI, the toxicological effect of an emission is calculated based on its Human Toxicity Potential (HTP). These HTPs are derived using a closed system, steady-state version of CalTOX, a multimedia fate and multiple exposure pathway model with fixed generic parameters for the United States. The contribution for human health cancer is measured in terms of benzene equivalents released per kilogram of emission. The contribution for human health non-cancer is measured in terms of emission.
- 7. Human health criteria. This accounts for measuring the ambient concentrations of particulate matter found to be associated with changes in background rates of chronic and acute respiratory systems as well as the mortality rate. TRACI uses DALY's (Disability Adjusted Life Years) measures to calculate the environmental impact in this category. The contribution to this impact category is given in terms of DALYs per tonne of emission.
- 8. *Eco-toxicity*. It uses Ecological Toxicity Potential (ETP) to quantitatively measure the ecological harm of a unit quantity of chemical released in the environment. ETP establishes a database that gives details of the ecological harm caused by a large set of toxic industrial and agricultural chemicals. The contribution to this impact category is measured in terms of 2,4-dichloro-phenoxyacetic acid equivalents released per kilogram of emission.
- 9. Fossil fuel use. The contribution in this impact category is calculated using

Fossil fuel index =
$$\sum_{i} N_i \times F_i$$

where N_i is the increase in energy input requirements per unit of consumption of fuel *i* and F_i is the consumption of fuel *i* per unit of product. The contribution in this impact category is measured in MJ of surplus energy per MJ of extracted energy in the process.

10. *Land use*. TRACI uses the density of threatened and endangered (T&E) species in a specific area as a proxy for environmental importance of land. It relates the location to be modified with the T&E species database to calculate the potential T&E displacement at that site. The contribution in this category is calculated using

Land use index =
$$\sum_{i} \frac{A_i \times (T\&E_i)}{CA_i}$$

where A_i is the human activity per functional unit of the product, T&E_i is the T&E species count for the county and CA_i is the area of the county under consideration.

11. *Water use*. This impact category of TRACI analysis is designed to capture the significant use of water in areas of low availability. It uses the total amount of water being used in terms of its mass or volume and accordingly using the corresponding characterization value to calculate the impact. The contribution in this impact category is measured in gallons.

TRACI has been developed to provide the most up-to-date possible treatment of impact categories for North America. It provides the provision of selecting the region (within US) where each process in the various life cycle phases of a product/service takes place. This helps in providing a more comprehensive customized environmental analysis for a process/service as it takes into account the current environmental health of that region and the consequent impacts of various stressors on it.

4. Design of an industrial ecosystem

Consider the agro-chemical complex situated in the Lower Mississippi River Basin as shown in Fig. 1. It presents the base case for this agro-chemical complex, which has been used for the current case study. There are thirteen production units in this complex along with



Fig. 1. Base case for industrial complex in Lower Mississippi River Corridor (Indala, 2004). (*Note*: Flow Rates Million TPY).

associated utilities for power, steam and cooling water and facilities for waste treatment. These production units in the base case are for following chemicals: ammonia, nitric acid, ammonium nitrate, urea, urea ammonium nitrate (UAN), methanol, granular triple super phosphate (GTSP), mono- and di-ammonium phosphate (MAP and DAP), sulfuric acid, phosphoric acid, acetic acid, ethylbenzene and styrene. Each plant contains more than one production unit. There is large amount of pure carbon dioxide produced in this complex which is directly released into the atmosphere and adds to the green house effect. The ammonia plant is the main source of carbon dioxide producing 0.75 million tons of CO₂ per year, and this plant accounts for almost 80% of the total emission of CO₂ into the atmosphere from this agro-chemical complex. The methanol, urea and acetic acid plants consume 0.14 million tons of CO₂ per year which leaves a surplus of 0.61 million tons of CO₂ per year being released into the atmosphere.

A new design has been proposed in order to minimize the carbon dioxide emission from this complex (Indala et al., 2004). This new strategy proposes to use pure carbon dioxide released from this complex as a raw material for manufacturing commercially useful products. It intends to expand the existing complex to form a new industrial ecosystem by incorporating the most suitable of the eighteen candidate new manufacturing processes. In the development of the new design scheme, a software tool, Chemical Complex and Cogeneration Analysis System, has been used to identify the optimal complex configuration from a superstructure of possible plants. This determines the best configuration of plants in a complex based on AIChE total cost assessment (TCA) using economic, energy and environmental and sustainable costs. TCA includes direct cost for manufacturing site, potentially hidden corporate and manufacturing site overhead costs, future and contingent liability costs, internal intangible costs and external costs. The proposed production units are designed to meet the market demand while consuming all the surplus carbon dioxide. Along with this, the other criteria include operating conditions (temperature and pressure requirements), reactant conversion, product selectivity and thermodynamic feasibility. These new plants consume pure carbon dioxide as a raw material to produce useful products like propylene, styrene, etc. using new manufacturing processes. Incorporating these new plants in this symbiosis helps in reducing the carbon dioxide emission to the atmosphere, hence reducing the contribution to global warming.

Eighteen processes are considered as candidates. These include four processes for methanol production, two processes for propylene, and one process each for ethanol, dimethyl ether (DME), formic acid, acetic acid, styrene, methylamines, graphite and synthesis gas, two processes for phosphoric acid production and two processes for recovering sulfur and sulfur dioxide. The optimum configuration of the new industrial ecosystem aims at consuming all of the carbon dioxide generated by the ammonia plant operating at full production capacity while achieving maximal profit. This optimization was conducted based on the superstructure methodology (Floudas, 1995). The mathematical model generated for this superstructure forms a Mixed Integer Non-Linear Problem (MINLP) which is solved using the software GAMS. In the new design scheme obtained through optimization, nine best-suited processes are selected from the pool of eighteen new processes for the industrial ecosystem to consume all the carbon dioxide, giving maximum economic benefits with high environmental sustainability. The operating capacity for each plant in base case and the new design scheme is given in Table 1. The total profit of the agro-chemical complex increases

	Base case capacity (tonnes/year)	New design scheme capacity (tonnes/year)
Ammonia	658,061	658,061
Nitric acid	178,525	169,967
Ammonium nitrate	226,796	215,924
Urea	99,790	97,626
Methanol	181,437	181,437
UAN	60,480	60,480
MAP	321,912	321,912
DAP	2,062,100	2,062,100
GTSP	822,284	822,284
Sulfuric acid	3,702,297	3,702,297
Phosphoric acid	1,394,950	1,394,950
Ethylbenzene	861,827	861,827
Styrene	753,279	0
Formic acid	n/a	77,948
Acetic acid (new method)	n/a	8165
Methylamines	n/a	16,763
Graphite	n/a	45,961
Synthesis gas	n/a	13,933
Propylene (from CO ₂)	n/a	41,429
Propylene (from Propane)	n/a	41,791
Styrene (new method)	n/a	362,237
DME	n/a	22,727

 Table 1

 Operating capacity for base case and new design scheme

from 378,325,617US\$/year (base case) to 459,608,034US\$/year (new design scheme) after incorporating these nine plants in the superstructure. These nine plants are: formic acid, acetic acid (new method), methyl amines, graphite, hydrogen/synthesis gas, propylene from carbon dioxide, propylene from propane dehydrogenation, styrene (new method) and DME plant. A brief description of these nine processes is given below:

 Formic acid production. This process proposes to produce formic acid by hydrogenation of carbon dioxide in aqueous solution using water as a solvent using Wilkinson's catalyst [CIRh(TPPTS)₃] (Dinjus, 1998):

$$CO_2(g) + H_2(g) \rightarrow HCOOH(l), \Delta H^\circ = -31 \text{ kJ/mol}, \Delta G^\circ = -31 \text{ kJ/mol}$$

This process operates at 25 °C and 40 bar which is less than the operating pressure and temperature of the conventional process that operates at 50 °C and 45 bar, respectively. The rate of formation of formic acid was reported to be 3440 mol per mol of catalyst. The value added economic model for this process gave a profit of 64.9 cents per kg of formic acid.

 Acetic acid production. Taniguchi et al. suggest acetic acid synthesis from methane and carbon dioxide in presence of vanadium catalyst VO(acac)₂ (acac: acetyl acetonate) (Taniguchi et al., 1998):

$$CH_4 + CO_2(g) \rightarrow CH_3COOH(l), \Delta$$
 $H^{\circ} = 36 \text{ kJ/mol}, \Delta G^{\circ} = 71 \text{ kJ/mol}$

This reaction is carried out at 350 K and 25 bar pressure. The feed gas composition is 0.95 mmol CH₄ and 3.784 mmol of CO₂. $K_2S_2O_8$ is also added during the reaction as an oxidizing agent and trifluoroacetic acid is added as a solvent. The yield of acetic acid based on methane is 97%. This process operates at a lower pressure and temperature than the conventional process which operates at 450 K and 35 bar. It is found to give a profit of 97.9 cents per kg of acetic acid.

3. *Methyl amine production*. This process uses CO₂, H₂ and NH₃ as a raw material for production of methyl amines (Arakawa, 1998). The catalyst used in this process is 51 wt.% Cu/Al₂O₃ and feed gas composition is H₂/CO₂/NH₃ = 3/1/1. The production is carried out at 277 °C and 6 bar. The reactions in this reactor are following:

$$CO_{2} + H_{2} \rightarrow CO + H_{2}O, \Delta \quad H^{\circ} = 41 \text{ kJ/mol}, \quad \Delta G^{\circ} = 29 \text{ kJ/mol}$$

$$CO + 2H_{2} \rightarrow CH_{3}OH, \quad \Delta H^{\circ} = -90 \text{ kJ/mol}, \quad \Delta G^{\circ} = -25 \text{ kJ/mol}$$

$$CH_{3}OH + NH_{3} \rightarrow CH_{3}NH_{2}, \quad \Delta H^{\circ} = -17 \text{ kJ/mol}, \quad \Delta G^{\circ} = -17 \text{ kJ/mol}$$

$$CH_{3}OH + CH_{3}NH_{2} \rightarrow (CH_{3})_{2}NH, \quad \Delta H^{\circ} = -37 \text{ kJ/mol}, \quad \Delta G^{\circ} = -30 \text{ kJ/mol}$$

This new process operates at a lesser pressure and temperature than the conventional process which operates at 390-450 °C and 14 bar. The value added economic analysis of this process shows a profit of \$1.24 per kg of methyl amines.

4. Graphite. This new process produces graphite by reduction of carbon dioxide through catalytic fixation in which methane is formed as an intermediate (Nishiguchi et al., 1998). This follows a two-stage reaction mechanism. In the first stage methane is decomposed into graphite and hydrogen, and in the second stage hydrogen produced is treated with carbon dioxide to produce methane and water. This methane is recycled back to the first stage.

$$2CH_4 \rightarrow 2C + 4H_2$$
, $\Delta H^\circ = -150 \text{ kJ/mol}$, $\Delta G^\circ = 101 \text{ kJ/mol}$

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O, \quad \Delta H^\circ = -165 \text{ kJ/mol}, \quad \Delta G^\circ = -113 \text{ kJ/mol}$$

Total:
$$CH_4 + CO_2 \rightarrow 2C + 2H_2O$$
, $\Delta H^\circ = -15.5 \text{ kJ/mol}$, $\Delta G^\circ = -12 \text{ kJ/mol}$

This process operates at a much lower temperature (500 °C) compared to the conventional process (2700 °C). It operates at atmospheric pressure producing a 70% conversion rate. The heat of reaction and Gibbs free energy for this process suggests that this process is thermodynamically feasible. The value added economic analysis shows that this process produces a profit of 65.6 cents per kg of graphite.

5. *Hydrogen/synthesis gas*. This process produces synthesis gas by CO₂ reforming of methane over a noble metal catalyst of 1% rhodium supported on alumina (Shamsi, 2002):

$$CH_4 + CO_2 \rightarrow 2H_2 + CO, \Delta$$
 $H^\circ = 247 \text{ kJ/mol}, \Delta G^\circ = 171 \text{ kJ/mol}$

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The conversion rate is 97% for both methane as well as carbon dioxide and is considered as high. It operates at atmospheric pressure, which is drastically lower than the conventional process that operates at 41 atm. The operating temperature for this process is 850 °C, which is in the same range as conventional process (760–980 °C). This process is thermodynamically feasible and a value added economic analysis shows that it gives a profit of 17.2 cents per kg of H₂.

6. *Propylene (from carbon dioxide)*. This production process produces propylene by the dehydrogenation of propane using carbon dioxide over Cr₂O₃/SiO₂ catalyst (Takahara et al., 1998):

 $C_3H_8 + CO_2 \rightarrow C_3H_6 + CO + H_2O, \Delta$ $H^{\circ} = 165 \text{ kJ/mol}, \quad \Delta G^{\circ} = 114.8 \text{ kJ/mol}$

This new process operates at a lower temperature (823 K) and pressure (1 atm) compared to the conventional process (temperature: 1143 K, pressure: 31–37 atm). The value added economic analysis of this process gave a profit of 4.3 cents per kg of propylene.

 Propylene (from propane dehydrogenation). This process produces propylene by dehydrogenation of propane over a proprietary platinum catalyst from UOP, called DeH-14 (C&EN, 2003):

$$C_3H_8 \rightarrow C_3H_6 + H_2$$
, $\Delta H^\circ = 124 \text{ kJ/mol}$, $\Delta G^\circ = 86 \text{ kJ/mol}$

This process operates at lower pressure (1 atm) and temperature (780–870 $^{\circ}$ C) compared to the conventional process (pressure: 31–37 atm, temperature: 1143 K). Even though it is an endothermic process, its energy requirement is less than the conventional process and it is three to four times more economical than the conventional process. The value added analysis of this process gives a profit of 2.5 cents per kg of propylene.

8. *Styrene (new method)*. This production method produces styrene through dehydrogenation of ethyl benzene using carbon dioxide over Fe/Ca/Al oxide catalyst (Mimura et al., 1998). The feed gas composition was CO₂/EB = 9/1 and the observed yield was 70%:

$$C_{6}H_{5}C_{2}H_{5} + CO_{2} \rightarrow C_{5}H_{5}C_{2}H_{3} + CO + H_{2}O, \Delta \quad H^{\circ} = 159 \text{ kJ/mol},$$

$$\Delta G^{\circ} = 112 \text{ kJ/mol}$$

This new process operates at 580 °C, which is low compared to the conventional process which operates at 690–700 °C. The energy requirement for this process $(323 \times 10^6 \text{ kJ/h})$ is also lower than the conventional process. A value added economic analysis of this process gives a profit of 10.9 cents per kg of styrene.

 Di-methyl ether (DME) plant. This process produces DME by hydrogenation of CO₂ over γ-Al₂O₃ modified with 1% silica used as catalyst (Jun et al., 2002):

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O_{,\Delta}$$
 $H^{\circ} = -49 \text{ kJ/mol}, \ \Delta G^{\circ} = 3.5 \text{ kJ/mol}$

$$CO_2 + H_2 \rightarrow CO + H_2O$$
, $\Delta H^\circ = 41 \text{ kJ/mol}$, $\Delta G^\circ = 29 \text{ kJ/mol}$

$$2$$
CH₃OH \rightarrow CH₃OCH₃ + H₂O, $\Delta H^{\circ} = -24$ kJ/mol,
 $\Delta G^{\circ} = -17$ kJ/mol

This process operates at $250 \,^{\circ}$ C and $0.53 \,^{\circ}$ atm giving a 70% conversion of methanol. The operating temperature for this process is lower than the temperature of the conventional process (250–368 °C). This process is thermodynamically favorable and this particular catalyst exhibits a better performance than the conventional catalyst (amorphous alumina treated with 10.2% silica). A value added economic analysis of this process gave a profit of 69.6 cents per kg DME.

5. Environmental impact analysis of different designs of the industrial ecosystem

Besides the economic concern, TRACI was used to conduct a comparative analysis of the environmental performance of the base case and the new design scheme of this agrochemical complex. The scope of this analysis is "Entry-to-Exit" due to data availability and practicality. It takes into account only the materials used inside this agro-chemical complex.

Plant	Input	MTPY	Output	MTPY
	Air	0.7088	CO ₂	0.6006
Ammonia	Natural Gas	0.2702	Purge (N ₂ : 22.46, H ₂ : 0.99, Ar: 76.55)	0.0119
	Steam	0.5143	Water	0.0923
Nitric acid	Air	0.9231	Vent (O ₂ : 4.32, N ₂ : 93.99, Ar: 1.60, CO ₂ : 0.07, NO: 0.02)	
	Steam	0.0374	H ₂ O	0.0299
Urea			Ammonia	0.0001
Urea			CO_2	0.0001
			Cooling Water	0.0374
Methanol	Water	0.0511	Vent (H ₂ : 3.33, CO ₂ : 81.29, CO: 15.38)	0.0008
	Natural gas	0.0682	Methanol	0.1771
Granular triple super			HF	0.0107
phosphate			Others (iron and aluminum sulfate 50% each)	0.0197
D	Boiling feed water	2.7793	CO ₂	0.3175
Power generation	Fuel	0.1158	Water	1.0316
Sulfuric acid	Air	7.8474	Vent (SO ₂ : 0.13, N ₂ : 98.13, Ar: 1.67, CO ₂ : 0.07)	6.0392
	Boiling feed water	5.8947	Blowdown	0.4245
	Water	0.7366	Others (inert impurity in sulfur feedstock)	0.0123
Phosphoric acid	Water	0.5371	Others (iron and aluminum sulfate 50% each)	1.997

Table 2

TRACI analysis data for base case	ΓRACI	analy	ysis	data	for	base	case
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The environmental impact of the resources used before entering industrial ecosystem and their fate after leaving the industrial ecosystem has not been accounted for in this study. For ease of calculation, only those environmental impacts that change from the base case to the new design scheme are compared. The results are calculated on the basis of the material input and waste output data for each plant in the base case and the new design scheme.

The TRACI analysis was carried out for the base case using the available data, based on the process flow diagram (Fig. 1). The input/output data for the base case is tabulated in Table 2. TRACI analysis was also carried out for the new design scheme (Fig. 2) and the input/output data for this new design scheme has been tabulated in Table 3. A comparison



Fig. 2. New design scheme for industrial complex in Lower Mississippi River Corridor (Indala, 2004). (*Note*: Flow Rates Million TPY).

Plant	Input	MTPY	Output	MTPY
	NG	0.2744	Purge (N ₂ : 22.46, H ₂ : 0.99, Ar: 76.55)	0.0121
Ammonia	Air	0.7200	Water	0.0938
	Steam	0.5225		
Nitric acid	Air	0.8800	Vent (O ₂ : 4.32, N ₂ : 93.99, Ar: 1.60, NO: 0.02)	0.7062
	Steam	0.0400	Ammonia	0.0001
Urea			CO_2	0.0001
Ulea			Cooling Water	0.0366
			Water	0.0293
CTED			Hydrogen fluoride	0.0100
GTSP			Others (iron and aluminum sulfate 50% each)	0.0200
	Air	7.8500	Vent (SO ₂ : 0.13, N ₂ : 98.13, CO ₂ : 0.07, Ar: 1.67)	6.0392
Sulphuric acid	BFW	5.8974	Blowdown (pure water)	0.4245
	Water	0.7366	Others (inert impurity in sulfur feedstock)	0.0123
Dhaamharia aaid	Water	0.5371	Others (iron and aluminum sulfate 50% each)	1.9970
Phosphoric acid			Water	4.2336
C +			CO (recovered as product)	0.0974
Styrene			Water	0.0627
Synthesis gas	NG	0.0600	CO (recovered as product)	0.1932
Deservises			CO (recovered as product)	0.0100
Propylene			Water	0.0089
Methyl amines	Ammonia	0.0161	CO (recovered as product)	0.0043
wieuryr annies			Water	0.0513
			CO (recovered as product)	0.0182
DME			MeOH (recovered as product)	0.0039
			Water	0.0406

Table 3			~			
TRACI	analysis	data	for	new	design	scheme

BFW, boiling feed water; NG, natural gas.

of the contribution of the agro-chemical complex in various impact categories for the base case and the new design scheme is given in Table 4.

A comparative analysis of the results of TRACI for the base case and the new design scheme in each impact category is discussed in the following section:

- 1. Acidification. In the base case, the contribution towards acidification is 920 H⁺ moles equivalent deposition/kg emission and in the new design scheme it is 919 H⁺ moles equivalent deposition/kg emission. Hence, there is no real difference in the contribution in the acidification category for these two design schemes, as shown in Fig. 3.
- 2. *Fossil fuel usage*. The fossil fuel usage in the new design scheme (22547.161 MJ surplus energy/MJ of extracted energy) has increased by 75% of what was consumed in the base case (12819.976 MJ surplus energy/MJ of extracted energy), as shown in Fig. 4. The reason for this increase is the energy use of the new plants added into the agro-chemical complex in order to consume excess carbon dioxide being released in the atmosphere.

Table 4

Comparison of base case and new design scheme in each impact category

Base case		New design scheme		
Process	Value	Process	Value	
Acidification (moles of H ⁺ eq	uivalent)			
Nitric acid	20	Nitric acid	19	
Sulfuric acid	879	Sulfuric acid	879	
Urea	21	Urea	21	
Total	920	Total	919	
Fossil fuel (MJ)				
Ammonia	1480	Ammonia	1480	
Methanol	368	Methanol	368	
Power generation	10,973	Power generation	20,191	
Tower generation	10,975	Acetic acid	12	
		Graphite	12	
			299	
		Synthesis gas		
Total	12,820	Total	22,547	
Global warming (kg CO ₂)				
Sulfuric acid	9	Sulfuric acid	9	
Nitric acid	1	Nitric acid	1	
Power generation	310	Power generation	571	
Urea	0	Urea	0	
Methanol	1			
Ammonia	1350			
Total	1672	Total	581	
Water (gal)				
Ammonia	138	Ammonia	138	
Sulfuric acid	1752	Sulfuric acid	1752	
Urea	10	Urea	10	
Methanol	14	Methanol	14	
Phosphoric acid	2213			
		Power generation	599	
Total	4126	Total	2512	
Eutrophication (kg N)				
Nitric acid	0.02	Nitric acid	0.02	
Urea	0.03	Urea	0.03	
Total	0.05	Total	0.05	
Human health non-cancer (lbs				
Sulfuric acid	0.01	Sulfuric acid	0.01	
Urea	0.70	Urea	0.70	
		Propylene	0.65	
Total	0.71	Total	1.36	
iotai	0.71	10(a)	1.50	

Table 4 (Continued)

Base case		New design scheme	
Process	Value	Process	Value
Photochemical smog (g NG	D_x equivalent)		
Methanol	0.00	Propene	279.93
Human health critera (DAI	LY)		
Sulfuric acid	0.24	Sulfuric acid	0.24



Fig. 3. Acidification values for base case and new design scheme.



Fig. 4. Fossil usage values for base case and new design scheme.

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Fig. 5. Global warming values for base case and new design scheme.

- 3. *Global warming*. The contribution to this category is reduced by 66% from base case (1671.96 CO₂ equivalents/kg emission) to the new design scheme (581.4 CO₂ equivalents/kg emission). The ammonia plant in the base case was a major contributor to the Global Warming. As can be seen from Fig. 5, the carbon dioxide emission from ammonia plant decreases largely in the new design scheme, as the new processes consume the carbon dioxide generated in the complex as raw material.
- 4. *Water usage*. The water usage reduces by 40% from the base case (4126.328 gal) to the new design scheme (2511.932 gal). This occurs due to the change in the manufacturing



Fig. 6. Water usage values for base case and new design scheme.



Fig. 7. Eutrophication values for base case and new design scheme.

methodology of phosphoric acid and switching from wet process to a HCl process for manufacturing phosphoric acid. As seen in Fig. 6, the water requirement for the power generation facility in the new design scheme is higher than that in the base case, still the reduction in water usage of phosphoric acid plant compensates for this increase.

- 5. *Eutrophication*. Similar to acidification, the contribution of the agro-chemical complex in eutrophication does not change from the base case, 0.048 nitrogen equivalents/kg, to the new design scheme, 0.047 nitrogen equivalents/kg, as shown in Fig. 7.
- 6. *Human health non-cancer*. The contribution to this environmental impact category increases by 90% from the base case (0.7144 toluene equivalents/kg emission) to the



Fig. 8. Human health non-cancer values for base case and new design scheme.



Fig. 9. Photochemical smog values for base case and new design scheme.

new design scheme (1.359 toluene equivalents/kg emission) because of the propylene plant, which has been added in the new design scheme, as shown in Fig. 8. This happens because of the residual propene released in the atmosphere.

- 7. *Photochemical smog*. The contribution of the agro-chemical complex increases manifold (6.22E+06%) from the base case (0.0045) to the new design scheme (279.926) as shown in Fig. 9. Again, the release of propene is responsible for this drastic increase in this impact category.
- 8. *Human health criteria*. The contribution of the agro-chemical complex to this category remains same for both the base case as well as the new design scheme.

As shown in the results, the environmental performance of the new design scheme for the agro-chemical complex has been improved manifold in terms of global warming and water usage, but on the other hand, its performance has deteriorated in terms of some other impact categories like fossil usage and human health. It is clear that the new design scheme will cause a tradeoff between different categories of environmental impacts.

6. Discussion and conclusion

Development of industrial ecosystems is one of the most promising methods available for sustainable development of industrial systems. For developing an eco-effective symbiosis of industries, it is vital to evaluate the environmental impacts of this symbiosis beforehand. This would provide clear guidance for improving the design and establishing a more efficient industrial symbiosis. LCA method can provide a comparative analysis of different design schemes of an industrial ecosystem to evaluate the corresponding environmental impacts.

As can be seen from the results of current case study, one alternative presents a better environmental performance for some impact potentials but worse on others. Thus, an attempt to optimize a process to reduce a particular environmental stress, for example global warming in this case, may end-up hurting the environment in terms of other environmental impacts like fossil fuel usage, human health and photochemical smog. One possible way to improve the design is to delete the propene plant from the superstructure, increase the operating capacity of the remaining carbon dioxide consuming plants and then optimize the superstructure again to consume all the carbon dioxide produced by the ammonia plant. This should reduce the contribution to photochemical smog and human health non-cancer categories. Another way is to rank the impact categories in order to make a choice. Various sociological as well as geographical factors need to be considered before ranking various environmental impact categories. It needs to be pointed out that the results of the current case study are based on limited data and its scope is limited to "Entry-to-Exit". If a more detailed LCA is conducted for the same industrial ecosystem with a wider scope, i.e., "Cradle-to-Grave" then the results obtained may be different from the results of the current case study.

Conclusively, LCA is a very useful and powerful tool to analyze and compare different designs for an industrial ecosystem by providing deep insight about various impacts caused by the production schemes. In order to justify the formation of such a symbiosis it is critical that a comprehensive LCA should be conducted for this industrial ecosystem to explore the probable advantages as well as disadvantages in order to make a more informed decision. This will help the decision-makers and stake-holders select the best scheme for the sustainable development of the industrial ecosystems.

Acknowledgements

This work is in-part supported by the Gulf Coast Hazardous Substance Research Center, the National Science Foundation under Grant CTS-0407494, and the Texas Advanced Technology Program under Grant no. 003581-0044-2003.

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