

Next Generation Steam Cracking Reactor Concept

Marco van Goethem

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PROEFSCHRIFT

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He has made everything beautiful in its time. He has also set eternity in the hearts of men; yet they cannot fathom what God has done from beginning to end. (Ecc. 3:11)

God heeft alles wat er is de goede plaats in de tijd gegeven, en ook heeft hij de mens inzicht in de tijd gegeven. Toch kan de mens het werk van God niet van begin tot eind doorgronden. (Pred. 3:11)

Be warned, my son, of anything in addition to them. Of making many books there is no end, and much study wearies the body. Now all has been heard; here is the conclusion of the matter: Fear God and keep his commandments, for this is the whole duty of man. (Ecc. 12:12-13a)

En tot slot, mijn zoon, nog deze waarschuwing: er komt geen einde aan het aantal boeken dat geschreven wordt, en veel lezen mat het lichaam af. Alles wat je hebt gehoord komt hierop neer: heb ontzag voor God en leef zijn geboden na. (Pred. 12:12-13a)

Preface

The work in front of you was initiated in the year 1998. In this year I received my Master of Science degree, which is the most logical moment to start with a PhD position. I already received a job offer from Technip Benelux B.V. (at that time KTI). In that same year my wife and I would get married and she would start her study at the college university in Rotterdam. The decision to take the job offer was clearly a reflected of my wish to start a family. My job at Technip was a continuation of my master's project, to develop an equation-based version of the SPYRO[®] program, which I claimed to be feasible. Together with several colleagues, under the guidance of Dr. Cor van Leeuwen (past away in 1999) the first version of this new program was created. During the annual performance evaluation I always mentioned my desire to do a PhD. Technip Benelux B.V. has an innovative working environment and exploratory research opportunities come along from time to time. This resulted mid 2001 in an invitation from my manager Simon Barendregt to write a research proposal for a PhD project. In July 2003 I started my research to the "next generation steam cracking process" in the Process System Engineering group at Technical University of Delft under the supervision of Johan Grievink, Peter Verheijen and Jacob Moulijn.

The research project had to be combined with my regular work at Technip, for four years I could spend two days per week on my PhD work. The challenge for my supervisors was to get me out of the engineering mindset and push me into the scientific mindset. This scientific working environment was a necessary prerequisite to obtain a deep understanding in the fundamentals of the steam cracking reactor. The partitioning of work was in the first couple of years not an issue but as my carrier progressed I had to execute higher priority project at Technip. This resulted in a delay of one and a half year. At the end of 2008 I had completed all my scientific work, which is described in four articles. After playing around with the phenomena patients I got the approval for the defence of my PhD thesis, early 2010. Now my work is completed, I can state that the final outcome of my research project fills me with pride.

At this point in time, I wish to express my gratitude to all the people who have contributed to this thesis. Firstly, I would like to thank Simon Barendregt for making this research project possible and his support during all these years.

Secondly, I am indebted to Johan Grievink for improving my abstract thinking and his effort to complete this thesis. I am grateful to Jacob Moulijn for showing the importance of the broad outlines. Special thanks for Peter Verheijen who encouraged me to seek my boundaries and beyond. Also his critical remarks and scientific awareness are very much appreciated.

Thirdly, I would like to thank all my colleagues at Technip Benelux B.V. and students at the Delft University of Technology, all of whom supported me during my research period. Special thanks to all my family and friends for their interest in my research work.

Finally, I thank my lovely wife Karin for her love, support and above all her patients to endure my long times behind my laptop. Also my children, Loïs, Jonas and Levi, I want to thank them for their sympathy when I was working instead of playing, irrespective of their understanding of my activities.

Delft, August 2010 Marco van Goethem

Summary

Next generation steam cracking reactor concept

The steam cracking process is an important asset in the hydrocarbon processing industry. The main products are lower olefins (ethylene, propylene, butylenes) and hydrogen, with ethylene being the world's largest volume organic chemical at a worldwide capacity of ≈ 120 million tonnes per year. Feed stocks are hydrocarbons (C₂₊) such as: ethane, LPG, naphtha's, gas condensates and gas oil. The olefin yield is predominantly determined by the steam cracking furnaces. These are retrofits of common heating furnaces made capable of adding a large energy flux at high temperature levels to drive endothermal cracking reactions.

Evolutionary design has led to the current state-of-the-art cracking furnaces. The steam cracking technology has developed from an empirical approach to design and operations to a deep, model-based understanding. Models can predict what is happening in the cracking coils and the resulting olefin yields, given the feed conditions, the coil configuration and incoming heat fluxes. Due to extensive optimisation of design and operation, current steam cracking has become "mature". Yet, a clear insight is lacking how far current olefin yields are removed from the theoretical maximum according to fundamental mechanisms. Finding a significant potential for yield improvement would justify a step-out in cracking reactor technology. Identifying such a potential is the main driver for this thesis research. The approach taken is to explore and exploit the fundamental opportunities the chemistry "offers" instead of taking the more restrictive view of what the current equipment is "capable of" or "limiting to".

The research goal is to search for the intrinsic optimal steam cracking reaction conditions, pushing the olefin yields to the maximum that the fundamental reaction kinetic models allow for. Such optimal conditions can serve as targets for developing a next generation steam cracking reactor. This search is based on mathematical modelling and optimisation, needed prior to any expensive experimental validation.

To get to that goal we have:

- **First** Identified alternative process concepts published in the literature and assessed against a set of ideal performance requirements;
- **Second** Developed the concepts and software for an equation based modelling tool suitable for optimisation of large scale reaction kinetic models;
- Third Developed a modelling strategy for olefins yield optimisation capable of embedding fundamental kinetic models into a model of a new reactor concept for homogeneous reactions with distributed feed allocation and macromixing;
- Fourth Applied the optimisation tool to the reactor concept model and an advanced reaction kinetic model for steam cracking, SPYRO[®], for a **model-based synthesis** of optimal reaction conditions for maximum olefin yields, covering a wider range of operating conditions than currently feasible.

First we have reviewed alternative process concepts from literature for the production of ethylene on industrial scale. These alternative process concepts are assessed on their compliance with a new set of ideal (performance) requirements. The features of an ideal process involve a maximum olefin yield, no remains of energy carriers or auxiliary chemicals in the product, minimal ecological impact, minimum energy input per unit product, high availability, and a low degree of complexity of the reaction section. It appears that specific energy requirements of the processes are poorly reported in the available literature. Therefore, these requirements are systematically determined from simulations with Aspen Plus software and the aid of SPYRO[®] for an ethylene plant with a fixed ethane feed. Although none of the reported processes fulfils all ideals, the new combination of the adapted firing furnace with ceramic reactors internals and the shock wave reactor come close. While this review is suited to identify the best available technology it is incapable to identify the maximum achievable yield. Therefore, we are taking the following optimisation approach as well.

Secondly, the yield optimisation approach needs advanced modelling and computation tools as enablers. SPYRO[®] Suite 7 was used as the reference software tool as it comprises an implementation of the required reaction kinetic model. Generating alternative software implementations of this kinetic model is practically out of reach due to excessive efforts. As the kinetic model needs to be coupled to a new reactor model and be interfaced with an optimiser, a symbolic modelling facility had to be added to the existing equation-based flow sheet package, SPYRO[®] Suite 7. The functional specifications for the symbolic modelling facility focus on minimising and easy detection of modelling errors by the modeller. For its implementation a sub-set of the gPROMS language is chosen, extended with some newly introduced attributes: spline construction, intermediate graphical results, and definition of a large number of simulations and optimisations via scenarios. The effectiveness of the symbolic model definition module was proven with this optimisation project.

Thirdly, the applied modelling and optimisation strategy is based on a physical decomposition approach focusing on the core chemistry & kinetics. I.e. the steam cracking process can be conceptually decomposed into several phenomena. The central phenomena are the chemical reactions, with stoichiometry and kinetics. Aspects of mechanistic energy transfer through the reactor wall or generated directly, and of momentum transfer are considered to be of secondary importance. The focus in this thesis is on the first step of this decomposition: finding optimal reaction conditions with respect to maximum olefin yields, using fundamental kinetics and species balances only. Energy and momentum balances must be addressed at a later stage of research. This decomposition is required due to a reduction of computational complexity and loads. As the reactions must occur in a reaction volume, a model of a new abstracted reactor concept is introduced. This concept, called d-RMix, allows homogeneous reactions to occur along a (one-dimensional) reactor volume coordinate, with a distributed allocation of feeds, withdrawal of products, and macro-mixing of the reaction medium. The temperature and (decreasing) pressure can be freely specified along the reactor volume coordinate. We have verified and validated this new d-RMix reactor model by using simple reaction-kinetic models (Van de Vusse) from the literature. Our results are compared with those published for another reactor synthesis method, namely the attainable region theory, and the match is perfect.

Fourth, having proven that our reactor synthesis tool is capable of reproducing existing test cases, it has been applied to olefin yield optimisation on basis of an industrially validated large kinetic scheme, $SPYRO^{\textcircled{B}}$. This scheme contains over 7000 reactions between 218 molecular and 27 radical species in the gas phase. The synthesis approach allows optimising the following degrees of freedom with respect to maximum olefin yield: feed distribution, product removal, intensity of macro-mixing, all along a reactor volume coordinate. Steam to feed ratio is kept fixed in these studies. Also the temperature profile is free along the reaction volume coordinate, though with a reaction temperature upper bound put at 1300 K, exceeding the current (metallurgical) bound by 100 K. The pressure is also a freely decreasing variable with a lower bound of 1 bar.

Results: For four different feed stocks optimisations of ethylene yield and of ethylene and propylene yields have been carried out with the following results. For the cracking of ethane a linear-concave unconstrained temperature profile with a (free) maximum temperature of ≈ 1260 K proves optimal, while all ethane should be supplied at the entrance of the reaction volume. The optimal conditions for ethane cracking are explained with the aid of the ethyl radical which is the most stable radical during ethane cracking. The ethyl radical is formed via hydrogen abstraction reactions of ethane. At higher temperatures ethyl decomposes to ethylene and at lower temperatures it is converted to ethane via a

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hydrogen abstraction reaction. The ethyl radical can also participate in addition reactions on unsaturated bounds and in radical termination reactions. The linearconcave temperature minimises the ethylene and ethyl concentration, limiting the secondary reactions, in the first part of the reaction volume to arrive at optimal ethylene yields. The theoretical maximum achievable ethylene yield for ethane cracking is found to be 66.8 wt% while in conventional cracking typically 55 wt% is considered to be the maximum value. This new optimum is constrained by the pressure at its lower bound of 1 bar. The resulting residence time is in the same order as with current technology.

For propane and heavier feed stocks an isothermal profile at the upper temperature bound is optimal, with dips at the beginning and the middle of the reaction volume coordinate. For these heavier hydrocarbon feeds a distribution along the reactor volume coordinate does result in higher yields. When optimising with respect to the sum of ethylene and propylene yields a significant higher propylene yield is obtained as compared with optimisation to ethylene yield only, hinting at economically attractive scenarios for shifting the balance from ethylene to propylene under suitable market conditions. Just as done for ethane cracking, the outcome of the optimisations are made plausible with the most stable radical, that is allyl $(CH_2CH = CH_2)$. Through the (distributed) injection of the fresh hydrocarbon feed the partial pressure is reduced which suppresses the secondary reactions and promotes the lower olefin producing initialisation reactions. The dips at the beginning and the middle of the reaction volume coordinate temper the ethylene consuming secondary reactions.

Having shown the potential for a significant yield increase, the next step on the research path to a new generation thermal cracking reactor will be to (experimentally) validate the model-based optimisation results. In the validation step the uncertainties in the optimal reaction conditions must be made visible. The SPYRO[®] kinetic model was applied outside the conventional operating window to arrive at the optimal reaction conditions. Therefore, in the next step possible uncertainties should be investigated by simulation and dedicated experiments. Especially the tendency to coke formation must be studied and modelled. If these model-based results are experimentally confirmed these optimal reaction conditions must be made possible by new (optimised) apparatus. The way forward would be to determine the required energy and momentum transfer rates to achieve the optimal reaction conditions within newly designed reactor geometry. This geometry should allow for short residence times with minimum pressure drop, plug flow regime and an axial distribution functionality of the hydrocarbon feedstock. Having established in this study that the steam cracking chemistry offers a potential for significantly higher olefins yields, these equipment engineering considerations pose a significant challenge to actually realise this potential and arrive at a next generation steam cracking reactor.

Marco van Goethem

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Chapter

Research objectives and approach

1.1 Introduction

Ethylene is world's largest organic petrochemical due to its application as raw material for intermediate base chemicals, such as polyethylene, ethylene oxide, and styrene. These base chemicals are applied in innumerable consumer products. Approximately 60% of the world ethylene demand is required for the production of polyethylene (Goodnight et al., 2008). The primary use of polyethylene is in plastic films for packaging and all kind of bags. Ethylene oxide is a raw material in the manufacturing of polyesters, ethylene glycols, surfactants and detergents. Styrene monomer is used mainly in polystyrene for packaging and insulation, as well as in styrene butadiene rubber. The usage of the consumer products is typical for prosperous societies and therefore the demand to ethylene is an indicator for prosperity.

The production of ethylene has been dominated by the steam cracking process since the end of World War II, with a worldwide production of ~128 million tonnes ethylene per year (2009). Propylene as main side product (~48 million tonnes) is often used as a swing to balance profitability. The feed stocks for steam cracking are hydrocarbons (C₂₊) such as ethane, liquefied petroleum gas(LPG), naphtha, gas condensate, and gas oil. Continuous research and development efforts are performed to achieve better ethylene yield and lower energy consumption. In addition, the use of alternative feed stocks such as biomass, natural gas, synthetic feed stocks from Fischer-Tropsch, methanol, and ethanol has also been pursued. In the next section we will highlight the limitations of the existing process structure both conversion by steam cracking and product separation, which is described in more detail in chapter 2. The focus is on the chemical conversion step, which is the steam cracking fundamentals.

1.2 Limitations of existing steam cracking technology

The current steam cracking technology has reached a stage of maturity in which improvements in yield and product selectivity are becoming increasingly difficult, due to engineering restrictions. The heart of the cracking technology is a highly heat integrated furnace with cracking coils suspended vertically in the radiant box through which the hydrocarbon feed, diluted with steam, flows (see Fig. 2.5). The hydrocarbons are being cracked at temperature levels above 600° C. at a low pressure (~ 1.5 bar) within a short residence time (< 1 sec). Due to the high reaction temperature the feed is preheated in the convection section of the furnace. The highly endothermic cracking reactions are being driven by an incoming high radiant heat flux ($\sim 95kW \cdot m^{-2}$) towards the cracking coil at a temperature level of $\sim 1050^{\circ}$ C external to the coil. The radiant heat flux is generated by combustion of fuel (mainly methane) at temperature levels of 1250°C. The radiant coil effluent is rapidly quenched (temperature $\sim 600^{\circ}$ C) to preserve the composition and to capture the thermal energy by the production of high pressure steam. The energy efficiency, the fraction of the fuel combustion energy used, of the furnaces achieved by the heat integration and the steam production is in the order of 90-94%. Typically, the ethylene yields are improved by raising the cracking temperature and reducing residence time. The increase in cracking temperature is obtained by increasing the firing duty inside the firebox through which the temperature of the cracking coils increase. Currently the metallurgy of the cracking coils is the limiting factor since the Cr-Ni alloys used have a maximum allowed tube skin temperature of $\sim 1150^{\circ}$ C.

The steam cracking process is an intermittent process because from time to time the production needs to be stopped to remove the coke deposit on the inside of the cracking coils via a controlled combustion under an atmosphere of steam and air. The removal of the coke deposit not only costs production time but also the cyclic temperature change reduces the life time of the hardware involved. A more extensive overview of conventional, currently applied steam cracking technology is presented in chapter 2.

The steam cracking process is known to be the most energy-consuming process in the chemical industry and globally uses approximately 8% of the sector's total primary energy use, excluding energy content of final products (Ren et al., 2006). Not surprisingly, a significant amount of effort has been put in reducing the energy requirement. Although currently the thermal efficiency of the cracking furnace is 94 %, an overall energy consumption reduction of the whole plant is required to meet environmental legislations on greenhouse gas emissions, such as CO_2 and NOx.

1.4 DRIVERS FOR SCIENTIFIC INNOVATIONS CRACKING TECHNOLOGY

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1.3 Drivers for scientific innovations in the steam cracking technology

Optimisation of design and operation of large capacity cracking furnaces justifies the need for accurate and reliable models for the reaction kinetics, the fluid flow and heat transfer. Although from the start of industrial-scale steam cracking general consensus was established about the free radical mechanism, due to the pioneering work of Rice and Herzfeld (1934), the first modelling of the steam cracking process was done with drastically simplified molecular kinetic models. This was done because modelling with such a large number of chemical species and reactions was not possible at that time. The availability of reliable kinetic and thermodynamic data (Benson, 1976) of the radical reactions involved made it viable to define and validate mechanistic kinetic models for practical conditions. In the 80s models were introduced involving more than 3000 chemical reactions with 150 molecular and radical species in the gas phase (Dente et al., 1979). The reactor model was kept simple by considering only one spatial coordinate in axial direction and assuming plug-flow for the gas. The effects of incoming heat transfer and pressure drop were taken into account. Through the developments in analysis techniques, economic interests for more heavy feed stocks e.g. vacuum gasoils, hydrotreated heavy gasoils, and the improvements made in computational sciences, hardware and software, the kinetics schemes were improved to meet the rising need of accurate predictions of the effluent composition of steam cracking units (Dente et al., 1992; Froment, 1992). In view of the large size and the repeating elements in the kinetic schemes, the creation of these schemes could be automated (Pierucci et al., 2005; van Geem et al., 2006). The values of the kinetics rate constants were estimated by ab-initio computations (Sabbe et al., 2007).

The cracking tube models have evolved from one to two-dimensional models for the proper description of the radial phenomena as for example the coke deposition in reaction tubes (van Geem et al., 2004). The radiant box is modelled threedimensionally to predict heat flux distributions, tube skin temperatures, NOx emissions (Habibi et al., 2007a,b; Frassoldati et al., 2007; Cuoci et al., 2007; Barendregt et al., 2008) and the effects of high emissive coatings on refractory walls (Stefanidis et al., 2008). The manufacturing of lower olefins via steam cracking is still the main processing route. Nevertheless, the contexts in terms of legislation, economy, safety, health and environment is changing over time and therefore research is required to adapted this production route to these changing boundaries. In the next section we will denote the context and the scope of our research.



Figure 1.1: Technical innovation options for ethylene production.

1.4 Context and scope of the research objectives

The research objectives are presented in a wider setting of achieving innovations for a chemical supply chain. These options can involve the product(s), the feeds and the processing, as shown in Fig. 1.1. The main application of lower olefins such as ethylene and propylene is in the making of polyolefins for the packaging industry. It is not unlikely that alternatives products will be used as substitutions in these applications. However, in this research we do not address this question. At present ethylene is mainly produced by steam cracking of hydrocarbons, such as ethane, naphtha, gas oil, but alternative feed sources and consequently conversion processes for lower olefins are becoming feasible. Neither these innovation options are dealt with in this study. We will focus on existing feed sources and their corresponding fundamental processing principles. Yet, we intend to break away from current processing techniques and therefore we consider alternatives for cracking within a tube that is suspended in a furnace, as well.

Many product and process inventions are driven and enabled by new knowledge. As a chemical manufacturing process is a complicated, multi-scale system, it is essential to indicate to which level(s) our research objectives are directed. Fig. 1.2 presents a multi-scale decomposition of what is relevant for our situation. A distinction is made between "Enabling technology", "Engineering" and "Reality" objects occurring in a physical reality. Engineering is a conceptual representation of the structure and behaviour of the "reality", useful for design of "real things" and optimization of their operation. In the central column of Fig. 1.2 "engineering" entities are stated and in the right hand side column the physical, "reality" are presented. Given the need for *chemical products* there must be suppliers. Usually, a producer has a portfolio of different chemicals. Which chemical products are produced by a supplier depends on what *business strategy*



Figure 1.2: Conceptual activities in development and design of chemical products and processes.

is applied. The business strategy directs and interacts with the manufacturing *policy and operations* that are available on a production site. The feed stock for a production site determines the operations that can be conducted and influence the manufacturing policy. The infrastructure of integrated process plants defines which feed stock can be applied and which processes can be built at a certain location. These factors influence the manufacturing policy and operations and vice versa. The feed stocks are converted to chemical products in an assembly of process equipments. Within the process equipment a single or multiple (intensified) *unit operations* are conducted/performed, for example reactions, phase changes and diffusional separations, etc. Process (unit) synthesis and optimization require the specification of a causal sequence of processing steps in terms of the required physical-chemical phenomena, such as reactions & mass, heat, momentum transport & transfer. Moving to the engineering column, the technology \mathcal{E} engineering trade-offs are to be posed as the formulation of the optimization problem in the context of a realisation of geometric degrees of freedom in design of equipment, and/or in the context of a realisation of temporal degrees of freedom by changing processing conditions. Simulations and optimisations for design & operations rely on the models of *physical-chemical phenomena*. These models are approximative descriptions of the behaviour (parameters/properties) of physical-chemical phenomena. The simulations and optimisations in business strategy, manufacturing policy and operations, technology & engineering and physical-chemical models are also critically dependent on efficient enabling technologies given in the left hand side column of Fig. 1.2, ICT and computational means.

The bottom level of the "Engineering" and "real things" columns in Fig. 1.2 are



Figure 1.3: Phenomena relevant for the steam cracking process.

the foundations of the chemical product and process design. The steam cracking process has evolved from an empirical understanding of performance and of the operations to an on-line use of rigorous models to optimise the performance and operations. The models have predictive capability with respect to what is happening in the cracking coils, given the coil configuration and the incoming heat fluxes as well as the feed conditions.

The objective of our research is to contribute to intensified cracking technology. By intensification we mean obtaining significantly higher olefin yields at better energy efficiency. To achieve this objective new operating conditions and design options will be searched for. Rather than starting experimentally, it is more efficient to do a model-based exploration first. To achieve inventions, going beyond marginal improvements to existing equipment, it is necessary to take a phenomena based modelling approach (Pohjola et al. (1994): "design is control over phenomena"). Therefore, it is expedient to analyse the phenomena playing a role in the steam cracking process (Fig. 1.3).

The central phenomena of the steam cracking process are the chemical reactions that drive the feed source to products under significant energy transfer required by the chemical reactions. Inside an axially distributed reaction volume the energy, momentum transfer and the distributed convective flow phenomena yield temperature, pressure and concentration distributions. The coking phenomena reduce the size of the reaction volume and increases resistance to incoming heat transfer. The coking rate is dependent on the local reaction conditions, temperature, pressure and concentrations and the composition of the reactor volume at its wall.

The main research issues can be now be stated as:

- 1. Are there viable alternative processing principles already offered in the literature which promise significant improvement of the olefin yields or in energy efficiency?
- 2. How far are olefin yields with current steam cracking technology removed from the maximum possible on fundamental grounds? What is, from the molecular perspective, the optimal path to maximum olefin yields and what

exactly are *intrinsic* limits to the maximisation of olefin yields? Can we find such limits, when using a fundamental reaction mechanism with rigorous thermodynamics and kinetics is considered, free from any additional rate constraints from the transport or transfer of heat and momentum?

3. Suppose there is scope indeed for significant yield improvements on basis of reaction thermodynamics and intrinsic kinetics. The optimum conditions may require temperature, pressure and velocity profiles that deviate considerably from those in existing steam cracking furnace designs. How can one design a new equipment set-up to get close to the optimal operating conditions for the theoretical maximum olefin yield? The challenge is to remove limitations on the energy and momentum transfers rates, as demanded for achieving the optimum yield conditions, as far as practically feasible at reasonable costs. Some of the new processing principles explored under 1 may contribute to inventing the required new cracking equipment.

1.5 Research approach

The problem statement above has been dealt with in practice in a heuristical sense. One looked at the application of a commonly known rule that short residence times at high temperature and low pressures should be applied to obtain a more selective steam cracking process. This loosely defined heuristic rule is applied in the development of the steam cracking furnace. Then, existing modelling tools, such as SPYRO[®] a dedicated simulation and optimisation program for the steam cracking process (Dente et al., 1979; van Goethem et al., 2001), are applied to arrive at the best design for a certain reactor configuration. This is the conventional approach. In this respect, we have observed that only limited research has been conducted to find the thermal and physical optimal reaction conditions for the steam cracking process (van Damme et al., 1984; Plehiers and Froment, 1987, 1991). Optimal is defined in the sense of giving maximised olefin yield. As mentioned, high temperatures give high yields but no conclusive research has been conducted with respect to the specific temperature profile that will give the highest possible yields. In particular, for a mature process it is important to know whether its performance is limited by equipment and operational constraints or by fundamental phenomena-based limits and whether there is still scope for further improvements. Similar observations can be made for the flow regime and the feed distribution: is plug flow indeed the best, must we supply all feed at the entrance of the reactor, etc?

We pursue a quest for the fundamental limits of the steam cracking process by making a decomposition into reaction fundamentals first and equipment engineering aspects for energy and momentum transfers next, while using modelling & computing as a vehicle to arrive a the optimal reactor configuration. This synthesis targeting approach consists of the following two steps:

STEP 1

Synthesize the optimal reaction conditions (under idealised assumptions) for achieving the highest olefin yield(s). These reaction conditions (temperature, pressure profiles and distribution allocation of species), are considered as free design decision variables along the reaction volume coordinate that can be manipulated to find better product yields. This formulation amounts to an optimal synthesis problem in a physico-chemical space. This synthesis problem will be solved for a range of practical feeds.

STEP 2

Translate the optimal reaction conditions into optimal geometry for (new) equipment and determine the required associated heat and momentum transfer fluxes.

This research, the synthesis targeting approach for the steam cracking process is enabled by the knowledge at the lowest decomposition level of a process. (see Fig. 1.2):

- 1. New computational and software engineering means are required and used for more efficient computations with large-scale, complex models.
- 2. Identifying the fundamental limits to olefin yields is based on hypothetical decoupling the reactions from inhibiting (limiting) heat and momentum transfer rates.

We are conceptually and computationally able to manipulate first-principle models of physical-chemical phenomena individually which is a key concept behind this research.

This thesis contains the realisation and outcome of STEP 1 in terms of optimal profiles for steam cracking for maximum olefin yields. The outcome of STEP 1 will be partially outside the application region of the current steam cracking processes. Therefore, it is recommended to do a validation of the STEP 1 results, possibly with experimental work, prior to continuing with STEP 2, the heat, momentum transfer and equipment engineering aspects. It is acknowledged that the expected high, fundamental ceilings to olefins yield, as obtained in STEP 1, may not yet be 100 % feasible in future practice due to still restrictive heat and momentum transfer or material limitations. Nevertheless, it will set a higher target for engineering development leading to intensified cracking units.

1.6 Structure of thesis

The existing steam cracking technology and an identification of its limitations is presented in chapter 2. Technical innovation options have been presented in Fig. 1.1 of this chapter, where the call-outs denote the options. From these options, the available alternative processing principles and technology will be covered with a review of the steam cracking technology available in the literature, chapter 3. We limit the scope of this work by considering some existing feed sources for the lower olefins, ethylene & propylene, production only.

None of these reported technologies addresses the question what is the maximum possible olefin yield from a fundamental perspective, allowing for a wider range of temperatures and pressures than currently considered. The option to optimise processing principles for current feeds and products is addressed by a new synthesis approach to identify the fundamental limits of the olefin production process and set fundamental targets for the future production processes of ethylene via the steam cracking chemistry.

In this research enhanced computational means, in terms of large mathematical problems being solved and optimised, are applied as vehicle to arrive at optimal reaction conditions. The effort and legal procedures required, to construct in the public domain a reliable kinetic model and transform this model into a fast and robust numerical reactor model, is considered a too large effort for this research project. Therefore we performed research on symbolic modelling of large systems of differential algebraic systems in SPYRO[®], which is described in chapter 4.

The fundamental ceiling of the olefin production is determined by the hypothetical decoupling from the heat and momentum transfer rates. The focus will be on the homogeneous reaction kinetics in the gas phase, options for distributed feed allocation, macro-mixing and distributed product withdrawal options for an abstracted one dimensional reactor concept. This amounts to developing a new distributed reactor synthesis model (d-RMix) which is presented and validated in chapter 5.

The application of this (reactor) synthesis approach to a large scale, industrially validated kinetic scheme is presented in the publication that is given in chapter 6. The result is a set of higher targets for olefin yields for a range of conventional feeds, to be realised in the next generation steam cracking reactor. Any proposed ultimate steam cracking reactor design can now be validated with the given constraints for the optimal olefin reaction conditions. We close this work with conclusions and some recommendations for the next research step, the required validation of results and engineering developments.

We have chosen to publish this work in several articles which constitute the chapters 3, 4, 5 and 6, therefore some overlap and differences will be present.

Chapter ∠

Current steam cracking technology

In this chapter we describe the state-of-the-art steam cracking process and highlight practical limitations of the current thermal cracking furnaces. This assessment of limitations is the basis for identifying the bandwidth of improvement between the current practical limitations and the fundamental restrictions, imposed by thermodynamics and intrinsic kinetic processes.

2.1 Location of steam cracking in the supply chain

We start with the location of the steam cracking process in the supply chain and subsequently zoom in on the plant, followed by the furnace and its internals. Along this description we will highlight current limitations of the process. The steam cracking process produces world's largest volume of organic petrochemical, ethylene, with a world wide capacity of ~ 128 million tones per year (Goodnight et al., 2008). Fig. 2.1 shows schematically where the steam cracking process is situated in the flow diagram of the petrochemical industry (Groenendaal and Gielen, 1999). The products of the steam cracking process are intermediates for the production of plastics (polyethylene, polypropylene), insulation materials and synthetic rubber. The feed stocks for the steam cracking process are hydrocarbons refined from crude oil and residual products obtained during the natural gas exploration. These hydrocarbons vary from light components such as ethane and propane to more complex mixtures such as naphthas, gasoils, and vacuum gas oils. In the US ethane is the predominant feed stock due to the large-scale exploration of the natural gas where large amounts of ethane are obtained as a residual product.

In Europe and Asia naphtha is the predominant feed stock. In the next 10 - 30 years, we expect to be in a transition phase, where oil is getting scarce and alternatives need to be found. The largest impact will be on fuels, because the



Figure 2.1: Schematic overview of petrochemical industry (Groenendaal and Gielen, 1999).

majority of the crude oil is used for the production of fuels. Approximately 1.5% of the crude oil is used for ethylene production (van Goethem et al., 2007). Therefore, only a small fraction of crude oil is used, suggesting that, in the transition period, the scarcity of crude oil will – supply-wise – not have a large impact for the chemical industry and hydrocarbon feeds will remain to be the obvious raw material. Though the feed cost effect can be very significant. It would not be logical to use biological raw materials, because they contain large amounts of heteroatoms that must be removed. With respect to the main outlet for ethylene, i.e., polyethylene, the situation is more complex. Biopolymers could be used to replace this polymer in certain applications. We assume that, in the transition period, the production of ethylene from hydrocarbons will remain a process of high importance.

2.2 Olefin plant

Fig. 2.2 shows a schematic of an olefins plant based on the steam cracking technology which consists of a hot and a cold section and a hydrocarbon recycle. The hot section consists of the cracking furnaces, the quench and the primary fractionator. The cracking furnace is the reactor of the plant where the (feed + recycle) hydrocarbons, diluted with steam, are cracked in the gas phase into lower olefins, such as ethylene and propylene at temperatures of around $800 - 850^{\circ}$ C and pressure of 1.5 bar with residence times of less than 1 second. In the quench, the reactor effluent composition is "frozen" by rapid cooling under the production of high pressure steam. In the primary fractionator, the water and fuel oil is removed from the reactor effluent. In the cold section, the reactor effluent is compressed, dried and chilled. In the subsequent distillation columns the reactor effluent is split in its products hydrogen, methane, ethane, ethylene, propane,



Figure 2.2: Schematic overview of an ethylene plant based on the steam cracking technology.

propylene and C4+ fraction. Depending on the specific plant the C4+ fractions can be separated further into butylene, butadiene, BTX and gasoline. The lowest temperatures in the cold section are approximately -200 - -170 °C at a pressure of 20 - 30 bars. These conditions are a necessity to make these separations possible (Zdonik et al., 1970; Grantom and Royer, 1987; van Geem et al., 2008).

This thesis is related to improving the chemical conversion concept of the steam cracking process; therefore, in the remainder of this chapter we will zoom into this section of the process.

2.3 Cracking furnace

A cracking furnace consists of a firebox and a side mounted stack, see Fig. 2.3. Inside the firebox the radiant coils are vertically mounted from the roof of the box. The amount of energy required for the cracking process is significant. This process has the largest energy consumption of all processes in the chemical industry (Ren et al., 2006) and it uses globally approximately 8% of the sector's total primary energy use ($\sim 20 \text{ MJ/kg } C_2H_4$). The energy is provided with bottom and/or side wall burners that combust a mixture of air and fuel, usually methane and hydrogen obtained in the cold section or any other fuel gas. Inevitably significant amounts of CO_2 are produced, approximately 180–200 million tons world wide (Ren et al., 2006). Reduction of this amount will contribute significantly to the goals of the Kyoto protocol. The NOx emission levels bound limit design and operation by the ever stricter regulations and pose a challenge for furnace designers that have



Figure 2.3: Schematic overview of two cracking furnaces.

to deliver intensified furnaces while maintaining the stringent emission levels. The intensification is different for retrofitting and for new designs. In the former the plot space of the furnace is kept the same while the capacity of the furnace increases, whereas in the latter the economy of scale favours the construction of extremely large furnaces.

To recuperate energy from the hot flue gasses of the firebox a convection section is constructed inside the stack to generate high pressure steam and preheat the hydrocarbon and dilution steam for the radiant coils. Fig. 2.4 gives an impression how the furnace shown schematically in Fig. 2.3 looks like in reality.

Fig. 2.5 shows a schematic of a typical cracking furnace and a steam system for a cracking furnace fed with a heavy feed stock. The convection section is a collection of different convection banks to recover energy from the hot flue gasses of the firebox. In the FPH-bank (Feed PreHeater) the hydrocarbon (HC) feed stock is preheated and afterwards mixed with a small amount of dilution steam (DS) and subsequently heated further in a so-called HTC-bank (High Temperature Coil). The main DS feed is super heated in a DSSH-bank (Dilution Steam Super Heater) and mixed with the heated HC(+DS) before it is heated in another HTCbank to the desired inlet temperature of the radiant coil of approximately 600°C. To recover more energy from the flue gasses a steam system is integrated into the cracking furnace and quench (transfer line exchanger). Boiling feed water (BFW)



Figure 2.4: The schematic furnace of Fig. 2.3 shown while being transported from construction yard to plant plot. (Technip Benelux B.V.)

for the steam drum is preheated in the ECO-bank (Economiser) to the saturation temperature of typically 100 bar steam. In the quench high pressure steam is generated with saturated water from the steam drum. The saturated steam is superheated in several HPSSH-banks (High Pressure Steam Super Heater) to yield high pressure steam (HPS) which is a product of the cracking furnace. The overall efficiency of the furnace is in the order of 90 - 94%, meaning that 6 - 10% of the energy generated by the combustion of the fuel is lost to the surroundings. The bottle neck for further reduction is the stack exit temperature. Currently this temperature is ~150°C, further reduction of temperature will cause condensation of acid components on the convection bank tubes, giving unacceptable corrosion rates.

2.4 Radiant coil

In the radiant coil the HC's are cracked in approximately 1-1000 ms, to amongst others lower olefins such as ethylene. The ethylene yields are correlated to the feed stock, ethane yields typically 75 wt% (ultimate) ethylene while vacuum gasoil's yields typically 20 wt% ethylene. The side products are propylene, butadiene, butylenes, BTX and fuels such as hydrogen, methane, fuel oil. The furnace operating conditions (e.g., temperature, steam-to-feed ratio) can be adjusted to influence the yield balance between ethylene and propylene for heavier feeds than ethane. The propylene yield (up to \sim 18 wt %) can be of very significant economic impact. In



Figure 2.5: Schematic overview of firebox, convection section and quench/steam system. HC= Hydrocarbon, DS= Dilution Steam, HPS=High Pressure Steam, FPH=Fead PreHeater, ECO=ECOnomizer, HTC=High Temperature Coils, HPSSH=High Pressure Steam Super Heater, DSSH=Dilution Steam Super Heater

order to obtain all these products in a purified state a significant separation effort is required (Moulijn et al., 2001). The cracking coil inner reaction temperature is severe, namely $600 - 850^{\circ}$ C, which results in an outside tube skin temperature of $1000 - 1075^{\circ}$ C. Higher yields are obtained when the reaction temperature is increased, but currently this is constrained by the metallurgy and coking of the applied cracking tubes in the furnaces. The maximum tube metal temperature for tubes made of Cr-Ni alloys is approximately 1150°C. In the transfer line exchanger the radiant coil its effluent is rapidly quenched. The reason for the rapid cooling of the reactor effluent from $\sim 850^{\circ}$ C to 600° C is the fact that the primary products, that is lower olefins, can react further into more unsaturated and more condensed species. The dilution steam is added to lower the hydrocarbon partial pressure, which reduces this secondary conversion of the desired lower olefins. It also reduces the coking rate in the radiant coil and the transfer line exchanger. The deposition of carbonaceous residue results in a higher pressure drop and higher tube skin temperatures (Bozzano et al., 2002; Cai et al., 2002; Heynderickx et al., 2005). To maintain a certain cracking severity (i.e. conversion, propylene-ethylene ratio) the heat input must be increased which leads to even faster coking deposition. After 20 - 60 days on stream the cracking furnace must be decoked. This is a controlled combustion of the coke on the tube wall by a steam-air mixture.

3

Ideal chemical conversion concept for the industrial production of ethylene from hydrocarbons¹

Abstract

This review considers and evaluates alternative process concepts for the production of ethylene on an industrial scale. A fundamental perspective is chosen, focusing on the ability to create a near-optimum conversion path from hydrocarbon (C_{2+}) feed to ethylene. The critical conversion aspects are: quickly achieving a high temperature at a low hydrocarbon pressure and, after a short reaction time, arresting the composition with a high ethylene content by rapid cooling. The features of an ideal process involve a maximum olefin yield, no remains of energy carriers or auxiliary chemicals in the product, minimal ecological impact, minimum energy input per unit product, high availability, and a low degree of complexity of the reaction section. The majority of the current ethylene production processes are an evolutionary redesign from earlier existing processes that is able to add a large amount of thermal energy in a short period of time and at elevated temperature levels in the range of $600 - 1200^{\circ}$ C, enabled by better high-temperature-resistant materials. The process concepts reviewed in this paper are examined from a different point of views namely, how well they meet the criteria of the ideal process. The specific energy requirements of the processes are limited in the available literature; therefore, these requirements are systematically determined with Aspen Plus software and the aid of SPYRO for an ethylene plant

 $^{^{1}}$ This chapter is a version with minor modifications of an article published in Industrial Engineering and Chemical Research (van Goethem et al., 2007)


Figure 3.1: Input-output diagram for the production of ethylene on industrial scale.

with a fixed ethane feed. A wide variety of process concepts is covered: dehydrogenation, direct heating, and indirect heating. Although none of the reported processes fulfils all ideals, the new combination of the adapted firing furnace with ceramic reactors internals and the shock wave reactor come close to it.

3.1 Introduction

Ethylene is the world's largest volume organic chemical, with a worldwide production of ~117 million tonnes per year in ~275 plants. Ethylene manufacturing is dominated by thermal cracking, and the process of thermal cracking has evolved significantly from the end of Word War II until the present. The plant size has increased from 10.000 tonne to 1.7 million tonne per year. The feed stocks for thermal cracking are hydrocarbons (C_{2+}) such as ethane, liquefied petroleum gas (LPG), naphthas, gas condensates, and gas oil. Continuous research and development efforts are performed to achieve better ethylene yield and lower energy consumption. In addition, the use of alternative feed stocks such as biomass, natural gas, synthetic feed stocks from Fischer-Tropsch, methanol, and ethanol has also been pursued.

Fig. 3.1 shows an overview of the different routes to ethylene on an industrial scale. Some of these routes have not yet been developed to an industrial scale



Figure 3.2: Percentage change of the world Gross Domestic Product and global installed C_2H_4 nameplate capacity(Nakamura, 2004; Lou, 2003)

process, but they have the potential to do so in the future. For example, a direct process from biomass to ethylene, at this moment, is not capable to produce ethylene at an industrial scale; however, the biological industry is promising and perhaps may be a topic of interest in the future. The prosperity of a society is one of the indicators for the demand of ethylene. An indicator for the global prosperity is the gross domestic product (GDP). Fig. 3.2 shows the annual change of both the world GDP and the installed ethylene nameplate capacity. Fig. 3.2 confirms that world GDP is a good indicator for the demand for ethylene. Because the economy in China and India is growing rapidly, the global prosperity, most probably, will also grow and, consequently, the demand for ethylene is expected to grow.

The current ethylene production facilities are heavily dependent on the availability of hydrocarbons from crude oil and light alkanes from gas fields, which will not last forever. This implies that we need to improve the current technologies and search for alternative processes, to produce ethylene in a more efficient way. Among others, a measure for the progress to more efficient thermal cracking processes is the decrease in the amount of energy needed to produce one kilogram of ethylene. Significant improvements to reduce the specific energy have been obtai-



Figure 3.3: The decrease in energy (Cole, 1996) required to produce a kilogram of C_2H_4 .

ned during the oil crisis in the 1980s. Fig. 3.3 shows the progress over the last 50 years. Considerable research has been conducted to improve the thermal cracking process and to find alternative routes to produce ethylene. During the oil crisis, the research objective was to crack crude oil directly; this generated several new thermal cracking processes, such as adiabatic cracking and fluidized bed cracking, among others (Hu, 1982) Often, a technology used for thermal cracking is derived from another technology. For example, the current state of the art thermal cracking furnace can be considered as an upgraded fired heater. The direct heating processes (for example, those using an advanced cracking reactor (ACR)) are derived from acetylene manufacturing processes. The fluidized-bed technologies find their origin in the fluid catalytic cracking (FCC) technologies. Generally, a process that can add a large amount of energy at a high-temperature level in a short period of time can be used for thermal cracking. Through this type of evolutionary process development, the focus is on what the existing technology can do and how this must be modified to obtain a good process for ethylene. This way of process development makes it hard to develop the "ideal" process for the production of ethylene. The developer is not focused on the conceptual process design but rather on the (re)design of an existing process.

Levenspiel (1988) stated that, before starting work on a particular process

concept, one should set criteria for the ideal never mind whether it is practical or not and see how close one can get to the ideal. This idea is used to review the existing process to produce ethylene on an industrial scale. This review is limited in scope by only considering processes that use hydrocarbons (C_{2+}) as feed stock. This implies that the dehydrogenation and cracking of the branches from Fig. 3.1 are reviewed.

In the next 10-30 years, we expect to be in a transition phase, where oil is getting scarce and alternatives need to be found. The largest impact will be on fuels, because the majority of the crude oil is used for the production of fuels. Approximately 1.5% of the crude oil is used for ethylene production. Therefore, on one hand, only a small fraction of crude oil is used, suggesting that, in the transition period, the scarcity of crude oil is not very important for the chemical industry. On the other hand, many chemicals are functionalized molecules and, as a consequence, biomass might be an intrinsically better feed stock than crude oil (derivatives). Therefore, biological routes can provide attractive alternatives for more functionalized molecules. When we use the term "functionalized", we mean molecules that embody atoms other than hydrogen and carbon (in particular, oxygen). For ethylene production in the transition period, hydrocarbon feeds are the obvious raw material. It would not be logical to use biological raw materials, because the heterogeneous atoms must be removed. With respect to the main product of ethylene (i.e., polyethene), the situation is more complex. Biopolymers could be used to replace this polymer in certain applications. We conclude that, in the transition period, the production of ethylene from hydrocarbons will remain a process of high importance.

With the selection of processes that use hydrocarbons as feed stock, we possibly ignore important process, such as the reaction of methanol to olefins (MTO). In the next section, we will briefly discuss these processes. Thereafter, the basic reaction stoichiometry and conditions are given. Engineering aspects are given subsequently. Before we will describe the processes, we will denote the criteria of what we consider to be an ideal process and how we are going to structure the different processes. After the description, we will qualitatively compare the different processes on the compliance with the ideal process criteria in the discussion. Besides looking back we will discuss the direction of development of the next generation ethylene processes with hydrocarbons as feed stock.

3.2 Overview biomass and natural gas process routes to ethylene

The biological route uses biomass as a feed source. As already stated, a direct route to ethylene is not yet available; however, an indirect biological route to ethylene is available through ethanol as an intermediate, which is produced, on an industrial scale, by biomass fermentation. The ethanol can be subsequently dehydrated to ethylene. The governing reactions can be summarized by

$$\begin{array}{rcl} 2 \ C_2 H_5 OH & \rightarrow \ \left(C_2 H_5 \right)_2 O & + \ H_2 O \\ & \left(\Delta H_{f298}^0 = -24 \ \mathrm{kJ/mol} \ \Delta G_{f298}^0 = -14 \ \mathrm{kJ/mol} \right), \end{array}$$

$$\begin{array}{rcl} (C_2H_5)_2\,O &\to& 2\;C_2H_4 \;+\; H_2O \\ & & \left(\Delta H^0_{f298} = -390\;\; \rm kJ/mol\;\; \Delta G^0_{f298} = -215\;\; \rm kJ/mol\right). \end{array}$$

These processes are based on the passage of ethanol vapor over solid catalysts at elevated temperatures $(315 - 500^{\circ}\text{C})$. Typical catalysts are based on activated alumina and phosphoric acid on a suitable support of zinc oxide with alumina. The reactors used are fixed or fluidized beds, operated at (near) isothermal or adiabatic conditions (Cole, 1996). Ethanol can also be produced from synthesis gas using a rhodium-based catalyst. The overall reaction is

$$2CO + 4H_2 \rightarrow C_2H_5OH + H_2O$$

 $(\Delta H_{f298}^0 = -256 \text{ kJ/mol } \Delta G_{f298}^0 = -122 \text{ kJ/mol}).$

Ethylene can also be directly produced from synthesis gas with the modified Fischer-Tropsch process, the reactions are

General:
$$nCO + 2nH_2 \rightarrow C_nH_{2n} + nH_2O$$

 $nCO + 2n + 1H_2 \rightarrow C_nH_{2n+2} + nH_2O$,

Ethylene : 2CO + 4H₂
$$\rightarrow$$
 C₂H₄ + 2H₂O
($\Delta H_{f298}^0 = -211 \text{ kJ/mol } \Delta G_{f298}^0 = -115 \text{ kJ/mol}$).

The production for ethylene, which is based on the Fischer-Tropsch reaction of synthesis gas, yields a broad spectrum of olefins. Successes have been made toward more-selective catalysts, but current catalysts give low selectivity toward ethylene, while methane formation is high. Snel (1987) gave an elaborate review on this type of production process. The selective MTO dehydration is another potential route to lower olefins. This process has evolved from Mobil's Methanol to Gasoline process, which converts methanol to gasoline, with alkenes as intermediates. An important issue for the production of lower alkenes is the suppression of the formation of aromatics. This can be accomplished using a zeolite or another type of molecular sieve catalyst. The overall reaction of methanol to ethylene is given by

$$\begin{array}{rcl} 2 \ CH_3OH & \to \ C_2H_4 & + \ 2H_2O \\ & \left(\Delta H^0_{f298} \ = \ -29 \ \mathrm{kJ/mol} \ \Delta G^0_{f298} = -64 \ \mathrm{kJ/mol} \right). \end{array}$$

In principle, the direct conversion of methane to ethylene is possible by applying the so-called "oxidative coupling", i.e., the catalytic reaction of methane with oxygen. The reaction produces ethane, which is converted to ethylene in situ, while higher hydrocarbons are also formed in small amounts through sequential reactions (Moulijn et al., 2001), the overall reactions are

$$2 CH_4 + 1/2O_2 \rightarrow C_2H_6 + 2H_2O (\Delta H_{f298}^0 = -177 \text{ kJ/mol } \Delta G_{f298}^0 = -160 \text{ kJ/mol}),$$

$$\begin{array}{rcl} C_2 H_6 &+& 1/2 O_2 &\to& C_2 H_4 &+& 2 H_2 O \\ && \left(\Delta H_{f298}^0 = -105 \ {\rm kJ/mol} \ \Delta G_{f298}^0 = -128 \ {\rm kJ/mol} \right) \end{array}$$

3.3 Process conditions

The favourable process conditions for the production of ethylene from hydrocarbon feed stocks are high temperature, low hydrocarbon partial pressure, and short residence times. These conditions are determined by thermodynamic and kinetic factors. Dehydrogenation is an endothermic process, as shown by the reactions

$$C_2 H_6 \rightarrow C_2 H_4 + H_2$$

 $(\Delta H_{f298}^0 = 137 \text{ kJ/mol } \Delta G_{f298}^0 = 101 \text{ kJ/mol}),$

$$C_3H_8 \rightarrow C_3H_6 + H_2$$

 $(\Delta H^0_{f298} = 124 \text{ kJ/mol } \Delta G^0_{f298} = 86 \text{ kJ/mol}).$

Fig. 3.4 indicates that, from a thermodynamic viewpoint, the reaction temperature should be high $(750 - 1000^{\circ}\text{C})$ for sufficient conversion. The reactions will occur in the gas phase, because the reactants and the products are at these temperature levels in the gas phase also. The energy required for the reactions can be supplied by energy carriers in the gas phase and by solids and liquids that are stable at these temperatures. In a somewhat abbreviated form for the production of monoalkenes, the equilibrium conversion is given by Eq. (3.1),

$$\varepsilon = \frac{\sqrt{K_p}}{\sqrt{K_p + P}},\tag{3.1}$$

where P is the total absolute pressure and K_p is the equilibrium constant for the dehydrogenation reaction. From Eq. (3.1), it follows that a process at vacuum would be the best in this respect; however, in the present industry, typically a pressure in the range of 1 - 5 bar is applied. It is generally agreed that a freeradical mechanism can describe the cracking process accurately (Dente et al.,



Figure 3.4: Equilibrium conversion for the dehydrogenation of ethane, propane, and isobutane at 1 bar. Data taken from Reid et al. (1988)

1979; Dente and Ranzi, 1983; Froment, 1992). Fig. 3.5 gives the mechanism for the simplest feed stock (namely, ethane). The reaction is initiated by cleavage of the C - C bond in an ethane molecule, resulting in the formation of two methyl radicals. Propagation proceeds by reaction of the methyl radical with an ethane molecule resulting in an ethyl radical and a methane molecule. The ethyl radical subsequently decomposes into ethylene and a hydrogen radical, which then attacks another ethane molecule, resulting in an ethyl radical and a hydrogen molecule. These two reactions dominate in the cracking of ethane. Termination results from the reaction of two radicals forming either a saturated molecule or a saturated molecule and an unsaturated molecule. Fig. 3.5 shows that the pyrolysis of ethane, besides ethylene as the main product, also produces methane and hydrogen. Small quantities of heavier hydrocarbons are also formed by termination reactions of larger radicals. These larger radicals are formed by the addition of radicals on unsaturated molecules.

A similar, although more complex, scheme applies to the thermal cracking of higher alkanes. The main reaction is the cracking of alkanes to alkenes and (smaller) alkanes. These types of reactions are considered to constitute the primary cracking network. The products resulting from primary cracking may undergo secondary reactions such as pyrolysis, dehydrogenation, and condensation. These secondary reactions may also lead to the formation of coke.

Fig. 3.6 summarizes the major reactions. The formation of coke is always

Initiation:
$$C_2 H_6 \rightarrow 2 C H_3^{\bullet} = 376.1$$

$$\begin{aligned} Propagation: CH_{3}^{\bullet} &+ C_{2}H_{6} \to CH_{4} &+ C_{2}H_{5}^{\bullet} \quad \Delta H_{f298}^{0} = -16.7 \\ C_{2}H_{5}^{\bullet} &\to C_{2}H_{4} &+ H^{\bullet} \quad \Delta H_{f298}^{0} = 151.1 \\ H^{\bullet} &+ C_{2}H_{6} \to H_{2} &+ C_{2}H_{5}^{\bullet} \quad \Delta H_{f298}^{0} = -14.1 \\ C_{2}H_{5}^{\bullet} &+ C_{2}H_{4} \to C_{4}H_{9}^{\bullet} &\Delta H_{f298}^{0} = -102.5 \\ C_{2}H_{5}^{\bullet} &\to etc. \end{aligned}$$

 $\begin{array}{rcl} Termination: \ H^{\bullet} & + H^{\bullet} & \rightarrow & H_2 & \Delta H^0_{f\,298} = -\,436.0 \\ C_2 H^{\bullet}_5 & + C H^{\bullet}_3 & \rightarrow & C_2 H_4 & + C H_4 & \Delta H^0_{f\,298} = -\,287.5 \\ etc. \end{array}$

Figure 3.5: Mechanism of Ethane Dehydrogenation/Cracking (After Moulijn et al. (2001)). The Heat of Reaction is Given in Units of $kJ \cdot mol^{-1}$.



Figure 3.6: Main Reactions Involved in Thermal Cracking of Higher Alkanes (From Chauvel and Lefebvre (1989).)

observed, even when lighter alkanes are used as feed stock. It is self-evident that the heavier the feed stock, the more coke is formed. Coking starts playing a role above 600°C. For some typical yield data for ethane and naphtha, the reader is referred to Ullmann's Encyclopedia of Industrial Chemistry (Grantom and Royer, 1987). The formation of the primary products is described well using first-order kinetics (Zdonik et al., 1970). The relationship between conversion, residence time, and reaction temperature for a first-order mechanism in a plug-flow tubular reactor is represented by Eq. (3.2),

$$\ln\left(\frac{1}{1-\xi}\right) = \int_{0}^{\tau} A \exp\left(\frac{-E_a}{R_{gas}T(t)}\right) dt, \qquad (3.2)$$

where ξ is the conversion, τ the residence time (given in seconds), A the frequency factor (expressed in units of s⁻¹), E_a the activation energy (expressed in units of J·mol⁻¹), T the temperature (given in Kelvin), and R_{gas} the universal gas constant (J·(mol·K)⁻¹). From Eq. (3.2), it is clear that, to achieve a certain level of conversion, many residence time and temperature combinations can be chosen. The thermodynamics (Fig. 3.4) prescribes the highest temperatures (>>600°C) to achieve reasonable conversions; the higher the temperature, the better, and, as a consequence, the residence time must be small (0.001 – 1s). Secondary cracking, where the products from the primary cracking reaction are cracked further, must be minimized and, as a consequence the residence time should be as low as possible to prevent further reactions. This demands that the rapid quenching (cooling) of the reaction effluent to temperature levels below 600°C.

3.4 Engineering aspects

Fig. 3.7 shows the overall architecture of an ethylene plant, in terms of the main functions and the recycle structure. This review focuses on processes that use hydrocarbons as feed stock. The scope is limited further by considering the conversion section of the ethylene plant. A dominating factor in the production of ethylene is the energy requirement of the process. Although this review is limited to the conversion section, we must consider the separation section as well for the comparison of the energy requirement. The conversion and separation section are interdependent, the size and the composition of the reactor effluent determine the separation effort, and the amount of fuel recovered in the separation section determines the amount of external fuel required. Therefore, we compare the different conversion sections with only one separation section. To limit the work further, we determine the minimum cooling and heating requirement according to the pinch technology (Douglas, 1988), instead of the actual energy requirement. The pinch technique allows us to determine these minimum energy requirements, respecting the second law of thermodynamics and by assuming that all streams



Figure 3.7: Input-output and recycle structure of an ethylene plant.

can exchange energy (no constraint on the amount of heat exchangers). The details of the pinch technique can be found in textbooks on process design (Douglas, 1988; Seider et al., 1999). Fig. 3.8 shows an example of a graphical representation of the determination of the minimum amount of heating and cooling requirement for an ethane plant based on the conventional cracking furnace. The input of the pinch technique is a flow sheet with closed mass and energy balances. The minimum approach temperature is assumed to be 10°C.

For the conversion or reaction section, we can distinguish four tasks that must be performed: (i) heating of feed and auxiliary chemicals; (ii) mixing of feed, auxiliary chemicals, and energy carriers; (iii) conversion of feed to products; and (iv) cooling of the reaction mixture. For the separation section, we consider three tasks that must be performed: (i) water removal, (ii) hydrogen/methane removal, and (iii) C_{2+} separation. The first separation task is for almost all the processes required, except for processes that do not use or produce water, such as, for example, membrane technology. The second separation task is also optional for some processes, because some processes separate hydrogen in the conversion section or methane is not formed, such as that observed in the oxidative dehydrogenation at low temperatures. The third separation task is for all the required processes. Fig. 3.9 (the solid items) shows a block diagram of the tasks that must be performed for an ethylene production plant. The reaction tasks of mixing and conversion have been combined, because these are dependent on the technology used. The separation is straightforward and similar to the classical process used in the thermal cracking process (see, for example, Zdonik et al. (1970)). Some processes use also oxygen as a feed stock. When we compare a process with and without oxygen as feed stock (for example, oxidative dehydrogenation (ODH) and thermal cracking), completely different results are obtained. The explanation is



Figure 3.8: Composite curve for an ethane cracking furnace producing 800 kt C_2H_4/yr ($\Delta T = 10^{\circ}$ C).

straightforward: the reaction section of the ODH process is energy neutral, whereas the thermal cracking process with indirect heating is heavily endothermic. Therefore, we cannot use the flow sheet (solid lines) as given by Fig. 3.9. Actually, in all the processes, oxygen is used in some way. For example, the thermal cracking furnace combusts (part) of the hydrogen and methane in the furnace to fulfil its energy requirement, the shock wave reactor requires superheated steam that is generated in a furnace, which needs fuel and oxygen, and the Advanced Cracking Reactor (ACR) combusts (part) of the hydrogen and methane with pure oxygen to generate the hot combustion gases wherein the hydrocarbon feed is injected. The purpose is to determine the minimum amount of energy in such a way that we can compare all the processes. Therefore, we use as much of the same separation section as possible to make a proper comparison of all the processes possible. Besides this obvious constraint, we also must introduce oxygen in all the systems. Therefore, we combust all the hydrogen and methane that exit the flow sheet as given by Fig. 3.9 at a temperature of $\sim 1550 - 1600^{\circ}$ C. The hot flue gases are subsequently cooled to a temperature of 210°C. The net result is that the energy of the hot combustion gases is added into the analysis, which yields a composite curve similar to that given by Fig. 3.10. The pinch analysis yields three deliverables, namely, the minimum heating requirement, the minimum cooling requirement, and the pinch temperature. The separation section is operated at fixed pressures of 20 - 30 bar. The minimum and maximum temperature are



Figure 3.9: Schematic flowsheet for an ethylene production unit. Dashed items are optional.

also reported, because they can change due to different compositions. The capacity of the ethylene plant for all the examined processes is ~800 kt C_2H_4/y (depending on selectivity), with a fixed ethane feed of 1.1 Mt C_2H_6/yr . Fig. 3.10 shows that the minimum heating requirement will be negative, which means that the process has an excess amount of energy at a high temperature. The smaller this (negative) value is, the more energy can be transformed to supply the need for energy elsewhere in the process. The minimum cooling requirement is a lower bound for the energy that must be put into the process to fulfil the minimum cooling requirement of the process. The results obtained with the pinch technique will be given in the discussion section (in Table 3.2). The flow sheets are solved with Aspen Plus (Aspen, 2001).

3.5 Requirements of the ideal thermal cracking process

As mentioned in the introduction, section 3.1, the production processes for ethylene on an industrial scale from hydrocarbon feed stocks have been derived from existing technology in an evolutionary way. The main focus on the process development of these processes was on how to modify these technologies to produce ethylene. In the previous section, we denoted that the focus is on the chemical conversion concept of the reported processes. This review examines if the ideal chemical conversion concept has been reported in the literature and the patents. For this, a set of criteria must be defined for the ideal conversion concept. Fig. 3.11 shows a black box model of an ethylene production process that will be the backbone of the defined criteria. Herein, we distinguish three entities, namely, output, input, and the internal system. We have defined three criteria for the output, which is the most important entity, and two each for the input and the system. These seven criteria are given below.

Maximum Ethylene Yields. This criterion is self-evident; the higher the yield



Figure 3.10: Composite curve (including combustion of H_2 and CH_4) for C_2H_6 cracking furnace 800 kt C_2H_4/yr ($\Delta T = 10^{\circ}$ C).

of the desired product, the smaller the amount of byproducts that must be separated from the main products and the smaller the recycle stream (Zdonik et al., 1970).

- Minimal Contamination of Product with Energy-Supplying Chemicals. The second requirement follows from the fact that we must generate a large amount of energy for the reaction. For example, when this energy is generated by combustion, the preferable oxidant is the oxygen in the air. When the combustion and reaction occur in the same space, there is nitrogen in the product gas. Also, combustion products of the fuel (such as CO and CO_2) can be in the effluent.
- Minimal Impact on the Environment. Much energy is generated by combustion, which produces a large amount of CO_2 and NOx. It is becoming more and more important to limit the production of these components.
- Low Ratio of Energy per Unit Product. The dehydrogenation or cracking of hydrocarbons is known to be energy intensive. However, the ideal process should attempt to achieve the lowest-possible energy consumptions per unit of product within its economic viability limits.
- Minimal Use of Auxiliary Chemicals. The fifth criterion is not very straightforward. It is customary to add steam, as demonstrated by the naming of these processes as "steam cracking". Steam is needed to reduce the coking rate



Figure 3.11: Black box of the process for ethylene production.

and improve selectivity by reducing the partial pressure of the hydrocarbons. For an ideal process, we do not want to add additional components such as steam, but also nitrogen or hydrogen. The additional components require energy for the separation of their products.

- Maximum Availability. With high temperatures, coke formation seems inevitable. The deposition of coke on the apparatus reduces the time-on-stream, plugs catalysts, etc., and this is not a desired phenomena.
- Low Degree of Complexity. Generally, complexity determines, among other parameters, the design effort, operating effort, containment of risk factors, and understanding, in case of troubleshooting. Financially, complexity is an issue when operability and maintainability are at stake. The cumulative financial loss from poor operability and maintainability over the life span of the plant are a few orders larger than the design and engineering cost.

In the next section, we elaborate on how the reviewed processes are structured. The evaluation of the processes with respect to the ideals is depicted in the discussion by means of a table (Table 3.1) with the respective scores of the criteria. Indicators for the criteria are shown in a black box schematic in the description of each process, as shown by Fig. 3.11. The methodology used to obtain the minimum energy requirement is denoted in the previous section.

3.6 Structuring of the information

In the next two sections, we will present the reviewed processes and prior to this presentation, we describe how the information is organized. The information gathered by the literature survey is structured approximately according to Fig. 3.12. The dehydrogenation technologies are subdivided into catalytical dehydrogenation, equilibrium shift, and ODH. In the literature, different types of ODH are



Figure 3.12: Structure of the reviewed oil-based production process for ethylene; this is a subset of all processes mentioned in Fig.3.1

reported. Not all of these types are, strictly speaking, oxidative dehydrogenation technologies but are "labeled" as such because of the fact that only recently has a consensus (Beretta et al., 2001a) been obtained on the true nature of the hightemperature ODH. Therefore, the low and medium versions of ODH are reported in the dehydrogenation section and the high-temperature process is reported under the thermal cracking section. The thermal and catalytic cracking branches in Fig. 3.1 are merged into one cracking branch. The reason for this is that the thermal cracking technologies are subdivided according to the way the energy is added to the system. As a result, the catalytical process fits into this subdivision seamlessly: the heating is applied in the same way, but a catalyst is present in the system. Direct heating with gases and solids is thoroughly examined, whereas direct heating with liquids can be observed as a curiosity. The indirect heating is the current state-of-the-art technology. All the reported technologies will be characterized with a black box (Fig. 3.11) containing typical values for: selectivity, conversion, minimum energy requirements, process conditions, auxiliary chemicals used. As already mentioned, the minimum energy requirement is estimated with the pinch technique for an ethylene plant that is processing 1.1 Mt C_2H_6/yr , the results are reported in the black box. The other items in the black box are taken from the literature. The selectivity is defined as the amount of ethylene divided by the amount of ethane converted (in moles). The conversion is defined as the amount of ethane converted divided by the initial amount of ethane.



Figure 3.13: Schematic overview of dehydrogenation processes.

3.7 Dehydrogenation processes

3.7.1 Catalytic dehydrogenation

Catalytic paraffin dehydrogenation for the production of olefins has been in commercial use since the late 1930s (Leveles, 2002). These processes include CA-TOFIN (from ABB Lummus), OLEFLEX (from UOP), Fluidized Bed Dehydrogenation (FBD) (from Snamprogetti), and Steam Active Reforming (STAR) (from Phillips Petroleum). The paraffins used in these commercial applications are mainly propane and isobutane for the production of propylene and isobutene, respectively. Smaller commercial-scale applications are reported for catalytic dehydrogenation of long-chain paraffins for the production of heavy linear olefins for the manufacture of biodegradable detergents (Bhasin et al., 2001). Dehydrogenation is generally conducted in the presence of a noble or heavy-metal catalyst such as platinum or chromium. The processes are performed at atmospheric pressure or under vacuum at $\sim 500 - 700^{\circ}$ C. Because propane and isobutane dehydrogenation is equilibrium-limited, the yield of product is limited in the applied temperature ranges. Despite the fact that the selectivity to the product is high (90%), the process requires a large separation effort to recycle the propane or isobutane. To improve the conversion per pass, the operating temperatures must be increased. This has a consequence that, as the selectivity drops, coke formation is enhanced and the time-on-stream is reduced. This process is not suited for the production of ethylene, because of its poor vield (Bhasin et al., 2001). To become of interest, the temperature range must be increased; however, this results in more coking, higher pressure decreases, and lower selectivity. This type of process for the production of ethylene from ethane seems to be a dead end. Fig. 3.13 gives the characteristics for the dehydrogenation of ethane; the conversion is estimated from thermodynamics at 600°C, and the selectivity is estimated from the literature (Bhasin et al., 2001). The amount of steam is taken from Golombok et al. (2000).

Another catalytic dehydrogenation process reported in the literature is the dehydrogenation of naphtha. Several catalysts are proposed for this purpose: alumina-KVO₃, alumina-CaO, alumina-TiO₂, alumina-SrO, alumina-MgO, alumina- Cr_2O_3 , and alumina-MnO (Golombok et al., 2000; Picciotti, 1997; Towfighi et al., 2002). An interesting observation was made by Golombok et al. (2000) on the catalytic dehydrogenation of naphtha. He stated that the increase in yield, with respect to the steam-cracking process, can be explained by the surface-to-volume ratio of the packed bed instead of the catalyst. This was concluded by comparing the results of measurements performed on catalysts with and without active components. The catalyst suppressed the coking activity and resulted in a lower ethylene yield, when compared with a packed bed without a catalyst. The catalyst gasifies coke and other components to carbon oxides (mainly CO and CO_2). The reason for the increase was ascribed to an effect of the available surface on the kinetics (Vasileva and Panfilov, 2002). The observation of the increased yield due to the packed bed and the effect of the catalyst on the coking rate was reinforced by other authors (e.g., Towfighi et al. (2002); Jeong et al. (2001, 2002)). The latter claimed that the increase in yield was due to improved heat transfer, in contradiction with Golombok et al. (2000). The observations made with the catalytic dehydrogenation of naphtha raise a question: Do the catalysts used for the dehydrogenation of propane and isobutane have the same effect? At this point, no references can be found that indicate that the catalyst for the production of propylene and isobutene from propane and isobutane really catalyze the formation of the product or also suppress coking reactions. Chauvel and Lefebvre (1989) already stated that the surface of the reactor influences the product yield. and this point requires further investigation.

3.7.2 Equilibrium shift

The production of olefins from (cyclo)-paraffins is through a dehydrogenation reaction. The conversion of dehydrogenation reactions can be enhanced when the produced hydrogen could be selectively removed. The enhancement of the conversion is of importance at low temperatures ($<600^{\circ}$ C) where the equilibrium conversion is low (see Fig. 3.4). Through the selective removal of hydrogen, the conversion can be "beyond the equilibrium conversion". The removal of hydrogen can be done with a membrane. As mentioned by Gobina and Hughes (1994) the membrane technology was first only suited for low-temperature ($<100^{\circ}C$) applications, because of the utilization of organic membranes. Currently, hightemperature, porous, ceramic, and metallic membranes can be applied, opening the route to the high-temperature dehydrogenation of lower alkanes to olefins. In the literature, (Champagnie et al., 1990; Minet et al., 1993; Gobina et al., 1995; Ziaka et al., 1993) several of these technologies have been reported. The basic configuration is a packed-bed reactor placed in a heater filled with a catalyst that promotes the dehydrogenation of ethane (or other hydrocarbons). The hydrocarbon is fed to the packed-bed reactor and, concurrently, the hydrogen is selectively



Figure 3.14: Schematic overview of equilibrium shift processes.

removed through the membrane. To increase the production, several of these reactors should be placed in parallel. The membrane reactors already have high selectivity (near 100%) in the temperature range of 500 – 600°C. The conversion level is 2 – 10% for the ethane cracking. This implies that a large recycle is needed, and this has a negative impact on the separation effort of the process. The membrane reactors require no dilution steam, because the temperature levels applied are not high enough for coking (coking starts to play a role above 600°C) to have a significant role. The reported conversions are several times ($4 \times - 8 \times$) higher than the thermodynamic equilibrium conversions. However, for economic application of this technology, the conversion must be increased. Increasing the temperature will result in higher conversions. This will also increase the coking rate, which has a negative effect on the permeability of the membrane and the performance of the catalyst. Fig. 3.14 shows the typical values for the membrane technology, where 97% for the selectivity is considered to be $\sim 100\%$ and 10% for the conversion is considered to be low.

3.7.3 Oxidative dehydrogenation

The ODH of paraffins for the production of olefins has been recognized as a potentially attractive alternative (Schmidt et al., 2000). Through the introduction of oxygen in the reaction system, the thermodynamic disadvantages of equilibriumlimited processes such as catalytic dehydrogenation and thermal cracking disappear. The presence of oxygen also limits the formation of coke on catalyst and reactor walls. The majority of the publications on ODH are on the ODH of ethane. The reported studies to date can broadly be classified as being conducted at lower temperatures of $300 - 400^{\circ}$ C, moderate temperatures of $400 - 600^{\circ}$ C, and at high temperatures of $600 - 800^{\circ}$ C (Bhasin, 2003). The ODH of ethane at lower temperatures is conducted with a reducible metal oxide catalyst, usually containing vanadium or molybdenum. Ethane is believed to react with molybdenum or vanadium oxide in the catalyst to form surface ethoxide, which can then



Figure 3.15: Mechanism of oxidative dehydrogenation (ODH) at low temperatures

undergo a β -elimination process to form ethylene (Fig. 3.15).

The surface ethoxide can be oxidized further to make surface acetate, which leads to acetic acid on hydrolysis. Selectivity to ethylene with these catalysts is in the range of $\sim 70\%$ at $\sim 70\%$ conversion of ethane (Bhasin et al., 2001; Silberova et al., 2003). Ethane ODH at moderate temperatures may be conducted with phosphorus/ molybdenum/ antimony oxide catalysts stabilized with one or more metal oxides. As opposed to the lower temperature catalysts, which have a tendency to produce coproducts, the moderate temperature processes have a tendency to produce only ethylene as olefin, and some also produce methane. Oxygenated products other than CO_x are largely absent. Zhang et al. (2003) reported selectivity at 400°C of 41 - 78% at a conversion level of 21 - 35% and high CO_x selectivity (22 – 59%). Wang et al. (2002) proposed an oxygen permeable membrane reactor for the ODH of ethane to ethylene. The selectivity is high (90%), but the conversion is low (20%). Fig. 3.16 gives the characteristic for ODH of ethane at moderate temperatures, where the selectivity and conversion are considered to be the average value for the reported studies. When the temperature of the process is increased, the conversion increases and the selectivity to ethylene decreases. Part of the ethane is combusted to form carbon oxides (mainly CO and CO_2), and, therefore, a lower selectivity is obtained. In these processes, rather large quantities of oxygen (on the same order of magnitude as the hydrocarbon feed) are used at relatively low temperatures $(300 - 600^{\circ} C)$. The hydrocarbon and oxygen are passed through a packed bed filled with a catalyst. High quantities of oxygen are required, because the ODH reaction is the only reaction that occurs at the relatively low temperatures involved. Unfortunately, at high oxygen concentrations, the reaction selectivity is low and high amounts of CO and CO_2 are formed. At these low temperatures, the conversion is controlled by oxygen content, and, in practice, conversion must be limited to maintain high selectivity. Therefore, these processes will result in large recycle streams, because of low conversions per pass. The ODH reaction is net exothermic, compared to the endothermic dehydrogenation-cracking reaction. Heat removal places an additional limitation on the conversion for ODH, because, as the temperature increases with the higher levels of oxygen required for conversion, selectivity de-



Figure 3.16: Schematic overview of ODH processes.

creases substantially (Gartside and Shaban, 1999). The "true" ODH catalyst for ethane must still be discovered (Bhasin, 2003).

3.8 Direct heating processes for production of ethylene

3.8.1 Precombusted gas reactors-adiabatic cracking reactor

The reactor consists of a combustion chamber, working at a pressure of 1-2 bar, where the fuel is burned with air or oxygen (Schrader, 1957). The hot (1200 -2700°C) combustion gases are mixed with the cracking feed. This feed can be a liquid feed or a gaseous feed. The mixing is enhanced by the use of a convergingdiverging nozzle to accelerate the hot gases. The feed can be added prior to, after, or in the throat of the nozzle. After a residence time on the order of milliseconds, the reaction fluid is rapidly quenched to fix its composition. Sogawa et al. (1968) discovered that when the hot gases with the cracking feed were accelerated to sonic (or supersonic) flow, the yields were enhanced further. According to Sogawa et al. (1968) this was due to a more uniform combustion that resulted in better mixing and the near elimination of coke formation. This concept was improved by many workers (e.g., Raniere and Schuman (1988) among others, proposed a reactor to crack methane to ethylene by controlling the temperature profile in the reactor). Bernard and Prudhon (1989) suggested using a cyclone as a reaction zone. Fuel and air-oxygen are combusted in a reaction chamber. The hot combustion gases and cracking feed are mixed in such a way that a helix stream is formed in the reaction chamber. Research in less-expensive feed stocks led especially to the adiabatic cracking reactor (ACR). To maintain or increase the profitability of the cracking process, the goal was to use crude oil directly, instead of products from the refineries (Wing, 1980). The fuels used to produce the hot combustion gases were hydrocarbons. These produced large amounts of CO and CO_2 . The CO production is considered to be a problem and ACRs were designed that shifted



Figure 3.17: Schematic of mixing-reaction-cooling zone of the adiabatic cracking reactor (ACR) reaction section. Data taken from Kamm and Tanaami (1979).

the CO to CO_2 through the injection of superheated steam in the hot combustion gases prior to the injection of the cracking feed (Read et al., 1981). The side effect of this injection was that a hydrogen-enriched mixture was formed that gave a positive effect on the olefin yield. Also, the coke deposits were virtually eliminated. Kamisaka et al. (1985, 1986) suggested that the addition of a CH_4/H_2 mixture to the hot combustion gases leads to an enhancement of the production of olefins. The benefit of this process is not only the enhancement of the olefin yield but also the near elimination of coke formation and the application of high pressures (2 – 70 bar). The latter enables downsizing of the equipment, recycle streams, etc. Hosoi and Keister (1975) and Baldwin and Kamm (1982, 1983) investigated the ACRs. The successful research in this technology resulted in the construction of a demonstration unit (Baldwin and Kamm, 1982) in 1979. It was observed that this technology is highly selective to ethylene and has an enormous flexibility in liquid feed stock (from crude oil distillates to naphthas).

The ACR consists of a combustion chamber, where methane is combusted with oxygen. The temperature of the hot combustion gases is regulated with superheated steam. The reaction section is a large venturi-shaped reactor (Fig. 3.17). The feed is injected in the throat section, where mixing, evaporation, and cracking occur simultaneously (Kamm and Tanaami, 1979). A shock wave occurs in the diffuser section of the reactor when the velocity of the hot gases in the throat section is (super)sonic. This shock wave causes the pressure and temperature



Figure 3.18: Schematic overview of precombustion processes.

to increase and the velocity drops back to subsonic levels. In other words, the kinetic energy is converted to sensible energy. This has a positive effect on the cracking reaction, because additional cracking can occur with this energy (Kamm et al., 1979). The research on this technology continued although no commercial plant has been built. Fukahara and Kamm (1990) investigated on-line decoking. One of the problems that needed to be addressed was the over-cracking in the hot section, where the cracking feed meets the hot combustion gases. Tellis et al. (1990) proposed a solution for this problem. The authors expect that this technology is waiting to be commercially applied, when the economic environment is right. It seems technically mature. Fig. 3.18 gives typical values for an ethane based precombustion process. The conversion and yield data reported are mainly for heavy feed stocks. Therefore, we estimate the selectivity and conversion with the aid of SPYRO (Dente et al., 1979; Grantom and Royer, 1987) and the typical conversion and selectivity for conventional thermal cracking of ethane. The amount of oxygen and steam are a result of the computation of the minimum energy requirement, the oxygen required for the combustion of the hydrogen and methane, and the amount of steam to limit the reactor its operation temperature $(1000^{\circ}C).$

3.8.2 Shock wave reactors

Until 1993, two options seemed to be possible for thermal cracking processes that applied direct heating with gases. The first option was injection of the cracking feed in hot combustion gases. The second option was to combust a portion of the cracking feed. Hertzberg et al. (1993, 1994) added another option. They supplied the energy needed for the cracking by means of gas dynamics. In other words, the cracking feed with dilution steam is brought to supersonic speeds and is then expanded. This results in a shock wave (see Fig. 3.19). This shock wave rapidly heats the cracking mixture to the desired cracking conditions. This so-called Shock Wave Reactor (SWR) enables one to perform mixing under the cracking



Figure 3.19: Schematic of reaction temperatures in the shock wave reactor (SWR), from Knowlen et al. (1995) (M = Mach number).

temperature and add the energy almost instantaneously. Therefore, this SWR can achieve very short residence times at a high-temperature level. When we compare the ACR and SWR technology (see Fig. 3.17 & 3.19), many similarities are observed: hot gas (energy carrier), diffuser, supersonic speeds, shock waves. The main difference between these technologies is the mixing zone. With the ACR technology, the mixing is performed at the reaction temperature; with the SWR, the mixing is performed below the reaction temperature. The latter is accomplished by converting the sensible energy (of the energy carrier) into kinetic energy at the beginning of the mixing zone.

Knowlen et al. (1995); Mattick et al. (1992) reported yields of 63% with a 70% conversion of ethane, which results in a selectivity of 90%. These numbers are 15 - 20% larger than those obtained with thermal cracking furnaces. However, these numbers are obtained by simulation. Although the simulation results are checked against shock tube measurements, no actual measurements are reported concerning the yield or conversion of this SWR. From a technological point of view, the SWR seems to be an interesting technique, because of the decomposition mixing-heating and reaction. Fig. 3.20 denotes the typical values for the shock wave technology where the amount of steam is taken from Hertzberg et al. (1993).



Figure 3.20: Schematic overview of shock wave processes.

3.8.3 Partial oxidation-oxidative dehydrogenation.

In this section, processes are discussed that use oxygen for the combustion, which generates the required energy for the endothermic homogeneous cracking reactions. The catalytical ODH of $C_2 - C_6$ hydrocarbons has been examined over noble metal catalysts supported on ceramic foam monoliths. Great interest has been aroused in the past decade by the results reported by Schmidt and co-workers on this topic (Schmidt et al., 2000; Bodke et al., 1999; Huff and Schmidt, 1993; Henning and Schmidt, 2002). High selectivity to olefins were reported in the investigation regarding the selective oxidation of light alkanes over platinum coated foam monoliths, operating adiabatically at extremely short contact times (1 - 10)ms). Selectivity of up to 70% for ethylene with a conversion of 80% for ethane were reported. A further improvement in the selectivity toward ethylene was the addition of hydrogen in the feed. The use of a Pt-Sn catalyst gave even higher selectivity of 80 - 85%, with a conversion of 60% for ethane (Bodke et al., 2000; Bharadwaj et al., 2003). Apparently, the Pt-Sn alloy favours the selective oxidation of hydrogen, which provides the thermal support for the highly selective dehydrogenation of ethane to ethylene. Another important observation is that, with the Pt-Sn catalyst and the hydrogen co-feed, the selectivity to CO_x decreases from $\sim 25\%$ to 5%. In conventional ethane thermal cracking, the selectivity to ethylene is 85% with a conversion of 65%, and the selectivity toward CO_x is <1%. It seems that ODH over a Pt-Sn catalyst with hydrogen as a co-feed gives equal or higher selectivity than the conventional cracking process. In the beginning, Huff and Schmidt (1993) and other authors (Flick and Huff, 1999; Front Freide et al., 1990) explained the results with a purely heterogeneous mechanism. Later, several authors reported that the homogeneous reaction mechanism gave the proper explanation for the observed yield with ODH at high temperatures and short contact times (Beretta et al., 2001a,b; Henning and Schmidt, 2002; Pavlova et al., 2003). The catalyst initiates the homogeneous cracking reactions and generates the CO, CO_2 , and H_2O . The use of oxygen has an impact on the



Figure 3.21: Schematic of diffusion flame reactor, after Sprauer (1964).

safety and reliability of the process. A challenge is the operation of this process, because hydrogen-oxygen and hydrocarbons are mixed and the composition is within the explosion limits. This requires a stringent operation discipline to prevent explosions and fires. The oxygen requirement has also an impact on the cost of the process. Without an oxygen supplier close to the plant, investments must be made for air separation units and the operation costs of these units.

Before 1960, the partial oxidation processes were not fully satisfactory, because of the necessity of using expensive refractory equipment to withstand the high temperatures involved in these processes. Sprauer (1964) proposed to use a diffusion flame reactor (Fig. 3.21). A diffusion flame is a flame where the fuel and oxidant are not mixed before combustion. The diffusion flame reactor features the injection of the hydrocarbon, in excess, into the flame. The hydrocarbon is partially burned to generate the energy needed for the cracking process. This process has been proposed for the production of both ethyne and ethylene. It is clear that the selectivity to ethylene in the diffusion flame reactor is not of interest for today's use. Green and Yan (1987) have improved the flame reactor. The product gas is selectively removed from the diffusion flame. This results in



Figure 3.22: Schematic overview of the partial oxidation-oxidative dehydrogenation processes.

a less over-cracked product and less CO_x in the product stream. Green (1987) proposed to use this process for the cracking of methane to ethylene at remote locations where methane is flared. However, this did not evolve to a commercial process, because of the low selectivity to valuable products.

The use of small quantities of oxygen at elevated temperatures has been considered. Layokun (1979) investigated the effect of adding 2 – 3% oxygen to a propane feed that reacts in an empty laboratory-scale pyrolysis tube. Nitrogen was used as a diluent instead of steam. The authors reported a slight improvement in primary olefin selectivity (to propylene). No reference was made to CO_x production or to the impact of such operation on ethylene furnaces. Choudhary and Mulla (1997) examined ethane pyrolysis with limited oxygen (0 – 20%). Their studies showed a substantial increase in CO_x and substantial decreases in the selectivity to ethylene as the amount of oxygen increased. Increasing oxygen from 0 vol % to 10 vol % of the feed increased the selectivity to CO from 2% to 7% and the selectivity to CO_2 from 0% to 0.4%, and it decreased the selectivity. Fig. 3.22 shows the typical values for the partial oxidation-ODH processes, and the selectivity and conversion are taken from the ODH processes (Bodke et al., 2000).

3.8.4 Direct heating with liquids.

Because of the high temperatures required for thermal cracking, the application of liquids for direct heating is restricted to liquid metals. Fair et al. (1957) presented the results obtained by passing light paraffins through a bath of molten lead. An excellent heat transfer was claimed and low coke formation was observed. The latter was attributed to the absence of a catalytic effect in the lead bath. The yields of the reactor at that time were considered to be equal to the yields obtained by tubular cracking in a furnace. However, lead was found in the quench and the



Figure 3.23: Schematic overview of thermal cracking process by direct heating with liquids.

downstream section. Bredeson et al. (1977) proposed a cracking reactor where this problem is eliminated. Letting them bubble through a "cold" lead bath cools the reaction products. The metals that were used must have a melting point of $<540^{\circ}$ C and have a high specific heat. Among the useful metals are lead, tin, bismuth, and cadmium, or an alloy of these elements in the molten state. Nagel and Bach (1996) proposed to use this technology to produce olefins from plastic waste in recycling applications. This technology is an interesting and different way of examining the problem but has no economical potential. Fig. 3.23 shows the typical values for the thermal cracking with direct heating by means of a liquid. Fair et al. (1957) claimed that the yield data are comparable with the thermal cracking in a conventional furnace; therefore, we have taken the same data.

3.8.5 Direct heating with solids.

Contrary to the heating by a liquid, heating with a solid energy carrier is not a curiosity. Catalytic cracking (FCC) was the first large-scale application of fluidized beds. The energy needed for the cracking (and the heating of the feed) is supplied by the recycled catalyst. The coke formation on the catalyst can be seen as a "mixed blessing", because, in the regenerator, this coke is burned off to produce the required energy for the cracking. The yield of lower olefins (ethylene and propylene) of a regular FCC unit is small. The increasing demand to lower olefins (in particular, to propylene) led to the development of the so-called deep catalytic cracking (DCC) process (Chapman et al., 2002). This process is similar to the FCC process, except for the catalyst (ZSM-5) and the cracking severity. This technology has been commercialized under different names: DCC (by Stone and Webster, Inc., and Sinopec Corporation/RIPP), PetroFCC (by UOP LLC), MAXOFIN (by Haliburton Kellogg Brown, and Root, ExxonMobil Research), and INDMAX (UCC) (by Indian Oil Corporation, Ltd.). Research in

less-expensive feed stocks led also to several technologies where solids were used to provide the energy for the thermal cracking process. In a process from Lurgi (Hu, 1982), hot sand is fluidized by a stream of feed and steam. Coke deposits on the sand particles. These are circulated through a burner, where the coke is pyrolyzed and the sand is heated before it is fed into the reactor. Similar to this sand cracker are other fluidized bed reactors with other solid heat carriers such as coke or inorganic oxides. Hu (1982) has given a more elaborate review of these processes. The main drive to use fluidized beds is to avoid down time to decoke the reactor. The coking and decoking are an integral part of the process itself. The coke is used to produce the energy for the thermal cracking. At this point, researchers have been successful in making fluidized-bed or entrained-flow technology suitable for the production of propylene. These processes, which are derived from the fluidized-bed technology, have not yet been made suitable for the production of ethylene in significant amounts. Any future developments are likely to be found in developing catalysts that are suitable in such an environment and avoid coking. The temperatures applied in the fluidized-bed reactors should be higher and the residence times should be shorter while maintaining plug flow to prevent over-cracking. It is a challenge for the proponents of fluidized beds to develop solutions here.

3.9 Indirect heating processes for production of ethylene

3.9.1 Conventional thermal cracking furnaces.

The conventional tubular cracking furnaces have reached a high level of maturity. The coil layout has developed significantly in the last 50 years, from a horizontal arrangement to a vertical arrangement, from long-residence-time coils to shortresidence-time coils, and from low surface-to-volume ratios to high surface-tovolume ratios. The main limitations in all these developments are the material properties of the coils. In fact, one can say that the main improvements in the conventional thermal cracking process are due to the improvements made by the material scientists. The thermal efficiency of a cracking furnace has increased from 84% in 1970 to 93% currently. This is accomplished by changing the convection in the furnace from natural to forced convection. This results in lower stack temperatures than in the past. Therefore, more heat exchangers can be added in the stack of the furnace. Fig. 3.24 denotes the typical characteristics for an ethane cracking furnace. Another development is the spatially controlled firing in the firebox (Chapman et al., 2002; Martens and Bellet, 1988). The intent of this concept is to provide the inlet tubes with a higher heat flux than the outlet tubes. The tubes and burners are arranged in such a way that this is possible. The fluid inside the inlet tubes is colder than that in the outlet tubes; thus, applying higher heat fluxes at the inlet tubes generally will not result in the tube skin temperatures exceeding the maximum allowed.



Figure 3.24: Schematic overview of thermal cracking by means of indirect heating.

In the unequal firing concept, one tries to give the inlet tubes more heat flux than the outlet tubes by putting more burners in the direction of the inlet tubes. As one can imagine, in a regular firebox this cannot be used in such a fashion that a continuously decreasing heat flux is obtained along the cracking coil. Kösters (1984) designed a firebox where such an optimal temperature profile can be achieved by a co-current flow of hot flue gases and cracked gases. Relatively high heat fluxes are applied at locations required by the endothermic pyrolysis reactions and a continuous lower heat flux as the cracking reactions proceeds. According to Kösters (1984) this thermal cracking process yields an optimal heat flux profile without the risk of overheating the coils. To increase the selectivity toward ethylene, higher temperatures are needed and the residence time should be as small as possible. Consequently, higher heat fluxes are required to supply the energy for the cracking. One way to accomplish this is to increase the driving force. This is realized by the increase of the tube skin temperatures. As stated previously, this is limited by the maximum allowed tube skin temperature. Another possible way to increase the heat flux is to increase the ratio o surface (for heat-transfer) area to reaction volume. In the early days of conventional thermal cracking furnaces, straight horizontal coils were used. The maximum heat flux was determined by the fact that coils bent by gravity when the temperatures were too high. Thereafter, vertical coils were used, which did not have this problem. To increase the surface-to-volume ratio, coils with different diameters of the individual tubes were applied (the so-called "swaged coils"; see Fig. 3.25c). Chambers and Potter (1974) introduced these coils in 1974. The swaging of coils is performed to have a higher surface-to-volume ratio in the beginning of the coil and less pressure decrease toward the end of the coil. Because of the larger diameter toward the exit, coke deposition, which is most pronounced near the coil outlet, has a lesser effect on the pressure drop than straight coils. High pressure drops have a negative effect on the ethylene yield.

The natural extension of these swaged coils is the application of split coils.



Figure 3.25: Examples of (a) split cracking coils, (b) a reverse split coil, and (c) swaged coils.

These coils have multiple parallel tubes in the first part of the coil (Yonezawa et al., 1983). In Fig. 3.25a, several coils layouts of different engineering companies are given. Plehiers and Froment (1991) proposed the reversed split coils (see Fig. 3.25b). These coils are actually the opposite of the split coils where the parallel tubes are applied at the outlet of a coil (see Fig. 3.25a). The reason to apply reversed split coils, according Plehiers and Froment (1991), is that these type of coils result in a more-optimal linear temperature profile than the conventional convex temperature profiles. The major drawback of this reverse split coils is that the diameter of the outlet tubes of the coil is relatively small and, therefore, are plugged quickly by coke formation. This is probably the reason no commercial implementations are offered.

3.9.2 Circumferential shape

Several different circumferential shapes have been tested or proposed (see Fig. 3.26a - e). Experiments are reported with annular coils, where the thermal cracking occurs in the annulus. The annulus has a higher surface- to-volume ratio than circular coils. The major drawback of annular coils, in comparison with split coils, is the fact that they can accommodate less coke than split coils. Also, oval tubes have been used as cracking coils (Sato, 1971; Aramaki et al., 1976). These coils clearly have a higher surface-to-volume ratio; however, after a certain time-on-stream, the oval coils change to regular round coils. The pressure forces inside the



Figure 3.26: Reported circumferential shapes: (a) circle, (b) oval, (c) extended-circle, (d) dumbbell, (e) annulus, (f) helix internal finning, and (g) straight longitudinal finning.

coil and the relative high temperatures of the tube wall cause this phenomenon.

3.9.3 Extended inside surface.

Another way of increasing the amount of energy supplied to a coil is to lower the heat resistance inside the cracking coil (e.g., by the application of finning inside the tubes; see Fig. 3.26f,g). Two types are proposed: the straight longitudinal finned tubes and the spiral type of finning (Magnam et al., 2002). Finned tubes improve the heat transfer but have a negative effect on the selectivity toward ethylene through the higher pressure drop. According to Magnam et al. (2002), the improvement in heat-transfer coefficient has a higher effect on selectivity than the decreasing effect of a higher pressure drop.

3.9.4 Coke inhibitors

Coke formation inside the coil makes it necessary to stop the production for the decoking of the coil. Bozzano et al. (2002) have recognized three types of coke formation: catalytic, thermal, and condensation. Often, after the decoking process, the coil is treated with some type of coke inhibitor (Chaudhuri et al.,



Figure 3.27: Schematic of ceramic block reactor with cross-heating chambers, after Busson et al. (2001a).

2005; Woerde et al., 2002), such as dimethyl disulphide (DMDS), to inhibit the fastest coke formation, namely, the catalytic coke formation. Coke formation by condensation is encountered when heavy feeds are cracked. In the 1980s, a process was developed to crack crude oil in a conventional coil. However, cracking of crude oil gives excessive coke formation by condensation. Yamaguchi et al. (1979) proposed the addition of atomized molten salts to the feed. The carbon and pitch (bitumen) formed by the pyrolysis do not stick to the wall but are gasified by the gas-water-shift reaction catalyzed by the melt (Li₂CO₃, Na₂CO₃, K₂CO₃). Thermal cracking must be executed at high temperatures, and, therefore, it is inevitable that thermal coke is formed. The proposed solution by Yamaguchi et al. (1979) can be used as a tool to extend the run lengths of the cracking furnaces.

3.9.5 Ceramic reactor

From the previous sections, it follows that the metallurgy of the coils is currently a limiting factor. There are no real alternatives with metal, but ceramic walls are an option. In the latter case, catalytic coke formation is avoided. Alagy et al. (1994) proposed to perform thermal cracking in a block reactor composed of silicon carbide (SiC). The firing is performed inside metal tubes that go through the SiC block. The hydrocarbons flow around the metal tubes (see Fig. 3.27). The cracking fluid flows in a cross-flow manner through the reactor with chambers that are heated by the combustion of gas or by electricity.

Ceramics are known for their poor resistance against cyclic temperature treatments. During the decoking phase, the temperatures are at a lower level. Therefore, Busson et al. (2001b) proposed to decoke the reaction zones one at a time. This prevents the cyclic temperature exposure of SiC. Duncan and Gondolfe (2002) proposed a pragmatic solution for the application of ceramics in



Figure 3.28: Schematic of overview of thermal cracking by means of indirect heating applying adapted firing and ceramics.

thermal cracking reactors. Ceramic plates are placed beside each other in such a way that rectangular channels are obtained, wherein thermal cracking occurs. These plates are placed in a furnace to supply the energy for the cracking. Alagy et al. (1988); Heynderickx et al. (1991) proposed the use of a ceramic honeycomb reactor for thermal cracking. This reactor can endure high temperatures (up to 1400°C) and also has a significantly higher surface-to-volume ratio than conventional tubular thermal cracking coils. No commercial implementation of ceramic thermal cracking reactors has occurred yet; however, they are candidates for future alternatives. Fig. 3.28 shows the typical values for a thermal cracking furnace with adapted firing and ceramics. The yield data are estimated with the aid of SPYRO (Dente et al., 1979; Grantom and Royer, 1987).

3.10 Results and discussion

The processes given in the previous sections have been related to each other, in terms of compliance with the ideal thermal cracking process requirements as mentioned in section 3.5. The results of the descriptions are summarized in Table 3.1, which shows the qualitative ranking of the different technologies, with respect to the ideal process criteria. The ranking of minimum energy requirement criteria is based on the outcome of the pinch technique, which is given in Table 3.2.

None of the reported processes have a close fit to all the criteria. We will examine two perspectives to these criteria, namely, from an engineering point of view and an environmental point of view. First, we will look at the process from the engineering point of view, where maximum yield (1), minimum contamination of product with energy supplying chemicals (2), minimum use of auxiliary chemicals (5), and availability (6) are most important. In this context, the cracking processes are interesting for both the direct and indirect heating processes. From the direct heating cracking process, the yield to ethylene has great potential, just

	Output Criteria			Input Criteria		Process Criteria					
	(1) maximum C ₂ H ₄	(2) minimum contamination	(3) minimum impact on environment	(4) minimum energy	(5) minimum auxillary chemicals	(6) maximum availability	(7) low complexity				
Dehydrogenation											
catalytic equilibrium shift ODH		** *** *	****	\$ \$ \$ \$	** *** *	¢¢¢					
Thermal Cracking: Direct Heating											
adiabatic cracking shock wave partial oxidation direct heating with liquids direct heating with solids direct heating with solids and catalysts		*****	*** ****	\$ \$ \$ \$ \$ \$ \$ \$ \$ \$ \$ \$ \$ \$ \$ \$ \$ \$ \$			¢ \$ \$ \$ \$ \$ \$ \$ \$ \$ \$ \$ \$ \$ \$ \$ \$ \$ \$ \$				
Thermal Cracking: Indirect Heating											
conventional furnace adapted firing furnaces ceramic reactors	** *** ***	44 44 44 44 44 44 44 44 44 44 44 44 44	*****		** *** ***	00 00 000	444 444 444 444				

Table 3.1: Qualitative Fit of the Thermal Cracking Process with the Requirements ofthe Ideal Process

by the nature of its heating (especially the gas-heated process, where the heating is fast and at a high temperature level). Despite the benefits of the direct heating, some remarks can be made. A possible drawback of the ACR (adiabatic cracking reactor) is the mixing of the relative cold hydrocarbons with the hot combustion gases, which can cause overcracking (the formation of acetylene, dienes, aromatics). This is concluded from the publications that had the intent of improving the mixing part of the ACR (Tellis et al., 1990). Another issue is the use of pure oxygen, which has a negative impact on operational costs. Besides, when no oxygen supplier is available, significant investments in air separation units is required. The SWR is an interesting technology, because the heating, mixing, and reaction are decoupled from each other, in contrast to the adiabatic cracking process, where the heating and reaction are decoupled. The SWR is capable of giving higher yields than the adiabatic cracking processes. A drawback of this technology is that it is complex. Also, the energy required to produce the superheated steam to generate the required supersonic velocities is a negative point. The partial oxidation, especially the high-temperature ODH, gives high yields and the reactor is small, in comparison with an equivalent conventional cracking furnace. A possible disadvantage is the safety of the process. Oxygen and hydrocarbons (and hydrogen) must be mixed together safely. A portion of the feed is combusted to produce the energy, which reduces the ethylene yield. Direct heating with liquids can be considered to be a curiosity, because the potential selectivity and conversion are moderate and special corrosive liquids must be used to make this work. Also, the number of papers and patents on this topic is limited. In contrast to direct heating with liquids, direct heating with solids is not a peculiarity. There is plenty of knowledge available on this process, because it is derived from the fluidized catalytic cracking (FCC) process. The major advantage of this technology is that coking and decoking are an integral part of the process. The

	conversion [%]	selectivity [%]	Q _{minH} [MJ/(kg C ₂ H ₄)]	Q _{minC} [MJ/(kg C ₂ H ₄)]	T_{max} [°C]	T_{\min} [°C]	T_{pinch} [°C]
		Dehydro	ogenation				
catalytical	25	96	21.1	26.1	1592	-176	-24
equilibrium shift	10	97	6.0	18.0	1584	-106	-20
ODH	30	66	-3.4	23.3	500	-108	306
		Thermal Crackin	g: Direct Heating				
adiabatic cracking	70	86	-3.3	11.6	849	-163	590
shock wave	70	90	9.7	11.4	1580	-168	587
partial oxidation	75	85	-1.8	8.9	1585	-163	793
direct heating with liquids (sacf) ^a	70	80	-6.1	3.1	1579	-159	-32
direct heating with solids	70	80	n.a. ^b				
direct heating with solids and catalysts	70	80	n.a. ^b				
	1	Thermal Cracking	g: Indirect Heating				
conventional furnace, CF°	70	80	-6.1	3.1	1579	-159	-32
ceramic/adapted firing reactors	70	86	-4.7	3.0	1596	-163	-33

Table 3.2: Minimum Energy Requirement of Reviewed ethylene Production Processes with a Fixed Ethane Feed of 1.1 Mt C_2H_6/yr (^a Same as that of the conventional furnace. ^b Not available. ^c The minimum energy requirements given are materialized in a real plant as given in Fig. 3.3)

selectivity and conversion are comparable with the conventional cracking process. The technology has already proven to be an alternative for the production of propylene but not yet for the production of ethylene. It is questionable (Picciotti, 1997) whether the performance of the fluidized-bed technology can be boosted to a higher level of conversion and selectivity, because the amount of solids needed over cracked gas to achieve current performance for ethylene production is already enormous.

The indirect heating cracking processes-especially the adapted firing furnaces - have the potential to produce ethylene in a more efficient way. The required shorter residence times can be achieved when the heat flux at the cold sections of the radiant coil would be increased. The main limitation of the conventional furnace is the metallurgy. When the ceramic reactors are more evolved, these limitations can be removed. From both developments, we can conclude that the combination of ceramic reactors and modified firing furnace is the way to achieve the next generation of thermal cracking furnaces. The dehydrogenation processes, catalytical dehydrogenation, and equilibrium shift produce, of all the processes, the most ethylene per unit of ethane feed, at the expense of significantly more energy to achieve the large recycles. These processes are applied in combination with their availability; therefore, they are of no interest, from an engineering point of view. To increase the yield of these dehydrogenation processes, the temperature must be increased, which also increases the coke formation that deactivates the catalyst. The ODH processes at low temperatures have great potential, because of the fact that they produce energy instead of consume energy, as all the other processes do. The major drawback is that the right catalyst still must be developed. When looking from an environmental point of view, the impact on environment (3), specific energy (4), and complexity (7) are important. The catalytic processes are not interesting, because of their energy requirements and the associated production of greenhouse gases. Table 2 shows that the equilibrium shift processes require less energy than the catalytical processes, despite the fact that the recycle stream is three times larger. The explanation for this observation is that the CH_4 separation column requires less energy for the separation, because there is no hydrogen in the feed of this column for the equilibrium shift processes. Although the indirect heating processes are known to be energy-intensive, they score very well in the minimum energy requirement. The temperature level of this process allows effective heat integration. Fuel is combusted with air to produce the required energy producing greenhouse gases that are released into the environment. The direct heating processes-adiabatic cracking and partial oxidation, although these require more energy-produce less greenhouse gases. The CO_2 is removed from the reaction effluent stream by some adsorption process; therefore, less greenhouse gases are produced. When the greenhouse gases would be removed from the flue gas of the thermal cracking furnaces, these processes would yield a process that performs well, from an environmental point of view.

3.11 Concluding remarks

All the ethylene used today is produced from hydrocarbons, and, obviously, quite some development has been performed to optimise and improve the processes involved, as is recounted above. We now ask ourselves what the future process routes and improvements could be. The overview of Fig. 3.1 shows the global possibilities. If we take into account the future scarcity of hydrocarbon resources, then, eventually, biological routes that are based on biomass have the most potential.

The hydrocarbon feed will remain important and, from a development point of view, there is scope, as the summary of Table 3.1 shows, that actually none of the processes are fulfilling the ideal expectations. The conventional processes fail on environmental impact or availability, and the alternative processes fail on complexity.

However, the attainable limits could have been reached. This is illustrated by the energy usage. Fig. 3.3 shows that some type of lower bound is encountered for conventional furnaces. Table 3.2 presents a refined analysis over various processes, showing the heat recovered from each process and the cooling requirement for each process. The possible limit shown by Fig. 3.3 will not be altered, because the conventional furnaces have the best energy performance.

We look first at the process conditions and chemistry. As noted, we intrinsically need high temperatures and short residence times. In the past, the catalytical processes have not been proven to provide alternatives for the thermal cracking furnaces. The coke formation and average selectivity prevent a breakthrough of this technology. If the proper catalyst for oxidative dehydrogenation (ODH) at lower temperatures ($<600^{\circ}$ C) were to be discovered, maybe this will change.

From an engineering point of view, the thermal cracking by direct heating with
gases are good, especially the shock wave reactor (SWR) that has a decoupling of the heating, mixing, and reaction, which can be optimised separately. There is room to improve this technology when we compare it with the evolution of the thermal cracking process, because the shock wave technology is in the pilot phase. Therefore, this requires a careful design of reactor unit.

Progress made by the materials scientists in the thermal cracking process proved to be of vital importance. Alternative materials, such as, for example, ceramics, must be investigated further to improve the thermal cracking process. The mechanical engineering should enhance the adjustment of the firing further to enable higher duties at the relative cold inlet section of the reactor. From an environmental point of view, the cracking processes with indirect heating are the most ideal processes. These processes could perform better when the greenhouse gases are removed from the flue gases.

The future process routes for ethylene will be examined in thermal cracking furnaces with a ceramic reactor and adapted firing. The shock wave reactor is a promising technology because the heating, mixing, and reaction can be controlled separately. The problems related to the heating of the steam must be solved. Also, the shock wave technology should be tested further, to determine whether the shock wave can produce the required energy for different feed stocks. Also, the scaling-up of this reactor is an interesting topic. However, when this technology prevails, it can be a breakthrough for the thermal cracking technology.

Chapter

Enhancing simulation program SPYRO with a symbolic modelling facility¹

Abstract

This paper describes the experience gained from the integration of symbolic modelling within an existing equation-based flowsheet package, $SPYRO^{\textcircled{(B)}}$ Suite 7. A demand for more flexibility led to the integration of a symbolic model definition module into the existing program. We elaborate on our motivations and choices made to our decision for the gPROMS language. The existing program is described, and in some detail the functionalities to minimise the modelling errors and to enhance the detection of them. The gPROMS language itself, the evolution of it and the selected subset are described. Additionally, new attributes of the language are described: spline construction, intermediate graphical results, and definition of a large number of simulations/optimisations. The symbolic model definition module is demonstrated on the determination of an attainable region and the thermal cracking of ethane. The symbolic modelling module proved to be cost effective and improved the quality of the main engine.

4.1 Introduction

The application of computer-aided process engineering in the industry was boosted in the late fifties by the introduction of the third generation programming langu-

 $^{^1{\}rm This}$ chapter is version with minor modifications of an article that is under revision at Computers and Chemical Engineering (van Goethem and Verheijen, 2010)

ages, such as FORTRAN. The simulation activities were focused in the beginning on individual pieces of equipment, for improving the knowledge and the operation and later on systems consisting of multiple units of equipment. In the eighties flowsheet simulators of unit operations were a common tool for all process engineers. In the nineties the dynamic simulators abandoned the research and development stage and yielded equation-based simulators, such as ASCEND (Abbott, 1996), DYMOLA (Cellier and Elmqvist, 1993), SPEEDUP (Perkins and Sargent, 1982), and gPROMS (Pantelides and Barton, 1993). From the late nineties until current date we are waiting for the physicochemical simulators, such as MODEL.LA (Bieszczad, 2000) or MODKIT (Bogusch et al., 2001) to leave the development phase. These simulators have not penetrated into the industrial practice due to a lack of commercial implementation of these tools (Klatt and Marquardt, 2009). Therefore they do not leave the development phase.

In this work we are dealing with a simulation tool, SPYRO[®] for the steam pyrolysis process that was introduced in the late seventies (Dente et al., 1979) and has evolved over the years such as other simulation tools. It started as a simulation program to describe the physical and chemical phenomena solely inside the radiant coil. It has evolved both on physicochemical as on application areas. Improvements in the kinetic schemes were made and models for other unit operations were added to become a full sequential modular simulator for the steam pyrolysis process. In the late nineties it became evident that the sequential modular paradigm on which the program is founded reached its limits for functional expansion. The increasing need for more flexibility of the modelling capabilities led to the development of an equation-based version, SPYRO², a more elaborated review of this is given by Barendregt et al. (2002). This increase in modelling capabilities is two fold. The first is the removal of certain structural limitations, such as a fixed predefined flow sheet for the simulation (van Goethem et al., 2001), enabling novel process designs. The second is the incorporation of mathematical optimisation capabilities (van Goethem et al., 2002). The latter yielded a modelling module for the definition of objective functions, inequality constraints and additional equality constraints (besides the predefined models). It proved fortuitous that the implementation of a module, where the optimisation problem could be formulated symbolically, provided additional flexibility. The features of this modelling module were limited. It is only applicable for optimisation and not for simulation, the modelling language used had a flat structure, no sub-models, no inheritance, and no structured equations (FOR-loop, IF-statement, CASE-statement). This initiated the integration of an advanced symbolic modelling module in an existing equation-based flow sheet package. This work can be generalised to incorporate symbolic modelling in any dedicated simulation/optimisation program. The aim of this paper is to present the experience gained by the integration of a symbolic module in an existing equation-based flowsheet program.

In the remaining part of this introduction we will elaborate on the motiva-

 $^{^2\}mathrm{SPYRO}^{\textcircled{B}}$ Suite 7 is abbreviated to SPYRO in the rest of this chapter.

tion and choices made. Thereafter we will describe the equation-based simulation/optimisation program, followed by the highlights of the modelling language that has been implemented. We will address the modifications of the language after its introduction. We discuss which subset of the modelling language is implemented for the specific requirements of the SPYRO program and describe the functionality that has been added to the modelling language. We will give an example to illustrate the benefits of the added functionality. Finally we will conclude with the experience gained.

4.1.1 Motivation and choices

The model equations, residuals, Jacobian matrix, sensitivity equations and derivatives in process simulators such as SPYRO are hard coded in optimised source code. Generally speaking the computation speed of these equations is high and the flexibility to change these equations is low. Depending on the quality of the package, it offers the flexibility to model all particular configurations of the process, in this case steam pyrolysis. The drawback is obviously that other processes cannot be modelled and the available computation power cannot be exploited without coding of new model equations. The coding of new models is time consuming, error prone and specialised people are required. The addition of a symbolic modelling module expands the package to other model equations without the need of specialised people and where the modeller can focus on the model equations solely and not on the IT and mathematical issues. The above motivated us to integrate a Symbolic Modelling Definition (SMD) module into a dedicated equation-based flowsheet package for steam pyrolysis. This leads to the following requirements for the SMD module. The SMD should facilitate to define process models, described by a NLAE, DAE or PDAE system, without the need of detailed knowledge of IT and mathematical techniques. Typically a process that can be described with a small number of species (10 to 20), are continuously operated, can contain discontinuities, and apply all kinds of heat and mass transfer processes. The module should also have facilities to connect with existing legacy models.

The topics to consider prior to the implementation of such a module are:

- 1. Selection of a suitable language for the SMD module
- 2. Integration structure of the SMD module with the existing flowsheet program

The first topic is the selection of a language to define the model equations. The modelling language is the interface between the modeller and the computeraided simulation tool. The third generation programming languages, such as C, C++, FORTRAN and Java, *language of computational procedures* (Bieszczad, 2000), provide the maximum flexibility for the development of process models. These languages are tailored for the description of solution procedures for mathematical models, not necessarily for the models itself and require a significant

amount of knowledge on programming, numerical mathematical techniques and time for design/coding and debugging of the models. Also the reusability of these models is inherently difficult as well as the modification to other applications of the programmed models (Bieszczad, 2000). Traditionally the language of unit operations has been applied by all modular flowsheet simulators. Despite the ability to supply user defined models this language of unit operations is restricted by the available models in the libraries and the dictated connection structure of the models. The equation-based packages provide the language of mathematical equations that overcomes the limitations of the procedural restrictions of the previously mentioned languages. This language allows the modeller to define the equations in a symbolic form, providing a focus on the model equations itself. The language embodies logical operators to facilitate conditional model definitions. Object-oriented programming concepts are implemented to organize and structure the mathematical description of the processes. The language of process modelling (also called language of physicochemical phenomena) has the ambitious goal to enable all chemical engineers to readily build and use models by supporting the model activity at the level of chemical engineering knowledge. Instead of defining the model equations, the modeller must define the assumptions taken, which species, phases, reactions, fluxes, flows are considered. He has to define the tasks, which describe the control actions and disturbances imposed on the processing system by its environment. In other words the interacting physicochemical phenomena are formulated. This language is still under development nevertheless it has a great potential since it would resolve some major deficiencies of current modelling tools (Cameron and Ingram, 2008).

The SPYRO program started as a package typically written in the *language* of computational procedures, evolved to a package using the language of unit operations, and subsequently to the language of mathematical equations. Obviously we consider both the language of equations and process modelling as the proper kind of language for the SMD module. Some of the available modelling tools are shown in Table 4.1 that features the language of mathematical equations and process modelling. These languages come in different forms, namely as a publication (PhD thesis, article, conference paper, open-source project, etc.), and as binaries (implemented in existing packages). All of the languages reported originate from academic research. A limited number have been commercialised. When a language is used that is published only, one needs to build the complete SMD module from scratch. This implies knowledge on programming, information technology, symbolic and discrete mathematics. The amount of work can be reduced if libraries are available, in the case of SPYRO several general purpose libraries for mathematical routines and all kind of utilities are present. The implementation of a language based on publications will generate the maximum flexibility since the module can be tailored to specific requirements, but will require a significant amount of effort. The use of an existing package (binaries) for the SMD module can be established through, amongst others, the CAPE-OPEN interface. This option will require a limited amount of effort but comes at a price of an additional license fee for the package. The flexibility will be limited because it depends on the willingness of the package supplier to add or change functionality to the SMD module. The application of an open-source SMD module, for example Modelica (http://www.modelica.org/), is conceptually flexible since the source code is available and can be established with limited effort. SPYRO is not open-source and therefore only an open-source project with a GNU L-GPL (GNU's Lesser General Public License) can be used for the SMD module, in all other cases special license should be obtained. We know from experience that a significant amount of effort is required for major changes of existing source code, especially when dealing with complex source code as required for the SMD.

In an industrial environment, reliability, flexibility, maintainability and cost of a new SMD module are important factors. The process modelling languages are still under development, and no need exists to research this kind of languages, and therefore not (yet) applicable in our industrial setting. When the SMD module is created from scratch the cost of the module is proportional to the spent man-hours which are significant and difficult to estimate. The cost when connecting SPYRO to an existing SMD module is easily estimated because it resembles roughly the license cost and the cost to create the interface. On the other hand the licence fees for a reliable, tool are significant and the flexibility to change or add new functionality is dependent on supplier. This led to the decision to create a SMD module from scratch because it gives the best reliability, flexibility and maintainability. With hindsight we observed that the costs to build the SMD module were modest, approximately a half man-year.

The available equation modelling languages do not differ much conceptually, although the syntax is quite different. Also the languages are all accessible through publications and are considered equally difficult to implement. We observed the application of the individual languages both in academia and industry to distinguish between the available languages. The gPROMS language, as proposed by Barton (1992), is selected because it has proven its value both in industry and academia. The language is also closely related to ABACUSS (Feehery and Barton, 1996) and the syntax is related to SPEEDUP (Perkins and Sargent, 1982), both are applied in industry and academia as well.

The second topic is related to the way the SMD module is integrated in the existing equation-based flowsheet package. In an equation-based program the solver and model equations are strictly separated. The communication between solver and models is basically done by a vector containing the unknowns, the residual vector and the derivative matrix (Jacobian). The SMD module will also generate unknowns, residuals and Jacobian matrices. The hard coded model equations and SMD equations can be solved with or without usage of each others variables. When the variables of both modules are integrated, the syntax needs to be created to use variables of the hard coded models in equations defined by the SMD module and vice versa. If they are not integrated the solver can determine the solution of the hard coded models and SMD module at the same time or separately. Our main objective is to model processes other than steam

Name of the system	A reference	Commercial package	Equation mo- delling langu- age	Process modelling language
ASCEND	Abbott (1996)		*	
ABACUSS	Tolsma et al. (2002)	*	*	
DAESIM STU- DIO	Hangos and Cameron (2001)	*		*
DYMOLA	Cellier and Elmqvist (1993)	*	*	
DYLAN	Lund (1992)		*	
gPROMS	Barton (1992); Pantelides and	*	*	
	Barton (1993)			
HPT	Woods (1993)			*
MODASS	Srlie (1990)			*
MODEL.LA	Bieszczad (2000)			*
MODELICA	Fritzson (1998)		*	
MODELLER	Westerweele and Preisig (1999)	*		*
MODEX	Meyssami and Åsbjørnsen (1989)			*
MODDEV	Jensen and Gani (1999)			
MODKIT	Bogusch et al. (2001)			*
OMOLA	Nilsson (1993)		*	
PROFIT	Telnes (1992)			*
PROMOT	Tränkle et al. (1997, 2000)			*

 Table 4.1: Selection of modelling tools (Adapted from Marquardt (1996))

pyrolysis therefore this integration of variables is deferred to a latter stage. The current model library is considered rich enough for the steam pyrolysis process. As a consequence we either offer models, defined in the SMD module, or hard coded models, to the solver. A second aspect of the second topic is the mode of operation, the SMD module can be build as an intermediate code generator, such as SPEEDUP (Perkins and Sargent, 1982) and DynoPC (Lang and Biegler, 2007), or as an interpreter, such as gPROMS (Pantelides and Barton, 1993), and AS-CEND (Abbott, 1996). The first operation mode requires code generation (in e.g. C/C++, or FORTRAN), compilation, linking which is time consuming even for a relative small number of equations. In the second mode the SMD is interpreted into data structures which can be evaluated directly without intervention of other programs. The advantage of this mode lies in the elimination of the compilation and linking steps, but has the disadvantage of being more memory intensive and less computationally effective than object code. Nowadays computer power make is possible to apply the interpreted mode of operation. When in the future models are build that cause performance issues in the SMD module we can develop a utility to generate source code, compile and link this as in the first operation mode.

4.2 Description of the SPYRO

The program features the simulation/optimisation of a flow sheet with predefined models, typical for steam pyrolysis: Firebox, Radiant Coils, Transfer-line exchangers, etc., and general purpose models such as: Feed, Product, Splitter, etc.. The program is divided into several functional sections, as schematically shown in Fig. 4.1. The Data Manager is the central section, the "spider in the web", controlling the data flow/storage of the program. The Graphical User Interface or Visualiser takes care of the visualisation of both the input and the output, this data is stored in an XML-file. The Solver-Optimiser Manager contains all the available numerical mathematical procedures for solving both linear and non linear systems of equations and optimisation problems.



Figure 4.1: Functional decomposition of the SPYRO program.

The Model Manager contains controls all the predefined models, residuals, analytical derivatives, initialisation output generation, etc.

The core of the chemical know-how of the SPYRO program are the equations for the pyrolysis and its kinetics (see "Kinetic Core" in Fig. 4.1). These are hard coded. The steam pyrolysis is described with a free radical mechanism, which is inherently stiff due to the different reaction velocities of the radicals and the molecular components. The latest kinetics scheme contains approximately 7000 reactions between 210 molecular components and 40 radical components. The steam pyrolysis process is described by a set of partial differential algebraic equations. The temporal dependency describes only slow phenomena, the formation of coke inside the radiant tubes (typical time scale is 40 - 60 days) and the number of temporal dependencies is small compared to the spatial dependencies. The numerical challenges are located in the description of these spatial properties, originating from the stiffness of chemistry model. The spatial dependencies are approximated effectively with the orthogonal collocation on finite elements technique (Lang and Biegler, 2007). Apart from the stiffness and other non-linear behaviour, the largest computation efforts is for the direct linear solver to perform a decomposition in reasonable time (~ 10 s) on a regular desktop PC (P4, 3.4 GHz, 2 GB RAM). The large Jacobian matrices (120.000 × 120.000 with $4 \cdot 10^6$ non-zeros) originate from the large number (~ 250) of equations of continuity and the presents of a 3D-Firebox model. The used solution system is such that we can solve 200.000 equations. This is sufficient for the pyrolysis calculations and also for the added SMD module.

4.2.1 Modelling error reduction

Several functionalities have been implemented to minimise the errors made by the modeller. This reduces the debugging time of the models submitted to the solving process. The functionalities vary from basic checking to the application of mathematical techniques in the core of the solver. Our vision is to provide clearly the relevant information to the modeller, both textually as well as graphically, based on mathematical progress indicators.

The first layer for checking is the visualiser (Fig. 4.1) that should be designed such that information is intuitively grouped and ordered logically, for example geometrical data should be separated from operational data (inlet temperature, flow rate, etc.). The Data Manager features a three level check procedure. The first level features the checks performed on one entity in a model, for example the lower, upper bound, the value of the sum of an array (mol fractions), etc. On the second level the consistency of a full model is checked, for example the specification of physical property systems with different reference states within one model. On the third level the consistency between different models is checked, for example the sequence of the sub-models of a radiant coil which have a predefined sequence. During the initialisation of the Model Manager, prior to the solving process, checks are performed whether the system is well-posed. Notification messages are issued, with possible root causes of these issues. When the modeller has defined a case that successfully passed all these checks and is submitted to the solution procedure, errors in the models can still be present.

The first type of modelling errors is of a numerical nature. The permutations applied in the direct linear solver, not only facilitate efficient factorisation but also give insight in the well-posedness of the problem. The transversal permutation yields information on the *structural singularity* of the system (Tolsma and Barton, 2000). The detection whether a proposed system of equations is *numerical structurally singular* is found easily in the pivoting process of the linear solver.

The second type of errors is an inconsistent (unphysical) definition of the problem, for example: description of a compressible flow through a tube where the specified flow rate is too large for the tubes geometry (pressure drop getting too high). The root cause is usually found by the inspection of different sets of output generated with a different number of iterations. The amount of data that needs to be inspected can be large and therefore the discovery of the root cause of the problem can be time consuming. Simulation programs report usually mathematical indicators to give insight in the progress of the solution procedure, such as damping factors, norm of residuals and correctors. This type of information does not give any insight in specific variables and residuals which possibly give rise to poor convergence behaviour as described above. In SPYRO we have added features to reduce the time to discover these errors of the second type. This is accomplished by reporting specific variables and residuals with the largest change during the solution procedure, besides the usual indicators. The following items benefit the modeller in the diagnostic phase(see also Fig. 4.2):

- 1. The variable with the largest violation of its bounds (used to compute the maximum damping factor).
- 2. The residual with the largest absolute value.
- 3. The variable with the largest absolute corrector step.
- 4. The variable with the largest relative corrector step (relative to the value of the variable).

Although this additional information gives valuable information, graphical intermediate results provide even faster and more insight in the solution procedure. Monitoring several intermediate results enables the modeller to draw conclusion on particular root causes of poor convergence behaviour of the model, for an example of the looking view see Fig. 4.2.

4.3 Description of the modelling language

We have selected the language as defined by Barton (1992), called gPROMS. The commercial implementations of this language are known under the names $gPROMS^{\textcircled{R}}$ (distributed by Process Systems Enterprise (PSE) Limited) and ABA-CUSS II (continued under the name JACOBIAN and distributed by Numerica Technology). For convenience we will label the language used in these programs as defined by Barton (1992): gPROMS³. This language is designed to formulate dynamic simulations of systems with combined discrete and continues processes of arbitrary complexity. The language proposed in its original form consists of four distinct entities, namely the *DECLARE*, *MODEL*, *TASK* and *SIMULATION* entity. The basic variable types, in terms of lower and upper bound and default value

 $^{^3 \}rm When we use the registered trademark token, <math display="inline">\textcircled{R}$, we refer to the program distributed by PSE Limited



Figure 4.2: Example of combined numerical solver output and graphical intermediate model results.

and stream types are defined in the DECLARE entity and are globally available to all model entities. MODEL entities describe both the continuous physicochemical mechanisms governing the time dependent behaviour of unit operations and any discrete changes resulting from these mechanisms. The TASK entities describe the external control actions or disturbances imposed on the modelled system. A SIMULATION entity defines a full dynamic simulation, where tasks are applied to instances of model entities Barton (1992). The definition of the language in a Backus-Naur From can be found in appendix B of the PhD thesis of Barton (1992).

A model for a complex process is constructed efficiently by the introduction of structure through the definition of several interconnected models. gPROMS provides three main functionalities in order to provide this structure.

- 1. The basic building block is a so-called primitive or root model, which contains no sub-models. Primitive models are constructed by the definition of attributes such as: parameters, variables, streams and equations (Barton, 1992).
- The second functionality is hierarchical sub-model decomposition (Elmquist, 1978). A model may be declared as a collection of interconnected submodels. Typically the connections represent physical streams of fluxes of mass, energy, electricity, etc..

3. The third functionality that is offered by gPROMS is the hierarchical model development through inheritance. The inheritance concept is well known from object-oriented programming languages. An inheritance hierarchy can be represented schematically by a directed tree, where the vertices signify the models and the edges signify the relationship "inherits from".

Languages are subject to changes and also gPROMS has changed after its introduction in 1992. We will highlight the changes relevant for our implementation. Developments in the (dynamic) optimisation community led to the need to have an entity for the definition of optimisation problems. The language is developed by two separate groups, gPROMS[®] (Process Systems Enterprise Ltd, 2004) and ABACUSS (Clabaugh, 2002), both groups added an *OPTIMISATION* entity as a fifth main entity. This is required to define typical relations for optimisation problems, for example: objection function, (in)equality constraints and control variables. In the gPROMS[®] group the emphasis is on adding or changing a *SI-MULATION* entity to an *OPTIMISATION* entity and in the ABACUSS group the *OPTIMISATION* entity is equal to a *SIMULATION* entity with additional features to define the typical optimisation features. The main *SIMULATION* oPTIMISATION entities show a differentiation between the two groups, through the naming of the entities and the attributes available inside the entity.

The language used by equation-based packages overcomes the limitations of the procedural languages. Nevertheless procedural functionality is still required, for example, to incorporate existing legacy code such as physical property packages. The way how the language enables to connect with external procedures stored in libraries is another explicit difference. In ABACUSS a formal robust, programming approach is taken, to minimise errors, by the definition of the *EXTERNAL* entity that defines the connection with external procedures (Tolsma et al., 2002). In gPROMS[®] the "foreign objects" have been introduces within the *MODEL* entity, which is less formal and more flexible. A parameter defines which external library should be accessed and procedures within this library are accessed such as variables in other models. If, for example, the parameter P defines the FOREIGN_OBJECT "ThermoPack" then the procedure to compute the liquid enthalpy is addressed within the model as follows: P.LiquidEnthalpy(T, p, x).

4.4 Language used

In this paragraph we address which elements of the gPROMS language will be used to fulfil the symbolic modelling requirements within SPYRO. Additionally, the new attributes will be discussed for the main entities: *DECLARE*, *MODEL*, *TASK*, *SIMULATION* and *OPTIMISATION*.

The *TYPE* attribute from the *DECLARE* entity, is implemented with an additional feature to have besides the upper and lower bound also a soft lower and soft upper bound, that are required by the numerical procedures within SPYRO. When these soft bounds are omitted they are assumed to be equal to the hard

bounds. The *STREAM* attribute of the *DECLARE* entity is not implemented, since it is not an essential functionality.

The attributes, *PARAMETER*, *UNIT*, *VARIABLE*, *SET*, and *EQUATION* of the *MODEL* entity have been applied. A minor change to the original gPROMS is the option to have a *PRESET* attribute in a *MODEL* entity, to make the initialisation of the variables more convenient. At this moment there is no requirement to model discontinuously operated processes and therefore we did not implement the CASE-equations and the IF-equations (also known as conditional equations), in the *MODEL* entity. The foreign objects can be used to define discontinues functions instead of the IF- and CASE-equations. This implies as well that temporal derivatives are not yet supported. Nevertheless DAE & PDAE systems are solved and optimised in an equation-based fashion, as for example done by Biegler and his co-workers (Lang and Biegler, 2007). For this purpose several additional functions, besides the standard functions such as: *sin, cos, erf, min, max, sigma,* etc., for Orthogonal Collocation on Finite Elements (OCFE) to compute the discretisation matrix, *ocmat,* location of the collocation points in a finite elements, *ocrloc,* and the distribution of the finite elements, *felr*.

The TASK entity is not implemented because there is no need to model discontinuously operated processes. The SIMULATION entity features all the attributes of the MODEL entity plus additional attributes for the output (MONITOR) and assignment (ASSIGN) of variables. The typical attributes for the time integration have been omitted such as, SCHEDULE, INITIAL. We adopted the ABACUSS approach for the OPTIMISATION entity because it is more in line with the whole language setup as defined by Barton (1992). The OPTIMISATION entity is equal to a SIMULATION entity with additional attributes for the specific optimisation requirements, such as MAXIMISE, MINIMISE, INEQUALITY, TIME INVARIANT, etc.

The features to improve the modelling efficiency in SPYRO proved fruitful. Therefore these items had to be incorporated into the language. We have added to the SIMULATION and OPTIMISATION entity two new attributes to enhance model debugging and simulation and optimisation efficiency. The first attribute is the display of intermediate model results to inspect the progress of the simulation and optimisation. As mentioned SPYRO features several functions to debug models. For this purpose we allow the modeller to specify 6 intermediate graph attributes. Fig. 4.2 shows, besides the usual numerical solver output the graphical intermediate model results. Within the *GRAPH* attribute the results of a series of consecutive expressions are interpreted as data sets for the graph where the first value of the result of an expression is considered to be the x-value, and the other values as y-values. Such a series of consecutive expressions is ideally defined with a FOR-equation, for example shown by Fig. 4.3. Note the subtle difference in the END-statement where we require ENDWITHIN to close a WITHIN statement, this is also required for the END statement of the *MODEL*, FOR-equation, etc. Reduction of errors is important in an industrial setting and for this reason we implemented this feature.

```
GRAPH1
WITHIN ModelOne DO
FOR i:=1 TO nSections DO
Time(i),Temperature(i);
ENDDO
ENDWITHIN
```

Figure 4.3: Example how to define a graph to display intermediate results during simulation/optimisation.

```
SCENARIO
VARY
# Parameter:= First value, last value, number of points;
Length := 1, 42, 200;
Diameter:=0.1, 0.5, 10;
OUTPUT
Yield, Conversion;
```

Figure 4.4: Example of a SCENARIO attribute to define 2000 simulation to inspect the dependency of the Yield and Conversion to different geometry values.

The second new attribute that is added, *SCENARIO*, defines consecutive simulations and optimisations to inspect the sensitivity of the results to model parameter values. This sensitivity is computed by performing a series of simulations or optimisations with different values for the parameters of interest. An example on how to define 2000 simulations within a *SCENARIO* attribute is given by Fig. 4.4.

The output of the sensitivity is augmented with the values of the parameters in the VARY block and a convergence indicator of the solver or optimiser.

Incorporation of external procedures are defined with the "foreign objects" concept from gPROMS[®] since this yields the most flexible options for the users while the responsibility to deliver robust external libraries is delegated. Robust external procedure functionality is provided by splines that have been incorporated in the gPROMS language. We have added the *SPLINE* attribute (see 4.5), additional to the *INTEGER*, *REAL*, *LOGICAL* and *FOREIGN_OBJECT* attributes of the *PARAMETER* section. The functions *splineconstr* and *splinevalue* have been added to respectively construct and evaluate a spline, the input and output operate both on scalars as on arrays as is the case in all other expressions.

```
PARAMETER
ST AS ARRAY(2) OF SPLINE
SET
ST:=SPLINECONSTR([0,1],[[0, 84],[1,2]],'cubic','linear');
EQUATION
42 = SPLINEVALUE(Solution,ST(1));
```

Figure 4.5: Example of a SPLINE attribute to define an array of 2 cubic splines with linear extrapolation, the construction and application of the spline in an equation.

4.5 Implementation of symbolic modelling

Fig. 4.1 shows the functional sections of the program, as shown, the SMD module is implemented as a separate module. The Model Manager provides the residuals and Jacobian matrices, when an instantiated SMD case is simulated/optimised the residuals and the Jacobian matrices are supplied by this extension. Currently no features are present to combine the predefined models with the SMD models. The kinetic core of SPYRO can be used through the "foreign object" functionality of the SMD. This has been tested on the model as explained in the second example with a foreign object for the production rate consisting of 3000 reactions between 150 species.

The SMD module is divided into several functional parts, as shown by Fig. 4.6. During the initialisation of the Model Manager the SMD input file is parsed and instantiated. The parser translates the input file into data structures that contain the MODEL, SIMULATION and OPTIMISATION entities (see Fig. 4.6), and it reports in case of errors, what and where the input file items need to be corrected. To facilitate parsing of the input file within an users preferred text editor, we added a separate interface to check the structural, semantic or lexical errors within the input file. When the parsing is successful the generated data structures are instantiated, and an active parameter array (P), an active variable array (X)and active equation/partial derivative arrays (R/J) are created (see Fig. 4.6). Additionally, the instantiator performs semantic checks which have been deferred by the parser due to the extensive model parameterisation applied in gPROMS. For example, the size of an array can be defined by parameters and during the process of instantiation the ultimate values of the parameters are known. Checks to determine, amongst others, dimensional correctness need therefore to be postponed until instantiation of the models. Appendix A denotes some details on how symbolically defined equations are translated into data structures that can be evaluated to yield numerical values and partial derivatives.



Figure 4.6: Functional decomposition of SMD module, see Figure 4.1 for the connection with SPYRO (SMD module).

4.6 Illustrative example

We present a simple and a complex example to illustrate the gained flexibility and the exploitation of the computation power of SPYRO for solving other models than the predefined flowsheet models. Although we have deferred to a latter stage, the integration of the predefined variables with SMD variables, the first example demonstrates that we can combine these two via a *FOREIGN_OBJECT*. During the implementation of the second example we added the functions to apply the OCFE technique more easily. This shows the flexibility when one develops such tools in-house. This is particular important in an industrial setting where efficiently is more important.

```
PARAMETER
  RelZ AS ARRAY(42) OF REAL
  ST
       AS
                       SPLINE.
  FO
       AS
                       FOREIGN OBJECT
SET
  # Define relative coordinate
  RelZ:=[0, 0.3, ..., 1];
  # Define corresponding temperature difference
  RelTemp:=[0, 0.42, ..., 1];
  # Construct the temperature spline
  ST:= SPLINECONSTR(RelZ,RelTemp,'qubic','linear');
  # Set the foreign object to the KS7F0B.DLL
  FO:="KS7Fob"; # The foreign object for ProdRates
EQUATION
  T(iCol,iFE) = Tlow + (Tval-Tlow)*
              SPLINEVALUE(Volume(iCol, iFE)/VolTot, ST);
  FOR iComp:= 1 TO noComp DO
    SIGMA(OCFEmat(iCol,:)*F(iComp,:,iFE))=VolTot*
        F0.ProdRates(F(:,iCol,iFE),P(iCol,iFE),T(iCol,iFE));
  ENDDO
```

Figure 4.7: Example on the use of SPLINE and FOREIGN_OBJECT attribute in a SMD input file for the comparison of ethylene yields for a isothermal and measured temperature profile.

4.6.1 Temperature profile comparison

In this example we will illuminate the use of the *SPLINE* and *FOREIGN_OBJECT* attributes. We are interested in the difference of ethylene yield for isothermal and some measured temperature profile for the steam pyrolysis of ethane with an outlet temperature of 850°C. The equation of continuity for the k^{th} component is described by equation (4.1).

$$\frac{dF_k}{dV} = R_k(F,T,P) \qquad V = 0 \quad F = F_0 \tag{4.1}$$

The chemical know-how of SPYRO is in its kinetic models for the production rates, R, of the pyrolysis process (see Fig. 4.1). These procedures have been made accessible for the SMD module through the application of a foreign object. Fig. 4.7 shows the declaration of foreign object (FO) which is similar to other parameters. In the *SET* section the FO is assigned to the desired external library, "KS7FOB.DLL". The spline parameter, ST, for the the measured temperature

profile is declared similar to other parameters and constructed in the SET section. In the equation section the temperature at a collocation point, iCol, in finite element, iFE, is defined equal to a value of the spline function, *splinevalue*. Fig. 4.7 shows as well the definition of the production rates, R, equal to external procedure "ProdRates" where the differential Eq. (4.1) is descretised with OCFE. Fig. 4.8 shows the results of the ethyleneversus ethane conversion for the isothermal and the measured temperature profile.



Figure 4.8: The conversion of ethane versus ethylene yield for a outlet temperature of 850° C.

4.6.2 Distributed reaction and mixing

In this example we demonstrate the effectiveness of the *SCENARIO* attribute in the *OPTIMISATION* entity and the available functions for OCFE for a more mature problem. We use the distributed reaction mixing (d-RMix) model (van Goethem et al., 2008), Eq.(4.2) to determine the attainable region (Kauchali et al., 2002) for the van de Vusse (1964) reaction scheme.

$$\frac{\partial F_{k,V}}{\partial V} = R_{k,V} + L(V)F_{0,k} - K(V)F_{k,V} + \int_{0}^{V_{t}} (F_{k,v}M(v,V) - F_{k,V}M(V,v)) dv$$
(4.2)

The first term of Eq. (4.2) represents the convective transport. The second term covers the net rate of formation of the k^{th} component. The third term indicates the distributive injection of the feed over the total available reaction volume. The fourth term accounts for a distributive removal of reaction material along the reaction coordinate. The fifth and the sixth term model the distributive reallocation of reaction material from one location (V) to another one (v), this is called "distributive mixing". The reaction scheme of the van de Vusse (1964) is given by (4.3). Additional information on the model formulation and the solution procedure can be found in van Goethem et al. (2008).

$$\begin{array}{ccc} A \xrightarrow{k_1 = 1} B \xrightarrow{k_2 = 1} C \\ 2A \xrightarrow{k_3 = 10} D \end{array} \tag{4.3}$$

Fig. 4.9 shows the definition of the discretisation matrix, OCFEmat, with the function, *ocmat*, which is parameterised with the number of collocation point, nCol, and the parameters for the Jacobi polynomials. To influence the density of collocation points we want to compute a series of finite element length which are smaller on the left hand side or on the right hand side of the domain. The function *felr* enables this with one assignment in the *SET* section. For similar reasons the relative location of the collocation points within a finite element can be retrieved with the *ocrloc* function.

Fig. 4.10 shows the attainable region determined with the geometric technique and the *d*-RMix (The attainable region is the region enclosed by the boundary and the *x*-axis in Fig. 4.10). The objective of this optimisation was to maximise the concentration of *B* at the exit of the reactor by adjusting the mixing kernel *M* and feed distribution function *L*. The effluent removal function, *K*, was defined zero, the total volume was set to an arbitrary value of 0.3 m^3 , and the exit concentration of *A* was fixed to the desired value. This is possible by using the volumetric flow rate entering (constant density) the reaction volume as a degree of freedom. Each point in the profile for the *d*-RMix is the outcome of an optimisation problem, the large number of points demonstrates the effectiveness of the *SCENARIO* attribute as shown in Fig. 4.9.

4.7 Concluding remarks

Simulation packages evolve with the scientific progress made in the area of the modelling languages. This can be observed on the steam pyrolysis simulation standard, SPYRO that started as a simulation tool for the process side of the radiant coils solely, progressed to a sequential modular flow sheet package and has evolved further to an equation-based flow sheet package for this process.

This work denotes the experience gained on how the equation-based solving power of the program is opened up to any model through the integration of a Symbolic Model Definition (SMD) module. The selection of a language for the

```
SET
 # Discretisation matrix
 OCFEmat :=OCMAT(nCol,Alpha,Beta);
 # Finite element relative length's
 # When Parm <0 Left side has higher FE density
 RelLenFE :=FELR(nFE,Parm);
 # Relative location collocation points within a FE
 RelLocCol:=OCRLOC(nCol,Alpha,Beta);
EQUATION
 FOR iComp:= 1 TO noComp DO
   SIGMA(OCFEmat(iCol,:)*F(iComp,:,iFE))=RelLenFE(iFE)*
           VolTot*(Prodrate(iComp) + MixIn(iCol,iFE,iComp -
          MixOut(iCol,iFE,iComp));
 ENDDO
SCENARIO
 VARY
   CaExit := 0.1, 0.99, 300;
 OUTPUT
   Cout,Qv;
```

Figure 4.9: Example of a SCENARIO attribute and OCFE functions to define 300 optimisations for the determination of an attainable region.



Figure 4.10: Attainable region for van de Vusse system [1, 1, 10] by CSTR/PFR/MIXING and d-RMix.

SMD module in an industrial setting is somewhat conservative since it should be reliable, flexible and maintainable at reasonable cost. The selection of the process modelling languages that are still under development (amongst others MODEL.LA, MODKIT) is not opportune because of the uncertainties accompanied by being under development.

The descriptive power of the available equation-based modelling languages does not differ significantly. The implementation of the available languages is considered equally difficult. The gPROMS language (Barton, 1992) is selected because is has proven itself over the years, both in industry as in academia.

The implementation was relative straight forward and took on the order of a half man-year. The language has been adapted to the specific requirements of the program, that is, supply the modeller with more information during the solution procedure. This means not only the numerical indicators of the mathematical progress but also indicators, both textual as graphical (GRAPH attribute), useful to the modeller to signify possible errors inside the model. The numerical algorithms allow soft lower and soft upper variable bounds, these have been added in the DECLARE entity to the TYPE attribute.

Series of simulations/optimisations are straightforwardly defined with the *SCENARIO* attributed.

The *FOREIGN_OBJECT* attribute provides a flexible connection to external executable libraries while the responsibility to create robust libraries is delegated.

This attribute requires programming knowledge and effort in e.g. C/C++ or FORTRAN 95. A robust way to incorporation of external procedural functionality is provided by the *SPLINE* attribute which is a natural extension of the language.

The symbolic module yielded the required additional flexibility for SPYRO, it provided a larger appeal on the underlying software as well through which its quality improved.

In the future we will implement dynamic optimisation based on an integration based method (implementation of the temporal derivative defined in gPROMS,), such as BDF. This will catalyse the implementation of discrete event modelling, for example decoking of transfer-line exchangers. The addressing of the variables defined by the hard-coded models in the SMD module and vice versa is also on the to-do list. We will add the *CONNECTION or STREAM* attribute to the *DECLARE* entity in order to more easily manipulate the passing of variables between modules. The functional extension of SPYRO is reached and therefore no graphical interface for the SMD module is foreseen.

Chapter 5

Towards synthesis of an optimal steam cracking reactor¹

Abstract

To develop new reactor options for steam cracking of ethane or other light hydrocarbons to lower olefins a fundamental process synthesis approach is taken. Firstly, an optimal reaction path and conditions are targeted, starting from a mechanistic reaction network. Secondly, to implement the optimal reaction path the reactor geometry and equipment are designed. This contribution focuses on the development of a targeting approach, for which a new distributive reactionmixing synthesis model is formulated and applied. The mixing kernel in the model provides freedom to redistribute the reaction mixture along a continuous reaction coordinate to optimise product yield. The model was validated for two applications. It reproduces the results for the Van de Vusse reaction network as obtained by the attainable region theory. When applied to a small reaction network for the conversion of ethane into ethylene, it reconfirms the existing result that for this network the plug flow mode at maximum temperature and minimum pressure gives the optimal olefin yield.

5.1 Introduction

This paper outlines an approach to the synthesis of an optimal reactor for steam cracking of ethane and other light hydrocarbons to lower olefins. The synthesis

 $^{^{1}}$ This chapter is a version with minor modifications of an article published in Chemical Engineering Research and Design (van Goethem et al., 2008)

objective is, given the mechanistic process reaction network and the feed sources, to maximise the amount of product per unit mass of feed.

We apply a fundamental approach which can be divided into two steps. The first step, targeting, is the determination of the optimal reaction path and conditions along a reaction coordinate in composition space, using reaction and mixing operations. The results are the product yield, as obtained from the optimal degree of mixing, the feed distribution function, the temperature profile and pressure profile. In the second step we will translate this optimal path in the required geometry for (new) equipment. In this paper we will concentrate on the first step. This approach, which suffices for a system of a single thermodynamic phase, is compatible with the more extensive design approach of Krishna and Sie (1994) for multi-phase reaction systems.

The steam cracking technology has developed from an empirical understanding of operations and of the performance of cracking furnaces to on-line use of rigorous models of furnace tubes based on first-principles reaction kinetics to optimise plant operations (van Goethem et al., 2007). The models have evolved from one to two-dimensional models for the proper description of the radial phenomena for example the coke decomposition in reaction tubes (van Geem et al., 2004). The radiant box is modelled three-dimensionally to predict heat flux distributions, tube skin temperatures and the NOx emissions (amongst others: Oprins et al. (2001); Oprins and Heynderickx (2003); Habibi et al. (2007a,b); Frassoldati et al. (2007); Cuoci et al. (2007)). The radical kinetic schemes are developed from the late seventies (Dente et al., 1979) onward to yield automated generation of kinetic schemes with lumped components to tackle the large number of species involved (> 10^6) (amongst others: van Geem et al. (2006); Ranzi et al. (2001)). To break away from the optimisation of reaction conditions in standard type of equipment in the above mentioned work, we no longer take the external conditions to the cracking process for granted but try to find the intrinsically best physicalchemical conditions along a reaction path for optimal product yield, exploiting fundamental insights captured in the available first-principles reaction-kinetic models. That is the first step, targeting, to synthesize the conditions defining the optimal reaction path. These reaction conditions (temperature, pressure and distribution allocation of species), are considered as free design decision variables that can be manipulated to find much better product yields. Such an approach forms an optimal synthesis problem. The second step of our approach - not covered in this article – is the translation of the optimal reaction path into optimal geometry for (new) equipment.

In our synthesis targeting approach the determination of the optimal reaction path is decomposed in three stages:

- Identification of the feasible window of physico-chemical conditions with a definition of a relevant product yield;
- 2. Determination of the optimal species distribution and product yield by running the reactions along a suitable reaction progress coordinate (e.g, space-

time or reaction volume) for pre-specified temperature and pressure profiles and by varying the distributions of the feed injection, of the product removal and internal mixing

3. Determination of the optimal temperature, pressure profiles and re-optimise the second stage till consistency is obtained.

Our motivation for the first stage (a) is to identify the feasible range of operating conditions with a target, such as: what is a practically relevant product yield, under what conditions (T, P, C) is the mechanistic reaction scheme applicable, catalyst used, number of phases, what type of heat transfer is allowed, can we allow discontinuities in temperature & pressure profiles, what is the limiting temperature and pressure for the best engineering materials available, etc.. The outcome of stage (a) is a set of feasibility constraints with a value function for the next synthesis stages.

Physical considerations imply that the information from the stages (b) and (c) should be computed simultaneously. Since we will be researching a complex system, steam cracking described by an extensive radical mechanism, containing strongly non-linear interactions between temperature and composition related variables, we decided to separate stages (b) and (c) in order to obtain partial optimisation problems that can be solved more easily. The optimisation of the T and P profiles is difficult for large reaction systems. This decomposition in two stages requires verification and re-iteration if the outcome of stage (c) influence the results obtained at stage (b).

There are a couple of reasons for developing and trying a new reactor synthesis model for targeting. Conceptually it seems attractive to find a general representation of the conversion process, which contains the standard ideal reactor types (batch, CSTR, distributive PFR) as limiting parametric cases and which is capable of combining such reactor types seamless in a single conversion "hull". Furthermore, the use of a synthesis model with continuous variables only (avoiding discrete synthesis decision variables) is computationally attractive in simulation and optimization calculations. The essence of the new synthesis model is the parallel consideration of reactions and species allocation by means of distributive macro-mixing, feed allocation and product removal along a reaction progress coordinate. We postulate a one dimensional coordinate along the reaction path since, higher dimensional coordinates would require a priori knowledge of the detailed reactor geometry.

Applying a new method to determine the mixing behaviour and the distribution of the feed we will explain it in the next chapter where we also compare it with other known synthesis methods. Thereafter the synthesis model is applied to the determination of the optimal reaction path for the steam cracking of ethane. Because we are exploring this methodology we use first a small kinetic model from the literature in order to keep the computational challenges limited. This is a preparatory step towards applying the proposed methodology to a large scale, rigorous kinetic scheme, $SPYRO^{\textcircled{R}}$, which is used in the industry (Dente et al., 1979; van Goethem et al., 2001).

5.2 Distributive reaction-mixing model (*d*-RMix)

In the synthesis of a reactor the optimal species distribution and product yield need to be determined. We propose a distributive, continuous species balance Eq. (5.1) that describes convective transport, reactions and the joint distributed injection of the feed, product removal and (macro-) mixing. These distributions are enabled by the introduction of two functions and one kernel namely: the first function for the feed distribution (L), the second function for the product removal (K) and a kernel for the mixing (M). Therefore we called this equation the distributive reaction-mixing model (d-RMix) The derivation of this equation is given in appendix B.

$$\frac{\partial C_{k,V}}{\partial t} = -\frac{\partial F_{k,V}}{\partial V} + R_{k,V} + L(V) F 0_k - K(V) F_{k,V} + \int_0^{V_t} (F_{k,v} M(v,V) - F_{k,V} M(V,v)) dv$$
(5.1)

[s] [m³]

In Eq. (5.1) the independent coordinates are:

	T (/	1
t		t	sime
V		t	the space-time coordinate
ho	ennee	tim	o coordinato is horo expressed as an increment

The space-time coordinate is here expressed as an incremental reaction volume, where this reaction volume ranges between zero and an upper bound, the total volume V_t [m³]. The subscript k is the identifier for k^{th} component. The dependent variables are:

C_k	the molar concentration of the k^{th} component,	$[mol \cdot m^{-3}]$
F	the molar flow rate	$[mol \cdot s^{-1}]$
R	the molar production rate as the net effect of	$[\text{mol}\cdot\text{m}^{-3}\cdot\text{s}^{-1}]$
	all reactions	
L	the feed distribution function	$[m^{-3}]$
F_0	the molar flow rate of the feed	$[mol \cdot s^{-1}]$
$M\left(V,v\right)$	the mixing kernel (amount mixed from loca-	$[m^{-6}]$
	tion V to v)	
K	product removal function	$[m^{-3}]$

The first term of Eq. (5.1) describes the molar accumulation of the k^{th} component per unit reaction volume. The second term represents the convective transport (which may also be extended to include gradient driven diffusion terms).

The third term covers the net rate of formation of the k^{th} component due to the joint effect of all reactions (stoichiometric summation over all volumetric reaction rates). The fourth term indicates the distributive injection of the feed over the total available reaction volume. The fifth term accounts for a distributive removal of reaction material along the reaction coordinate; e.g. at locations where the product flow has a (local) maximum. It is not a separation function because it does not account for selective removal of species, for example by means of membranes.

The sixth and the seventh term model the distributive re-allocation of reaction material from one location (V) to another one (v). This is called "distributive mixing". The sixth term represents the material coming in at the reference location V from all other locations. The seventh term accounts for the local reaction mixture distributed to all other locations (outgoing). The mixing allows for by-passing and back mixing of varying level of intensity.

The supply and removal functions L and K are made spatially dependent. Considering steady state operation temporal dependency, relevant in case of dynamic operations such as start up and shutdown strategies, is ignored. For the same reason we consider the mixing kernel M not to be temporal dependent.

Since the supply and removal functions, L, K and the mixing kernel M, represent flows, they are independent of the species. But they are subject to physical feasibility constraints (see, appendix B). To prevent negative flow rates the supply and removal functions, L and K, should have non-negative values. A constraint is added to ensure that all of the available feed is released in the reaction volume. The mixing kernel, M, should also be non-negative, a special condition is defined for the conservation of mass. It is obvious that the forward and backward mixing should neither change the conservation of mass (by artificially creating mass as a mathematical incident) nor give rise to negative flows. These conditions impose lower and upper bounds on the mixing kernel M.

The distributive reaction-mixing model (d-RMix) contains three state vectors, C, F, R, and therefore two additional equations need to be defined, namely:

- 1. Relations between, net rates of formation R, and concentrations, C, are provided by the stoichiometric scheme and reaction kinetics.
- 2. Relations between concentrations, C, and molar flow rates, F, can be established for the gas phase systems at atmospheric pressures by means of the ideal gas law, linking molar density and molar fractions to concentrations

When augmenting the species balances with these equations, and associated boundary and initial values, a complete set of equations is obtained. The degrees of freedom for decision making in synthesis are given by the supply and removal functions and the mixing kernel.

The second stage (b) of the reactor synthesis problem is now made up by the above set of model equations, the feasibility constraints on the process conditions and on the supply and removal functions and the mixing kernel. The stoichiometry and the reactions kinetics are assumed to be known, with given specified temperature and pressure profiles. Using the product yield as a target value function to be optimised the synthesis degrees of freedom, K, L, M, can be determined. Since there are infinitely many degrees of freedom the synthesis optimisation problem is reduced to a finite dimensional one by discretisation of reaction volume coordinate (see Fig. B.1).

The simulator/optimiser used in this work is described by van Goethem et al. (2002). We apply an equation based approach, which means that we approximate the solution with the technique orthogonal collocation of finite elements (OCFE), yielding a set of non-linear algebraic equations that can be solved and/or optimised. The mixing kernel, M, is approximated as piecewise linear. The model is coded such that the number of piecewise linear sections can be set independently of the number of finite elements of the OCFE method. This is done in order to be able to increase the modelling detail there were steep gradients occur. At the bounds of the piecewise linear sections of M the L and K can be active to inject or remove fluid.

5.3 Distributive reaction-mixing model (*d*-RMix) – ideal reactors

The generic nature of the distributive reaction-mixing model should allow for a reduction to the ideal reactor types. We show in detail in appendix C how the ideal reactor models (PFR, DSR and CSTR) are derived. The PFR and the DSR are straightforwardly derived. The derivation of the CSTR is less straight forward, because the distributed system must yield constant concentrations along the volume coordinate. We have validated the d-RMix results of the van de Vusse (1964) reaction scheme with the analytical CSTR solution. The reaction scheme and the results are also given by (Kauchali et al., 2002):

$$\begin{array}{ccc} A & \stackrel{k_1 = 1}{\longrightarrow} B & \stackrel{k_2 = 1}{\longrightarrow} C , \\ & 2A & \stackrel{k_3 = 10}{\longrightarrow} D . \end{array} \tag{5.2}$$

The desired product is B, while C and D are considered by products. The molar production rates are given by:

$$R_{A} = -k_{1}C_{A} - 2k_{3}C_{A}^{2},$$

$$R_{B} = k_{1}C_{A} - k_{2}C_{B},$$

$$R_{C} = k_{2}C_{B},$$

$$R_{D} = k_{3}C_{A}^{2}.$$
(5.3)

We assume steady state and constant density and temperature. The flow rate entering the reactor is $F_0 = [1, 0, 0, 0] \text{ mol} \cdot \text{s}^{-1}$. The relation between molar flow rate and concentration is given by the relations:

$$F_i = C_i \frac{\phi_m}{\rho} \tag{5.4}$$



Figure 5.1: Concentrations of A and B for the analytical CSTR and d-RMix (constant mixing kernel M_m of 500 m⁻³) results for Van de Vusse scheme [1, 1, 10].

and

$$\phi_m = M w_A \left(F_A + F_B + F_C + 2F_D \right) \,, \tag{5.5}$$

were ϕ_m , ρ are respectively the mass flow rate and the density. We define the volumetric flow rate entering the reactor to be unity. This implies, see Eq. 5.4, that the value of the concentration is equal to the molar flow rate (at the boundary). Therefore the concentrations can be evaluated with the following relation:

$$C_{i,V} = \frac{F_{i,V}}{F_{A,V} + F_{B,V} + F_{C,V} + 2F_{D,V}} \frac{\rho}{Mw_A} \quad V \in [0, V_t] , \qquad (5.6)$$

where the density and molar mass ratio are defined by the boundary condition for component A:

$$\frac{\rho}{Mw_A} = 1. \tag{5.7}$$

Fig. 5.1 shows the results of the comparison between the analytical solution and the solution obtained with the distributive reaction-mixing model (d-RMix). Each solution point of the d-RMix is a solution of (C.6) with a different total volume. We conclude that the CSTR results are properly predicted.

5.4 Relation of the distributive reaction-mixing model (*d*-RMix) with the attainable region theory

The attainable region is defined as the full set of product composition vectors that can be achieved by all possible steady state reactor networks, using only the processes of reaction and mixing (Kauchali et al., 2002). Feinberg and Hildebrandt (1997) have shown that the conventional reactors, PFR, CSTR and differential side stream reactors DSR, shape the boundaries of the attainable region. The synthesis is determined by optimisation of discrete reactor superstructures, with geometric techniques (Hildebrandt and Glasser, 1990; Kauchali et al., 2002), more recently the method of bounding hyperplanes and IDEAS (Abraham and Feinberg, 2004; Zhou and Manousiouthakis, 2006) have been proposed.

In the previous 2 sections we have demonstrated that the *d*-RMix embodies these three reactor types. To demonstrate the capabilities of our *d*-RMix we have determined the boundary of the attainable region for the kinetic scheme (5.2), which is also reported by Kauchali et al. (2002). Fig. 5.2 shows both results of the geometric technique and the *d*-RMix, each point in the profile for the *d*-RMix is the outcome of an optimisation problem. (The attainable region is the region enclosed by the boundary and the *x*-axis in Fig. 5.2) The objective of this optimisation was to maximise the concentration of *B* at the exit of the reactor by adjusting the mixing kernel *M* and feed distribution function *L*. The effluent removal function, *K*, was defined zero, the total volume was set to an arbitrary value of 0.3 m³, and the exit concentration of *A* was fixed to the desired value. This is possible by using the volumetric flow rate entering (constant density) the reaction volume as a degree of freedom, is equivalent to selecting a "residence time".

We again solved the Van de Vusse system (5.2) with a different set of kinetic constants [10, 1, 0.145]. Fig. 5.3 shows the comparison of the results obtained with the geometrical method using CSTR, PFR and mixing as the basic blocks and the *d*-RMix. On the basis of these two cases we conclude that the *d*-RMix can predict attainable regions and the inherent richness of *d*-RMix to generate each of the reactor types used in the attainable region theory. Yet a full theoretical proof of equivalents or overlap is left open.

5.5 Testing by application to steam cracking process using a small reaction network

Having introduced and tested the d-RMix we will discuss its application to steam cracking of ethane. This process is also called steam cracking or steam pyrolysis. The process consists of converting hydrocarbons (typically alkanes, cyclo-alkanes, gas oils, vacuum gas oils) in the presence of steam to ethylene, propylene, hydrogen, methane and a large number of heavier olefins, alkanes and aromatics. The



Figure 5.2: Attainable region for Van de Vusse system [1, 1, 10] by CSTR/PFR/MIXING and d-RMix.



Figure 5.3: Attainable region for Van de Vusse system [10, 1, 0.145] by CSTR/PFR/MIXING and d-RMix.

i th	Reaction	Order	$\begin{array}{l} ko_i \\ [\mathrm{s}^{-1}] \text{ or} \\ [\mathrm{m}^3 \cdot \mathrm{mol}^{-1} \cdot \mathrm{s}^{-1}] \end{array}$	$ E_{a_i} \\ [J \cdot mol^{-1}] $
1	$C_2H_6 \to C_2H_4 + H_2$	1	4.65×10^{13}	273,020
2	$C_2H_4 + H_2 \rightarrow C_2H_6$	2	8.75×10^{5}	$136,\!870$
3	$2C_2H_6 \to C_3H_8 + CH_4$	1	3.85×10^{11}	$273,\!190$
4	$C_3H_6 \rightarrow C_2H_2 + CH_4$	1	9.81×10^{8}	$154,\!580$
5	$C_2H_2 + CH_4 \rightarrow C_3H_6$	2	5.87×10^{1}	$29,\!480$
6	$C_2H_2 + C_2H_4 \to C_4H_6$	2	1.03×10^{9}	172,750
7	$C_2H_4 + C_2H_6 \rightarrow C_3H_6 + CH_4$	2	7.08×10^{10}	$253,\!010$

Table 5.1: Reaction scheme and kinetic parameters for steam cracking of ethane (Froment and Bischoff, 1979).

state-of-the-art process is performed in multiple parallel tubular reactors (also called radiant coils) placed in a furnace (also called firebox or radiant box). The hydrocarbons mixed with steam, flow through the radiant coils with a residence time of 100 – 1000 milliseconds and a feed rate per coil for the hydrocarbons of approximately 200 – 2.000 kg·h⁻¹ at a pressure of $\sim 1 - 4$ bars. Within the radiant coil the mixture is heated from ~ 850 K to ~ 1150 K and therewith cracked and dehydrogenated to smaller unsaturated hydrocarbons. At the coil exit the reaction mixture is rapidly quenched to preserve the composition. The major product of the process is ethylene. The ethylene yields range from 20 – 50 wt%. For a more elaborated review of this process the reader is referred to van Goethem et al. (2007).

As mentioned in the introduction we will initially use a small kinetic scheme found in the literature (Froment and Bischoff, 1979) for testing purpose, this scheme is given in Table 5.1.

The stoichiometric coefficient matrix of the reaction system is defined by Eq. (5.8) were the i^{th} row represent the i^{th} reaction as given in Table 5.1 and the k^{th} column represents the k^{th} component as given in Table5.2.

$$\alpha = \begin{pmatrix} 0 & 0 & 1 & -1 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & -1 & 1 & 0 & 0 & 0 & -1 & 0 \\ 1 & 0 & 0 & -2 & 0 & 1 & 0 & 0 & 0 \\ 1 & 1 & 0 & 0 & -1 & 0 & 0 & 0 & 0 \\ -1 & -1 & 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & -1 & -1 & 1 & 0 & 0 & 0 & 0 \end{pmatrix}$$
(5.8)

The individual reaction rates are determined by:

$$r_i = k_i \prod_{k=1..n} C_k^{\kappa_k}, \qquad \kappa_k = \begin{cases} 1 & \alpha_{i,k} < 0 \\ 0 & else \end{cases}, \qquad i = 1..n_{reac}, \qquad (5.9)$$

Component	CH_4	C_2H_2	C_2H_4	C_2H_6	C_3H_6	C_3H_8	C_4H_6	H_2	H_2O
Number k	1	2	3	4	5	6	7	8	9
$F_0 \; [\mathrm{mol} \cdot \mathrm{s}^{-1}]$	0	0	0	HC	0	0	0	0	$HC \cdot SDR$

Table 5.2: The component numbers and the feed flow rate definitions.

were the reaction constants are defined by the Arrhenius equation:

$$k_i = ko_i \exp\left(\frac{-Ea_i}{R_{gas}T}\right) \qquad i = 1..n_{reac}.$$
(5.10)

The molar production rate of the nine components is computed according:

$$R_k = \sum_{i=1}^{n_{reac}} \alpha_{i,k} r_i \quad k = 1..n.$$
 (5.11)

The concentrations can be related to the molar flow rates with the aid of the ideal gas law:

$$C_{k} = \frac{F_{k}}{\sum_{k=1..n} F_{k}} \frac{P}{R_{gas} T} \qquad k = 1 .. n .$$
 (5.12)

The residence time in the reaction volume is determined according:

$$t = \int_{0}^{V_{t}} \frac{P}{R_{gas} T \sum_{k=1}^{n} F_{k}(V)}.$$
(5.13)

The feed flow rate of the feed and the component numbers are defined in Table 2. The feed is considered of pure ethane (HC) with a steam dilution ratio (SDR) ratio of 0.5.

5.5.1 Stage a: identification of the feasible window of physico-chemical conditions

As mentioned several hydrocarbon feed stocks can be used for steam cracking. In this research we have limited ourselves to ethane due to the availability of small kinetic schemes in the literature and the explorative nature of the research to the d-RMix model. The maximum allowed tube skin temperatures, approximately 1300 - 1350 K, depend on the metallurgic properties of the radiant coils. In the future we expect that new or better materials will become available and therefore the maximum process fluid temperature is considered to be 1300 K, instead of ~1150 K. When indirect heat is applied, such as in current cracking furnaces, the tube skin temperature will than be approximately 1450 - 1500 K. Vacuum

is considered not to be an option because of the large throughput of an ethylene plants therefore the pressures should be larger than 1 bar. The distribution of the feed is considered to be possible at discrete locations. Removal of process fluid is assumed not to be an option. This process is a high temperature process and coking is an important side effect of steam cracking, especially at elevate temperatures. Removal of process fluid is done at high temperatures, giving rise to extensive coking and plugging of removal apparatus. This effect is considered less for the feed injection because the feed stream is usually at lower temperatures.

5.5.2 Stage b: determination of the optimal species distribution

According to Levenspiel (1999) the ideal flow regime for a $A \rightarrow B \rightarrow C$ reaction scheme is plug flow. Steam cracking is such a system, primary cracking yields the desired products, which are mono alkenes, and secondary cracking includes further dehydrogenation of the desired product to di-alkenes, aromatics, etc.. We will investigate if we can draw the same conclusion with our *d*-RMix (5.1). In the previous section, where we related the *d*-RMix to the attainable region theory, the reaction path was defined in concentration space. For a system with a small number of components this is useful because it is easy to visualize. We could determine the optimal mixing behaviour for the same reason in composition space of ethane and ethylene, since these are the most important. This is not possible when we consider the cracking of heavier feed stocks, because the reactant is not a single component. Therefore we selected, from an engineering point of view, the conversion-yield space. The conversion gives an indication on the separation effort, unreacted ethane is recycled back and the yield gives approximately the ethylene yield of the plant. The conversion and yield are defined as follows

$$\xi = \frac{F_{C_2H_6,0} - F_{C_2H_6,V_t}}{F_{C_2H_6,0}}, \qquad (5.14)$$

$$Y = \frac{F_{C_2H_4,V_t}}{F_{C_2H_6,0}}.$$
(5.15)

When dealing with heavier feed stocks, for example naphtha's, gas oils and vacuum gas oils, the definition of the conversion, as given by Eq. (5.14), is not usable because the feed stock consist of a large number of components of which none is predominant. There are other conversion indicators available for these types of feed stocks as denoted by Golombok et al. (2001). When heavier feed stocks are considered not only ethylene is important for the yield, but nowadays propylene is also important. Therefore a weighted sum of ethylene and propylene can be used as a yield function.

In order to get some insight into the conversion-yield space of the reaction system given in Table 5.1, we simulated the isothermal (and isobaric) cracking of ethane for several temperatures with a PFR model. The results are given in Fig. 5.4. Each point in the figure is obtained by solving the PFR model with a


Figure 5.4: *PFR conversion – yield plots for the cracking of ethane at 1000, 1100, 1200 and 1300K at 1 bar.*

T [K]	x[-]	$\frac{Y}{[\text{mol}\cdot\text{mol}^{-1}]}$	$\frac{HC}{[\text{mol} \cdot \text{s}^{-1}]}$	t [s]
1000	0.61	0.51	$\begin{array}{c} 0.007 \\ 0.070 \\ 0.466 \\ 2.915 \end{array}$	6.862
1100	0.85	0.74		0.629
1200	0.95	0.86		0.075
1300	0.98	0.91		0.011

Table 5.3: Conversion, C_2H_6 flow rate, residence time at maximum yield for different temperatures of Fig. 5.4.

given ethane inlet flow rate (*HC*, see Table 5.2), the *SDR* is kept the same (0.5). Again we selected arbitrarily 0.3 m^3 as total reactor volume. The same numerical strategy was applied as mentioned earlier.

When we inspect the graphs in Fig. 5.4 we see a clear maximum. On the left hand side of the maximum the primary cracking is predominant, that is, the ethylene concentration is too low and the residence time is too short to have significant amount of secondary reactions. On the right hand side the secondary reactions are predominant, that is, ethylene is cracked further to unwanted side products (in our simple kinetic scheme to C_3H_8). The maximum values are reported in Table 5.3, these values are used for the explanation of the optimal temperature profiles in stage (c).

In this stage we need to establish if the mixing and distribution of the feed



Figure 5.5: Optimal yield determined with d-RMix @ 1100 & 1200K. The PFR yields are shown as well.

injection can give higher yields than the isothermal/isobaric PFR value for a given conversion (residence time, feed flow rate). We address this question by solving an optimisation problem with the objective to maximise the yield (5.15). The ethane flow rate (=HC) is fixed for each optimisation. The free variables are the feed distribution function L and mixing kernel, M. We used between 5 – 10 sections to approximate L and M (= 30 – 110 free variables). We solved this optimisation problem for several values of HC, for 1100 and 1200 K the results are shown in Fig. 5.5. Similar results are obtained for 1000 and 1300 K, not shown in this paper.

The results plotted in Fig. 5.5 indicate that no extension of the PFR profiles is obtained. This is consistent with the numerical optimisation result for the mixing kernel, M, which becomes zero over the whole domain, for example the PFR as denoted in appendix C. Also the feed distribution function, L, is equal to the PFR model in all optimisations that is all the feed is added at the entrance of the reactor. The mixing kernel, M, is non-zero at high conversions where the yield is dropping. We can also, from Fig. 5.5, observe that the yield of the d-RMix is equal to yield of the PFR. Therefore we can conclude that the PFR gives the optimal distribution of the species for isothermal and isobaric operation.

5.5.3 Stage c: determination of the optimal temperature and pressure profiles

In the previous section we have concluded that the PFR provides the optimal species distribution for the used kinetic scheme (Table 5.1). In this stage we determine what the optimal temperature and pressure profile is for this species distribution. If another temperature is obtained than isothermal we need to iterate between stage (b) and (c).

We used the same model as for stage (b) to determine the optimal temperature and pressure profiles. These optimal profiles are obtained by solving an optimisation problem with the objective to maximise the yield (5.15). The ethane flow rate, HC, is fixed for each optimisation. The free variables are the temperatures and pressures in the different sections. We used between 20 - 25 sections to approximate piecewise linear the temperature and pressure profiles. The pressure is forced to be larger than 1 bar by an inequality constraint. The temperature is forced to be larger than 600 K and smaller than some maximum temperature [1000, 1100, 1200, 1300 K]. At each maximum temperature we solved this problem for different values of the ethane feed flow rate HC. We observed that the isothermal temperature and isobaric pressure PFR profiles give the highest yield (the same results were obtained as in stage (b)) when the ethane feed rate HC was larger and equal than reported in Table 5.3 (the conversion and residence time are than smaller as reported in this table).

Profiles as given by Fig. 5.6 are obtained when the HC value is smaller (residence time larger than reported in Table 5.3) than the values reported in Table 5.3. In the first part of the volume, at the lower temperatures in Fig. 5.6, all the reactor velocities are practically zero, suggesting that this part of the reactor is "switched off". The resulting conversions, yields are equal to the values reported as can be seen from Table 5.4. The residence time at the maximum temperature for Fig. 5.6 is also given in Table 5.4. This value is similar to the one reported in Table 5.3. Therefore we can conclude that the optimal profile is isothermal at the maximum allowed temperature. Although we specify an ethane flow rate, HC, which will result in a larger residence time than the optimal one. This gives equal optimal yields as reported in Table 5.3. As mentioned in stage (a), vacuum is the optimum pressure for steam cracking, at least from a thermodynamic perspective. The determined optimal pressure profiles are always at the lower bound of 1 bar which confirms the previous statement.

5.6 Concluding remarks

Synthesis of a one-dimensional optimal reaction path where convective transport and reaction, together with distributive feed injection, effluent removal and mixing, are considered, can be performed by means of a new continuous distribu-



Figure 5.6: Optimal temperature profile with maximum T of 1100 K and ethane feed rate of 0.034 mol·s⁻¹.

Input			Result	S		
T_{min} [K]	T_{max} [K]	$\frac{HC}{[\text{mol}\cdot\text{s}^{-1}]}$	x[–]	$Y \\ [mol \cdot mol^{-1}]$	t[s]	$t@T_{max}$ [s]
600	1100	0.034	0.85	0.74	1.74	0.65

Table 5.4: Input and output values for the problem corresponding with Fig.5.6.

ted species balance equation with differential and integral terms. The synthesis is accomplished through the introduction of three terms, representing a feed distribution function, an effluent removal function and a mixing kernel. Therefore w e have called this approach the distributive reaction-mixing synthesis model, d-RMix. We have shown that the d-RMix embodies the ideal CSTR, PFR and DSR models.

The distributive functions and kernel are determined by optimisation to yield an optimal product yield under physical feasibility constraints, and limits on process conditions for example temperature and pressure.

We have demonstrated that the d-RMix is related to the attainable region theory. In the future the added value of this d-RMix approach needs to be proven.

We have applied the *d*-RMix to the steam cracking of ethane, using an elementary kinetic reaction model. We extended the operation window in terms of maximum allowed temperature for future new or better materials to accommodate this process. We concluded that the PFR is the optimal species distribution mode. It is also shown that isothermal and isobaric operation of the reactor at the maximum allowed temperature and lowest allowed pressure is the optimal one, at least when the residence time does not exceed the optimal one.

Chapter 6

Model-based, thermo-physical optimisation for high olefin yield in steam cracking reactors¹

Abstract

The steam cracking practice seems to have reached a stage of maturity which makes it increasingly difficult to improve ethylene yield. In order to determine whether there is still scope for yield improvements it is helpful to know what the optimal reaction conditions for the steam cracking process are. This work presents a model-based synthesis approach that enables to determine the optimal thermal and physical reaction conditions for a particular feed, maximising olefin yield. A distributive reaction mixing synthesis model has been combined with an industrially proven large kinetic scheme, SPYRO[®], which contains over 7000 reactions between 218 molecular and 27 radical species. The model combination allows optimising the following degrees of freedom with respect to olefin yield: feed distribution, product removal, macro-mixing, along a reaction volume coordinate. The reaction temperature upper limit is put at 1300 K, exceeding the current (metallurgical) bound by 100 K. For the cracking of ethane a linear-concave unconstrained temperature profile with a maximum temperature of $\sim 1260 \text{K}$ proves optimal which is lower than allowed while all ethane should be supplied at the entrance of the reaction volume. For propane and heavier feed stocks an isothermal profile at the upper temperature bound, with dips at the beginning and the middle of the reaction coordinate is optimal, while distribution of the hydrocarbon feed

 $^{^{1}}$ This chapter is a version with minor modifications of an article published in Chemical Engineering Research and Design (van Goethem et al., 2010)

along the reactor coordinate results in higher yields. The theoretical maximum achievable ethylene yield for ethane cracking is found to be 66.8 wt% while in conventional cracking typically 55 wt% is considered to be the maximum value. This optimum is constrained by the pressure which is at its lower bound. The resulting residence time is in the same order as with current technology for ethane cracking, but for the more heavy feed stocks they are one order of magnitude smaller which will be a challenge for designing.

6.1 Introduction

In this work we aim to find the optimal olefin yields by varying the thermal and physical processing conditions for the steam cracking process by relaxing some current, practical engineering constraints. This process produces world's largest volume organic chemical, namely ethylene, with a worldwide capacity of ~120 million tonnes per year (Goodnight et al., 2008). The steam cracking process was discovered half a century ago and its understanding has evolved from an empirical description to a detailed knowledge of its fundamentals, in terms of chemical mechanism, kinetics, process requirements, design methods, etc. The practical state-of-the-art in steam cracking has reached a stage of maturity in which improvements in yield and product selectivity are becoming increasingly difficult due to engineering restrictions. Typically, the ethylene yields are improved by raising the cracking severity. These severe conditions are constrained by the metallurgy of the applied cracking tubes in the furnaces. Currently the maximum tube metal temperature for tubes made of Cr-Ni alloys is approximately 1400 K.

The heart of a cracking furnace is the radiant coil through which the hydrocarbons flow diluted with steam in a turbulent plug flow regime. These hydrocarbons are alkanes such as ethane, liquefied petroleum gas (LPG), naphtha's, gas condensates, and gas oil. The temperature increases from approximately 900 K to 1100 K in 0.001-1 seconds. Fig. 6.1 shows typical temperature profiles along the tube for different feed stocks. In first instance the alkanes are cracked to the desired olefins, mainly ethylene and propylene and smaller alkanes. This is referred to as primary cracking (Fig. 6.2) which is described accurately with first order kinetics. However, secondary reactions take place. This is the subsequent cracking, dehydrogenation, condensation, etc of the (desired) products from the primary cracking to diolefins, aromatics and eventually coke. Second-order kinetics describes the secondary cracking quite well. From basic chemical reaction engineering principles (Levenspiel, 1999), it follows that plug flow is the preferred flow regime. Steam dilution is applied to reduce the effects of secondary cracking reactions and coke formation. Coking plays a role when the reaction temperature is above 900 K. Coke deposition on the inner tube wall limits the time on stream of the steam cracking furnace. Steam dilution is effective in slowing down the coking rate. So is low pressure, chosen in the range of 1-5 bars.

Having pointed out that current engineering restrictions prevent further potential improvements the issue arises how much room for improvement there is left from the fundamental reaction kinetics perspective, if some engineering restrictions could be relaxed.



Figure 6.1: Typical (convex, from a flow direction perspective) temperature profiles of a steam cracking furnace for different feed stocks. (Grantom and Royer, 1987).

In this respect, we have observed that only limited research has been conducted to find the thermal and physical optimal reaction conditions for the steam cracking process (van Damme et al., 1984; Plehiers and Froment, 1987, 1991). Optimal in the sense of giving maximised olefin yield. As mentioned, higher temperatures give higher yields but no conclusive research has been conducted with respect to the specific temperature profile that will give the highest possible yields. In particular, for a mature process it is important to know what its fundamental limits are and whether there is still scope for further improvements. Similar observations can be made for the flow regime and the feed distribution: is plug flow indeed the best, must we supply all feed at the entrance of the reactor, etc? The aim of this work is to find the maximum olefin yield(s) achievable for this process with given reaction mechanism and kinetics and to explore the limits of the steam cracker process.

Such exploration is possible through the availability of detailed kinetic schemes (Dente and Ranzi, 1983; Clymans and Froment, 1984; Pierucci et al., 2005; van Geem et al., 2006), that can predict the effluent slate of steam cracking accurately.



Figure 6.2: Main reactions involved in steam cracking of higher alkanes (Chauvel and Lefebvre, 1989).

Our approach is to consider a (reference) volume with one coordinate (not a 3D-geometry), along which cracking reactions occur. There is freedom to vary the temperature, pressure and allocation of reactants over a wider range than usual. This will enable us to search for the optimal reaction conditions for olefin yields. The term "thermal-physical" conditions as used in this study refers to the presence of temperature and pressure profiles as well as distribution of feed and macro-mixing effects in the reaction volume. The term does not refer to the use of an energy balance or considerations of fluid flow and heat transfer.

The method and computational techniques to determine the optimal reaction conditions were described and tested in (van Goethem et al., 2008), using a small scale, lumped network for steam cracking. This small kinetic scheme was used to prove the computational viability but due to its simplicity the results are not accurate. Therefore in the current work we apply a realistic large scale, state-of-the-art, reaction network, SPYRO[®], covering over 7000 reactions between 218 molecular and 27 radical species. SPYRO[®] is used in many industrial simulation and optimisation studies (van Goethem et al., 2002). Optimisation studies are carried out with five different feed stocks. We do not use a specific reactor design (2D or 3D) but an abstracted reaction volume with one reaction coordinate to find the theoretical optimal yields of lower olefins.

6.2 Synthesis targeting approach

To break away from the optimisation of reaction conditions in standard type of equipment for steam cracking, we no longer take restrictive external conditions to the cracking process for granted but try to find the intrinsically best conditions along a reactor coordinate for optimal product yield, exploiting fundamental insights captured in the available first-principles reaction-kinetic models. The synthesis targeting approach consists of two steps. The first step is targeting: i.e., to synthesize the optimal reaction conditions (under idealised assumptions). These reaction conditions (temperature, pressure profiles and distribution allocation of species), are considered as free design decision variables along the reaction volume coordinate, that can be manipulated to find better product yields. This formulation amounts to an optimal synthesis problem. The second step of our overall approach – not covered in this article – is the translation of the optimal reaction conditions into optimal geometry for (new) equipment and to determine the required associated heat and momentum transfer fluxes.

For reasons of mastering the computational complexity the first step in our synthesis targeting approach, the determination of the thermal-physical optimal reaction conditions, is decomposed in three stages,

- 1. Identification of the feasible window of thermal-physical conditions with a definition of a relevant product yield;
- 2. Determination of the optimal species distribution and product yield by running the reactions along a suitable reaction progress coordinate (e.g, spacetime or reaction volume coordinate) for pre-specified temperature and pressure profiles and by varying the distributions of the feed injection, of the product removal and internal (macro-)mixing.
- 3. Determination of the optimal temperature, pressure profiles and re-optimise the second stage till consistency is obtained.

Our motivation for the first stage (1) is to set the stage for the subsequent optimisation. I.e., to identify the feasible range of operating conditions for targets, such as: what is a practically relevant product yield; under what conditions (T, P, C) is the mechanistic reaction scheme applicable; catalyst used; number of thermodynamic phases; what type of heat transfer is allowed; can we allow discontinuities in temperature & pressure profiles; what is the limiting temperature and pressure for the best engineering materials available, etc.. The outcome of stage (1) is a set of feasibility constraints with a value function for the next synthesis stages.

Physical considerations imply that the information from the stages (2,3) should be computed simultaneously. In principle, the stages (2,3) can be executed simultaneously when using a distributive reaction mixing (*d*-RMix) synthesis model (van Goethem et al., 2008). Nevertheless two separate stages have been defined because we are optimising a complex system. After all, steam cracking is described by an extensive radical mechanism, containing strongly non-linear interactions between temperature and composition related variables. This decomposition in two stages requires verification and re-iteration if the outcome of stage (3) influences the results obtained at stage (2). A short description of the optimisation problem and the model is given in the following section.

6.3 Thermal-physical optimality

6.3.1 Stage a: identification of a window of feasible thermal and physical conditions

The window of feasible reaction conditions is expressed by means of inequality constraints on variables in the optimisation model. Fig. 6.3 gives the schematic overall structure of the total model. The total model consists of four sub-models:

- 1. an objective function for the definition of the thermal-physical optimality,
- 2. a distributive, species balances based reactor model with differential and algebraic equality constraints and algebraic inequality constraints,
- 3. an input model, connecting feed characteristics with boundary conditions for the reactor model, and
- 4. a reaction kinetic model.

These sub-models will be explained in more detail in the following sections.

6.3.2 Objective function

The optimisation problem is formulated with a single objective, rather than several objectives in parallel as in Pareto type of optimisation. We have selected two alternative optimality criteria, each of which is used individually in an optimization, depending on the feed and operating scenario. The first optimality criteria is to maximise the ethylene yield, see Eq. (6.1), and the second one is to maximise the ethylene plus propylene yields together, Eq. (6.2). The main product of the steam cracking process is ethylene, explaining the first objective function, but the side product, propylene, is increasingly more important because of its economic value. Therefore we have selected the second objective function to validate whether different optimal conditions are required for maximising both ethylene and propylene. We will not consider the latter objective for the ethane feed because no significant amounts of propylene are formed. For compactness we will label optimisations with maximum ethylene, Eq. (6.1) as objection function as Max E and for optimality (6.2) we will use Max E+P.



Figure 6.3: Schematic overall structure of the applied model.

Objective functions Max E and Max E+P:

$$\max Y_{C_2H_4}$$
 or $\max Y_{C_2H_4} + Y_{C_3H_6}$,

where:

$$Y_{C_2H_4} = \frac{F_{C_2H_4}M_{C_2H_4}}{\phi_m - F_{H_2O}M_{H_2O}}\Big|_{V=V_t},$$
(6.1)

$$Y_{C_3H_6} = \frac{F_{C_3H_6}M_{C_3H_6}}{\phi_m - F_{H_2O}M_{H_2O}}\Big|_{V=V_t}.$$
(6.2)

6.3.3 Input model connecting feeds and boundary conditions for reactor model

This sub-model translates the conventional experimental characterisation of a feed to the boundary condition (species flow and composition) as required by the reaction model. The range of feed stocks for steam cracking varies from ethane, LPG, naphtha to gasoils. Nowadays several techniques are available to determine the detailed composition of these feed stocks, e.g. gas chromatography, gas chromatography combined with mass spectrometry, and high performance liquid chromatography. Unfortunately these techniques are time consuming and error

Feed label	Characteristics	Typical maximum
		temperature [K] in
		existing processes.
Ethane	100% C2H6	1145
Propane	100% C3H8	1155
Naphtha	PIONA[wt%] = 31.5, 36.1, 0.0, 24.7,	1145
	7.7; SG15/15 [-] = 0.7061; ASTM-	
	$D86[^{\circ}C] = IBP:39.8, BP50:87.4,$	
	FBP:167.4	
NaphthaArom	PIONA[wt%] = 21.7, 32.3, 0.0, 27.6,	1135
	18.4; SG15/15 = 0.7742; ASTM-	
	$D86[^{\circ}C] = IBP:130, BP50:151.4,$	
	FBP:163.6	
HGO	SG20/4 = 0.858; SC = 0.31%;	1125
	$RI = 1.4448; ASTM-D86[^{\circ}C]$	
	= IBP:147, BP10:233.4, BP30:	
	266.7, BP50:299.1, BP70:335.3,	
	BP90:375.2, FBP:433.	

Table 6.1: Selected feed stocks, where PIONA = paraffin, iso-paraffin, olefins, naphthenes and aromatics (PIONA), SG20/4 = specific gravity @20°C/4°C, SG15/15 = specific gravity @15°C/15°C, SC = sulphur content, ASTM-D86 standard can be found in API Technical data book (1992), IBP = initial boiling point, BP*0 = boiling point @ *0% of the volume evaporated, FBP = final boiling point.

prone and therefore not widely spread in the industry where more practical properties are applied to express the composition, such as specific density, H/C ratio, mean molecular mass, Paraffin, Iso-paraffin, Olefins, Naphthenes and Aromatics (PIONA) weight fractions and a ASTM boiling curve (Daubert, 1994). We have decided to apply the latter composition indices to make comparison with existing data more straightforward. Table 6.1 denotes the feed stocks selected for our yield optimisation studies.

The first two feeds have been selected because these are the smallest pure components that can be applied in the steam cracking process. The other three feeds are typical feeds with increasing amounts of larger molecules such as naphthenic and aromatic components. We have selected these feeds to verify if observations made on the cracking of lighter feed stocks also hold for more heavy feeds and vice versa. The optimisation results will also provides an overview of the thermal and physical optimal conditions of the whole feed stock spectrum. The conversion of the feed characteristics (given in Table 6.1) to detailed mass fraction based composition for all species in the reaction kinetic model, xwt_{HC} , is performed with the feed characterisation tools of SPYRO[®] Suite 7.

In addition to the hydrocarbon feed, steam is needed. We will apply a mass-

based Steam Dilution Ratio (SDR) of 0.5 (steam over hydrocarbons), being a typical value in practical steam cracking. A single ratio is used as to limit the amount of computations.

6.3.4 Distributive model along reaction volume coordinate

Distributive reaction-mixing model (*d***-RMix)** In the synthesis of a reactor the optimal species distribution and product yield need to be determined. In view of the very short residence times and the fast reaction dynamics only steady sate situations will be studied and optimised. We will use continuously distributive (van Goethem et al., 2008) species balances that describe convective transport, reactions and the injection of the feed, product removal and (macro-) mixing, the latter three functioning as distributions along a reaction volume coordinate. The steady state version is given by Eq. (6.3) (for a schematic of the model see Fig. B.1 in (van Goethem et al., 2008). The three distributions are enabled by the introduction of two functions and one kernel namely: the first function for the feed distribution (L), the second function for the product removal (K) and a kernel for the (macro-) mixing (M). Therefore we called this equation the distributive reaction-mixing model (d-RMix)

Molar-balance for k^{th} component, along reactor coordinate V:

$$\frac{\partial F_{k}(V)}{\partial V} = R_{k}(C,T,P) + L_{j}(V)F0_{k} - K(V)F_{k}(V) + \int_{0}^{V_{t}} (F_{k}(v)M(v,V) - F_{k}(V)M(V,v))dv.$$
(6.3)

All HC have the same feed distribution function $L_j(V)$ while steam has an independent one, j = HC for $k \neq H_2O$ and $j = H_2O$ for $k = H_2O$. Boundary condition for Eq. (6.3) are given below:

$$F_k(V) = \phi_m \frac{xwt_k}{Mw_k} \quad \text{for V} = 0.$$
(6.4)

Feeds weight fraction composition:

$$xwt_k = \begin{cases} \frac{SDR}{1+SDR} & k = H_2O\\ \frac{xwt_{HC,k}}{1+SDR} & else \end{cases}$$
(6.5)

where

$$\sum_{\substack{k=1\\k \neq H_2O}}^{nComp} xwt_{HC,k} = 1.$$
(6.6)

Change of residence time with the reaction volume coordinate (V):

$$\frac{d\tau}{dV} = \frac{\rho(V)}{\sum_{m=1}^{nComp} F_m(V) M w_m} , \quad V = 0 , \quad \tau = 0 , \quad (6.7)$$

where the density is defined by the ideal gas law. The relation between the molar flow rate and the concentration is defined by the ideal gas law as well:

$$C_k = \frac{F_k}{\sum_{m=1}^{nComp} F_m} \frac{P}{RT}$$
(6.8)

and

$$\rho = \sum_{m=1}^{nComp} c_m M w_m \,. \tag{6.9}$$

The first term of Eq. (6.3) describes the convective transport of the k^{th} component, the second term covers the net rate of formation of the k^{th} component due to the joint effect of all reactions (stoichiometric summation over all volumetric reaction rates). The third term indicates the distributive injection of the feed over the total available reaction volume. We allow two different distribution functions: one for the hydrocarbon feed stock (i = HC) and one for the steam feed $(i = H_2O)$; i.e., all hydrocarbons are distributed in an identical way, which may differ from the steam distribution. The fourth term accounts for a distributive (collective) removal of reaction material along the reaction volume coordinate; e.g. at locations where the product flow has a (local) maximum. It is not a separation function because it does not account for selective removal of species, for example by means of membranes. The fifth and the sixth term define the distributive reallocation of reaction material from one location (V) to another one (v). This is called "distributive mixing". The fifth term represents the material coming in at the reference location V from all other locations. The sixth term accounts for the local reaction mixture distributed to all other locations (outgoing). The mixing allows for bypassing and back mixing of locally varying level of intensity.

The distributive reaction-mixing model (d-RMix) contains three physical state vectors, C, F, R, and therefore two additional sets of equations need to be defined, namely:

- Relations between net rates of formation R, and concentrations, C, are provided by the large scale reaction-kinetic scheme SPYRO[®] (Dente et al., 1979; van Goethem et al., 2001). The latest kinetic scheme, KS7, consists of 7000 reactions between 245 components of which 27 components are radicals.
- 2. Relations between concentrations, C, and molar flow rates, F, are established by the ideal gas law since the pressures are relative low (1 5 bar) (Eq. (6.8)).

While the use of a reaction volume coordinate of a reference volume is convenient for the computations, but it is less suitable for making comparisons with results of other studies. Residence time is better suited for that purpose. Therefore, the d-RMix model has been extended with a residence time Eq. (6.7).

The boundary condition for the molar flow rate vector, F, is defined by the composition of the hydrocarbon feed stock, xwt_{HC} , and the Steam Dilution Ratio (SDR). The total mass flow rate in Eq. (6.4) is a free variable that basically defines the residence time and the conversion of the feed with a fixed total volume. This volume, V_t , was chosen (0.3 m^3) such that the numerical values of the species molar flow rates, F, in Eq. (6.3) are in the range of 1–100. Also, the resulting residence times are of a practical order of magnitude. This range of values resulted in systems of equations that gave no issues with respect to numerical conditioning.

The reaction-mixing model does not include energy and momentum balances at this stage of research. The temperature and pressure profiles can be freely specified within a physically feasible range. The required local heat transfer rates to achieve the optimum temperature profile are not computed. While the practical importance of having feasible heat transfer rates is acknowledged, the thermal engineering aspects are postponed till insights have been obtained in the theoretical optimum reaction conditions.

6.3.5 Kinetic model

The kinetic modelling involves the choices of the relevant chemical components, the essential reactions and their kinetics. This is all included in the SPYRO[®] kinetic scheme, applied in this work. It is a detailed mechanistic kinetic scheme (Dente and Ranzi, 1983; Dente et al., 1992; Ranzi et al., 2001), which consists of several radical (1 - 3) and molecular (4) elementary reaction classes that are briefly summarised in as follows (Ranzi et al., 2001):

(1) Initialisation

(1a) Unimolecular:

 $CH_3 - (CH_2)_2 - CH_3 \rightarrow 2 C_2 H_5^{\bullet}$

(1b) Bimolecular:

 $CH_3 - CH_3 + CH_2 = CH_2 \rightarrow 2 C_2 H_5^{\bullet}$

(2) Propagation reactions

(2a) Alkyl radical decomposition:

$$CH_2 = CH - CH_2^{\bullet} \rightarrow CH_2 = C = CH_2 + H^{\bullet}$$

(2b) Alkyl radical isomerisation via a 1 - 4 and 1 - 5 H-transfer:

 $CH_3 - (CH_2)_3 - CH_2^{\bullet} \rightarrow CH_3 - (CH_2)_2 - CH^{\bullet} - CH_3$

(2c) H-abstraction of molecules:

 $CH_3^{\bullet} + CH_3 - CH_3 \rightarrow C_2H_5^{\bullet} + CH_4$

(2d) Addition of radicals on unsaturated molecules:

$$C_2H_5^{\bullet} + CH_2 = CH_2 \rightarrow CH_3 - CH_2 - CH^{\bullet} - CH_3$$

(3) Termination reactions

- (3a) Recombination of radicals forming one molecule (reverse of (1a))
- (3b) Recombination of radicals forming two molecules (reverse of (1b))

(4) Molecular reactions

(4a) Olefin isomerisation via a four centre reaction

$$CH_3 - CH = CH - CH_3 \rightarrow CH_2 = CH - CH_2 - CH_3$$

(4b) Olefin dehydrogenation

$$CH_2 = CH - CH_2 - CH_3 \rightarrow CH_2 = CH - CH = CH_2 + H_2$$

(4c) Olefin decomposition by ene-mechanism

$$CH_2 = CH - (CH_2)_2 - CH_3 \rightarrow CH_2 = CH - CH_3 + CH_2 = CH_2$$

(4d) Cyclo-hexane decomposition to diolefin plus olefin and reverse via the Diels-Alders, six-centre reaction

$$Cy - C_6H_6 \rightarrow CH_2 = CH - CH = CH_2 + CH_2 = CH_2$$

The kinetic scheme contains components up to 42 carbon atoms. The total number of modelled components would be in the order of millions when all possible species are considered that are present in hydrocarbon feed and effluent slate. Evidently, simplifications have to be applied to limit the number of components and reactions. The major assumptions in the kinetic scheme are related to the generalisation of the Hydrogen abstraction reactions, the instantaneous decomposition of large radicals into their final products and the lumping of isomers and intermediate components. Fig. 6.4 shows the simplification method applied for H-abstraction of n-octane. The n-octyl radicals can isomerise through internal H-abstraction reactions, and decompose through smaller radicals for example nhexyl and olefins (ethylene) via β -scission reactions; finally this process stops at the smaller radicals which are assumed stable. These reactions are lumped under



Figure 6.4: H-abstraction reactions of n-octane.

the assumption of an average cracking temperature to one overall reaction which is also shown in Fig. 6.4.

Coke deposition is a kinetically controlled process (Bozzano et al., 2002; Dente et al., 1983), determined by the interplay between gas phase and metal wall catalysed reactions. The actual coking rate depends on the local boundary layer conditions and therefore on the actual design of a cracking tube. However, in this exploratory work we do not consider a specific reactor geometry but an abstracted reaction volume with one reaction coordinate to find the theoretical optimal olefin yields. The design of the pertaining optimal (new) reactor equipment is a subsequent step, beyond the scope of this article. In the present work we do not make statements on the actual shape, on the construction material of the reactor equipment, nor on the energy supplying mechanism (direct, indirect, or \cdots . Nevertheless, to get a coarse indication of the coking behaviour at the optimal reaction conditions, the coking deposit model of SPYRO[®] is applied, where the effluent composition, pressure and temperature will be used to evaluate the coking rate. The main features of the SPYRO[®] coking model can be schematically described as follows (Bozzano et al., 2002):

1. The metals of the conventional steam cracking coils act as a heterogeneous poly-addition catalyst forming an initial fouling deposit very similar in its morphology to the polymer formed with conventional Ziegler-Natta catalysts. When a uniform coverage is present on the metallic surfaces, the coking rate is controlled by the diffusion of the monomers into the polymeric layer. Furthermore, cross linking reactions in the polymer layer further reduce the monomer diffusivity due to the increasing of path tortuousness. Due to the higher temperatures, this contribution lasts only a few hours in the coils.

- 2. The initial coke deposit is covered by a continuous layer of polymeric material which, after a certain amount of time, is transformed into coke. This polymeric layer seals the coke deposit and hereby inhibits the decoke by steam. The porosity of the deposit is created by the successive transformations from polymers to coke, with specific volume contractions and cleavage of the deposited material.
- 3. The limiting step in the deposit growth is the reactions of saturated radicals and molecule at the surface of the polymeric material (often referred to as fouling).
- 4. The trapping of high boiling point species into the polymeric matrix is relevant for gasoil cracking. In the case of liquid pyrolysis, the cracking of alkyl chains of heavy poly-aromatic species strongly rises the amount of asphaltenes. These poly-aromatic components, due to their low stability, can flocculate and can become important contributors to the fouling process.

With a given composition (at the boundary layer), composition, temperature and pressure the coking model return the coke deposit rate in $kg \cdot m^{-2} \cdot s^{-1}$.

6.3.6 Inequality constraints along reaction volume coordinate

Steam cracking starts to occur above ~900 K and this value is considered to be the lower bound for the process temperature (T). Nowadays available materials limit the upper process temperature to ~1200 K (corresponding with a tube metal temperature of ~1400K), typical maximum applied temperatures for various feeds are shown in Table 6.1. We expect that in the future better heat resistant materials will become available and therefore we define 1300 K as the maximum allowed process temperature (T_{max}). The pressure (P) has a lower constraint of 1 bar because we consider underpressure (vacuum) not to be an option for a process with such a large throughput as applied in ethylene plants. With the constraints for the temperature and pressure defined we need to define the feasible window for the feed distribution (L) and product removal (K) functions and mixing kernel (M) in Eq. (6.3). The mixing kernel has no constraints other than the ones to have physical feasible solutions (e.g. non-negative flows and mass conservation features) (van Goethem et al., 2008).

6.3.7 Degrees of freedom in optimisation

Inspection of the system of equations defined in by Eq. 6.3 until 6.8 shows that the following variables and functions can be freely varied (within the imposed set of inequality constraints):

1. Total mass flow rate, ϕ_m , entering the reaction volume,

- 2. The Steam-Dilution Rate (SDR) (feed to steam ratio),
- 3. The feed distribution functions for, respectively the steam and the hydrocarbon feed: $L_{H_2O}(V)$ and $L_{HC}(V)$,
- 4. The temperature and pressure profiles along the reaction volume coordinate, T(V), P(V),
- 5. The (macro-)mixing kernel M(V, v).

Due to the continuous distribution, temperature, pressure functions and the mixing kernel there are infinitely many degrees of freedom.

6.3.8 Approach to solving the distributed optimisation problem

The synthesis problem has now been formulated as a distributed non-linear optimisation problem with infinite degrees of freedom. Its mathematical structure is similar to the optimizing design problems for differential side stream reactors, chapter 19 in Biegler et al. (1997), and optimal control problems. However, we prefer to numerically solve a finite dimensional non-linear programming (NLP) problem. Such a NLP problem is obtained by discretising the distributive external input variables along the reaction volume coordinate. The feed distribution, mixing and product removal is considered possible on discrete locations along the reactor volume coordinate.

The simulator and optimiser used in this work is described elsewhere (van Goethem et al., 2002). We apply an equation-based approach, which means that we approximate the solution of the differential equations with the technique orthogonal collocation of finite elements (OCFE), yielding a set of non-linear algebraic equations that can be solved and/or optimised. The mixing kernel, M, in the reaction model is approximated as piecewise linear. The model is coded such that the number of piecewise linear sections can be set independently of the number of finite elements of the OCFE method. This is done in order to be able to increase the modelling detail there were steep gradients occur. At the bounds of the piecewise linear sections of M the L and K functions can be active to inject or remove fluid. The temperature and pressure profiles are approximated in the same way as the mixing kernel.

Fig. 6.5 shows a schematic overview of the optimisation problem that we need to solve in order to determine the optimal thermal and physical conditions. The fixed inputs are the SDR, xwt_{HC} and the total volume, V_t . The total mass flow rate in Eq. (6.4) is a free variable that basically defines the residence time and the conversion of the feed with a fixed total volume.



Figure 6.5: Feasible window of thermal and physical conditions, where SDR = SteamDilution Ratio (Steam/HC), Tmax = maximum allowed temperature.

6.3.9 Stage b,c: determination of optimal species distribution, temperature pressure profiles

In the stages b,c the functions L, K, M and the T and P profiles need to be determined to obtain the optimal olefins production. We attempted to determine all the free variables simultaneously but we were unsuccessful. Our approach prescribes first the determination of the optimal species distribution (L, K and M), stage b, using predefined P, T profiles. Subsequently, the optimal temperature and pressure profiles (for optimised L, K and M distributions) were determined (stage c). We performed stage b on a subset of the feeds, Ethane & NaphthaArom, followed by stage c and subsequent verification. We optimised approximately 400 cases, starting from different numerical initial values for the model variables, under different temperature and pressure profiles. In all cases we observed that plug flow (M = 0) is the preferred flow regime. By generalising this observation we postulate that the solution of the mixing kernel, M, for all the feeds is equal to zero, implying a plug-flow regime. So, these computational results confirm the insights from basic chemical reaction engineering. By removing this mixing term in the component balances, the *d*-RMix model changes from an Integro-DAE system to a DAE system. Through this simplification we are now able to perform stages b and c simultaneously.

On the evaluation of optimised solutions A reference solution is required in order to be able to assess whether the found optimal conditions are of significance. The considered reference solutions are summarised in Table 6.2. The OptPath solution is the outcome of our model (optimization) as defined in Eq. (6.3) until (6.8) and Fig. 6.5. We consider two reference cases, where temperature profiles have been pre-set:

Solution label	Description
OptPath	Optimal solution of NLP thermal-physical reaction
	problem, as defined by Figure 6.
IsoT	Optimised solution with an IsoThermal (& isobaric)
	PFR
TT	Optimised solution with a Typical Temperature pro-
	file as applied in cracking furnace (& isobaric). Tmax
	is a degree of freedom
OptLHC	A simulation run generated by combining the opti-
	mal <i>LHC</i> profile of an OptPath solution with iso-
	thermal and isobaric PFR conditions (applied for
	diagnostic purposes in discussion of heavy feed stock
	results)

Table 6.2: Reference solution cases

- (R1) IsoT, an isothermal Plug Flow Reactor (PFR) profile and
- (R2) TT, having a Typical Temperature PFR profile, as shown in Fig. 6.1 for the Max E and Max E+P optimisations.

The pressure profile in the reference cases is a flat one at minimum pressure. There is no feed distribution (L(V) = 0), no mixing (M(V, v) = 0) and no product removal (K(V) = 0). The SDR is fixed at 0.5, while the feed mass intake rate is the only free variable for the optimiser to achieve the optimal values for objectives defined by Eq. 6.1 & 6.2. These specifications of the profiles define the reference cases.

A remark is in order on the applied numerical representation of the temperature profiles along the reaction volume coordinate. The shape of the temperature profiles in Fig. 6.1 is captured in a normalised temperature function, f_{T-norm} , as given by Eq. (6.10). For each of the five feed stocks a normalised temperature function is recorded. These functions are implemented as a (B-spline) lookup table. The inverse function (6.11) can be used to compute the typical temperature as function of the reaction volume coordinate V. The initial temperature of the TT (at the volume entrance) is set equal to the lower bound (900 K) while the outlet temperature is a free variable that can be set equal to the maximum allowable value defined for the OptPath case:

$$f_{T-norm}(x) = \frac{T_x - T_{x=0}}{T_{x=1} - T_{x=0}} \qquad x = \frac{V}{V_t} \qquad x \in [0,1] , \qquad (6.10)$$

$$T(V, T_{\max}) = 900 + (T_{\max} - 900) f_{T-norm} (V/V_t)$$
. (6.11)

Results of the optimisation cases The optimisation cases involve the five different feed stocks which are each optimised for two objective functions: maximum ethylene and maximum of ethylene and propylene. The case with ethane feed and ethylene + propylene yield drops out as no significant amount of propylene is generated, giving the virtually same results as optimization with ethane feed and ethylene yield. For each viable combination of feed stock and objective function three different situations with respect to the temperature profile are considered. The three temperature profile cases in the optimisation are one free profile case (OptPath) and two cases with a reference profile (IsoT and TT), as specified in Table 6.2. In each case all available degrees of freedom of the NLP problem are considered, with the exception of the macro-mixing (M = 0). There are some common results for all cases.

We observe that the pressure in all the optimisations is made equal to its lower bound of 1 bar. This confirms existing conclusions from basic chemical reaction kinetic insights.

The solution for the removal function, K, is in all optimisations equal to zero. So, intermediate product removal does not have any advantage to obtain higher objective function values.

The case specific results are given in Table 6.3 for all the feed stocks (as defined in Table 6.1), two different objective functions (max E and max E+P) and for three temperature profiles (Table 6.2).

For each optimisation scenario four key variables are listed, viz., the maximum achieved temperature, the actually achieved ethylene yield, the sum of actually achieved ethylene and propylene yields, and the residence time.

The results for optimal injection strategies are diverse. It is advantageous to inject all dilution steam at the entrance in all cases. While for all hydrocarbon feed cases – except ethane – a distributed allocation yields higher olefins. The ethane should be injected at the entrance of the reactor volume. The optimal distribution function profiles, $L_{HC}(V)$, of the other four hydrocarbon feed are given for Max E and Max E+P respectively by Fig. 6.6 and Fig. 6.7. The optimal temperature profiles for the OptPath reference cases with the Max E objective function is shown by Fig. 6.8. Fig. 6.9 shows the optimal temperature profiles for the feed stocks that produce a significant amount of propylene, for the two objective functions, Max E and Max E+P. The small steps in the optimal temperature profiles are the effect of the discretisation applied in the mathematical modelling and are approximations to a smooth solution for the obtained profiles.

6.4 Discussion

First three main effects on product yields will be discussed: (a) having ethane as a feed; (b) distribution of hydrocarbon feeds; (c) factors favouring propylene

 $^{^{1}}$ Note that only the markers are a solution of the optimisations. The lines are added for visual effects, are not part of the solution.

feed stock	PFR	Max T[K]		C_2H_4	yield	C_2H_4	+	Reside	ence
	type			[wt-dry%]		C_3H_6	yield	time [s	5]
						[wt-dry %]			
	Max:	E	E+P	E	E+P	E	E+P	E	E+P
Ethane	OptPath	1231	n.a.	66.75	n.a.	67.83	n.a.	0.197	n.a.
	IsoT	1185	n.a.	65.62	n.a.	66.64	n.a.	0.067	n.a.
	TT	1225	n.a.	66.66	n.a.	67.70	n.a.	0.165	n.a.
Propane	OptPath	1300	1300	52.03	49.14	57.43	60.31	0.019	0.011
	IsoT	1300	1300	51.67	48.91	57.41	60.24	0.007	0.003
	TT	1300	1300	48.83	46.08	55.33	58.42	0.039	0.019
Naphtha	OptPath	1300	1300	42.53	39.07	48.46	52.70	0.009	0.003
	IsoT	1300	1300	41.42	36.86	46.57	51.85	0.007	0.002
	TT	1170	1104	33.68	29.68	38.54	43.76	0.776	0.712
NaphthaArom	OptPath	1300	1297	37.12	33.91	42.28	46.25	0.010	0.003
	IsoT	1300	1300	36.14	31.54	40.53	45.19	0.008	0.001
	TT	1182	1103	30.42	26.66	34.75	39.48	0.562	0.511
HGO	OptPath	1300	1300	36.16	32.58	41.31	45.95	0.015	0.003
	IsoT	1288	1284	35.40	30.70	39.88	44.82	0.010	0.002
	TT	1233	1144	31.22	27.30	36.00	41.07	0.275	0.235

Table 6.3: Optimal temperature, olefin yields and residence time for different feeds \mathcal{C} optimisation goals (max $E \mathcal{C}$ max E+P).

yield. After this discussion the optimisation results obtained in this study are compared with the few literature data on steam cracking yield optimisations. This is followed by an analysis of the sensitivities of the olefin yields with respect to uncertainties in feed composition. Thereafter we denote our findings on the coking phenomena. Finally, we shortly discuss the implications of these results for the next necessary step: the equipment engineering research.

6.4.1 Having ethane as a feed

Table 6.3 shows, not unexpectedly, that the ethane feed stock gives the highest olefin yields among the feed stocks considered. Interestingly, compared to the optimal temperature profile (OptPath) the typical temperature profile (TT) results in only a marginally lower maximum yield. So, current temperature profiles are suited to obtain the maximum (once through) yields for ethane cracking when cracking reactors can be build that can withstand reaction fluids at ~1230 K. Fig. 6.10A depicts the sensitivity of optimal ethylene yield to the maximum allowed temperature. The OptPath solution does not change with higher maximum temperature bounds and the TT solution coincide with the OptPath solution at the mentioned (maximum) temperature. The ethylene selectivity (ethylene yield (6.1) divided by the ethane conversion), also in the ethylene producers community called the ultimate yield, of ethane feed stock is important because it is the net ethylene yield of a plant when all the unconverted ethane is recycled. Fig. 6.10C shows this selectivity as a function of the maximum allowed temperatures.



Figure 6.6: Optimal feed distribution function for the feed stocks, LHC, for Max E^{1} .

maximum selectivity is obtained at the temperatures of 1145 K. This coincides with currently applied reaction conditions which are around 1145 K (Table 6.1). However, the typical industrial ethane conversions at that temperature level of 1145 K are 70% while the selectivity for the typical temperature (TT) profile is obtained with a conversion of 92%. So, there is still scope to improve the current ethane cracking technology.

Currently applied reaction temperatures are lower than the maximum yield temperatures. Therefore the yield will increase with higher temperatures. So, when considering an upper bound on the temperature, it might be expected a priori that the isothermal temperature profile is the best candidate. However, the optimisations show that a linear-concave profile is the optimal temperature profile. Why this is so, can be explained by analysing the reaction mechanism. In Fig. 6.10B & 6.10D we plotted the ethylene and ethyl (C_2H_5) radical concentrations (the most stable radical for ethane cracking) for respectively the OptPath and IsoT PFR types. The ethyl radical is formed by propagation reactions, Habstraction reaction of ethane. At higher temperatures ethyl can decompose to ethylene and at lower temperatures it 'reacts' to ethane through an H-abstraction reaction. Other typical reactions of ethyl radicals are addition to unsaturated bonds and radical termination reactions. Fig. 6.10B and 6.10D show that the optimal (OptPath) temperature profile (shown in Fig. 6.8 for the ethane feed case) minimises the ethylene and ethyl concentration in the first part of the reaction



Figure 6.7: Optimal feed distribution function for the feed stocks, LHC, for $Max E+P^1$.

volumes, which reduces secondary cracking reactions (initialisation reactions and radical addition to C_2H_4) of ethylene.

Table 6.3 and Fig. 6.8 show a clear difference in the maximum temperature in an optimised profile between ethane and the other feed stocks. For ethane a gradually rising profile is found, the maximum not reaching the temperature upper bound, whereas for the heavier feeds the maximum temperature is equal to the upper bound of 1300 K. This can be explained from the kinetics. Heavier feed stocks, such as propane, require the breakage of more C - C bonds to obtain ethylene as product, as compared to ethane cracking. The breakage is favoured by higher temperatures which explain this observation, the activation energies for C - C scissions are generally speaking larger than for C - H scissions (van Geem, 2006). The application of temperatures higher than 1231 K (see Fig. 6.10A) will not generate more ethylene which implies that the theoretical maximum achievable (once through) ethylene yield for ethane cracking is 66.8%. The maximum ethylene yield in conventional cracking is typically 55 wt%.

6.4.2 The effects of distribution of hydrocarbon feed on the yield

Fig. 6.6 and Fig. 6.7 indicate that Propane, Naphtha, NaphthaArom and HGO have an optimal feed distribution along the first part of the reaction volume. As compared with ethylene yield optimization (Fig. 6.6), the feed must be distributed



Figure 6.8: Optimal temperature profiles(OptPath) for Max E optimisation for all feed stocks.

more uniformly and further into the reaction volume, in order to maximise the E+P yield, as shown in Fig. 6.7.

Fig. 6.11A shows for the NaphtaArom feed a comparison of the ethylene profile obtained by the IsoT case and the profile obtained by the application of the hydrocarbon feed function (L_{HC}) of the OptPath case at isothermal conditions (we label this simulation case OptLHC, see Table 6.2). The difference between the two curves shows the impact of the distribution of the hydrocarbon feed along the reaction volume for the Max E optimality.

This difference can be made plausible by considering the role of the most stable allyl radical (ALP, $CH_2CH = CH_2$). Its concentrations differ significantly when we compare the IsoT and OptLHC profiles (see Fig. 6.11B). Allyl is produced by first-order initiation reactions together with primary olefins, such as ethylene, propylene. With the increase of ethylene and allyl concentrations the secondary cracking reactions, H-abstraction and radical addition reactions will play a larger role. This is indicated by the decrease of the allyl radical and the smaller slope of ethylene. With the injection of fresh feed the secondary cracking reactions are suppressed and initialisation is promoted again until the secondary cracking would start playing a role again. The distribution of the hydrocarbon feed results in larger ethylene yield compared with the injection of all feed at the entrance of the volume. Fig. 6.11C & D show the additional effect of the temperature curves



Figure 6.9: Optimal temperature profiles (OptPath) for Max E and Max E+P optimisation for propylene generating feed stocks.

on top of the feed distribution. The lower initial temperature (see Fig. 6.9C) tempers the ethylene production, indicated by the lower allyl concentration. The temperature is lowered after having been on the maximum as to reduce the consumption of the ethylene by H-abstraction and radical addition reactions. The above reasoning explains the optimal ethylene yield for the NaphthaArom feed stock. The same phenomena are observed for the Propane, Naphtha and HGO feeds.

6.4.3 Factors that influence the propylene yield

In the Max E+P optimisations the propylene yield is also important. The propylene yields are indirectly denoted in Table 6.3: subtract the C_2H_4 yield from the $C_2H_4+C_3H_6$ yield for both Max E and Max E+P. It is generally agreed that milder or less severe cracking conditions favour the production of propylene. This is confirmed when comparing the residence times for the Max E and Max E+P optimisations at the same temperature levels. We observe a significantly smaller



Figure 6.10: A: ethylene yield versus maximum allowed temperature (Tmax). C: Selectivity (or ultimate) ethylene yield as function of Tmax. B & D: ethylene and ethylene yield versus scaled reaction volume coordinate at Max T for OptPath & IsoT (data given in Table 5) for the ethane feed stock.

residence time, for the Max E+P optimisations (see Table 6.3). When optimising with respect to Max E+P the propylene yields double or triple when comparing with the corresponding Max E results. We observe for the Max E+P optimality the same trends for hydrocarbon feed distribution and non-isothermal temperature profiles, as obtained with the Max E optimisations. This is not surprising since the Max E+P optimisations co-maximise ethylene yields as well. Fig. 6.12 shows the differences between propylene, ethylene and allyl concentration profiles, as obtained with OptPath optimisations for the NaphtaArom feed with Max E and Max E+P criteria.

Fig. 6.12A shows that despite the smaller residence time in the first part of the volume, similar propylene yields are obtained as for the Max E optimisation. The ethylene yield on the other hand (see Fig. 6.12B), is lower for the Max E+P optimisation in the first part of the volume, due to the smaller residence times.



Figure 6.11: (A, B): ethylene and allyl curves, maximising the ethylene yield (Max E) at the maximum T as denoted in Table 6.3 for the OptLHC and IsoT PFR type with the NaphthaArom feed stock. (C,D): Same as A & B but than for the OptPath and OptLHC PFR type. $ALP = allyl radical, CH_2CH = CH_2$.

The allyl radical concentration (see Fig. 6.12C) is similar to one for the IsoT with Max E optimisation in Fig. 6.11B. This indicates significant promotion of propylene producing initialisation reactions. In the second part of the volume the Max E+P optimised temperature (see Fig. 6.9C) is reduced below the Max E temperatures, slowing down secondary cracking. This lower temperature level in the second part of the volume prevents further cracking of propylene to ethylene and other products, as seen in Fig. 6.12A. The combined effect of smaller residence time, feed distribution and different temperature gives an overall higher ethylene plus propylene yield as shown by Fig. 6.12D.



Figure 6.12: NaphthaArom feed stock results for the OptPath PFR type of the MaxE and Max E+P optimisations: (A) propylene (C_3H_6), (B) ethylene (C_2H_4), (C) Allyl radical (ALP) and (D) ethylene plus propylene.

6.4.4 Comparison of results with reported optimisations in the literature

We intended to compare our results with other reported optimal reaction conditions for the steam cracking process. Surprisingly, almost no research has been published to find the optimal reaction conditions for steam cracking. In the mideighties, some research was conducted to finding the optimal temperature profile, both by experiments and simulations (van Damme et al., 1984). This research provided a basis for the development of *reversed split* and *Uno-Quattro coils* (Plehiers and Froment, 1987, 1991). Cracking of light naphtha was carried out in a pilot reactor where the temperature profile could be manipulated. The outcomes of the experiments show that linear temperature profiles give rise to higher yields than with the typical (convex) temperature profiles as given by Fig. 6.1. At first sight, this might seem in contradiction with the work here: except for ethane feed cases, the optimal temperature profiles are far from linear (see Fig. 6.9). These different results could be due to a different choice of boundary conditions in both studies. In the published research by Froment, the residence time and the conversion were kept constant when comparing the linear and the convex profiles. In order to achieve the same conversion and residence time for the linear profiles a higher temperature is required. In our research, the maximum temperature is kept constant which will yield different conversions and residence times for the examined temperature curves.

6.4.5 Sensitivity of optimal olefin yield with respect to feed composition

The optimal olefin yields are obtained by varying the process conditions, using a fundamental model with some fixed inputs, shown in Fig. 6.5. These yields are likely to be sensitive to the fixed inputs. For instance, the composition of the feed stocks in the steam cracking process varies significantly. Therefore, we did already examine five typical feed stocks in order to establish possible trends in the optimal reaction conditions when applying the different feed types. To gain a more detailed evaluation of the sensitivity of the optimal yields to the feed stock composition we also will examine the effect of possible measurement errors in the Naphtha feed stock. The Naphtha feed definition (see Table 6.1) has eight parameters, namely four PI(O)NA weight fractions, three boiling points (IBP, BP50 and FBP) and one specific gravity (SG). To study the yield sensitivity to parametric feed measurement errors, Monte Carlo sampling generates fifteen normally distributed measurements for each feed input. The measurements are assumed to have a relative error of 5% except for the three temperatures were we used an absolute error of 5 K. Then, for each of these Naphtha feed compositions an OptPath type of optimisation for max E is carried out with a maximum allowed temperature of 1200K. The results are presented in Table 6.4.

We did not observe any changes in the optimal profiles for the temperature, pressure, the steam distribution function and the product removal function. However, the optimal hydrocarbon distribution function did depend on the feed characteristics, see Table 6.5. The first part of the L_{HC} did not change significantly, only the part close to zero, see Fig. 6.6. The results reveal that the impact of possible measurement errors in the feed composition generates changes in the optimal E and E+P yields, but the differences are marginal. The most sensitive feed characteristic in the Monte Carlo simulation is the specific gravity (SG) which yields the largest differences in the yields and the residence time. The effect of the errors in the PIONA and the boiling curve are negligible and allow for larger uncertainties in the feed characteristics.

In addition to the effects of parametric uncertainties in feed composition on olefin yields, a similar uncertainty analysis could – in principle – be performed with respect to uncertainties in the SPYRO[®] kinetic parameters. This has been skipped in this phase of research as the SPYRO[®] kinetic scheme was extensively validated with experimental data and proven to be robust over thirty years of experience with the industrial use of this model.

ref_value	E yield 40.93wt%	E+P yield $47.02 wt%$	Res. Time 0.068 s
Feed characteristics	st d diff [$\%$]	st d diff [$\%$]	Std diff [$\%$]
Р	0.251	0.309	0.076
Ι	0.037	0.062	0.022
Ν	0.137	0.186	0.042
А	0.187	0.229	0.015
IBP	0.131	0.120	0.035
BP50	0.063	0.081	0.017
FBP	0.002	0.003	0.004
SG	0.435	0.670	0.313

Table 6.4: Effect of errors in feed composition (feed composition $\pm 5\%$ and temperature $\pm 5 K$) on the optimised yields of E and E+P and the residence time. Naphtha feed optimised for max E, with OptPath type and $T_{max} = 1200K$. diff(i) =(measurement(i)-ref_value) where i=1:15, std = standard deviation.

LHC ref_value [m^{-3}]:	0.113	0.184	0.229	0.205	0.144	0.084	0.040	0.002
Feed characte- ristics	avg ref di	ff [%]						
Р	-0.006	-0.025	-0.032	-0.023	-0.001	0.040	0.109	5.675
Ι	-0.013	-0.016	-0.012	-0.003	0.010	0.025	0.044	1.446
Ν	-0.026	-0.085	-0.101	-0.066	0.015	0.148	0.395	14.510
А	0.043	0.044	0.032	0.007	-0.025	-0.065	-0.126	-4.300
IBP	-0.001	0.013	0.020	0.025	0.017	-0.027	-0.518	5.245
BP50	0.016	0.041	0.039	0.016	-0.018	-0.061	-0.126	-5.154
FBP	-0.010	-0.015	-0.013	-0.005	0.007	0.023	0.052	1.597
SG	-0.670	-0.060	0.237	0.111	-0.180	-0.403	-4.067	138.062

Table 6.5: Effect of errors in feed composition (see Table 6.4) on the L_{HC} function. Naphtha feed optimised for max E, with OptPath type and Tmax=1200K. ref diff(i) = (measurement(i)-ref_value)/ref_value where i=1:15, avg = average value. Note that only the reference values (ref_value) that are non-zero are given.

6.4.6 Coking phenomena

Coking is an important phenomenon in the steam cracking processes, occurring at the inner surfaces of the reactor wall. Using an abstracted reactor concept in this work, we do not consider the surface walls yet as part of the reactor design. Therefore coking is only tentatively discussed. The detailed discussion on coking must be deferred to the next phase of a more specific reactor design. In order get insight in the coking tendency we computed the coking rate with the effluent composition, pressure and temperature as it would be in a tube wall made of alloys used in conventional steam cracking furnaces. Fig. 6.13 shows for the NaphthaArom feed stock the coking rates for the solutions and objective functions. Acetylene is known to be a precursor (Albright and Marek, 1988) for (radical) coke deposit and is therefore shown in this figure as well. We can confirm that there is correlation between acetylene and the coking rate but it is a weak one. The exponential dependency of the coking rate on the temperature is clearly shown, particularly in the Max E+P optimisation (see Fig. 6.9C as well). The coking deposit will pose a challenge to design the (new) optimal reactor equipment when it would be made from the conventional Cr-Ni alloys as is currently done.

6.4.7 The implications of these results for the next step of the research

The first step has involved a model-based determination of the optimal reaction conditions and olefin yields. The next step must involve research into the equipment engineering aspects (e.g., required heat fluxes to achieve desired temperature profiles). A strong sensitivity of the optimal reactions conditions to the feed composition would make our approach useless for further practical applications. This not being the case, the second step becomes feasible. An important consideration in the second step is an experimental validation of the validity of the SPYRO[®] kinetic scheme under the found optimal conditions.

6.5 Concluding remarks

A method for the determination of the optimal thermal and physical reaction conditions, initially tested and validated with several simplified kinetics schemes (van Goethem et al., 2008), is effectively applied for steam cracking using an industrially proven large kinetic scheme SPYRO[®]. Optimum reaction conditions (temperature, pressure, feed distribution profiles) for maximising olefin yields have been obtained for five practical feeds, while relaxing the upper reaction temperature constraint to 1300 K.

The results show that for a wide range of feed stocks some macro-mixing is not helpful and that plug flow is indeed the optimal flow regime. Distribution of the steam feed and intermediate removal of reaction fluid gives no improvement in ethylene or ethylene plus propylene yield.



Figure 6.13: NaphthaArom feed stock results for the coking rate and the acethylene yields for the OptPath, IsoT and TT PFR type of the Max E and Max E+P optimisations, at the effluent composition, pressure and temperature: (A) coking rate for Max E, (B) acetylene (C_2H_2) for Max E, (C) coking rate for Max E+P and (D) acetylene (C_2H_2) for Max E+P

In case of ethane cracking, the feed should be entered in the beginning of the reactor. The optimal temperature profile is linear/concave and has a (free) maximum value of 1231 K. At the optimal conditions the ethylene yield is marginally (0.13%) larger than with the currently applied typical temperature profiles. The selectivity is maximal at the currently applied maximum process temperature of 1145 K, but the optimal ethane conversion is high, 92%, where as in practice the once-through conversion is typically 70%. The optimisations show there is still scope for improvements in ethane cracking. Since in the optimisations the cracking was not constrained any more by the maximum temperature bound we can conclude the maximum achievable ethylene yield for ethane cracking to be 66.8 wt%, while typically 55 wt% is considered to be the maximum achievable in conventional cracking.

For the heavier feed stock, the maximum temperatures were all constrained by the upper bound of 1300 K, needed for the difficult breakage of C-C bonds to yield ethylene. Compared to typical temperature profiles the overall increase in reaction temperature along the reaction volume coordinate results in significant improvements in ethylene and ethylene + propylene yields. Maximum ethylene is obtained with temperature curves that increase rapidly to the maximum allowed value and after a short period drop and increase again towards the end of the reactor coordinate. Maximum ethylene + propylene require isothermal conditions in the first part of the reaction volume, followed by a decrease in temperature.

The distribution of heavy feed along the reaction volume coordinate results in improvements of yields for both Max ethylene and Max ethylene + propylene optimality. The optimal feed distribution is for Max ethylene + propylene optimality more uniform and spread out.

The propylene yield in the Max ethylene + propylene optimality doubles or triples compared to its yield under Max ethylene optimality, which offers an interesting perspective for propylene market constrained situations.

The optimal residence times for all feed stocks are in the range of 1 - 1000 ms, the residence times smaller than 100 ms are a challenge for design.

The findings on the optimal reaction conditions are marginally sensitive to changes in the feed composition. The largest effect (<0.1% ethylene plus propylene yield) is generated by inaccurate specific gravity characteristics of the Naphtha feed composition. A five degrees variance in the boiling curve has a negligible effect on the outcome of the optimisations.

The application of a large kinetic scheme instead of the small kinetic schemes applied in the testing and validation phase of our method presented no additional numerical problems, which is an implicit indication of the robustness of our modelling and optimisation method.

The work presented gives a method and a promising perspective to pursue new developments to drive the steam cracking process to its fundamental chemical optimum. Although, the SPYRO[®] kinetic scheme was extensively validated with experimental data and proven to be robust over thirty years of industrial experience, experimental work needs to be done to verify the idealised, modelderived hydrocarbon feed distribution function, temperature and pressure profiles. If validated, equipment and material engineering work is required to achieve the required heat transfer with high temperature resistant materials.


Conclusions and recommendations

In the following four sections we will present the main conclusions from this work, on respectively the ideal processing route for lower olefins from hydrocarbons, enhancing a simulation program for the steam cracking process, the reactor synthesis approach for a single phase and the higher olefins yields by optimising the steam cracking conditions. The final section in this chapter is dedicated to the recommendations resulting from this research.

7.1 Ideal processing route for lower olefins from hydrocarbons

In the next 10-30 years, when crude oil is getting scarcer, one can expect a transition phase to alternative feeds. A minor fraction of crude oil is used for making chemicals. As many chemicals are functionalized molecules (with "functionalized" we mean molecules that embody atoms other than hydrogen and carbon, in particular, oxygen), biomass might be an intrinsically better feed stock than crude oil by offering more closely related molecular building blocks. Therefore, biological routes can provide attractive alternatives for more functionalized molecules. However, for lower olefins production, for which approximately 1.5% of the crude oil is being used, hydrocarbon feeds are expected to remain the obvious raw material in the transition period. With respect to the main product of olefins, polyolefins, the situation is more complex: biopolymers could be used to replace these polymers in certain applications. Overall, we conclude that, in the transition period, the production of lower olefins from hydrocarbons will remain a process of high importance. Therefore we argued that the steam cracking of hydrocarbons will continue to offer a viable process route to lower olefins. In our research we have reviewed how features of published steam cracking process concepts match with the ideal process, according to the following criteria: maximum olefin yield, no remains of energy carriers or auxiliary chemicals in the product, minimal ecological impact, minimum energy input per unit product, high availability, and a low degree of complexity of the reaction section. Out of the wide variety of process concepts, classified as dehydrogenation, direct heating, and indirect heating, none meets all objectives (Table 3.1 & 3.2). The new combination of the adapted firing furnace with ceramic reactors internals comes close to it. Also, the shock wave reactor shows potential due to its functional separation of mixing, heating, reaction and cooling operations. The minimum and maximum energy requirements, obtained with the pinch analysis technique, indicated that heat integration of the shock wave reactor concept will be challenging.

7.2 Enhancing SPYRO with symbolic modelling

The role of enabling technologies, such as ICT, computer hardware and numerical models, is of vital importance in current practice of research and development. The scientific progress made in these enabling technologies generates driving forces to take the engineering activities to the next level of sophistication (Fig. 1.2). In this research the challenge was to couple a very large scale reaction-kinetic model to a new, distributed and flexible reactor model. Thus there was a need for a software environment where models could be rapidly implemented or changed and which could handle distributed models with a large number of species. Transfer of the reaction-kinetic model to a state-of-the-art modelling & computing environment (e.g. gPROMS) was ruled out for reasons of excessive effort and legal constraints. Therefore the enhancement of SPYRO[®] with symbolic modelling module was a necessity to overcome the problems of using FORTRAN, or any other third generation programming language.

The symbolic module yields the required additional flexibility for SPYRO[®], and provided a larger appeal on the underlying software as well, through which its quality improved. The diagnostics or debugging phase of the modelling is accelerated through the reporting, in human readable strings, of specific variables and residuals with the largest absolute and relative change during the solution process. The use of the extended SPYRO[®] reduced the amount of work significantly. This reduction is in the order of a few man years, since this would be the time to construct a computational efficient and reliably predictive model with the information and computational tools in the public domain. This enhancement of the SPYRO[®] program resulted in a tool that was very effective in this research work and provided quantitative insights in found improvements as well.

7.3 Reactor synthesis approach for a single phase reactor

In view of the multi-scale nature of process design problems and the complexity of the design decision making, finding an effective decomposition approach is often the key to success. Krishna and Sie (1994) formulated a (decomposition) strategy to design multiphase reactors, comprising three successive levels of design. The design of the catalyst is the first level, while the reactant and energy injection strategy forms the second level and the third level involves the choice of hydrodynamic flow regime with associated phase transfer rate laws. In our case, having a single phase reaction system without a need for a catalyst, the associated design problem is essentially that of level two. Ignoring options of dynamic modes of operations and energy injections, we have developed a new reactor synthesis model, d-RMix, that encompasses the mass injection strategies at level two of Krishna and Sie (1994). This synthesis model features a one-dimensional reaction volume coordinate along which the following physical operations are considered: convective mass transport and multiple reactions, together with distributive feed injection, effluent removal and macro-mixing. The energy injection strategy of level two is replaced by a free temperature profile. The third level, the choice of hydrodynamic flow regime has been omitted; instead we have a free pressure profile. The synthesis is enabled through the introduction of three additional functions along the reaction volume coordinate, representing a feed distribution function, an effluent removal function and a mixing kernel. This has resulted in a new model formulation, involving continuous distributed species balance equations with differential and integral terms. We have called this approach the distributive reaction-mixing synthesis model, d-RMix. We have shown that the d-RMix embodies the ideal CSTR, PFR and DSR (Differential Side-stream Reactor) models as special cases by making particular choices for the distribution functions. The free distributive functions and kernel are determined by optimisation to maximise a product yield, such as ethylene or ethylene + propylene under physical feasibility constraints, and limits on process conditions such as for example temperature and pressure. We have demonstrated that the d-RMix is related to the design method for a reactor network by the attainable region theory and that we can numerically reproduce several results obtained with that technique. All features of the reactor synthesis model, distributed feed allocation and product removal, macro-mixing, have been addressed in the testing. The successful application of the d-RMix to the optimal reaction conditions for steam cracking reactors, with SPYRO[®] proofs the effectiveness of this reactor synthesis model. The conclusions of the latter are given in the following section.

7.4 Higher olefin yields by optimised steam cracking conditions

The quest to the optimal reaction conditions for improved olefin yields with the steam cracking reactor initiated this research project. We observed that limited public domain research had been conducted to find the thermal and physical optimal reaction conditions. The available research addresses optimal reaction conditions in the context of the radiant coil geometry as applied in current technology. In order to break away from this technology we have decoupled all the phenomena so we can optimise the separate phenomena individually. Optimum reaction conditions (temperature, pressure, feed distribution profiles) for maximising olefin yields have been obtained for five practical feeds, while relaxing the upper reaction temperature constraint to 1300 K (versus 1200 K nowadays).

The nature of the feed stocks is important in practice and in our research since these have different cracking behaviour and product slate. Therefore we have tested a range of feed stocks ranging from ethane to heavy gas oils. The computational results show that for all tested feed stocks some macro-mixing is not helpful and that plug flow is indeed the optimal flow regime. Distribution of the steam feed and intermediate removal of reaction fluid gives no improvement in ethylene or ethylene plus propylene yield. The optimal operation pressure was found to be at the lower bound of 1 bar.

In case of ethane cracking, all ethane feed should be entered in the beginning of the reactor. The optimal temperature profile is increasing between linearly and concave and has a (free) maximum value of 1231 K. At the optimal conditions the ethylene yield is marginally (0.13%) larger than with the currently applied typical temperature profiles. The selectivity is maximal at the currently applied reaction temperature of 1145 K, while the optimal ethane conversion is high, 92%, where as in practice the once-through conversion is typically 70%. The optimisations show there is still scope for yield improvements in ethane cracking. Since the optimisations indicate a free optimal temperature, below the maximum temperature bound, we conclude the maximum achievable ethylene yield for ethane cracking to be (around) 66.8 wt%, while typically 55 wt% is obtained in conventional cracking. The optimal conditions for ethane cracking are explained with the aid of the ethyl radical which is the most stable radical during ethane cracking. The ethyl radical is formed via hydrogen abstraction reactions of ethane. At higher temperatures ethyl decomposes to ethylene and at lower temperatures it is converted to ethane via a hydrogen abstraction reaction. The ethyl radical can also participate in addition reactions on unsaturated bounds and in radical termination reactions. The linear-concave temperature profile minimises the combination concentration of ethylene and ethyl concentration, limiting the secondary reactions, in the first part of the reaction volume to arrive at optimal ethylene yields.

For the heavier feed stocks, the maximum temperatures were all constrained by the imposed future material upper bound of 1300 K. Compared to current temperature profiles an increase in reaction temperature along the reaction volume coordinate results in significant improvements in ethylene and ethylene + propylene yields. Maximum ethylene yield is obtained with temperature curves that increase rapidly to the maximum allowed value followed by a short period drop and increase again towards the end of the reaction volume coordinate. Maximum ethylene + propylene yield requires isothermal conditions in the first part of the reaction volume, followed by a decrease in temperature.

The distribution of heavy feed along the reaction volume coordinate results in improvements of yields for either ethylene or ethylene + propylene optimality. The optimal feed distribution for ethylene + propylene yield optimality is more uniform and spread out compared to that in the case of ethylene optimality.

Just as done for ethane cracking, the outcome of the optimisations are made plausible with the most stable radical, that is allyl $(CH_2CH = CH_2)$. Allyl is formed by ethyleneand propylene producing initialisation reactions, and consumed by secondary reactions. With increasing olefin concentrations the secondary reactions will play a larger role and consequently reduce the lower olefin yields. Through the injection of the fresh hydrocarbon feed the partial pressure is reduced which suppresses the secondary reactions and promotes the lower olefin producing initialisation reactions. The dips at the beginning and the middle of the reaction volume coordinate temper the ethylene consuming secondary reactions.

7.5 Recommendations

In this work the finding of optimal processing principles for the steam cracking process has been addressed. The outcome shows room for significant olefin yield improvements and therefore we advise to pursue research, to capture this potential into new equipment and optimal reaction conditions. The continued research will necessarily have a dual approach, modelling and experimental. Recommendations are given for advancements in the enabling computational infrastructure to incorporate physically more complete and detailed reactor models which handle energy and fluid flow aspects and account for coking. At the experimental side it is recommended to test the validity of the obtained computational results and to explore the use of ceramic materials to achieve higher temperature and lower coking rates.

7.5.1 Validity of optimised processing principles for steam cracking

To translate the optimal reaction conditions into (new) optimal apparatus it will be important to make the uncertainties in the optimal reaction conditions visible. The SPYRO[®] kinetic model has been applied outside the regular operations to arrive at the optimal reaction conditions. As a consequence the predictions can have a larger uncertainty as in the regular situations. Therefore the validity of the SPYRO[®] kinetic scheme at temperatures up to 1300 K should be investigated. Regarding reaction-kinetics the currently available ab-initio calculations can make experimental validation work more effective since these calculations reduce the number of experiments. Ab-initio is particularly useful for research to the fundamentals of the coking phenomena where experiments are cumbersome.

Concerning the distributive features some experimental work is required to verify the predictions of the idealised model-derived hydrocarbon feed distribution function, temperature and pressure profiles. Particularly to the mixing associated with the injection of the hydrocarbon feeds along the reaction volume coordinate is a point of concern. If kinetics and effects of distribution are validated, additional equipment and material engineering work is required to achieve the required heat transfer with high temperature resistant materials. Attention has to be given to the materials effect on coking formation in the high temperature regime (> 1200 K) and the effect on the reactor availability and performance.

7.5.2 Enabling computational technologies

Technological developments are enabled by state of the art methods and tools as well as skilled engineer-scientists. At the tool side the functionality of the implemented Symbolic Modelling Definition module should be extended with temporal derivatives, to allow dynamic optimisations. This extension will probably enhance the quality of the underlying software which is always a good thing for actively used software. The extension must include a user manual with some hands on examples which would increase the usability of this module for main stream (chemical) engineers.

When it comes to equipment engineering the physical property models play an important role since these connect the thermodynamic state variables (pressure, temperature, entropy, etc.) to the non-state variables (mass flow rate, energy flows, etc.), which determine the size of the equipment. It would be very efficient to have access to physical property modules from other flow sheet packages. Considering the use of CAPE-OPEN possibilities brings the application of general purpose simulators, such as gPROMS, JACOBIAN, SPEEDUP, etc., into the picture.

The distributed allocation of hydrocarbon feeds to the reaction volume will demand study of injection mechanisms. For this purpose (and wider) the combination of micro-scale models (mostly 3D) and macro-scale models (1D or 2D) are often required to provide the right insights. The combination of detailed equipment modelling with CFD and more aggregated simulators is therefore of interest.

In this work we have implemented symbolic modelling in the existing simulation package since it was resource effective. In view of the impossibility to move the reaction kinetic model to a general purpose tool, a possible further extension of SPYRO[®] with CAPE-OPEN or connectivity with CFD packages should be done on the basis of a structured evaluation.

In this research the need for flexible modelling was addressed by the implementation of a Symbolic Model Definition module in an existing simulation and optimisation package. The application of this symbolic modelling in chemical engineering research revealed that the (main stream) chemical engineers must have some skills in all kind of (numerical) mathematics. Although these skills are instructed at the universities these are not often actively applied, due to the current available simulation software that do not necessary require these skills. Particularly, the lack of experience surfaces when new models need to be assembled from scratch, this requires the combination of physical models and numerical (mathematical) model. Therefore engineers are required that are more skilled in these topics to address these modelling activities. The further development of a package providing the modelling language of the physicochemical phenomena or the language of process modelling would contribute to this.

7.5.3 Reactor synthesis approach for a single phase reactor

The d-RMix model solved elegantly the formulated research question but inherently defers other important questions to a later stage. Firstly, there is the fundamental theoretical question to what extent d-RMix covers the scope of the attainable region theory, or even goes wider. Analysing mathematically the relationship between the two synthesis methods is recommended to enforce the scientific foundations of the d-RMix.

Secondly, through the use of an abstract geometry in the d-RMix model, and the focus on the species balances and reaction part only, certain engineering aspects are inherently excluded. The way forward would be to determine the required energy and momentum rates to achieve the optimal reaction conditions and geometry. The geometry should provide a short residence time with a small pressure drop, plug flow regime and distribution functionality of the hydrocarbon feed stock. The temperature level of the energy supplier should be modestly higher than the optimal cracking temperature to prevent high temperature gradients on surfaces whereon coke can deposited. The resulting optimal geometry and optimal reaction conditions should also be examined on flexibility to accommodate turn down of the capacity of the reactor. Another phenomenon is coke deposit which is strongly related to the material properties and the contact surface of the reactor walls. These can only be considered when a particular geometry is applied.

Therefore we recommend to extend the *d*-RMix model with the energy and momentum balances and a rigorous model for coke deposition. The energy injection modelling can be relatively easily developed, even without the explicit definition of the reactor volume geometry. The momentum phenomenon on the other hand can only be considered with an explicit reactor volume geometry, since this phenomenon requires the definition of velocity and considerations on friction losses. The inclusion of a code deposition model is more challenging since it requires kinetics for the particular materials.

The translation of any obtained macro-mixing kernel in d-RMix to a physical realisation is a challenging task. For the steam cracking process the mixing kernel is fortunately zero, leading to plug flow. However, the system with Van de Vusse reactions gave a non-zero mixing kernel. The translation of an obtained macromixing kernel into a feasible reactor volume geometry demands further research and engineering ingenuity. The translation of the distribution functions for the reactants and product can be correlated more easily to geometrical parameters such as porosity, perforations, etc. but will require research to arrive at a generic protocol.

7.5.4 Engineering aspects of processing route for lower olefins

The review of all reported processing principles was completed with a minimum and maximum energy requirement according the pinch analysis of the process. This was done for an ethane feed with an equal separation section for all alternatives. Possibly slightly different conclusions regarding energy consumption could be obtained when considering optimised separation sections for each processing principle. This would also give the opportunity to make stronger statements on the real energy consumption instead of the minimum and maximum energy requirements. We considered the pollutants such as NOx and SOx and CO_2 in a qualitative way, when tackling the flow sheets with more detail this allowed to review the emissions in a quantitative manner. The coking phenomenon was also looked at from a qualitative perspective this can be treated more directly to get a more accurate statement on coking rate and thus on the time on stream per annum for each process.

The pinch analysis revealed that the heat integration of the shock wave reactor is challenging. The shock wave reactor is from an engineering point of view an interesting technology since it features a decoupling of mixing, heating and reaction. Therefore we consider it worthwhile to investigate possible alternatives for the large amount of high pressure steam, the prime source of the challenge, for example other fluids, combination with other high temperature processes to allow efficient heat integration, etc.

The research to the thermo-physical optimisation for high olefin yield in steam cracking reactors (see chapter 6) revealed that for ethane cracking the currently applied temperature profiles are applicable. The coking rates for ceramic material is known to be several orders of magnitude lower than the typical alloys used for radiant coils, making this material suitable to crack all feed stocks. Therefore we consider it worthwhile to investigate if ceramic radiant coils suspended in furnaces with adapted firing can offer the next generation ethane steam cracking technology. For the heavy feed stocks the adapted firing furnace with ceramic reactor internals will allow to achieve the higher temperatures. However, it will require a necessary step out in design to find the optimal reaction volume(s) geometry for the cracking of heavy feed stocks since the optimal profiles have no resemblance with the typical (or adapted firing) reactor temperatures and injection policies.

Appendix A

Basic symbolic mathematics

The core of the SMD module is the procedure to evaluate symbolic algebraic expressions. Our implementation, in FORTRAN 95, is based on a binary-tree representation of algebraic equations (see e.g. Pantelides, 1988; Tolsma and Barton, 1998). The tree of the general algebraic expression (A.1) is shown Fig. A.1.

$$r = f(x)^{g(x)} \tag{A.1}$$

The vertices in the tree represent operators, such as addition, subtractions, multiplication, functions, etc., and the edges denote the sequence of evaluation, often referred as LHS and RHS (Left/Right Hand Side) of the operator. The root vertex represents the result of the algebraic expression and the leaves of the tree represent the individual variables, parameters, constants, etc., in between the vertices represent the operators.

$$\frac{\partial r}{\partial x} = f(x)^{g(x)} \left(\frac{\partial g}{\partial x} \ln \left(f(x) \right) + \frac{g(x)}{f(x)} \frac{\partial f}{\partial x} \right)$$
(A.2)

Once the expression tree of an algebraic expression is available the partial derivative expression tree can be constructed by recursively applying the rules of differentiation, for example Eq. (A.2), which is the differentiation rule of Eq. (A.1). During the construction of the derivative tree of Eq. (A.1) Eq. (A.2) needs to be added to the derivative tree, the vertices that are added are shown in Fig. A.2. The algorithm to construct a derivative tree from a residual tree is given by Fig. A.3.

The evaluation of the expression trees is performed from the leafs to the roots of the tree. This is accomplished with a depth first evaluation procedure, as shown by Fig. A.4.



Figure A.1: Example of residual represented by a binary tree



Figure A.2: Binary tree of differentiation rule for Eq. (A.1), or its tree in Fig. A.1

```
DIFF( R(Vertex), D(Vertex) )
  SELECT CASE(R(Vertex).Operator)
 CASE(CONSTANT)
    RETURN D(Vertex).Value=0
 CASE(VARIABLE)
    RETURN D(Vertex).Value=1
 CASE(PLUS)
    ADD D(Vertex).LHS
    ADD D(Vertex).RHS
    D(Vertex).Operator=PLUS
    DIFF( R(Vertex).LHS, D(Vertex).LHS )
    DIFF( R(Vertex).RHS, D(Vertex).RHS )
    RETURN
 CASE()
        :
    Similar code for other operators
        :
  ENDCASE
END DIFF
```

Figure A.3: Recursive algorithm for the creation of a derivative tree, D, from a residual tree, R

```
Real EVALUATE(T(Vertex) )
 SELECT CASE(T(Vertex).Operator)
 CASE(CONSTANT)
   RETURN T(Vertex).Value = 42
 CASE(VARIABLE)
   rval = GET_FROM_X(T(Vertex).Position)
   RETURN T(Vertex).Value = rval
 CASE(PLUS)
   lhs_val = EVALUATE( T(Vertex) LHS )
   rhs_val = EVALUATE( T(Vertex) LHS )
   RETURN lhs_val + rhs_val
 CASE()
        :
   Similar code for other operators
        :
 ENDCASE
END EVALUATE
```

Figure A.4: Evaluation algorithm of a tree, T.

Appendix B

Derivation of the *d*-RMix model

In this appendix the *d*-RMix and its constraints are derived. Consider a series of finite volumes, as shown by Fig. B.1. There is a flow of material from the entrance to the exit. On top of this flow all the finite volumes can exchange material with one another and product can be removed from all these finite volumes. The k^{th} component balance of the i^{th} finite volume is given by Eq. (B.1):

$$\frac{\partial C_{k,\ i/N}\Delta V}{\partial t} = F_{k,\ (i-1)/N} - F_{k,i/N} + R_{k,i/N}\Delta V + L(i/N)F_{0k}\Delta V - K(i/N)F_{k,i/N}\Delta V + \Delta V \sum_{j=1}^{N} F_{k,j/N}M(j/N,i/N)\Delta V - \Delta V \sum_{j=1}^{N} F_{k,i/N}M(i/N,j/N)\Delta V.$$
(B.1)

In all equations denoted in this work we have for the sake of compactness, denoted the dependency to the reaction volume for the concentration, molar flow rate and net production rate (C, F, R) in the subscript, for example $C_{k,V} = C_k(V)$. When we let the number of finite volumes go to infinity, the following differential-integral Eq. (5.1) is obtained:

$$\frac{\partial C_{k,V}}{\partial t} = -\frac{\partial F_{k,V}}{\partial V} + R_{k,V} + L(V) F_{0k} - K(V) F_{k,V} + \int_{0}^{V_{t}} (F_{k,v}M(v,V) - F_{k,V}M(V,v)) dv.$$
(B.2)

The feed distribution, and product removal functions and mixing kernel: L, K,



Figure B.1: Schematic of the d-RMix principle for 3 interconnected finite volumes.

M, are independent of the species and subject to physical feasibility constraints, such as non-negative flows in the system:

$$L(v) \geq 0 \qquad v \in [0, V_t] , \qquad (B.3)$$

$$M(v, V) \ge 0 \ v, V \in [0, V_t],$$
 (B.4)

$$K(v) \geq 0 \qquad v \in [0, V_t] . \tag{B.5}$$

Eq. (B.2) is defined for one feed stream, we note that this model can be extended for multiple feed streams by the definition of multiple feed distribution functions. All the available feed should be released inside (and/or by pass) the reactor:

$$\int_{0}^{V_{t}} L(v) \, dv = 1.$$
 (B.6)

The mixing kernel, M, cannot contribute to the overall production of a component in the total reaction volume, only locally, therefore the mixing kernel should fulfil the following conservation constraint:

$$\int_{0}^{V_{t}} \int_{0}^{V_{t}} M(v, V) \, dv \, dV = \int_{0}^{V_{t}} \int_{0}^{V_{t}} M(V, v) \, dv \, dV \,. \tag{B.7}$$

The total molar flow rate of the k^{th} component, leaving the reaction volume (see Fig. B.1) is a summation of the feed that is by-passed and the amount extracted from the reaction volume. This is defined by the following equation:

$$F_{out,k} = L(V_t) F 0_k + \int_0^{V_t} K(v) F_{k,v} dv.$$
 (B.8)

The final item that must be defined is the molar flow rate at the entrance of the reaction volume, this is given by the following equation:

$$F_{k,0} = L(0) F_{0k}.$$
 (B.9)

Appendix Distributive reaction-mixing model – ideal reactors

The use of the word "reactor" in this section is conceptual and concerns reaction volumes with idealised flow patterns; it does not refer to specific equipment.

C.1 PFR

The distributive reaction-mixing model Eq. (5.1) embodies the PFR, DSR and CSTR models as special cases. First we will show how the PFR results are obtained. We define the following feed injection function, mixing kernel and extraction functions (L, M, K):

$$L(v) = \begin{cases} 1 & v = 0 \\ 0 & else \end{cases},$$

$$M(v,\mu) = M_m \,\delta(v-\mu) \quad M_m \geq 0 \,(\text{mixing at } v = \mu \text{ only}),$$

We only add feed at the entrance of the reactor and extract no fluid along the reactor coordinate. We allow only mixing towards and from the same location. Substitution of the functions, kernel L, K, M gives (V > 0):

K(v) = 0.

$$\frac{\partial C_{k,V}}{\partial t} = -\frac{\partial F_{k,V}}{\partial V} + R_{k,V} + \int_0^{V_t} M_m \,\delta\left(v - V\right) \left(F_{k,v} - F_{k,V}\right) dv \,. \quad (C.1)$$

The boundary Eq. (B.9) changes to

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$$F_{k,0} = L(0) F_{0k} = F_{0k}.$$
 (C.2)

The integral in Eq. (C.1) vanishes, yielding the standard equation for the description of the PFR:

$$\frac{\partial C_{k,V}}{\partial t} = -\frac{\partial F_{k,V}}{\partial V} + R_{k,V} \qquad F_{k,0} = F_{0k}.$$
(C.3)

C.2 DSR

The Differential Side-stream Reactor (DSR) model is derived in a similar fashion as for the PFR, where the feed and product removal functions, L, K, are defined as non-zero functions for the whole or part of the reaction coordinate V, as given by:

$$\frac{\partial C_{k,V}}{\partial t} = -\frac{\partial F_{k,V}}{\partial V} + R_{k,V} + L(V)F0_k - K(V)F_{k,V} \quad F_{k,0} = F0_k.$$
(C.4)

C.3 CSTR

For the CSTR model we define that the feed is only injected at the entrance of the reactor, no fluid is removed along the reactor coordinate and a constant mixing rate is applied. This is defined by the following equations:

$$L(v) = \begin{cases} 1 & v = 0 \\ 0 & else \end{cases}$$
$$M(v, \mu) = \frac{M_m}{V_t},$$
$$K(v) = 0.$$

The boundary Eq. (B.9) changes to

$$F_{k,0} = L(0) F_{0k} = F_{0k}.$$
 (C.5)

,

Substitution of the functions, kernel L, K, M gives (V > 0) the following equation:

$$\frac{\partial C_{k,V}}{\partial t} = -\frac{\partial F_{k,V}}{\partial V} + R_{k,V} + \frac{M_m}{V_t} \int_0^{V_t} (F_{k,v} - F_{k,V}) dv.$$
(C.6)

When the mixing rate is high $(M_m >> 1)$ the integral in Eq. C.6 remains small only when $|F_{k,v} - F_{k,V}| \rightarrow 0$. In other words, the gradient of the flow will vanish except where the feed enters the reaction volume; there an almost



Figure C.1: Typical d-RMix profiles for a CSTR with a mixing constant of 500 m⁻³, total volume is 0.3 m^{-3} .

infinite gradient will be observed. Fig. C.1 gives an indication how the profiles look similar to model a CSTR with the *d*-RMix. These profiles are for reaction scheme (5.2), a total volume of 0.3 m^{-3} , and a mixing constant M_m of 500 (m⁻³).

Taking the integral $\int_{-\infty}^{V_t} dV$ over Eq. C.6 and introducing the uniform conditions inside V_t due to a very high M_m one obtains:

$$V_t \frac{dC_k}{dt} = F_{k,0} - F_{k,V_t} + V_t R_k.$$
 (C.7)

This is the CSTR species balance.

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Nomenclature

Symbols

A	frequency factor	$[s^{-1}]$
A	area	$[m^2]$
C	molar concentration	$\left[\text{mol} \cdot \text{m}^{-3} \right]$
E_a	activation energy	$J \cdot \text{mol}^{-1}$
Е	ethylene (yield)	[wt%]
E+P	ethylene plus propylene (yield)	[wt%]
F	molar flow rate	$\left[\text{mol} \cdot \text{s}^{-1} \right]$
F_0	molar flow rate of the feed	$\left[\text{mol} \cdot \text{s}^{-1} \right]$
h	height	[m]
K	product removal function	[m ⁻³]
k	reaction constant	$\left[s^{-1} \right]$ or
		$[m^3 \cdot mol^{-1} \cdot s^{-1}]$
K_p	equilibrium constant	[Pa]
k^{\uparrow}	reaction constant	$\begin{bmatrix} s^{-1} \end{bmatrix}$ or
		$[m^3 \cdot mol^{-1} \cdot s^{-1}]$
ko	reaction constant	$\left[s^{-1} \right]$ or
		$m^3 \cdot mol^{-1} \cdot s^{-1}$
L	feed distribution function	[m ⁻³]
M	Mach number	[-]
M(V, v)	the mixing kernel (amount mixed from	[m ⁻⁶]
	location V to v)	
Mw	molecular mass	$[\text{kg·mol}^{-1}]$
n	number of components	[-]
n_{reac}	number of reactions	[-]
P	pressure	[Pa]
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<i>R</i> molar production rate as the net effect	$\left[\text{mol} \cdot \text{m}^{-3} \cdot \text{s}^{-1} \right]$
of all reactions	
R_{gas} universal gas constant	$[J \cdot mol^{-1}K^{-1}]$
r radius	[m]
r reaction rate	$\left[\text{mol} \cdot \text{m}^{-3} \cdot \text{s}^{-1} \right]$
r_{RH} ratio radius-height	$[m \cdot m^{-1}]$
S steam	[-]
SDR steam dilution ratio	$[\text{kg}\cdot\text{kg}^{-1}]$
T temperature	[K]
t residence time	[s]
V, v space-time coordinate	$[m^3]$
V_t total volume	$[m^3]$
x_{wt} wet feed mass fractions	[-]
xwt_{HC} hydrocarbon feed mass fractions	[-]
Y yield	$[\text{mol·mol}^{-1}]$

Subscript

k	counter for components	[-]
i	counter for reactions	[-]
j	identifier for the j^{th} feed type $[HC,$	[-]
	H_2O]	
V, v	identifier for the location in the reaction	$[m^{3}]$
	volume	

Greek symbols

ΛV finite volume element	1
ΔV infine volume element [m°	
$\Delta H_{f,298}^0$ heat of formation at 25°C and standard [J·m	$10l^{-1}$]
pressure	
$\Delta G_{f,298}^0$ Gibbs energy of formation at 25°C and [J·m	$10l^{-1}$]
standard pressure	
ε equilibrium conversion [-]	
ζ conversion [mod	$1 \cdot \text{mol}^{-1}$]
κ zero/one function as defined by $[-]$	
Eq. (5.9)	
ξ conversion [-]	
ρ density [kg·	m^{-3}]
au residence time [s]	
ϕ_m total mass flow rate [kg·s	s^{-1}]

Acronyms

Advanced cracking reactor
American Society for testing and materials
Boiling feed water
Benzene, toluene and xylene
Continues stirred tank reactor
Differential algebraic equation
Deep catalytic cracking
Dimethyl disulphide
Dilution steam
Differential side-stream reactor
Dilution steam super heater
Economiser
Fluidized bed dehydrogenation
Fluid catalytic cracking
Feed pre-heater
Final boiling point
Gross domestic product
Hydro carbon
Heavy Gas Oil
High temperature coil
High pressure steam
High pressure steam super heater
Initial boiling point
Left hand side
Liquefied petroleum gas
Methanol to olefins
Natural gas
Non-linear algebraic equation
Partial differential algebraic equation
Plug flow reactor
Paraffins iso-paraffins olefins naphthenes and aromatics
Right hand side
Steam dilution ratio
Specific gravity
Symbolic model definition
Steam active reforming
Shock wave reactor
Orthogonal collocation on finite elements
Oxidative dehydrogenation

Samenvatting

Het concept voor de volgende generatie stoomkraak reactoren

Het stoomkraakproces is een belangrijk onderdeel van de koolwaterstof verwerkende industrie. De belangrijkste producten zijn lagere olefinen (etheen, propeen, butenen) en waterstof. Etheen is hiervan volumetrisch gezien 's werelds grootste organisch chemisch product, met een wereldwijde capaciteit van ≈ 120 miljoen ton per jaar. De voedingen voor dit proces zijn koolwaterstoffen (C₂₊) zoals: ethaan, LPG, nafta's, gas condensaten en gasolie. De opbrengst van de olefines wordt voornamelijk bepaald door het ontwerp van de stoomkraak fornuizen. Deze fornuizen zijn aangepaste verwarmingsovens die in staat zijn om op hoge temperaturen een hoge energieflux te realiseren om de endotherme kraak reacties te laten verlopen.

De huidige state-of-the-art kraakoven technologie is ontstaan vanuit een evolutionair ontwerp. Het is gestart vanuit een empirische benadering van het ontwerp en de operatie van de ovens, naar een diep, modelgebaseerd begrip hiervan. Modellen hebben de mogelijkheid om te voorspellen wat er gebeurd in de kraakbuizen en wat de resulterende opbrengsten aan olefinen zijn, gegeven de voedingssamenstelling, de kraakbuis configuratie en de inkomende energie stromen. Door de uitgebreide optimalisatie van het ontwerp en de operatie, is het huidige stoomkraak proces "volwassen" geworden. Toch ontbreekt er een helder inzicht over hoe ver de huidige olefine opbrengsten verwijderd zijn van de theoretisch maximum haalbare, volgens de fundamentele basis mechanismen. Het vinden van een mogelijkheid voor een significante opbrengstverbetering zou een revolutionaire verandering in kraakreactor technologie kunnen rechtvaardigen. Het identificeren van een dergelijk potentieel is de belangrijkste drijfveer voor dit onderzoek. Er is gekozen voor een benadering waarin onderzocht en gebruikt wordt wat de kansen zijn van wat de chemie fundamenteel te "bieden" heeft, in plaats van de meer beperkte aanpak om te onderzoeken waartoe de huidige apparatuur "in staat is"

of waarin deze "beperkt is".

Het onderzoeksdoel is om de intrinsieke optimale stoomkraak reactiecondities te vinden, die de opbrengsten aan olefinen maximaliseren, gebruik makend van fundamentele reactie-kinetiek modellen. Deze optimale omstandigheden kunnen dan dienen als richtlijn voor de ontwikkeling van een volgende generatie stoomkraak reactor. Dit onderzoek is gebaseerd op mathematische modellering en optimalisatie, dat vooraf gaat aan enige dure experimentele validatie.

Om dat doel te bereiken:

- 1. zijn de in de literatuur gepubliceerde alternatieve proces concepten getoetst tegen een reeks van ideale voorwaarden;
- zijn concepten en software ontwikkeld voor een vergelijkings gebaseerd modellerings programma dat geschikt is voor de optimalisering van grootschalige reactie-kinetiek modellen;
- 3. is een modellerings strategie ontwikkeld om de opbrengsten van olefinen te optimaliseren, die fundamentele kinetische modellen integreert in een nieuw reactor concept voor homogene reacties met een gedistribueerde voeding en macro-menging;
- 4. zijn optimalisatie technieken toegepast op het nieuwe reactor concept model en een geavanceerd reactie-kinetiek model voor stoomkraken, SPYRO[®], om een **model gebaseerde synthese** uit te voren op de optimale reactie omstandigheden voor een maximale olefine opbrengst, met een breder scala aan operationele condities dan die op dit moment haalbaar zijn.

Eerst hebben we de alternatieve proces concepten uit de literatuur voor de productie van etheen op industriële schaal onderzocht. Deze alternatieve proces concepten zijn beoordeeld op hun overeenstemming met een reeks van ideale (prestatie) eisen. De eigenschappen van een ideaal proces zijn: een maximale olefine opbrengst, geen overblijfselen van de energiedragers of hulpchemicaliën in het product, een minimale ecologische impact, een minimale toevoeging van energie per eenheid product, een hoge beschikbaarheid en een lage mate van complexiteit van de reactie sectie. Het blijkt dat de specifieke energie benodigdheden van de processen slecht zijn gerapporteerd in de beschikbare literatuur. Daarom zijn deze energie benodigdheden systematisch bepaald op basis van simulaties uitgevoerd met Aspen Plus software en SPYRO[®] voor een etheen fabriek met een zelfde ethaan voeding. Hoewel geen van de gerapporteerde processen voldoet aan alle idealen, komen er twee dicht in de buurt. Deze twee zijn de nieuwe combinatie van de kraakoven met aangepaste branders met keramische reactoren als binnenwerk en de schokgolf reactor. Dit onderzoek naar de alternatieve processen is weliswaar geschikt voor het vinden van de beste beschikbare technologie, het is echter niet geschikt om de maximaal haalbare olefine opbrengst te identificeren. Daarom is de volgende optimalisatie aanpak ook uitgevoerd.

Ten tweede: de optimalisatie van de opbrengst wordt mogelijk gemaakt door geavanceerde modellering en berekenings technieken. SPYRO[®] Suite 7 werd gebruikt als referentie software, omdat het een implementatie van het vereiste reactie-kinetiek model bevat. Het genereren van alternatieve reactie-kinetiek modellen en implementeren in bruikbare software is buiten het bestek van dit onderzoek gelaten om wille van beschikbare tijd. Een voorziening om symbolisch te modelleren is toegevoegd aan het bestaande vergelijking gebaseerde simulatie en optimalisatie pakket, SPYRO[®] Suite 7, zodat de optimalisering functionaliteit kan worden toegepast op een nieuw reactor model. De functionele specificaties voor de symbolische modellerings voorziening zijn gericht op het minimaliseren en eenvoudig detecteren van fouten gemaakt door de modelleur. Voor de implementatie is een onderdeel van de gPROMS taal gekozen. Deze is uitgebreid met een aantal nieuwe attributen: spline constructie, tussentijdse grafische resultaten en de definitie van een groot aantal simulaties en optimalisaties door middel van scenario's. De effectiviteit van de symbolische modellerings voorziening is bewezen met dit optimalisatie project.

In de derde plaats is de toegepaste modellering en optimalisatie strategie gebaseerd op een fysische decompositie die de chemie en de reactie-kinetiek benadrukt. D.w.z. het stoomkraak proces kan conceptueel worden ontleed in verschillende verschijnselen. De centrale verschijnselen zijn de chemische reacties, met stoichiometrie en kinetiek. Mechanistische aspecten zoals de energie overdracht (via de reactorwand of rechtstreeks), en de impulsoverdracht worden van secundair belang geacht. De focus in dit proefschrift ligt op de eerste stap van deze ontleding, namelijk: het vinden van optimale reactie condities om tot een maximale olefine opbrengst komen, op basis van fundamentele kinetiek en component balansen. Energie- en impulsbalansen moeten worden onderzocht in een later stadium van het onderzoek. De decompositie is nodig om de berekeningscomplexiteit en werkbelasting te verminderen. De reacties zijn verondersteld plaats te vinden in een abstract reactie volume. Een nieuw reactor model concept is hiertoe geïntroduceerd. Dit concept, genaamd d-RMix, beschrijft een (één-dimensionaal) reactor volume, met een gedistribueerde voeding injectie, gedistribueerde productextractie en macro menging van het reactie medium, waarin homogene reacties optreden. De temperatuur en de (dalende) druk kan vrij worden gespecificeerd als functie van de coördinaat van het reactor volume. De nieuwe d-RMix reactor is geverifieerd en gevalideerd met behulp van eenvoudige reactie-kinetiek modellen (Van de Vusse) uit de literatuur. De verkregen resultaten zijn vergeleken met de resultaten die gepubliceerd zijn voor een andere reactor synthese methode, namelijk de "bereikbare regio theorie", en zijn identiek bevonden.

Als vierde is, na bewezen te hebben dat de nieuwe reactor synthese model in staat is om bestaande testcases te reproduceren, het model toegepast is op de optimalisatie van olefine opbrengsten m.b.v. een industrieel gevalideerd groot kinetische schema genaamd SPYRO[®]. Dit schema bevat meer dan 7000 reacties in de gasfase tussen 218 moleculaire en 27 radicaal componenten. De reactor synthese maakt het optimaliseren van de volgende vrijheid met betrekking tot de

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maximale opbrengst aan olefine mogelijk: voeding distributie, product verwijdering en intensiteit van de macro-mixing, langs de reactor volume coördinaat. De verhouding van stoom en voeding is constant gehouden tijdens dit onderzoek. Het temperatuur profiel is vrij te bepalen langs de coördinaat van het reactor volume, de bovengrens van de reactietemperatuur is vastgesteld op 1300 K, een marge van meer dan 100K met de huidige (metallurgische) bovengrens. De druk is ook een vrij te variëren variabele met een ondergrens van 1 bar.

Resultaten: De volgende resultaten zijn behaald voor de optimalisatie van de etheen opbrengst en de etheen plus propeen opbrengst voor vier verschillende voedingssoorten. Voor het kraken van ethaan een vrij optimum is verkregen, een lineair-concaaf temperatuurprofiel met een maximum temperatuur van ≈ 1260 K. Alle ethaan moet worden toegevoegd aan de ingang van het reactie volume. Deze optimale reactie condities voor het kraken van ethaan kan worden verklaard met behulp van het ethyl radicaal dat het meest stabiele radicaal is bij het kraken van deze voeding. Het ethyl radicaal wordt gevormd via waterstof abstractie reacties van ethaan. Bij hogere temperaturen valt ethyl uiteen in etheen en bij lagere temperaturen wordt het omgezet in ethaan via de teruggaande waterstof abstractie reacties. Het ethyl radicaal kan ook deelnemen aan additie reacties met onverzadigde verbindingen en aan radicaal terminatie reacties. Het lineairconcaaf temperatuurprofiel minimaliseert de etheen en ethyl concentraties in het eerste deel van het reactie volume, waardoor de secundaire reacties worden gereduceerd. Hierdoor wordt een optimale etheen opbrengst verkregen. De theoretisch maximaal haalbare etheen opbrengst voor het kraken van ethaan kraken is 66.8 gewichtsprocent, terwijl in conventionele stoomkraken doorgaans 55 gewichtsprocent wordt beschouwd als de maximale waarde. Dit optimum wordt begrensd door de druk die op de ondergrens van 1 bar zit. De resulterende verblijftijd is in dezelfde orde als bij de huidige technologie.

Voor propaan en zwaardere voedingen is het optimale temperatuursprofiel een isotherm profiel, waarbij de temperatuur gelijk is aan de gestelde bovengrens met een dip aan het begin en het midden van de reactie volume coördinaat. Voor de zwaardere koolwaterstof voedingen leidt de distributie van de voeding over de coordinaat van het reactie volume tot hogere opbrengsten. Bij het optimaliseren van de som van etheen en propeen wordt een aanzienlijk hoger propeen opbrengst verkregen dan bij de optimalisatie van enkel de etheen opbrengst. Dit wijst op economisch aantrekkelijk scenario's voor een verschuiving van etheen naar propeen onder geschikte marktomstandigheden. Net zoals voor het kraken van ethaan is een verklaring voor dit resultaat te vinden in het meest stabiele radicaal. Hier is dat het allyl radicaal $(CH_2CH = CH_2)$. Door de (gedistribueerde) injectie van de verse voeding wordt de partiële druk van de koolwaterstoffen verminderd, waardoor de secundaire reacties worden onderdrukt en de olefine producerende initialisatie reacties bevorderd. De dips in het begin en het midden van de coördinaat van het reactie volume onderdrukken de consumptie van etheen door secundaire reacties.

Na aangetoond te hebben dat er een aanzienlijk potentieel is om de opbrengst

te verhogen, zal de volgende stap in het onderzoek naar een nieuwe generatie thermische kraak reactoren, zijn om (experimenteel) te valideren of de resultaten verkregen op basis van model optimalisering correct zijn. In de validatie stap zullen de onzekerheden in de optimale reactie condities zichtbaar moeten worden gemaakt. Om te komen tot de optimale reactie condities, is het SPYRO[®] kinetiek model gebruikt buiten het conventionele toepassingsgebied. Dien ten gevolge moeten in de volgende stap mogelijke onzekerheden worden onderzocht door middel van simulaties en gerichte experimenten. Vooral de vorming van cokes dienen te worden bestudeerd en gemodelleerd. Als deze modelgebaseerde resultaten experimenteel zijn bevestigd, dan moeten deze optimale reactie condities mogelijk worden gemaakt in nieuwe (geoptimaliseerde) apparaten. De daarop volgende stappen zijn, om de benodigde energie- en impulsoverdracht snelheden voor de optimale reactie condities vast te stellen in de geometrie van een nieuw te ontwerpen reactor. Deze geometrie moet het volgende mogelijk maken: een korte verblijftijd met een minimum aan drukval, propstroming en axiale distributie functionaliteit van de koolwaterstof voeding. In dit onderzoek is vastgesteld dat de stoomkraak chemie aanzienlijk potentieel bied voor hogere olefinen opbrengst, de gevonden optimale reactie condities vormen een significante uitdaging voor de apparatuur ontwerpers om dit potentieel ook daadwerkelijk te realiseren in de volgend generatie stoomkraak reactor.

Marco van Goethem

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Curriculum vitae

Marco Willie Marie van Goethem was born in Terneuzen, the Netherlands, on 22 September 1971. From 1984 until 1988, he attended secondary school, followed by a technical secondary school until 1991. In the same year he started his studies at the department of chemical engineering on the University of Applied Sciences in Utrecht, the Netherlands and received his Bachelor's degree in 1995. Thereafter he continued his studies at the department of chemical engineering on the Delft University of Technology, the Netherlands. In June 1998 Marco van Goethem defended his Master thesis: "Modeling of Reactors with Large Reaction Systems" and obtained his M.Sc. degree with honours in chemical engineering. His Master thesis was awarded the Unilever Research Award in 1999. He joined in July 1998 the Pyrotec department of Technip Benelux B.V. (previously known as KTI B.V.) as Process Modelling Engineer. Marco van Goethem worked on an equation based simulation program for the steam cracking process, SPYRO[®], he received for this work in 2003 Technip's Jacques Franquelin Award. In July 2003 he started a part time Ph.D. research project to the optimal reaction conditions for the steam cracking process at the Process Systems Engineering section in the department of chemical engineering, Delft University of Technology under the supervision of Johan Grievink, Jacob Moulijn and Peter Verheijen. At Technip Benelux B.V. he continued part-time his process modelling activities, amongst others, the development of the NOX Post Processor, a simulation program capable to predict accurately the NO_x in the flue gasses from industrial furnaces, in 2008 he received a Jacques Franquelin Award for this work. In that same year he was promoted to Principal Process Modelling Engineer, responsible for all technical activities in the Pyrotec department. The research work which was done in 2003 -2008 results in a Ph.D. thesis entitled: "Next Generation Steam Cracking Reactor Concept".

Colophon

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The steam cracking process is an important asset in the hydrocarbon processing industry. The main products are lower olefins and hydrogen, with ethylene being the world's largest volume organic chemical at a worldwide capacity of ~120 million tonnes per year. Feed stocks are hydrocarbons such as: ethane, LPG, naphtha's, gas condensates and gas oil.

The research goal of this thesis is to search for the intrinsic optimal steam cracking reaction conditions, pushing the olefin yields to the maximum that the fundamental reaction kinetic models allow for. To get to that goal we have: firstly, identified and assessed alternative process concepts published in the literature. Secondly, developed the concepts and software for an equation based modelling tool suitable for optimisation of large scale reaction kinetic models. Thirdly, developed a new reactor concept, *d*-RMix for homogeneous reactions with distributed feed allocation, product removal and macro-mixing. Fourthly, applied the optimisation tool to the new reactor concept model and an advanced reaction kinetic model for steam cracking, SPYRO[®].

For four different feed stocks optimisations of ethylene yield and of ethylene plus propylene yields have been carried out. For the cracking of ethane a linear-concave unconstrained temperature profile with a (free) maximum temperature of ~1260 K proves optimal. For propane and heavier feed stocks an isothermal profile at the upper temperature bound is optimal, with dips at the beginning and the middle of the reaction volume coordinate. For these heavier hydrocarbon feeds a distribution along the reactor volume coordinate does result in higher yields. Having established that the steam cracking chemistry offers a potential for significantly higher olefins yields, these equipment engineering considerations pose a significant challenge to actually realise this potential and arrive at a next generation steam cracking reactor.

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