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Life Cycle Optimization for Sustainable Operations in a Petrochemical Complex

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This paper addresses the optimal operation of a petrochemical complex under economic and environmental criteria. The site mathematical model includes linear and nonlinear simplified models for single plants to calculate site production taking into account main operating variables, intermittent deliveries and inventory variable profiles. The objective function considers the maximization of total profit and the minimization of environmental impact, subject to constraints on mass balances, bounds on product demands, equipment capacities and intermediate and final product storage tanks limitations. The environmental objective is measured with the global warming potential (GWP) and Eco-indicator 99 metrics according to the life cycle assessment procedures. The resulting mixed integer nonlinear programming (MINLP) models have been implemented in GAMS. The bi-criteria MINLP model is solved with the ε-constraint method. The resulting pareto-optimal curve shows the tradeoff between the economic and environmental aspects to pursuit a sustainable operation of an existing integrated petrochemical complex. The optimal solution shows that polyethylene plants have the best environmental and economic performances in the entire complex. As compared to current situation, optimization results show that the petrochemical complex can satisfy product demands while improving the environmental behavior by decreasing greenhouse gases emissions in almost 26 %, from 1,018 to 750.42 kt CO_2-eq/y.

1. Introduction

The petrochemical industry provides numerous commodities for modern society and much effort has been devoted to optimize production processes and economic performance. There is still need for the inclusion of environmental targets to ensure sustainable production of petrochemical products. There is a lack of literature source related to rigorous optimization strategies which explicitly take into account environmental impact as objective function. Environmental concerns are considered as part of the objective design and not as additional constrains in similar design process systems (Ciumei et al., 2004). In this context, life cycle assessment (LCA) is a standard procedure to evaluate the environmental performance of a process (Guillén-Gosálbez and Grossmann, 2009). It calculates environmental loads associated to a product, a process or activities from raw material acquisition and others supplies required for the production to the final disposition of products (ISO-14040, 2006). The first step of LCA application consists in setting boundaries for the LCA analysis; defining the objective of the analysis, the functional units and the environmental metrics followed by identification and quantification of the energy and material used in a process. The next step is the estimation of waste released to the environment. Obtained results are converted into a set of environmental impacts that can be aggregated into different groups, eleven impact categories are proposed (PRé-Consultants, 2000). The eleven impact categories are aggregated into three damage models: to human health, to ecosystem quality and to resource.

In this work, we carry out multiobjective optimization of a currently operating petrochemical complex (Schulz et al., 2003), considering both economical and environmental objectives. The site comprises two natural gas liquids (NGL) processing plants, two ethylene plants, a caustic soda and chlorine plant, a VCM plant, a PVC

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plant, three polyethylene plants (LDPE, HDPE, LLDPE), an ammonia and an urea plant. Linear mathematical models have been derived for the NGL, ethylene and polyethylene plants, based on rigorous existing models tuned with actual plant data. Simplified models take into account variations in production with key plant operating variables, such as temperature and pressure in separation units. Available yield data for chemical transformations and utilities consumption have been used to model the rest of the petrochemical complex.

The present work addresses the development of the mathematical model of a petrochemical complex where the objective function considers the maximization of total profit and the minimization of environmental impact, subject to constraints on mass and energy balances, bounds on product demands, equipment capacities and intermediate and final product storage tanks limitations. In addition, there are constraints on the final products distribution by ship, train or truck while storage tanks capacities are satisfied. The environmental objective is measured with the global warming potential (GWP) and Eco-indicator 99 metrics according to the life cycle assessment procedures. The resulting problem is a mixed integer nonlinear programming (MINLP) optimization problem, implemented in GAMS (Brooke et al., 2011).

2. Petrochemical complex description

The complex under study comprises two natural gas processing plants, whose main objective is to extract ethane from natural gas to use it as raw material in ethylene plants. Natural Gas Plant I, next to the complex, is fed with 24 Mm^3/d of natural gas. Residual gas (mainly methane) is recompressed to pipeline pressure; part of it is taken as feed for the ammonia plant and the rest is delivered as sales gas. Pure ethane, propane, butane and gasolines are plant products. Natural Gas Plant II has its cryogenic sector (referred to as Demethanizing Plant) several kilometers away from the conventional separation train (NGL Fractionation Plant). The demethanizing plant is fed with 36 MMm^3/d of natural gas. Light gases are separated from the heavy ones (ethane, propanes, butanes and gasolines) and injected to the natural gas pipeline. The rich gas mixture (5 Mm^3/d of heavy gases) is stored in thermal vessels and pumped to the petrochemical complex where it is fed to containers to equalize the charge, i.e. to damp any pulsation or flow changes that may occur anywhere along the pipeline. The feed mixture undergoes a conventional distillation train in the NGL Fractionation Plant to obtain LPG (Liquefied Petroleum Gas: propane, butane and gasoline) and ethane. Ethylene plants process 2,300 t/y of pure ethane; ethylene is provided as raw material to polyethylene and VCM plants and the rest is exported. The ammonia plant production is 2,050 t/d, most of which is fed to the urea plant to produce 3,250 t/d of urea. In these processes, 1.28 Mm^3/d of natural gas is used as raw material. Urea, ammonia, polyethylenes and PVC are delivered by ship, train and trucks.

3. Methodology

3.1 Life Cycle Optimization of a Petrochemical Complex

The main objective of LCA is to provide quantitative environmental criteria in order to compare different alternatives of design and operational conditions. LCA is integrated with optimization tools to simultaneously evaluate the main operating conditions of the petrochemical complex. LCA evaluates the complex from an environmental point of view, and optimization tools provide information about operational condition and identify the optimal design in terms of environmental impact minimization (Azapagic and Clift, 1999). Environmental impact evaluation is performed following LCA principles, determined by ISO – 14040 (2006). The LCA is conducted in four steps: definition of goal and scope, life cycle inventory (LCI), life cycle impact assessment (LCIA) and interpretation.

Definition of Goal and Scope: The objective is to determine the petrochemical complex LCA. The functional unit of the LCA is the production in terms of tons of generated products. Environmental impact is evaluated in transport, steam generation, emissions related to natural gas supply, electricity consumption and emissions of all operational units of the petrochemical complex. The impact is quantified by means of GWP metric, a relative measure that compares global warming impact of a certain mass of a chemical product to global warming impact of a similar mass of carbon dioxide (whose GWP is standardized to 1) and Eco-indicator 99, a damage oriented method for life cycle environmental impact assessment of process, activity and products (Piemonte et al., 2014, PRé-Consultants, 2000)..

Life Cycle Inventory: This step aims to analyze all input/output data associated to the operation of the units of the petrochemical complex. The inventory of LCA is taken in transport, steam generation, emissions related to natural gas supply, electricity consumption and emissions of all operational units of the petrochemical complex.

Life Cycle Impact Assessment: Contributions corresponding to environmental impacts are calculated based on inventory analysis. GWP and Eco-Indicator 99 are the metrics used to quantify environmental impact. Global Warming Potential (GWP) is calculated as the sum of GWP of each source of emission. The

Intergovernmental Panel on Climate Change (IPCC) provides the generally accepted values for GWP of greenhouse gases (Solomon et al., 2007). GWP is calculated over a specific time horizon, IPPC of 2007 recommends a 100 y horizon (Gebreslassie et al., 2013). In LCA context, a specific evaluation method of environmental impact is Eco-Indicator 99 (EI99) (Piemonte et al., 2014, Guillén-Gosálbez and Grossmann, 2009) where 11 impact categories are proposed (PRé-Consultants, 2000). The 11 impact categories are aggregated into 3 damage models (damage to human health, damage to ecosystem quality and damage to resource) that are converted in only one EI99 measurable. Damaging factors, which relate LCA results and impact categories, are given by the specific damage models available of each category (PRé-Consultants, 2000). Pieragostini et al. (2011) used this method for a bioethanol plant in Argentina, as it is the most used LCA method.

Interpretation: At this step, the calculated LCI and LCIA results are interpreted with respect to the goal and scope of the LCA study and recommendations for decision-making are given.

3.2 Mathematical Formulation

The life cycle optimization of a petrochemical complex is formulated as an MINLP problem which determines the optimal operation of petrochemical complex considering the economic performance and environmental impact objective functions. Binary variables are associated to intermittent product delivery. MINLP models have been formulated, with different objective functions: minimization of GWP and multiobjective optimization for profit maximization and environmental impact minimization, respectively. Additionally, approximate mixed integer linear models (MILP) have also been formulated applying linearization techniques to bilinear equations (Schulz et al., 2005) to obtain valid initial points for MINLP problems. The bi-objective function is the maximization of total profit, defined as the difference between sales revenue and total operating cost plus penalties for not meeting demands and inventory and the minimization of environmental impact. Three major types of constraints are included in the model formulation: mass balance constraints, economic analysis constraints, and life cycle environmental impact constraints. A brief description of plants and their mathematical models is given in Schulz et al. (2005). The environmental objective is measured with the global warming potential (GWP) and Eco-indicator 99 metrics All model elements are calculated for the following components: CO_2, N_2, CH_4, C_2H_6, C_3H_8, C_4H_{10}, C_5H_{12}, C_6H_{14}, C_2H_4, C_3H_6, LDPE, LLDPE, HDPE, EPE, H_2, C_2H_2, C_4H_8, VCM, EDC, PVC, NH_3, $(NH_2)_2CO$.

Environmental Impact

The environmental impact analysis of the petrochemical complex is developed following LCA principles. Environmental constrains related to the optimization problem are inventory analysis and environmental impact constraints.

Inventory Analysis Constraints: Total emissions calculated in the LCI analysis(LCI_b^{tot}) consists of transport (LCI_b^{trans}), steam generation (LCI_b^{steam}), natural gas supply (LCI_b^{ng}), electricity consumption (LCI_b^{elec}) and operational unit (LCI_b^{emiss}) emissions of the entire petrochemical complex, as shown in Eq(1).

$$\left(\mathrm{LCI}_b^{tot}\right) = \left(\mathrm{LCI}_b^{trans}\right) + \left(\mathrm{LCI}_b^{steam}\right) + \left(\mathrm{LCI}_b^{ng}\right) + \left(\mathrm{LCI}_b^{elec}\right) + \left(\mathrm{LCI}_b^{emiss}\right) \tag{1}$$

Different types of emissions are calculated according to emissions carbon footprint per functional unit and total consumption, as indicated in Eq(2).

$$\mathrm{LCI}_b^{cat} = \mathrm{LCIE}_{b,cat}\bar{F}_{cat} \quad \forall\ b, cat\ \in \{trans, steam, ng, elec, emiss\} \tag{2}$$

where $\bar{F}_{cat}$ represents the total mass of transported raw material, total cubic meters of steam water consumed, total cubic meters of natural gas consumed, total kWh of electricity consumed, and total emissions released in kg during the operation of the petrochemical complex. LCI_b^{cat} are the LCI input of the petrochemical complex of chemical species *b* in each unit.

Environmental Impact Constraints: Obtained results from LCI are translated into different categories of environmental damage. GWP is calculated as the sum of GWP of each source of emission(GWP_{cat}), as indicated Eq(3).

$$\mathrm{GWP}_{cat} = \sum_b \mathrm{LCI}_b^{cat}\phi_{cat} \quad \forall cp, cat\ \in \{trans, steam, ng, elec, emiss\} \tag{3}$$

ϕ_{cat} is the damage factor that relates GWP of chemical species *b* to GWP of the carbon dioxide. Damage factors of each type of greenhouse gases emissions are obtained from Solomon et al. (2007). Environmental performance is modeled minimizing GWP or Eco-Indicator 99.

$$\mathrm{GWP} = \sum_{\mathrm{b}} \mathrm{GWP_{cat}} \qquad (4)$$

Eco-Indicator 99: Environmental impacts associated to each impact category are calculated from LCI analysis Eq. (1) and damage factor of the model is calculated as indicated in Eq. (5).

$$\mathrm{IMP_c} = \sum_{\mathrm{b}} \mathrm{LCI_b d\, f_{bc}} \quad \forall \mathrm{c} \qquad (5)$$

where $\mathrm{IMP_c}$ indicates the damage caused in the impact category *c*, $\mathrm{LCI_b}$ is the value associated to chemical species *b* in the LCI analysis and $\mathrm{df_{bc}}$ is the coefficient associated to chemical species b of the damage model *c*. These coefficients, that relate LCI analysis and impact categories, are given by specific damage model for each category and are available in the literature (PRé-Consultants, 2000; Ecoinvent Center, 2009). Finally, impact factors are aggregated into damage categories *d* $(\mathrm{DAM_d})$, which are transformed into only one indicator EI99, as shown below.

$$\mathrm{DAM_d} = \sum_{\mathrm{c} \in \mathrm{CD(d)}} \mathrm{IMP_c} \quad \forall \mathrm{d} \qquad (6)$$

$$\mathrm{EI99} = \sum_{\mathrm{d}} \mathrm{DAM_d nf_d w\, f_d} \qquad (7)$$

In Equation (6), $\mathrm{CD(d)}$ represents the different impact categories included in the damage category *d*, $\mathrm{nf_d}$ refers to factor normalization and $\mathrm{wf_d}$ refers to factor weighing (PRé-Consultants, 2000). Environmental performance is modeled minimizing EI99 given by Eq. (7).

3.3 Solution Method

LCA and bi-objective optimization combined provides an adequate environment to rigorously and systematically identify opportunities for improvement in the environmental and economic fields. Therefore, the bi-criteria optimization problem is formulated as follows:

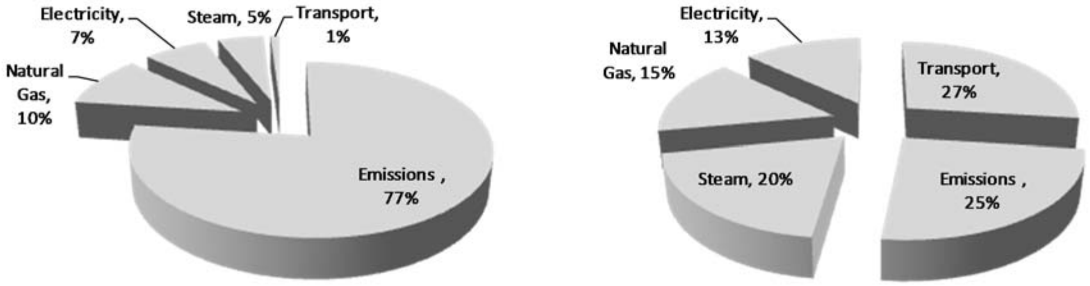
$$\begin{aligned} &\max_{\mathrm{x}} \quad \text{Total Profit} \\ &\min_{\mathrm{x}} \quad \mathrm{GWP} \\ &\mathrm{s.t.} \\ &\qquad \mathrm{h(x)} = 0 \\ &\qquad \mathrm{g(x)} \le 0 \\ &\qquad \mathrm{x} \in \mathrm{R} \end{aligned} \qquad (8)$$

Where equality constraints are associated to mass balance constraints, economic analysis constraints, and life cycle environmental impact constraints. Inequality constraints are given by specific requirements of the model, such as equipment capacities, storage limitations and bounds on production and products demands. The objective function takes GWP as a measure of the environmental impact. The solution to this bi-criteria optimization problem is given by a set of Pareto optimal points.

4. Numerical Results and Discussion

The MINLP model has 7,989 equations, 6,742 continuous variables and 200 binary variables. It is formulated in GAMS 24.1.3 modelling environment (Brooke, 2013) and solved with DICOPT (CONOPT3 and CPLEX), respectively. The MINLP problem is solved in eight major iterations. The Pareto optimal operations with ten points are generated in 1,503 CPU s.

As compared to current situation, optimization results for GWP minimization show that the petrochemical complex can satisfy product demands, while improving the environmental impact decreasing greenhouse emissions in almost 26 %, from 1,018 to 750.42 kt $\mathrm{CO_2}$-eq/y in terms of GWP, while still fulfilling product demands and environment policies. Figure 1 shows both GWP distributions, before and after minimization, for GHGs and environmental impacts associated to transport, steam usage, electricity and natural gas for the petrochemical complex. The main impact is given by associated emissions. Figure 3 shows environmental impact in terms of Eco-Indicador 99 and its eleven impact categories so as to minimize GWP for the petrochemical complex. As it can be seen, the most important environmental impact is fossil fuel exhaustion, followed by breathing effects, climate change and carcinogenic effects. The main impact is associated to process emissions, followed by natural gas usage, electricity, steam usage and in a lower proportion transport. This is due to the fact that the main raw material is natural gas, which is transported by pipelines. Therefore, to reduce environmental impact, the main focus must aim at reducing emissions associated to each process unit.



a b

Figure 1: LCA for petrochemical complex before (a) and after (b) GWP minimization

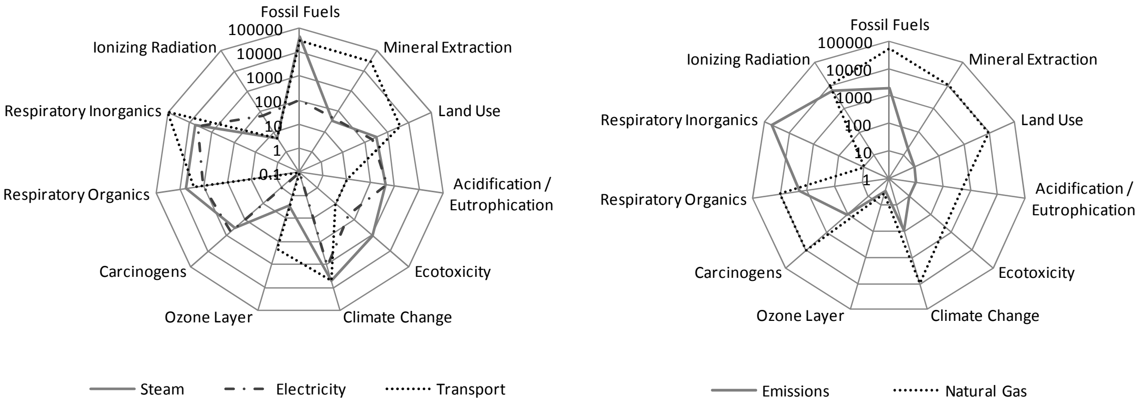


Figure 2: Petrochemical complex environmental impact with Eco-Indicator 99

Figure 3 shows Pareto optimal solutions. The y-axis of the Pareto curve represents the total profit and the x-axis is GWP. The Pareto curve shows the optimal trade-off operations of the petrochemical complex and each Pareto point represents optimal design of the petrochemical complex with a unique combination between the total profit and GWP.

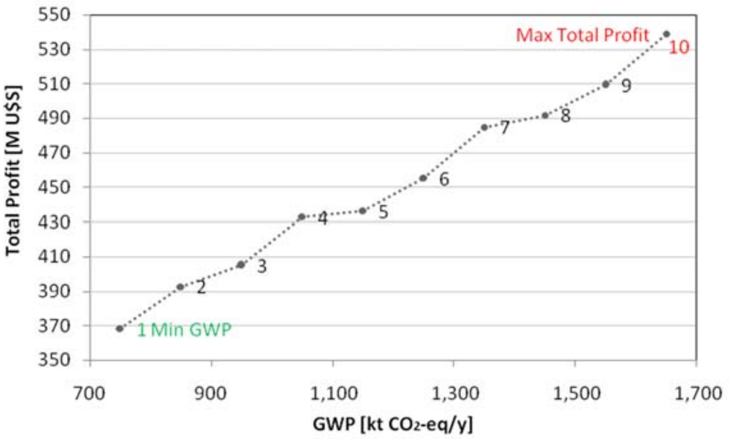


Figure 3: Pareto Curve for petrochemical complex

This is not always the case when dealing with an entire site, composed of several plants. Optimal solutions show that polyethylene plants have the best environmental performances in the entire complex. Greenhouse gases emissions can be reduced in almost 26 % with 30 % profit reduction, without taking into account carbon credits. Therefore, the inclusion of carbon credits and other emission markets within the model will provide a better economical performance associated to this environmental impact.

5. Conclusions

In this work, we have formulated MINLP models for GWP minimization and simultaneous optimization of economical and environmental objectives for an operating petrochemical complex in Argentina. The model takes into account mass balances, economic equations, and life cycle environmental impact constraints. Traditionally, LCA can be applied systematically with good results. However, including detailed process information within mathematical models provides better insights on environmental behaviour. In our case study, optimization results show that greenhouse gases emissions can be reduced in almost 26%, while still fulfilling product demands and environmental legislation. The inclusion of carbon credits and other emission markets within then model is part of current work.

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