SUSTAINABILITY IN CHEMICAL ENGINEERING

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Rezumat: Activitățile industriale aparțin unuia, sau mai multora din cele patru domenii majore ale ingineriilor: electrică, mecanică, chimică şi civilă. Prin fluxurile informaționale cu celelalte trei domenii inginerești, cu matematica, fizica, chimia teoretica, biologia, știința materialelor, informatica ş.a, ingineria chimică constituie nucleul descoperirilor în cercetarea științifică. În dezvoltarea durabila a societății, ingineria chimică are de asemenea un rol major, prin necesitățile de folosire a resurselor de materii prime şi energie regenerabile, reducere a numărului şi cantităților de produse secundare nedorite şi a riscurilor de poluare, crearea de noi materiale cu proprietăți superioare şi reutilizabile etc. În consecință, sunt necesare o serie de noi paradigme pentru fundamentarea noii inginerii chimice sustenabile. În cadrul prezentării, vor fi expuse o serie de astfel de paradigme. Acestea deriva din principalele practici actuale din industriile de proces, care în scopul dezvoltării durabile sunt imperios necesar a fi îmbunătățite. De asemenea, vor fi prezentate direcțiile specifice în evoluția cercetării din ingineria chimică, rezultate din respectivele paradigme. Pentru noile tehnologii durabile se va impune aplicarea în practică a celor mai adecvate soluții, obținute cu ajutorul tehnicilor de optimizare multicriterială. În final, ideile expuse vor fi concretizate printr-un studiu de caz.

Cuvinte cheie: dezvoltare durabilă, inginerie chimică,optimizare multicriterială.

Abstract: The industrial activities belong to one, ore more of the four main engineering fields: electrical, mechanical, chemical and civil. Through the informational fluxes connected to the others three engineering fields, to mathematics, physics, theoretical chemistry, biology, material science, computer science, and others, chemical engineering is the nucleus of discovery in science research. Also, in the sustainable development of the society chemical engineering play a main role, due to the requirements to use renewable raw materials and energy sources, to reduce number and amounts of secondary undesirable products and the pollution risks, to realise new renewable materials with high properties, etc. Consequently, new paradigms are necessary for the new sustainable chemical engineering. In this presentation several such paradigms will be exposed. These paradigms emerge from the actual main practices of the process industries, which to the aim of sustainable development must strongly to be improved. The specific directions of chemical engineering research evolution, derived from the new paradigms, will be presented. For the new sustainable technologies the most adequate solutions, obtained with multiobjective optimization techniques, will be implemented. Finally, the exposed ideas will be materialized through a case study.

Keywords: sustainability, chemical engineering, multiobjective optimization.

Chemical engineering is one of the four main engineering fields beside electrical, mechanical, and civil engineering. Our life cannot be conceived without any of these fields. Through the informational fluxes connected to the others three engineering fields, to mathematics, physics, theoretical chemistry, biology, material science, computer science, and others, chemical engineering is the nucleus of discovery in science research (Fig. 1).

In the sustainable development of the society chemical engineering play a main role, due to the requirements to use renewable raw materials and energy sources, to reduce number and amounts of secondary undesirable products and the pollution risks, to realise new renewable materials with high properties, etc.

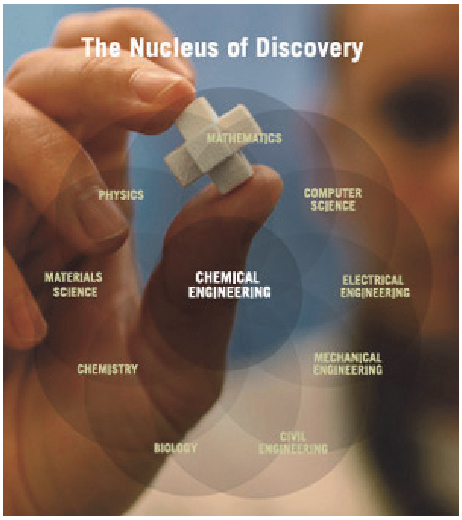

Fig. 1. Nucleus of discovery: Chemical Engineering (web.mit.edu).

A comprehensive definition of sustainability is as *the optimal growth path that maintains economic development while protecting the environment and optimizing the social conditions with the boundary of relying on limited, exhaustive natural resources* (Stiglitz, 1974). Therefore, sustainability clearly does not men to preserve, but to develop responsibly. Our world has limited resources with a fast growing population and a limited carrying capacity of our planet. Therefore, besides the **economic** structure of a process, **environmental** and **social** aspects should be considered. Sustainability becomes more and more important in modern economy, and in 1999 the Dow Jones Sustainability Indices were started. Corporate sustainability is considered a business approach that creates long-term shareholder value by embracing opportunities and managing risks deriving from **economic, environmental, and social development.** All these three parts are important in truly sustainable development. They are not independent of each other, but rather there are manifolds interactions between them (Fig. 2).

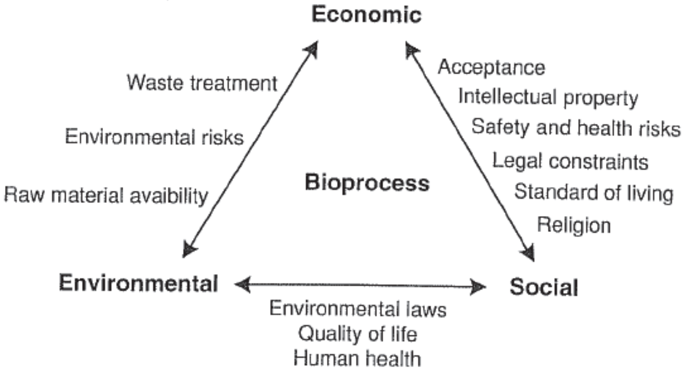

Fig. 2. Economic, environmental and social sustainability (Heinzle et al., 2006).

In the actual evolution new paradigms are necessary for the new sustainable chemical engineering. These paradigms emerge from the actual main practices of the process industries, which to the aim of sustainable development must strongly to be improved. Current chemical practices must be transformed into new paradigms in sustainable chemistry (Table 1 from Workshop Report: Chemistry for a Sustainable Future, National Science Foundation on Sustainability and Chemistry, May 30 – June 1, 206 Arlington, VA).

As a result of these new paradigms, research in a number of specific areas is necessary and includes:

- Supplying the building blocks for material synthesis by research into tailorable, e.g. genetically engineered, renewable energy feedstocks. (This would allow for the use of more renewable alternative energy sources and, in particular, decrease society’s reliance on petroleum.)

Table 1

Transformation of current chemical practices into new paradigms in sustainable chemistry

Current chemical practices	New paradigms in sustainable chemistry
Chemicals and materials synthesized from petroleum-derived molecules	• Tailorable, *e.g.* genetically engineered, renewable feedstocks supply the building blocks for material synthesis • Thermoprocessible plastics produced by simple modifications of oxygenated biomaterials
Products are assembled by covalent bonds that must be degraded prior to re-utilization	Materials held together by non-covalent forces that can be disassembled under specific conditions
• Conversions require stoichiometric quantities of reagents • Accessory compounds, *e.g.* chiral auxilliaries, protecting groups, etc., are often required • Most carbon-carbon bond formation is under thermodynamic, rather than kinetic, control	Reactions promoted by highly selective and active catalysts
Reactions carried out in a variety of volatile organic solvents tailored for each reaction type	A single solvent, *e.g.* near-critical water, that allows tunable properties for multiple types of chemical reactions
Reaction discovery and process optimization is often a slow process	• *In situ* spectroscopy for real-time monitoring of reactions over time scales from nanoseconds to hours during the discovery phase • Higher level at which computations can be used to predict new catalytic systems
A large number of candidate materials are prepared and screened with respect to their properties	Accurate computational approaches to predicting the properties of novel materials reduces development effort
Specialized macroreactors are usually used for each synthetic step	The future chemical plant will consist of modular microreactors that can be rapidly assembled in multiple combinations to create new processes
Each unit operation advances the synthesis by a single step	Multiple reactions carried out in a single vessel promoted by compatible catalysts
Product separation and purification is often difficult and energy-intensive	Highly selective, nanomaterials-based separations methods avoid the need for distillation

• Increasing alternative fuel use by searching for thermoprocessible plastics produced by simple modifications of oxygenated biomaterials.

• The development of highly active and selective catalysts would minimize the production of side products and solve problems associated with thermodynamic, rather than kinetic, control.

• Lessening present energy conversion inefficiencies by developing single solvent, e.g. near-critical water, which allows tunable properties for multiple types of chemical reactions.

• Making the process of developing new materials less difficult by in situ spectroscopy for real-time monitoring of reactions over time scales from nanoseconds to hours during the discovery phase.

• Improving new materials development by creating tools to make higher-level computations. (Chemists could more easily predict new catalytic systems and to develop more accurate computational approaches for predicting the properties of novel materials.)

• Developing modular microreactors that can rapidly assemble in multiple combinations to create new processes. (These microreactors should be developed for use in chemical plants.)

• Developing compatible catalysts that allow for multiple reactions to be carried out in a single vessel.

• Avoiding difficult and energy intensive product separation and purification by developing highly selective, nanomaterials-based separations methods that avoid the need for distillation.

- Developing tunable reaction conditions to allow multisteps in the same pot (oxidation, condensation, reduction or making a monomer + polymerize), i.e. find ways to make the incompatible…compatible.
- Developing massively scalable synthesis (environ-friendly) of useful nanoparticles/materials.
- Improving molecular study of degradation/life cycle analysis of aggregates.
- Developing triggered self-disassembly.
- Developing new materials that are biodegradable.
- Developing catalysts with environmentally friendly metals (not precious metals or heavy metals) or non-metal catalysts.
- Investigating environ/health implications nanotubes and nanoparticles should be determined in advance.
- Establishing design rules for nanomaterials.
- Exploiting size/property relationships of molecular and nanoscience and investigating unique morphologies and control issues.

Always we must have in minded that: “**research is the conversion of money into knowledge, while innovation is the conversion of knowledge into money**”.

For the new sustainable technologies, multiobjective optimization techniques have a paramount role in the implementation of the most adequate solutions. An illustrative case study which presents optimal sustainable design of a chemical process using a multiobjective technique is exposed bellow.

Case study: *Optimal economical, environmental and social design of the biodiesel production from soybean oil.*

Over the past three decades there has been intense investigation on the development of fuel producing processes that are based on the use of renewable agricultural materials as feedstock. This activity is driven by the quest of fuel self-reliance as well as reducing emissions of particulates, hydrocarbons and carbon monoxide. The majority of efforts have been concentrated on bioethanol and biodiesel. Biodiesel consists of the simple alkyl esters of the fatty acids found in agricultural acylglycerol-based fats and oils. It has been shown to give engine performance similar to that of conventional fuels. The process (Fig. 3 from SuperPro Designer 8.5 Examples) has been split into three sections: the *Reaction*, the *Biodiesel Refining*, and the *Glycerol Purification* section.

The *Reaction Section* consists of:

- The raw material storage tanks for the methanol (TNK-101), the catalyst (TNK-102) and the soybean oil (TNK-103)
- The two reactors (R-101 and R-102)
- A decanter centrifugal separator (DC-101)

The soybean oil is directly fed to the reactor (R-101). Methanol and the catalyst are mixed and 90% of the mixture is fed to the first reactor. The rest (10%) is fed to the second reactor. Methanol reacts with soybean oil and yields biodiesel and glycerol. Product is removed at a rate equal to the rate of charging the reactants and catalyst. The average residence time of materials in the reaction is 1 h. Glycerol, a co-product of the *acylglycerol transesterification*, separates from the oil phase as the reaction proceeds. The reaction extent is approximately 90%. The material is then fed to a centrifugal separator (DC-101) where the biodiesel and the soybean oil that has not reacted are separated from the glycerol-rich co-product phase. The latter, is sent to the glycerol recovery unit. The biodiesel stream, which also contains unreacted methanol, soybean oil and catalyst is fed into a second stirred tank reactor (R-102) along with the addition of the methanol-catalyst stream from the splitter (FSP-101). The reaction conditions are the same. The reaction extent in the second reactor is 90% which yields a combined conversion efficiency of 99%. Again the mixture of methyl esters (biodiesel), glycerol, unreacted substrates and catalyst exiting the second reactor is fed to another centrifugal separator (DC-102).

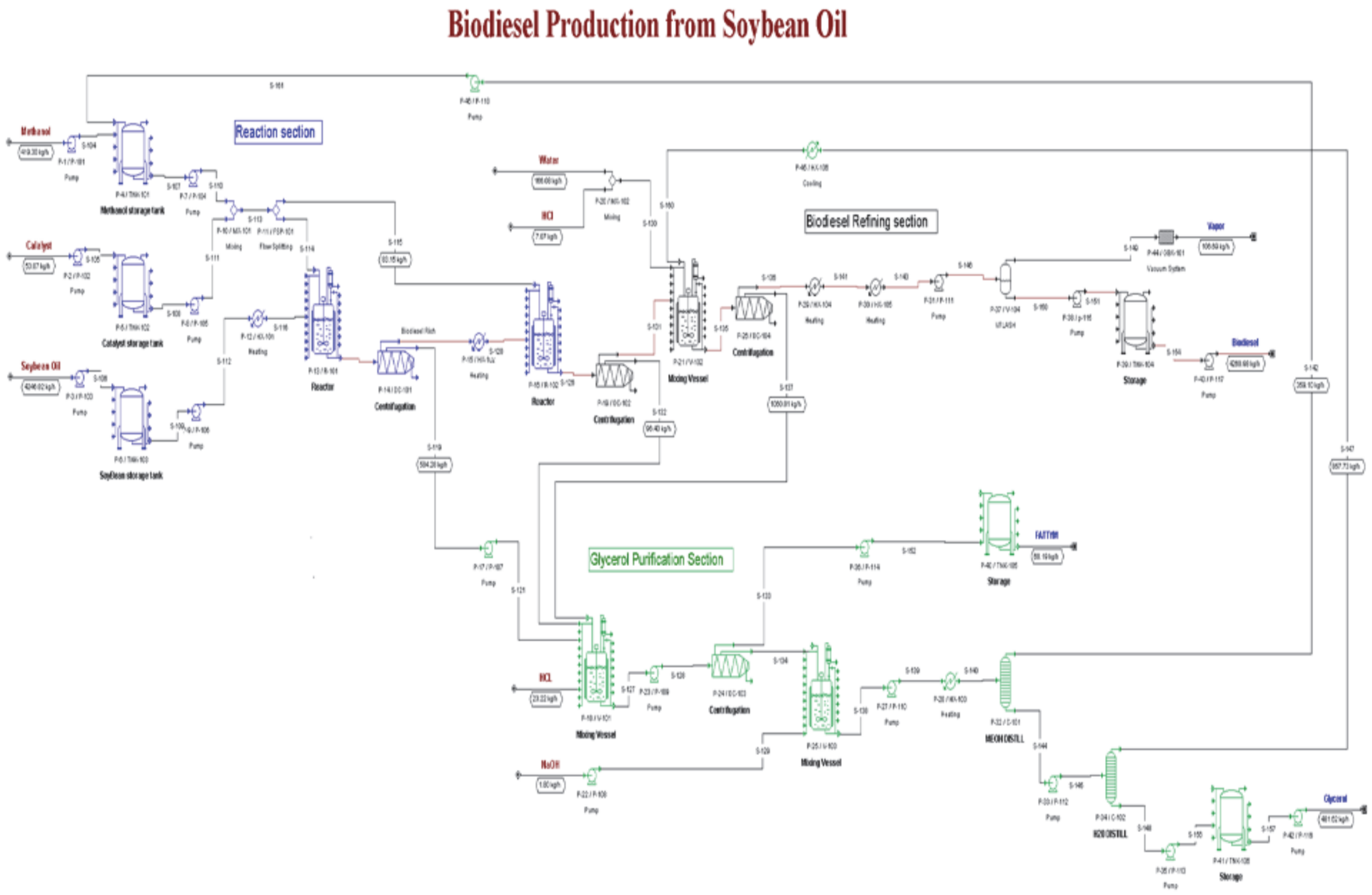

Fig. 3. The process for biodiesel production from soybean oil.

Biodiesel Refining Section consists of:

- Two continuous centrifugal separators (DC-102 & DC-104)
- A mixing vessel (V-102)
- A vacuum dryer system (V-104 & GBX-101)
- The Biodiesel storage tank (TNK-104)

The crude biodiesel stream is washed with acidified water at a pH of 4.5 in a mixing tank (V-102) to neutralize the catalyst and turn any soaps into free fatty acids. The material is then fed to a continuous centrifugal separator (DC-104) to separate the biodiesel from the aqueous phase, which is fed to the glycerol recovery section. The crude biodiesel product must contain a maximum of 0.050% w/w water. This is achieved by using a vacuum dryer system (V-104 & GBX-101). It lowers the water content from 2.3% to app. 0.04%.

Glycerol Purification Section consists of:

- Two mixing vessels (V-101 & V-103)
- A centrifugal separator (DC-103)
- Two distillation columns (C-101 & C-102)
- Two storage tanks (TNK-105 & TNK-106)

Glycerol produced during trans-esterification requires purification before it can be sold. The equipment is sized to remove methanol, the fatty acids, and most of the product to yield an 80% pure glycerol which is then sold to industrial glycerol refiners at a price of \$0.33/kg. Both glycerol streams (S-119 & S-132) and fatty acid contaminants (S-137) exiting the reactors are pooled and treated with acid (HCl) in V-101 to convert soaps into free fatty acids which are subsequently removed by centrifugation (DC-103). The fatty acid stream is destined to disposal. The glycerol stream is then neutralized with caustic soda (in V-103). The methanol contained in the glycerol stream is recovered by distillation (C-101) and recycled back to the first reactor (R-101). Finally the glycerol stream is concentrated to reach 80% purity by another distillation step (C-102) that removes the water, which is recycled back to the mixing vessel V-102.

The multiobjective optimization problem consists in establish the optimal biodiesel annual production of the plant with the next three objectives:

$f1$ = maximize the profit (k\$/year) : economical objective

$f2$ = minimize VOC emissions (kg/h) : ecological objective

$f3$ = maximize number of jobs of chemical operators: social objective

This multiobjective optimization problem was solved using the Matlab Genetic Algorithm "*gamultiobj*". Genetic Algorithms are stochastic search techniques that evolve a population of initial solutions. By adequate selection of the algorithm parameters it can be obtained global optimum, or close near optimum solution. The values of the independent variables v_i (input flowrates of raw materials) and the resulting process, economical and ecological data after simulation with SuperPro Designer was transferred between Matlab and SuperPro Designer using an original Matlab graphical user interface (GUI)- based on Component Object Module (COM) technology, named Objective Function (Fig. 4).

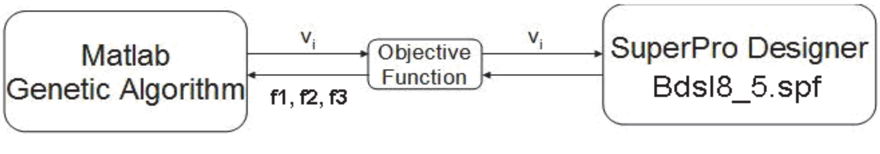

Fig. 4. The data transfer between Matlab and SuperPro Designer.

Some sets of the values of the three objectives are represented in Fig. 5. It can be observed that for biodiesel annual productions corresponding to high profit values, despite increasing of the number of jobs, the VOC emissions are important, which is undesirable.

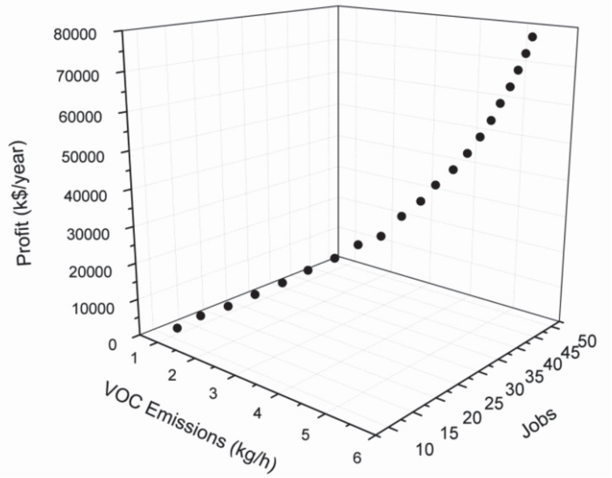

Fig. 5. Some sets of the values of the three objectives.

The goal of the multiobjective genetic algorithm is to find a set of solutions in that range (ideally with a good spread). The set of solutions is also known as a Pareto front. All solutions on the Pareto front are optimal. Two Pareto fronts from which it can be selected the best compromise solutions are exposed in Fig. 6 and Fig. 7. A compromise solution is: biodiesel production 3110 t/year, profit 10820 k$/year, VOC emissions 2.006 kg/h and 16 jobs of chemical operators. Another optimal solution is: biodiesel production 9210 t/year, profit 66560 k$/year, VOC emissions 5.375 kg/h and 42 jobs of chemical operators.

Traditionally multiobjective optimization of design and operation in chemical engineering was done manually, step by step in a trial and error approach. This type is time consuming and obtained solution confidence is low. Also, the number of objectives implied cannot be large. The presented client-server application, based on Component Object Module (COM) technology, calls automatically the SuperPro Designer simulator inside optimization loops for various sets of input variables. Due to the link with Matlab, SuperPro Designer functionality is greatly extended by the use of Matlab toolboxes (optimization, statistics, graphical tools, etc.).

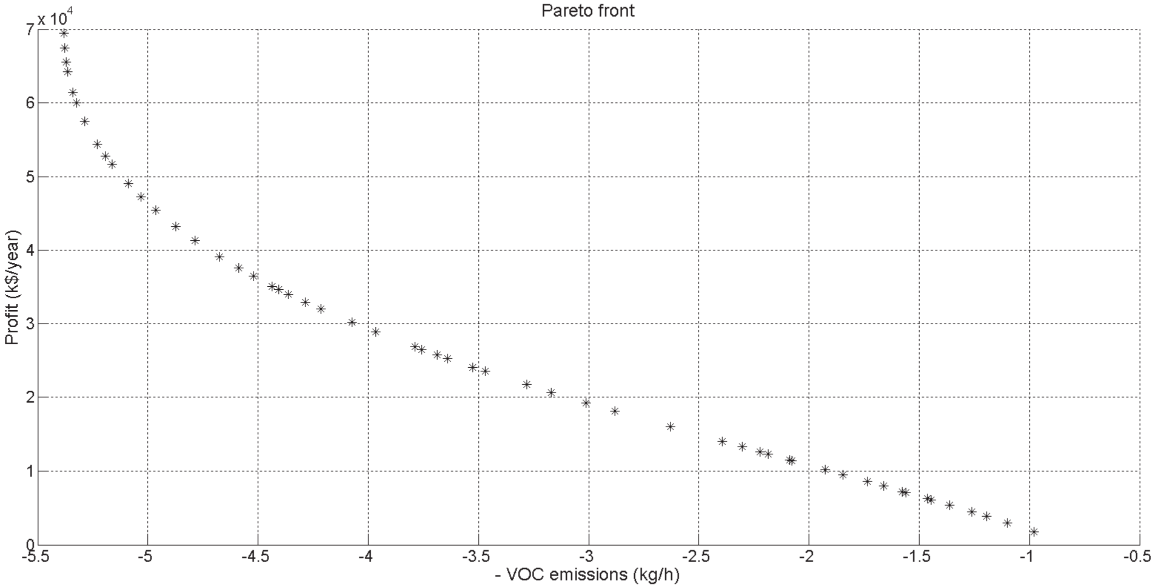

Fig. 6. Pareto front Profit – VOC emissions.

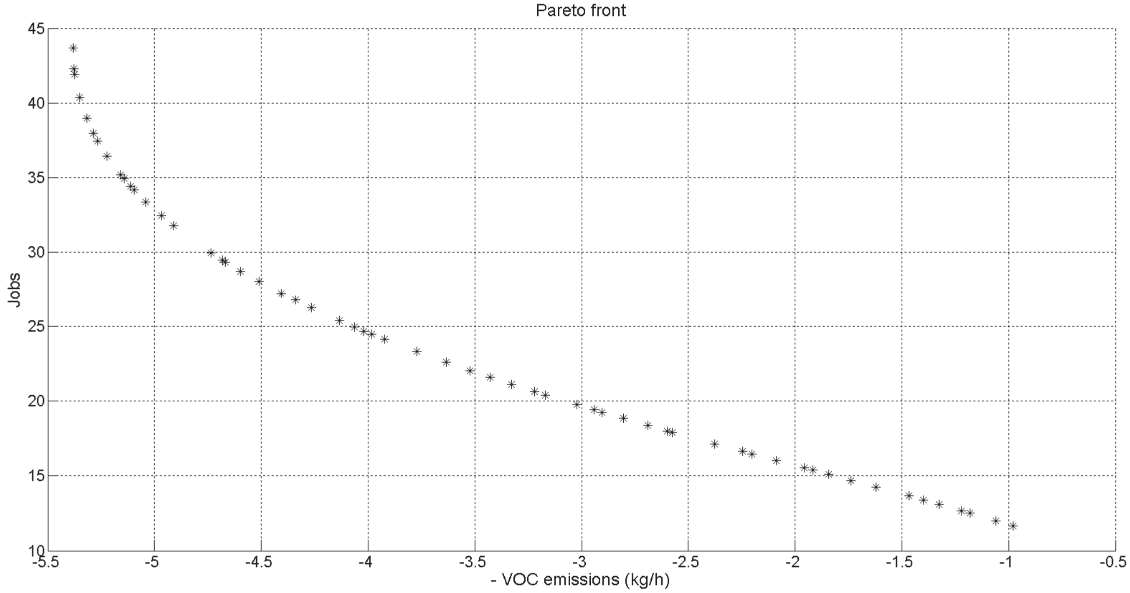

Fig. 7. Pareto front Jobs – VOC emissions.

The multiobjective optimization is in agreement with the actual tendency in design and operation of economical, environmental and social sustainable processes. This can be used in both design and operation phase of a plant. In the design stage it can be used to render a sustainable design. In the exploitation stage it can be used to determine the best economic and environmental condition for obtaining product, every time when the final product amount or quality parameters are modified due to various client specifications.

The optimal design and operation of sustainable processes must be an imperative task not only in chemical engineering, but also in every engineering field. The multiobjective optimization is a power tool for this purpose.

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