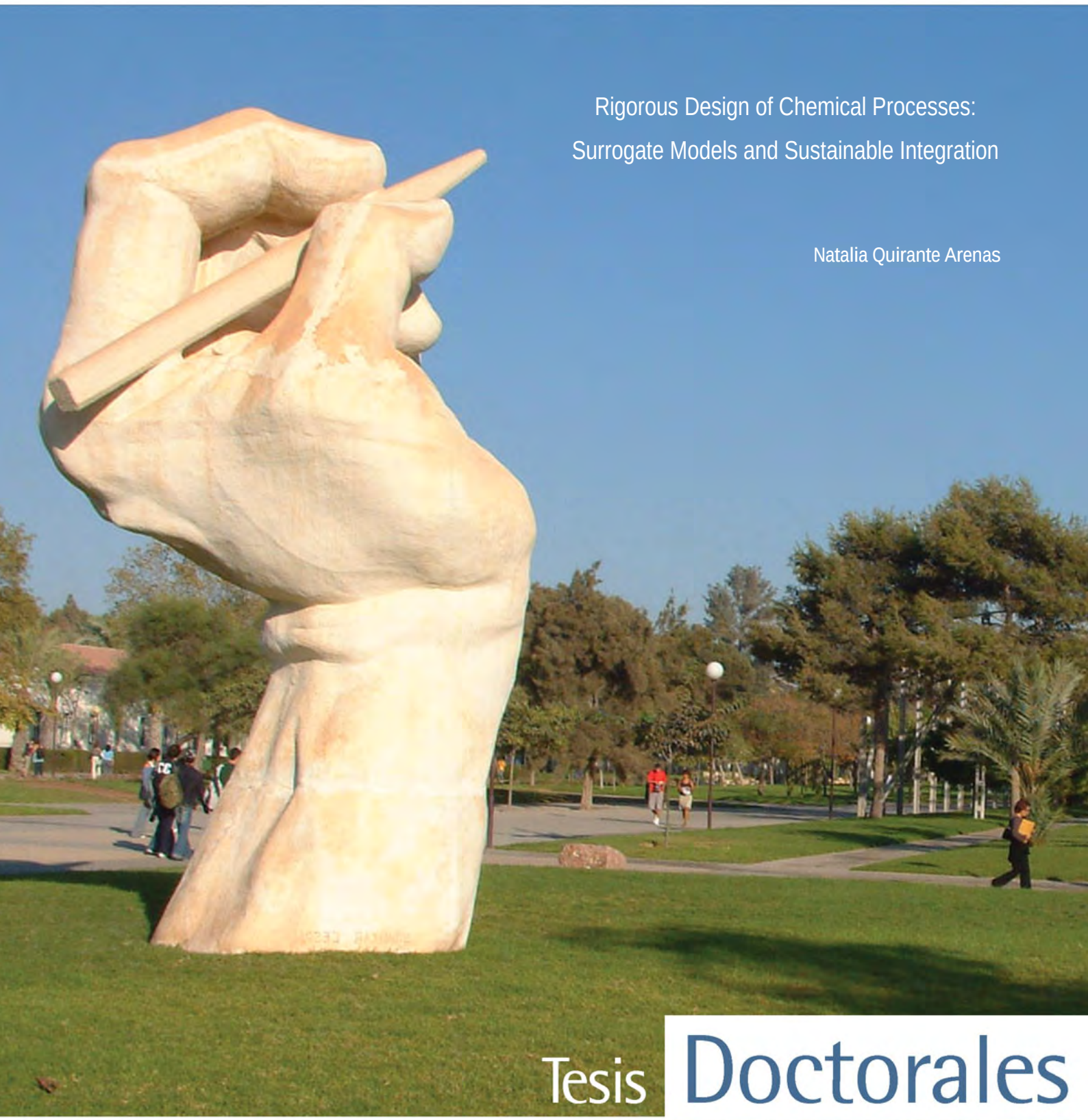
Universitat d'Alacant
Universidad de Alicante

Rigorous Design of Chemical Processes: Surrogate Models and Sustainable Integration

Natalia Quirante Arenas



Tesis Doctorales

www.eltallerdigital.com

UNIVERSIDAD de ALICANTE

[>>COnCEPT] Computer Optimization in Chemical Engineering Processes and Technologies

Rigorous Design of Chemical Processes:
Surrogate Models and Sustainable Integration

PhD Thesis

Natalia Quirante Arenas

Alicante, December 2017

Universitat d'Alacant
Universidad de Alicante

Universitat d'Alacant
Universidad de Alicante
Escuela Politécnica Superior

Instituto Universitario de Ingeniería de Procesos Químicos

Rigorous Design of Chemical Processes:

Surrogate Models and Sustainable Integration

Natalia Quirante Arenas

Tesis presentada para aspirar al grado de
DOCTORA POR LA UNIVERSIDAD DE ALICANTE

MENCIÓN DE DOCTORA INTERNACIONAL

DOCTORADO EN INGENIERÍA QUÍMICA

Dirigida por:
JOSÉ A. CABALLERO SUÁREZ

Ayudas para Contratos Predoctorales
para la Formación de Doctores 2013

Ref: BES-2013-064791

GOBIERNO DE ESPAÑA
MINISTERIO DE ECONOMÍA Y COMPETITIVIDAD
Unión Europea
Fondo Europeo de Desarrollo Regional
"Una manera de hacer Europa"

Universitat d'Alacant
Universidad de Alicante

© Natalia Quirante Arenas, 2017

Cover design: Laura Quirante Arenas.
Printing and binding: The University of Alicante Press.

Universitat d'Alacant
Universidad de Alicante
ESCUELA POLITÉCNICA SUPERIOR
Instituto Universitario de Ingeniería de Procesos Químicos

D. JOSÉ ANTONIO CABALLERO SUÁREZ, Catedrático del Departamento de Ingeniería Química de la Universidad de Alicante

CERTIFICA:

Que Dña. NATALIA QUIRANTE ARENAS, Ingeniera Química, ha realizado bajo mi dirección, en el Instituto de Ingeniería de los Procesos Químicos de la Universidad de Alicante, el trabajo que con el título "Rigorous Design of Chemical Processes: Surrogate Models and Sustainable Integration" constituye su memoria para aspirar al grado de Doctora en Ingeniería Química, reuniendo a mi juicio las condiciones necesarias para ser presentada y juzgada por el tribunal correspondiente.

Y para que conste a los efectos oportunos, firmo el presente Certificado en Alicante, a 8 de noviembre de 2017.

Fdo. Dr. José A. Caballero Suárez

Universitat d'Alacant
Universidad de Alicante

Table of Contents

Universitat d'Alacant
Universidad de Alicante

Universitat d'Alacant
Universidad de Alicante

Universitat d'Alacant
Universidad de Alicante

Universitat d'Alacant
Universidad de Alicante

List of Tables

Universitat d'Alacant
Universidad de Alicante

Universitat d'Alacant
Universidad de Alicante

List of Figures

Universitat d'Alacant
Universidad de Alicante

Universitat d'Alacant
Universidad de Alicante

SUMMARY
Resumen

Universitat d'Alacant
Universidad de Alicante

Summary

The development of efficient chemical processes, from an economic and environmental point of view, is one of the main objectives of the Chemical Engineering. To achieve this goal, in the last years, advanced tools are being used for design, simulation, optimization, and synthesis of chemical processes, which allow us to obtain more efficient processes and with the least possible environmental impact.

Reducing energy consumption is one of the most important aspects to consider when designing efficient processes. The global energy consumption of the industrial sector represents approximately 22.2 % of the total energy consumption. Within this sector, the chemical industry accounts for around 27 %.[1] Therefore, the global energy consumption of the chemical industry is approximately 6 % of all the energy consumed in the world.

Bearing in mind that the energy consumed is mainly generated by combustion of fossil fuels, any improvement in the design of chemical processes could reduce the energy consumption, reducing also the environmental impact.

The work collected in this Doctoral Thesis has been carried out in the research group COnCEPT[2] of the University of Alicante during the years 2014 and 2017.

The main objective of this Thesis is based on the development of simulation and optimization tools in order to improve process energy efficiency, which reduces the environmental impact. Specifically, this Doctoral Thesis is composed of two main studies, which are the concrete objectives to achieve:

* Study and evaluation of surrogate models to improve the simulation-based optimization of chemical processes.
* Development of new models for the simultaneous optimization and heat integration of chemical processes.

The first objective is based on the study and evaluation of surrogate models to replace complex models implemented in process simulators. The simulation-based optimization has some disadvantages. On the one hand, each unit operation is considered as a “black box” inside the simulators, therefore, algebraic equations that define the models are not available. Consequently, its derivatives must be calculated

by numerical differentiation what is very expensive to compute. Even in the case in where the CPU time is not excessive, most of the black box models introduce numerical noise, thus avoiding to estimate accurate derivatives. Additionally, the lack of convergence of a simulation during the optimization makes the whole procedure fail. For this study, the first part of this Thesis is composed of three papers; two of them have been published in international journals of high-impact factor and the third has been sent and is under review in another of these journals.

In the first work, different configurations of distillation columns have been studied. The basic idea to solve these problems is to replace distillation columns or complex arrangements by surrogate models generated from rigorous models. Surrogate models are computationally efficient[3] and they ensure an acceptable degree of accuracy.[4] During the development of this Thesis, Kriging algorithm[5] was selected to build the surrogate models, thanks to its ability to obtain accurate surrogate models from relatively small sampling data. The results from this work show that it is possible to obtain accurate surrogate models (with errors below 5 %) with up to seven degrees of freedom. This study has been collected in the Publication 1: "Rigorous Design of Distillation Columns Using Surrogate Models Based on Kriging Interpolation".

The main objective of the second work is the multiobjective optimization of the sour water stripping plant of a refinery, considering simultaneously the economics, heat integration and environmental impact. The idea of this paper arises from the satisfactory results of the first work, with the purpose of implementing the use of surrogate models in the optimization of large-scale processes. The strategy followed consists of replacing by surrogate models based on Kriging interpolation only those units or modules that could produce numerical problems, like distillation columns. Units that do not introduce numerical noise, such as heat exchangers, pumps, mixers, and splitters, are maintained in the simulator. Moreover, the equations related to heat integration and life cycle assessment are defined as explicit equations. The results show that it is possible to perform the multiobjective optimization of large-scale processes using surrogate models. In addition, the multiobjective optimization allows large energy savings (around 39 % in heating and 25 % in cooling) regarding the economically optimized plant, without taking into account neither the heat integration nor the environmental impact. At the same time, multiobjective optimization allows us to reduce the environmental impact around 49.5 % regarding the non-optimized plant. This study can be found in the Publication 2: "Large Scale Optimization of a Sour Water Stripping Plant Using Surrogate Models".

The main objective of the third work is the optimization of a Vinyl Chloride Monomer (VCM) process superstructure using surrogate models. The idea of this paper arises from the satisfactory results of the second work, with the purpose of implementing the use of surrogate models in the optimization of superstructures (i.e., to extend the study to Mixed-Integer Nonlinear Programming (MINLP) problems). In this case, surrogate models based on Kriging interpolation are used to replace distillation columns and reactors, because these units could produce numerical problems during the optimization. All the possible alternatives to produce VCM are proposed through the superstructure. Heat integration was also studied after the optimization, which allow us to know the energy savings. In this work, financial risk is also studied in order to know the risk of not obtaining the expected profit. The results show that heat integration allows energy savings, with the consequent reduction of the environmental impact. Furthermore, the financial risk study reflects that the risk of not achieving the expected profit is very low (around 5 %). Therefore, the results are remarkably satisfactory. The results of this research are under review in an international high-impact journal, under the title: "Hybrid Simulation-Equation Based Synthesis of Chemical Processes". (Publication 3)

The second part of this Thesis is composed of two new papers, which have been published in international high-impact journals. In this case, a new alternative strategy is developed for the simultaneous optimization and heat integration of chemical processes. Most of the methods developed in the field of heat integration assume that input and output process stream temperatures are fixed and known *a priori*. In other words, heat integration is carried out only after fixed all the process operation conditions. However, it is known that the simultaneous optimization of the process conditions and the heat integration might produce significant savings in the total cost of the process.[6] Several works have been published following the idea developed by Duran and Grossmann.[7-9] Nevertheless, in this work, we develop a new strategy for the simultaneous process optimization and heat integration through the modification of the Pinch Location Method.

The first work consists of the modification of the 'max' operators that Duran and Grossmann used to deal with the problem. We use a disjunction to deal directly with the 'max' operators, instead of explicitly dealing with the positions of the different streams in relation to the pinch (as occurs in the model proposed by Grossmann et al.[7]). The advantage of this model is that we use an additional variable to reformulate the problem, which reduces the number of binary variables and the number of equations. The results obtained with the proposed disjunctive formulation show that

our model is very competitive from the point of view of CPU time, compared to the disjunctive model proposed by Grossmann et al.[7] and Navarro-Amorós et al.[8] Furthermore, the proposed model improves the relaxation gap. The results of this study have been compiled in the Publication 4: "A Novel Disjunctive Model for the Simultaneous Optimization and Heat Integration".

The second work considers that during the simultaneous optimization and heat integration of chemical processes there might exist streams that are not classified *a priori*, that is, that they cannot initially be classified as hot or cold streams. Additionally, an extension of the model is presented to allow the area estimation assuming vertical heat transfer, where all the 'kink' points on the hot and cold balanced composite curves are determined and an implicit ordering is used to determine adjacent points in the balanced composite curves for the area estimation. The proposed new formulation has proved to be robust and numerically efficient in large-scale problems. Furthermore, the total number of variables and equations is lower than that of the alternative formulations,[8,10] which makes the proposed disjunctive model very competitive. The results of this research are collected in the Publication 5: "Disjunctive Model for the Simultaneous Optimization and Heat Integration with Unclassified Streams and Area Estimation".

Finally, in order to aspire to the International PhD Mention, a three-month research stay was conducted. The stay took place in the School of Chemical Engineering and Analytical Science (The University of Manchester),[11] one of the most outstanding universities in this field of study. During the stay, I acquired the knowledge for the correct development of a life cycle inventory. The inventory was based on data available in the literature. Also, I learned to build a Life Cycle Assessment (LCA) model using GaBi software,[12] a commercial software widely used in the academia and industry. As a case study, the inventory of a membrane system for the oxy-combustion process for CO_2 capture was applied.

References

[1] International Energy Agency. *World Energy Outlook 2016*. Paris, France; 2016.

[2] COnCEPT (Computer OptimizatioN of Chemical Engineering Processes and Technologies). University of Alicante. http://web.ua.es/concept.

[3] Papalambros PY, Wilde DJ. *Principles of Optimal Design: Modeling and Computation*. 2nd ed. New York: Cambridge University Press; 2000.

[4] Chung PS, Jhon MS, Biegler LT. The Holistic Strategy in Multi-Scale Modeling. *Adv Chem Eng* 2011; 40:59-118.

[5] Krige DG. *A Statistical Approach to Some Mine Valuations and Allied Problems at the Witwatersrand* [Master's Thesis]. South Africa: University of Witwatersrand; 1951.

[6] Duran MA, Grossmann IE. Simultaneous Optimization and Heat Integration of Chemical Processes. *AIChE J* 1986; 32(1):123-138.

[7] Grossmann IE, Yeomans H, Kravanja Z. A Rigorous Disjunctive Optimization Model for Simultaneous Flowsheet Optimization and Heat Integration. *Comput Chem Eng* 1998; 22:S157-S164.

[8] Navarro-Amorós MA, Caballero JA, Ruiz-Femenia R, Grossmann IE. An Alternative Disjuntive Optimization Model for Heat Integration with Variable Temperatures. *Comput Chem Eng* 2013; 56:12-26.

[9] Hui CW. Optimization of Heat Integration with Variable Stream Data and Nonlinear Process Constraints. *Comput Chem Eng* 2014; 65:81-88.

[10] Kong L, Avadiappan V, Huang K, Maravelias CT. Simultaneous Chemical Process Synthesis and Heat Integration with Unclassified Hot/Cold Process Streams. *Comput Chem Eng* 2017; 101:210-225.

[11] School of Chemical Engineering and Analytical Science. The University of Manchester. http://www.ceas.manchester.ac.uk/

[12] Thinkstep, Inc. *GaBi* [Computer Software]. Stuttgart, Germany: Thinkstep Inc; 2017.

Universitat d'Alacant
Universidad de Alicante

Universitat d'Alacant
Universidad de Alicante

Resumen

El desarrollo de procesos químicos eficientes, tanto desde un punto de vista económico como desde un punto de vista ambiental, es uno de los objetivos principales de la Ingeniería Química. Para conseguir este propósito, durante los últimos años, se están empleando herramientas avanzadas para el diseño, simulación, optimización y síntesis de procesos químicos, las cuales permiten obtener procesos más eficientes y con el menor impacto ambiental posible.

Uno de los aspectos más importantes a tener en cuenta para diseñar procesos más eficientes es la disminución del consumo energético. El consumo energético del sector industrial a nivel global representa aproximadamente el 22.2 % del consumo energético total, y dentro de este sector, la industria química representa alrededor del 27 %.[1] Por lo tanto, el consumo energético de la industria química a nivel global constituye aproximadamente el 6 % de toda la energía consumida en el mundo.

Además, teniendo en cuenta que la mayor parte de la energía consumida es generada principalmente a partir de combustibles fósiles, cualquier mejora de los procesos químicos que reduzca el consumo energético supondrá una reducción del impacto ambiental.

El trabajo recopilado en esta Tesis Doctoral se ha llevado a cabo dentro del grupo de investigación COnCEPT,[2] perteneciente al Instituto Universitario de Ingeniería de los Procesos Químicos de la Universidad de Alicante, durante los años 2014 y 2017.

El objetivo principal de la presente Tesis Doctoral se centra en el desarrollo de herramientas y modelos de simulación y optimización de procesos químicos con el fin de mejorar la eficiencia energética de éstos, lo que conlleva a la disminución del impacto ambiental de los procesos. Más concretamente, esta Tesis Doctoral se compone de dos estudios principales, que son los objetivos específicos que se pretenden conseguir:

* Estudio y evaluación de los modelos surrogados para la mejora en la optimización basada en simuladores de procesos químicos.

* Desarrollo de nuevos modelos para la optimización de procesos químicos y la integración de energía simultánea.

Universitat d'Alacant
Universidad de Alicante

El primero de los objetivos principales de la presente Tesis se basa en el estudio y la evaluación de los modelos surrogados para sustituir modelos complejos implementados en simuladores de procesos. La optimización basada en simuladores presenta varios inconvenientes. Por un lado, las operaciones unitarias son tratadas como "cajas negras" dentro de los simuladores, por lo que las ecuaciones algebraicas que definen los modelos son desconocidas. Por ello, sus derivadas deben ser estimadas por diferenciación, necesitando unos tiempos de CPU elevados. Además, algunos de estos modelos introducen ruido numérico, por lo que sus derivadas no pueden ser calculadas con precisión. Asimismo, en algunos puntos el modelo simulado podría tener problemas de convergencia, lo que hace que todo el procedimiento de optimización falle. Para este estudio, la primera parte de la Tesis se compone de tres trabajos, dos de los cuales han dado lugar a dos publicaciones en revistas de alto impacto internacional y el tercero ha sido enviado y se encuentra bajo revisión en otra de estas revistas científicas.

En el primero de los trabajos realizados se estudian diferentes configuraciones de columnas de destilación. La idea básica para solventar los problemas que plantea la optimización basada en simuladores es la de sustituir las columnas de destilación, o disposiciones complejas de columnas, por modelos surrogados generados a partir de modelos rigurosos, los cuales son computacionalmente eficientes[3] y aseguran un grado de precisión aceptable.[4] Durante el desarrollo de esta Tesis, el algoritmo de Kriging[5] fue el seleccionado para construir los modelos surrogados, gracias a su capacidad de obtener modelos surrogados precisos a partir de conjuntos de datos reducidos. Los resultados obtenidos a partir de este trabajo muestran que es posible obtener modelos surrogados precisos (con errores medios por debajo del 5 %) con hasta siete grados de libertad. La investigación llevada a cabo para este estudio se recoge en la Publicación 1: "Rigorous Design of Distillation Columns Using Surrogate Models Based on Kriging Interpolation".

El segundo de los trabajos tiene como objetivo principal la optimización multiobjetivo de la planta de tratamiento de aguas de una refinería de petróleo, teniendo en cuenta simultáneamente el coste de operación del proceso, la integración de energía y el impacto ambiental de la planta. La idea de este trabajo surge a partir de los resultados satisfactorios obtenidos del primer trabajo, con la intención de implementar el uso de los modelos surrogados en la optimización basada en simuladores de procesos a gran escala. La estrategia seguida consiste en sustituir, por modelos surrogados basados en interpolación Kriging, solamente aquellas unidades de la planta que puedan introducir problemas numéricos durante la optimización,

como son las columnas de separación. Aquellas unidades que no introducen ruido numérico, como intercambiadores de calor, bombas, mezcladores y separadores, se mantienen en el simulador. Además, todas las ecuaciones relacionadas con la integración de energía, así como con el análisis de ciclo de vida, son definidas en forma de ecuaciones explícitas. Los resultados obtenidos muestran que la optimización multiobjetivo de procesos a gran escala usando modelos surrogados es posible. Ésta permite grandes ahorros energéticos (en torno al 39 % en calentamiento y al 25 % en enfriamiento) respecto a la planta optimizada económicamente y sin tener en cuenta la integración de energía ni el impacto ambiental. Al mismo tiempo, la optimización multiobjetivo permite reducir los impactos ambientales alrededor del 49.5 % con respecto a la planta sin optimizar. Los resultados obtenidos en este estudio constituyen la Publicación 2: "Large Scale Optimization of a Sour Water Stripping Plant Using Surrogate Models".

El objetivo principal del tercer trabajo consiste en la optimización de una superestructura para obtener el mejor proceso para la fabricación del monómero de cloruro de vinilo. La idea de este trabajo surge a partir de los resultados satisfactorios obtenidos del segundo trabajo, con la intención de implementar los modelos surrogados en la optimización de superestructuras (es decir, con la intención de ampliar el estudio a problemas de programación no lineal con variables binarias (MINLP)). En este caso, los modelos surrogados basados en interpolación Kriging son utilizados para sustituir tanto columnas de destilación como reactores químicos, debido a que estas unidades podrían introducir problemas numéricos en la optimización. A través del desarrollo de la superestructura se plantean todas las alternativas de interés para la producción del cloruro de vinilo. Una vez optimizada la planta, se genera la red de integración de energía, lo que nos permite conocer el ahorro energético que se puede conseguir. En este trabajo también se estudia el riesgo financiero de la instalación, para conocer el riesgo de no conseguir el beneficio esperado. Los resultados obtenidos muestran que los modelos surrogados también pueden ser empleados para resolver problemas a gran escala de optimización basada en simuladores. Por otra parte, la integración de energía permite obtener importantes ahorros energéticos, con la consiguiente reducción del impacto ambiental. Así mismo, el estudio del riesgo financiero refleja que el riesgo de no obtener el beneficio esperado es muy bajo (aproximadamente del 5 %). Por lo tanto, los resultados obtenidos son muy satisfactorios. Los resultados obtenidos en este estudio se encuentran en revisión en una revista de alto impacto internacional, bajo el título: "Hybrid Simulation-Equation Based Synthesis of Chemical Processes". (Publicación 3)

La segunda parte de esta Tesis está compuesta por dos nuevos trabajos, que también han sido publicados en revistas científicas de alto impacto internacional. En este caso, aparece la idea de desarrollar una estrategia alternativa para la optimización de procesos y la integración de energía simultánea, para redes de intercambiadores de calor. La gran mayoría de los métodos desarrollados en el campo de la integración energética asumen que las temperaturas de entrada y salida de una red de intercambiadores de calor son fijas y conocidas *a priori*. En otras palabras, la integración de calor se lleva a cabo solo después de haber fijado todas las condiciones de operación del proceso. Sin embargo, es sabido que la optimización de las condiciones del proceso y la integración energética simultanea pueden producir importantes ahorros en el coste total del proceso.[6] Varios han sido los trabajos publicados siguiendo la idea desarrollada por Duran y Grossmann.[7-9] No obstante, en esta parte se pretende desarrollar una nueva estrategia para la optimización y la integración de energía simultánea a partir de una modificación del método de localización del Pinch.

En el primero de éstos trabajos se plantea modificar los operadores 'max' con los que Duran y Grossmann tratan el problema, aplicando una disyunción directamente sobre el operador, en lugar de trabajar con la posición de las corrientes con respecto al Pinch (como se hace en el modelo propuesto por Grossmann et al.[7]). La ventaja que presenta este modelo es que se utiliza una variable suplementaria para reformular el sistema, lo que reduce el número de variables binarias y el número de ecuaciones. Los resultados obtenidos con la formulación disyuntiva propuesta muestran que nuestro modelo resulta muy competitivo, desde el punto de vista del tiempo de resolución, frente a los modelos de Grossmann et al.[7] y Navarro-Amorós et al.[8] Además, el modelo propuesto mejora la solución del problema relajado. Los resultados de este estudio se recogen en la Publicación 4: "A Novel Disjunctive Model for the Simultaneous Optimization and Heat Integration".

El segundo de los trabajos parte de la idea de considerar que durante la optimización de procesos e integración energética simultánea pueden existir corrientes que no estén clasificadas *a priori*, es decir, que en un primer momento no se puedan clasificar como corrientes frías o calientes. Asimismo, se presenta una extensión del modelo que permite la estimación del área de intercambio asumiendo que la transferencia de calor es vertical, donde se determinan todos los puntos de curvatura de las curvas balanceadas compuestas y, además, se realiza el ordenamiento para determinar los puntos adyacentes en las curvas compuestas y poder así estimar el área de intercambio. La nueva formulación ha demostrado ser

robusta y numéricamente eficiente en problemas a gran escala. Al mismo tiempo, el número total de variables y ecuaciones del modelo es menor que el de las reformulaciones alternativas,[8-10] lo que provoca que el modelo propuesto sea muy competitivo. Los resultados derivados de esta investigación se encuentran recogidos en la Publicación 5: "Disjunctive Model for the Simultaneous Optimization and Heat Integration with Unclassified Streams and Area Estimation".

Finalmente, para poder optar a la Mención de Doctora Internacional, se realizó una estancia de investigación de tres meses en la Escuela de Ingeniería Química y Ciencias Analíticas[11] de la Universidad de Manchester (Reino Unido), con el fin de mejorar los conocimientos en el área del análisis de ciclo de vida y estudio del impacto ambiental, en una de las universidades más destacadas dentro de este campo de estudio. Durante la estancia se adquirieron los conocimientos necesarios para construir un inventario de ciclo de vida basado en datos disponibles de distintas referencias bibliográficas. También se aprendió a construir los modelos para la Evaluación del Ciclo de Vida usando el software GaBi,[12] un software comercial ampliamente utilizado en el mundo académico y en la industria. Como caso de estudio, se realizó el inventario de un sistema de membranas aplicado al proceso de oxi-combustión para la captura de CO_2.

Referencias

[1] International Energy Agency. *World Energy Outlook 2016*. Paris, France; 2016.

[2] COnCEPT (Computer OptimizatioN of Chemical Engineering Processes and Technologies). Universidad de Alicante. http://web.ua.es/concept.

[3] Papalambros PY, Wilde DJ. *Principles of Optimal Design: Modeling and Computation*. 2nd ed. New York: Cambridge University Press; 2000.

[4] Chung PS, Jhon MS, Biegler LT. The Holistic Strategy in Multi-Scale Modeling. *Adv Chem Eng* 2011; 40:59-118.

[5] Krige DG. *A Statistical Approach to Some Mine Valuations and Allied Problems at the Witwatersrand* [Master's Thesis]. South Africa: University of Witwatersrand; 1951.

[6] Duran MA, Grossmann IE. Simultaneous Optimization and Heat Integration of Chemical Processes. *AIChE J* 1986; 32(1):123-138.

[7] Grossmann IE, Yeomans H, Kravanja Z. A Rigorous Disjunctive Optimization Model for Simultaneous Flowsheet Optimization and Heat Integration. *Comput Chem Eng* 1998; 22:S157-S164.

[8] Navarro-Amorós MA, Caballero JA, Ruiz-Femenia R, Grossmann IE. An Alternative Disjuntive Optimization Model for Heat Integration with Variable Temperatures. *Comput Chem Eng* 2013; 56:12-26.

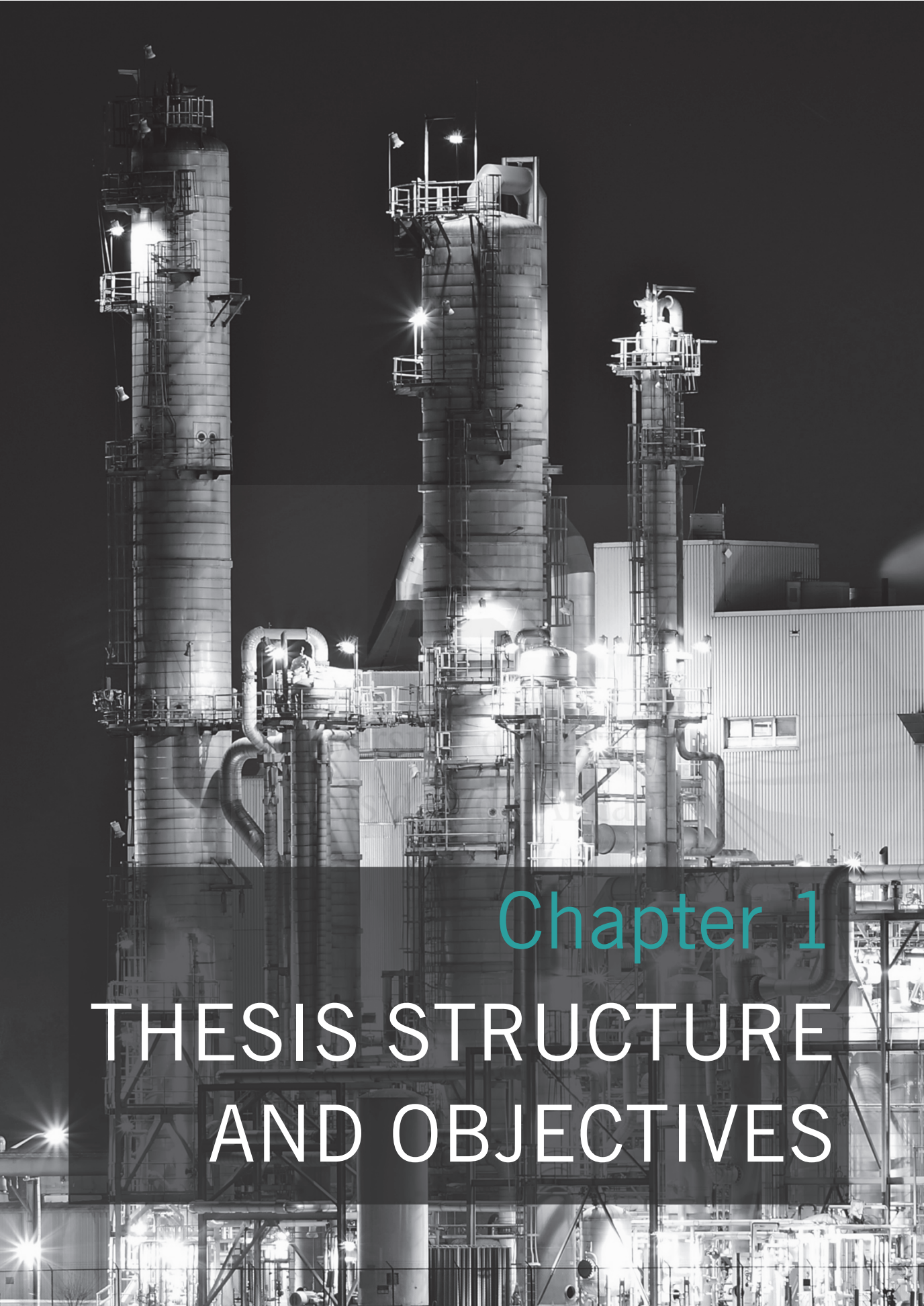
[9] Hui CW. Optimization of Heat Integration with Variable Stream Data and Nonlinear Process Constraints. *Comput Chem Eng* 2014; 65:81-88.

[10] Kong L, Avadiappan V, Huang K, Maravelias CT. Simultaneous Chemical Process Synthesis and Heat Integration with Unclassified Hot/Cold Process Streams. *Comput Chem Eng* 2017; 101:210-225.

[11] Escuela de Ingeniería Química y Ciencias Analíticas. Universidad de Manchester. http://www.ceas.manchester.ac.uk/

[12] Thinkstep, Inc. *GaBi* [Computer Software]. Stuttgart, Germany: Thinkstep Inc; 2017.

Universitat d'Alacant
Universidad de Alicante



Chapter 1

THESIS STRUCTURE AND OBJECTIVES

Universitat d'Alacant
Universidad de Alicante

Chapter 1.

Thesis Structure and Objectives

The work developed in this Doctoral Thesis has been carried out in the research group COnCEPT belonging to the Institute of Chemical Processes Engineering of the University of Alicante, between the years 2014 and 2017, under the National Sub-Program for Training, Grants for predoctoral contracts for doctoral training (BES-2013-064791), associated with projects CTQ2012-37039-C02-02 "*Metodologías para el diseño avanzado de procesos químicos sostenibles: optimización, intensificación; eficiencia energética y sostenibilidad"* and CTQ2016-77968-C3-2-P (AEI/FEDER, UE) "*Desarrollo de herramientas sistemáticas para el modelado y optimización de procesos más sostenibles con integración de aspectos económicos, ambientales y sociales*", by the Spanish Ministry of Economy, Industry, and Competitiveness.

The main purpose of Chapter 1 is to define the objectives and the structure followed in the development of this Thesis.

Universitat d'Alacant
Universidad de Alicante

1.1. Thesis Objectives

The main objective of this Thesis is based on the development of simulation and optimization tools in order to improve the energy efficiency of chemical processes, which reduces the environmental impact. Specifically, this Doctoral Thesis is composed of two main studies, which are the concrete objectives to be achieved:

* Study and evaluation of surrogate models to improve the simulation-based optimization of chemical processes.
* Development of new models for the simultaneous optimization and heat integration of chemical processes.

1.2. Thesis Structure

In terms of its structure, this Thesis is clearly divided into five chapters. The present Chapter 1 defines the main objectives and the structure of the Thesis.

The next chapter begins with an introduction, which presents an overview of the most important methods and tools used during the development of this Thesis. First, a general introduction to global energy problems and how to solve them introduces Chapter 2. A brief overview of the use of process simulators can be found below. Also, a short introduction to the different types of mathematical programming problems to be solved is presented. Additionally, a concise summary of surrogate models can be found. This introductory chapter also includes sections related to the most important aspects of heat integration and environmental impact assessment. Finally, Chapter 2 ends with the references used in this introductory chapter.

The results of the different studies are presented in Chapter 3, where the different papers that are part of this Thesis are shown. Four of these papers are published in international high-impact journals, and one more paper is awaiting publication (under review).

Below is presented Chapter 4, which summarizes the most relevant conclusions derived from the research.

Finally, the most important scientific contributions carried out during the research period are found in Chapter 5.

Universitat d'Alacant
Universidad de Alicante

1.2.1. Publications Included in this Thesis

This Doctoral Thesis is presented as a compendium of publications. The following papers are part of the present Thesis:

* **Publication 1**: Quirante N, Javaloyes J, Caballero JA. Rigorous Design of Distillation Columns Using Surrogate Models Based on Kriging Interpolation. *AIChE Journal* 2015; 61(7):2169-2187. http://onlinelibrary.wiley.com/doi/10.1002/aic.14798/full

* **Publication 2**: Quirante N, Caballero JA. Large Scale Optimization of a Sour Water Stripping Plant Using Surrogate Models. *Computers & Chemical Engineering* 2016; 92:143-162. http://doi.org/10.1016/j.compchemeng.2016.04.039

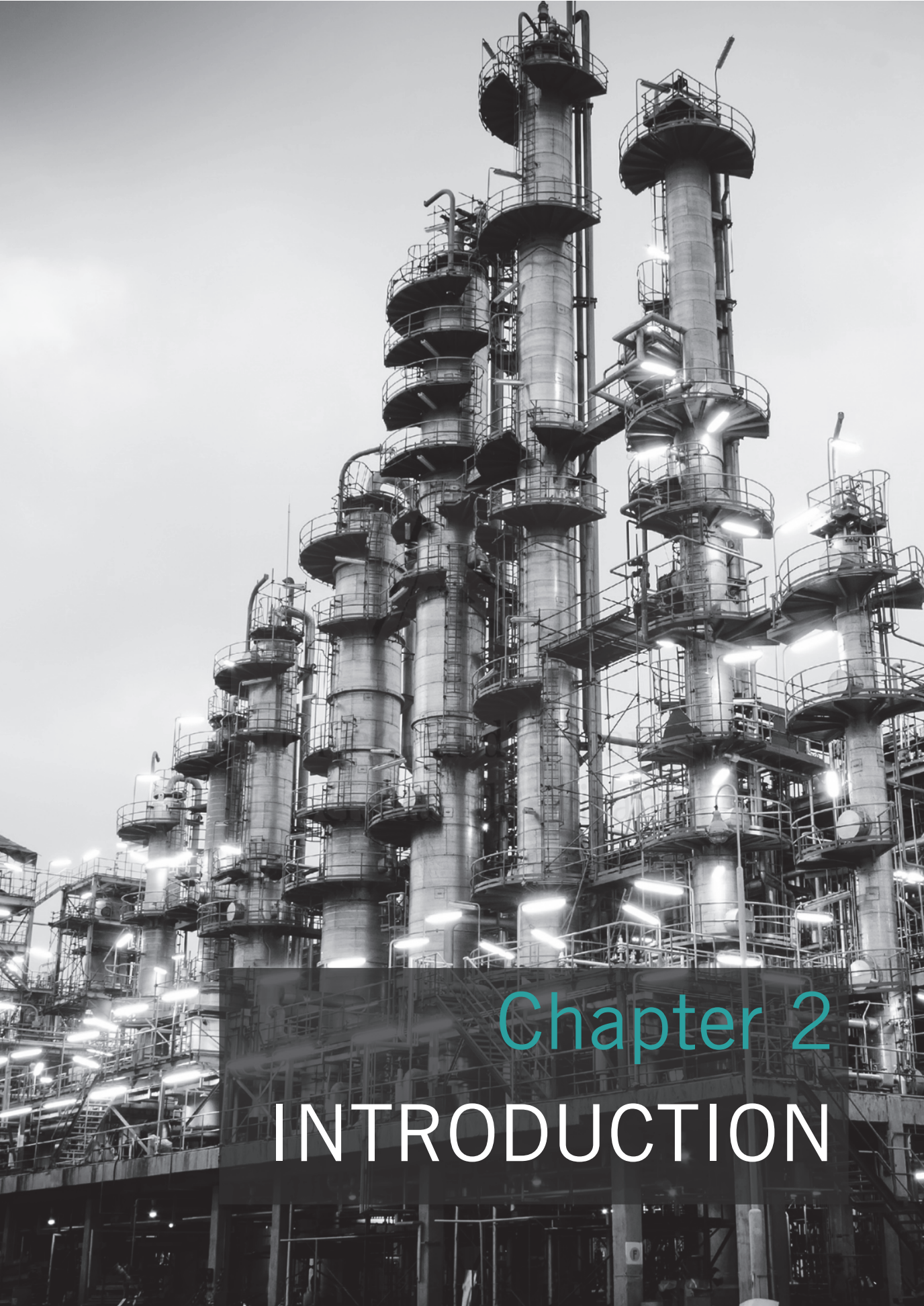
* **Publication 3**: Quirante N, Javaloyes J, Caballero JA. Hybrid Simulation-Equation Based Synthesis of Chemical Processes. Sent to: *Chemical Engineering Research & Design* [Under review].

* **Publication 4**: Quirante N, Caballero JA, Grossmann IE. A Novel Disjunctive Model for the Simultaneous Optimization and Heat Integration. *Computers & Chemical Engineering* 2017; 96:149-168. http://doi.org/10.1016/j.compchemeng.2016.10.002

* **Publication 5**: Quirante N, Grossmann IE, Caballero JA. Disjunctive Model for the Simultaneous Optimization and Heat Integration with Unclassified Streams and Area Estimation. *Computers & Chemical Engineering* 2018; 108:217-231. https://doi.org/10.1016/j.compchemeng.2017.09.013

Universitat d'Alacant
Universidad de Alicante

Universitat d'Alacant
Universidad de Alicante



Chapter 2
INTRODUCTION

Universitat d'Alacant
Universidad de Alicante

Chapter 2.
Introduction

During the development of this Thesis, different methods and tools have been used in order to achieve the objectives defined in Chapter 1.

The main goal of this chapter is to describe the basic concepts on which the different studies are based and to explain some aspects related to its implementation in this work.

2.1. Global Energy Demand

Reducing energy consumption is one of the most important aspects to take into account when designing efficient processes. The global energy consumption of the industrial sector represents approximately 22.2 % of the total energy consumption. Within this sector, the chemical industry accounts for around 27 %.[1] Therefore, the global energy consumption of the chemical industry is approximately 6 % of all the energy consumed in the world. Figure 2.1 illustrates the energy consumption by sector.

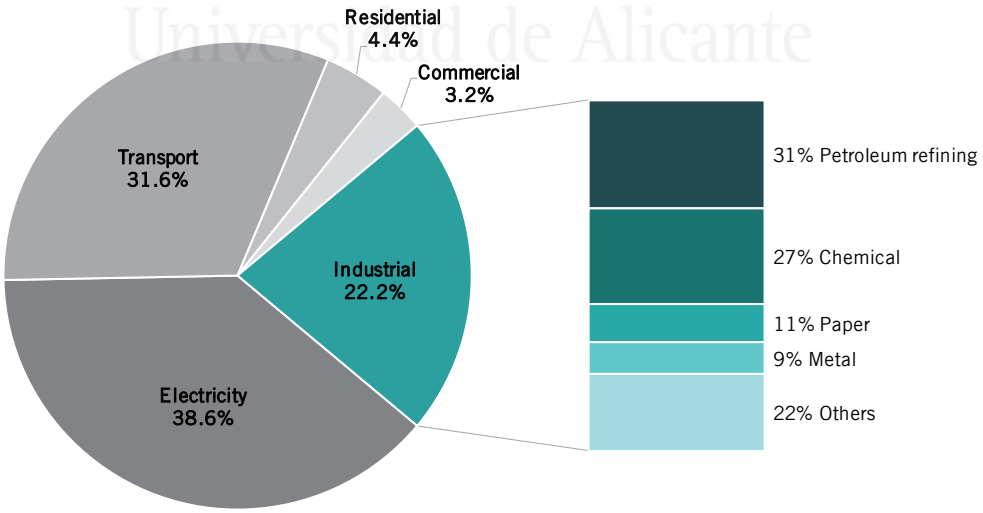


Figure 2.1. Energy consumption by sector (May 2016).[1]

Analyzing the chemical industry energy consumption, most of the chemical processes are involved in purifying components. Consequently, a large part of the energy consumed in many industrial sectors can be attributed to separation processes. Distillation is the most common separation process in the chemical industry. It has an extensive product history and is still reported as "the method of choice for many separations, and the method against which other options must be compared".[2,3] It is estimated that in the United States there are 40,000 distillation columns in operation, which handle more than 90 % of separations and purifications.[4]

In conclusion, it is estimated that distillation columns account for about 3 % of the total US energy consumption and recent reports show that this number has not been undergoing fundamental changes to date.[4-6] This fact together with the fact that the energy consumed is mainly generated by combustion of fossil fuels make that any improvement in the design of chemical processes could reduce the energy consumption, with the consequent reduction of the environmental impact.[7]

2.2. Process Simulators

The simulation, design, and optimization of chemical processes, which include several processing units interconnected by process streams, are part of the main activities of process engineering. The correct development of these tasks requires multiple subtasks, such as material and energy balances, equipment sizing, and calculation of the capital and operating costs, among others.

Universidad de Alicante

Historically, the performance of these tasks has been a complicated work due to the complexity of the models developed for the representation of chemical processes. Fortunately, computer development has made possible to study these processes. Nowadays, a large number of computer programs are able to carry out these tasks, especially, the software dedicated to the simulation of chemical processes.

Process simulation can be defined as the employment of computer software resources to develop mathematical models for the construction of an accurate and representative model of a chemical process in order to analyze, study, and understand its behavior during steady state plant operations and to evaluate other possible working conditions.[8] All these studies are possible because process simulators include an accurate description of physical properties of pure components and complex mixtures, rigorous models for unit operations, and numerical

techniques for solving large systems of algebraic and differential equations. Furthermore, through a process simulator, it is possible to obtain an extensive computer image of a running process, which is a valuable tool to understand the operation of a complex chemical plant and can serve to continuously improve the process or to develop new ones.

Within the process engineering, depending on the final objective, different types of problems can be solved with the aid of a process simulator. Even though the main objective of process simulators is the simulation, efforts have been made to include design, optimization, and synthesis capabilities (see Figure 2.2). This is also one of the objectives of this Thesis.

* **Simulation problem**: where the variables associated with the input streams for each unit of the process and the parameters of all the units should be specified. In other words, the simulator calculates the output streams according to the inputs and the parameters of that unit (the degrees of freedom are equal to zero).
* **Design problem**: where some of the design variables are unknown (e.g., the reactor volume, number of trays of a distillation column, the heat exchanger area, etc.). To solve this problem, we should add as many constraints to the output streams as degrees of freedom has the problem.
* **Optimization problem**: where the process efficiency is evaluated according to the input streams and the design variables in order to minimize its behavior based on economic, environmental, or social criteria. This type of problems can present equations of equality and inequality and the number of equations can be equal or greater than the number of variables.
* **Synthesis problem**: where an open structure with different operation and equipment alternatives for each of the system tasks is considered. Through this type of problems, we can determine the optimal configuration that minimizes or maximizes some key aspects of the problem, such as its economy or its environmental impact. The equations change according to the selected equipment, which makes solving synthesis problems a hard task.

Process simulators simplify the work of process engineers, allowing us to solve a wide variety of design, simulation, optimization, and synthesis problems.

Universitat d'Alacant
Universidad de Alicante

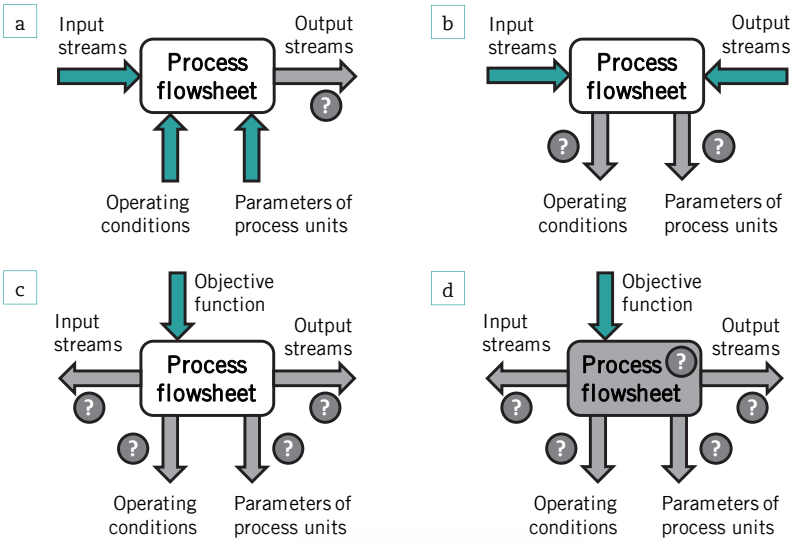


Figure 2.2. Process engineering problems: (a) Simulation. (b) Design. (c) Optimization. (d) Synthesis.

The use of process simulators can offer several advantages:

* Ease and simplicity in the complete study of all material and energy process streams.
* Investigate the formation and separation of byproducts and impurities.
* Evaluate the plant behavior when input streams or product demand change.
* Analyze how to reduce the environmental impact.
* Enhance process safety and control.
* Optimize the economic performance of the plant.

Universitat d'Alacant
Universidad de Alicante

2.2.1. Architecture of Process Simulators

The architecture of a process simulator is determined by the strategy of computation. Depending on how the process is described (modular or nonmodular) and depending on the method used to solve the resulting equations (sequential or simultaneous), process simulators can be classified into three types:

* Sequential-Modular simulators.
* Simultaneous-Nonmodular or Equation-Oriented simulators.
* Simultaneous-Modular simulators.

2.2.1.1. Sequential-Modular Simulators

The Sequential-Modular architecture is based on the concept of modularity, which extends the chemical engineering concept of unit operation to a "unit calculation" of the computer code (i.e., subroutine) responsible for the calculations of a single process unit.[9] The equations for each process unit (material and energy balances, equilibrium equations…) are grouped together in a subroutine or module. Consequently, each module calculates the output streams from the given input streams and parameters for that particular process unit, regardless of the source of input information or where the output information goes. In this way, the output streams become the input streams for the following unit and so on. This method is similar in principle to the traditional method of calculating unit operations by hand.

This calculation strategy is used by the most of the steady state simulators, as Aspen Plus, Aspen HYSYS, CHEMCAD, ProSim, Design II or SuperPro.

2.2.1.2. Equation-Oriented Simulators

In the Equation-Oriented approach, the complete model of the plant (flowsheet) is expressed in the form of one large dispersed system of nonlinear algebraic equations that is simultaneously solved for all the unknowns. This methodology is more flexible than the Sequential-Modular architecture. However, it requires more programming effort and is computationally expensive.

This strategy is followed by simulators like gPROMS, Abaqus, Ascend, VMGSim, Aspen Custom Modeler and Aspen Plus in EO mode.

2.2.1.3. Simultaneous-Modular Simulators

In the Simultaneous-Modular approach, the solution strategy is a combination of the Sequential-Modular and the Equation-Oriented methods. These flowsheeting programs use the traditional modular structure, but also solve a system of simultaneous equations that includes all the stream variables. The main difference here is the ease with which a system of equations can be solved compared to the Equation-Oriented method, in that the system of equations and the solution are simplified. Specifically, for each unit, an additional module is written, which approximately relates each output value by a linear combination of all input values.

Accordingly, rigorous models are used at the process unit level, which are solved sequentially, while linear models are used at flowsheet level and are solved globally.

2.2.2. Sequential-Modular Approach

The simulation of a steady state operation of a chemical plant can be represented by a system of nonlinear algebraic equations:

$$f(x)=0 \tag{2.1}$$

where f is a vector of functions and x is a vector of variables describing the input and output streams of a particular unit operation as well as the design parameters of that unit (e.g., reactor volume, reflux ratio for distillation columns, area of heat exchangers…).

The vector of functions f is derived from the conservation equations for mass, energy and momentum, physical and chemical equilibrium among species and phases, and additional constitutive equations that describe the rates of chemical transformation or transport of mass and energy. The system of equations described in Eq.(2.1) has a strong nonlinear character, particularly due to the relationship among physical properties and state variables. It is worth noting that estimation of physical properties can consume up to 90 % of the computation time.[10]

The system of equations generated during the simulation of a chemical plant may include thousands of equations and variables. The task of solving this problem can be especially difficult if a single model that includes the entire plant is considered. The strategy adopted by a Sequential-Modular process simulator is to write the balance equations for each unit separately. Therefore, Eq.(2.1) is rewritten as follows:

$$f_i(x)=0 \qquad i=1,\ 2,\ ...,\ n_u \tag{2.2}$$

where f_i is a subset of vector f with the functions associated with unit i, and n_u is the number of units in the plant.

Taking into account that the variables associated with the streams entering the plant and design variables for the units always have to be defined and that the information flow in the mathematical model is the same as in the flowsheet (the process simulator Aspen HYSYS is a remarkable exception where a bi-directional flow of information is possible), Eq.(2.2) can be rewritten as is shown in Eq.(2.3).

$$x_i^{out}=g\left\{x_i^{in}\right\} \qquad i=1,\ 2,\ ...,\ n_u \tag{2.3}$$

where x_i^{in} and x_i^{out} are subsets of the variables associated with the input and the output streams of unit *i*, respectively, and n_u is the number of unit operations in the flowsheet.

In this approach, the output stream for a given unit *i* becomes the input stream for a downstream unit and the calculation proceeds as before until all the units have been visited. Consequently, it is possible to compute an entire flowsheet without recycling streams by using sequentially Eq.(2.3). However, a process with recycle streams must be decomposed into one or several calculation sequences, and then an iterative strategy has to be adopted. The solution approach for flowsheets containing recycle streams is more complex and includes a topological analysis to determine the computational sequence and the corresponding tear streams. This strategy also requires iterative calculations for all units in the recycle loop, as the calculated value for the recycle stream may differ from the initial estimation.

2.2.2.1. Advantages of the Sequential-Modular Approach

The Sequential-Modular approach exhibits clear advantages for process flowsheeting over the Equation-Oriented approach, which explains why actually it is the dominant method of steady state simulation. Table 2.1 shows a list of advantages and disadvantages of sequential-modular process simulators.

Universitat d'Alacant
Universidad de Alicante

TABLE 2.1. Advantages and disadvantages of the sequential-modular approach.

Advantages	Disadvantages
* Robustness and reliability. * The flowsheet architecture is easily understood, since it closely follows the process flow diagram. * The unit blocks can be easily added to the flowsheet (or removed from the flowsheet). * The models of the different units can be prepared and tested separately leading to a library of unit modules. * Specific solution methods are developed for each process unit. * Easy control of convergence, both at the unit and flowsheet level.	* The simulators are well suited for process simulation, but not for dynamic simulation, optimization or design. * Present difficulties with flowsheets involving a large number of recycles. * Rigid direction of computation (usually, outputs from inputs).

2.2.3. Structure of a Process Simulator

The internal structure of a sequential-modular process simulator is divided into three clearly differentiated sections:

1. The central logic or general logic of the simulator.
2. The module responsible for physicochemical estimations.
3. The unit module library, i.e., each of the equipment modules.

The interconnections between the basic components of a typical simulation package are shown in Figure 2.3.

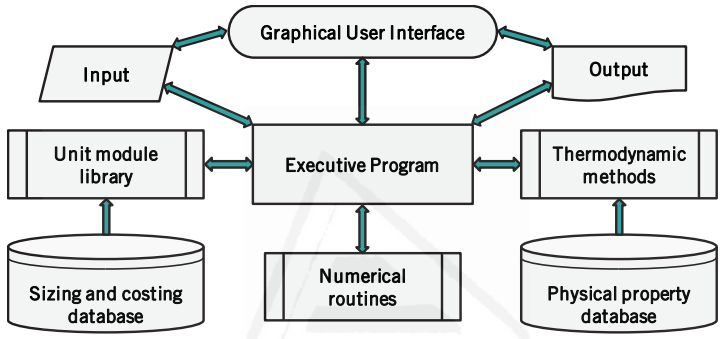


Figure 2.3. Components of sequential-modular process simulator software.

Each component shown in Figure 2.3 is described below:

* **Flowsheet builder (graphical user interface)**: provides the user an interface to generate the flowsheet of the plant under a graphical environment.
* **Executive program (flowsheet solver)**: the heart of any process simulator. It controls the sequence of the calculations and the overall convergence of the simulation.
* **Numerical routines**: a collection of mathematical methods for solving systems of linear, nonlinear, and differential equations.
* **Component data bank**: a database with the required parameters to calculate the physical properties needed.
* **Thermodynamic property prediction methods**: a set of thermodynamic methods to estimate the physical and thermodynamic property data.
* **Unit module library**: subroutines to perform energy and material balances and design calculations for the typical process engineering units.
* **Data output generator**: report the results of the simulation by tables and graphical displays.

2.2.3.1. General Logic of Process Simulators

The graphical user interface (GUI) is a key component of the process simulator. It should be characterized by flexibility and a user-friendly environment. The GUI communicates directly with the input/output data modules and the executive program. The input system is able to detect inconsistencies and errors in data entry in order to minimize the time employed in simulation tasks. In this way, inconsistent values within the problem context are immediately notified to the user through a validation system that emits error and warning messages.

The executive program is responsible for managing the various tasks that must be executed in order to perform the simulation of a given flowsheet. The flowsheet of a chemical process usually involves a large number of unit operations (reactors, separation units, heat exchangers…) connected by process streams (material and energy streams). The approach used to solve these flowsheets depends largely on its complexity. The simplest case to solve by a sequential-modular simulator is an acyclic system (without material streams or energy recycles), since the information occurs in a single direction. However, most of the chemical processes have several recycles, particularly those plants that are highly integrated. In that case, the problem cannot be solved directly, and an iterative procedure must be adopted. It becomes necessary to 'tear' a stream inside the loop and to introduce a convergence block. Initial values must be provided for the output streams of the convergence block. Then, the complete flowsheet can be calculated and the inputs to the convergence block compared with the outputs. If the convergence criteria are met, then the calculation stops. In other cases, a suitable numerical method may be used to provide new estimates for the tear stream and the iteration then continues.

Universitat d'Alacant
Universidad de Alicante

To implement these solution methods it is necessary to take into account a series of preliminary considerations, such as:

* Which unit operations must be solved simultaneously? (This is known as **partitioning**).
* In what order should we solve the grouped unit operations? (This is known as **precedence ordering**).
* Which streams should we tear in each group? (This is known as **tearing**).

There are several algorithms to perform these tasks, and most of them were developed in the late 1960s and 1970s.[11]

Methods for partitioning and precedence ordering are based on path-searching and are closely related to graph theory. These methods can be found in the works developed by Sargent and Westerberg,[12] Ledet and Himmelbrau,[13] Kehat and Shacham,[14] and Tarjan,[15] among others.[16-18]

Once the partition is complete, if we group all the units that form a partition (also called in graph theory as a strongly connected component) in a new theoretical node that group them, the resulting flowsheet must be acyclic, making it easy to obtain the order of precedence to solve the problem. The acyclic flowsheet can be formed by nodes that do not receive information from others (initial nodes), nodes that do not transfer information to others (terminal nodes), and the strongly connected component units (maximum cycles) that are obtained by means of one of the aforementioned algorithms.

The next issue concerns how to proceed to solve the partitions containing more than a single unit by choosing a set of tear streams for each. Several algorithms following different tear criteria have been proposed to find the tear streams. Process simulators such as Aspen Plus include the algorithm developed by Upadhye and Grens.[19] This method finds an optimal set of tear streams that yields the best convergence for fixed-point methods of solving the flowsheet. Other methods for finding the tear streams are the "Set Covering Problem" proposed by Pho and Lapidus[20] and the method proposed by Barkley and Motard,[21] among others.

Once the process simulator knows which units form a maximum cycle, the order of precedence and the tear stream corresponding to each maximum cycle, an iterative process is performed to solve the flowsheet. Flowsheeting programs employ methods that limit the number of iterations required to solve the flowsheet. The main methods described in the literature to solve the large sets of nonlinear algebraic equations that arise in flowsheeting problems are fixed-point methods, like direct substitution method, Wegstein's method,[22] or dominant Eigenvalue; Quasi Newton methods, like Broyden's method;[23] and if it is possible to get accurate derivative information, the Newton-Raphson method.

Finally, once the flowsheet is calculated, the process simulator must retain the results and display them in the appropriate places. The operating scheme of a sequential-modular simulator is illustrated in Figure 2.4.

Universitat d'Alacant
Universidad de Alicante

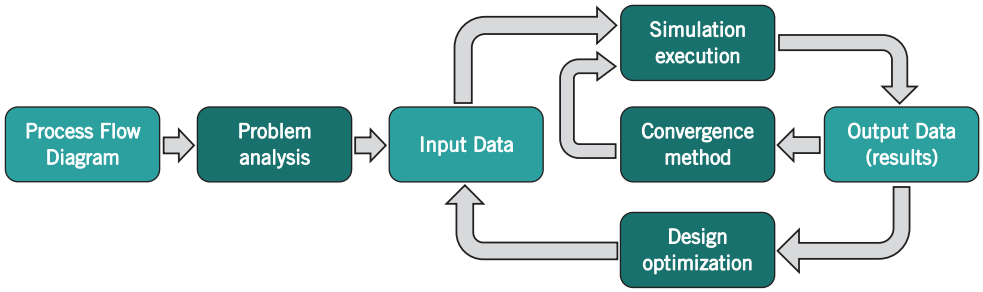


Figure 2.4. Operating scheme of a sequential-modular process simulator.

2.2.3.2. Physical Property Service Facilities

In a process simulation, the physical property service is an essential part of the software package, since the quality of process design ultimately depends on how the laws of physics and chemistry apply to the problem. A brief summary of the different property data required in a simulation of a chemical process is given in Table 2.2.

TABLE 2.2. Types of property data and their corresponding specific properties.

Property type	Specific properties
Phase equilibrium	Boiling and melting points, vapor pressure, fugacity and activity coefficients, solubility, BIPs.
PVT behavior	Density, molar volume, compressibility, critical properties, acentric factor.
Thermal properties	Heat capacity, latent heat, ionic conductivity, enthalpy, entropy.
Transport properties	Viscosity, thermal conductivity, diffusion coefficients.
Chemical reaction equilibrium	Equilibrium constants, association/dissociation constants, enthalpy of formation, enthalpy of combustion, heat of reaction, Gibbs free energy of formation, reaction rates.
Boundary properties	Surface tension.
Molecular properties	Virial coefficients, ion radius and volume, molecular weight, and dipole moment.
Safety characteristics	Flash point, explosion limits, toxicity, maximum working place concentration, lower and upper flammability limits.

The physical property service has to perform a series of tasks, but the most useful of these is to provide the user with a large data bank of components and allow data entry in order to create new components. It also has to continuously supply estimates for a number of different physical properties while the estimation is running, and provide the user with property values of interest during the calculation and/or once the simulation is finished.

Phase equilibrium represents one of the most important physical properties, since many chemical process simulations involve distillation, stripping, evaporation or liquid-liquid separation. The solution of the mass and heat balances for these unit operations requires predicting the separation of chemical mixtures between the liquid and vapor phases. To predict phase equilibria, a thermodynamic property method must be chosen from a set of thermodynamic methods implemented in the software. In Table 2.3 are listed the main thermodynamic property models available in commercial process simulators.

TABLE 2.3. Thermodynamic property models available in commercial simulators.

Model category	Model name	Guidelines
Equation of state (EOS)		
Ideal	Ideal gas law	For systems close to ideality. Light gases, similar hydrocarbons, petroleum pseudo-components.
Cubic equations of state	Peng-Robinson (PR)	For gas processing, refinery, and petrochemical processes. PR obtains better liquid densities than SRK.
	Soave-Redlich-Kwong (SRK)	For gas processing, refinery, and petrochemical processes. For polar systems, SRK makes a better prediction than PR.
Virial equations of state	Hayden-O'Connell	Predicts solvation of polar compounds and dimerization in the vapor phase, as occurs with mixtures containing carboxylic acids.
	Lee-Kesler-Plöcker	Hydrocarbon systems that include the common light gases. It can be used in gas processing, refinery, and petrochemical applications.
Steam	ASME steam tables	For water or steam (no parameter requirements).
Activity coefficient models		
BIP	NRTL	Recommended for highly nonideal chemical systems. It can be used for VLE and LLE applications.
	Wilson	Recommended for highly nonideal systems, especially alcohol water systems. It cannot be used for LLE calculations.
	van Laar	Describes nonideal liquid solutions with positive deviations from Raoult's law.
	UNIQUAC	For highly nonideal chemical systems, VLE and LLE applications.
Group contribution	UNIFAC	If there are no interaction parameters. For any combination of polar and nonpolar compounds.
Electrolyte models	Electrolyte NRTL	Aqueous electrolyte.

Universidad de Alicante

TABLE 2.3. Thermodynamic property models available in commercial simulators (continued).

Model category	Model name	Guidelines
Special models		
Vapor pressure models	API Sour	For correlating NH_3, CO_2 and H_2S volatilities from aqueous sour water systems (from 20 °C to 140 °C).
Liquid fugacity models	Chao-Seader	Pure component fugacity coefficients for liquids.
	Grayson-Streed	Extension of the Chao-Seader model. It is not recommended for systems containing hydrogen.
Specific models	Amine package	For systems with amines (MEA, DEA, TEA, MDEA, DGA, and DIPA).
	Glycol package	For the triethylene glycol (TEG)-water mixture.
	OLI electrolyte	For predicting the equilibrium properties of a chemical system including phase and reactions in a water solution.

2.2.3.3. Unit Module Library

Sequential-modular process simulators come with a large library of modules (unit operations). Unit models are encapsulated as procedures and can be considered as "black boxes" that perform a large number of subtasks and calculations. Modular process simulators are highly robust solving each unit operation with numerical methods tailored to the specific characteristics to each one of these units. These include from specific inside-out algorithms to "flash" a material stream, going through detailed methods for reactors and heat exchangers until complex methods for distillation. Some of the unit operations built into commercial flowsheeting programs are:

* **Column operations**: absorber, liquid-liquid extractor, reboiled/refluxed absorber, distillation, 3-phase distillation.
* **Electrolyte operations**: neutralizer, precipitator, crystallizer.
* **Heat transfer operations**: air cooler, cooler/heater, fired heater, heat exchanger.
* **Piping operations**: mixer/tee, pipe segment, valves.
* **Reactor operations**: Gibbs reactor, equilibrium reactor, conversion reactor, plug flow reactor, continuous-stirred tank reactor.
* **Rotating operations**: centrifugal compressor, centrifugal expander, pumps.
* **Solid separation operations**: baghouse filter, cyclone, hydrocyclone, rotary vacuum filter, simple solid separator.

Universitat d'Alacant
Universidad de Alicante

2.3. Synthesis and Process Design

Process synthesis is the step in design where the chemical engineer chooses the conditions, component parts, and how to interconnect them in order to create a new flowsheet.

The design and synthesis of processes originally began with the concept of "unit operation". According to Little's definition, unit operations are a variety of generic building blocks that can be assembled to compose processes for any of a large variety of applications.[24] Until the late 60's, this concept was the key in the design of processes. However, Rudd et al.[25] proposed the concept of "process synthesis" in 1973 and, since then, this topic has contributed to the development, design, and operation of chemical processes, which is currently considered as the basis for the design of processes.[26-30]

Traditionally, process synthesis is a systematic methodology to obtain the optimal configuration of a process, with the aim of maximizing the economic performance, maximizing the energy efficiency, or minimizing the environmental impact. The optimal design will be obtained through the combination of all the different possibilities (different types of feeds, unit operations...) in order to obtain the desired products, taking into account the requirements established and the regulations applied. A simplified scheme of a synthesis problem is shown in Figure 2.5.

Universitat d'Alacant
Universidad de Alicante

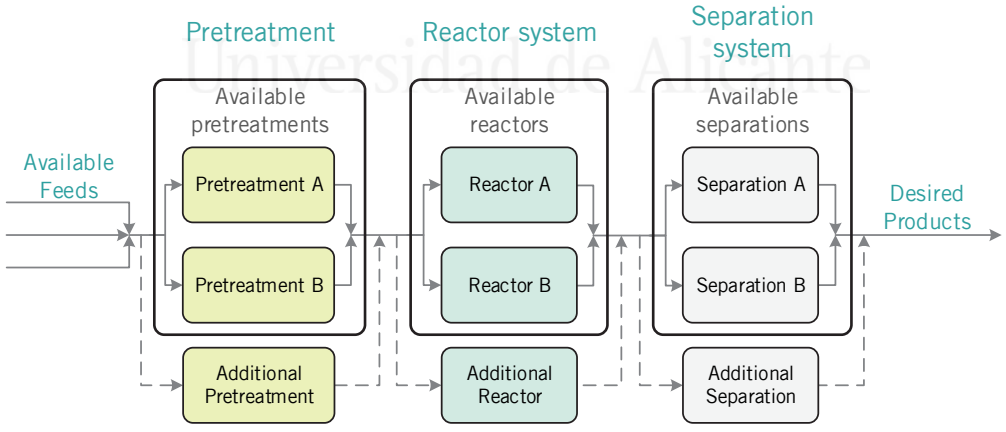


Figure 2.5. Simplified scheme of a synthesis problem.

2.3.1. Methodologies in the Synthesis of Processes

Since the 70's, several advances have been developed in the area of chemical process synthesis.[26,29] Methodologies for cost and energy minimization in the synthesis of processes can be classified into three groups: methods based on heuristics rules, methods based on mathematical programming, and hybrid methods (which combine both methods).[30]

2.3.1.1. Methods Based on Heuristic Rules

Heuristic methods are based on the experience accumulated over the years by researchers and engineers. The first systematic method based on heuristic rules was developed in 1971 by Siirola and Rudd.[31] The objective of this method was the development of separation sequences for multicomponent mixtures.

The main methodology within this field of study was developed during the 80's. Hierarchical heuristic methods divide the whole design problem into a series of decision levels, where the most suitable configuration is established successively by means of heuristic rules. The methodology proposed by Douglas[27,32] follows a strategy where decision-making is done from the top to the bottom, allowing us to obtain good flowsheets. However, the main disadvantage of this methodology is the ignorance of the interactions between the levels, due to its sequential nature, which does not guarantee the optimal design of a process.

This hierarchy can be represented symbolically by the layers of the "onion diagram" shown in Figure 2.6. The diagram emphasizes the sequential, or hierarchical, nature of process design.

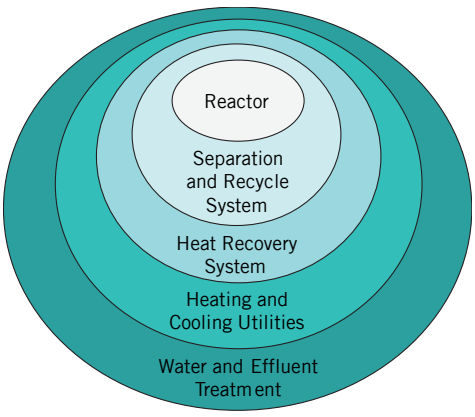


Figure 2.6. The onion diagram of process design.

Heuristic methods have been used in several applications, such as separation sequences,[33,34] process flowsheets,[31] waste reduction,[35] metallurgical process design,[36] or HEN synthesis.[37] Model levels are classified according to the type of decision taken.

Level 1: Processing Mode: Batch or Continuous

At this first level, it is decided whether the process will develop in continuous or discontinuous.

Continuous processes are designed to operate 24 hours a day, 7 days a week, throughout the year at almost constant conditions before the plant is shut down for maintenance. In contrast, batch processes are designed to operate intermittently, with some, or all, of the process units being frequently shut down and started up. During the bath operating cycle, the units are filled with material, perform their desired function for a specific period, are shut down, drained, and cleaned before the cycle is repeated.

Discontinuous processes are typical of the pharmaceutics, plastic, and food industry. They are selected if one of the following points is met:

* When the product has to be in the market in a reduced space of time.
* When the annual demand for a product is covered in a short period of time.
* When the process is in a preliminary phase exposed to some variations and improvements.
* When the product price is much higher than the manufacturing costs.
* When the product has a short life on the market before another product replaces it.

In practice, most industrial processes are continuous because they are cheaper with respect to the operating and capital costs, even in small-scale industrial processes.

Level 2: Input-Output Structure of the Flowsheet

At this level, feed and product streams involved in the overall process are studied. The input-output structure defines the overall material balance boundary of the flowsheet, therefore, byproducts and inerts should be considered. In addition, it is desired to recover more than 99 % of all valuable materials.

Level 3: Reactor System and Recycle Structure

At this point, the number of reactors employed in the process and the recycled streams are studied. In addition, the effect of the different operation conditions on each of the reactors is also studied. The operating conditions include the diluent effect of the inerts in the feed streams and the effect of the pressure on the chemical equilibrium reached in each reactor.

Level 4: Separation System

Generally, the unreacted feed is recovered and recycled to the reactors in order to minimize the cost of the raw materials. Additionally, products and byproducts are separated and extracted from the process. Possible means of reducing emissions by using alternative separation techniques or by rearranging existing ones are evaluated. The interactions of the separation system with the reactor and recycle systems are also considered.

This level is divided into two sublevels: recovery of liquid streams and recovery of vapor streams. The recovery process for vapor streams is more expensive than the separation for liquid streams. Liquid separation processes are commonly carried out in distillation columns.

Universitat d'Alacant
Universidad de Alicante

Level 5: Heat Exchanger Network

At the last level, the energy systems required by the process are evaluated. The main tool for use at this level is "The Pinch Analysis". It provides a powerful insight into process integration and is known for its use in heat exchanger network design.

In addition, it has other powerful applications to reduce the environmental impact of industrial processes.[38,39] For example, heat exchanger networks can reduce fuel firing and steam consumption, which in turn, reduces the production of greenhouse gases and the use of water treatment chemicals.

After maximizing heat recovery in the heat exchanger network, those heating and cooling duties not serviced by heat recovery must be provided by external utilities (i.e., furnace heating, use of steam, steam generation, cooling water, air-conditioning or refrigeration). Thus, utility selection and design follows the design of the heat recovery system.

Level 6: Total Site Integration

Maximizing heat recovery at the process level is a good step toward a better performance of industrial facilities. However, industrial processes are usually organized in larger sites and are served by a common utility system. The processes interact with each other via the utility system. There are significant benefits to be gained from considering the complete sites as integrated energy systems, evaluating and optimizing the energy generation, distribution, use, and recovery.[40,41] Therefore, total site integration has been applied to several chemical industrial sites.[42]

A typical chemical site (Figure 2.7) usually consists of a number of production and auxiliary processes. These processes require the supply of different utilities in order to carry out their functions. Such utilities are:

* **Process heating**. Steam is usually the preferred heating medium because of its high specific heat content in the form of latent heat and superheat. High-temperature processes, however, may require heating with hot oil or directly with flue gas in furnaces.
* **Process cooling**. This is performed by using cooling water, ambient air, or refrigerants.
* **Power demands**. These arise from the need for driving process equipment –such as pumps, compressors, mills, etc. and also lighting and electric heating (where high accuracy and responsiveness are required).–
* **Water supply and disposal**. It includes mainly the supply of freshwater –usually treated water to satisfy the water quality requirements– as well as the water treatment, recycling, and disposal.

The selection and design of the utilities is made more complex by the fact that the process will most likely operate within the context of a site comprising several different processes that are all connected to a common utility system. Thus, the design of the water and aqueous treatment system occurs at the last level.

Level 7: Water System Design

In the past, water has been assumed to be an unlimited low-cost resource. However, there is now increasing awareness of the danger to the environment caused by the overextraction of water.

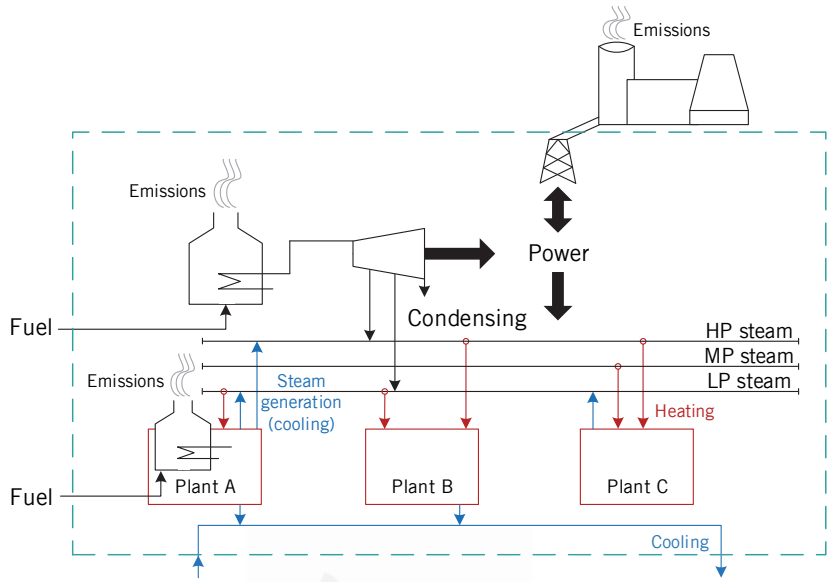


Figure 2.7. Typical total site industry.

Figure 2.8 shows a schematic of a simplified water system for a processing site. Raw water enters the process, it is used in various operations, it becomes contaminated and it is discharged to effluent. All of the effluents are mixed together with contaminated stormwater, and are treated centrally in a wastewater treatment system and discharged to the environment.

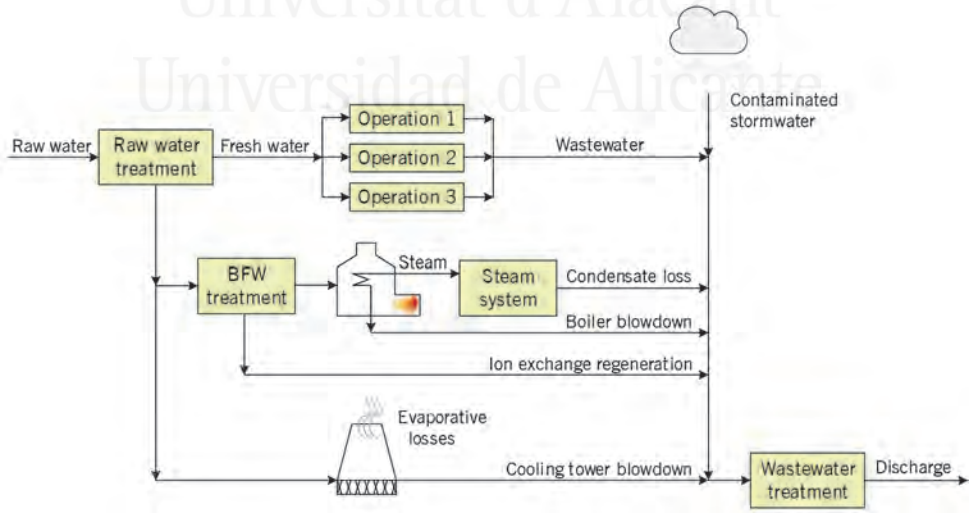


Figure 2.8. Typical water and effluent treatment system.

Water consumption and wastewater generation can be reduced through reuse, regeneration reuse and regeneration recycling (Figure 2.9).

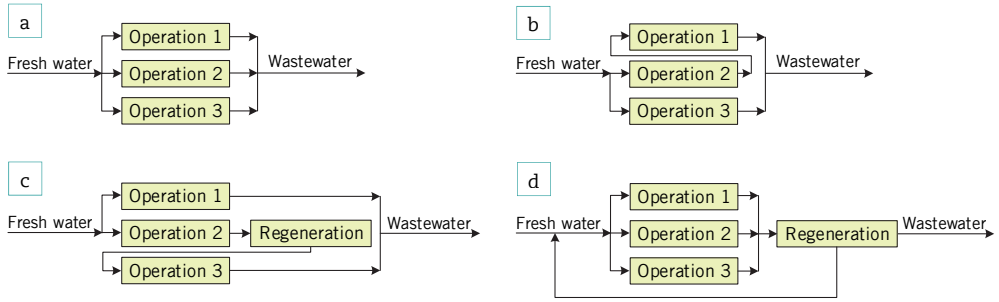


Figure 2.9. Water reuse and regeneration. (a) Fresh water used in all operations. (b) Water reuse. (c) Regeneration reuse. (d) Regeneration recycling.

The capital cost of wastewater treatment operations is generally proportional to the total flow of water and the operating cost generally increases with decreasing concentration for a given mass of contaminant to be removed. Thus, if two streams require different treatment operations, it makes no sense to mix them and treat the two streams in both treatment operations. This will increase both capital and operating costs.

Various primary, secondary and tertiary treatment processes are available to achieve the required discharge concentrations. Maximum water reuse can be identified from limiting water profiles. These identify the most contaminated water that is acceptable in an operation. A composite curve of the limiting water profiles can be used to target the minimum water flow rate. While this approach is adequate for simple problems, it has some severe limitations. A more mathematical approach using the optimization of a superstructure allows all of the complexities of multiple contaminants, constraints, enforced matches, capital and operating costs to be included. A review of this area can be found in Mann and Liu.[43]

Universitat d'Alacant
Universidad de Alicante

2.3.1.2. Methods Based on Mathematical Programming

The methodology based on mathematical programming is focused on considering, through mathematical equations, the relations between the different subsystems and the process economic balance. This approach uses optimization techniques to select the configuration and parameters of the processing system.[44-47] Superstructures containing alternative processing units and their interconnections are modeled as optimization problems involving continuous and discrete (binary) variables.

The mathematical programming approach consists of three major steps. The first is the development of a representation of alternatives from which the optimal solution is selected. The second is the formulation of a mathematical program (see Eq.(2.4)) that generally involves discrete and continuous variables for the selection of the configuration and the operating levels, respectively. The third is the solution of the optimization model from which the optimal solution is determined.

$$\begin{aligned} &\min\ z = f(x,y) \\ &s.t.\ \ h(x,y) = 0 \\ &\quad g(x,y) \le 0 \\ &\quad x \in X \subseteq \mathbb{R}^n \qquad y \in \{0,1\}^m \end{aligned} \tag{2.4}$$

where $f(x,y)$ is the objective function, $h(x,y)$ are the equations that describe the performance of the system and $g(x,y)$ are inequalities that define the specifications or constraints for feasible choices. The variables x are continuous and generally correspond to the state or design variables, while y are the discrete variables, which generally are restricted to take 0-1 values to define the selection of an item or an action.

Significant advances have taken place with this methodology, which offers the possibility of developing automated tools to support the exploration of alternatives and the optimization of chemical processes by design engineers.[48]

Closely related to the selection of the superstructure is the selection of the level of detail of the optimization model. A common misconception about the mathematical programming approach is that the models are always detailed and require a lot of information. This, however, is not necessarily true.

In general, mathematical programming models can be classified into three main classes:

* **Aggregated models**: These refer to high-level representations in which the design or synthesis problem is greatly simplified by an aspect or objective that tends to dominate the problem at hand (for example, the LP transshipment model for predicting the minimum utility cost and the minimum number of units in heat exchanger networks[49] and mass exchanger networks,[50] and the set of heat integration constraints based on the pinch location method[51,52]).
* **Shortcut models**: These refer to fairly detailed superstructures that involve cost optimization (investment and operating costs), but in which the

performance of the units is predicted with relatively simple nonlinear models in order to reduce the computational cost, and/or for exploiting the algebraic structure of the equations, especially for global optimization (for example, the synthesis models for heat exchanger networks,[53,54] distillation sequences,[55,56] and process flowsheets[57,58]).

* **Rigorous models**: These also rely on detailed superstructures, but involve rigorous and complex models for predicting the performance of the units. The area of synthesis of distillation sequences (ideal and nonideal) is perhaps the one that has received the most attention for developing rigorous models.[59-62]

2.3.1.3. Hybrid Methods

The methods described above have some advantages and disadvantages if we compare them.[63,64] However, these methods are considered to be competitive and complementary, because they are referred to different aspects of design. Therefore, the combination of the heuristic methods with the mathematical programming is the way followed in process synthesis. For example, Daichendt[65] presented a model that combined mathematical programming and hierarchical decomposition to design large-scale chemical processes. A hybrid methodology that combined mathematical programming and thermodynamic aspects to design multi-column distillation systems was also proposed.[66,67]

Several hybrid models have been developed and applied to different chemical processes, such as heat exchanger networks, distillation sequences, complex reactor networks, and water networks.[68-71]

2.4. Mathematical Programming for the Synthesis of Chemical Processes

The optimization of a chemical process is a complex procedure that can be described through a mathematical model. The mathematical models developed can include continuous and/or discrete variables, and are described by linear and/or nonlinear equations. Different mathematical formulations are established depending on the type of the equations and variables. These formulations are described below.

2.4.1. Linear Programming

A linear programming problem can be defined as the problem of minimizing or maximizing a linear function (objective function) subject to linear constraints. The constraints can be equalities or inequalities.[72]

Linear programming (LP) problems can be expressed by the following equation (Eq.(2.5)).

$$\begin{aligned} &\min\ (or\ \max)\ \ c^T x \\ &s.t.\ \ A x \le b \\ &\quad x \ge 0 \end{aligned} \tag{2.5}$$

where A is a rectangular matrix (m x n) of known coefficients, x is a column vector of variables to solve of dimension n, b is a column vector of known coefficients of dimension m, and c is a column vector of known coefficients of dimension n. The expression $c^T x$ is the objective function, and the constraints $A x \le b$ form the feasible region.

Linear programming problems can be solved by means of two different techniques: the simplex method and the interior-point method. The simplex method[72,73] solves linear programs by moving along the boundaries from one vertex (extreme point) to the next. The interior-point algorithm[74,75] improves a feasible interior solution point of the linear program by steps through the interior.

Linear programming problems vary from small to large scale. In fact, linear programming models can be very large in practice; some have many thousands of constraints and variables. They are used to solve planning, scheduling, and design problems.

2.4.2. Nonlinear Programming

A nonlinear programming (NLP) program is similar to an LP program, since it involves minimizing or maximizing an objective function subject to constraints. The difference is that a nonlinear program includes at least one nonlinear function, which could be the objective function or some or all of the constraints. Many real systems are inherently nonlinear, so it is important that the optimization algorithms are able to handle them.

Nonlinear programming problems can be generally expressed by the following equation (Eq.(2.6)).

$$\begin{aligned} &\min \ (or \ \max) \quad f(x) \\ &s.t. \ \ h(x) = 0 \\ &\qquad g(x) \le 0 \\ &\qquad x \in X \subseteq \mathbb{R}^n \end{aligned} \tag{2.6}$$

where x is an n vector of continuous variables, $f(x)$ refers to the objective function, $h(x)$ is the set of equality equations defining the process and $g(x)$ is a set of inequality constraint functions added to the problem.

Nonlinear programming problems can be convex or nonconvex (see Figure 2.10). A set of points (or a region) is defined as a convex set in the n-dimensional space if, for all pairs of points x_1 and x_2 in the set, the straight line segment joining them is also entirely in the set.

Figure 2.10. Example of (a) convex and (b) nonconvex sets.

An important feature of this type of problems is that global optimal solutions can be guaranteed for the case where the problem is convex, i.e., the objective function is convex and the constraints form a convex set (the inequality constraints are nonlinear convex functions, and the equalities are linear).

It is not possible to prove that a given algorithm will find the global optimum of a nonlinear programming problem unless the problem is convex. For nonconvex problems, however, many algorithms find at least a local optimum. Due to the nonconvex functions, the problem might be infeasible. Therefore, nonlinear programming problems are generally hard to solve.

The two major methods for solving NLP problems are: the successive quadratic programming (SQP) algorithm[76,77] and the reduced gradient method.[78,79] However, growing interest in efficient optimization methods has led to the development of interior-point or barrier methods for large-scale nonlinear programming. In particular, these methods provide an attractive alternative to active set strategies in handling problems with large numbers of inequality constraints.[80]

In the case of the SQP algorithm, the basic idea is to solve in each iteration a quadratic programming subproblem of the form:

$$\begin{aligned} \min\ & \nabla f\left(x^k\right)^T d+\frac{1}{2}d^T B^k d \\ s.t.\ & h\left(x^k\right)+\nabla h\left(x^k\right)^T d=0 \\ & g\left(x^k\right)+\nabla g\left(x^k\right)^T d\le 0 \end{aligned} \tag{2.7}$$

where x^k is the current point, B^k is the estimation of the Hessian matrix of the Lagrangian, and d is the predicted search direction.

An important point about the SQP algorithm is the fact that the quadratic programming with the exact Hessian matrix of the Lagrangian in B can be shown to be equivalent to applying Newton's method to the Karush-Kuhn-Tucker conditions. Thus, a fast convergence can be achieved with this algorithm.

On the other hand, in the reduced gradient method, the basic idea is to solve a sequence of subproblems with linearized constraints, where the subproblems are solved by variable elimination. Reduced gradient methods are very effective in solving large nonlinear optimization problems.

In addition, multiple solvers use the interior-point method for nonlinear programming, such as IPOPT and KNITRO. As a barrier method, IPOPT estimates solutions for a sequence of barrier problems. Then decreases the barrier parameter, and continues the solution of the next barrier problem from the approximate solution of the previous one.

Several works can be found in the literature concerning nonlinear programming.[81-83]

2.4.3. Mixed-Integer Linear Programming

A large number of optimization models described by linear equations can contain continuous variables and a subset of variables that are restricted to integer values (most commonly to 0-1). The general form of the Mixed-Integer Linear Programming (MILP) problems is given by Eq.(2.8).

$$\begin{aligned} &\min\ (or\ \max)\quad c^T x + d^T y \\ &s.t.\ \ A\,x + B\,y \le b \\ &\qquad x \in X \subseteq \mathbb{R}^n \\ &\qquad y \in \{0,1\}^m \end{aligned} \tag{2.8}$$

where A and B are rectangular matrices of known coefficients, x is an n vector of continuous variables, y corresponds to a vector of m binary variables, b is a vector of known coefficients of dimension m, and c and d are vectors.

The MILP problem is very useful for modeling a number of discrete decisions with the binary variables y. Typical examples are: multiple choice constraints, implication constraints, and disjunctive constraints.

A large number of optimization problems can be described by MILP model. Examples include the optimization of production operations including planning and scheduling, optimization of supply chains involving logistics and distribution, multiple period optimization,[84] and process synthesis using simplified models without nonlinearities.[85]

The standard method for solving MILP problems is the Branch and Bound (B&B) method.[86,87] For the MILP, we begin by first solving the relaxed LP problem. The problem stops when is solved, that is, when integer values are obtained for the binary variables. On the other hand, if no integer values are obtained, the basic idea is then to examine, using bounds, a subset of nodes in a binary tree to locate the global mixed-integer solution. In the tree, the binary variables are successively restricted one by one to 0-1 values at each node where the corresponding LP is solved. This can be done efficiently by updating the successive LPs through few dual simplex iterations. In Figure 2.11 is illustrated the branch and bound method.

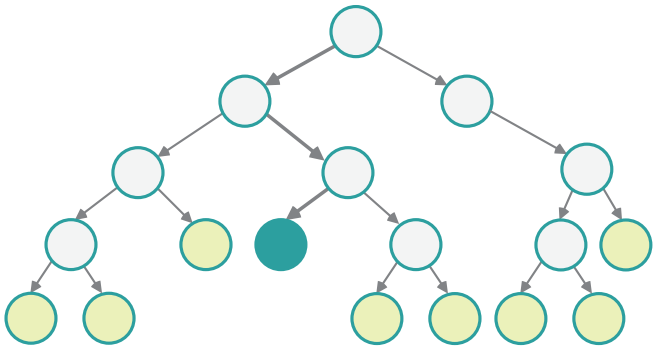


Figure 2.11. Branch and bound method.

However, B&B algorithms may not be able to effectively solve large problems due to the exponential number of subproblems that may have to be solved, particularly when the LP relaxation is poor. Therefore, MILP solvers have implemented more sophisticated versions denoted by Branch and Cut (B&C) algorithms, in which valid inequalities denoted by cutting planes are added to the linear relaxations in order to reduce the size of the feasible space without eliminating any feasible integer solution (see Figure 2.12).

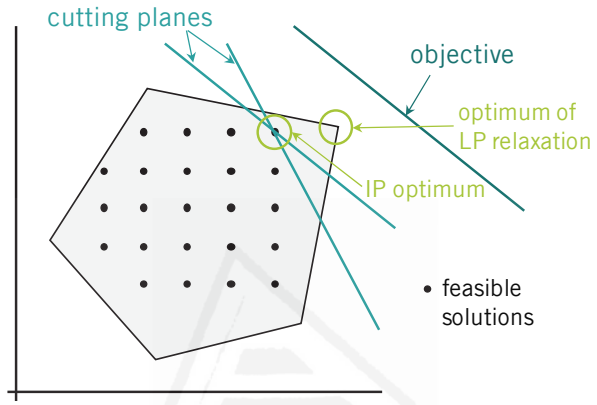


Figure 2.12. Cutting plane method.

There are seven general approaches to enhance the solution of a MILP model:

1. **Alternative formulations**. The goal is to develop a smaller and/or tighter model based on a different problem representation, different modeling techniques, or the (dis)aggregation of variables.
2. **Tightening and valid inequalities**. A tighter LP relaxation of a given model can be achieved via the addition of valid inequalities and by bounding/fixing variables, both of which can be performed before or during the B&B search.
3. **Extended reformulation**. They provide a tighter approximation of the convex hull of the integer feasible points, as do valid inequalities; however, reformulations typically rely on introducing new variables and replacing some starting constraints.[88]
4. **Decomposition methods**. The idea is to decompose the original problem into smaller subproblems that can be solved much faster. There are two types: methods that exploit the mathematical structure of the model, for example, Bender's decomposition[89] and Lagrangean relaxation/decomposition,[90] and

methods that exploit the physical structure of the problem, for example, decomposition into assignment and sequencing subproblems.

5. **Algorithmic enhancements**. They are typically improvements of the basic algorithm, including automatic generation of valid inequalities, advanced search strategies, preprocessing techniques using domain knowledge, and problem-specific heuristics.[91,92]
6. **Hybrid methods**. The idea is to combine MILP with another solution method that has complementary strengths. They are typically based on a decomposition of the original problem into two subproblems, one solved using MILP methods and one solved using a method like constraint programming.[93]
7. **Parallel computing**. The goal is to design methods that harness parallel computational resources, including enhancements that will allow the parallel implementation of the basic B&B algorithm.[94] Decomposition approaches are also likely to benefit from parallelization.

Real world problems tend to be large and complex. However, it is clear that in the recent years truly remarkable progress has been made in the solution of MILP problems.[95-98] The ability to solve more complex problems has been supported by:

a) Advances of computational resources in terms of speed and memory, leading to faster calculations.
b) Developments of new and improved algorithms and preprocessing techniques.
c) Modeling systems that speed up the definition of problems.

Some of the powerful commercial solvers are CPLEX,[99] Gurobi,[100] and XPRESS-MP.[101] Probably the solver CPLEX is currently the most used because it has available a set of different solvers, tools, and interfaces for different languages and software.

2.4.4. Mixed-Integer Nonlinear Programming

Mixed-Integer Nonlinear Programming (MINLP) programs involve nonlinear functions, and continuous and integer variables. An MINLP problem can be generally expressed by Eq.(2.9).

$$
\begin{aligned}
&\min\ (or\ \max)\quad c^T x + f(x)\\
&s.t.\ \ h(x) = 0\\
&\qquad g(x) \le 0\\
&\qquad A\,x = a\\
&\qquad B\,y + C\,x \le d\\
&\qquad E\,y \le e\\
&\qquad x \in X = \left\{ x \mid x \in \mathbb{R}^n,\ x^L \le x \le x^U \right\}\\
&\qquad y \in \{0,1\}^m
\end{aligned}
\tag{2.9}
$$

where f, h, and g are assumed to be convex and differentiable functions, x is an n vector of continuous variables, y corresponds to a vector of m binary variables, b is a vector of known coefficients of dimension m, and c and d are vectors of known coefficients of dimension n.

Many process systems engineering applications are modeled using MINLP: process synthesis,[102] planning and scheduling,[103] process control,[104] and molecular computing,[105] among others. MINLP programs can be solved with the branch and bound method. An important drawback of the branch and bound method for MINLP is that solving the NLP subproblems can be costly since they cannot be easily updated as in the case of the MILP. Therefore, in order to reduce the computational cost involved in solving many NLP subproblems, several techniques can be used, such as the Outer-Approximation method,[51,106] the Generalized Benders decomposition,[82,107] the extended cutting plane algorithm or the LP/NLP based Branch and Bound.

Universitat d'Alacant
Universidad de Alicante

2.4.4.1. Outer-Approximation

In the Outer-Approximation (OA) algorithm, the resolution of the problem is made through an iterative sequence of NLP subproblems and master MILP subproblems. NLP subproblems, with fixed values of the integer variables, provide the upper bound of the problem, while the master problems provide the lower bound. Algorithm convergence is achieved when both boundaries –lower and upper– differ by a value less than an established tolerance.

2.4.4.2. Generalized Benders Decomposition

Generalized Benders decomposition (GBD) is similar to OA method, but they differ in the linear master problem. In particular, the master problem of the GBD only

considers the discrete variables and the active inequalities. This fact makes the computational cost required for the resolution of the master problem is less than the time required when using OA. On the other hand, the lower bounds predicted in the relaxed problem are less than or equal to those obtained using OA. Additionally, this fact is responsible for the greater number of iterations required to solve the problem, compared to the OA method.

2.4.4.3. Extended Cutting Plane

The Extended Cutting Plane (ECP) method[108-110] follows a similar concept as the OA, but it avoids solving NLP subproblems. In this method, at a given solution of the master MILP, all the constraints are linearized. A subset of the most violated linearized constraints is then added to the master problem. Convergence is achieved when the maximum violation lies within the specified tolerance. The algorithm provides a non-decreasing lower bound after each iteration.

The main strength of the method is that it relies solely on the solution of MILPs, for which powerful algorithms are readily available. Similarly to the OA method, it solves the problem in one iteration if the equations are linear. There are two main downsides in the algorithm. The first one is that convergence can be slow.[111] The second one is that the algorithm does not provide an upper bound (or feasible solution) until it converges.

Universitat d'Alacant
Universidad de Alicante

2.4.4.4. LP/NLP Based Branch and Bound

The LP/NLP based branch and bound method[112] is a single tree search, that can be considered as a hybrid algorithm between B&B and OA. The algorithm is first initialized in a similar manner as the OA. When an integer solution is found, an NLP problem is solved and all open nodes in the search tree are updated.

This method, compared to the OA, generally reduces the number of evaluated nodes, but increases the number of NLPs solved. Recent work shows that the use of modern MILP solvers and advanced MILP tools greatly improve the performance of this method.[113] The extension of this method to GBD and ECP is straightforward.

2.4.5. Generalized Disjunctive Programming

Generalized Disjunctive Programming (GDP) is an alternative approach to the traditional algebraic mixed-integer programming formulation, which involves algebraic constraints, logic disjunctions, and logic propositions.[58,114-119]

Starting from the disjunctive programming proposed by Balas,[114] Raman and Grossmann[119] developed an alternative formulation for the process synthesis, which not only facilitates the development of the models by making the formulation process intuitive, but it also maintains in the model the underlying logic structure of the problem that can be exploited to find the solution more efficiently. Process Design[120] and Planning and Scheduling[97] are some of the areas where GDP formulations have shown to be successful.

The general structure of a GDP can be represented as shown in Eq.(2.10).

$$\begin{aligned} &\min\ Z = \sum_{k\in K} c_k + f(x) \\ &s.t.\ \ g(x) \le 0 \\ &\quad \bigvee_{i\in D_k} \begin{bmatrix} Y_{ik} \\ r_{ik}(x) \le 0 \\ c_k = \gamma_{ik} \end{bmatrix} \qquad k \in K \\ &\quad \Omega(Y) = True \\ &\quad x^{lo} \le x \le x^{up} \\ &\quad x \in \mathbb{R}^n,\ c_k \in \mathbb{R}^1,\ Y \in \{True, False\} \end{aligned} \tag{2.10}$$

where f is a function of the continuous variables x in the objective function, and g is the set of global constraints. The disjunctions $k \in K$ are composed of a number of terms $i \in D_k$ that are connected by the 'OR' operator. The main characteristic of the disjunction is that if Y_{ik} is true, then its constraints are enforced to be $r_{ik}(x) \le 0$ and $c_k = \gamma_{ik}$. Otherwise, they are ignored.

2.4.5.1. Solution Methods for Solving GDPs

Different methods have been developed in order to directly solve GDP problems. Solution methods for solving GDPs can be classified into two different categories: direct solution methods and reformulation methods. A simplified scheme of the different GDP solution alternatives is presented in Figure 2.13.

Universitat d'Alacant
Universidad de Alicante

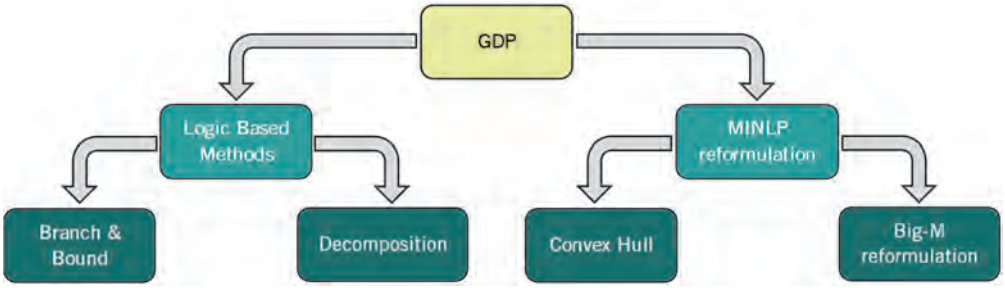


Figure 2.13. GDP solution alternatives.

Specifically, two solution methods are commonly used, the Branch and Bound method,[121] and the Logic-Based Outer-Approximation method.[58]

The basic idea in the Branch and Bound method is to directly branch on the constraints corresponding to particular terms in the disjunctions, while considering the convex hull of the remaining disjunctions. Although the tightness of the relaxation at each node is comparable with the one obtained when solving the convex hull reformulation with an MINLP solver, the size of the problems solved are smaller and the numerical robustness is improved.

For the case of Logic-Based Outer-Approximation methods, the main idea is to solve iteratively a master problem given by a linear GDP, which will give a lower bound of the solution and an NLP subproblem that will give an upper bound.

In order to take advantage of the existing MINLP solvers, GDPs are often reformulated as an MINLP by using either the Big-M reformulation[87] or the Convex hull formulation.[121] In these reformulations, the disjunctive constraints are expressed in terms of algebraic equations and the propositional logic is expressed in terms of linear equations.

The Big-M reformulation is shown in Eq.(2.11).

$$
\begin{aligned}
&\min\ Z = f(x) + \sum_{i\in D_k}\sum_{k\in K}\gamma_{ik}y_{ik} \\
&s.t.\ \ g(x)\le 0 \\
&\quad r_{ik}(x)\le M(1-y_{ik}) \qquad i\in D_k,\ k\in K \\
&\quad \sum_{i\in D_k} y_{ik} = 1 \qquad k\in K \\
&\quad Ay \ge a \\
&\quad x\in\mathbb{R}^n,\ y_{ik}\in\{0,1\}
\end{aligned}
\tag{2.11}
$$

where the variable y_{ik} has a one to one correspondence with the Boolean variable Y_{ik}. Note that when $y_{ik} = 0$ and the parameter M is sufficiently large, the associated constraint becomes redundant; otherwise, it is enforced. Also, $Ay \geq a$ is the reformulation of the logic constraints in the discrete space.

The Convex hull formulation yields as follows:

$$
\begin{aligned}
&\min\ Z = f(x) + \sum_{i \in D_k} \sum_{k \in K} \gamma_{ik} y_{ik} \\
&s.t.\ \ g(x) \leq 0 \\
&\quad x = \sum_{i \in D_k} v^{ik} && k \in K \\
&\quad y_{ik} r_{ik}\left(v^{ik} / y_{ik}\right) \leq 0 && i \in D_k,\ k \in K \\
&\quad 0 \leq v^{ik} \leq y_{ik} x^{up} && i \in D_k,\ k \in K \\
&\quad \sum_{i \in D_k} y_{ik} = 1 && k \in K \\
&\quad Ay \geq a \\
&\quad x \in \mathbb{R}^n,\ v^{ik} \in \mathbb{R}^n,\ y_{ik} \in \{0,1\}
\end{aligned}
\tag{2.12}
$$

Note that the size of the problem is increased by introducing a new set of disaggregated variables v^{ik} and new constraints. On the other hand, the Convex hull formulation is generally tighter than the Big-M reformulation when the discrete domain is relaxed.[122,123] This behavior is illustrated in Figure 2.14.

Figure 2.14. Solution to the relaxed problem using: (a) the Convex hull formulation, and (b) the Big-M reformulation.

2.5. Surrogate Models

The simulation-based optimization of chemical processes using commercial simulators, in many cases, is impractical. One reason is that the objective functions coming from computer simulations are often analytically intractable due to discontinuities, non-differentiabilities, and inherent numerical noise. Another

reason, and in many cases even more important, is the high computational time (in some cases, the simulation time can be as long as several hours, days, or even weeks per single design). Since conventional optimization algorithms require tens, hundreds or even thousands of objective function calls per run (depending on the number of design variables), the computational cost of the whole optimization process may not be acceptable. The feasible handling of these unmanageable functions can be accomplished using surrogate models.

2.5.1. Introduction to Surrogate-Based Methods

Surrogate-based optimization[124,125] has been suggested as an effective approach to the design with time-consuming computer models. The basic concept of surrogate-based optimization is that an iterative process involving the creation, optimization, and updating of a fast and analytically tractable surrogate model replaces the direct optimization of the computationally expensive model. The design obtained through the optimization of the surrogate model is verified by the evaluation of the high-fidelity model. Because most of the operations are performed on the surrogate model, surrogate-based optimization reduces the computational cost of the optimization process compared to the optimization of the high-fidelity model directly, without resorting to any surrogate.

For optimization problems, surrogate models are considered good approximation models of the simulation models, which are built from sampled data obtained by sampling the design space using appropriate design of experiments methodologies.[125] A key issue for building accurate surrogate models is based on the strategy followed to distribute the sample data.

Additionally, once the surrogate model is built, the accuracy of the metamodel must be evaluated.

2.5.2. Design of Experiments

To build a surrogate model, design of experiments (DoE)[126-128] methods are generally used to determine the locations of the sampling points in the design space. The objective of DoE is to maximize the amount of information obtained from a limited number of sampling points.[126]

When sampling, there is a clear tradeoff between the number of points used and the amount of information that can be extracted from these points. Samples are usually separated as much as possible in order to capture global trends in the design space.

There are different DoE methods commonly used, such as Latin Hypercube Sampling,[129,130] Orthogonal array design,[125] Monte Carlo Sampling,[126] or Hammersley.[131]

In this thesis, the 'maxmin' approach has been used with the general goal of maximizing the minimum distance between two sampling points.

2.5.2.1. Maxmin Approach

The 'maxmin' approach is the technique used to distribute of a set of points in a domain, where the minimum distance between two points is maximized.

The 'maxmin' problem is formulated as an NLP problem as follows (Eq.(2.13)): Consider the distribution of N points (i) in a D-dimensional space (d):

$$\begin{aligned} & x_{i,d} = d \text{ dimension component of point } i \\ & \text{maxmin } \left\{ distance_{i,j} \right\} \\ & distance_{i,j} = \sqrt{\sum_{d=1}^{D} \left(x_{i,d} - x_{j,d} \right)^2} \qquad \forall\, i,j \in Points \;/\; i \neq j \\ & 0 \leq x_{i,d} \leq 1 \end{aligned} \tag{2.13}$$

To avoid maximizing the result of the 'min' operation that introduces non-differentiabilities, the previous problem is reformulated by transferring the 'min' operation to the constraints and using the auxiliary variable α.

$$\begin{aligned} & \max \alpha \\ & s.t.\ \alpha \leq \sqrt{\sum_{d=1}^{D} \left(x_{i,d} - x_{j,d} \right)^2} \qquad \forall\, i,j \in Points \;/\; i \neq j \\ & \quad 0 \leq x_{i,d} \leq 1 \end{aligned} \tag{2.14}$$

Alternatively, it is possible to minimize the square of the distance without modifying the result, instead of minimizing the distance. The only modification proposed in Eq.(2.14) is to fix 2^D points to the extremes of the interval to avoid extrapolations in the optimization near the 'corners' of the hypercube.

The distribution of 40 sampling points using different techniques for a two-dimensional problem is illustrated in Figure 2.15.

Universitat d'Alacant
Universidad de Alicante

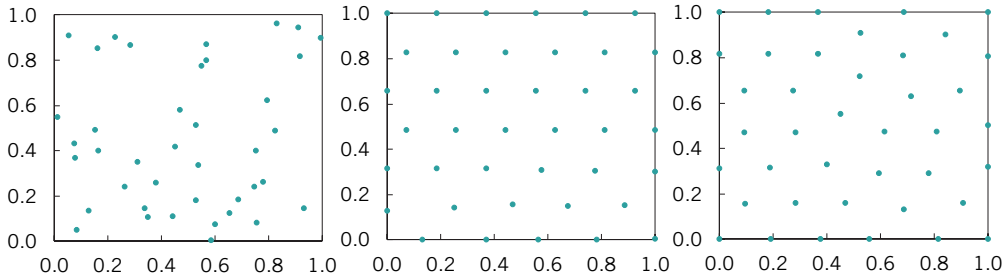


Figure 2.15. Distribution of 40 points: random distribution (left), uniform distribution (middle), 'maxmin' approach (right).

2.5.3. Surrogate Modeling Techniques

There are a large number of surrogate modeling techniques available in the literature. In this section, the most popular techniques are described.

2.5.3.1. Polynomial Regression Models

Polynomial regression[125] is a form of linear regression in which the relationship between the independent variable x and the dependent variable $f(x)$ is modeled as an nth degree polynomial in x.

The simplest examples of regression models are the first- and the second-order polynomial models (Eq.(2.15) and Eq.(2.16), respectively).

$$f(x) = \beta_0 + \sum_{j=1}^{n} \beta_j x_j \tag{2.15}$$

$$f(x) = \beta_0 + \sum_{j=1}^{n} \beta_j x_j + \sum_{i=1}^{n} \sum_{j \leq 1}^{n} \beta_{ij} x_i x_j \tag{2.16}$$

2.5.3.2. Multivariate Adaptive Regression Splines

Multivariate Adaptive Regression Splines (MARS) is an implementation of techniques for solving regression-type problems, with the main purpose of predicting the values of a continuous dependent variable from a set of independent variables.[132]

MARS is a nonparametric statistical method based on the strategy of dividing and conquering in which the training data sets are divided into separate piecewise linear segments (splines) of differing gradients (slope).

The general MARS model equation is given in Eq.(2.17).[133]

$$f(x) = \beta_0 + \sum_{j=1}^{n} \beta_j h_j(x) \tag{2.17}$$

where $f(x)$ is predicted as a function of the predictor variables x, β_0 and β_j are parameters, and $h_j(x)$ are basis functions.

2.5.3.3. Radial Basis Functions

Radial basis function approximation[134,135] exploits linear combinations of n radially symmetric functions φ.

$$f(x) = \sum_{i=1}^{n} \omega_i \varphi(\|x - x_i\|) + p(x) \tag{2.18}$$

where ω_i are the ith unknown weight coefficient, $\varphi(\|x - x_i\|)$ are the basis functions that depend on the Euclidean distance between the observed point x_i and the untried point x, and $p(x)$ is the global trend function which is taken as a constant.

Universitat d'Alacant
Universidad de Alicante

2.5.3.4. Kriging

Kriging[136] is an interpolation method that takes into account the data observed at all sampling points. Kriging provides a statistical prediction of an unknown function by minimizing its mean squared error. It can be equivalent to any order of polynomials and, therefore, it is very suitable for a highly nonlinear function with multiple extremes.

The Kriging fitting is composed of a polynomial expression and a deviation from that polynomial.

$$y(x) = f(x) + Z(x) \tag{2.19}$$

where $Z(x)$ is a stochastic Gaussian process that represents the uncertainty over the mean of $y(x)$ with expected value zero. The covariance for two points x_i and x_j is

given by a scale factor σ^2 that can be fitted to the data and by a spatial correlation function $R(x_i,x_j)$. The choice of the spatial correlation function will determine how the model fits the data. There are many choices for the spatial correlation function, but the most common one used in Kriging models is the exponential function given by Eq.(2.20).[137]

$$R\left(x_i,x_j\right)=\exp\left(-\sum_{l=1}^{d}\theta_l\left(x_{i,l}-x_{j,l}\right)^{P_l}\right)=\prod_{l=1}^{d}\exp\left(-\theta_l\left(x_{i,l}-x_{j,l}\right)^{P_l}\right) \tag{2.20}$$

where $\theta_l \geq 0$ and $0 \leq P_l \leq 2$ are adjustable parameters.

The influence of the sampled data points on the point to be predicted becomes weaker as their distance increases. The value of θ_l indicates how fast the correlation goes to zero as we move in an lth coordinate direction. The parameter P_l determines the smoothness of the function which is usually fixed to 2 (Gaussian Kriging) in all the coordinates.

An important advantage of Kriging models is that the degree of the polynomial $f(x)$ does not significantly affect the fit quality because $Z(x)$ captures the most significant behavior of the function.[138] A constant term μ (Ordinary Kriging) is enough for a good prediction.[139,140]

To estimate the values of the parameters σ^2, θ_l, P_l, and μ, we maximize the logarithm of the likelihood function of the obtained data y.

$$\log\left(L\right)=-\frac{n}{2}\ln\left(2\pi\right)-\frac{n}{2}\ln\left(\sigma^2\right)-\frac{n}{2}\ln\left(\left|R\right|\right)-\left(\frac{-\left(y-1\mu\right)^T R^{-1}\left(y-1\mu\right)}{2\sigma^2}\right) \tag{2.21}$$

where y is the vector of obtained responses (n x 1), **1** is a vector of ones (n x 1) and n is the number of sampled points.

Differentiating Eq.(2.21) with respect to μ and σ^2 and equating it to zero, the optimal values for μ and σ^2 are obtained after some algebra.

$$\hat{\mu}=\frac{1^T R^{-1} y}{1^T R^{-1} 1} \tag{2.22}$$

$$\hat{\sigma}^2=\frac{\left(y-1\hat{\mu}\right)^T R^{-1}\left(y-1\hat{\mu}\right)}{n} \tag{2.23}$$

To interpolate a new point x_{new}, we have to add the point (x_{new}, y_{new}) to the data and compute the augmented likelihood function keeping all the parameters at the previously calculated values. With all the parameters constant, the log-likelihood function is only a function of y_{new}. Consequently, the predicted value for y_{new} will be the value that maximizes the augmented likelihood function. The final predictor of the Kriging method is given by Eq.(2.24).

$$\hat{y}(x_{new}) = \hat{\mu} + r^T R^{-1}\left(y - 1\hat{\mu}\right) \tag{2.24}$$

where r (n x 1) is the vector of correlations $R(x_{new}, x_i)$ between the sample design points and the point to be correlated.

Kriging has proven to be useful in a wide variety of fields.[134,140,141] The main reason is that Kriging metamodels combine computational efficiency with relatively small sampling data. Due to these characteristics, the Kriging algorithm has been selected to build the metamodels in the studies carried out in this Thesis.

2.5.3.5. Artificial Neural Networks

Artificial Neural Networks (ANNs) model is based on a large collection of simple neural units (artificial neurons), loosely analogous to the observed behavior of a biological brain's axons.

The basic structure of a neural network[142] is the neuron. A neuron performs an affine transformation followed by a nonlinear operation (see Figure 2.16a). If the inputs to a neuron are denoted as $x_1, \ldots, x_n$, the neuron output y is computed as shown in Eq.(2.25).

$$f(x) = \frac{1}{1 + \exp(-\eta / T)} \tag{2.25}$$

where $\eta = w_1 x_1 + \ldots + w_n x_n + \gamma$, with $w_1, \ldots, w_n$ being regression coefficients. γ is the bias value of a neuron, and T is a user-defined (slope) parameter.

The most common neural network architecture is the multilayer feed-forward network (see Figure 2.16b).

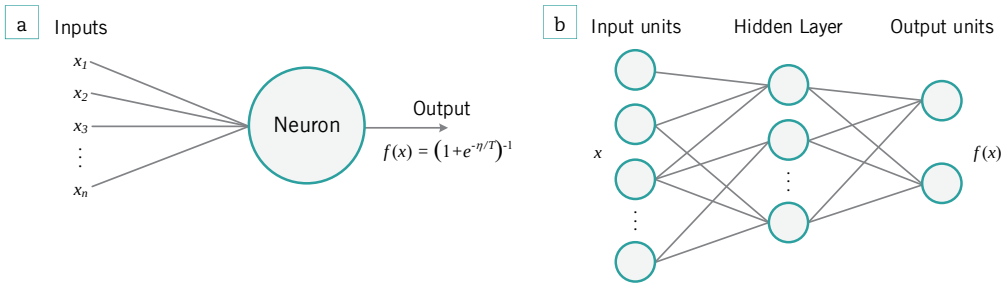


Figure 2.16. Neural networks: (a) Neuron basic structure. (b) Two-layer feed-forward neural network architecture.

2.5.4. Model Validation

The last step in the construction of the surrogate model is the validation stage. The approach followed to validate the accuracy of the model is the "cross-validation".[125,139]

Cross-validation is an extremely popular methodology to verify the predictive capabilities of a model generated from a set of samples. In the cross-validation approach, a point is removed and its value is re-evaluated with the rest of the points. This procedure is repeated with all the sampling points.

Additionally, the model allows us to estimate the prediction error with all the error measures obtained in this process.

Universitat d'Alacant
Universidad de Alicante

2.6. Heat Integration

In industrial processes, the need to heat or cool down fluids frequently appears. When a process has a certain number of process streams that should be heated or cooled, the idea of taking advantage of the process streams to heat other streams arises, attempting to minimize heat and cold utilities and, at the same time, minimizing capital and operating costs. The configuration of the process streams exchanging heat and the configuration of which equipment should exchange heat is known as heat exchanger network.

Due to its importance, the synthesis of heat exchanger networks is one of the most studied areas of process synthesis and, consequently, it presents a greater degree of development.

In the following sections, the most important aspects of the heat integration will be developed.

2.6.1. Fundamentals of Pinch Analysis

The pinch analysis is a systematic technique to analyze the heat flow through an industrial process based on fundamental thermodynamics.[143] The Second Law of Thermodynamics requires that the heat flows naturally from hot to cold objects. This key concept is embodied in the hot and cold composite curves (Figure 2.17), which represents the overall heat released and heat demanded of a process as a function of temperature.

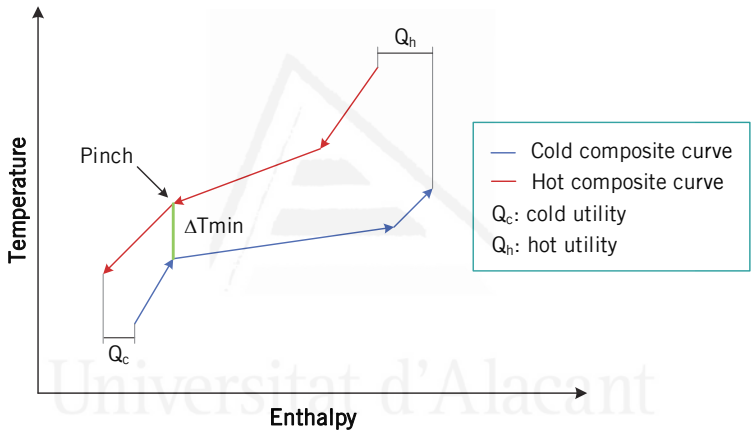


Figure 2.17. Example of composite curves.

The hot composite curve represents the sum of all the heat sources (hot streams) within the process in terms of heat load and temperature level. Similarly, the cold composite curve represents the sum of all the heat sinks (cold streams) within the process. When these curves are placed together on a single temperature-enthalpy diagram (as in Figure 2.17), it is evident that heat can be recovered within the process wherever there is a portion of the hot composite curve above a portion of the cold composite curve; that is, heat can flow from a higher temperature part of the process to a lower temperature part. To keep the size of the heat recovery equipment reasonable, the temperature difference (approach) must be larger than a defined minimum allowable temperature approach, ΔT_{min}.

Most of the processes display a pinch –a region where the vertical separation of the curves approaches and eventually reaches the ΔT_{min} value–. The pinch divides the process into two different regions:

* Above the pinch, some heat integration is possible (where the hot composite curve sits above the cold composite curve), but there is a net heat deficit and an external utility heat source (Q_h) is required.
* Below the pinch, some heat integration is possible (where the hot composite curve sits above the cold composite curve), but there is a net heat surplus and an external utility heat sink (Q_c) is required.

The distinction between the net heat source and the net heat sink regions is a key feature of the pinch approach, and it forms the basis for the pinch principle: "Do not transfer heat across the pinch".

Pinch analysis is commonly used to improve heat integration schemes in new process designs, to reduce either capital cost or energy demand, or both.[144]

2.6.2. Heat Exchanger Networks

The heat exchanger network synthesis problem is one of the most studied problems in process synthesis and the development of cost-efficient heat exchanger networks has proven to be a challenging task. In the synthesis process, decisions about the level of heat recovery, as well as the network structure, size, and type of heat exchangers are made. A network resulting in the most economical overall solution when considering both utility costs and investment costs for all units of the energy recovery network is targeted. During the last three decades, a large number of methods have been proposed for the design task. These methods are thoroughly presented in the reviews by Gundersen and Naess[145] and Furman and Sahinidis.[146]

The general objective is to find out the structure of a heat exchanger network, which facilitates the task of cooling a given set of hot streams and heating a given set of cold streams to the desired levels with a minimum of investment and operating costs. Basically, there are two types of approaches to solving the synthesis problem of heat exchangers network:

* Sequential methods.
* Simultaneous methods.

2.6.2.1. Sequential Methods

The sequential methods attempt to reduce the computational complexity of the problem by decomposing the main problem into subproblems, which are then solved sequentially.[49,147-150] The subproblems are solved with the aim of obtaining:

a) The minimum utility cost.
b) The minimum number of exchanger units.
c) The minimum capital cost of the network.

The sequential synthesis does not guarantee the optimal design of a heat exchanger network with the minimum total cost, but it guarantees a valid heat exchanger network.

2.6.2.2. Simultaneous Methods

The simultaneous methods solve the problem without any decomposition. They make use of superstructures consisting of a variety of structural possibilities and optimize them to remove redundant features. The tradeoff between capital cost (fixed costs of heat exchanger units and area costs) and operating cost (hot and cold utility costs) is considered in a single rigorous optimization framework in the simultaneous design approach for heat exchanger networks.[53,151-154]

The main drawback of the simultaneous heat exchanger network design approaches is the difficulty in solving these large size models.

Universitat d'Alacant
Universidad de Alicante

2.7. Environmental Impact Assessment

Environmental impact assessment is a key aspect of many large-scale planning applications. It is a technique used to understand the potential environmental impacts associated with the manufacture of a product or an activity.

The most commonly used technique to assess environmental impacts is the Life Cycle Assessment (LCA). This technique takes into account environmental aspects and potential impacts associated with all the stages of a product's life from cradle to grave (i.e., supply of raw materials for the production of a product, the manufacturing of intermediates, and the final product, including packaging, transportation, distribution, use of the product and disposal of the product after use).[155]

Figure 2.18 shows all the stages of the life cycle of a product.

Figure 2.18. Life cycle of a product (from cradle to grave).

Specifically, an LCA can help to evaluate the potential impacts by:

* Compiling an inventory of relevant energy and material inputs and environmental releases.
* Evaluating the potential environmental impacts associated with identified inputs and releases.
* Interpreting the results to help make a more informed decision about the human health and environmental impacts of products, processes, and activities.

The procedures of the Life Cycle Assessment are part of the ISO 14000 environmental management standards: in ISO 14040:2006[156] and ISO 14044:2006.[157]

2.7.1. Phases of an LCA

According to the ISO 14040 and 14044 standards, a Life Cycle Assessment is carried out in four phases (see Figure 2.19):

1. Goal and scope definition.
2. Life Cycle Inventory (LCI).
3. Life Cycle Impact Assessment (LCIA).
4. Interpretation.

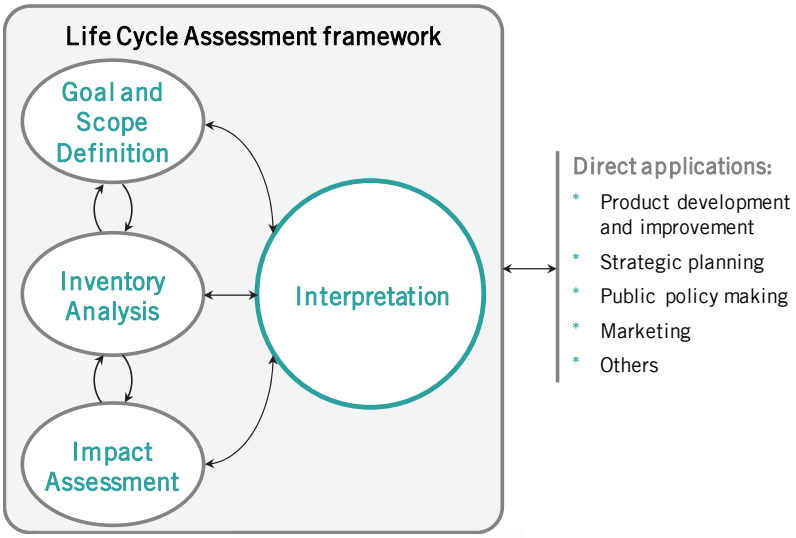


Figure 2.19. Phases of a life cycle assessment.

2.7.1.1. Goal and Scope Definition

The LCA starts with an explicit statement of the goal and scope of the study. Following the ISO standards, the goal and scope of an LCA should be clearly defined and consistent with the intended application. Some technical details that can be considered are:

* The functional unit, which defines what precisely is being studied and quantifies the service delivered by the product system, providing a reference to which the inputs and outputs can be related. Additionally, the functional unit is an important basis that enables alternative goods, or services, to be compared and analyzed.
* The system boundaries.
* Any assumptions and limitations.
* The allocation methods used to partition the environmental load of a process when several products or functions share the same process.
* The impact categories chosen.

The scoping determines which processes will be included, which environmental concerns will be considered, what economic or social good is provided by the products or services in question, resolves any technical issues and defines the audience for the LCA.

Universitat d'Alacant
Universidad de Alicante

2.7.1.2. Life Cycle Inventory (LCI)

The inventory provides information about all environmental inputs and outputs from the product system involved in the Life Cycle Assessment. This involves modeling of the product system, data collection, and verification of data for inputs and outputs for all parts of the product system. Inputs include: inputs of water, raw materials, energy, and chemicals. Outputs include: air emissions, releases to water, and solid waste.

2.7.1.3. Life Cycle Impact Assessment (LCIA)

The aim of this phase is the assessment of the significance of potential environmental impacts based on the LCI results. The Life Cycle Impact Assessment (LCIA) should include the following elements:

* Selection of impact categories, category indicators, and characterization models.
* Classification stage, where the inventory parameters are sorted and assigned to specific impact categories.
* Impact measurement, where the categorized LCI flows are characterized, using one of many possible LCIA methodologies, into common equivalence units that are then summed to provide an overall impact category total.

Universitat d'Alacant
Universidad de Alicante

2.7.1.4. Interpretation

Life cycle interpretation is a systematic technique to identify, quantify, check, and evaluate information from the results of the LCI and/or the LCIA. The results from the inventory analysis and impact assessment are summarized during the interpretation phase.

The result of the interpretation phase is a set of conclusions and recommendations for the study. This phase should include:

* Identification of significant issues based on the results of the LCI and LCIA of a Life Cycle Assessment.
* Evaluation of the study considering completeness, sensitivity, and consistency checks.
* Conclusions, limitations, and recommendations.

2.7.2. ReCiPe Indicator

The indicator used in this Thesis for Life Cycle Impact Assessment (LCIA) has been the ReCiPe 2008.

ReCiPe 2008 comprises two sets of impact categories with associated sets of characterization factors.[158] Eighteen impact categories are addressed at the midpoint level:

* Climate change (CC).
* Ozone depletion (OD).
* Terrestrial acidification (TA).
* Freshwater eutrophication (FE).
* Marine eutrophication (ME).
* Human toxicity (HT).
* Photochemical oxidant formation (POF).
* Particulate matter formation (PMF).
* Terrestrial ecotoxicity (TET).
* Freshwater ecotoxicity (FET).
* Marine ecotoxicity (MET).
* Ionizing radiation (IR).
* Agricultural land occupation (ALO).
* Urban land occupation (ULO).
* Natural land transformation (NLT).
* Water depletion (WD).
* Mineral resource depletion (MRD).
* Fossil fuel depletion (FD).

At the endpoint level, most of these midpoint impact categories are converted and aggregated into the following three endpoint categories:

* Damage to human health (HH).
* Damage to ecosystem diversity (ED).
* Damage to resource availability (RA).

Figure 2.20 illustrates the relations between the LCI parameter, the midpoint indicator, and the endpoint indicator.

Universitat d'Alacant
Universidad de Alicante

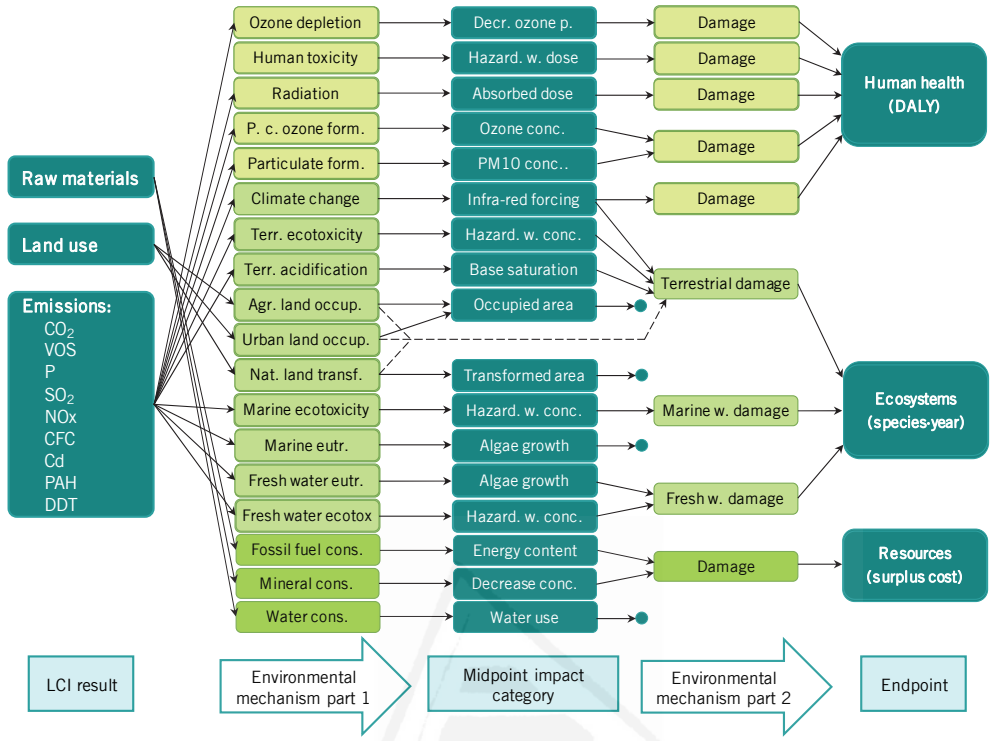


Figure 2.20. Relationship between LCI parameters (left), midpoint indicator (middle), and endpoint indicator (right) in ReCiPe 2008.

The method follows three versions using the Tompson's theory of cultural perspectives.[159] According to this theory, consistent sets of subjective choices on time horizon, assumed manageability, etc. can be grouped around three perspectives:

* Individualist (I): short-term perspective.
* Hierarchist (H): balance between short and long-term perspective.
* Egalitarian (E): very long-term perspective.

2.8. References

[1] International Energy Agency. *World Energy Outlook 2016*. Paris, France; 2016.

[2] Kister HZ. Are Column Malfunctions Becoming Extinct –or Will They Persists in the 21st Century? *Chem Eng Res Des* 1997;75(6):563-589.

[3] Kunesh JG, Kister HZ, Lockett MJ, Fair JR. Distillation: Still Towering Over Other Options. *Chem Eng Prog* 1995;91(10):43-54.

[4] Humphrey JL. Separation Processes: Playing a Critical Role. *Chem Eng Prog* 1995; 91(10): 31-41.

[5] Engelien HK, Skogestad S. Selecting Appropriate Control Variables for a Heat-Integrated Distillation System with Prefractionator. *Comput Chem Eng* 2004; 28(5):683-691.

[6] Mix TW, Dueck JS, Weinbeerg M. Energy Conservation in Distillation. *Chem Eng Prog* 1978; 74:1949-1955.

[7] Soave G, Feliu JA. Saving Energy in Distillation Towers by Feed Splitting. *Appl Thermal Eng* 2002; 22(8):889-896.

[8] Diwekar UM. Green Process Design, Industrial Ecology, and Sustainability: A Systems Analysis Perspective. *Resour Conserv Recy* 2005; 44(3):215-235.

[9] Shannon PT. The Integrated Use of the Digital Computer in Chemical Engineering Education. *Chem Eng Educ* 1963; 3:11-22.

[10] Dimian AC. Integrated Design and Simulation of Chemical Processes. In: Dimian AC, editor. *Computer Aided Chemical Engineering*. Amsterdam, The Netherlands: Elsevier; 2003. Vol 13.

[11] Martín M. *Introduction to Software for Chemical Engineers*. 1st ed. Boca Raton, FL, USA: CRC Press; 2014.

[12] Sargent RWH, Westerberg AW. "SPEEDUP" in Chemical Engineering Design. *Trans Inst Chem Eng* 1964; 42:190-197.

[13] Ledet WP, Himmelblau DM. Decomposition Procedures for the Solving of Large Scale Systems. *Adv Chem Eng* 1970; 8:185-254.

[14] Kehat E, Shacham M. Chemical Process Simulation Programs II. Partitioning and Tearing System Flowsheets. *Process Technol* 1973; 18:115-118.

[15] Tarjan R. Depth-First Search and Linear Graph Algorithms. *SIAM J Comput* 1972; 1(2): 146-160.

[16] Friedler F, Tarjan K, Huang YW, Fan LT. Graph-Theoretic Approach to Process Synthesis: Polynomial Algorithm for Maximal Structure Generation. *Comput Chem Eng* 1993; 17(9): 929-942.

[17] Friedler F, Tarjan K, Huang YW, Fan LT. Graph-Theoretic Approach to Process Synthesis: Axioms and Theorems. *Chem Eng Sci* 1992; 47(8):1973-1988.

[18] Wu W, Henao CA, Maravelias CT. A Superstructure Representation, Generation, and Modeling Framework for Chemical Process Synthesis. *AIChE J* 2016; 62(9):3199-3214.

[19] Upadhye RS, Grens EA. Selection of Decompositions for Chemical Process Simulation. *AIChE J* 1975; 21(1):136-143.

[20] Pho TK, Lapidus L. Topics in Computer-Aided Design: Part I. An Optimum Tearing Algorithm for Recycle Systems. *AIChE J* 1973; 19(6):1170-1181.

[21] Barkley RW, Motard RL. Decomposition of Nets. *Chem Eng J* 1972; 3:265-275.

[22] Wegstein JH. Accelerating Convergence of Iterative Processes. *Commun ACM* 1958; 1(6): 9-13.

[23] Broyden CG. A Class of Methods for Solving Nonlinear Simultaneous Equations. *Math Comput* 1965; 19(92):577-593.

[24] King CJ. From Unit Operations to Separation Processes. *Separ Purif Method* 2000; 29(2): 233-245.

[25] Rudd DF, Powers GJ, Siirola JJ. *Process Synthesis.* New Jersey, USA: Prentice Hall; 1973.

[26] Barnicki SD, Siirola JJ. Process Synthesis Prospective. *Comput Chem Eng* 2004; 28(4): 441-446.

Universitat d'Alacant
Universidad de Alicante

[27] Douglas JM. A Hierarchical Decision Procedure for Process Synthesis. *AIChE J* 1985; 30(3): 353-362.

[28] Nishida N, Stephanopoulos G, Westerberg AW. A Review of Process Synthesis. *AIChE J* 1981; 27(3):321-351.

[29] Westerberg AW. A Retrospective on Design and Process Synthesis. *Comput Chem Eng* 2004; 28(4):447-458.

[30] Yuan Z, Chen B, Gani R. Applications of Process Synthesis: Moving from Conventional Chemical Processes towards Biorefinery Processes. *Comput Chem Eng* 2013; 49:217-229.

[31] Siirola JJ, Rudd DF. Computer-Aided Synthesis of Chemical Process Designs. From Reaction Path Data to the Process Task Network. *Ind Eng Chem Fund* 1971; 10(3):353-362.

[32] Douglas JM. *Conceptual Design of Chemical Processes*. New York: McGraw-Hill; 1988.

[33] Seader JD, Westerberg AW. A Combined Heuristic and Evolutionary Strategy for Synthesis of Simple Separation Sequences. *AIChE J* 1977; 23(6):951-954.

[34] Nath R, Motard RL. Evolutionary Synthesis of Separation Processes. *AIChE J* 1981; 27(4): 578-587.

[35] Douglas JM. A Hierarchical Decision Procedure for Process Synthesis. *AIChE J* 1985; 30(3): 353-362.

[36] Linninger AA. Metallurgical Process Design – A Tribute to Douglas' Conceptual Design Approach. *Ind Eng Chem Res* 2002; 41(16):3797-3805.

[37] Lewin DR. A Generalized Method for HEN Syhnthesis Using Stochastic Optimization – II: The Synthesis of Cost-Optimal Networks. *Comput Chem Eng* 1998; 22(10):1387-1405.

[38] Rossiter AP, Rutkowski MA, McMullen AS. Pinch Technology Identifies Process Improvements. *Hydrocarb Process* 1991; 70(1):63-66.

[39] Spriggs HD, Smith R, Petela EA. Pinch Technology: Evaluate the Energy/Environmental Economic Trade-Offs in Industrial Processes. In: Tester JW, Wood DO, Ferrari NA, editors. *Energy and the Environment in the 21st Century*. Cambridge, MA, USA: Massachusetts Institute of Technology; 1990.

[40] Dhole VR, Linnhoff B. Total Site Targets for Fuel, Co-generation, Emissions, and Cooling. *Comput Chem Eng* 1993; 17:S101-S109.

[41] Klemeš JJ, Varbanov PS, Alwi SRWW, Manan ZA. *Process Integration and Intensification: Saving Energy, Water and Resources*. Berlin, Germany: Walter De Gruyter; 2014.

[42] Matsuda K, Hirochi Y, Tatsumi H, Shire T. Applying Heat Integration Total Site Based Pinch Technology to a Large Industrial Area in Japan to Further Improve Performance of Highly Efficient Process Plants. *Energy* 2009; 34(10):1687-1692.

[43] Mann JG, Liu YA. *Industrial Water Reuse and Wastewater Minimization*. New York: McGraw-Hill; 1999.

[44] Grossmann IE. MINLP Optimization Strategies and Algorithms for Process Synthesis. In: Siirola JJ, Grossmann IE, Stephanopoulos, editors. *Foundations of Computer-Aided Process Design*. Amsterdam, The Netherlands: Elsevier; 1990:105-132.

[45] Grossmann IE. Mixed-Integer Programming Approach for the Synthesis of Integrated Process Flowsheets. *Comput Chem Eng* 1985; 9(5):463-482.

[46] Grossmann IE. Mixed-Integer Nonlinear Programming Techniques for the Synthesis of Engineering Systems. *Res Eng Des* 1990; 1(3):205-228.

[47] Grossmann IE. Mixed-Integer Optimization Techniques for Algorithmic Process Synthesis. In: Anderson JL, editor. *Advances in Chemical Engineering*. Amsterdam, The Netherlands: Elsevier; 1996. Vol 23. p. 171-246.

[48] Grossmann IE, Caballero JA, Yeomans H. Mathematical Programming Approaches to the Synthesis of Chemical Process Systems. *Korean J Chem Eng* 1999; 16(4):407-426.

[49] Papoulias SA, Grossmann IE. A Structural Optimization Approach in Process Synthesis. Part II: Heat Recovery Networks. *Comput Chem Eng* 1983; 7(6):707-721.

[50] El-Halwagi MM, Manousiouthakis V. Synthesis of Mass Exchange Networks. *AIChE J* 1989; 35(8):1233-1244.

[51] Duran MA, Grossmann IE. An Outer-Approximation Algorithm for a Class of Mixed-Integer Nonlinear Programs. *Math Program* 1986; 36(3):307-339.

[52] Grossmann IE, Yeomans H, Kravanja Z. A Rigorous Disjunctive Optimization Model for Simultaneous Flowsheet Optimization and Heat Integration. *Comput Chem Eng* 1998; 22: S157-S164.

[53] Yee TF, Grossmann IE, Kravanja Z. Simultaneous Optimization Models for Heat Integration III. Process and Heat Exchanger Network Optimization. *Comput Chem Eng* 1990; 14(11): 1185-1200.

[54] Ciric AR, Floudas CA. Heat Exchanger Network Synthesis without Decomposition. *Comput Chem Eng* 1991; 15(6):385-396.

[55] Aggarwal A, Floudas CA. Synthesis of General Distillation Sequences-Nonsharp Separations. *Comput Chem Eng* 1990; 14(6):631-653.

[56] Yeomans H, Grossmann IE. Nonlinear Disjunctive Programming Models for the Synthesis of Heat Integrated Distillation Sequences. *Comput Chem Eng* 1999; 23(9): 1135-1151.

[57] Kocis GR, Grossmann IE. Relaxation Strategy for the Structural Optimization of Process Flow Sheets. *Ind Eng Chem Res* 1987; 26(9):1869-1880.

[58] Türkay M, Grossmann IE. Logic-Based MINLP Algorithms for the Optimal Synthesis of Process Networks. *Comput Chem Eng* 1996; 20(8):959-978.

[59] Bauer MH, Stichlmair J. Superstructures for the Mixed-Integer Optimization of Nonideal and Azeotropic Distillation Processes. *Comput Chem Eng* 1996; 20(S1):S25-S30.

[60] Bauer MH, Stichlmair J. Design and Economic Optimization of Azeotropic Distillation Processes using Mixed-Integer Nonlinear Programming. *Comput Chem Eng* 1998; 22(9): 1271-1286.

[61] Smith EMB, Pantelides CC. Design of Reaction/Separation Networks Using Detailed Models. *Comput Chem Eng* 1995; 19(1):83-88.

[62] Grossmann IE, Aguirre PA, Barttfeld M. Optimal Synthesis of Complex Distillation Columns Using Rigorous Models. *Comput Chem Eng* 2005; 29(6):1203-1215.

[63] Bedenik NI, Pahor B, Kravanja Z. An Integrated Strategy for the Hierarchical Multilevel MINLP Synthesis of Overall Process Flowsheets Using the Combined Synthesis/Analysis Approach. *Comput Chem Eng* 2004; 28(5):693-706.

[64] Ponce-Ortega JM, Mosqueda-Jiménez FW, Serna-González M, Jiménez-Gutiérrez A, El-Halwagi MM. A Property-Based Approach to the Synthesis of Material Conservation Networks with Economic and Environmental Objectives. *AIChE J* 2011; 57(9):2369-2387.

[65] Daichendt MM, Grossmann IE. Integration of Hierarchical Decomposition and Mathematical Programming for the Synthesis of Process Flowsheets. *Comput Chem Eng* 1998; 22(1):147-175.

[66] Jaksland CA, Gani R, Lien KM. Separation Process Design and Synthesis Based on Thermodynamic Insights. *Chem Eng Sci* 1995; 50(3):511-530.

[67] Hostrup M, Gani R, Kravanja Z, Sorsak A, Grossmann IE. Integration of Thermodynamic Insights and MINLP Optimization for the Synthesis, Design and Analysis of Process Flowsheets. *Comput Chem Eng* 2001; 25(1):73-83.

[68] Kravanja Z, Grossmann IE. Multilevel-Hierarchical MINLP Synthesis of Process Flowsheets. *Comput Chem Eng* 1997; 21:S421-S426.

[69] Tay DHS, Ng DKS, Kheireddine H, El-Halwagi MM. Synthesis of an Integrated Biorefinery via the C–H–O Ternary Diagram. *Clean Technol Environ* 2011; 13(4):567-579.

[70] Tay DHS, Ng DKS, Sammons NE, Eden MR. Fuzzy Optimization Approach for the Synthesis of a Sustainable Integrated Biorefinery. *Ind Eng Chem Res* 2011; 50(3):1652-1665.

[71] Verheyen W, Zhang N. Design of Flexible Heat Exchanger Network for Multi-Period Operation. *Chem Eng Sci* 2006; 61(23):7730-7753.

[72] Dantzig GB, Thapa MN. *Linear Programming: 1: Introduction.* Heidelberg, Germany: Springer; 1997.

[73] Nash JC. The (Dantzig) Simplex Method for Linear Programming. *Comput Sci Eng* 2000; 2(1):29-31.

[74] Karmarkar N. A New Polynomial-Time Algorithm for Linear Programming. *Combinatorica* 1984; 4(4):373-395.

[75] Adler I, Resende MC, Veiga G, Karmarkar N. An Implementation of Karmarkar's Algorithm for Linear Programming. *Math Program* 1989; 44(1-3):297-335.

[76] Han S-P. Superlinearly Convergent Variable Metric Algorithms for General Nonlinear Programming Problems. *Math Program* 1976; 11(1):263-282.

[77] Powell MJD. A Fast Algorithm for Nonlinearly Constrained Optimization Calculations. In: Watson GA, editor. *Numerical Analysis*. Heidelberg, Germany: Springer; 1978. Vol 630. p. 144-157.

[78] Murtagh BA, Saunders MA. Large-Scale Linearly Constrained Optimization. *Math Program* 1978; 14(1):41-72.

[79] Murtagh BA, Saunders MA. A Projected Lagrangian Algorithm and its Implementation for Sparse Nonlinear Constraints. In: Buckley AG, Goffin JL, editors. *Algorithms for Constrained Minimization of Smooth Nonlinear Functions*. Heidelberg, Germany: Springer; 1982. p. 84-117.

[80] Wächter A, Biegler LT. On the Implementation of an Interior-Point Filter Line-Search Algorithm for Large-Scale Nonlinear Programming. *Math Program* 2005; 106(1):25-27.

[81] Biegler LT. *Nonlinear Programming. Concepts, Algorithms, and Applications to Chemical Processes*. Philadelphia, PA, USA: Society for Industrial and Applied Mathematics (SIAM); 2010.

[82] Floudas CA. *Nonlinear and Mixed-Integer Optimization: Fundamentals and Applications.* Oxford, UK: Oxford University Press; 1995.

[83] Griva I, Nash S, Sofer A. *Linear and Nonlinear Optimization*. 2nd ed. Philadelphia, PA, USA: Society for Industrial and Applied Mathematics (SIAM); 2009.

[84] Grossmann IE. Enterprise-Wide Optimization: A New Frontier in Process Systems Engineering. *AIChE J* 2005; 51(7):1846-1857.

[85] Biegler LT, Grossmann IE, Westerberg AW. *Systematic Methods of Chemical Process Design.* New Jersey: Prentice Hall; 1997.

[86] Dakin RJ. A Tree-Search Algorithm for Mixed-Integer Programming Problems. *Comput J* 1965; 8(3):250-255.

[87] Nemhauser GL, Wolsey LA. *Integer and Combinatorial Optimization.* New Jersey, USA: John Wiley & Sons; 1999.

[88] Pochet Y, Wolsey LA. *Production Planning by Mixed-Integer Programming*. Heidelberg, Germany: Springer; 2006.

Universidad de Alicante

[89] Benders JF. Partitioning Procedures for Solving Mixed-Variables Programming Problems. *Numer Math* 1962; 4(1):238-252.

[90] Fisher ML. The Lagrangian Relaxation Method for Solving Integer Programming Problems. *Manage Sci* 2004; 50(12):S1861-S1871.

[91] Atamtürk A, Savelsbergh MWP. Integer-Programming Software Systems. *Ann Oper Res* 2005; 140(1):67-124.

[92] Johnson EL, Nemhauser GL, Savelsbergh MWP. Progress in Linear Programming-Based Algorithms for Integer Programming: An Exposition. *INFORMS J Comput* 2000; 12(1):2-23.

[93] Hooker JN. *Integrated Methods for Optimization.* 2nd ed. Heidelberg, Germany: Springer; 2011.

[94] Bussieck MR, Ferris MC, Meeraus A. Grid-Enabled Optimization with GAMS. *INFORMS J Comput* 2009; 21(3):349-362.

[95] Achterberg T, Koch T, Martin A. MIPLIB 2003. *Oper Res Lett* 2006; 34(4):361-372.

[96] Kondili E, Pantelides CC, Sargent RWH. A General Algorithm for Short-Term Scheduling of Batch Operations - I. MILP formulation. *Comput Chem Eng* 1993; 17(2):211-227.

[97] Méndez CA, Cerdá J, Grossmann IE, Harjunkoski I, Fahl M. State-of-the-art Review of Optimization Methods for Short-Term Scheduling of Batch Processes. *Comput Chem Eng* 2006; 30(6):913-946.

[98] Shah N, Pantelides CC, Sargent RWH. A general algorithm for short-term scheduling of batch operations - II. Computational issues. *Comput Chem Eng* 1993; 17(2):229-244.

[99] IBM. *IBM ILOG CPLEX Optimization Studio CPLEX User's Manual, Version 12 Release 6.* Armonk, NY, USA: IBM Corp.; 2013.

[100] Gurobi Optimization Inc. *Gurobi Optimizer Reference Manual, Version 7.* Houston, TX, USA: Gurobi Optimization Inc; 2017.

[101] FICO Inc. *XPRESS Optimization Suite Release 8.1.* California, USA: FICO Inc; 2017.

[102] Grossmann IE, Caballero JA, Yeomans H. Advances in Mathematical Programming for the Synthesis of Process Systems. *Lat Am Appl Res* 2000; 30(4):263-284.

[103] Pinedo M. *Scheduling: Theory, Algorithms, and Systems.* 5th ed. Heidelberg, Germany: Springer; 2016.

[104] Bertsekas DP. *Dynamic Programming and Optimal Control.* 4th ed. Nashua, NH, USA: Athena Scientific; 2012.

[105] Achenie LEK, Gani R, Venkatasubramanian V. *Computer Aided Molecular Design: Theory and Practice.* Vol 12. Amsterdam, The Netherlands: Elsevier; 2003.

[106] Fletcher R, Leyffer S. Solving Mixed-Integer Nonlinear Programs by Outer-Approximation. *Math Program* 1994; 66(1-3):327-349.

[107] Geoffrion AM. Generalized Benders decomposition. *J Optim Theory Appl* 1972; 10(4): 237-260.

[108] Westerlund T, Pettersson F. An Extended Cutting Plane Method for Solving Convex MINLP Problems. *Comput Chem Eng* 1995; 19:131-136.

[109] Westerlund T, Skrifvars H, Harjunkoski I, Pörn R. An Extended Cutting Plane Method for a Class of Non-Convex MINLP Problems. *Comput Chem Eng* 1998; 22(3):357-365.

[110] Westerlund T, Pörn R. Solving Pseudo-Convex Mixed-Integer Optimization Problems by Cutting Plane Techniques. *Optim Eng* 2002; 3(3):253-280.

[111] Kelley JE. The Cutting-Plane Method for Solving Convex Programs. *J Soc Ind Appl Math* 1960; 8(4):703-712.

Universidad de Alicante

[112] Quesada I, Grossmann IE. An LP/NLP Based Branch and Bound Algorithm for Convex MINLP Optimization Problems. *Comput Chem Eng* 1992; 16(10):937-947.

[113] Abhishek K, Leyffer S, Linderoth J. FilMINT: An Outer-Approximation-Based Solver for Convex Mixed-Integer Nonlinear Programs. *INFORMS J Comput* 2010; 22(4):555-567.

[114] Balas E. Disjunctive Programming and a Hierarchy of Relaxations for Discrete Optimization Problems. *SIAM J Algebra Disc Meth* 1985; 6(3):466-486.

[115] Beaumont N. An algorithm for Disjunctive Programs. *Eur J Oper Res* 1990; 48(3):362-371.

[116] Hooker JN. *Logic-Based Methods for Optimization: Combining Optimization and Constraint Satisfaction*. New Jersey, USA: John Wiley & Sons; 2000.

[117] Hooker JN, Osorio MA. Mixed Logical-Linear Programming. *Discrete Appl Math* 1999; 96-97:395-442.

[118] Lee S, Grossmann IE. Logic-Based Modeling and Solution of Nonlinear Discrete/ Continuous Optimization Problems. *Ann Oper Res* 2005; 139(1):267-288.

[119] Raman R, Grossmann IE. Modelling and Computational Techniques for Logic-Based Integer Programming. *Comput Chem Eng* 1994; 18(7):563-578.

[120] Grossmann IE, Caballero JA, Yeomans H. Advances in Mathematical Programming for Automated Design Integration. *Korean J Chem Eng* 1999; 16:407-426.

[121] Lee S, Grossmann IE. New Algorithms for Nonlinear Generalized Disjunctive Programming. *Comput Chem Eng* 2000; 24(9–10):2125-2141.

[122] Grossmann I, Lee S. Generalized Convex Disjunctive Programming: Nonlinear Convex Hull Relaxation. *Comput Optim Appl* 2003; 26(1):83-100.

[123] Vecchietti A, Lee S, Grossmann IE. Modeling of Discrete/Continuous Optimization Problems: Characterization and Formulation of Disjunctions and their Relaxations. *Comput Chem Eng* 2003; 27(3):433-448.

[124] Bandler JW, Cheng QS, Dakroury SA, Mohamed AS, Bakr MH, Madsen K, Søndergaar J. Space Mapping: The State of the Art. *IEEE T Microw Theory* 2004; 52(1):337-361.

[125] Queipo NV, Haftka RT, Shyy W, Goel T, Vaidyanathan R, Tucker PK. Surrogate-Based Analysis and Optimization. *Prog Aerospace Sci* 2005; 41(1):1-28.

[126] Giunta A, Wojtkiewicz S, Eldred M. Overview of Modern Design of Experiments Methods for Computational Simulations. *41st Aerospace Sciences Meeting & Exhibit*. Reno, NV, USA: American Institute of Aeronautics and Astronautics; 2003.

[127] Koehler JR, Owen AB. Computer Experiments. In: Ghosh S, Rao CR, editors. *Handbook of Statistics: Design and Analysis of Experiments*. Amsterdam, The Netherlands: Elsevier; 1996. Vol 13. p. 261-308.

[128] Santner TJ, Williams BJ, William WI. *The Design and Analysis of Computer Experiments.* Heidelberg, Germany: Springer; 2003.

[129] Iman RL, Helton JC, Campbell JE. An Approach to Sensitivity Analysis of Computer Models: Part 1. Introduction, Input Variable Selection and Preliminary Variable Assessment. *J Qual Technol* 1981; 13(3):174-173.

[130] McKay MD, Beckman RJ, Conover WJ. A Comparison of Three Methods for Selecting Values of Input Variables in the Analysis of Output from a Computer Code. *Technometrics* 1979; 21(2):239-245.

[131] Kalagnanam JR, Diwekar UM. An Efficient Sampling Technique for Off-Line Quality Control. *Technometrics* 1997; 39(3):308-319.

[132] Friedman JH. Multivariate Adaptative Regression Splines. *Ann Stat* 1991; 19(1):1-141.

[133] Hastie T, Tibshirani R, Friedman JH. *The Elements of Statistical Learning: Data Mining, Inference, and Prediction.* Heidelberg, Germany: Springer; 2001.

[134] Forrester AIJ, Keane AJ. Recent Advances in Surrogate-Based Optimization. *Prog Aerosp Sci* 2009; 45(1–3):50-79.

[135] Wild SM, Regis RG, Shoemaker CA. ORBIT: Optimization by Radial Basis Function Interpolation in Trust-Regions. *SIAM J Sci Comput* 2008; 30(6):3197-3219.

[136] Krige DG. *A Statistical Approach to some Mine Valuation and Allied Problems on the Witwatersrand* [Master's Thesis]. South Africa: University of Witwatersrand; 1951.

[137] Sacks J, Welch WJ, Mitchell TJ, Wynn HP. Design and Analysis of Computer Experiments. *Stat Sci* 1989; 4(4):409-423.

[138] Papalambros PY, Wilde DJ. *Principles of Optimal Design: Modeling and Computation.* 2nd ed. New York: Cambridge University Press; 2000.

[139] Jones DR, Schonlau M, Welch WJ. Efficient Global Optimization of Expensive Black-Box Functions. *J Glob Optim* 1998; 13(4):455-492.

[140] Kleijnen JPC. Kriging Metamodeling in Simulation: A Review. *Eur J Oper Res* 2009; 192(3): 707-716.

[141] Beck J, Friedrich D, Brandani S, Fraga ES. Multi-Objective Optimisation Using Surrogate Models for the Design of VPSA systems. *Comput Chem Eng* 2015; 82(SC):318-329.

[142] Haykin SO. *Neural Networks and Learning Machines.* 3rd ed. Cambridge, UK: Pearson; 2008.

[143] Linnhoff B, Townsend DW, Boland D, Hewitt GF, Thomas BEA, Guy AR, Marsland RH. *A User Guide on Process Integration for the Efficient Use of Energy*. Institute of Chemical Engineers, Oxford: Pergamon Press; 1982.

[144] Linnhoff B. Pinch Analysis: Building on a Decade of Progress. *Chem Eng Prog* 1994; 90(8): 32-57.

[145] Gundersen T, Naess L. The Synthesis of Cost Optimal Heat Exchanger Networks. *Comput Chem Eng* 1988; 12(6):503-530.

[146] Furman KC, Sahinidis NV. A Critical Review and Annotated Bibliography for Heat Exchanger Network Synthesis in the 20th Century. *Ind Eng Chem Res* 2002; 41(10): 2335-2370.

[147] Ahmad S, Linnhoff B, Smith R. Cost Optimum Heat Exchanger Networks 2. Targets and Design for Detailed Capital Cost Models. *Comput Chem Eng* 1990; 14(7):751-767.

[148] Linnhoff B. Pinch Analysis – A State-of-the-Art Overview. *Chem Eng Res Des* 1993; 71(A5): 503-522.

[149] Linnhoff B, Ahmad S. Cost Optimum Heat Exchanger Networks 1. Minimum Energy and Capital Using Simple Models for Capital Cost. *Comput Chem Eng* 1990; 14(7):729-750.

[150] Linnhoff B, Hindmarsh E. The Pinch Design Method for Heat Exchange Network. *Chem Eng Sci* 1983; 38:745-763.

[151] Ciric AR, Gu D. Synthesis of Nonequilibrium Reactive Distillation Processes by MINLP Optimization. *AIChE J* 1994; 40(9):1479-1487.

[152] Floudas CA, Grossmann IE. Synthesis of Flexible Heat Exchanger Networks for Multiperiod Operation. *Comput Chem Eng* 1986; 10(2):153-168.

[153] Yee TF, Grossmann IE. Simultaneous Optimization Models for Heat Integration II. Heat Exchanger Network Synthesis. *Comput Chem Eng* 1990; 14(10):1165-1184.

[154] Fraga ES, McKinnon KIM. Discrete Programming and Data Analysis for Heat-Integrated Process Synthesis in Early Design. *Ind Eng Chem Res* 2004; 43(1):144-160.

[155] Rebitzer G, Ekvall T, Frischknecht R, Hunkeler D, Norris G, Rydberg T, Schmidt WP, Suh S, Weidema BP, Pennington DW. Life Cycle Assessment. Part 1: Framework, Goal and Scope Definition, Inventory Analysis, and Applications. *Environ Int* 2004; 30(5):701-720.

Universitat d'Alacant
Universidad de Alicante

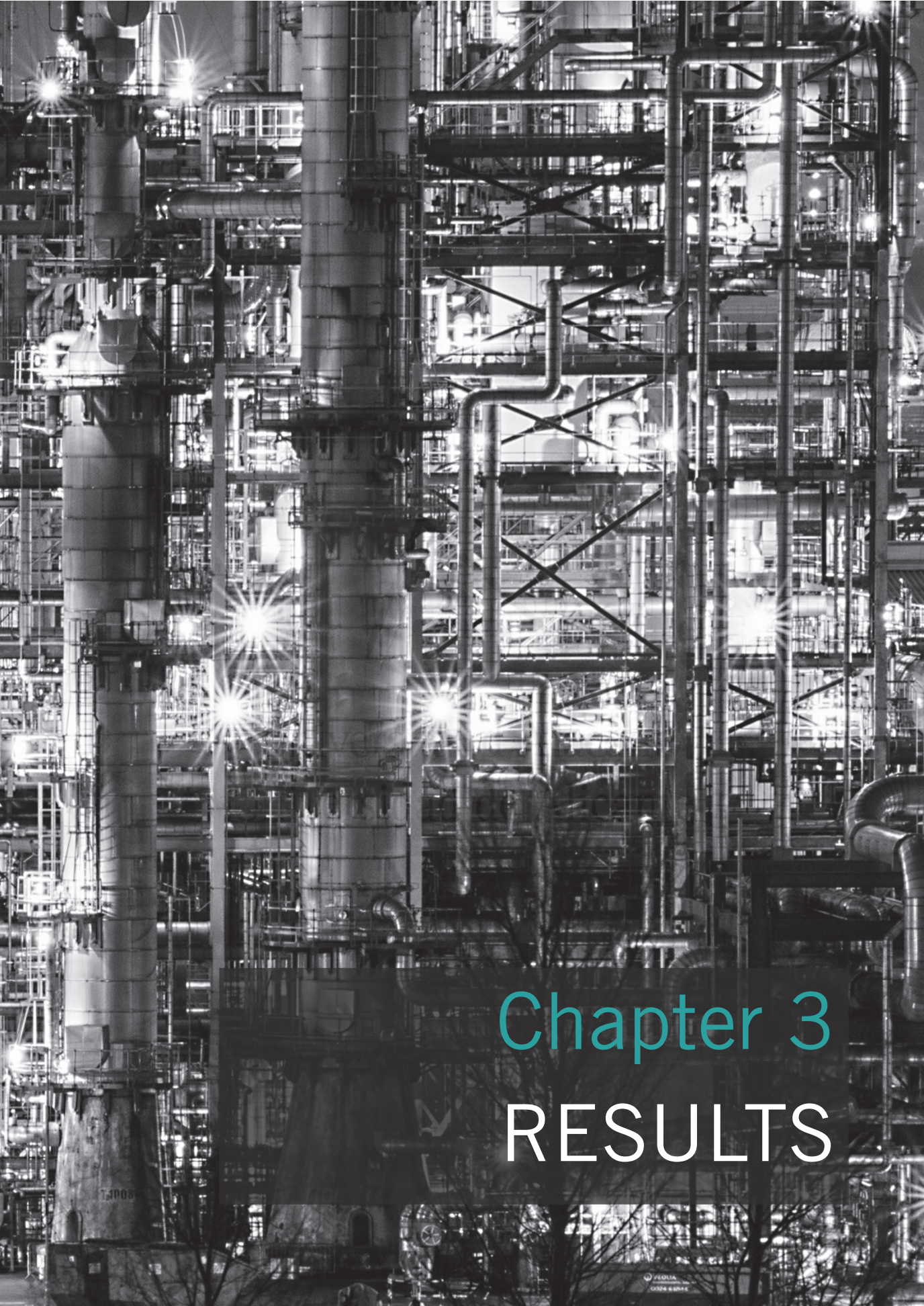
[156] ISO 14040:2006. *Environmental Management – Life Cycle Assessment – Principles and Framework.* Geneva, Switzerland: International Organization for Standardization (ISO); 2006.

[157] ISO 14044:2006. *Environmental Management – Life Cycle Assessment – Requirements and Guidelines.* Geneva, Switzerland: International Organization for Standardization (ISO); 2006.

[158] Goedkoop M, Heijungs R, Huijbregts M, Schryver AD, Struijs J, Van Zelm R. *ReCiPe 2008. A Life Cycle Impact Assessment Method which Comprises Harmonised Category Indicators at the Midpoint and the Endpoint Level. Report I: Characterisation*. 1st ed. Bilthoven, The Netherlands: National Institute for Public Health and the Environment (RIVM); 2009.

[159] Thompson M, Ellis RJ, Wildavsky A, Wildavsky M. *Cultural Theory*. 1st ed. Colorado, CO, USA: Westview Press; 1990.

Universitat d'Alacant
Universidad de Alicante



Chapter 3
RESULTS

Universitat d'Alacant
Universidad de Alicante

Chapter 3.

Results

Different studies have been developed throughout the present Thesis in order to achieve all the objectives established at the beginning of the work. In this chapter, the results of this Thesis are presented. These results correspond to four articles published in different international journals of high-impact factor and one paper that has been submitted and is under review in another of these journals.

* **Publication 1**: Quirante N, Javaloyes J, Caballero JA. Rigorous Design of Distillation Columns Using Surrogate Models Based on Kriging Interpolation. *AIChE Journal* 2015; 61(7):2169-2187.
  http://onlinelibrary.wiley.com/doi/10.1002/aic.14798/full

* **Publication 2**: Quirante N, Caballero JA. Large Scale Optimization of a Sour Water Stripping Plant Using Surrogate Models. *Computers & Chemical Engineering* 2016; 92:143-162.
  http://doi.org/10.1016/j.compchemeng.2016.04.039

* **Publication 3**: Quirante N, Javaloyes J, Caballero JA. Hybrid Simulation-Equation Based Synthesis of Chemical Processes. Sent to: *Chemical Engineering Research & Design*. [Under review].

* **Publication 4**: Quirante N, Caballero JA, Grossmann IE. A Novel Disjunctive Model for the Simultaneous Optimization and Heat Integration. *Computers & Chemical Engineering* 2017; 96:149-168.
  http://doi.org/10.1016/j.compchemeng.2016.10.002

* **Publication 5**: Quirante N, Grossmann IE, Caballero JA. Disjunctive Model for the Simultaneous Optimization and Heat Integration with Unclassified Streams and Area Estimation. *Computers & Chemical Engineering* 2018; 108:217-231.
  https://doi.org/10.1016/j.compchemeng.2017.09.013

Universitat d'Alacant
Universidad de Alicante

Universitat d'Alacant
Universidad de Alicante

3.1. Publication 1. Rigorous Design of Distillation Columns Using Surrogate Models Based on Kriging Interpolation

Distillation has been, and probably will continue to be, the most important technique in the chemical industry. In fact, almost 90 % of recovery and purification operations are distillation processes. The main problem of distillation is the high cost of this unit operation, since approximately 3 % of the energy consumed globally is due to distillation processes. Therefore, a reduction of energy consumption of the chemical processes will have a huge impact on the world energy demand and, in addition, this reduction will contribute to decreasing the environmental impact.

Additionally, the rigorous design of a distillation column is an arduous problem in chemical process engineering, since it involves the simultaneous optimization of continuous decisions related to operating conditions and discrete decisions related to the number of trays in each column section. In the case of column sequences, the design includes decisions related to column connectivity.

Consequently, there is a growing interest in the design and optimization of chemical processes. Mathematical models allow us to solve such problems, and the use of software is an essential tool for solving complex mathematical models. For this reason, the demand for computationally efficient process models in many engineering applications has been increasing in recent years.

Universitat d'Alacant
Universidad de Alicante

In general, most of the process models have a modular structure to which users have limited internal access and, furthermore, some of these models need a noteworthy CPU time and their derivatives cannot be accurately estimated due to the generation of numerical noise.

On the other hand, the design of distillation columns or distillation sequences is a difficult problem that has been dealt with superstructure approaches. However, these methods have not been widely used because they lead to mixed-integer nonlinear programs, which are hard to solve and involve initialization procedures of high complexity. To solve this problem, there is a growing trend towards the integration of optimization models with surrogate models because they are computationally efficient and, at the same time, they ensure an acceptable degree of accuracy.

Surrogate models can be used at different levels: substituting the complete model, replacing some components, or developing a local approach to the whole model followed by any trust region algorithm.

In this paper, we propose the replacement of distillation columns or complex sequences by surrogate models. For this study, surrogate models are based on Kriging interpolation and they are generated through rigorous distillation models. We focus on Kriging metamodels because they combine computational efficiency with relatively small sampling data.

Examples of different complexity were performed in order to study and verify the effectiveness of the method. All examples were simulated using Aspen HYSYS v.7.3 and solved using state-of-the-art optimizers (CONOPT and SNOPT) available in TOMLAB-MATLAB. The Kriging surrogate models were calibrated using MATLAB.

In all the cases studied, the results show that it is possible to obtain accurate surrogate models, with errors below 5 %. It is proved that the error increases slightly as the number of independent variables increases. However, this strategy provides excellent results compared to the results obtained with the simulator.

In conclusion, surrogate models allow us to simulate the behavior of the distillation columns and they allow us to perform a fast and reliable optimization of industrial processes.

Universitat d'Alacant
Universidad de Alicante

AIChE JOURNAL
An Official Publication of the American Institute of Chemical Engineers
AIChE

Rigorous Design of Distillation Columns Using Surrogate Models Based on Kriging Interpolation

Natalia Quirante, Juan Javaloyes and José A. Caballero

AIChE Journal, 61 (2015), pp. 2169 – 2187. (DOI 10.1002/aic.14798)

Article Info

Article history:
Manuscript received 2 Dec 2014
Manuscript revised 6 March 2015
Accepted 21 March 2015
Available online 16 June 2015

Keywords:
Simulation
Optimization
Design (distillation columns)
Kriging algorithm
Mathematical modeling

Abstract

The economic design of a distillation column or distillation sequences is a challenging problem that has been addressed by superstructure approaches. However, these methods have not been widely used because they lead to mixed-integer nonlinear programs that are hard to solve and require complex initialization procedures. In this article, we propose to address this challenging problem by substituting the distillation columns by Kriging-based surrogate models generated via state-of-the-art distillation models. We study different columns with increasing difficulty and show that it is possible to get accurate Kriging-based surrogate models. The optimization strategy ensures that convergence to a local optimum is guaranteed for numerical noise-free models. For distillation columns (slightly noisy systems), Karush-Kuhn-Tucker optimality conditions cannot be tested directly on the actual model, but still, we can guarantee a local minimum in a trust region of the surrogate model that contains the actual local minimum.

Universitat d'Alacant
Universidad de Alicante

Universitat d'Alacant
Universidad de Alicante

3.2. Publication 2. Large Scale Optimization of a Sour Water Stripping Plant Using Surrogate Models

The simulation of a chemical process can incorporate a large number of linear and nonlinear equations. Even a small chemical process can include thousands of variables and equations. In some cases, it is possible to write and solve the complete set of equations by using an appropriate modeling system. Nevertheless, the more complex the model, the more difficult the convergence will be. Therefore, it is possible to use a modular approach to calculate the model, instead of solving all the equations simultaneously.

Surrogate models have recently been proposed as an alternative to modular process models because they are computationally efficient and they guarantee a satisfactory degree of accuracy. Surrogate models combine mathematical functions, based on data generated from the simulation, to approximate the input-output relationship of the simulation. While the original simulation model could be hard to solve, noisy or time-consuming, the metamodel is relatively easy to solve and noise-free.

On the other hand, the increasing energy global demand and the strict standards that regulate carbon dioxide emissions in order to mitigate the greenhouse effect and its consequences are the main reasons for developing techniques for the efficient and sustainable energy use. The most effective method to reduce energy consumption, and thus to reduce costs, is the use of energy from process streams through thermal integration between cooling and heating systems. Additionally, the reduction of energy consumption can achieve the minimization of environmental impacts.

In this paper, a large-scale sour water stripping plant is optimized. The objective of the sour water treatment is to remove sulfides and ammonia from water that comes from a petrochemical complex.

For this purpose, a hybrid approach was followed in which only some parts of the plant (those that could introduce numerical problems in the optimization) are substituted by surrogate models, some units are maintained in the process simulator (those that do not introduce numerical noise), and the equations related to heat integration and Life Cycle Assessment (LCA) are defined in terms of explicit equations.

In this work, Kriging interpolation is used to build the metamodels because they combine relatively small sampling data with computational efficiency. In order to build accurate Kriging models, a good distribution of sampling points is required. The 'maxmin' approach was selected to distribute the sampling data. Furthermore, an analysis based on feasibility and degrees of freedom considerations was performed in order to aggregate some equipment into a single and more robust surrogate model.

In this work, the optimization of the operating conditions of the sour water stripping plant is carried out first, evaluating the environmental performance through an LCA. Then, the heat integration concept is introduced, simultaneously optimizing the operating conditions and the heat integration, and analyzing the environmental impact.

The models were simulated on Aspen HYSYS v.8.4 and the Kriging surrogate models were calibrated using MATLAB. As NLP solver, we use CONOPT available through TOMLAB-MATLAB.

The disjunctive formulation of the Pinch Location Method proposed by Grossmann et al. was considered in order to perform the simultaneous optimization and heat integration of the process. The ReCiPe indicator was used to evaluate the environmental impacts.

The results show that the heat integration reduces the economic performance of the process and, at the same time, it reduces the environmental impact.

In conclusion, the difficulties related to the lack of convergence of some black box models, the relatively large CPU time to converge or the introduction of numerical noise can be overcome with the use of surrogate models. Even though the optimization cannot guarantee the global optimum due to the nonconvex character of the model, the procedure has demonstrated to be robust and reliable.

Universitat d'Alacant
Universidad de Alicante

Contents lists available at ScienceDirect

Computers and Chemical Engineering

journal homepage: www.elsevier.com/locate/compchemeng

Large Scale Optimization of a Sour Water Stripping Plant Using Surrogate Models

Natalia Quirante and José A. Caballero

Computers & Chemical Engineering, 92 (2016), pp. 143 – 162.

(DOI 10.1016/j.compchemeng.2016.04.039)

Article Info

Article history:

Manuscript received 3 Nov 2015

Manuscript revised 26 April 2016

Accepted 26 April 2016

Available online 21 May 2016

Keywords:

Process simulation

Process optimization

Kriging interpolation

Heat exchanger network

Life cycle assessment

Abstract

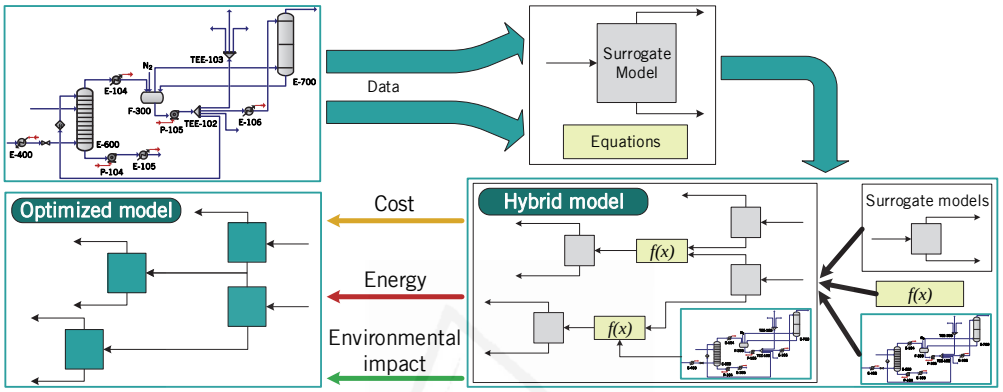
In this work, we propose a new methodology for the large-scale optimization and process integration of complex chemical processes that have been simulated using modular chemical process simulators. Units with significant numerical noise or large CPU times are substituted by surrogate models based on Kriging interpolation. Using a degree of freedom analysis, some of those units can be aggregated into a single unit to reduce the complexity of the resulting model. As a result, we solve a hybrid simulation-optimization model formed by units in the original flowsheet, Kriging models, and explicit equations.

We present a case study for the optimization of a sour water stripping plant in which we simultaneously consider economics, heat integration and environmental impact using the ReCiPe indicator, which incorporates the recent advances made in Life Cycle Assessment (LCA).

The optimization strategy guarantees the convergence to a local optimum inside the tolerance of the numerical noise.

Universitat d'Alacant
Universidad de Alicante

Graphical Abstract



Highlights

* We develop an efficient multi-objective optimization method using surrogate models based on Kriging interpolation.
* We solve a hybrid simulation-optimization model formed by units of the flowsheet with low numerical noise, Kriging models, and explicit equations.
* The hybrid approach (Kriging models, simulation and explicit equations) has proved to be robust and reliable.

Universitat d'Alacant
Universidad de Alicante

3.3. Publication 3. Hybrid Simulation-Equation Based Synthesis of Chemical Processes

An important technique for the synthesis of chemical processes consists of superstructure optimization-based methods. This methodology takes into account the complete network, which is composed of all the unit operations, their connections, and other constraints. The solution of the mathematical model identifies which of the initial units and their connections are maintained in the optimal structure. These methods are used because they offer a simultaneous optimization of the superstructure and the operating conditions. However, superstructure optimization-based methods are complex to solve because the resulting model is a large-scale nonconvex mixed-integer nonlinear problem.

A difficult problem occurs when a sequential-modular process simulator is used as a black box to describe the behavior of the system; the presence of numerical noisy unit operations.

In this work, this problem is addressed by combining process simulators and surrogate models. The superstructure includes all the alternatives of interest of the process that we need to optimize and is implemented at the level of the process simulator. Surrogate models based on Kriging interpolation replace those unit operations that are inherently noisy and/or need a notable CPU time to converge. The units that do not introduce numerical noise are maintained in the process simulator. Thus, the final model is composed of Kriging surrogate models, unit operations maintained in the process simulator, and explicit equations.

Several Kriging models are built, with a maximum of five independent variables. A sensitivity analysis is carried out to determine if some units need or not to be merged into a single metamodel. Furthermore, an efficient distribution of the training points is required in order to build robust and accurate surrogate models. An *a priori* infill procedure, the 'maxmin' approach, has been used to achieve a good distribution.

To illustrate the proposed approach, the optimization of the well-known vinyl chloride monomer (VCM) production process is performed. The VCM superstructure considered is divided into three sections: direct chlorination, oxychlorination, and pyrolysis. The main objective is to determine the best flowsheet topology to maximize the profit of the process.

The vinyl chloride monomer production process is simulated in Aspen HYSYS v.8.4 and the surrogate models are built in MATLAB from training data sets obtained from the process simulator. Additionally, the equations related to capital and operating costs are implemented as explicit equations. The final model, objective function, constraints, and surrogate models are written in a proprietary modeling language interfaced with TOMLAB-MATLAB, which connects MATLAB with Aspen HYSYS to optimize the process.

Heat integration is the most effective technique to reduce the costs of a process, which is achieved through the thermal integration between heating and cooling systems. Therefore, in order to improve the energy efficiency of the plant, the heat exchanger network of the VCM process is designed. The results show that utility requirements are considerably decreased in the heat integrated process, which implies a reduction in the operating costs.

In addition, the economic feasibility of the optimized VCM process is evaluated assuming uncertainty in the prices of raw material and products. The concept of financial risk is employed to analyze the risk of not meeting the profit target obtained in the optimal process.

Universitat d'Alacant
Universidad de Alicante

Hybrid Simulation-Equation Based Synthesis of Chemical Processes

Natalia Quirante, Juan Javaloyes and José A. Caballero

Sent to: Chemical Engineering Research & Design.

Article Info

Article history:

Manuscript received 18 Jun 2017

Manuscript revised:

Accepted:

Available online:

Keywords:

Simulation

Optimization

MINLP

Kriging algorithm

Vinyl Chloride Monomer process

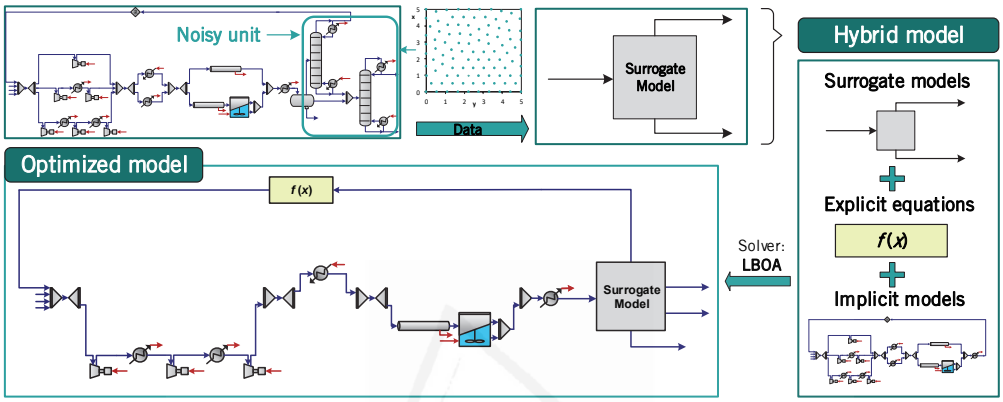
Abstract

A challenging problem in the synthesis and design of chemical processes consists of dealing with hybrid models involving process simulators and explicit constraints. Some unit operations in modular process simulators are slightly noisy or require large CPU times to converge. In this work, this problem is addressed by combining process simulators and surrogate models. We have replaced some unit operations, which cannot be used directly with a gradient-based optimization, by surrogate models based on Kriging interpolation. To increase the robustness of the resulting optimization model, we perform a degree of freedom analysis and aggregate (or disaggregate) parts of the model to reduce the number of independent variables of the Kriging surrogate models (KSMs). Thus, the final model is composed of KSMs, unit operations (maintained in the process simulator) and also explicit equations.

The optimization of the well-known vinyl chloride monomer (VCM) production process is performed to test the proposed approach. The effect of the heat integration is also studied. In addition, the economic feasibility of the optimized process is calculated assuming uncertainty in raw material and product prices.

Universitat d'Alacant
Universidad de Alicante

Graphical Abstract



Highlights

* A methodology for the optimization of complex chemical processes is developed.
* A hybrid model is solved (simulation units, Kriging models and explicit equations).
* Optimization of VCM process is performed to show the performance of our approach.
* This approach has proved to be robust and reliable to solve complex problems.
* Additionally, heat integration and economic feasibility are studied.

Universitat d'Alacant
Universidad de Alicante

3.4. Publication 4. A Novel Disjunctive Model for the Simultaneous Optimization and Heat Integration

Energy consumption has a high influence on the total cost of a process. Consequently, heat integration is a key factor in determining the optimal design of a chemical process. Therefore, if the energy consumption and the energy losses are minimized, the economic benefits of a chemical plant will increase.

The most important technique to reduce energy consumption is through the implementation of heat exchanger networks. The purpose is to determine the minimum utility requirements of a process, and identify the maximum possible grade of heat recovery as a function of the minimum temperature difference within the heat exchanger network.

The most important methodology to minimize the energy consumption of a chemical process is based on the concept of Pinch Location Method.

The objective of this work is to present a disjunctive reformulation of the Pinch Location Method. This work introduces a new disjunctive formulation for the simultaneous optimization and heat integration of systems with variable inlet and outlet stream temperatures. The proposed disjunctive model also considers the possibility of using different utilities. The starting point is the original compact formulation of the Pinch Location Method where the 'max' operators are modeled by means of a disjunction.

Universitat d'Alacant
Universidad de Alicante

Several examples of different complexity were presented to illustrate the performance of the novel approach. Examples include: fixed and variable stream temperatures; variable stream temperatures by simulating the behavior of the system through a penalty function; simultaneous process optimization and heat integration of a chemical process using a hybrid simulation-optimization approach (where the flowsheet is solved by a commercial process simulator and the heat integration model is included in form of equations); and variable stream temperatures using multiple utilities.

Calculations of fixed and variable stream temperature problems were performed in GAMS. Calculations of the simultaneous process optimization and heat integration problem were carried out in TOMLAB-MATLAB and the simulations were performed on Aspen HYSYS v.8.4.

The results show that the new formulation is very competitive from the point of view of CPU time and includes fewer binary variables and equations than the best-known disjunctive formulation (the disjunctive version developed by Grossmann et al.), although the number of total variables is slightly larger. The new model has also shown to have equal or lower relaxation gap than the Grossmann model, thus reducing computational time and numerical difficulties related to nonconvex approximations.

One of the main features of the novel model is that it can be 'added' to any model with almost no modifications of the existing model, and consequently, its implementation is simple.

Universitat d'Alacant
Universidad de Alicante

Contents lists available at ScienceDirect

Computers and Chemical Engineering

journal homepage: www.elsevier.com/locate/compchemeng

A Novel Disjunctive Model for the Simultaneous Optimization and Heat Integration

Natalia Quirante, José A. Caballero and Ignacio E. Grossmann

Computers & Chemical Engineering, 96 (2017), pp. 149 – 168.

(DOI 10.1016/j.compchemeng.2016.10.002)

Article Info

Article history:

Manuscript received 25 Jul 2016

Manuscript revised 3 Oct 2016

Accepted 4 October 2016

Available online 8 October 2016

Keywords:

Heat integration

Variable temperatures

Disjunctive model

Simultaneous optimization

Abstract

This paper introduces a new disjunctive formulation for the simultaneous optimization and heat integration of systems with variable inlet and outlet temperatures in process streams as well as the possibility of selecting and using different utilities. The starting point is the original compact formulation of the Pinch Location Method, however, instead of approximating the 'maximum' operator with smooth, but nonconvex functions, these operators are modeled by means of a disjunction. The new formulation has shown to have equal or lower relaxation gap than the best alternative reformulation, thus reducing computational time and numerical problems related to nonconvex approximations.

Highlights

* An alternative disjunctive model for simultaneous optimization and heat integration.
* It allows the possibility of selecting and using different utilities.
* The novel disjunctive reformulation has a good relaxation gap.
* Examples with different complexity illustrate the performance of the novel approach.

Universitat d'Alacant
Universidad de Alicante

3.5. Publication 5. Disjunctive Model for the Simultaneous Optimization and Heat Integration with Unclassified Streams and Area Estimation

The total cost of a chemical process can be greatly influenced by energy consumption. Therefore, in order to increase the economic benefits of a chemical plant, the minimization of the energy consumption is a key factor in determining the optimal design of a chemical process. The most important technique to reduce energy consumption is through the implementation of heat exchanger networks.

One of the major advances in chemical process engineering was the discovery that it is possible to calculate the least amount of hot and cold utilities required for a process without knowing the heat exchanger network. This advance motivated the introduction of the pinch concept and the pinch design method, for the design of heat exchanger networks (HEN).

The most important methodology to minimize the energy consumption of a chemical process is based on the concept of pinch location method. From the 1970s to the present, hundreds of papers related to heat integration have been published.

A common situation that appears when the temperatures are not fixed, particularly regarding on the optimization of superstructures, is that *a priori* it is not possible to decide if a process stream is a hot (it requires cooling) or a cold (it requires heating) stream. To illustrate this behavior, consider the outlet stream from one of two alternative reactors (A or B) which is sent to a separation unit. Initially, as shown in Figure 3.5.0, we cannot determine if the stream is a hot or cold stream before solving the model.

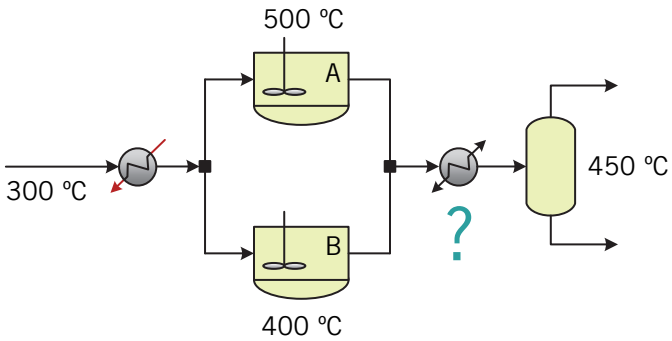


Figure 3.5.0. Example of an unclassified process stream.

The objective of this work is to present a disjunctive reformulation of the Pinch Location Method, based on the formulation developed in Section 3.4. This work introduces a disjunctive formulation for the simultaneous optimization and heat integration of systems with unclassified process streams, variable inlet and outlet stream temperatures, variable flow rates, isothermal process streams, and multiple utilities.

The proposed disjunctive model also presents an extension to allow the estimation of the area assuming vertical heat transfer. The model takes advantage of the disjunctive formulation of the 'max' operator to explicitly determine all the 'kink' points in the hot and cold balanced composite curves. The formulation uses an implicit ordering to determine adjacent points in the balanced composite curves for area estimation.

Four case studies were presented to illustrate the performance of the proposed approach. The first three examples include a large number of process streams, and the fourth example introduces the area estimation and illustrates the effect of the preprocessing on the numerical behavior of the model. The calculations of the problems were performed in GAMS, using BARON as a solver.

The results show that the new disjunctive model has excellent numerical performance, even in large-scale models. The proposed model has the advantage of reducing the number of equations and binary variables, which allows the reduction of CPU time when solving problems.

In addition, the model has been extended to simultaneously estimate the area of the heat exchanger network, and consequently its investment cost. Although the performance of the model depends on the characteristics of the problem –how large are the bounds on the temperatures and the degree of overlap between those bounds–, it is possible to obtain good solutions with a relatively small gap for medium size problems.

Universitat d'Alacant
Universidad de Alicante

Contents lists available at ScienceDirect

Computers and Chemical Engineering

journal homepage: www.elsevier.com/locate/compchemeng

Disjunctive Model for the Simultaneous Optimization and Heat Integration with Unclassified Streams and Area Estimation

Natalia Quirante, Ignacio E. Grossmann and José A. Caballero

Computers & Chemical Engineering, 108 (2018), pp. 217 – 231.

(DOI 10.1016/j.compchemeng.2017.09.013)

Article Info

Article history:

Manuscript received 20 Jun 2017

Manuscript revised 13 Sep 2017

Accepted 14 September 2017

Available online 20 Sep 2017

Keywords:

Simultaneous optimization

Heat integration

Variable temperatures

Disjunctive model

Unclassified streams

Abstract

In this paper, we propose a disjunctive formulation for the simultaneous chemical process optimization and heat integration with unclassified streams –streams that cannot be classified *a priori* as hot or cold streams and whose final classification depends on the process operating conditions–, variable inlet and outlet temperatures, variable flow rates, isothermal process streams, and the possibility of using different utilities.

The paper also presents an extension to allow area estimation assuming vertical heat transfer. The model takes advantage of the disjunctive formulation of the 'max' operator to explicitly determine all the 'kink' points on the hot and cold balanced composite curves and uses an implicit ordering for determining adjacent points in the balanced composite curves for area estimation.

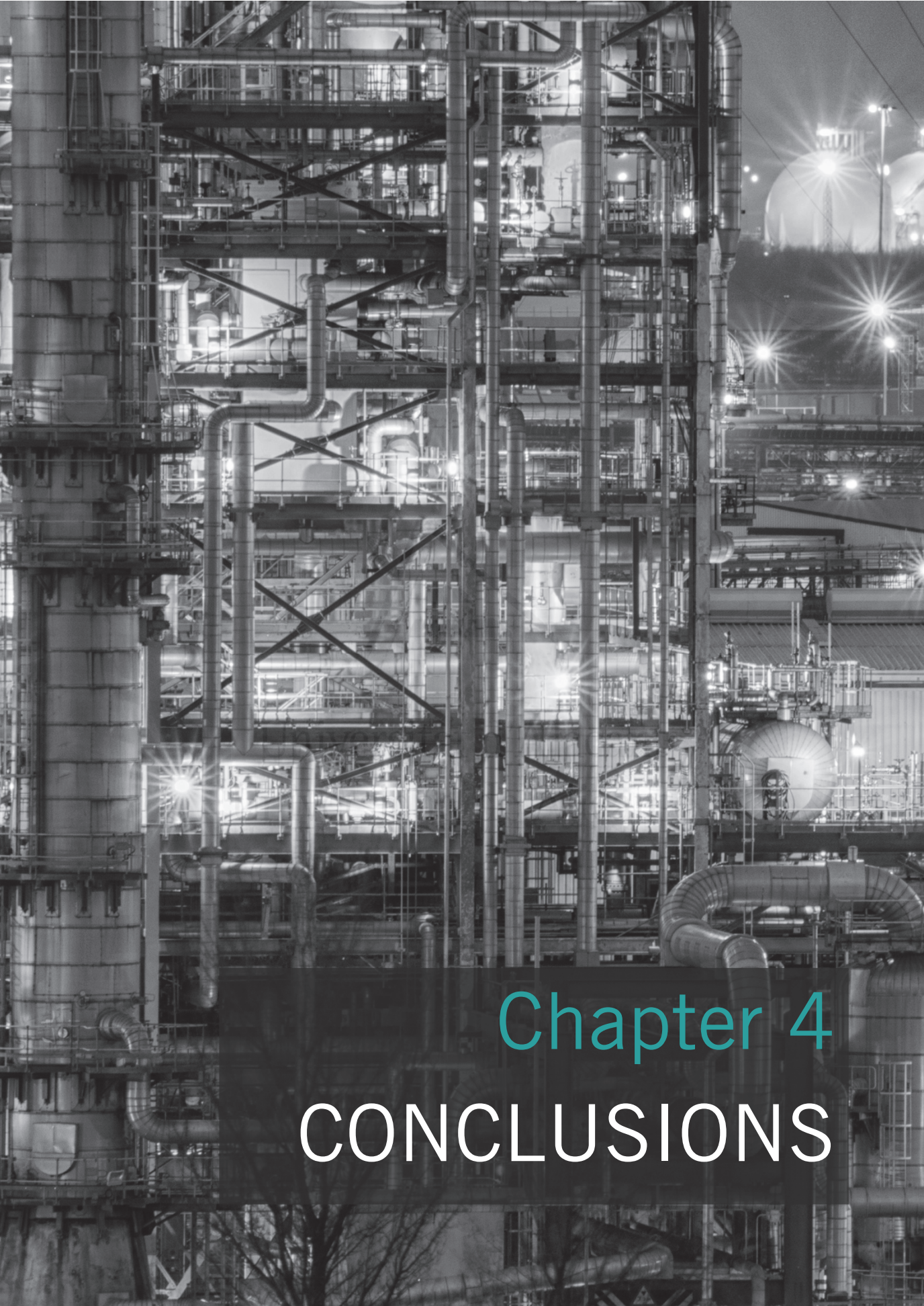
The numerical performance of the proposed approach is illustrated with four case studies. Results show that the novel disjunctive model of the pinch location method has excellent numerical performance, even in large-scale models.

Universitat d'Alacant
Universidad de Alicante

Highlights

* Disjunctive formulation for simultaneous optimization and heat integration.
* It involves unclassified process streams with variable inlet/outlet temperatures.
* Extension of the model to allow area estimation assuming vertical heat transfer.
* Four examples illustrate the numerical performance of the proposed approach.
* The disjunctive formulation has excellent numerical performance.

Universitat d'Alacant
Universidad de Alicante



Chapter 4
CONCLUSIONS

Universitat d'Alacant
Universidad de Alicante

Chapter 4.

Conclusions

Taking into consideration the results presented in Chapter 3, the most important conclusions of this Doctoral Thesis are highlighted below.

In order to achieve the first main objective of this Thesis, surrogate models have been studied and evaluated to facilitate and substantially improve the simulation-based optimization of chemical processes.

* The strategy developed and presented in Publication 1 discusses how to solve the problems associated with the resolution of optimization models based on simulators. The basic idea is to replace the rigorously simulated models (of different configurations and column sequences) by surrogate models. In order to build the metamodels, the Kriging algorithm was selected, since this algorithm allows obtaining accurate surrogate models from small data sets.

  The results obtained with the Kriging metamodels are very close to those obtained when performing the rigorous simulation of the systems, presenting average errors below 5 %. The mean error increases slightly when the number of independent variables becomes greater, although it is possible to obtain accurate surrogate models with up to seven degrees of freedom. However, in all cases, the strategy followed provides excellent results compared to those obtained with the rigorous simulation. In conclusion, this technique allows replacing, in a fast and accurate way, the unit operations that might produce numerical problems during the optimization by surrogate models generated from rigorous models.

* The objective of Publication 2 consists of the multiobjective optimization of a sour water treatment plant from an oil refinery. The objective function was simultaneously to minimize the operating costs of the process, the energy consumption and the environmental impact of the treatment plant. The presented procedure is based on the implementation of surrogate models in order to optimize large-scale processes based on simulators. Therefore, the strategy followed is to replace for surrogate models all those process units that can generate numerical problems during the optimization, keeping in the

simulator the remaining units that do not introduce numerical noise. In addition, the equations related to heat integration and the equations related to life cycle assessment are defined as explicit equations.

The results obtained show that it is possible to use surrogate models to optimize this type of optimization problems. At the same time, the multiobjective optimization allows achieving great economic and energy savings. In addition, as a consequence of the multiobjective optimization, the reduction of the environmental impact can be significant, about 49 % with respect to the plant without optimizing. In conclusion, this technique allows replacing the unit operations that might produce numerical problems during the optimization by surrogate models generated from rigorous models, which makes it easy to optimize this type of problems in an accurate way.

* In Publication 3, the optimization of a superstructure using surrogate models is proposed. All units that might produce numerical problems in the optimization are replaced by metamodels based on Kriging interpolation, in this case, both distillation columns and chemical reactors. Through the superstructure, all the alternatives of interest are proposed to produce the desired product. Once the plant is optimized, the heat exchanger network is generated and the financial risk of the plant is studied.

  The results obtained from this study show that surrogate models can also be employed to solve mixed-integer nonlinear programming problems. In addition, heat integration achieves significant energy and economic savings, with the consequent reduction of the environmental impact. The use of surrogate models in the simulation-based optimization of chemical processes is, in fact, highly satisfactory. This work is currently under review.

Within the second general objective of this Thesis, an alternative methodology has been developed for the simultaneous optimization of chemical processes and heat integration.

* In Publication 4, a new model is proposed to reduce the numerical difficulties associated with the use of the 'max' function. For this, a disjunction is applied directly to the operator. An important feature of the presented model is that a supplementary variable is used to reformulate the system, which is translated into a reduction in the number of binary variables and the number of equations.

This fact makes this model very competitive compared to the other models, obtaining better results both in calculation time and in the degree of relaxation of the problem.

The results obtained show that the model developed is very competitive compared to the models proposed by Grossmann et al. and Navarro-Amorós et al.

* Finally, Publication 5 extends the study carried out in the previous publication, considering that in a system there may be process streams that are not classified *a priori* as hot or cold streams. In addition, an extension of the model is presented to estimate the area of the heat exchanger network (and therefore, to estimate the costs) assuming vertical heat transfer.

  As in the previous publication, the presented model contains a smaller number of variables and equations that the other alternative reformulations. This fact makes the developed model very competitive compared to the other models. In addition, the results show that the new reformulation is robust and numerically efficient in large-scale problems.

Universitat d'Alacant
Universidad de Alicante

Universitat d'Alacant
Universidad de Alicante

Conclusiones

Considerando los resultados expuestos en el Capítulo 3, a continuación se destacan las conclusiones más relevantes de esta Tesis Doctoral.

Dentro del primer objetivo general de la Tesis se han estudiado y evaluado los modelos surrogados para facilitar y mejorar sustancialmente la optimización de los procesos químicos basada en simuladores.

* La estrategia desarrollada y presentada dentro de la Publicación 1 plantea cómo solventar los problemas asociados a la resolución de modelos de optimización basados en simuladores. La idea básica consiste en sustituir los modelos simulados rigurosamente (de distintas configuraciones y secuencias de columnas) por modelos surrogados. Para construir los metamodelos se empleó el algoritmo de Kriging, ya que este algoritmo permite obtener modelos surrogados precisos a partir de conjuntos de datos reducidos.

  Los resultados obtenidos con los modelos Kriging son muy próximos a los obtenidos al realizar la simulación rigurosa de los sistemas, presentando errores medios por debajo del 5 %. El error medio se incrementa ligeramente al aumentar el número de variables independientes, aunque es posible obtener modelos surrogados precisos con hasta siete grados de libertad. Sin embargo, en todos los casos, la estrategia seguida proporciona excelentes resultados comparados con los obtenidos con la simulación rigurosa. En conclusión, esta técnica permite sustituir, de forma rápida y precisa, operaciones unitarias que podrían producir problemas numéricos durante la optimización por modelos surrogados generados a partir de los modelos rigurosos.

* El objetivo de la Publicación 2 consiste en la optimización multiobjetivo de una planta de tratamiento de aguas provenientes de una refinería de petróleo. La función objetivo consistía en minimizar simultáneamente el coste de operación del proceso, el consumo de energía y el impacto ambiental de la planta de tratamiento. El procedimiento presentado se basa en la implementación de los modelos surrogados con el fin de optimizar procesos a gran escala basados en simuladores. De este modo, la estrategia seguida consiste en sustituir por modelos surrogados todas aquellas unidades del proceso que puedan generar problemas numéricos durante la optimización, manteniendo en el simulador el

Universitat d'Alacant
Universidad de Alicante

resto de unidades que no introducen ruido numérico. Asimismo, las ecuaciones relacionadas con la integración energética y el análisis del ciclo de vida de la instalación se definen en forma de ecuaciones explicitas.

Los resultados obtenidos muestran que es posible el uso de los modelos surrogados para optimizar este tipo de problemas de optimización. Al mismo tiempo, la optimización multiobjetivo permite conseguir grandes ahorros económicos y energéticos. Además, como consecuencia de la optimización multiobjectivo, la reducción del impacto ambiental puede llegar a ser muy significativa, en torno al 49 % con respecto a la planta sin optimizar. En conclusión, esta técnica permite sustituir las operaciones unitarias que podrían producir problemas numéricos durante la optimización por modelos surrogados generados a partir de modelos rigurosos, facilitando la optimización de este tipo de problemas de una manera precisa.

* En la Publicación 3 se plantea la optimización de una superstructura usando modelos surrogados. Todas las unidades que podrían introducir problemas numéricos en la optimización se sustituyen por metamodelos basados en interpolación Kriging, en este caso, tanto columnas de destilación como reactores químicos. Mediante la superestructura se plantean todas las alternativas de interés para producir el producto deseado. Una vez optimizada la planta, se genera la red de integración de energía y se estudia el riesgo financiero de la planta.

  Los resultados obtenidos de este estudio muestran que los modelos surrogados también pueden ser empleados para resolver problemas de programación no lineal con variables binarias. Además, con la integración energética se consiguen importantes ahorros energéticos y económicos, con la consiguiente reducción del impacto ambiental. Definitivamente, el uso de los modelos surrogados para optimizar procesos basados en simuladores resulta muy satisfactorio. Este trabajo se encuentra actualmente en la fase de revisión.

Dentro del segundo objetivo general de la Tesis, se ha desarrollado una metodología alternativa para la optimización de procesos químicos y la integración de energía simultánea.

* En la Publicación 4 se plantea un nuevo modelo para eliminar las dificultades numéricas asociadas a con el uso de la función ‘max’. Para ello, se aplica una

disyunción directamente sobre el operador. Una característica importante del modelo presentado es que se utiliza una variable suplementaria para reformular el sistema, lo que se traduce en una reducción del número de variables binarias y el número de ecuaciones. Este hecho hace que este modelo resulte muy competitivo frente a otros modelos, consiguiendo mejores resultados tanto en tiempo de cálculo como en el grado de relajación del problema.

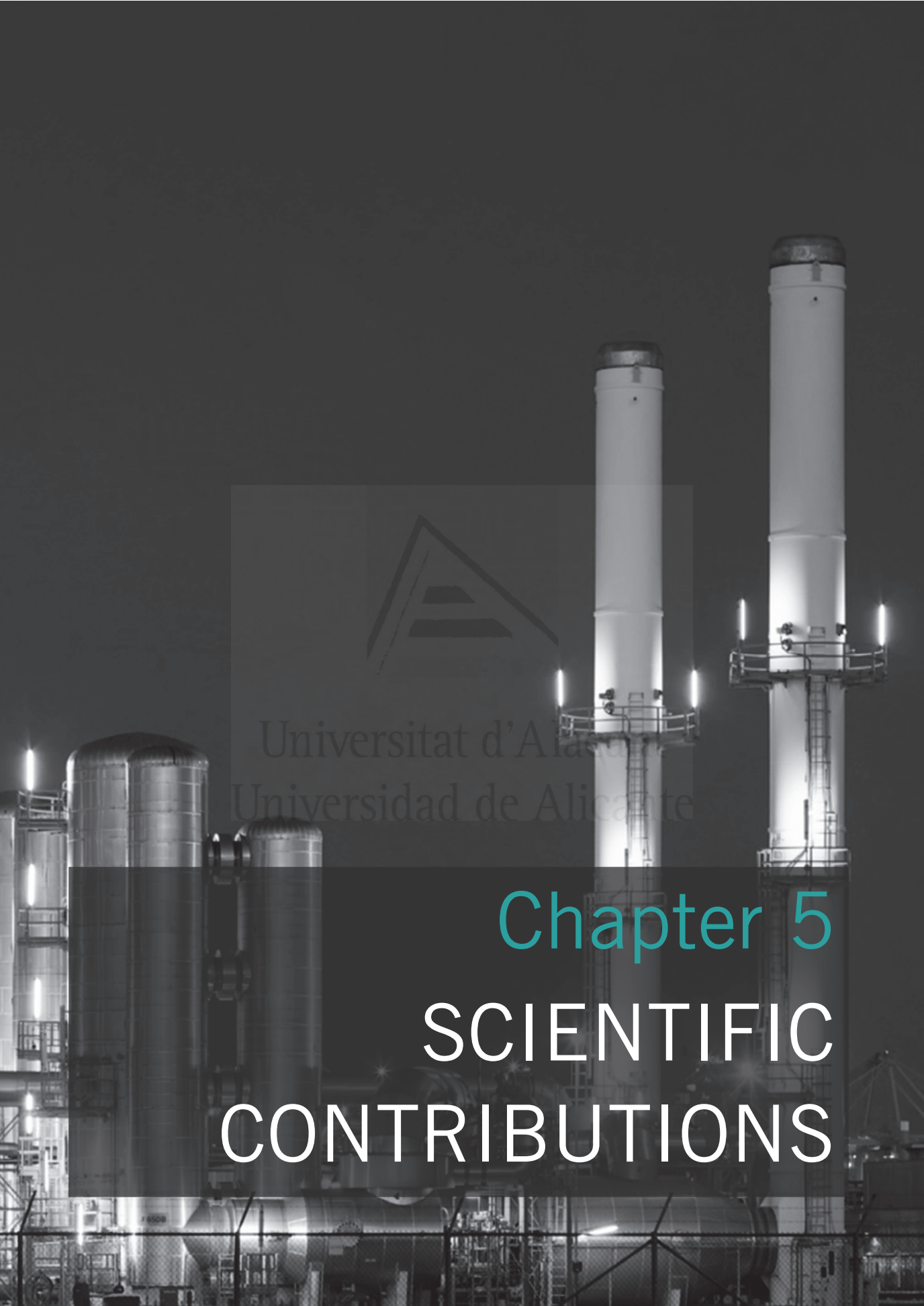
Los resultados obtenidos muestran que el modelo desarrollado es muy competitivo en comparación a los modelos propuestos por Grossmann et al. y Navarro-Amorós et al.

* Por último, en la Publicación 5 se extiende el estudio realizado en la publicación anterior, considerando que en un sistema pueden existir corrientes de proceso que no estén clasificadas como corrientes frías o calientes, *a priori*. Además, se presenta una extensión del modelo para estimar el área de intercambio (y por consiguiente, estimar los costes) asumiendo que la transferencia de calor es vertical.

  Del mismo modo que en la publicación anterior, el modelo presentado contiene un menor número de variables y ecuaciones que el de las reformulaciones alternativas. Este hecho hace que el modelo desarrollado resulte muy competitivo frente a los otros modelos. Además, los resultados demuestran que la nueva reformulación es robusta y numéricamente eficiente en problemas a gran escala.

Universidad de Alicante

Universitat d'Alacant
Universidad de Alicante



Universitat d'Alacant
Universidad de Alicante

Chapter 5

SCIENTIFIC CONTRIBUTIONS

Universitat d'Alacant
Universidad de Alicante

Chapter 5.

Scientific Contributions

In addition to the publications that have been used to develop this Doctoral Thesis, the candidate has collaborated in other projects, which have led to the publication of journal articles, book chapters, and conference contributions. All these scientific contributions are presented in Chapter 5.

5.1. Journal Articles

* **Quirante N**, Javaloyes J, Caballero JA. Hybrid Simulation-Equation Based Synthesis of Chemical Processes. Sent to: *Chemical Engineering Research & Design*. [Under review].

* **Quirante N**, Grossmann IE, Caballero JA. Disjunctive Model for the Simultaneous Optimization and Heat Integration with Unclassified Streams. *Computers & Chemical Engineering* 2018; 108:217-231.

* **Quirante N**, Caballero JA, Grossmann IE. A Novel Disjunctive Model for the Simultaneous Optimization and Heat Integration. *Computers & Chemical Engineering* 2017; 96:149-168.

* **Quirante N**, Caballero JA. Large Scale Optimization of a Sour Water Stripping Plant Using Surrogate Models. *Computers & Chemical Engineering* 2016; 92: 143-162.

* **Quirante N**, Javaloyes J, Caballero JA. Rigorous Design of Distillation Columns Using Surrogate Models Based on Kriging Interpolation. *AIChE Journal* 2015; 61(7): 2169-2187.

Universitat d'Alacant
Universidad de Alicante

5.2. Book Chapters

* **Quirante N**, Caballero JA, Grossmann IE. A New Disjunctive Formulation for the Simultaneous Optimization and Heat Integration with Cold/Hot and Unclassified Streams. In: Espuña A, Graells M, Puigjaner L, editors. *Computer Aided Chemical Engineering*; Amsterdam, The Netherlands: Elsevier; 2017. Vol 40: p. 2167-2172. ISBN: 978-0-444-63965-3.

* Vázquez D, **Quirante N**, Ruiz-Femenia R, Fernández MJ, Salcedo-Díaz R, Gómez-Rico MF, Caballero JA. Systematic Methods for Inherently Safer Process Design: Comparison among Inherent Safety Indexes by Dimensionality Reduction. In: Espuña A, Graells M, Puigjaner L, editors. *Computer Aided Chemical Engineering*; Amsterdam, The Netherlands: Elsevier; 2017. Vol 40: p. 1237-1242.
ISBN: 978-0-444-63965-3.

* Onishi VC, **Quirante N**, Caballero JA. Synthesis of Work and Heat Exchanger Networks with Unclassified Process Streams at Sub-Ambient Conditions. In: Varbanov PS, Su R, Lam HL, Liu X, Klemeš JJ, editors. *Chemical Engineering Transactions*; Italy: AIDIC Servizi S.r.L; 2017. Vol 61.
ISBN: 978-88-95608-51-8.

* **Quirante N**, Caballero JA. Optimization of a Sour Water Stripping Plant Using Surrogate Models. In: Kravanja Z, Bogataj M, editors. *Computer Aided Chemical Engineering*; Amsterdam, The Netherlands: Elsevier; 2016. Vol 38: p. 31-36.
ISBN: 978-0-444-63428-3.

* **Quirante N**, Javaloyes J, Ruiz-Femenia R, Caballero JA. Optimization of Chemical Processes Using Surrogate Models Based on a Kriging Interpolation. In: Krist V, Gernaey JKH, Rafiqul G, editors. *Computer Aided Chemical Engineering*; Amsterdam, The Netherlands: Elsevier; 2015. Vol 37: p. 179-184.
ISBN: 978-0-444-63429-0.

5.3. Conference Contributions

* **Quirante N**, Caballero JA, Grossmann IE. *A New Disjunctive Formulation for the Simultaneous Optimization and Heat Integration with Cold/Hot and Unclassified Streams*. Presentation format: Poster. "27th European Symposium on Computer Aided Process Engineering". Barcelona (Spain). 01/10/2017 – 05/10/2017.

* Vázquez D, **Quirante N**, Ruiz-Femenia R, Fernández MJ, Salcedo-Díaz R, Gómez-Rico MF, Caballero JA. *Systematic Methods for Inherently Safer Process Design: Comparison among Inherent Safety Indexes by Dimensionality Reduction*. Presentation format: Poster. "27th European Symposium on Computer Aided Process Engineering". Barcelona (Spain). 01/10/2017 – 05/10/2017.

* **Quirante N**. *CO_2 Reuse in Direct DME Synthesis from Syngas*. Presentation format: Oral. "CAPE Forum 2017". Athens (Greece). 06/09/2017 – 08/09/2017.

* Onishi VC, **Quirante N**, Ravagnani M, Caballero JA. *Synthesis of Work and Heat Exchanger Networks with Unclassified Process Streams at Sub-Ambient Conditions*. Presentation format: Oral. "20th Conference on Process Integration, Modelling and Optimisation for Energy Saving and Pollution Reduction". Tianjin (China). 21/08/2017 – 24/08/2017.

* **Quirante N**, Caballero JA. *Optimization of a Sour Water Stripping Plant Using Surrogate Models.* Presentation format: Oral. "26th European Symposium on Computer Aided Process Engineering". Portorož (Slovenia). 12/06/2016 – 15/06/2016.

* Salcedo-Díaz R, Ruiz-Femenia R, Caballero JA, Javaloyes J, **Quirante N**. *Aplicación de la teoría de la simulación modular para el manejo eficiente de los simuladores de procesos comerciales*. Presentation format: Poster. "III Congreso de Innovación Docente en Ingeniería Química". Alicante (Spain). 21/01/2016 – 23/01/2016.

* **Quirante N**, Javaloyes J, Ruiz-Femenia R, Caballero JA. *Optimization of Chemical Processes Using Surrogate Models Based on a Kriging Interpolation.* Presentation format: Oral highlight + poster. "12th International Symposium on Process Systems Engineering and 25th European Symposium on Computer Aided Process Engineering". Copenhagen (Denmark). 31/05/2015 – 04/06/2015.

* **Quirante N**, Javaloyes J, Caballero JA. *Optimization Using Surrogate Models Based on a Kriging Interpolation: Application to the Rigorous Design of Distillation Columns.* Presentation format: Oral. "13th Mediterranean Congress of Chemical Engineering". Barcelona (Spain). 30/09/2014 – 03/10/2014.

* **Quirante N**, Caballero JA. *Logic-Based Algorithms for the Integration of Different Models in the Synthesis of Chemical Processes: Application to the Design of a Power Utility Plant*. Presentation format: Poster. "13th Mediterranean Congress of Chemical Engineering". Barcelona (Spain). 30/09/2014 – 03/10/2014.

* Javaloyes J, **Quirante N**, Ruiz-Femenia R, Caballero JA. *Optimization of chemical processes using chemical simulators and machine learning algorithms*. Presentation format: Poster. "13th Mediterranean Congress of Chemical Engineering". Barcelona (Spain). 30/09/2014 – 03/10/2014.

* Reyes-Labarta JA, Javaloyes J, **Quirante N**, Caballero JA. *Analysis of the improving in conventional distillation columns through the optimal design of equivalent internally heat-integrated distillation columns*. Presentation format: Poster. "13th Mediterranean Congress of Chemical Engineering". Barcelona (Spain). 30/09/2014 – 03/10/2014.

5.4. Conference Attendance

* Computer Aided Process Engineering Center (CAPE) "27th European Symposium on Computer Aided Process Engineering (ESCAPE-27)". Barcelona (Spain). 01/10/2017 – 05/10/2017.

* Computer Aided Process Engineering (CAPE) "CAPE Forum 2017". Athens (Greece). 06/09/2017 – 08/09/2017.

* Process Integration Research Consortium "XXXIII PIRC Annual Research Meeting 2016". Manchester (UK). 12/10/2016 – 13/10/2016.

* Computer Aided Process Engineering Center (CAPE) "26th European Symposium on Computer Aided Process Engineering (ESCAPE-26)". Portorož (Slovenia). 12/06/2016 – 15/06/2016.

* Departamento de Ingeniería Química e Instituto Universitario de Ingeniería de los Procesos Químicos de la Universidad de Alicante "III Congreso de Innovación Docente en Ingeniería Química". Alicante (Spain). 21/01/2016 – 23/01/2016.

* Computer Aided Process Engineering Center (CAPE) "12th International Symposium on Process Systems Engineering & 25th European Symposium on Computer Aided Process Engineering (PSE2015/ESCAPE-25)". Copenhagen (Denmark). 31/05/2015 – 04/06/2015.

* Sociedad Española de Química Industrial e Ingeniería Química "13th Mediterranean Congress of Chemical Engineering (13MCCE)". Barcelona (Spain). 30/09/2014 – 03/10/2014.

5.5. Research Stay Abroad

* School of Chemical Engineering and Analytical Science. University of Manchester (United Kingdom [UK]).
* Principal investigator: Prof. Robin Smith.
* Duration: 3 months (from 01/09/2016 to 01/12/2016).
* Summary of developed activity:

  During the stay, I acquired the knowledge for the development of a life cycle inventory. The inventory was based on data available in the literature. Also, I learned to build an LCA model using GaBi software, a commercial software widely used in the academia and industry. As a case study, the inventory of a membrane system for the oxy-combustion process for CO_2 capture was applied.

This research stay has been possible thanks to the support provided by the Spanish Ministry of Economy and Competitiveness. Grants for pre-doctoral mobility for short stays in Spanish and foreign R&D centers 2016 (EEBB-I-16-11761).

Universitat d'Alacant
Universidad de Alicante

5.6. Award

* 2nd Prize of the EURECHA Student Contest Problem 2017.
* Organized by: European Committee for the Use of Computers in Chemical Engineering Education (EURECHA).
* Title: Carbon CO_2 Reuse in Direct DME Synthesis from Syngas.
* Authors: Carrero A, Medrano JD, **Quirante N**.
* Presentation of the work in CAPE-Forum Conference. Athens, Greece. 06/09/2017 – 08/09/2017.

Rigorous Design of Chemical Processes:

Surrogate Models and Sustainable Integration

Natalia Quirante Arenas

The development of efficient chemical processes, from an economic and environmental point of view, is one of the main objectives of the Chemical Engineering. To achieve this goal, in the last years, advanced tools are being used for design, simulation, optimization, and synthesis of chemical processes, which allow us to obtain more efficient processes and with the least possible environmental impact.

The main objective of this Thesis is based on the development of simulation and optimization tools in order to improve process energy efficiency, which reduces the environmental impact. Specifically, this Doctoral Thesis is composed of two main studies, which are the concrete objectives to achieve:

* Study and evaluation of surrogate models to improve the simulation-based optimization of chemical processes.
* Development of new models for the simultaneous optimization and heat integration of chemical processes.

Universitat d'Alacant
Universidad de Alicante