UNIVERSITÀ DEGLI STUDI DI PADOVA

DIPARTIMENTO DI INGEGNERIA INDUSTRIALE

CORSO DI LAUREA MAGISTRALE IN INGEGNERIA CHIMICA E DEI PROCESSI INDUSTRIALI

Tesi di Laurea Magistrale in
Ingegneria Chimica e dei Processi Industriali

Modelling of an industrial plant for vinyl chloride production

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ANNO ACCADEMICO 2015/2016

Abstract

Vinyl chloride is one of the leading chemicals, used mainly for manufacturing polyvinyl chloride (PVC). The vinyl chloride production is almost exclusively realised through the so-called balanced process, where ethylene, chlorine and oxygen are converted into the product, involving 1,2-dichloroethane as intermediate. In this thesis a complete flow-sheet representing the whole plant is developed by using the gPROMS® ProcessBuilder process simulator. Design alternatives have been analysed in order to represent an optimal process configuration close to the real practice. Molecular kinetic models are implemented in each reactor unit considering main reactions and most significant side reactions. The thermodynamic model reliability is ensured by regression and implementation of binary interaction parameters from experimental data for the main binary mixtures involved in the process. The accuracy of simulation results is verified by comparison with plant and unit operations data available from the literature.

Process Systems Enterprise Ltd. (London, UK) is gratefully acknowledge for technical and financial support.

Riassunto

Il cloruro di vinile è uno dei più importanti composti prodotti nell'industria chimica. La sua notevole importanza è data dal fatto che è quasi esclusivamente utilizzato come monomero per la produzione del polivinilcloruro (PVC), una delle principali *commodity plastics*, la terza in termini di capacità annuale dopo polietilene (PE) e polipropilene (PP). Per tale motivo è comune identificare direttamente tale specie chimica come VCM (Vinyl Chloride Monomer). Inoltre, è opportuno evidenziare che, grazie alla spinta di paesi in via di sviluppo come Cina e India, la capacità produttiva del cloruro di vinile è in continuo aumento in impianti di sempre maggiori dimensioni. Inoltre, le condizioni in cui viene condotto il processo per la produzione del cloruro di vinile rendono molto vantaggioso l'utilizzo di software per la simulazione di processo: ad esempio, data la scala di produzione, anche un piccolo miglioramento tecnico porta a un consistente vantaggio economico. L'obbiettivo di questo lavoro di tesi, dunque, consiste nella sintesi di un modello in grado di rappresentare il processo completo in modo affidabile. Ciò è realizzato attraverso la convalida di un modello termodinamico tramite dati sperimentali e modellando in modo dettagliato le unità principali che costituiscono il processo.

Nel lavoro di tesi è stato modellato il processo comunemente noto come *balanced process*, per mezzo del quale avviene più del 90% della produzione di VCM. Esso prevede essenzialmente tre reattori e due sezioni di purificazione. Due reattori sono sfruttati per la clorurazione dell'etilene a 1,2-dicloroetano (EDC): nel primo reattore si effettua una clorurazione diretta con cloro, la quale avviene in una fase liquida essenzialmente composta dallo stesso prodotto che ha anche funzione di solvente; nel secondo, invece, si esegue un'ossiclorurazione dell'etilene con HCl e ossigeno che avviene esclusivamente in fase gassosa. Il terzo reattore, infine, è costituito da una fornace in cui si trasforma il dicloroetano in cloruro di vinile e HCl attraverso un processo di cracking non catalitico. É opportuno sottolineare che l'acido cloridrico prodotto in questa sezione viene riciclato ed utilizzato come reagente nel processo di ossiclorurazione. L'alimentazione di HCl al reattore è costituita esclusivamente da una portata di riciclo: complessivamente non vi è presenza di HCl né in ingresso né in uscita al processo in quanto ciò che è prodotto viene completamente consumato. Per tale motivo il processo di produzione del cloruro di vinile è comunemente definito bilanciato (*balanced*). D'altra parte, sono necessarie due sezioni di separazione atte a purificare rispettivamente l'intermedio di processo EDC e il cloruro di vinile. La prima sezione rimuove ogni impurità prodotta nel processo purificando sia il dicloroetano proveniente dalla clorurazione, sia quello non convertito nella fornace di cracking. Viceversa la sezione di purificazione del VCM non rimuove alcuna impurità ma separa i componenti principali HCl, EDC e VCM. L'acido cloridrico

è inviato praticamente puro al reattore di ossiclorurazione, il dicloroetano viene riciclato alla rispettiva sezione di purificazione, mentre è possibile ottenere cloruro di vinile con un grado di purezza tale da poter essere utilizzato direttamente nel processo di polimerizzazione.

Al fine di ottenere una simulazione accurata del processo, soprattutto per quanto concerne le sezioni di purificazione, è necessario disporre di un modello termodinamico affidabile e convalidato. È stato selezionato il modello a coefficienti di attività NRTL (Non-Random Two Liquid) in quanto capace di descrivere in modo opportuno un sistema di specie chimiche fortemente interagenti. Tale modello è combinato con l'equazione di stato RK (Redlich-Kwong) al fine di poter descrivere adeguatamente l'equilibrio liquido-vapore a pressioni relativamente alte. Successivamente, per la convalida del modello si è utilizzato il software Multiflash$^{\mathrm{TM}}$ in modo tale da aggiustare i parametri di interazione binaria (BIPs) sulla base di dati sperimentali di solubilità o di equilibrio liquido-vapore. Sono state prese in considerazione le principali miscele binarie coinvolte nei processi di separazione di fase.

Si è osservato che complessivamente i risultati sono accurati: l'errore relativo sulla stima della pressione di vapore è inferiore ad 1% per le miscele formate da EDC+tricloroetilene, EDC+1,1,2-tricloroetano e EDC+Cl_2. Per la miscela binaria formata da EDC+etilene l'errore relativo massimo è prossimo al 3%. Tuttavia, l'accuratezza della simulazione non può essere garantita per miscele che coinvolgono HCl e VCM nel calcolo dell'equilibrio di fase. La causa principale di questo errore è data dalla mancanza di possibilità di prevedere con i dati a disposizione il comportamento del acido cloridrico oltre la propria temperatura critica (51.5°C). Oltre questo limite i valori di tensione di vapore di HCl, calcolati con l'equazione di Antoine fornita dal software, risultano inattendibili e influenzano direttamente il calcolo di equilibrio eseguito attraverso il modello NRTL-RK. Inoltre, è stato osservato che le stesse equazioni di Antoine disponibili non rappresentano in modo appropriato i dati sperimentali di tensione di vapore per HCl e VCM puri: tale errore influenza chiaramente la regressione dei parametri di interazione binaria per le miscele EDC+HCl, EDC+VCM e VCM+HCl.

Di conseguenza, il limite del modello termodinamico appena descritto rende la simulazione del processo non completamente accurata se confrontata con i dati disponibili. Infatti, poiché la prima colonna del treno di purificazione del cloruro di vinile opera parzialmente al di sopra della temperature critica di HCl è possibile ottenere un risultato accurato in termini di composizione al distillato ma non al residuo, il quale contiene EDC e VCM in prevalenza. Tale errore influenza le unità a valle, specificatamente la colonna per la rimozione di EDC da VCM e la colonna di purificazione finale del prodotto. Il resto dell'impianto è simulato in modo accurato rispetto alle informazioni disponibili da fonti di letteratura: ad esempio, la sezione di purificazione del dicloroetano rispetta i limiti di composizione per l'alimentazione al cracking e gli stessi reattori rispecchiano i risultati attesi in termini di conversione e selettività.

Per la modellazione delle unità principali costituenti l'impianto è stato utilizzato il simulatore di processo gPROMS® ProcessBuilder, fornito da Process Systems Enterprise Ltd. Si è ottenuto un *flow-sheet* completo in grado di rappresentare l'intero impianto chiudendo 7 ricicli di materia e specificando la conversione dei reagenti ai reattori principali attraverso delle unità di controllo. Il reattore per la clorurazione diretta è simulato attraverso un reattore perfettamente mescolato dove la miscela è considerata all'equilibrio di fase in modo da rappresentare la condizione di ebollizione della miscela stessa. La cinetica implementata è di tipo molecolare e rappresenta, oltre

alla reazione principale, la produzione di 1,1,2-tricoloroetano, ossia il sottoprodotto principale. Per il processo di ossiclorurazione, viceversa, è stato utilizzato un reattore tubolare ed è stata implementata una cinetica in grado di rappresentare, oltre alla produzione di 1,2-dicloroetano, la formazione di sottoprodotti come 1,1,2-tricloroetano e CO_2. Analogamente, per simulare il processo di cracking del dicloroetano è stato utilizzato un reattore tubolare. La cinetica implementata è di tipo molecolare e fornisce risultati accurati nonostante il meccanismo reale sia di tipo radicalico: ciò garantisce una minore complessità senza inficiare la precisione del risultato per il livello di dettaglio richiesto in questa fase. I risultati sono accurati in termini di conversione e selettività per quanto riguarda i reattori utilizzati per la clorurazione, mentre l'unità di cracking è stata convalidata anche in termini di composizione di uscita. Inoltre, sono stati applicati modelli rigorosi per il calcolo dei bilanci di materia e di energia nelle colonne di distillazione, assumendo per ogni stadio l'equilibrio termodinamico. In questo caso i risultati ottenuti sono stati verificati in base alla composizione degli *streams* principali. I parametri dimensionali per le diverse unità sono stati opportunamente scelti sulla base delle informazioni ottenute dalle fonti di letterature oppure attraverso analisi di sensitività.

A conclusione del lavoro, sono state proposte diverse attività future per migliorare la modellazione del processo reale al simulatore. Innanzitutto, come evidenziato anche in precedenza, sono necessari dati sperimentali aggiuntivi in modo da poter rappresentare il comportamento reale di HCl in miscela al di sopra della propria temperatura critica. Successivamente, è opportuno migliorare l'accuratezza dell'equazione di Antoine per la stima della pressione di vapore di HCl e VCM in quanto tale proprietà ha un effetto significativo sul valore dei parametri di interazione binaria da regredire.

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Introduction

Vinyl chloride [75-01-4] (or chloroethane) is one of the world's most important commodity chemicals. It is a colourless flammable gas at ambient temperature. The main application of vinyl chloride is the production of polyvinyl chloride (PVC), which is one of the most widely used commodity plastics. About 98% of the entire amount is used in the polymer manufacture: for this reason it is common to refer to vinyl chloride with the abbreviation VCM (Vinyl Chloride Monomer). Furthermore, the worldwide production capacity of PVC and VCM is constantly growing mainly thanks to developing countries like China and India. At the same time the average plant capacity is increasing: for instance, in the 1990s the largest plant in the USA produced about 635 ktons/yr, while today there are several plants producing over one million tons of VCM per year.

The use of computer simulations tools can be very convenient in such conditions where even minor improvements may lead to substantial effects in the process profitability. In the past, the VCM technology was among the first to take advantage from improvements suggested by process simulators, mainly in order to solve problems concerning hazard, safety and pollution. As result, the modern VCM plants are today among the cleanest and safest in the chemical process industries (Dimian and Bildea, 2008). However, there are still many possibilities of optimisation and improvement thanks to the specific features of the VCM process.

More than 90% of the VCM production is based on the so-called balanced process. It involves two highly exothermic reactors (direct chlorination and oxychlorination) for the production of 1,2-dichloroethane and one highly endothermic reactor performing the cracking of 1,2-dichloroethane to VCM: therefore, an example of improvement, feasible thanks to simulation software, is the design of a heat integration network. An optimised network allows to save a significant amount of energy and, as a consequence, to reduce operative costs. At the same time, due to the complexity of the balanced process, connectivity between units and interactions between recycles clearly affect the usual operation and the controllability of the plant. The control structures, for instance, may involve variables belonging to different part of the plant and the simulation software can be exploited to understand positive and negative effects on a specific unit or to create design alternatives.

However, in order to achieve feasible and useful results to improve the plant performance, it is essential that a reliable and validated model of the process is available. Therefore, the aim of the thesis is to develop a plant model and to validate the thermodynamic model in order to properly represent the real behaviour of the main unit operations. The tool used for modelling and simulating the plant is the gPROMS® ProcessBuilder, developed by PSE (Process System Enterprise Limited), leading supplier of advanced process modelling software and model-based engineering. Furthermore, physical properties information are supplied by the Multilfash^{TM} software, developed by Infochem Computer Services Limited.

The thesis begins analysing the most important chemical routes for industrial applications that are actually used. Furthermore, after a brief market analysis for VCM and PVC, the motivation for this work is discussed.

In Chapter 2 the balanced process is described in detail by analysing the three reactors and the two sections for 1,2-dichloroethane and vinyl chloride purification respectively. Typical operative conditions are reported and design alternatives are discussed. If selections of design alternatives have been required, the reasons of the choice are specified.

In Chapter3 the two software, used for modelling of units and thermodynamic properties, are presented and it is reported how they have been exploited to develop and validate the VCM plant model.

In Chapter4 methods and results of thermodynamic model validation are reported. The NRTL activity model combined with the Redlich-Kwong equation of state is used to predict the vapour-liquid equilibria. Furthermore, it is highlighted as the prediction of pure components physical properties must be accurate: above all, the vapour pressure highly affects the simulation results. The validation is performed through regression of binary interaction parameters from experimental vapour-liquid data or solubility data for main binary mixtures involved.

Chapter 5 presents the modelling of the three reactors and detailed information about unit types, design parameters and kinetic models is supplied. Results are reported and compared with the available information from references in order to show the reliability of prediction in terms of conversion, selectivity or outlet composition.

In Chapter 6 the modelling of distillation trains for 1,2-dichloroethane and vinyl chloride purification is discussed. Simulation results are compared with available data.

Some final remarks and a discussion on future works conclude the thesis.

Chapter 1

Production technologies and thesis motivation

This first chapter represents a brief introduction to the balanced process in order to show the reasons why it is successfully established. The advantages that can be achieved by process modelling and simulation are explained. The analysis pass through most important chemical alternative routes for industrial applications. Besides, a market overview of the product and its main derivative is proposed.

1.1 Chemical routes

Vinyl chloride was obtained for the first time in 1830-1834 by V. Regnault through dehydrochlorination of 1,2-dichloroethane with alcoholic potash, on the contrary the synthesis by thermal cracking of the same raw material dates back to 1902. At that time however, due to the lack of a proper technological support, these processes did not lead to industrial and commercial applications. Industrial production of vinyl chloride started in 1930s, thanks to the work developed in 1912 by F. Klatte who obtained the monomer through catalytic hydrochlorination of acetylene. Despite the high energy requirement and the high pollution level, the acetylene route was almost exclusively applied until 1940-1950 and it is still used in China. The acetylene route could be substituted by ethylene-based processes, especially after the introduction of large-scale oxychlorination (by Dow Chemical, 1955-1958), which led to the so-called integrated balanced process, now used almost exclusively. The acetylene-based process will be briefly described in the following section, whereas the balanced process represents the core of this thesis.

It should be noted that from a pure chemical point of view the easiest way to vinyl chloride monomer would be the ethane chlorination. Anyway, despite the substantial reduction in raw material cost, the ethane route is still not attractive if compared to the ethylene-based process, which has been widely optimised over time leading to higher yields and energy efficiency (Dreher et al., 2012).

1.1.1 Acetylene route

The acetylene-based process is the oldest process for vinyl chloride monomer production. It has been mainly used in the past, and when ethylene became available at very competitive price, it started to be gradually replaced by the ethylene-based

Table 1.1: PVC capacity in China on April 2006. (Source Fryer (2006))

Sources	**Producers**	**Capacity [ktpa]**
CaC_2 & Cl_2	79 producers	6855
C_2H_4 & imported DCE	Liaoning Jinhua Chemical	80
	Cangzhou Chemical	115
imported VCM	13 producers	1550
captive C_2H_4 & Cl_2	Shanghai Chlor-alkali	420
	Qilu Petrochemical	600
	Beijing No.2 Chemical	160
	Tianjin Dagu	320

process. As reported by Fryer (2006), the dominant process in China in 2006 was still based on acetylene, which is produced from calcium carbide. Table 1.1 briefly sums up the Chinese production of polyvinyl chloride according to the different sources. It is evident that most of Chinese producers takes advantage of low-price resources available in their country through acetylene-based process for vinyl chloride production. Indeed, the attraction to this technology in China is due mostly to the fact that all raw materials are domestically available: unlike natural gas, coal reserves are abundant and coke and energy requirements are satisfied by very cheap hydroelectric power generation facilities. Thanks to the latter also hydrogen chloride is easily available, coming from chlorine and hydrogen produced by electrolysis (Benyhaia, 2009). From coal and limestone, coke and calcium oxide are respectively obtained, then they are heated over 2000°C in order to produce calcium carbide and carbon monoxide. At the end, according to the reaction (1.1) acetylene is produced.

$$CaC_2 + 2H_2O \longrightarrow CH{\equiv}CH + Ca(OH)_2 \tag{1.1}$$

The industrial production of vinyl chloride through acetylene is based on the catalytic hydrochlorination represented by reaction (1.2). The most commonly used catalyst is mercury(II) chloride on activated carbon in concentration of 2-10%wt.

$$CH{\equiv}CH + HCl \xrightarrow[HgCl_2]{} CH_2{=}CHCl \qquad \Delta H^0_{298} = -99.2\ \text{kJ/mol} \tag{1.2}$$

Catalyst volatility represents a limiting factor for the reaction operation, so different additives can be used in order to contain activity decrease. Industrially the reaction (1.2) occurs in the gas-phase at 0.1-0.3 MPa and 100-250°C with residence time lower than 1 s. Fixed-bed multitubular reactors are almost exclusively applied and, thanks to anhydrous conditions, most equipments are made in carbon steel. A simple scheme of the plant is represented in Figure 1.1. Reactor effluents that are sent to the purification train are composed mainly of vinyl chloride, hydrogen chloride and unconverted acetylene, so a first distillation column removes light components in order to recycle most of them to the reactor while the vinyl chloride is withdrawn as residue. Pure vinyl chloride is obtained at the top of the second column while heavy bottoms are sent to the stripper as well as the liquid coming from the scrubber. The top product of the stripper (mainly acetylene and vinyl chloride) is recycled back to first purification step and heavies are discharged from the bottom. Acetylene conversion and selectivity to vinyl chloride are respectively around 99% and higher than 98%.

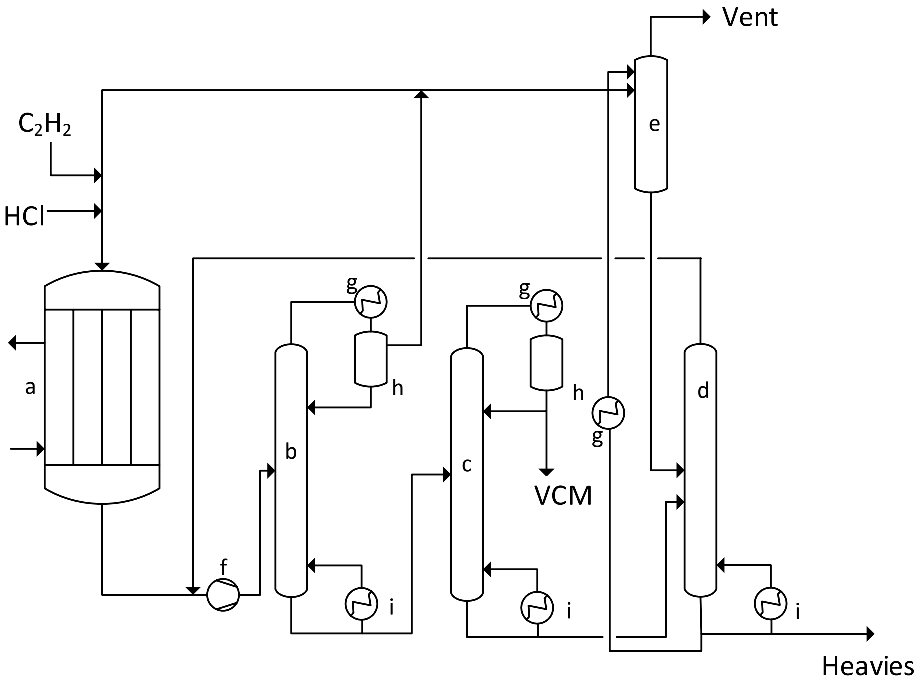

Figure 1.1: Acetylene-based production. a) reactor; b) lights column; c) VCM column; d) heavies stripper; e) vent wash tower; f) compressor; g) cooler; h) knock-out drum; i) reboiler. Dreher et al. (2012).

1.1.2 Ethylene route

Ethylene is the most used raw material for the vinyl chloride monomer manufacture: the production is carried out exclusively through this route. The usual route contemplates to pass through the 1,2-dichloroethane as intermediate for the production of vinyl chloride, chlorinating the ethylene according to direct chlorination (1.3a) and oxychlorination (1.3b) reactions and finally performing the pyrolysis (1.3c) in a cracking furnace:

$$CH_2{=}CH_2 + Cl_2 \longrightarrow ClCH_2{-}CH_2Cl \tag{1.3a}$$

$$CH_2{=}CH_2 + 2\ HCl + 1/2\ O_2 \longrightarrow ClCH_2{-}CH_2Cl + H_2O \tag{1.3b}$$

$$ClCH_2{-}CH_2Cl \longrightarrow CH_2{=}CHCl + HCl \tag{1.3c}$$

According to the classic route, thanks also to optimisation over the years, problems of selectivity and by-products can be avoided. In fact, as Dreher et al. (2012) reported, more than 90% of the vinyl chloride whole produced amount is based on the balanced process (a simplified block flow diagram is shown in Figure 1.2). The plant structure is made by three different reactors and two separation section for the purification of the intermediate and of the product respectively. Ethylene is usually split in almost equal parts and supplied to the two chlorination units, direct chlorination and oxychlorination, where reactions (1.3a) and (1.3b) occur respectively yielding selectively to 1,2-dichloroethane (EDC). After purification EDC is vaporised and sent to the furnace where pyrolysis (1.3c) occurs. After cracking reactor the process stream is mainly composed by vinyl chloride, hydrogen chloride and unreacted 1,2-dichloroethane and it is

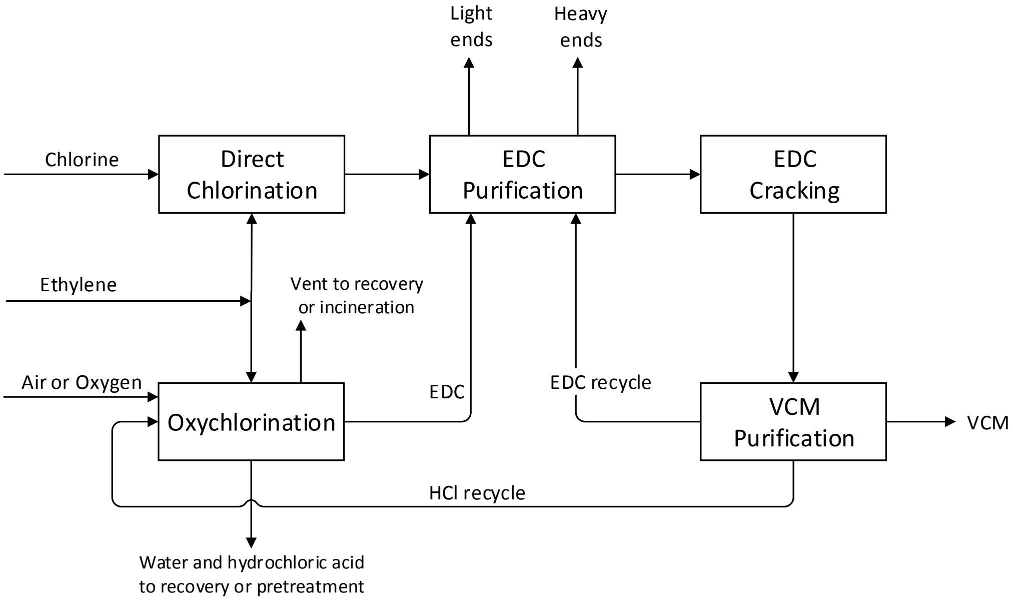
Light ends
Heavy ends
Chlorine
Direct Chlorination
EDC Purification
EDC Cracking
Ethylene
Vent to recovery or incineration
Air or Oxygen
Oxychlorination
EDC
EDC recycle
VCM Purification
VCM
HCl recycle
Water and hydrochloric acid to recovery or pretreatment

Figure 1.2: Block flow diagram of balanced process for vinyl chloride manufacture. From Dreher et al. (2012).

sent to the VCM purification section where almost pure HCl and VCM are drawn. As the Figure 1.2 highlights, two main recycle streams are present: the 1,2-dichloroethane is fed back to its purification section while hydrogen chloride is supplied to the oxychlorination reactor after recovery by distillation. Furthermore, it must be evident that during steady state operation a feed of fresh hydrogen chloride is absent and the same pyrolysis reactor provides the entire amount of reactant required by the oxychlorination section. This is the reason why it is called balanced process: the overall reaction, which does not involve hydrogen chloride, can be easily derived by summation of reactions (1.3a), (1.3b) and (1.3c):

$$2\ CH_2{=}CH_2 + Cl_2 + 1/2\ O_2 \longrightarrow 2\ CH_3{=}CHCl + H_2O \tag{1.4}$$

Furthermore, the balanced process is very well disposed for heat integration, since it makes available combinations of highly exothermic step with high energy requiring unit operations. Energy demand for purification steps, for example, can be easily integrated with heat recovered from direct chlorination step or quenching section, and an optimisation of the energy recovery network allows for a consistent reduction of the overall costs. For this reason the process is usually described as integrated balanced process.

1.2 Market analysis

The main application of vinyl chloride is the production of polyvinyl chloride (PVC). With over 98% of VCM used in PVC manufacture, the demand is very dependent on the fortunes of the PVC market. The remaining 2% of VCM is consumed in the production

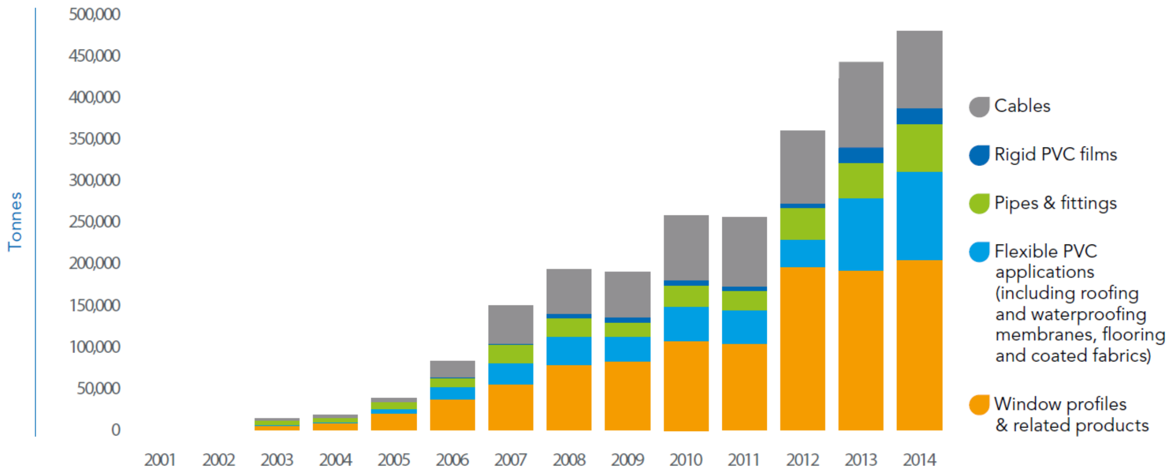

Figure 1.3: Amount of recycled PVC according to its application between 2001 and 2014. From VinylPlus (2015).

of polyvinylidene chloride and chlorinated solvents. PVC is the third most widely used synthetic plastic polymer of the thermoplastic family, after polyethylene (PE) and polypropylene (PP). The PVC market is highly dependent on the construction sector which consumes around 75% of the overall throughput. Typical applications are window profiles, pipes, conduits, fitting and insulation for electrical wiring because of its fire retardant properties. As a consequence of the recession in the construction sector, PVC has been one of the slowest growing commodity polymers in Europe (ICIS, 2007). Furthermore, nearly all European countries have improved their performances in terms of recycled PVC productivity: the increase in volume is due in particular to the consolidation of the PVC profiles recycling schemes in France and Poland (VinylPlus, 2015). Figure 1.3 shows this growth according to most important applications.

On the other hand, a stronger demand growth has been seen in Asia thanks to the boom in housing and infrastructures projects, in particular in China and India. As said above, the use of acetylene as raw material for the VCM production has been very significant for Chinese producers. However, since the last quarter of 2008, Chinese acetylene-based VCM/PVC producers have lost their cost competitive position as ethylene prices fell following the collapse in crude oil prices from 140$/bbl to 40$/bbl. Only producers integrated to cheap coal sources have remained competitive. Therefore, as stated by Benyahia (2009), new ethylene-based VCM projects are economically feasible in the Far East, India and also in the Middle East: the overall rates of return (ROR) are estimated around 27% and pay back periods (PBP) around 6 years for a plant located in the Middle East.

Furthermore, it must be highlighted the tendency to increase the plant capacity for the ethylene-based VCM production. In the 1990s the largest plant in the USA had a capacity of about 635 ktons/yr, but currently there are several plants over one million tons/yr (Dimian and Bildea, 2008). On the other hand, Figure 1.4 shows the average plant capacity according to its location: both in the Western Europe and in China an average size of 300 ktons/yr can be assumed for an ethylene-based plant. This is also the value that has been considered in the present case for the process simulation. Figure 1.4 shows also that the average size of acetylene-based plants is significantly smaller than a conventional ethylene-based plant: the average capacity is around 80

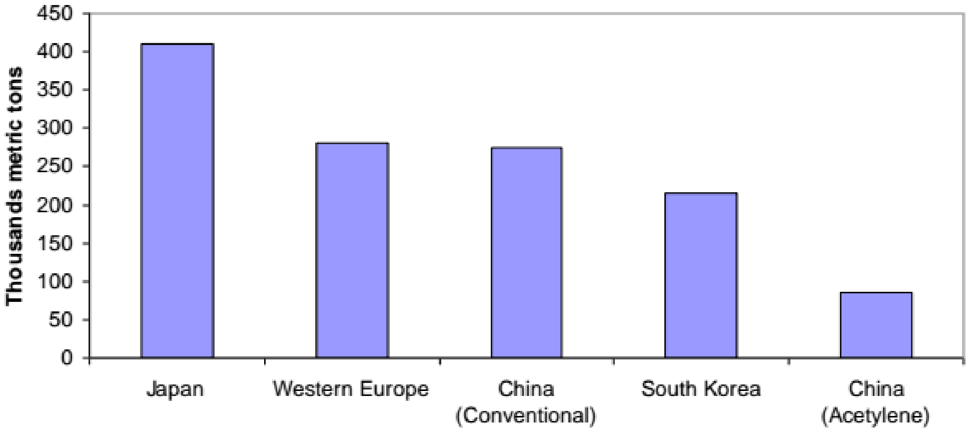

Figure 1.4: Average size of VCM plant capacity by country. From Khan and Benyahia (2007)

ktons/yr.

1.3 Motivations

It is clear, at this point, that the vinyl chloride production is made through a large-scale plant involving different reaction and separation sections, interconnected in a complex process with recycles. At this scale, computer simulation, process optimisation and advanced computer-control techniques play a determinant role since even slight improvements have a great economic impact.

For example, the balanced process is highly suitable for heat integration because of its structure with high exothermic and endothermic sections. In these conditions an optimised heat integration structure allows to reduce the energy consumption and leads to great economic advantages. At the same time, it may be difficult to achieve high purity vinyl chloride because numerous impurities are generated in different reaction sections and strong interactions are present between recycle streams and units. Thus, by using simulation tools, process configuration can be designed and optimised in order to reduce the impurities amount and the interactions between units. Process simulation allows to achieve a more efficient impurity control, reducing the amount of wastes to be discharged or treated.

However, any model used for these purposes must be consistent with the real plant behaviour and validated on experimental thermodynamic data. Therefore, the aim of the present work is the synthesis of a model for the simulation of a vinyl chloride plant based on a reliable thermodynamic model and considering all the necessary unit operations into an optimal flow-sheet.

Chapter 2

Balanced process

The chapter illustrates the balanced process reactors and separation trains configurations, giving details of unit types according to the different possibilities that are available for industrial application and the choices that have been made for the specific plant modelled.

2.1 Process configuration

As briefly described in the previous chapter there are three reactor units and two distillation trains, working simultaneously and interacting:

- direct chlorination;
- oxychlorination;
- pyrolysis and quench;
- vinyl chloride purification;
- 1,2-dichloroethane purification.

Figure 2.1 represents a simplified flow-sheet in which it is possible to see the overall process configuration. Every section will be discussed with more details in this chapter. At this level, however, it is clear that direct chlorination and oxychlorination reactors work in parallel and also that the former does not need specific treatment or purification before being fed to distillation train. On the other hand, the oxychlorination outlet needs to be washed with caustic soda solutions in order to remove acid residuals. The two chlorination outlets are mixed before 1,2-dichloroethane purification and they are jointly treated in the downstream units, distillation columns and cracking, but the pyrolysis reactor is not strictly sequential to them. Hydrogen chloride is the main by-product of the EDC cracking and it is recovered as almost pure at the top of the first column after the quench: this flow-rate controls the performance and the capacity of the oxychlorination reactor, since HCl is usually the limiting reactant and there is no make-up of this component. At the later stage, the main product is obtained at the required purity, while the residual is recycled back for purification. Therefore, it is possible to see that all impurities end at the 1,2-dichloroethane purification section, which, indeed, has to treat outlet products coming from three different reactors: even at this level it is clear that minimising impurities formation from each source is essential for a proper operation of the whole plant.

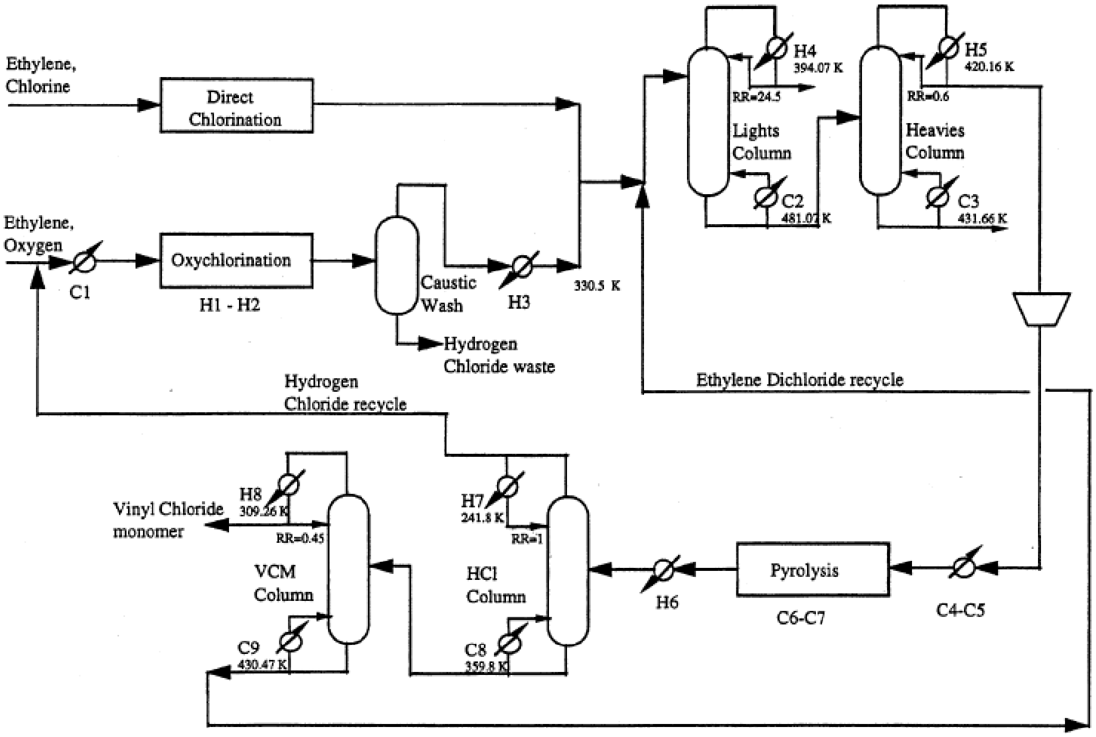
Ethylene,
Chlorine
Direct
Chlorination
Ethylene,
Oxygen
C1
Oxychlorination
H1 - H2
Caustic
Wash
H3
330.5 K
Hydrogen
Chloride waste
Hydrogen
Chloride recycle
H4
394.07 K
RR=24.5
Lights
Column
C2
481.07 K
H5
420.16 K
RR=0.6
Heavies
Column
C3
431.66 K
Ethylene Dichloride recycle
H8
309.26 K
Vinyl Chloride
monomer
RR=0.45
VCM
Column
C9
430.47 K
H7
241.8 K
RR=1
HCl
Column
C8
359.8 K
H6
Pyrolysis
C6-C7
C4-C5

Figure 2.1: Simplified balanced process flow-sheet. (Lakshmanan et al., 1999)

2.2 Direct chlorination

As the very name highlights, chlorination of ethylene can be performed directly using chlorine according to the reaction (2.1) in presence of a Lewis acid catalyst: iron(III) chloride ($FeCl_3$) is the most commonly used. Although the feed is clearly in vapour phase, the chlorination is carried out exclusively in the liquid phase and the gas phase process has no industrial applications. Liquid phase direct chlorination conversions up to 100% with 99% selectivity are possible. The most important secondary product is 1,1,2-trichloroethane, formed by further chlorination of dichloroethane according to the reaction (2.2).

$$CH_2{=}CH_2 + Cl_2 \xrightarrow[FeCl_3]{} ClCH_2{-}CH_2Cl \quad \Delta H^0_{298} = -220 \text{ kJ/mol} \tag{2.1}$$

$$ClCH_2{-}CH_2Cl + Cl_2 \longrightarrow ClCH_2{-}CHCl_2 + HCl \tag{2.2}$$

A very specific feature of this process is that reactants, as well as the catalyst, are dissolved in the solvent which is the product 1,2-dichloroethane. However the catalyst is used in diluted concentration, namely between 0.1 and 0.5%wt, since this does not affect selectivity. Indeed, the most important phenomenon that must be controlled for a proper operation is the absorption rate of reactants, especially ethylene which is less soluble than chlorine in the solvent/product. For this reason a proper choice of reactor with an efficient sparging system, able to ensure high dissolution rates, is paramount.

The feed usually is in stoichiometric condition or with a slight excess of ethylene (0.5-1.0% by volume, as reported by Benyahia (2005)) in order to reach complete conversion of chlorine. During the past ethylene excess was higher in order to minimised

Table 2.1: Extent of 1,1,2-trichloroethane (TCE) formation according to temperature condition, catalyst and oxygen amount (Benyahia, 2005).

Iron chloride in EDC $[g/m^3]$ as Fe	**Oxygen in feed** $[\%vol]$ in Cl_2	**Temperature** $[°C]$	**TCE formed** $[ppmw]$
50	0.5	60	2000
2000	0.5	60	1500
50	2.5	60	500
2000	2.5	60	400
50	0.5	84	50000
2000	0.5	84	5000
50	2.5	84	10000
2000	2.5	84	2000

by-products formation, but nowadays after optimisation of reactor performances it can be reduced or even avoided, erasing cost entries due to reactant recovery. However, a high purity ethylene feed is needed in order to improve selectivity. Chlorine stream, on the other hand, is usually characterised by a small presence of oxygen, from 0.5 to 2.5% by volume. Oxygen works as a catalyst for the process since it inhibits the free-radical route which leads to highly chlorinated products. Hence it allows the catalysed ionic route to go ahead leading to higher selectivity. Table 2.1 shows the effect of oxygen on selectivity, reporting values of the main impurity (1,1,2-trichloroethane) for different catalyst amount and operative temperature.

Furthermore, another essential feature that must be highlighted is the high exothermicity of the reaction, first of all because of the amount of heat that can be recovered and collected: production of 1 ton of 1,2-dichloroethane suffices for generating approximately 1 ton of steam, according to Benje (2005). This feature leads then to the possibility to perform the process in two different way, taking advantage of the reaction heat directly vaporising the 1,2-dichloroethane (high temperature chlorination) or recovering it by heat exchange (low temperature chlorination). This two options will be analysed further in detail in this chapter. Furthermore, thanks to anhydrous condition and relatively low temperature, carbon steel can be used as construction material.

2.2.1 Reactor type

In this section two different reactor configurations are compared: stirred tank and bubble column reactor. The comparison is made taking into account the works developed by Balasubramanian et al. (1966) and Orejas (1999) respectively for each unit type. These experimental analysis were both developed for low temperature chlorination applications: between 32 and 56°C for stirred tank reactor and around 62°C for the bubble column. A proper choice on the direct chlorination reactor type is essential since the process is mainly controlled by transport phenomena and in particular, as stated above, by the ethylene absorption in the liquid mixture: in fact, ethylene solubility is about seven time smaller if compared to chlorine.

The work developed by Balasubramanian et al. (1966) on direct chlorination reaction rate confirms this behaviour: they proposed a general kinetic model performing experimental tests in a stirred tank reactor. Figure 2.2 shows a representation of the

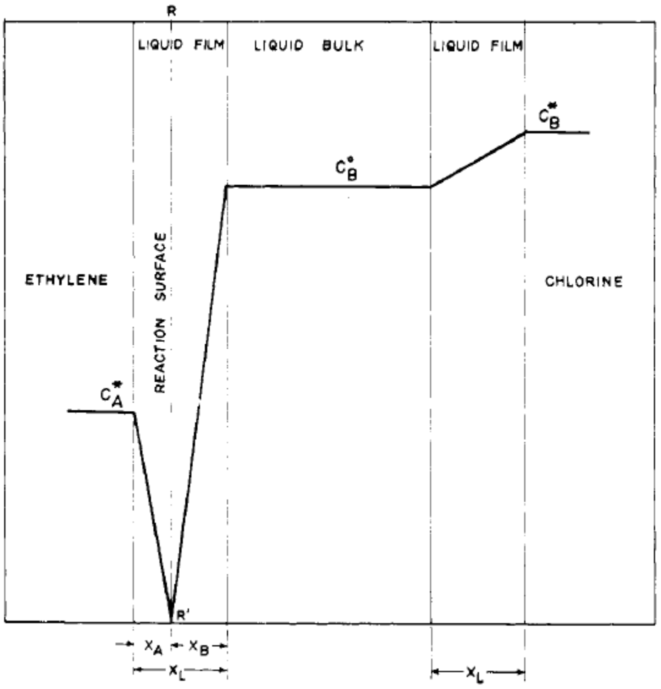

Figure 2.2: Representation of film model. C_i^* are equilibrium concentrations of species A, B and C which are respectively ethylene, 1,2-dichloroethane and chlorine. It shows that in the stirred tank reactor the reaction occurs instantaneously within the liquid film between the ethylene bubble and the liquid (Balasubramanian et al., 1966).

proposed film model. The reaction occurs instantaneously within the liquid film at the interface between ethylene bubble and the liquid. As a consequence it is evident that ethylene absorption is the rate-determining step of the process, and in order to improve the reactor performance the mass transfer rate must be increased.

This can be done, for example, by the employment of a bubble column reactor, which is widely used for direct chlorination industrial application. Figure 2.3 is a schematic representation of this type of unit: ethylene and chlorine, both in gaseous state, are fed to the reactor through different distributors. They are dissolved in the liquid 1,2-dichloroethane, that circulates in the loop, and react within the riser part in order to yield more dichloroethane. In the downcomer part the liquid is cooled by means of an heat exchanger, making possible temperature control. The work developed by Orejas (1999), using this reactor configuration, shows that the chemical reactions that are taking place at the interface between gaseous ethylene and liquid phase are not fast with respect to the mass transfer of the same hydrocarbon, contrary to the result obtained with a stirred tank reactor. Figure 2.4 indicates clearly this difference since it is evident the presence of ethylene in the liquid phase. However, it must be highlighted that the diffusion of the reactants into the liquid bulk is small and most of the reaction occurs within the liquid phase. For this reason it is extremely important to design properly the unit: an adequate contact time must be ensured for gas dissolution and in order to avoid excessive liquid carry-over in the vapour phase. Furthermore, the reactor needs a proper supply system: for example a simple but effective expedient used for maintain an high selectivity is the introduction of ethylene into the circulating reaction medium at a point upstream with respect to the chlorine feed (Benje, 2005).

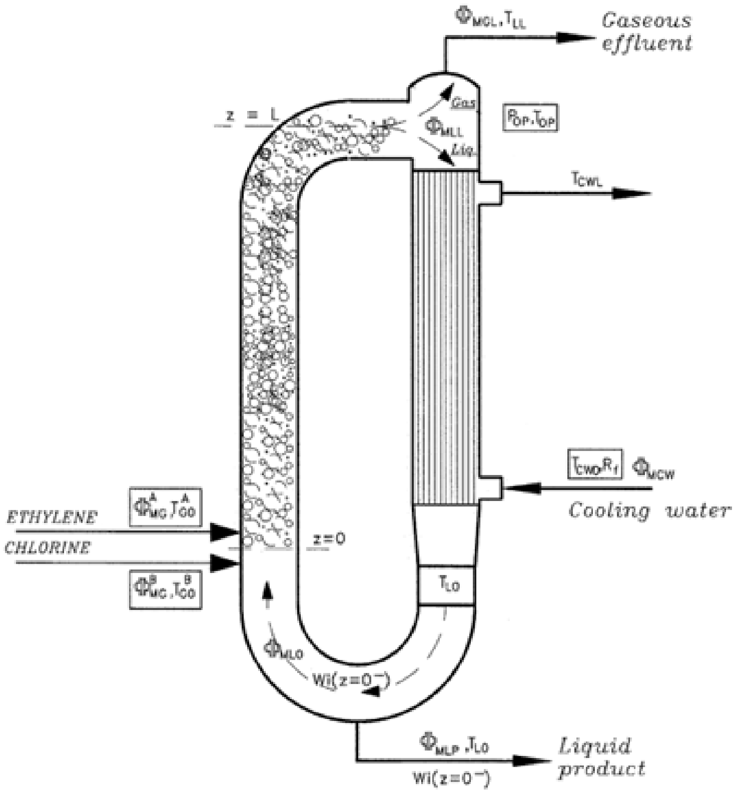
ΦMGL,TLL
Gaseous effluent
z = L
Gas
ΦMLL
Liq.
POP,TOP
TCWL
TCWO,RT ΦMCW
Cooling water
ETHYLENE
CHLORINE
ΦAMG,TAGO
ΦBMG,TBGO
z=0
TLO
ΦMLO
Wi(z=0−)
ΦMLP,TLO
Wi(z=0−)
Liquid product

Figure 2.3: Bubble column reactor with external loop recirculation. Specific application for low temperature chlorination with product drawn in the liquid phase (Orejas, 2001).

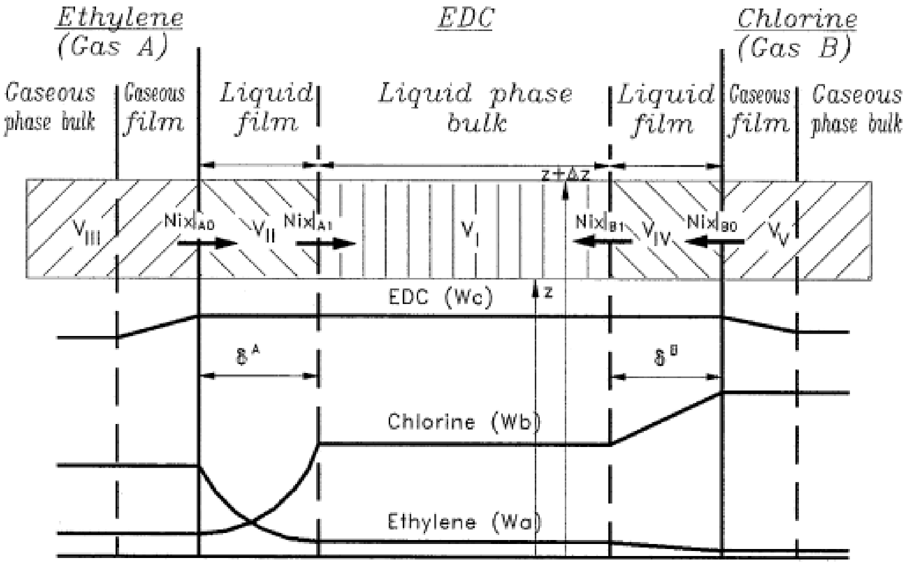
Ethylene (Gas A)
EDC
Chlorine (Gas B)
Gaseous phase bulk
Gaseous film
Liquid film
Liquid phase bulk
Liquid film
Gaseous film
Gaseous phase bulk
z+Δz
VIII
NixA0
VII
NixA1
VI
NixB1
VIV
NixB0
VV
EDC (Wc)
z
δA
δB
Chlorine (Wb)
Ethylene (Wa)

Figure 2.4: Schematic representation of the concentration profile of ethylene, chlorine and dichloroethane (EDC) in a bubble column reactor. Contrary to the result obtained with a stirred tank reactor, in this case there is a presence of ethylene in the liquid phase bulk (Orejas, 1999).

2.2.2 Chlorination temperature

Although each producer has modified and optimised the process according to his requirements, two different main technologies can be identified. The distinction is based on the operating temperature, so they are typically called:

LTC Low Temperature Chlorination, operating below the mixture boiling point;

HTC High Temperature Chlorination, operating above the mixture boiling point.

The mixture is mostly composed by 1,2-dichloroethane (NBP=82.4°C) with a small amount of heavy impurities, mainly 1,1,2-trichloroethane (NBP=113.9°C), and dissolved unconverted reactants. Figure 2.5 represents schematically how this two technologies are applied. In Figure 2.5*a* LTC is described: the reactor is a gas-liquid contact column in which reactants are fed in the gas phase whereas the product comes out in the liquid phase. The latter is cooled through an external heat exchanger producing steam and controlling the temperature in the range between 50-70°C since part of the cold 1,2-dichloroethane is recycled back to the column. Cooling can be performed either by an external heat exchanger, as represented, or by internal transfer devices, as cooling coils for example. Pressure is mostly needed to maintain the reacting mixture in the liquid phase, and it is generally close to the atmospheric value. Unconverted gasses are vented from the top of the column. Due to low operating temperature, this process is advantageous for achieving higher selectivity (over 99%) and limiting by-product formation.

On the other hand, Figure 2.5*b* represents how HTC can be performed. The reaction is conducted at the boiling point of the mixture, within the range of 1.5-5.0 bar and 85-140°C, often at about 100°C. Also in this case pressure is required just to ensure that the mixture contained in the reactor remains in the liquid phase. At the same time it is possible, by increasing pressure, to reduce the size of ethylene and chlorine bubbles and thus increase the interface surface enhancing mass transfer. Furthermore, the boiling configuration takes advantage of the high heat of reaction, which is 6-7 times greater than the heat of vaporisation of 1,2-dichloroethane, because the reactor may work as a reboiler for the distillation column D-1: the product outlet is in the vapour phase so it can be directly fed at the bottom of the distillation column, whereas the liquid residue is recycled back to the reactor helping to cool the system. Furthermore, some process configurations consider other liquid recycle streams, mainly composed by EDC, that can be fed to the direct chlorination section. For instance, the side stream drawn from the column D-1 is mainly composed of 1,2-dichloroethane and trichloroethylene as impurity. This chlorinated species is hard to remove by distillation since it forms a low-boiling azeotrope with 1,2-dichloroethane. As a consequence the recycle of this stream to the reactor allows further chlorination of this impurity, leading to heavy products which can be easily removed. The HTC reactor, however, can be designed either as integrated to the column or as a stand-alone unit: the heat can be anyway recovered efficiently with external heat exchangers and the steam produced can be supplied to distillation columns downstream.

From a strictly theoretical point of view, the HTC process is less selective than the LTC because of the higher temperature at which it is performed. However, many sources, patents or producers, as Dreher et al. (2012), Calcagno and Di Fiore (1975) or Vinnolit GmbH & Co. KG claim that, by proper reactor design or modified catalyst formulation, yields comparable to the LTC process are feasible. Furthermore, once

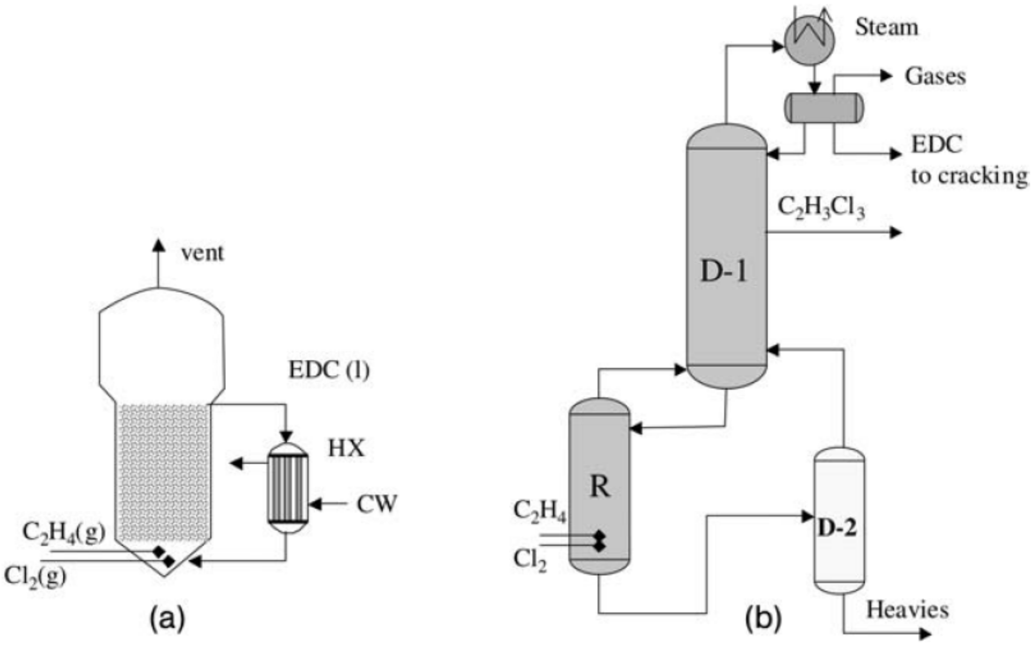

Figure 2.5: (a) Low-temperature chlorination reactor made by a gas-liquid contact column; (b) High-temperature chlorination where the reactor R works as the reboiler for the dichloroethane purification. From Dimian and Bildea (2008).

established that operating at high temperature high selectivity can be reached, the HTC process becomes advantageous in term of energy efficiency and product purity. In fact, the heat recovery from the product of the HTC process is more efficient as compared with the LTC process, because the outlet stream is at higher temperature. As an alternative, Figure 2.6 shows how the heat can be recovered externally both by condensation of the gas product and by cooling of an external liquid loop. It shows also that there is no need of specific purification steps after the reactor: the outlet stream, since it comes out in vapour phase, is iron free. As a consequence, there is no need of catalyst recovery which actually requires at least two steps. In fact, for the LTC process the catalyst removal is performed at first by washing the product with a caustic soda solution and then drying the product by azeotropic distillation (1,2-dichloroethane and water is an azeotropic mixture). Hence, as reported by Benyahia (2005), if the boiling reactor is chosen, there is no need to wash the product and no drying is required. It is just needed to avoid liquid entrainment.

2.3 Oxychlorination

As stated above, the oxychlorination reactor works in parallel with direct chlorination aiming the production of 1,2-dichloroethane. However, its behaviour and its features are quite different from the direct chlorination process. First of all, the oxychlorination reaction (2.3) occurs in gas phase in order to avoid corrosive problem due to the presence of acid aqueous solutions. Liquid phase oxychlorination has no industrial applications. Gaseous ethylene and oxygen react with hydrogen chloride, coming from the vinyl chloride purification section, in presence of an heterogeneous catalyst, usually copper(II) chloride, $CuCl_2$. Typical values of selectivity and conversion are lower

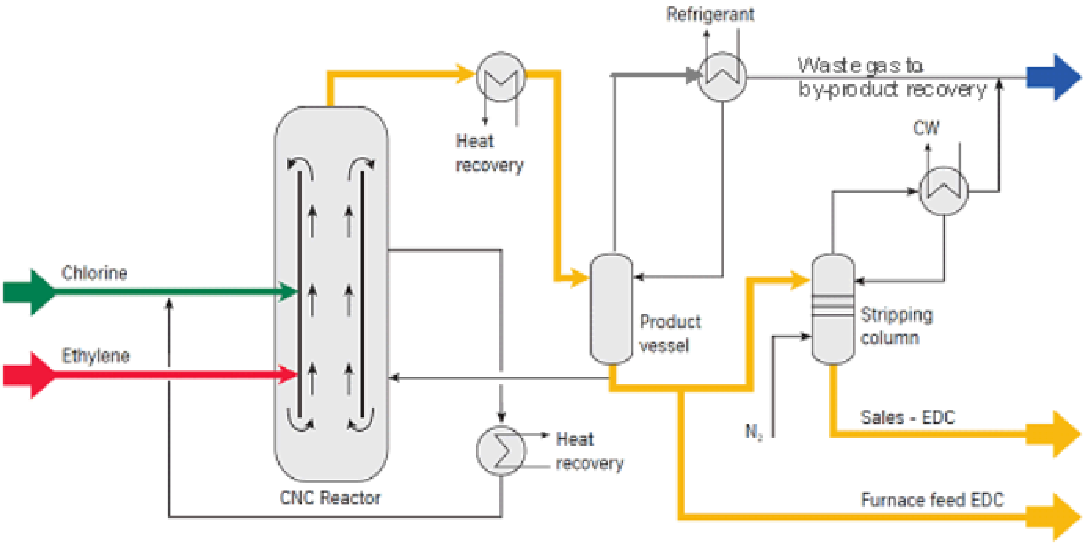

Figure 2.6: High-temperature chlorination with heat recovery from the vapour effluent condensation and the external liquid loop. The scheme shows also that there is no need of washing and drying the product outlet. From Vinnolit GmbH & Co. KG website.

with respect to the direct chlorination: the former varies from 91% to 96% whereas the latter usually stays in a range between 80% and 97% (ethylene-based) according to specific operative conditions. Main side products are 1,1,2-trichloroethane, coming from further chlorination of 1,2-dichloroethane (2.4), and carbon oxides coming from ethylene combustion. Reaction (2.5) represents the complete combustion of ethylene to carbon dioxide.

$$CH_2{=}CH_2 + 2\ HCl + 0.5\ O_2 \xrightarrow[CuCl_2]{} ClCH_2{-}CH_2Cl + H_2O \qquad \Delta H^0_{298} = -295\ kJ/mol \tag{2.3}$$

$$ClCH_2{-}CH_2Cl + HCl + 0.5\ O_2 \longrightarrow ClCH_2{-}CHCl_2 + H_2O \tag{2.4}$$

$$CH_2{=}CH_2 + 3\ O_2 \longrightarrow 2\ CO_2 + 2\ H_2O \tag{2.5}$$

Other by-products that can be found as traces in the outlet stream are: 1,1-dichloroethane, monochloroethane, tetrachloroethane, trichloroethylenes, vinyl chloride, acetaldehyde and other chlorinated derivatives. Feed composition changes according to the process configuration: for instance, oxygen can be supplied both as pure or as air. This two processes, oxygen-based and air-based, will be described in detail later in this section. Ethylene feed flow-rate is typically related to this choice but, in any case, polymerisation grade ethylene is supplied in order to minimise the by-product formation and purification problems. On the other hand, the hydrogen chloride stream contains acetylene as impurity, coming from the EDC cracker side reactions. According to its amount, acetylene can affect selectivity of oxychlorination reactor. Hence it is essential to control properly the furnace operation in order to limit its formation, otherwise selective catalytic hydrogenation should be taken into account in order to remove this impurity.

Table 2.2: Water partial pressure and corresponding acceptable range of temperature and material for oxychlorination reactor. (Benyahia, 2005).

Material	**Steam pp** [*bar*]	**Temperature** [°*C*]
Mild steel	1.0	200-260
	1.5	None
Stainless steel 316	1.0	190-300
	1.5	210-300
	2.0	None
Iconel	1.0	160-280
	1.5	190-280
	2.0	220-280
Hastelloy	1.0	160-300
	1.5	170-300
	2.0	180-300

Temperature and pressure ranges are quite large and change according to the specific case and requirement of the producer. For example, two reactor types are industrially used: fixed-bed or fluidised-bed reactor (the choice between them will be discussed later in this section). When a fluidised-bed reactor is used, the operating temperature is generally lower and kept more or less constant between 220-240°C; on the other hand if a fixed-bed is chosen the temperature is usually higher and can go up to 300°C. Operating pressure is usually about 4-6 bar.

However, operating at these conditions, even if the system is in gas phase corrosion problems are not completely solved. As Benyahia (2005) reported, a proper choice on construction material is required because corrosion can occur at temperature well above the theoretically calculated dew point. This phenomena is due to a complex erosion and corrosion mechanism, but it can be controlled acting on the dew point of the mixture: the key parameter in this case is the partial pressure of steam in the reactor product. Table 2.2 describes typical choices according to this key parameter and operating temperature.

2.3.1 Catalyst and mechanism

Oxychlorination catalyst and mechanism have been widely studied in order to understand and optimise the process. As said above, cupric chloride is often used as active species: it is generally dispersed as fine powder with diameter between 100-200 μm over a high surface alumina support. Furthermore, alkali and alkaline earth or aluminium chlorides are added in order to reduce catalyst volatility and improve reaction rates and selectivity. According to Dreher et al. (2012), $CuCl_2$ is usually added in concentration of 3-12%wt of the total catalyst amount and alkali salts are added in nearly double amount. Catalyst is prepared to the alumina support by imbibition method followed by drying or by special spry techniques. Furthermore, this step of catalyst preparation is quite important since it has been proved that alumina plays an active role in the oxychlorination process. It must be clear that high surface alumina is preferred as support because it allows to control catalyst parameters as surface area, pore volume and size, but at the same time uncovered alumina affects selectivity. As reported by Finocchio et al. (1998), alumina is very active in performing dehydrochlorination of chloroalkanes, hence it does not affect ethylene conversion but is responsible for further dehydrochlorination and oxychlorination cycles involving 1,2-dichloroethane. As a consequence, increasing the $CuCl_2$ coverage has a double effect: improving the catalyst activity and reducing the EDC conversion performed by Al_2O_3 support. Typically the optimum value of cupric chloride is the one that allows to have a complete monolayer coverage of the support. Furthermore, $CuCl_2$ not only is a catalyst but it also works as chlorinating agent. As tested by Wachi and Asai (1994), the mechanism illustrated by the following set of reactions well describes the behaviour of the real process:

$$CH_2{=}CH_2 + 2\ CuCl_2 \longrightarrow ClCH_2{-}CH_2Cl + 2\ CuCl \tag{2.6a}$$

$$2\ CuCl + 0.5\ O_2 \longrightarrow CuO{-}CuCl_2 \longrightarrow CuO + CuCl_2 \tag{2.6b}$$

$$CuO + 2\ HCl \longrightarrow 2\ CuCl_2 + H_2O \tag{2.6c}$$

Addition reaction (2.6a) is the ethylene chlorination step in which copper chloride oxidation state is reduced from II (cupric) to I (cuprous). In the following step, on the other hand, catalyst is regenerated through reactions with oxygen and hydrogen chloride. For this reason they also suggest to split chlorination and regeneration steps in order to improve yield, enhance the waste separation efficiency and prevent flammable mixtures keeping separate oxygen and ethylene. Furthermore, this work, as well as the one developed by Arganbright and Yates (1962), confirms that the oxychlorination rate-determining step is ethylene adsorption on catalyst surface. These information have been taken into account especially for the definition of the kinetic model of this process.

2.3.2 Air-based and oxygen-based process

As anticipated, two process alternatives that find industrial applications are available: air-based and oxygen-based oxychlorination. As oxygen source for oxychlorination, air has been widely used in the past due to its low cost. Another advantage linked to the use of air is that the presence of nitrogen dilutes the stream entering the unit and it allows an easier temperature control: this effect is very important especially for fixed-bed reactors where temperature is higher and local hot spots must be avoided. On the other hand, by-production of nitrous oxides is favoured using air-based configuration. The most significant difference between these two alternatives, however, is that the large amount of nitrogen in the vent gas makes the stream 20-100 times bigger and, as a consequence, the final treatment becomes prohibitively expensive (Dreher et al., 2012). By choosing an oxygen-based system, this function is directly realised by ethylene: an higher excess (up to 60% over HCl) is required in order to dilute the system and control temperature but, as shown in Figure 2.7, a gas recycle (mainly composed by ethylene and oxygen) is now necessary. Only a small amount, anyway, needs to be vented and treated, so most of the gaseous effluent will be recycled to the reactor. This solution also allows to reduce conversion per pass, improving yields. Therefore, as stated by Magistro and Cowfer (1986), with emission-control standards becoming more severe, the ratio of oxygen-based to air-based plants will increase. Therefore, an oxygen-based process should be preferred.

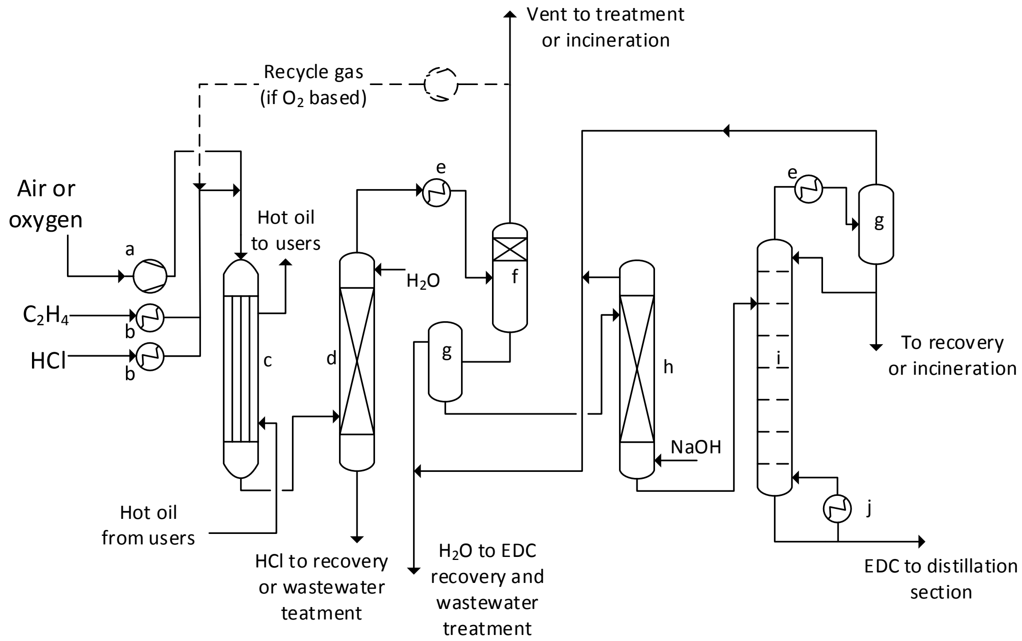
Vent to treatment or incineration
Recycle gas (if O_2 based)
Air or oxygen
a
C_2H_4
b
HCl
b
Hot oil to users
c
d
e
H_2O
f
g
h
NaOH
e
g
i
j
To recovery or incineration
Hot oil from users
HCl to recovery or wastewater teatment
H_2O to EDC recovery and wastewater treatment
EDC to distillation section

Figure 2.7: Oxychlorination process scheme showing the gas recycle for oxygen-based alternative. a) compressor; b) preheater; c) fixed-bed reactor; d) quench tower; e) cooler; f) degasser; g) separator; h) wash tower; i) azeotropic drying tower; j) reboiler. From Dreher et al. (2012)

Figure 2.7 shows also that in both cases product treatments are required before the distillation section. First of all, gaseous effluent are quenched with water in order to cool down the system and remove unconverted hydrogen chloride. After cooling, gases are then vented or recycled, whereas the liquid stream is purified from water and residual hydrogen chloride through the use of decanter, caustic washing and azeotropic distillation column.

2.3.3 Fixed-bed and fluidised-bed reactors

For industrial application two reactor design are in service: fixed-bed and fluidised-bed reactors. Table 2.3 lists some producers showing which technology they apply. It is evident, however, that fluidised-bed reactors are more widely used. Fixed-bed reactors resemble multi-tube heat exchanger with the catalyst packed in vertical tubes, so the heat can be removed easily with a cooling medium on the shell side. The catalyst is immobilised within the tubes in the form of small pellets, granules or extruded. Uniform packing is important in order to ensure uniform pressure drops, flow and residence time through each tube. Furthermore, generally catalyst activity profile is not constant because of the high exothermicity of the reaction: temperature control is more difficult in fixed-bed reactor, thus typical solutions are dilution of the catalyst with inert graphite or dilution of the stream with nitrogen. Operating temperature of 230-300°C and pressure of 2.5-15 bar are typical for oxychlorination with a fixed-bed reactor.

On the other hand, fluidised-bed reactors are typically cylindrical vessel equipped

Table 2.3: List of producers according to reactor type applied for oxychlorinaiton. (Dreher et al., 2012)

Fixed-bed Reactor	Fluidised-bed Reactor
Dow Chemical	B.F. Goodrich
Stauffer	Hoechst
Toyo Soda	Pittsburgh Plate Glass (PPG)
Vulcan	Ethyl Corp.
	Solvay
	ICI
	Mitsui Toatsu Chemical

with internal cooling coils in order to remove the heat of reaction and cyclones for catalyst loss minimisation. Figure 2.8 represents a simplified structure of this unit. Catalyst is supplied as fine powder (10-200 μm). Fluidisation ensures intimate contact between feed and product vapours, catalyst and heat transfer surfaces, leading to a uniform temperature profile. Indeed, fluidised-bed behaviour in this application can be assumed as isothermal: typical temperature value is lower than fixed-bed reactors and it ranges between 220-240°C, whereas pressure varies between 2.5 and 6 bar. Performances in term of selectivity and conversion are equivalent, even if backmixing for fluidised-bed can lead to a decrease of efficiency. Therefore, thanks to these features it is usually preferred to a fixed-bed reactor.

2.4 Pyrolysis

After production and purification of the intermediate 1,2-dichloroethane, vinyl chloride is finally produced by thermal cracking according to reaction (2.7). The reaction is highly endothermic and occurs in a gas phase, through a radical-based mechanism:

$$\mathrm{ClCH_2{-}CH_2Cl \longrightarrow CH_2{=}CHCl + HCl} \quad \Delta H^0_{298} = 100.2\ \mathrm{kJ/mol} \tag{2.7}$$

The process can be carried out both in the presence and in the absence of catalyst, but the latter choice is preferred by producers since with a proper design of the reactor conversion and yield close to the former configuration can be achieved, whereas additional costs for catalysis are avoided. For instance, if Wacker uses catalytic cracking, Dow Chemical, Ethyl Corp., B.F. Goodrich, Hoechst, ICI, Mitsui Toatsu, Monsanto, Stauffer prefer the non-catalytic route (Dreher et al., 2012). Yields to vinyl chloride is around 95-99%, but conversion must be kept in the range of 50-60% in order to maintain high selectivity. Initiators and promoters, however are added in order to improve process selectivity. Chlorine is easily available in the plant and is often used as initiator or promoter since it enhances chain propagation, as well as other chlorine delivering compounds, like tetrachloromethane (CCl_4) and trichloromethane (chloroform, $CHCl_3$). At the same time, 1,2-dichloroethane fed to the furnace must be pure over 99%. As reported by Benyahia (2005), the feed usually contains 500 ppm (wt) of 1,1,2-trichloroethane and 1 ppm of iron, coming from the direct chlorination catalyst. Moisture must be kept below 10 ppm. Other species, as trichloroethylene and oxygen, enhance coke deposition on the coil walls so their amount has to be minimised.

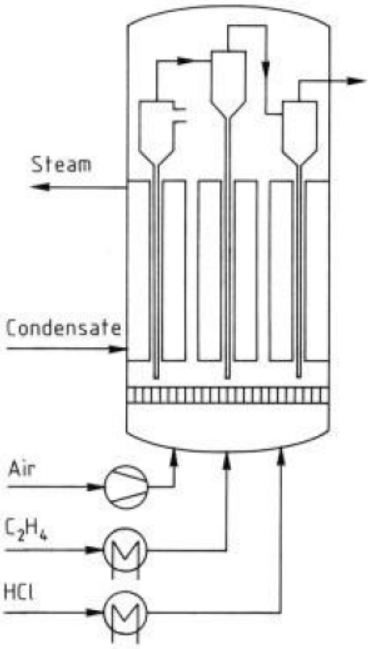

Figure 2.8: Fluidised-bed for oxychlorination process. Gaseous streams are fed from the bottom of the vessel, while the product is drawn from the top after catalyst recovery through a series of cyclones. From Dreher et al. (2012)

However, despite these precautions and expedients, a large variety of by-product is still present. Beside tars and coke, it is possible to find at the furnace outlet impurities such as ethylene, acetylene, vinylacetylene, 1,3-butadiene, chloroprene, benzene, chlorobenzene, dichloroethylenes, 1,1-dichloroethane, trichloroethanes, methyl chloride, methylene chloride, chloroform and tetrachloromethane (Dreher et al., 2012).

Figure 2.9 shows a schematic representation of the reactor. It is composed by one or more coils placed in a furnace. Coil length values are up to 1200 m and typical construction materials are chromium-nickel alloys and Incoloy. The structure can be split in two different sections: the radiant section (lower part) at higher temperature where reactions occur, and the convective section (upper part) where exhaust gases preheat the feed up to the point in which reaction rates become significant (400-420°C). The feed, then, is vaporised externally with an heat exchanger before being supplied to the radiation section. The vaporisation can be made either with steam or the pyrolysis effluent in order to save as much heat as possible from the system. The heat required for the reaction is supplied by a series of burners placed in the furnace chamber and fed typically with natural gas. Reaction temperature ranges from 480°C to 550°C, while pressure varies between 3 and 30 bar. However, it is common to use higher pressure in order to reduce furnace size, improve heat transfer and make downstream separation easier.

2.4.1 Quench

The furnace effluent must be quickly cooled by quenching in order to stop pyrolysis reactions, prevent further vinyl chloride decomposition and minimise additional by-product formation. Furthermore, quench columns are not only cooling units, but they ensure also a first coarse separation of the effluent before the distillation train. Essential

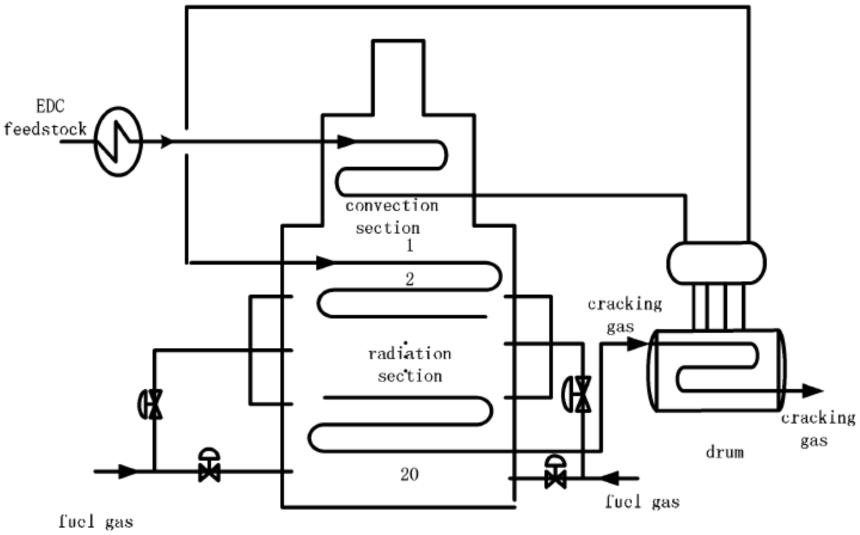

Figure 2.9: Schematic representation of the 1,2-dichloroethane (EDC) cracking furnace. The feed is preheated and vaporised in the convection section while the reaction occurs in the radiation section. From Li et al. (2013)

is the removal and the purge of heavies, tars and coke residuals. Several alternatives for quench column design are available but they can be distinguished according to the liquid quench source. Indeed, Figure 2.10 represents two configurations: effluent can be cooled through a recirculation of part of the liquid coming out at the bottom of the same column (a), or alternatively it can be done employing a liquid stream coming from a downstream unit operation (b). The system shown in Figure 2.10*a* makes use of flash separation with liquid recycle and external cooling, whereas the alternative configuration shown in Figure 2.10*b* takes advantages of the liquid coming from a downstream flash after cooling of the vapour outlet. Then, the main difference is related to the heat recovery accomplished by the heat exchanger: the disadvantage of alternative (a) is the energy loss because of the low temperature at which the recovery is achieved (Dimian and Bildea, 2008).

2.5 Vinyl chloride purification

Essential tasks of this section are the achievement of monomer grade vinyl chloride and the recovery of HCl and EDC, reactants for oxychloriantion and pyrolysis process respectively. Impurities are not discharged in this part of the plant and almost all cracking by-products are sent with 1,2-dichloroethane to purification. The effluent stream coming from the pyrolysis reactor is fed to the quench, which performs a first separation. As proved by Bruzzi et al. (1998), if the actual quench column is followed by a pre-fractionator (a simple flash as in Figure 2.10*b* or a reboiled stripping), many advantages in terms of product purity and energy saving can be achieved. After this unit operation, however, the outlet effluent coming from pyrolysis (composed by HCl, 1,2-dichloroethane and vinyl chloride almost in equimolar amount) is split in two streams: a vapour stream rich in HCl and vinyl chloride, and a liquid stream rich in EDC and vinyl chloride. Both of them are fed to the distillation train, whose configuration is represented in Figure 2.11.

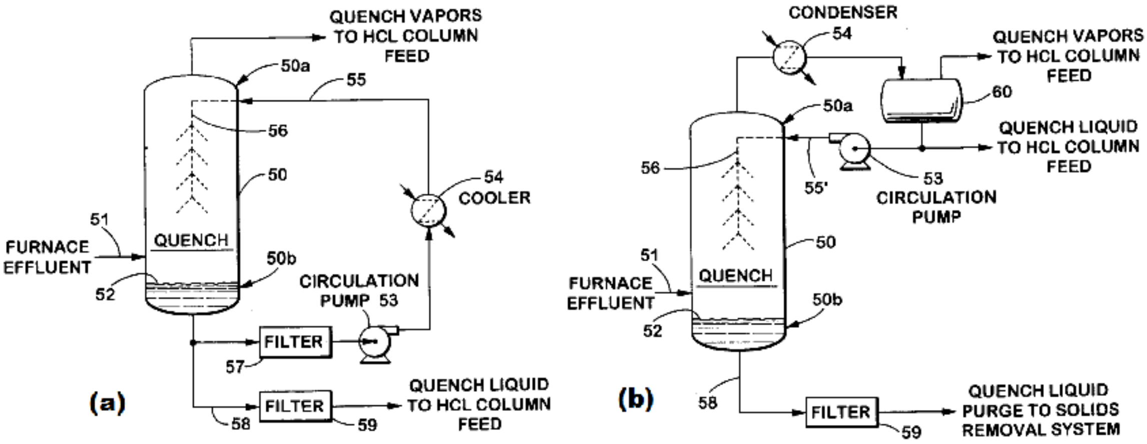
QUENCH VAPORS TO HCL COLUMN FEED
50a
55
56
50
54
COOLER
51
FURNACE EFFLUENT
QUENCH
50b
52
CIRCULATION PUMP 53
FILTER
57
(a)
FILTER
58
59
QUENCH LIQUID TO HCL COLUMN FEED
CONDENSER
54
QUENCH VAPORS TO HCL COLUMN FEED
60
50a
56
QUENCH LIQUID TO HCL COLUMN FEED
53
55'
CIRCULATION PUMP
50
51
QUENCH
FURNACE EFFLUENT
50b
52
(b)
58
FILTER
59
QUENCH LIQUID PURGE TO SOLIDS REMOVAL SYSTEM

Figure 2.10: Quench column alternatives. a) furnace effluent is quenched by recycling and cooling a liquid stream from the same unit; b) furnace effluent is quenched with a liquid stream obtained by condensing and flashing the vapour stream coming out from the same column. From Best (1996)

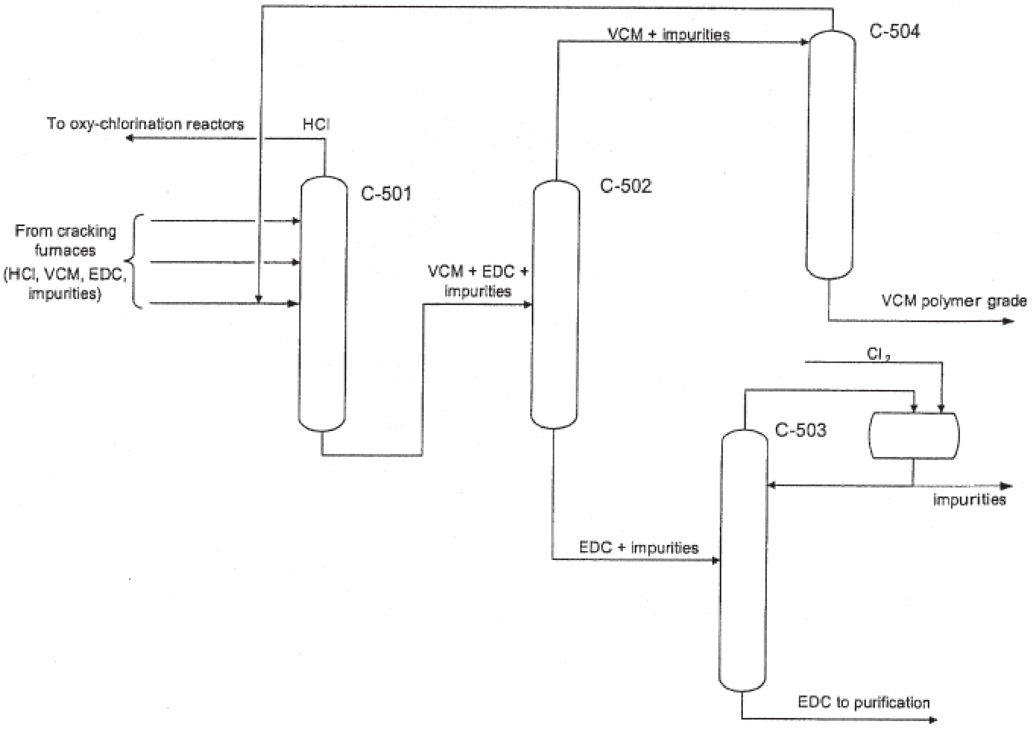
VCM + impurities
C-504
To oxy-chlorination reactors
HCl
C-501
C-502
From cracking furnaces (HCl, VCM, EDC, impurities)
VCM + EDC + impurities
VCM polymer grade
Cl₂
C-503
impurities
EDC + impurities
EDC to purification

Figure 2.11: Direct-like purification train for polymer grade vinyl chloride. Column C-501 recovers HCl for oxychlorination, column C-502 recovers 1,2-dichloroethane, while the product is obtained at the bottom of the column C-504. Top distillate of the last column is recycled back at the beginning of the train in order to limit the vinyl chloride loss. Column C-503 is considered as part of EDC purification train. From Bezzo et al. (2004)

Table 2.4: Vinyl chloride monomer composition specification. From Dimian and Bildea (2008).

property	Maximum level [ppm]
acetylene	2
acidity, as HCl by wt	0.5
acetaldehyde	0
alkalinity, as NaOH by wt	0.3
butadiene	6
1-butene	3
2-butene	0.5
ethylene	4
propylene	8
ethylene dichloride (EDC)	10
non-volatiles	150
water	200
iron by wt	0.25

For typical industrial application the sequence is direct-like: at first the lightest component (HCl) is recovered, then vinyl chloride and 1,2-dichloroethane are separated. The main advantage of this arrangement is that the scheme can better accommodate for the heat integration between different columns by varying the pressure level. Furthermore, it can ensure higher product purity and also higher flexibility during operation. It also takes advantage of the high operating pressure of pyrolysis: if the heaviest component (EDC) were removed first, the temperature at the bottom would be too high or an intermediate compression would be necessary in order to have an efficient purification between vinyl chloride and hydrogen chloride.

Figure 2.11 shows that three distillation columns are exploited in order to reach polymer grade vinyl chloride (99.99+%). Composition specification for polymer grade vinyl chloride are available in Table 2.4. The first unit is a 45-real-tray column receiving the feed from the quench. The distillation column operates above 10 bar with a partial condenser, so gaseous hydrogen chloride is fed to the oxychlorination reactor with a purity around 99.8%wt. Top temperature ranges between -30°C and -20°C, whereas the bottom temperature is about 100°C. The VCM loss at the top is around 20 ppm by wt and the HCl residual at the bottom must stay below the threshold value of 100 ppm by wt. The residue of this column is supplied to the rest of the train, which operates at 5 bar. The second column separates 1,2-dichloroethane and most of the heavy impurities from the vinyl chloride: it is a 70-tray column with total condenser. The residue is recycled to the EDC purification train, since it contains most of the impurities produced by cracking, while the liquid distillate is fed to the top tray of the product column. The bottom contains about 200 ppm by wt of vinyl chloride which is lost in the dichloroethane purification; in the top stream around 150 ppm by wt of HCl are still present, so further purification is required. Top and bottom temperature are about 30°C and 150°C respectively. The last column is a 30-tray column with total condenser able to reach polymer grade purity vinyl chloride at the bottom. The liquid distillate at the top, containing vinyl chloride and light impurities is recycled back to the first column in order to limit product loss. Therefore, this configuration

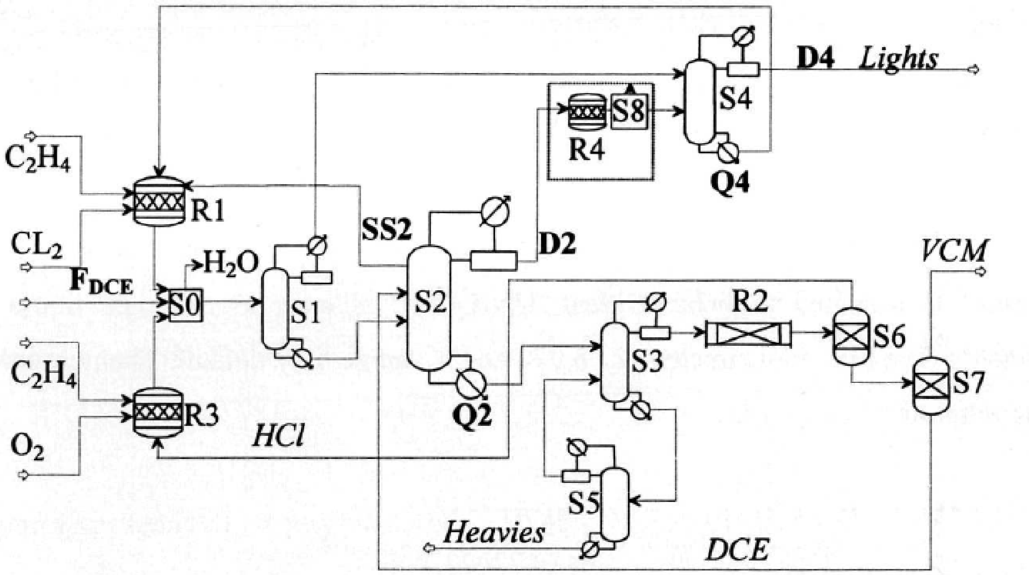

Figure 2.12: Balanced process flow-sheet with detailed representation of the EDC purification train with optional chlorination unit R4. Chlorination units outlets are mixed and purified from water and acids (S0) and from very light components (S1). Lights are removed at first (S2) with an additional column (S4) for limiting EDC loss. EDC for pyrolysis is obtained at the top of the column S3 and column S5 limits the loss of EDC. From Groenendijk (2000)

for product purification section is able to achieve monomer grade VCM and further purification units, typically required for finishing the product, are avoided. As reported by Cowfer and Best (1987), neutralisation of acid residual was usually required and performed by washing the product with a caustic soda solution. As a consequence, also a drying unit was added in order to keep water concentration below its limit value.

2.6 Dichloroethane purification

If the vinyl chloride purification section is required for the recovery of the main by-product (hydrogen chloride) and unconverted 1,2-dichloroethane, the EDC purification train is essential for impurities removal since all undesired products are vented in this section. As stated by Dimian et al. (2001), impurities removal in vinyl chloride process is known to be difficult because species can accumulate in the recycle loop and cause unstable operation. Three of them can be identified as the most important ones: chloroprene, trichloroethylene and tetrachloromethane. The effect of tetrachloromethane is not negative for the whole plant performance: it is considered a "good" impurity since it works as a catalyst for the pyrolysis process, decreasing temperature and enhancing selectivity. Usually its value is kept around the optimum value of 2000 ppm by wt. On the other hand, control of chloroprene and trichloroethylene removal is critical since they are unsaturated components: CLP can polymerise easily if above 8%wt, plugging equipment, and TRI enhances coke production in the furnace. According to Groenendijk (2000) threshold values for chloroprene and trichlorothylene in the EDC stream are 100 and 600 ppm by weight respectively. Therefore, modelling of 1,2-dichlorothane purification will be focus on the removal of "bad" impurities.

Figure 2.12 represents a simplified flow-sheet of the balanced process for vinyl chloride production, but the EDC distillation section is represented in detail. Direct chlorination and oxychlorination reactors outlets are mixed and jointly treated before distillation section. The unit S0 simulates a washing and drying unit, required for the removal of water and acid residuals, as unconverted hydrogen chloride, from reactor units. Pre-treatments are completed by column S1, which performs a separation of very light components, mostly unconverted ethylene, oxygen and carbon dioxides: for oxygen-based oxychlorination this stream is partially recycled back to the reactor in order to limit the loss of reactants (because of the feed excess). Otherwise they are completely vented, like in the scheme proposed. Advantages of oxygen-based configuration have been already discussed in section 2.3.2. Crude dry and recycled EDC are sent to distillation column S2 for the light removal: it is a 47-tray column operating at high reflux ratio and slightly above atmospheric pressure. Due to the low-boiling azeotropic mixture formed by trichloroethylene and 1,2-dichloroethane, accumulation problems close to the top may be prevented by recycling a side stream back to the direct chlorination reactor, in order to convert impurity in to higher chlorinated species easily removable as heavy. In the real practice, due to this thermodynamic constraint and CLP composition limit, high amount of EDC is still present on top distillate of light column S2. Therefore, an additional unit (S4) is required to limit its loss: it is a 10-tray distillation column operating close to atmospheric pressure. Top distillate is vented, whereas the bottom residue has to be recycled back to the direct chlorination reactor in order to convert impurities, if the optional chlorination reactor R4 is not used.

Impurities leave the process as lights or heavies: the main high-boiling component that must be removed is 1,1,2-trichloroethane, since it is the most abundant. As reported by Benyahia (2005), typical TCE amount in the cracking feed is 500 ppm by weight. A single column is typically not enough in order to achieve purity specification on EDC and at the same time limit its loss: an additional column is required. The the first column S3 (6-tray) operates above atmospheric pressure. Highly pure EDC is obtained as top distillate and is sent to cracking furnace, while the residue is fed to the unit S5, which is a vacuum distillation column (13-tray) working at 0.2 bar. Hence, heavies are vented at the bottom of this column and 1,2-dichloroethane recovered at the top is recycled to unit S3. The heavies removal from EDC is easier than lights and it does not require an intermediate conversion or a stream recycled to the reactor unit.

2.6.1 Flow-sheet alternatives

After the introduction of the intermediate chlorination reactor R4 three alternative configurations are available by changing the connection between units. Figure 2.13 displays three possible configurations analysed by Groenendijk (2000) in terms of degree of separation achieved and dynamic controllability of the plant. All of them allow to avoid the recycle of the S4 residue to the direct chlorination reactor: therefore, some common main advantages can be observed. First of all, the direct chlorination unit works cleaner and as a consequence selectivity is enhanced but, above all, the whole plant dynamic behaviour is improved. The impurities path is shorter and feedback effects are reduced, therefore dynamic response is faster and plant performance and controllability are improved.

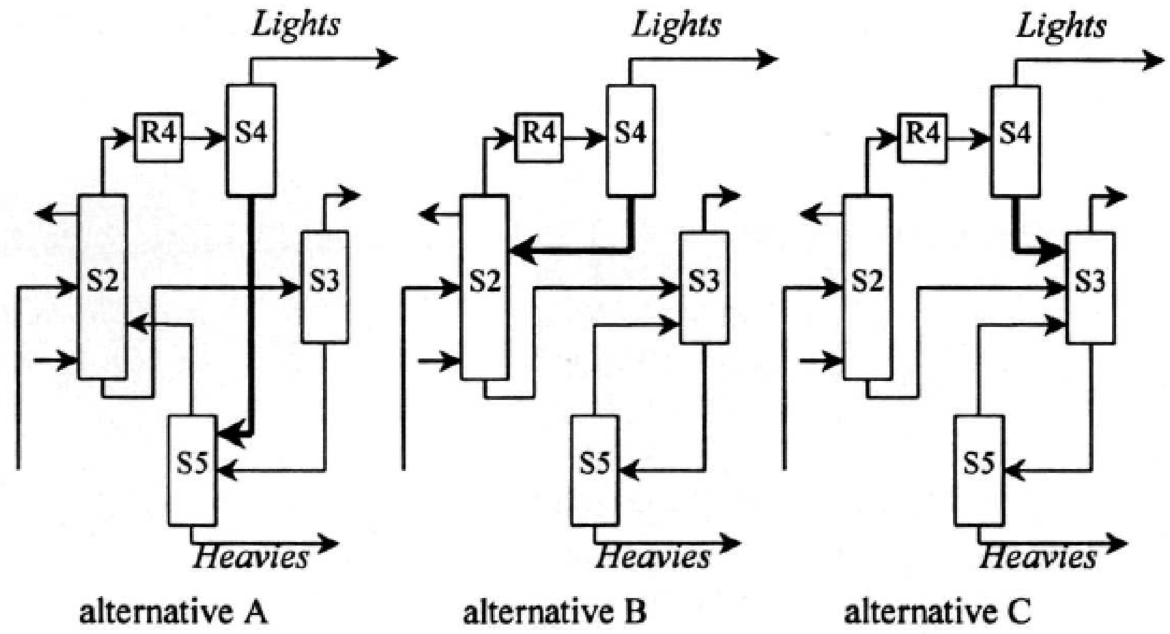

Figure 2.13: EDC purification alternative configurations after introduction of chlorination unit R4. (Groenendijk, 2000)

Each alternative is based on a different connection of S4 residue stream. In the alternative A the bottom stream of column S4 is fed to the heavy column S5. However, the S5 top distillate is recycled back to the main light column S2 instead of heavy column S3. This allows to reduce the heavies amount in column S2, which is the key unit of this purification section. According to alternative B, the S4 residue is sent back to the upstream light column, while other connections are as previously described: this configuration allows to further shorten the impurities path. On the other hand, the S4 residue can be fed directly to the heavy column S3, according to alternative C in Figure 2.13. The latter configuration is the simplest but also the least safe one: a fail on column S4 would directly affect purity of the cracking feed stream. On the contrary, alternative A is technologically the safest, but the impurities path is longer if compared with other alternatives, hence the dynamic response is slower. Alternative B is simpler, the system response is faster and it reduces interactions between light train and heavy train. Furthermore, as displayed in Figure 2.11, in the real practice the chlorination can be performed adding chlorine to the reflux drum of the EDC purification column: higher chlorinated components, that are produced at this step, are treated at first in the distillation column S2. Therefore, alternative B is also the closest solution to real practice configurations.

Chapter 3

Software and tools

Software used for modelling and thermodynamic properties validation are presented in this chapter. Briefly main features of the equation oriented approach and gPROMS® ProcessBuilder are discussed at first. Then Multiflash™ tools for thermodynamic properties calculation are described.

3.1 gPROMS® ProcessBuilder

The gPROMS® platform, developed by Process System Enterprise Ltd., provides a family of different products for advanced process modelling, involving all essential functionalities as flowsheeting, custom modelling, parameter estimation, optimisation and physical properties calculation. ProcessBuilder is the tool used for the model development and the simulation of the plant analysed in this work. It provides high-fidelity steady-state and dynamic models for all common units through the gPROMS® Model Libraries (gMLs) and high-fidelity predictive models for complex reactor and separation systems through the Advanced Model Libraries (AMLs). For the present case, modelling and simulations have been performed with the *beta4* release of the gML library. Furthermore, ProcessBuilder allows the use of these models by simple "drag & drop" techniques for flowsheeting environment, but at the same time, it preserves the capability of easily developing and implementing custom models thanks to the gPROMS® structure. Custom modelling constitutes a key topic for simulation technology and it allows great flexibility: it guarantees to any particular user to achieve the detail level required for each specific case, which not even the most complete model library is able to ensure.

3.1.1 Equation oriented approach

Two different approaches for process flowsheeting can be distinguished: sequential modular (SM) and equation oriented (EO). Traditionally most of commercial steady-state flowsheeting tools have adopted the SM approach because of its robustness and relative ease of implementation. On the other hand, gPROMS® is based on the equation oriented approach. Software based on SM approach solve each unit operation sequentially and individually, according to the flow direction. Individual modules are developed for each unit operation and process: they perform material and energy balances based on the thermodynamic model selected. Hence, every module computes its output stream that represents the input values for the following module. On the contrary, EO tools are able to solve the whole problem simultaneously, considering it as a non-linear equations system. The overall system is composed by mathematical models for every unit operation and connectivity relations and it is solved through optimisation techniques, as those based on Newton's method (Pantelides et al., 2015). Of course, they are more difficult to construct and troubleshooting can be more complex with respect to SM software, but major advantages can be identified. For instance, using the SM approach a recycle stream needs to be guessed, the calculation through the entire sequence needs to be repeated and the initial guess replaced with the new value obtained, hence basically several iteration through the loop may be required in order to get convergence. This problem typically becomes more acute in processes with multiple interacting recycles, as the one considered in the present case. Furthermore, addition of overall process specifications or optimisation tasks are accomplished through calculator units that add additional loops. This information loops are handled like material recycles, increasing complexity and computational time. On the other hand, EO approach is more efficient in the handling of multiple interacting recycles and optimisation task, thanks to its structure that treats the entire set of variables and equations simultaneously. Moreover, custom modelling is more flexible and codes implementation is easier since the addition of a new unit operation model only requires the definition of its equations set and the solution is achieved at flowsheet level.

3.1.2 Initialisation procedure

As stated by Pantelides et al. (2015), whilst the EO approach is potentially much more powerful in terms of the scope of problems that could be addressed, only the SM approach was capable of providing the degree of robustness that is necessary to support the wide deployment of these tools. But recent technological developments are enhancing usability of EO tools, thanks also to progresses achieved in the initialisation procedure area. Model initialisation procedure (MIP) is basically a sequence of calculations used to achieve gradually a solution for complex models, enhancing robustness. It operates both at unit model level (U-MIP) and at flow-sheet level (F-MIP). At unit-level initialisation procedure is simply a sequence of models ordered according to increasing complexity. The first model solved is very simple and a solution can be find starting from very poor initial guesses. On the other hand, the last model is the final one with the maximum level of complexity and it is solved thanks to more accurate initial guess variables obtained by previous calculations. At flow-sheet level initialisation procedure is essentially a set of mathematical algorithms for combining U-MIPs, allowing reliable and efficient convergence. For the specific case, sequential initialisation procedure option has been applied in order to exploit the robustness of the SM approach, obtaining accurate initial guesses for the solution of the entire flowsheet. By specifying this option each unit is initialised sequentially, according to the flow direction, with open recycles. Once convergence has been obtained, the software closes recycles according to user specifications in order to complete MIP. Also at this level, sequence of closure can be specified in order to help the solver to reach convergence since multiple interacting recycles are present. Convergence problems in steady-state simulation may be caused by infeasible specifications in combination with recycle loops, hence flexibility on recycle breakers closure sequence allows the stable operation of the solver, ensuring users to achieve the solution. Once MIP has reach convergence and a base-case is achieved, the software allows to save a variable set in order to perform following simulations and sensitivity analysis supplying this accurate set of initial guesses, saving a meaningful amount of time and ensuring robustness and solution accuracy.

3.2 The thermodynamic package

Multiflash^{TM} is a powerful system for modelling physical properties and phase equilibria, developed by Infochem Computer Services Ltd. It supports all commonly-used thermodynamic and transport properties, including a wide rage of equation of state and activity models. Two data banks are supplied for pure component data:

- Infodata, developed by Infochem Computer Services Ltd;
- DIPPR (Design Institute for Physical Properties), from AIChE.

The latter one is the one exploited in the present case. The software can be used as stand-alone or in conjunction with other software: for instance, in gPROMS® ProcessBuilder it can be easily implemented in any model as a foreign object containing all thermodynamic information required. In order to properly specify the foreign object it is required to generate a file with *mfl* extension from the Multiflash^{TM} Windows interface. This file must contain the complete list of components and the thermodynamic model that is used in the simulation. Binary interaction parameters, if available, are included in this file, otherwise they have to be added at this level. Afterwards the file containing the thermodynamic information can be imported from the ProcessBuilder and specified in the source units.

3.2.1 Excel® interface for Multiflash^{TM}

Another software which can be used in combination with Multiflash^{TM} is Microsoft Excel®. This option is simply supplied by Infochem Computer Service Ltd as add-in for this software, hence is very easy to install. It allows to obtain and display pure component properties, as critical temperature and pressure, and use these values in a normal Excel® flow-sheet, but above all, it allows to perform every calculation in the this environment for any binary, ternary or very complex mixture. The key task that must be accomplished is the initialisation of the flow-sheet where MF functions are called. Cells where this simple code is implemented are called at the end of each MF functions, since it specifies following essential information:

- pure component databank;
- thermodynamic model;
- binary interaction parameters set;
- number of BIPs in the set;
- gas phase thermodynamic model;
- liquid phase (or phases) thermodynamic models;
- list of components;

- unit of measure.

These information can be supplied manually as in the case reported in Appendix A or simply defining a *mfl* file, as actually happen for the gPROMS® platform. In the latter case it is enough to include the MF file specifying its path in the initialisation cell, as in the following example:

```
include ''C:/Folder/VCM.mfl''
```

In the present case, this software has been used for BIPs regression, and further information are required in order to allow the user to modify their values. BIPs set has to be specified again and following specification can be supplied:

- temperature dependence order for BIPs;
- thermodynamic model type (activity or EOS);
- BIPs unit of measure.

Otherwise default specifications are applied.

Chapter 4

Thermodynamic validation

This chapter explains how thermodynamic properties are calculated by the software: description of the chosen thermodynamic model is reported explaining reasons of its selection. Binary interaction parameters are reported specifying regression method and analysing results.

4.1 Thermodynamic model

Results accuracy during process modelling is highly affected by the thermodynamic model used for the simulation. Especially for distillation columns a proper selection of the thermodynamic model is essential in order to give a suitable representation of vapour-liquid equilibria (4.1) and separations.

$$f_i^v = f_i^l \tag{4.1}$$

Fugacities of component i in vapour (f_i^v) and in liquid phase (f_i^l) can be described by two groups of equations: equation of state methods or activity coefficient methods. Equation of state can be used over wide ranges of temperature and pressure. Any thermodynamic property, such as fugacity coefficients for each phase (ϕ_i^v, ϕ_i^l), can be calculated from the equation of state:

$$f_i^v = \phi_i^v y_i p \tag{4.2}$$

$$f_i^l = \phi_i^l x_i p \tag{4.3}$$

where y_i and x_i are respectively vapour and liquid phase molar fraction. They are often used for ideal or slightly non-ideal systems such as hydrocarbon systems. On the other hand, activity models are suitable for the prediction of polar and non-polar compound mixtures even when they show very strong non-ideality. For the case under study, most of the component pairs exhibit quite strong liquid-phase interaction, so an activity model sounds more suitable. The complete list of components used for the simulation is presented in Table 4.1. When modelling thermodynamic properties with activity models, however, equations of state are still required since this method allows to calculate just the liquid phase fugacity of a general component i. Indeed, this approach is also called $\gamma - \phi$: vapour phase fugacity is calculated according to equation (4.2), while liquid phase fugacity is derived through the activity coefficient γ_i as follows:

$$f_i^l = \gamma_i x_i f_i^0 \tag{4.4}$$

where f_i^0 is the standard-state fugacity. The activity coefficient γ_i represents the deviation of the mixture from ideality. However, according to the equation of state used, allowed pressure range varies: for example, assuming the gas phase behaviour as ideal, pressure should be limited to 3-5 bar, whereas if Redlich-Kwong or another EOS is used pressure limit is higher, of the order of 10-20 bar (Computer Services Ltd, 2013). For this reason in order to simulate the vinyl chloride production an activity model has been chosen and more specifically the NRTL (Non-Random Two Liquid) model coupled with Redlich-Kwong EOS has been used. Of course, the model has to be validated with experimental data in order to represent properly the real behaviour of the system and this will be the object of the following section 4.2.

A clear example of advantages and accuracy of the prediction with NRTL-RK model is shown in Figure 4.1. It represents the vapour-liquid equilibrium for the binary mixture 1,2-dichloroethane and trichloroethylene at 760.0 mmHg: binary interaction parameters have been regressed for both the models according to the available experimental data. Actually the reported comparison stresses two aspects: at first it shows the reliability of the activity method for the description of an interacting system. For instance, the prediction of the azeotropic point at atmospheric pressure is 82.2°C with 43.3%wt in EDC and the reference value from Horsley (1973) is 82.1°C and 43.5%wt. But at the same time the analysis highlights the requirement of a good prediction for the pure component vapour-pressure, since a wrong estimation of this property may lead to significant errors in the equilibrium prediction and these cannot be compensated by regression of binary interaction parameters. For instance, for any activity model pure vapour pressure data are essential and the inaccurate representation of this property is one of the main sources of error. Pure component information required for the NRTL model are vapour pressure and saturated liquid density, but the former is the most important for vapour-liquid equilibria predictions. The software applies the Antoine equation (4.5) for all the component used in the simulation, except for nitrogen and carbon dioxide for which the Wagner equation (4.6) is exploited.

$$\ln P = a_1 + \frac{a_2}{T + a_3} + a_4 T^{a_6} + a_5 \ln T + \frac{a_7}{T^2} \tag{4.5}$$

$$\ln P = \ln P_c + \frac{w_1 \tau + w_2 \tau^{3/2} + w_3 \tau^3 + w_4 \tau^6}{T_r} \tag{4.6}$$
$$\text{where } T_r = \frac{T}{T_c} \text{ and } \tau = 1 - T_r$$

Antoine parameters a_i, Wagner parameters w_i, critical temperature T_c [K] and critical pressure P_c [Pa] are available from DIPPR databank. These correlations are based on regression of pure component experimental data; hence, as mentioned by Poling et al. (2001), they are very accurate in the range of experimental data, but they should not be used outside these constraints. Moreover, reliability of Antoine model will be discussed in section 4.2.1, comparing it with available experimental data.

Using the selected method the activity coefficient is calculated through the partial derivative of the excess Gibbs energy G^E over the number of moles of component i, as follow:

$$\ln \gamma_i = \frac{\partial G^E}{\partial n_i} \tag{4.7}$$

Table 4.1: Components list. Pure component data available from DIPPR Databank.

Tag	Name
O2	oxygen
H2O	water
HCl	hydrogen chloride
Cl2	chlorine
C2H4	ethylene
C2H2	acetylene
VCM	vinyl chloride
EDC	1,2-dichloroethane
TCE	1,1,2-trichloroethane
N2	nitrogen
CLP	chloroprene
TRI	trichloroethylene
DCB	1,4-dichlorobutane
CO2	carbon dioxide
HCB	hexachloro-1,3-butadiene

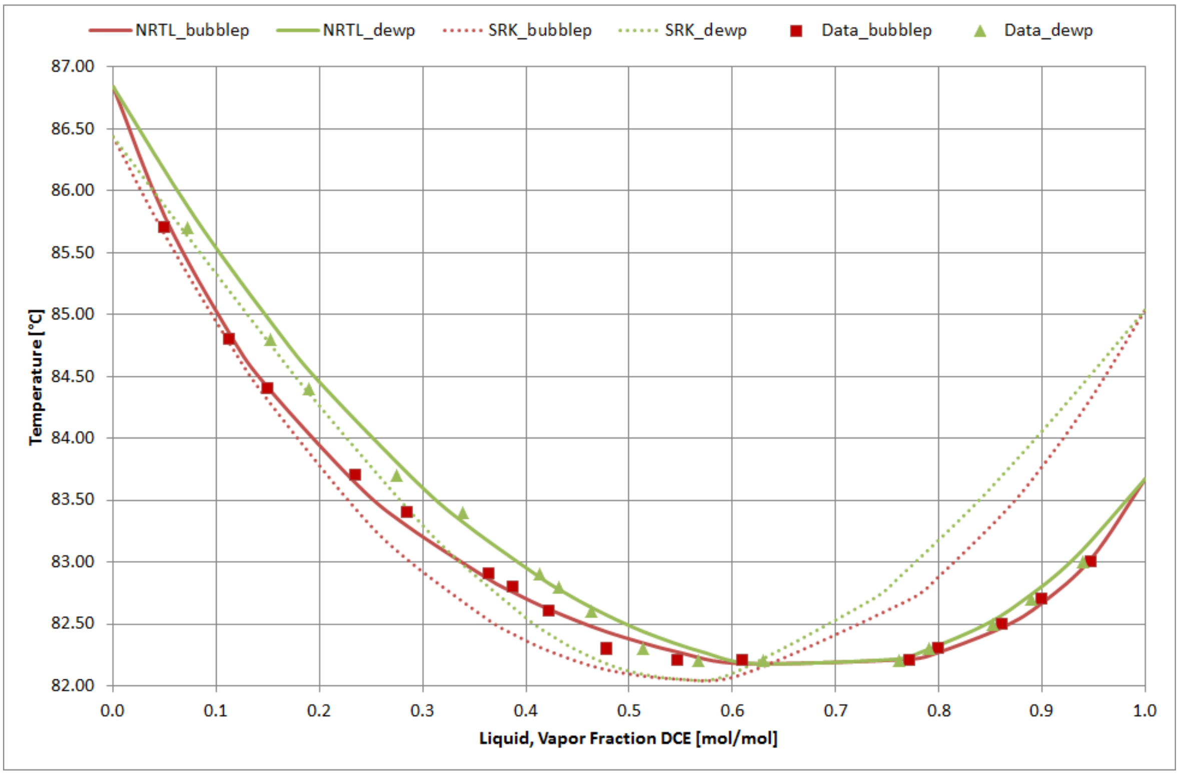

Figure 4.1: Comparison between prediction of isobaric vapour-liquid equilibrium obtained by Soave-Redlich-Kwong equation of state and NRTL-RK model, for the mixture 1,2-dichloroethane + trichloroethylene. Binary interaction parameters have been regressed for both models according to experimental data at 760 mmHg.

Furthermore, for a generic mixture, the NRTL model defines G^E according to the following equation:

$$G^E = \sum_i n_i \frac{\sum_j n_j A_{ji} G_{ji}}{\sum_j n_j G_{ji}} \tag{4.8}$$

where A_{ij} is the binary interaction parameter and G_{ij} is the Gibbs energy for a mixture made of generic components i and j calculated from equation (4.9).

$$G_{ij} = \exp\left(-\frac{\alpha_{ij} A_{ij}}{RT}\right) \tag{4.9}$$

Furthermore, since the relation

$$\alpha_{ij} = \alpha_{ji} \tag{4.10}$$

is always valid, the NRTL model contains three parameters for each binary mixture: two energy parameters and α_{ij}, which is called non-randomness factor. It can be considered to represent the non-ideality of the molecular rearrangement of the component molecules in the vicinity of a given molecule (Kato, 1982). If the behaviour is totally random α_{ij} is zero, but typical values range between 0.2 and 0.47. When experimental data are scarce, the value can be set arbitrarily and a typical choice is 0.3 (Prausnitz et al., 1998), which is also the default value supplied by Multiflash$^{\mathrm{TM}}$.

4.2 Model validation

No binary interaction parameters were available in Multiflash$^{\mathrm{TM}}$ for the components taken into account in the present case, so at first it has been necessary to identify key mixtures for which A_{ij} are required. For this preliminary study distillation columns and direct chlorination reactor have been considered, since these are the main units is which vapour-liquid equilibrium is involved: oxychlorination and pyrolysis systems involve mixtures that are exclusively in the gas phase. Direct chlorination process, as discussed in Chapter 2, is controlled in terms of conversion and selectivity by mass transfer of gaseous reactant into the liquid medium. Therefore, a proper prediction of ethylene and chlorine solubility in 1,2-dichloroethane is essential for the purpose of the simulation. Considering EDC purification section, on the other hand, it is essential to predict properly the removal of trichloroethylene from the light column because of the low-boiling point azeotropic mixture. At the same time it is necessary to properly describe the behaviour of the mixture 1,2-dichloroethane+1,1,2-trichloroethane since the latter is the most abundant heavy impurity. Other components, that are in low amount or that are significantly heavier or lighter than 1,2-dichloroethane, can be considered not affecting meaningfully the overall behaviour or very easy to remove. Furthermore considering the vinyl chloride purification, three components have been taken into account, due to their amount and importance for the process: vinyl chloride, 1,2-dichloroethane and hydrogen chloride. It is clear that also these three binary mixtures must be considered. Table 4.2 lists components pairs for which experimental data have been regressed in order to obtain binary interaction parameters. Experimental data regression is not the only method available for the estimation of binary interaction parameters, but it is certainly the more reliable. For lack of experimental data and databank properties alternative solution could be fitting ”pseudo-experimental” data generated with a predictive equation of state or a validated model. The ideal regression

Table 4.2: Key mixtures for which binary interaction parameters have been regressed with corresponding source of experimental data.

Component 1	**Component 2**	**Source**
1,2-dichloroethane	chlorine	(Evstigneev et al., 1985)
1,2-dichloroethane	ethylene	(Stoeck, 1985)
1,2-dichloroethane	1,1,2-trichloroethane	(Araten, 1957)
1,2-dichloroethane	trichloroethylene	(Cheric)
1,2-dichloroethane	vinyl chloride	(Preuss and Moerke, 1988)
1,2-dichloroethane	hydrogen chloride	(Cheric)
vinyl chloride	hydrogen chloride	(Preuss and Moerke, 1988)

for parameters estimation requires experimental data at plant operation conditions: in the present case available data from literature sources have been chosen according to temperature, pressure and composition ranges. Where it is was not possible to obtain information at operative conditions, selection was made in order to obtain data as close as possible to them. Furthermore, it must be pointed out that for the HCl recovery column additional complete mixture data are required: since the bottom temperature is higher than hydrogen chloride critical temperature ($T_{c,HCl} = 51.5$ °C), its pure vapour pressure value is obtained by extrapolation by the software in order to find a solution, but the Antoine equation should not be used out of the temperature range (Poling et al., 2001) in order to predict mixture properties.

4.2.1 Binary interaction parameters estimation

Each regression has been performed with Excel® interface for Multiflash™ since this solution allows to use exactly the same thermodynamic model that will be used in the simulation. It just requires for the initialisation few strings of code containing the following specifications: pure component databank, thermodynamic model, binary interaction parameters set, gas phase and liquid phase thermodynamic model used for the equilibrium calculation, component names and unit of measure for thermodynamic variables used in the flow-sheet. An example of code is reported in Appendix A. It is important to note that binary interaction parameters are function of temperature and for NRTL model they can be described both in dimensional (A_{ij}, [J/mol]) or adimensional mode ($\frac{A_{ij}}{RT}$) as following respectively:

$$A_{ij} = a'_{ij} + b'_{ij}T + c'_{ij}T^2 \tag{4.11a}$$

$$\frac{A_{ij}}{RT} = a_{ij} + \frac{b_{ij}}{T} + c_{ij}T \tag{4.11b}$$

where a'_{ij}, b'_{ij}, c'_{ij} and a_{ij}, b_{ij}, c_{ij} are simple parameters for dimensional and adimensional forms respectively. For the present case, the adimensional mode (4.11b) has been always specified in order to avoid errors during the implementation in the software database. Of course the two forms are not independent and it is easy to convert adimensional values to their dimensional form if required. Also the non-randomness parameter is temperature dependent but this effect is usually neglected. Furthermore for the case under study, the default value of 0.3 has been kept constant for each binary mixture.

The regression is performed through minimisation of the sum of squared errors for the prediction of temperature, if isobar vapour-liquid equilibrium data are available, or pressure, if isothermal data are used. Non-linear solver has been applied for the minimisation of the objective function using default convergence tolerance. Furthermore, the *multistart* option has been used in order to find a global optimum instead of a local, since it allows to perform several calculation starting from different initial guesses. On the other hand, varying binary interaction parameters over a wide range may lead to invalid numerical values. Therefore, in order to avoid invalid solutions an additional parameter (c_{num}) has been added to the sum of squared errors. Using an `IF` condition the parameters is set to zero when a valid solution is found or it is set to $1 \cdot 10^{+20}$ if one or more values of calculated pressure and temperature are invalid numbers: it is implemented according to equation (4.13) in case of isothermal data (analogous for isobaric). The complete objective function is reported in equation (4.12) for the case of isothermal vapour-liquid equilibria (analogous formula is applied on temperature for isobaric data set):

$$f_{obj} = \left[\sum_{i}^{NP} \left(P_{calc} - P_{data} \right)^2 \right] + c_{num} \tag{4.12}$$

$$c_{num} = \begin{cases} 0, & \text{if } \sum_i P_{i,calc} \in \Re \\ 1 \cdot 10^{+20}, & \text{otherwise} \end{cases} \tag{4.13}$$

where the objective function is identified by f_{obj}, P_{calc} and P_{data} [Pa] are the calculated and experimental pressure respectively, and NP is the number of points.

Furthermore, each data set thermodynamic consistency has been tested by correlative method, checking relative error on temperature or pressure and, where possible, the absolute error on vapour fraction prediction. Finally, regressed binary interaction parameters are reported in Table 4.3.

Direct chlorination reactor

Initially the direct chlorination reactor has been validated through ethylene and chlorine solubility data. The reactor works at about 2 bar and 110°C. Figure 4.2 shows a comparison between original prediction and the actual prediction with binary interaction parameters. It proves that at the same pressure the amount of dissolved ethylene is always lower than the one originally predicted without BIPs. Solubility curves are straight lines, hence the behaviour at this condition can be properly represented also by using a simpler method like an Henry constant. Furthermore, it is evident that for decreasing concentration of dissolved ethylene the difference between old and new predictions is reduced at any temperature: this observation will be useful in order to understand the effect on simulation results, proposed in the next chapter. On the other hand, Figure 4.3 shows the relative error on the pressure estimation after fitting: maximum error value is 3.2% and their distribution is random, so the data set is considered consistent and the prediction is accurate.

At the later stage, chlorine solubility prediction has been adjusted according to experimental data at atmospheric pressure, as illustrated by Figure 4.4. Few points were available but for low concentration and high temperature (closer to operative condition) the difference between original and adjusted prediction is lower. Figure 4.5 confirms the accuracy of the prediction, even if this is clearly influenced by the few available experimental points.

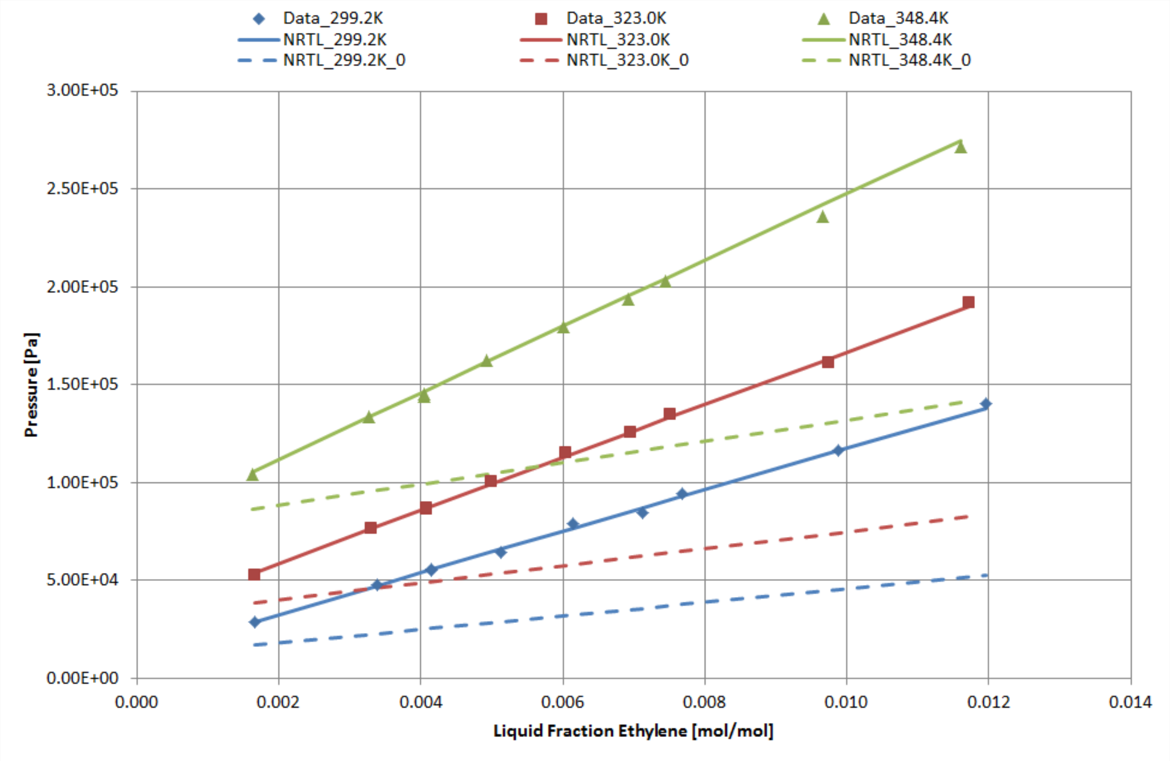

Figure 4.2: Solubility of ethylene in 1,2-dichloroethane at different temperatures. Comparison between NRTL model before (dashed line) and after (continuous line) fitting of experimental data.

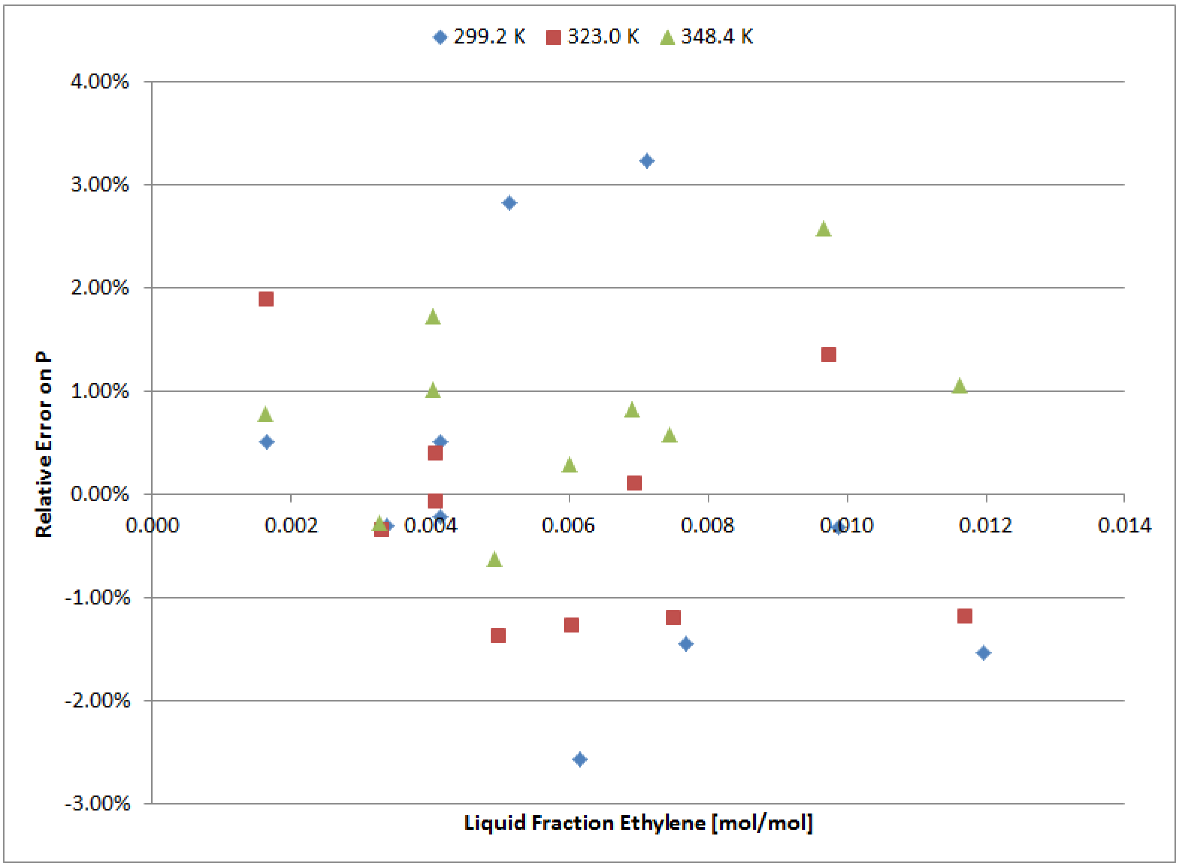

Figure 4.3: Relative error on pressure after fitting for ethylene solubility in 1,2-dichloroethane.

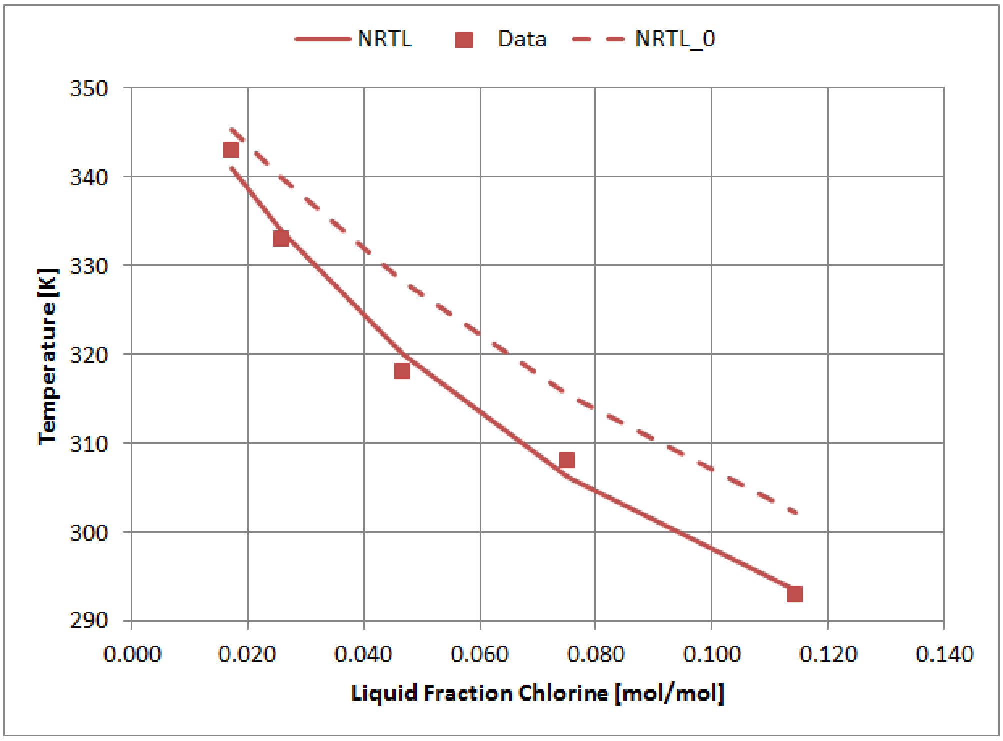

Figure 4.4: Solubility of chlorine in 1,2-dichloroethane at atmospheric pressure. Comparison between NRTL model before (dashed line) and after (continuous line) fitting of experimental data.

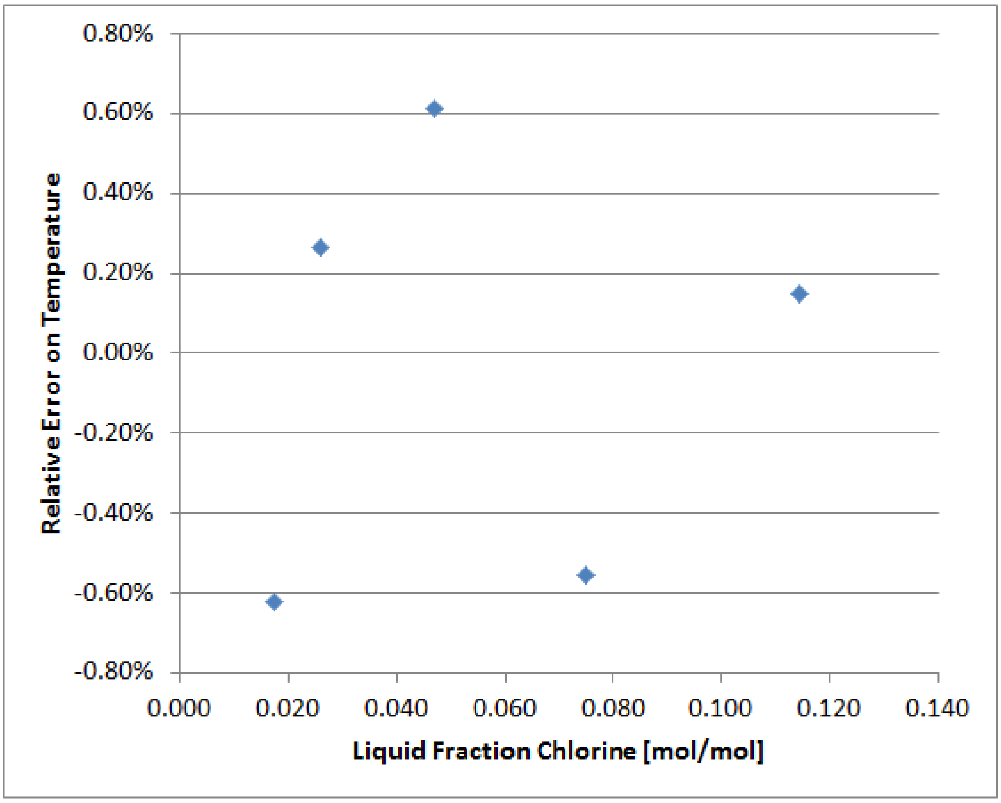

Figure 4.5: Relative error on temperature after fitting for chlorine solubility in 1,2-dichloroethane.

Table 4.3: Regressed parameters values of binary interaction parameters obtained by fitting of experimental data for NRTL-RK model. Non-randomness parameter α_{ij} is constant and equal to 0.3 for all the binaries.

Component i	**Component j**	a_{ij} $[-]$	b_{ij} $[K]$	c_{ij} $[K^{-1}]$
EDC	Cl_2	-0.0857247	-0.0048817	–
Cl_2	EDC	0.4340391	-0.0033955	–
EDC	C_2H_4	0.5144321	0.0165664	–
C_2H_4	EDC	0.7963315	0.0127459	–
EDC	TCE	-0.9285118	-10.00000	–
TCE	EDC	1.430896	-10.00000	–
EDC	TRI	8.434875	-2701.789	–
TRI	EDC	9.633237	-3556.939	–
EDC	VCM	13.8593	0.08770312	0.005747944
VCM	EDC	41.62886	0.1940586	-0.06153572
EDC	HCl	-0.7529631	-0.0057478	0.0053578
HCl	EDC	-0.7769685	-0.006156	-0.0001827
VCM	HCl	-0.6560299	-62.98315	–
HCl	VCM	1.338497	-49.68659	–

EDC purification

Another binary mixture that can be useful for direct chlorination reactor validation is 1,2-dichloroethane+1,1,2-trichloroethane, since the latter is the most important impurity for this unit. On the other hand, a proper prediction of the vapour-liquid equilibrium of this binary mixture is essential for simulation of EDC purification train. Data were available at atmospheric pressure but it has to be noticed that not all distillation columns work close to this condition: the light section and the first heavy column work slightly above the atmospheric pressure, whereas EDC loss reduction in the heavy section is performed by vacuum distillation at 0.2 bar. However, as highlighted by Araten (1957) and by Figure 4.6, the mixture behaves ideally and the prediction even without BIPs regression may be considered accurate. Never the less, regressed parameters have been used in order to increase accuracy: Figure 4.7 shows the values of error on temperature and vapour fraction predictions.

The most important contribution for EDC purification train validation is supplied by 1,2-dichloroethane+trichloroethylene binary mixture. As Figure 4.8 displays, the original prediction describes the mixture as ideal while the two components are strongly interacting. The binary system is characterised by the presence of a low-boiling azeotrope at 82.2°C which complicates operations: conversion of this impurity to heavier components is required in order to limit 1,2-dichloroethane loss at the lights end. Figure 4.9 confirms thermodynamic consistency and prediction accuracy.

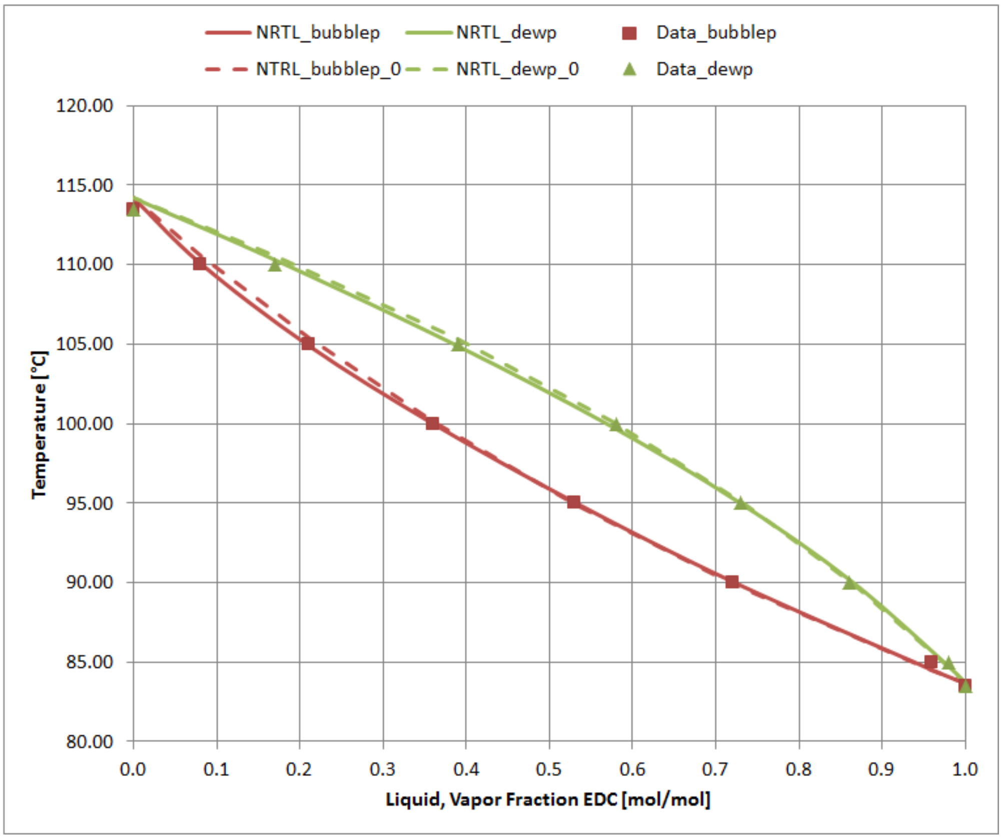

Figure 4.6: Vapour-liquid equilibrium of 1,2-dichloroethane+1,1,2-trichloroethane at 760mmHg. Comparison between NRTL model before (dashed line) and after (continuous line) fitting of experimental data.

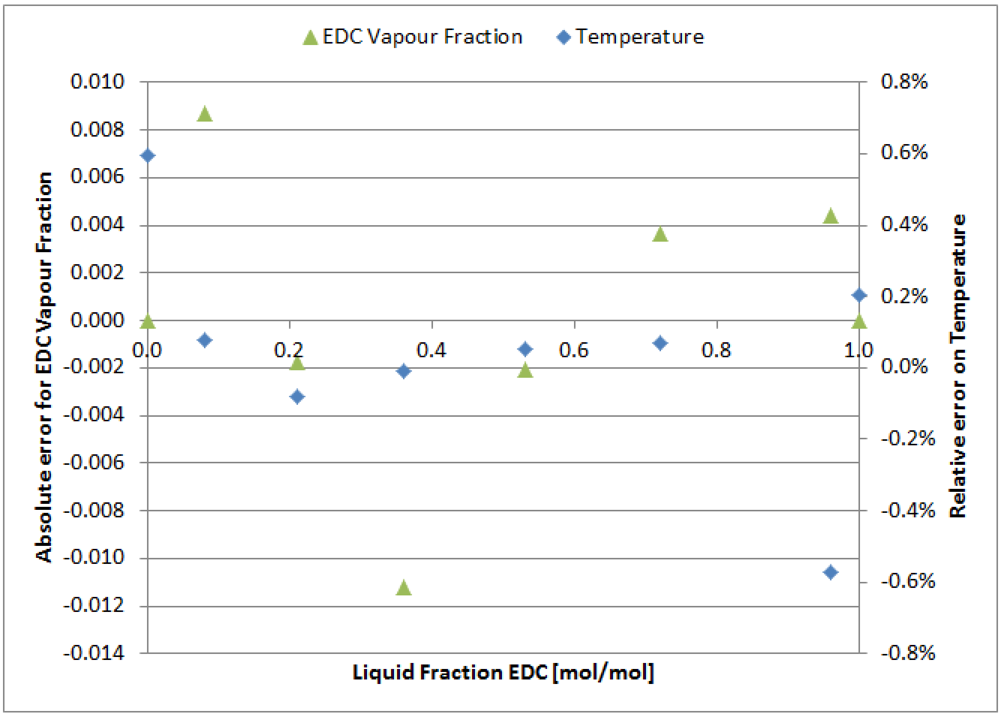

Figure 4.7: Relative error on temperature and absolute error on vapour fraction after fitting for 1,2-dichloroethane+1,1,2-trichloroethane mixture.

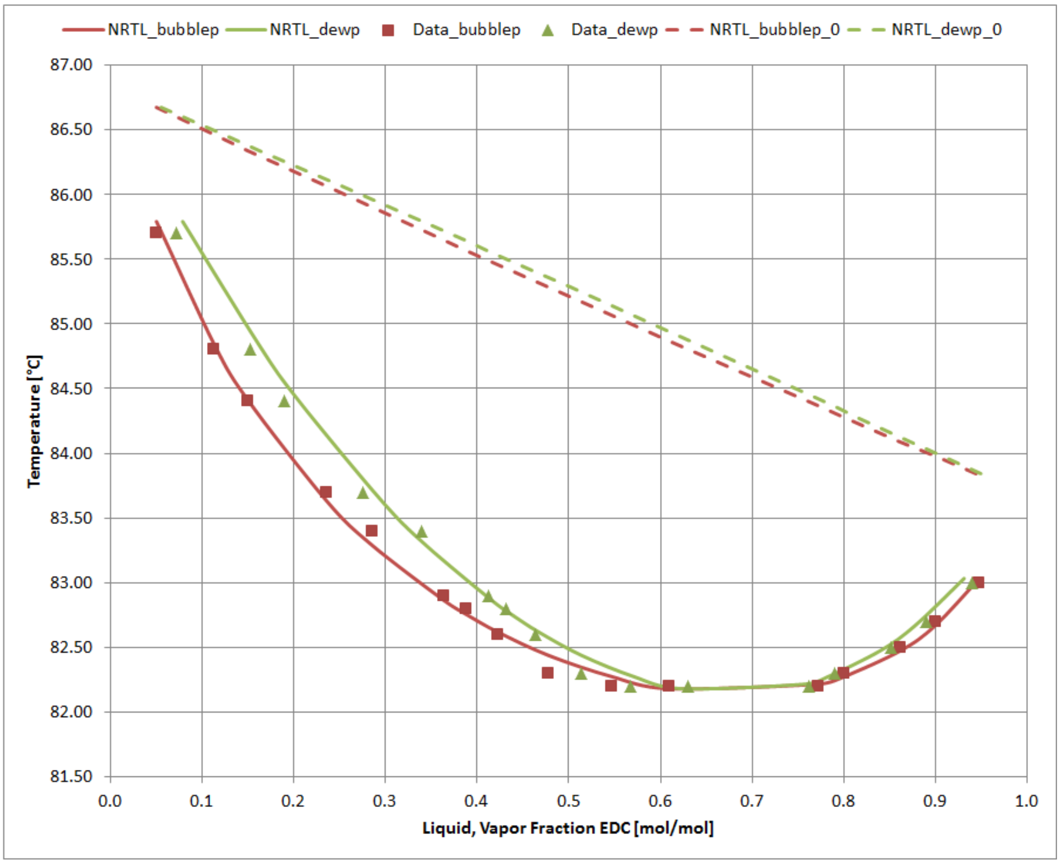

Figure 4.8: Vapour-liquid equilibrium of 1,2-dichloroethane+trichloroethylene at 760 mmHg. Comparison between NRTL model before (dashed line) and after (continuous line) fitting of experimental data.

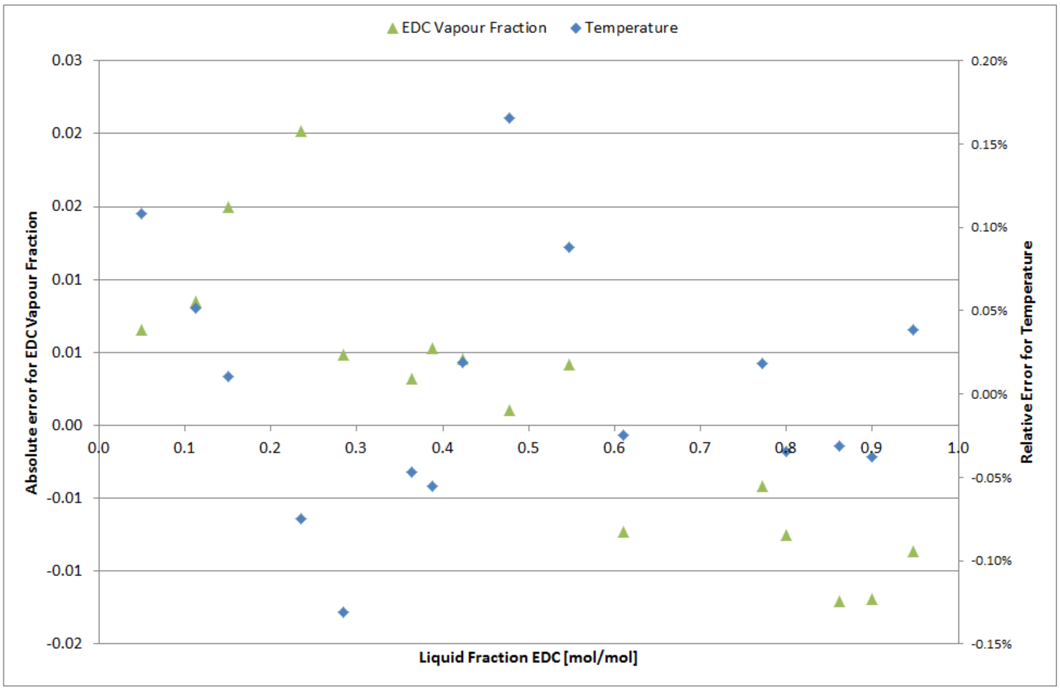

Figure 4.9: Relative error on temperature and absolute error on vapour fraction after fitting for 1,2-dichloroethane+trichloroethylene mixture.

VCM purification

For vinyl chloride purification train validation, the first analysed binary mixture is 1,2-dichlorothane+hydogen chloride because of its importance in modelling of the first column for HCl recovery. This unit operates at 11.0 bar, top and bottom temperature are respectively about -30°C and 100°C. Two vapour-liquid equilibrium data set have been fitted simultaneously: they are both isothermal and temperatures are -30°C and 0°C. Figure 4.10 and Figure 4.11 show fitting results for the set at -30°C: results for vapour-liquid equilibrium at 0°C are similar and their representation is neglected since it may appear redundant. The relative volatility is very high and the original prediction does not significantly deviate from the one adjusted with binary interaction parameters. The relative error on pressure prediction is assessed below 4% (below 3% for set at 0°C), except for the mixture rich in EDC below atmospheric pressure: for this condition relative error ranges are around 8-12%. Higher relative error values are due to very low value of pressure for mixture rich of EDC: for example, an absolute error of -0.0338 bar over an experimental value of 0.2882 bar leads to a relative error of -11.7%. It must be noticed, however, that in the simulated plant there are no mixtures at this conditions since the column for hydrogen chloride recovery operates at high pressure. Therefore, according to values of errors on the prediction of mixture rich of HCl, the result can be considered accurate. However, further tests, without considering experimental points corresponding to worst predictions, have been performed in order to reduce the relative error but the accuracy is not affected by these changes.

As stated previously, inaccuracy on vapour-liquid equilibrium prediction may be caused by pure vapour pressure erroneous estimation since its value cannot be modified by BIPs and it affects the equilibrium calculation among the entire composition range. For example, it can be noticed from Table 4.4 that, for the binary mixture just discussed, the Antoine model underestimates HCl vapour pressure and the difference between the prediction and the experimental value is about 0.3-0.5 bar. Problems on hydrogen chloride vapour pressure prediction are clear, since the same error can be found from the data for HCl+VCM binary mixture. On the other hand, as stated by Bezzo et al. (2004), the use of Soave-Redlich-Kwong equation of state model, in order to estimate pure hydrogen chloride vapour pressure, ensures higher accuracy. Further tests with SRK have been performed on the separation train in order to assess differences between simulations based on different thermodynamic models. Simulation results will be discussed in Chapter 6, but it can be said in advance that no meaningful differences were found. Table 4.5 reports the comparison between experimental data and SRK predictions for pure hydrogen chloride and vinyl chloride. It shows that absolute errors are typically lower for HCl, especially for lower temperatures. Antoine model estimation for 1,2-dichloroethane vapour pressure is accurate. Vinyl chloride vapour pressure is generally well predicted except for values at 70°C and 100°C: the latter point is the worst predicted since the absolute error is higher than 0.8 bar. In this case, the SRK EOS behaves similarly to the Antoine equation since the svinyl chloride vapour pressure is well predicted only at lower temperature by both the models according on available data.

For vinyl chloride+1,2-dichloroethane mixture solubility data at different temperatures (40, 70, 100°C) are available. Predictions at 70°C and 100°C are highly affected by the error on pure VCM vapour pressure. For example, Figure 4.13 shows the relative error on pressure prediction for fitted data for testing consistency. Relative errors seem to be not randomly distributed among composition range, and this may denote the presence of a systematic error, which in this case unfortunately cannot be corrected without additional data. First, the fitting has been performed on the entire data set available, but in order to reduce the error further analysis have been performed. Figure 4.12 shows the entire data set, the original prediction and the prediction after regression of binary interaction parameters for point that have been considered. Since VCM+EDC mixture is essential for modelling of the first and the second column of vinyl chloride purification train, their operating conditions are considered. Vinyl chloride is recovered from 1,2-dichloroethane in the second column which operates at 5 bar, the distillate is almost pure VCM at 30°C. Furthermore, the HCl recovery column, operating at 11 bar is able to achieve at the bottom a mixture made almost exclusively by VCM and EDC in equimolar amount (50-50%). For this reason it is assumed that an accurate prediction of pure vinyl chloride at higher temperature is not required for the purposes of the simulation: thus, it was decided not to consider the data above the actual operating conditions, and this allowed obtaining a higher accuracy in the temperature range of interest, without affecting the prediction of the second column. The relative error for solubility prediction at 40°C, as expected, is slightly affected by this change, but maximum errors at 70°C and 100°C can be reduced respectively from 8% to 7% and from 8% to 5%.

For the last binary mixture, four solubility data set of hydrogen chloride in vinyl chloride are available at different temperatures (-20, -10, 20 and 50°C). This mixture affects the entire vinyl chloride purification train since hydrogen chloride impurities are still present in EDC recovery column and are finally removed from the main product (and recycled) in the last finishing column. As Figure 4.14 shows, the original prediction does not differ significantly from the one adjusted with binary interaction parameters. However, as Figure 4.15 displays, accuracy is improved especially for mixture rich of VCM, whereas for remaining composition range it is basically the same.

Table 4.4: Comparison between pure vapour pressure data and prediction from Multiflash^{TM} Antoine model.

Mixture	**Pure**	**Temperature** [°C]	**Vapour Pressure** [kPa] Data	 Prediction	 Delta
EDC+HCl	HCl	-30.00	1097.64	1068.40	-29.24
		0.00	2616.88	2562.87	-54.01
HCl+VCM		-20.00	1487.00	1461.25	-25.75
		-10.00	1992.00	1953.93	-38.07
		20.00	4259.00	4206.34	-52.66
EDC+VCM	VCM	40.00	603.00	604.68	+1.68
		70.00	1257.00	1233.33	-23.67
		100.00	2312.00	2229.32	-82.68
HCl+VCM		-10.00	118.00	119.41	+1.41
		20.00	338.00	342.27	+4.72
		50.00	780.00	779.56	-0.44
EDC+HCl	EDC	-30.00	0.36	0.37	+0.01
		0.00	2.68	2.83	+0.15
EDC+VCM		40.00	21.00	20.88	-0.12
		70.00	65.00	64.99	-0.01
		100.00	164.00	163.92	-0.08

Table 4.5: Comparison between pure hydrogen chloride vapour pressure data and prediction from Multiflash^{TM} Soave-Redlich-Kwong equation of state.

Mixture	**Pure**	**Temperature** [°C]	**Vapour Pressure** [kPa] Data	 Prediction	 Delta
EDC+HCl	HCl	-30.00	1097.64	1086.15	-11.49
		0.00	2616.88	2642.12	+25.24
HCl+VCM		-20.00	1487.00	1496.45	+9.45
		-10.00	1992.00	2010.41	+18.41
		20.00	4259.00	4316.34	+57.34
EDC+VCM	VCM	40.00	603.00	602.24	-0.76
		70.00	1257.00	1226.95	-30.05
		100.00	2312.00	2225.62	-86.38
HCl+VCM		-10.00	118.00	124.93	+6.93
		20.00	338.00	344.11	+6.11
		50.00	780.00	775.18	-4.82

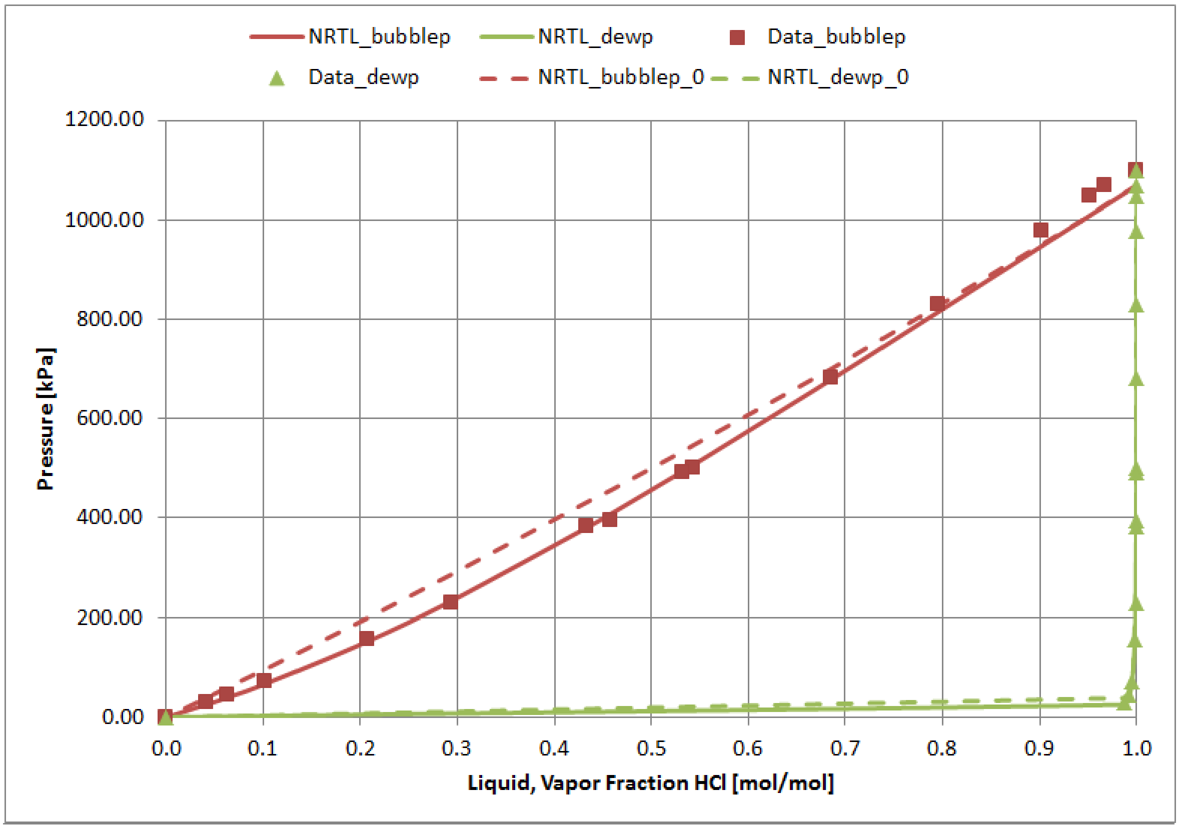

Figure 4.10: Vapour-liquid equilibrium of 1,2-dichloroethane+hydrogen chloride at temperature of -30°C. Comparison between NRTL model before (dashed line) and after (continuous line) fitting of experimental data.

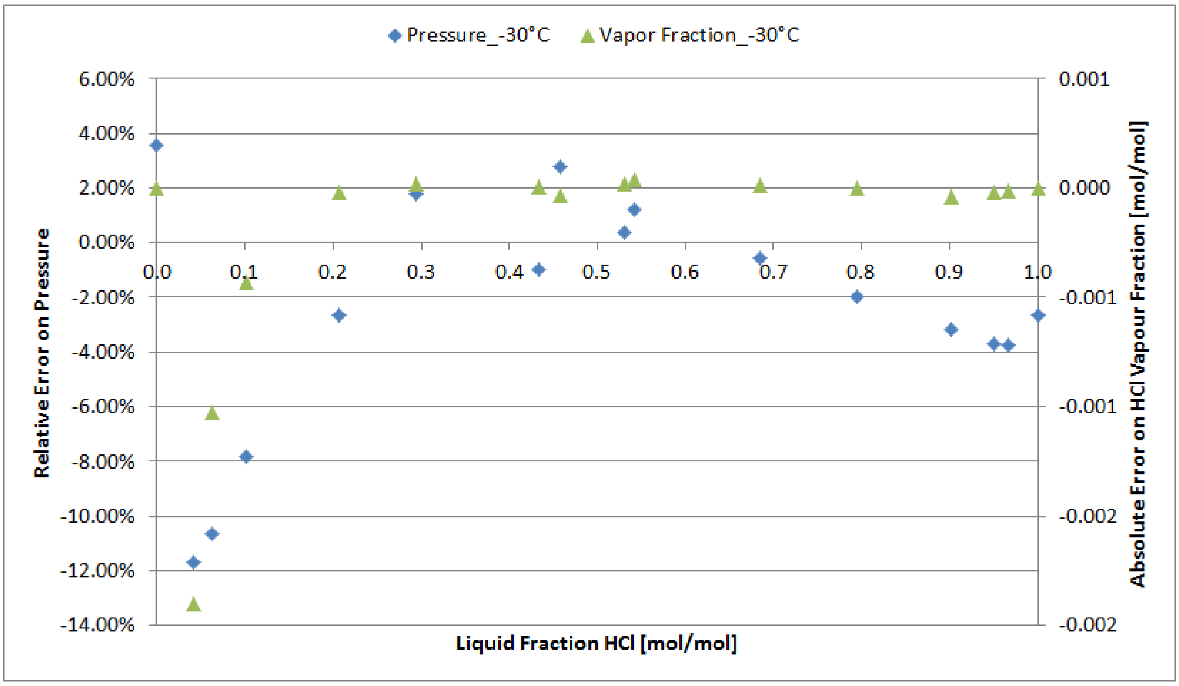

Figure 4.11: Relative error on pressure and absolute error on hydrogen chloride vapour fraction after fitting for 1,2-dichloroethane+hydrogen chloride mixture.

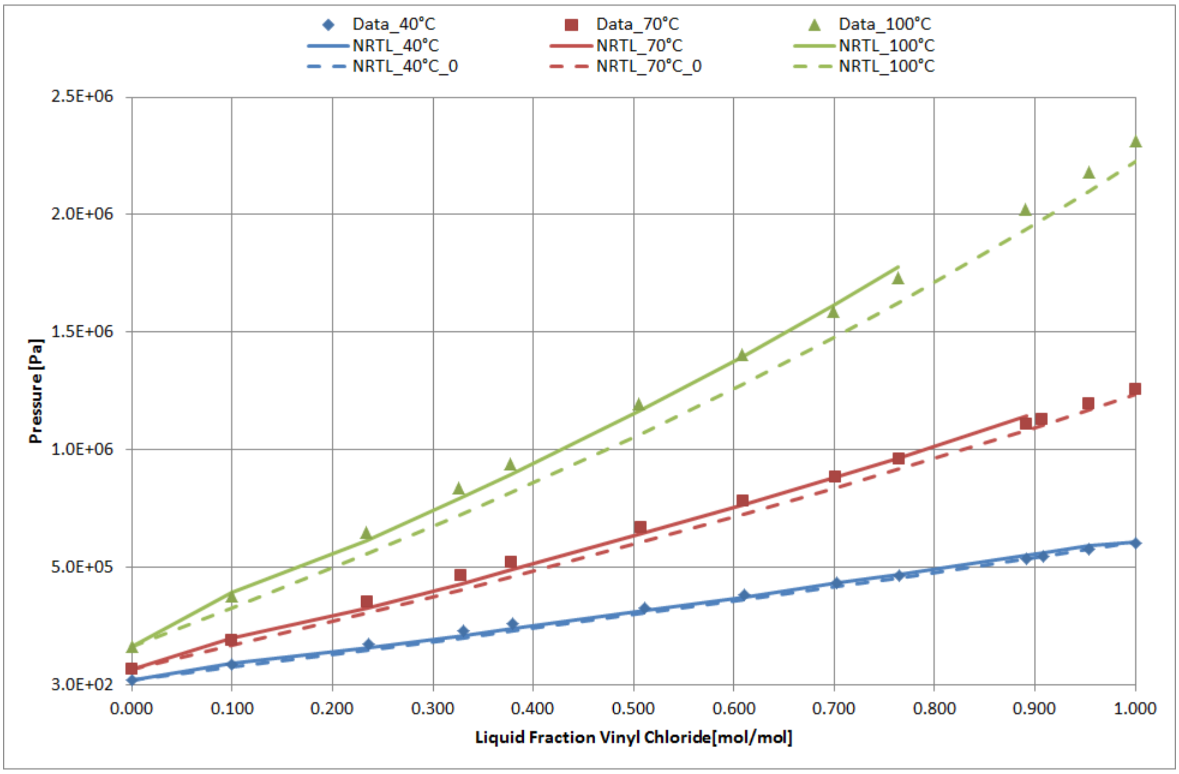

Figure 4.12: Solubility of vinyl chloride in 1,2-dichloroethane at different temperatures. Comparison between NRTL model before (dashed line) and after (continuous line) fitting of experimental data.

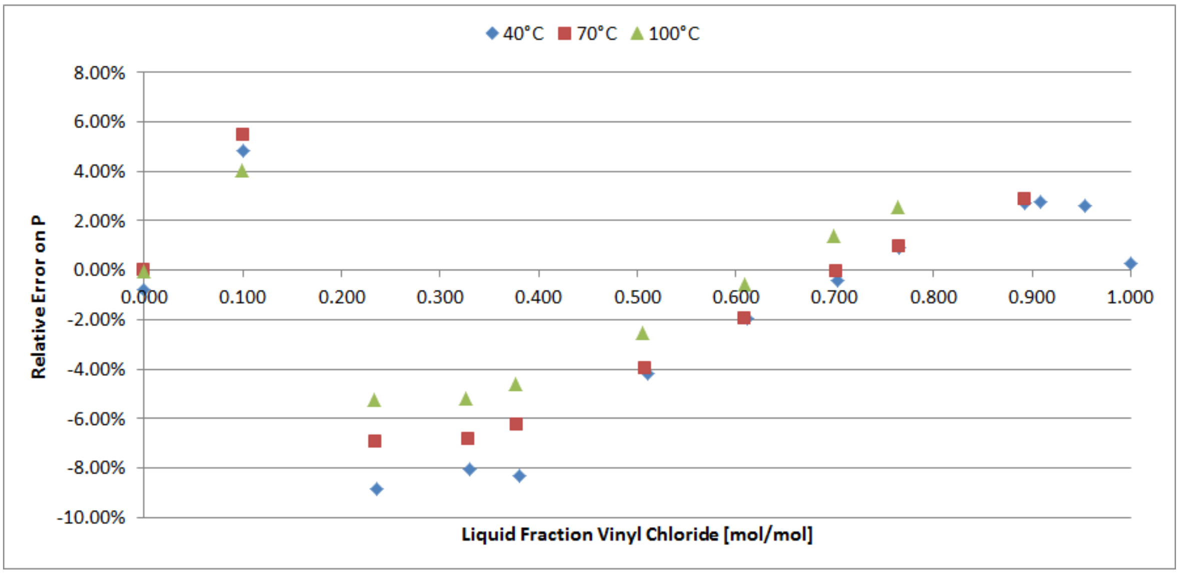

Figure 4.13: Relative error on pressure after fitting for 1,2-dichloroethane+vinyl chloride mixture.

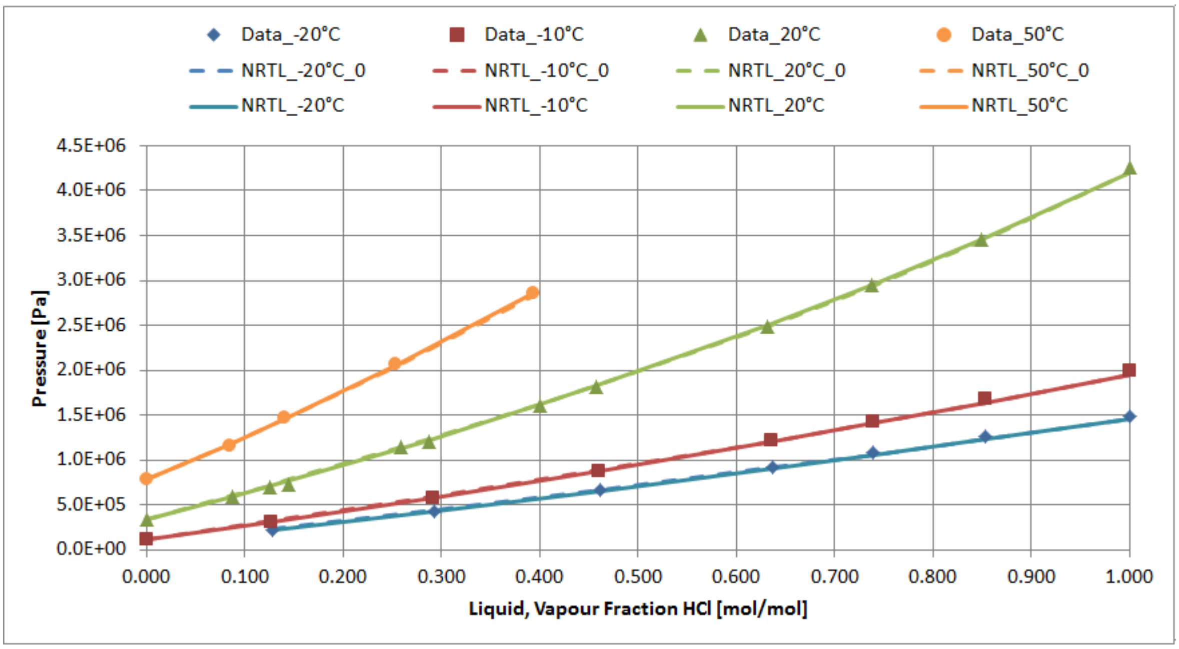

Figure 4.14: Solubility of hydrogen chloride in vinyl chloride at different temperatures. Comparison between NRTL model before (dashed line) and after (continuous line) fitting of experimental data.

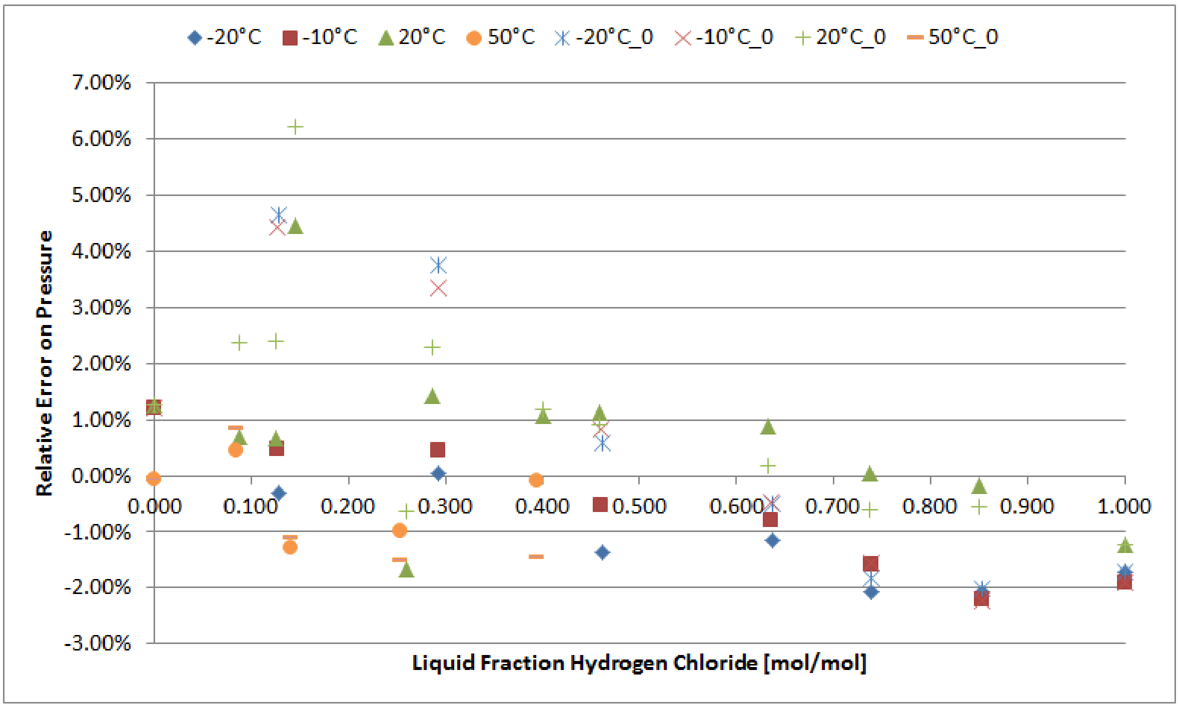

Figure 4.15: Relative error on pressure after fitting for hydrogen chloride+vinyl chloride mixture.

Chapter 5

Reactors modelling

In this chapter modelling of the three reactor units is described giving details about unit type, kinetic models and results obtained.

5.1 Direct chlorination

Direct chlorination is performed in a bubble column reactor: the liquid hold-up is composed mainly by 1,2-dichloroethane, which is the product but is also acting as solvent. Chlorine and ethylene react once dissolved in the liquid phase. In order to simulate properly the liquid hold-up, reactor_VLE_gML is used: unlike a simple stirred tank reactor, this model performs a flash calculation of the mixture simulating the vaporisation of the liquid as it happens in real practice. Reactor is assumed to be isothermally operating at 110°C and 15 psig. Feed flow-rates and composition are determined according to the case study performed by Dimian and Bildea (2008) in order to obtain a plant capacity of 300 kton/yr. Chlorine flow-rate of 20014 kg/h with 0.5%wt of oxygen is fed to the reactor, whereas ethylene is supplied with 1.0% molar excess over chlorine, which is the limiting reactant. However, an additional stream must be added in order to initialise the reactor kinetic in the liquid phase: it is a solvent flow-rate of pure 1,2-dichloroethane, but, after convergence is achieved, the flow-rate is stopped since in the real practice there is no supply of pure solvent. The pilot reactor studied by Wachi and Morikawa (1986) is taken as reference for design specifications. It is a boling bubble column composed by a riser of 6 m height with diameter equal to 0.2 m, with external loop (down-comer) of same geometry. The reaction occurs in the riser part so only this is considered in the simulation. However, the effect of design parameters has been tested by sensitivity analysis and results are presented in the following section 5.1.2.

5.1.1 Kinetic model

Direct chlorination kinetic models are available for low and high temperature chlorination, but usually tests have been performed on a restricted range of temperature, hence the choice must be accurate. Very often literature references describe kinetic models suitable for low temperature chlorination where experimental tests have been performed at 30-60°C, as for Wachi and Morikawa (1986) or Orejas (2001). For the present case, the kinetic proposed by Wachi and Morikawa (1987) is taken as reference, since the model has also been validated through experimental tests for higher temperature. However, the model they proposed is limited to the main reaction, whereas the purpose of the simulation is to predict also the by-production of 1,1,2-trichloroethane, since it is the main impurity for direct chlorination process. Therefore, simple kinetic mechanism (5.1) is considered. Kinetic parameters for side reaction were obtained from a low temperature chlorination case, but, as will be reported later, they have been adjusted in order to obtain a proper prediction.

$$\mathrm{CH_2{=}CH_2 + Cl_2 \xrightarrow{k_1} ClCH_2{-}CH_2Cl} \tag{5.1a}$$

$$\mathrm{ClCH_2{-}CH_2Cl + Cl_2 \xrightarrow{k_2} Cl_2CH{-}CH_2Cl + HCl} \tag{5.1b}$$

Addition reaction of chlorine to ethylene (5.1a) occurs through a ionic mechanism and it is catalysed by dissolved $FeCl_3$. On the other hand, side reaction (5.1b) occurs by substitution of hydrogen atom with chlorine through radical chain mechanism. The initiation of substitution reaction is usually considered thermal or photochemical. The presence of oxygen in the system, however, enhances selectivity inhibiting free-radical route: it is common to feed this component within chlorine inlet stream as 0.5-2.5 % by volume. Reaction rates expressions, on the other hand, are simplified power law equations that do not take into account the real mechanism but at the same time are suitable for prediction of reactor performance:

$$r_1 = k_1 C_{et} C_{cl} \tag{5.2a}$$

$$r_2 = k_2 C_{et} C_{cl}^2 \tag{5.2b}$$

where C_{et} and C_{cl} [kmol/m^3] are molar concentrations of ethylene and chlorine respectively, and k_j are kinetic constants calculated through the Arrhenius equation (5.3).

$$k_j = k_j^0 \exp\left(\frac{-E_{a,j}}{RT}\right) \tag{5.3}$$

As briefly mentioned above, kinetic parameters values for equations (5.2a) and (5.2b) are obtained from different references, respectively Wachi and Morikawa (1986) and Orejas (2001). Values of parameters are summarised in Table 5.1. An interesting observation on the kinetic model is derived by performing the ratio between (5.2b) and (5.2a).

$$\frac{r_2}{r_1} = \frac{k_2}{k_1} C_{cl} \tag{5.4}$$

Correlation (5.4) clearly shows that selectivity depends just on chlorine concentration and that a higher amount of Cl_2 in the liquid phase promotes substitution reaction. Furthermore, since the reaction rates are determined by dissolved gases concentration and the outlet stream depends on flash calculation, it is evident that a proper validation with data is required (see chapter 4). Above all, solubility of reactants must be predicted with accuracy for a detailed modelling, since the reaction mostly occurs within the liquid film between ethylene and the liquid mixture, and chlorine concentration directly affects selectivity.

Table 5.1: Kinetic parameters for direct chlorination process (Wachi and Morikawa, 1986) and (Orejas, 2001).

Parameter	**Value**	**u.o.m**
k_1^0	$5.36{\cdot}10^2$	$m^3{\cdot}mol^{-1}{\cdot}s^{-1}$
k_2^0	$8.517{\cdot}10^9$	$m^6{\cdot}kmol^{-2}{\cdot}s^{-1}$
$^{E_{a,1}}/_{R}$	2518	K
$^{E_{a,2}}/_{R}$	7282.21	K

5.1.2 Results

For the simulation, the work developed by Wachi and Morikawa (1986) is used as reference since it is a detail modelling of a boiling bubble column validated through experimental data on a pilot reactor. Reactor height (L) is 6 m and diameter (D) is 0.2 m. A sensitivity analysis was performed in order to check the effect of design specifications on the simulation. For example, Figure 5.1 shows that the liquid level specification slightly affects chlorine conversion and selectivity: the value 0.7 m/m has been chosen as specification. Furthermore, the reactor size has been tested keeping the aspect ratio L/D constant. Figure 5.2 proves that also size effect is negligible on the reactor performance in terms of conversion and selectivity, hence values used by the reference paper are used. At the moment, despite conversion is close enough to expected values (total conversion of chlorine can be achieved), selectivity is higher than typical values for direct chlorination: this can be due to the assumption on side reaction kinetic model but, before that, the effect of binary interaction parameters has to be tested. Simulations have been performed before and after the addition of binary interaction parameters for the following binary mixtures:

- 1,2-dichloroethane+ethylene;
- 1,2-dichloroethane+chlorine;
- 1,2-dichloroethane+1,1,2-trichloroethane.

but also this modification does not affect the reactor behaviour. Table 5.2 shows the composition of the liquid phase in the reactor: ethylene and chlorine molar fractions have respectively order of magnitude of 10^{-2} and 10^{-4} and, as proved in Chapter 4, the difference on prediction of solubility before and after binary interaction parameters addition decreases for lower concentration of gas in the mixture. Therefore, after validation of thermodynamic model through experimental data, in order to achieve a proper prediction of the direct chlorination outlet, side reaction pre-exponential factor k_2^0 has been modified in order obtain selectivity of 99%. Activation energy is kept constant since its value is mainly determined by thermodynamic properties of the system. On the other hand, pre-exponential factor is a statistical parameters which represents the probability of collision between molecules, and increasing temperature it is higher. Figure 5.3 shows how chlorine conversion is almost total but slightly increases according to this kinetic parameter and, above all, it displays that selectivity quickly decreases. 1,2-dichloroethane over ethylene selectivity of 99.00% is achieved for k_2^0 equal to $1.37{\cdot}10^{15}$ $m^6{\cdot}kmol^{-2}{\cdot}hr^{-1}$. Furthermore, a check on 1,1,2-trichloroethane production can be carried out: its amount in the outlet stream obtained from the

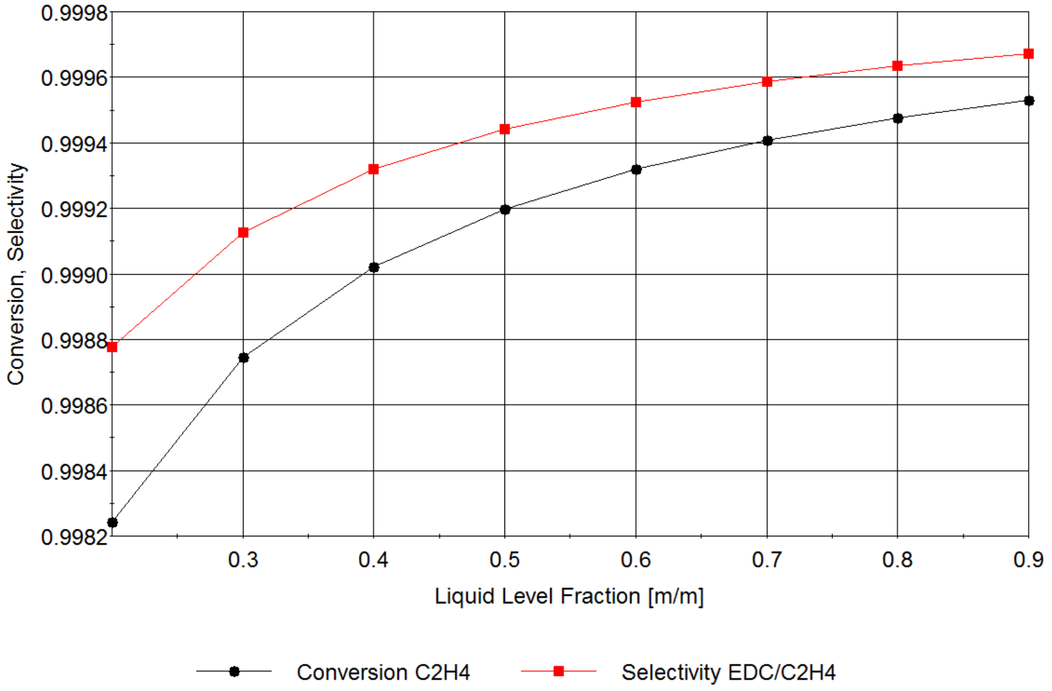

Figure 5.1: Sensitivity analysis on reactor liquid level. Effect on chlorine conversion and selectivity.

simulation is equal to 13255 ppm by wt and it is within the range of 50000-5000 ppm by wt reported by Benyahia (2005) for high temperature chlorination and 0.5% by volume of oxygen in the chlorine feed (value changes according to catalyst amount).

Thanks to the design of 1,2-dichloroethane purification section, the direct chlorination reactor has no complex interactions with other units: a stream rich in EDC from purification section is typically recycled back to the direct chlorination reactor in order to convert TRI into higher chlorinated component that are easier to remove by distillation. However, as discussed in section 2.6.1, the use of an additional reactor placed in the EDC purification section leads to several advantages and allows to avoid this recycle. Thus all the inputs to the direct chlorination reactor are source units or user specifications: therefore, the model just described is implemented without any modification in the main flow-sheet.

5.2 Oxychlorination

The fluidised-bed reactor is the most common choice for the oxychlorination process. In order to represent this system it is common to use a two-phase model considering a bubble phase and a surrounding dense phase. Furthermore in many papers where fluidised-bed operation is modelled in detail, like those proposed by Al-Zahrani et al. (2001) and Moreira and Pires (2010), a one-dimension model is implemented and it is assumed that the bubble gas phase is in a plug flow. For this reason a simple tubular reactor model seems more suitable for the purpose of the simulation. The tubular reactor is made up of a single channel with inner diameter of 0.8 m. Smooth pipe pressure drop correlation is used. Outer diameter is equal to 1.0 m: inside the

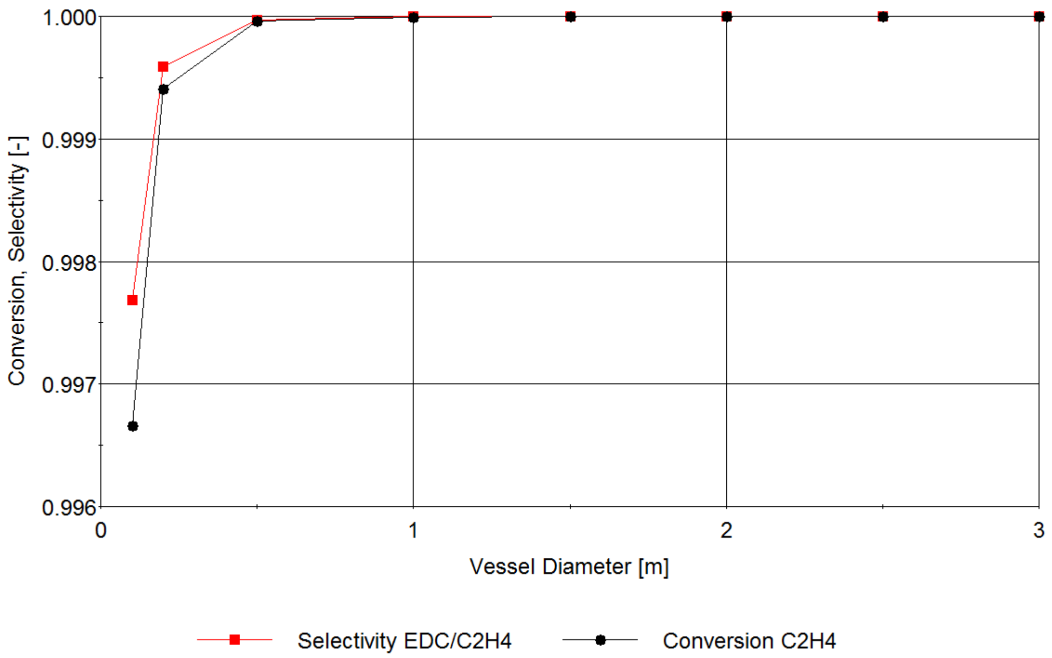

Figure 5.2: Sensitivity analysis on reactor size varying vessel diameter and keeping constant aspect ratio $^L/_D$. Effect on chlorine conversion and selectivity.

Table 5.2: Liquid phase composition in direct chlorination reactor before modification of side reaction pre-exponential factor k_2^0.

Component	**Mass fraction** $[kg/kg]$	**Molar fraction** $[mol/mol]$
oxygen	0.003578	0.010893
hydrogen chloride	0.000151	0.000403
chlorine	0.000421	0.000579
ethylene	0.003092	0.010760
1,2-dichloroethane	0.992206	0.976963
1,1,2-trichloroethane	0.000552	0.000403

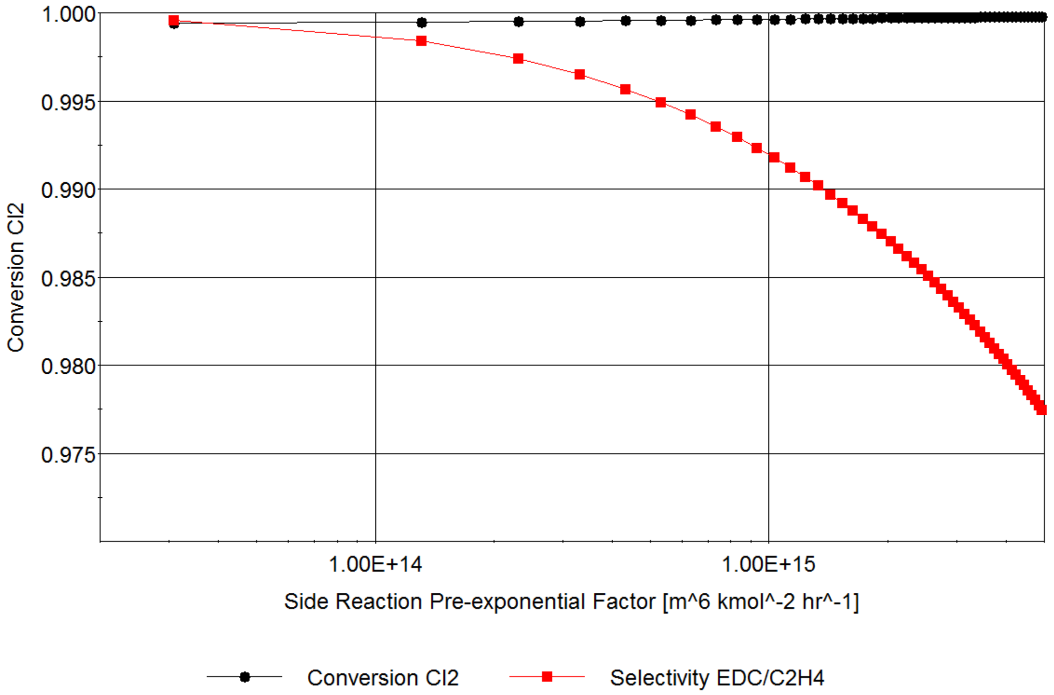

Figure 5.3: Sensitivity analysis on pre-exponential factor of side reaction k_2^0. Effect on chlorine conversion and selectivity.

Table 5.3: Design parameters for oxychlorination reactor (Al-Zahrani et al., 2001).

Parameter	**Value**	**u.o.m.**
inlet temperature	460	K
utility temperature	360	K
channel to wall heat transfer coefficient	500	$W{\cdot}m^{-2}{\cdot}K^{-1}$
bed bulk density, ($\rho_{b,bed}$)	1369	$kg{\cdot}m^{-3}$
pellet bulk density, ($\rho_{b,pellet}$)	3075	$kg{\cdot}m^{-3}$
pellet diameter, (d_p)	80	µm

shell a constant temperature utility is used in order to remove the heat of reaction. The catalyst is considered fixed, therefore the unit is actually modelled as a fixed-bed reactor where pellets have spherical shape. However, fluidised-bed behaviour still can be properly represented since, according to heat transfer specifications, near-isothermal operation can be achieved, as it is made in practice through fluidisation. Heat transfer specifications and catalyst properties are chosen according to the work developed by Al-Zahrani et al. (2001) and are summarised in Table 5.3. The length of the reactor is not specified since it is adjusted in order to reach a desired conversion of hydrogen chloride. Inlet flow-rates are estimated according to the overall mass balance from Dimian and Bildea (2008), a case study for a 300kton/yr capacity plant; therefore a scale-up is not required when the reactor is implemented in the main flow-sheet.

5.2.1 Kinetic model

The oxychlorination kinetic mechanism has been discussed in section 2.3, drawing also attention to the ethylene adsorption, since it is considered as rate-determining step. As a consequence, the oxychlorination reaction is usually represented through a Langmuir-Hinselwood kinetic model, as suggested by Wachi and Asai (1994), where the reaction rate depends on catalyst concentration, adsorbed ethylene amount and is not directly influenced by hydrogen chloride or oxygen concentrations. On the other hand, the representation of by-products formation is required and usually this is achieved by implementation of a simpler model, as power law model. Therefore, the molecular mechanism applied for the simulation of oxychlorination process is proposed by reactions set (5.5). Of course it is not the real mechanism, but it is simpler and above all is able to represent properly the system.

$$\mathrm{CH_2{=}CH_2 + 2\ HCl + 0.5\ O_2 \xrightarrow[CuCl_2]{k_1} ClCH_2{-}CH_2Cl + H_2O} \tag{5.5a}$$

$$\mathrm{ClCH_2{-}CH_2Cl + HCl + 0.5\ O_2 \xrightarrow{k_2} Cl_2CH{-}CH_2Cl} \tag{5.5b}$$

$$\mathrm{CH_2{=}CH_2 + 3\ O_2 \xrightarrow{k_3} 2\ CO_2 + 2\ H_2O} \tag{5.5c}$$

$$\mathrm{4\ HCl + O_2 \xrightarrow{k_4} 2\ Cl_2 + 2\ H_2O} \tag{5.5d}$$

Reaction (5.5d) is also called Deacon reaction and it is required since side reaction rates are controlled by the partial pressure of chlorine in the system. Therefore, the kinetic model is reported by following expressions of reaction rates r_j:

$$r_1 = \frac{k_1 K_a C_c P_{et}}{RT + K_a P_{et}} \tag{5.6a}$$

$$r_2 = k_2 P_{edc} P_{cl}^{1/2} \tag{5.6b}$$

$$r_3 = k_3 P_{ox} P_{et} P_{cl}^{1/2} \tag{5.6c}$$

$$r_4 = k_4 P_{ox} P_{cl}^{-1} \tag{5.6d}$$

where P_i [bar] is the partial pressure of generic component i: oxygen (ox), ethylene (et), 1,2-dichloroethane (edc) and chlorine (cl). Furthermore, K_a [m^3_{cat}/mol] is the adsorption constant, C_c [mol/m^3_{cat}] is the concentration of cupric chloride in the catalyst and k_j are kinetic constants calculated from Arrhenius equation (5.3). Table 5.4 summarises all the values of the kinetic parameters used for the modelling.

Since two different kinetic models are used at same time, i.e. Langmuir-Hinshelwood (5.6a) and power law, it is necessary to implement a custom kinetic model in the project file. Furthermore, for the specific case the custom kinetic model allows to avoid numerical errors due to the reaction order of chlorine in the reaction (5.6d). Since there is no chlorine in the feed, a division by zero may occur. Therefore, the partial pressure of chlorine in the model has been replaced by the following function: `MAX( x('CHLORINE'), 1e-10)`. The core of the custom kinetic model is reported in Appendix A: at first required parameters have been added to default gPROMS parameters, then in the `SET` section their values are assigned and stoichiometric matrix is defined. Once parameters have been set in the `EQUATION` sections the kinetic model

Table 5.4: Kinetic parameters for oxychlorination process (Moreira and Pires, 2010).

Parameter	Value	u.o.m.
K_a	0.63	$m^3_{cat}\cdot mol^{-1}$
C_c	[1]993	$mol\cdot m^{-3}_{cat}$
k^0_1	269	s^{-1}
k^0_2	$1.4\cdot 10^5$	$kmol\cdot m^{-3}_{cat}\cdot s^{-1}\cdot Pa^{-1.5}$
k^0_3	$5.2\cdot 10^{-5}$	$kmol\cdot m^{-3}_{cat}\cdot s^{-1}\cdot Pa^{-2.5}$
k^0_4	$0.28\cdot e^{11.73}$	$kmol\cdot m^{-3}_{cat}\cdot s^{-1}$
$E_{a,1}$	37800	$J\cdot mol^{-1}$
$E_{a,2}$	128040	$J\cdot mol^{-1}$
$E_{a,3}$	112000	$J\cdot mol^{-1}$
$E_{a,4}/R$	14594.8	K

has been easily implemented. At the same time the Arrhenius equation for the kinetic parameter calculation is implemented with a logarithmic expression: the same form is applied for the specification of the adsorption constant.

5.2.2 Results

The first simulation has been tested according to the pilot plant data supplied by Al-Zahrani et al. (2001) even if it is an air-based process: the inlet is composed by ethylene and hydrogen chloride in stoichiometric ratio at 400 kPa. Hydrogen chloride over oxygen ratio is equal to 3.5, so the latter is clearly in excess. Therefore, it is specified a conversion of hydrogen chloride of 99.3%. Other specifications were assumed as discussed above. The result shows that the reactor behaviour is almost isothermal and the temperature profile along the channel is displayed in Figure 5.4. Furthermore, ethylene conversion is calculated as 98.2% when pilot plant data achieved 98.3% (-0.1% error). The inner diameter has been chosen according to a sensitivity analysis on ethylene conversion, selectivity and tube length: hydrogen chloride conversion value is fixed at 99.3%. Tube diameter value ranges between 0.3-1.0 m: Figure 5.5 shows that the effect on ethylene conversion and selectivity is negligible since curves are flat. However, as confirmed by Figure 5.6, the tube length significantly varies according to the inner diameter in order to reach specifications. Therefore, since according to Moreira and Pires (2010) bed height is 11.1 m (minimum fluidisation height is 8.1 m), the value of inner diameter equal to 0.8 m properly represents this condition and it is chosen as design specification. The oxychlorination reactor for vinyl chloride plant simulation is modelled according this specification, even if its feed is not exactly the same: first of all, hydrogen chloride feed is a recycle stream, hence its flow-rate and composition depend on the pyrolysis outlet and purification columns results. Furthermore, ethylene and hydrogen chloride are not in stoichiometric ratio but the hydrocarbon is fed with excess, since the flow-sheet simulates an oxygen-based oxychloriantion process.

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[1] Value of $CuCl_2$ concentration in catalyst is obtained from Wachi and Asai (1994) who are, however, used as reference by Moreira and Pires.

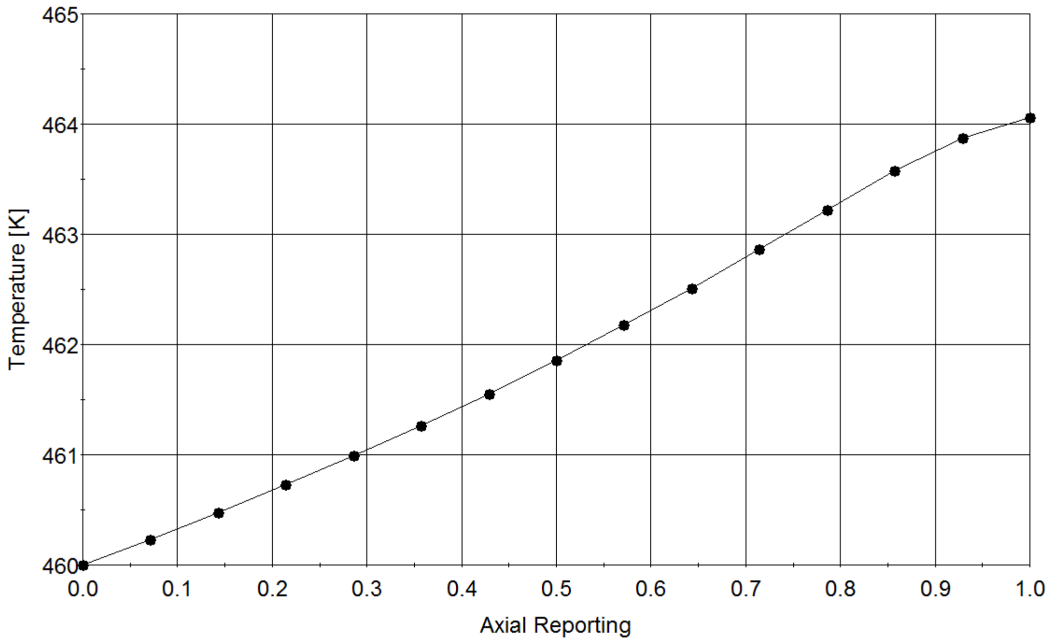

Figure 5.4: Oxychloriantion reactor temperature profile. Simulation performed with stoichiometric feed ratio between HCl and ethylene.

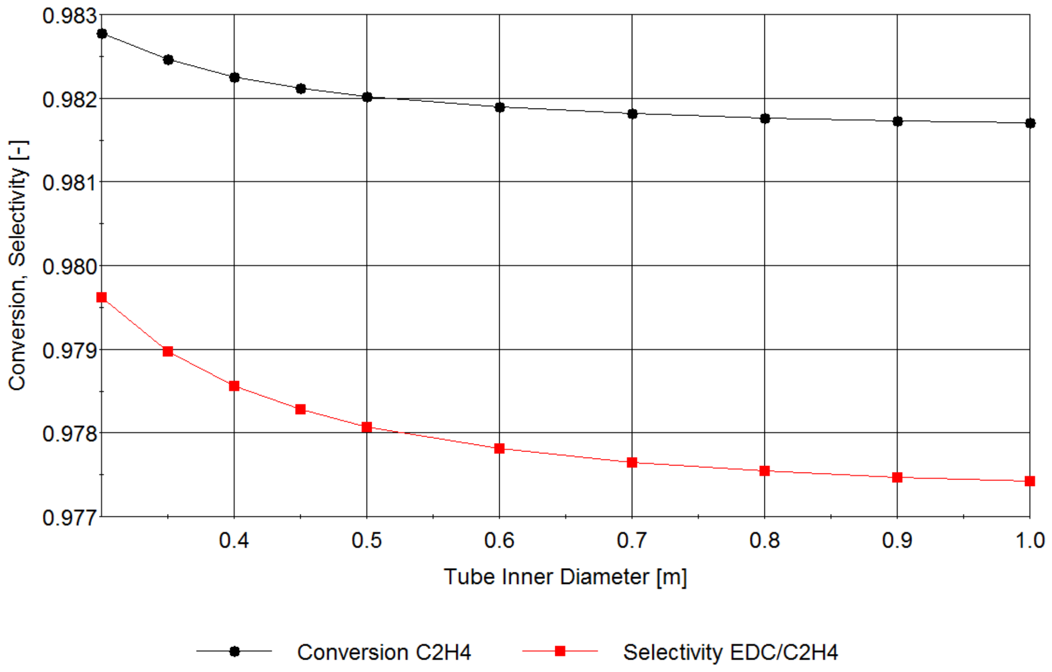

Figure 5.5: Oxychlorination reactor sensitivity analysis on tube inner diameter. Effect on ethylene conversion and 1,2-dichloroethane selectivity.

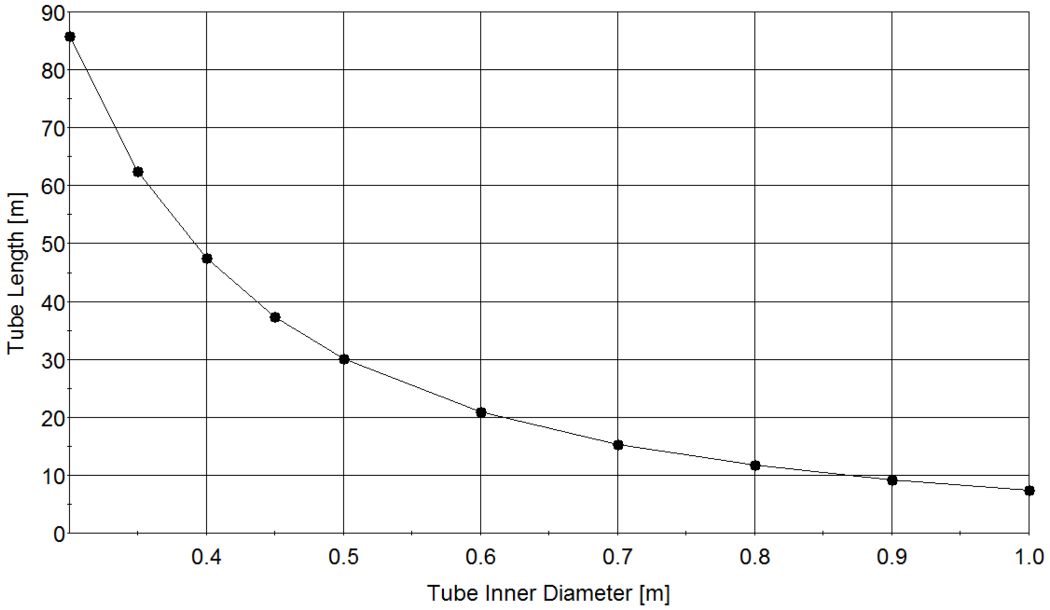

Figure 5.6: Oxychlorination reactor sensitivity analysis on tube inner diameter. Effect on tube length.

5.3 Pyrolysis

Since the real furnace is made by one or a series of coils the plug flow reactor is the typical choice for simulating the pyrolysis reactor. In the specific case the unit tubular_reactor_gML has been implemented: it is a one-dimensional model in which mass, energy and momentum balances are solved according to the axial direction. Tubular reactor geometry specifications have been supplied according to the case study by Dimian and Bildea (2008) and simulation outputs at first have been compared to their results. Tubular reactor is made by 16 channel with inner diameter equals to 0.1 m. The reactor length is adjusted according to the specified conversion, fixed at 51%. The heat is removed using an utility at constant temperature equal to the suggested reaction temperature (530°C): an high utility flow rate (100 kg/s) is specified in order to ensure this condition. Furthermore, in order to properly predict impurities, two conversion reactors have been added: Figure 5.7 shows the detail of the pyrolysis unit from the flow-sheet, stressing the need of a recycle breaker unit between the conversion reactors (circled in red). Since the tubular reactor length is adjusted according to conversion, during initialisation the stream, that is fed to the last conversion reactor, varies in flow-rate and composition but, due to the tight specifications of this reactor, an error can occur. The recycle breaker ensures the proper work of the conversion reactor since it is closed after that tubular reactor specified conversion has been achieved.

5.3.1 Kinetic model

The pyrolysis kinetic mechanism is radical, such as the simplified one reported by reaction set (5.7), and it involves several different species and several elementary

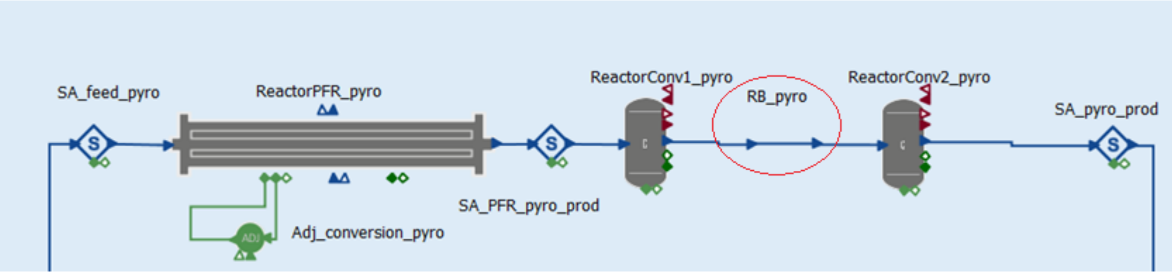

Figure 5.7: Detail of reactors system used for the simulation of EDC cracking furnace.

reactions:

$$\text{EDC} \longrightarrow \text{ClCH}_2\text{—}\dot{\text{C}}\text{H}_2 + \text{Cl}\cdot \tag{5.7a}$$

$$\text{Cl}\cdot + \text{EDC} \longrightarrow \text{ClCH}_2\text{—CHCl}\cdot + \text{HCl} \tag{5.7b}$$

$$\text{ClCH}_2\text{—CHCl}\cdot \longrightarrow \text{VCM} + \text{Cl}\cdot \tag{5.7c}$$

The reaction mechanism of dichloroethane cracking is extremely complex and, as a consequence, also kinetic models able to predict it can be highly complex. For example the kinetic model proposed by Borsa (1999) involves 818 elementary reactions and 135 species, of which 64 are radical. Even though radical kinetic models are essential for a rigorous simulation of the cracking furnace, simple molecular mechanisms have been proposed in order to reduce the complexity and to decrease computational time. Furthermore, due to the high selectivity of the pyrolysis reactor they can also predict properly its behaviour and by-product formation, if the detail level required for the simulation is not too high and the number of species is limited. Since the aim of this thesis is to model the whole plant and not just a specific unit, a molecular model has been chosen in order to represent the key reactions of the pyrolysis process. It is made by three irreversible reactions: beside the main reaction (5.8a), it predicts the rate of formation of acetylene by vinyl chloride cracking (5.8b) and the by-production of ethylene and chlorine (5.8c).

$$\text{ClCH}_2\text{—CH}_2\text{Cl} \longrightarrow \text{CH}_2\text{=CHCl} + \text{HCl} \tag{5.8a}$$

$$\text{CH}_2\text{=CHCl} \longrightarrow \text{C}_2\text{H}_2 + \text{HCl} \tag{5.8b}$$

$$\text{ClCH}_2\text{—CH}_2\text{Cl} \longrightarrow \text{C}_2\text{H}_4 + \text{Cl}_2 \tag{5.8c}$$

Reaction rates are calculated through a power law model (5.9) in which kinetic constants are estimated according to the Arrhenius equation (5.3). Values of kinetic parameters are reported in Table 5.5.

$$r_j = k_j \prod_{i=1}^{NC} C_i^{n_{ij}} \tag{5.9}$$

Reaction rates are of first-order since it is assumed that the mechanism is purely molecular and reaction are irreversible.

The impurities prediction, however, is completed by the use of two conversion reactors working in series according to stoichiometry and conversion proposed in the case

Table 5.5: Kinetic parameters for 1,2-dichloroethane pyrolysis (Dimian and Bildea, 2008).

Reaction	**Pre-exponential factor** $[s^{-1}]$	**Activation Energy** $[cal \cdot mol^{-1}]$
(5.8a)	$1.14{\cdot}10^{14}$	58000
(5.8b)	$5.00{\cdot}10^{14}$	69000
(5.8c)	$1.00{\cdot}10^{13}$	72000

Table 5.6: Conversion specification and reference reactant for conversion reactors (Dimian and Bildea, 2008).

Reaction	**Reference reactant**	**Conversion** [%]
(5.10a)	acetylene	50
(5.10b)	1,2-dichloroethane	100-$S_{\%}$
(5.10c)	chlorine	50
(5.10d)	chlorine	20
(5.10e)	chlorine	30

study by Dimian and Bildea. These two reactors are called ReactorConv1_pyro and ReactorConv2_pyro in the flow-sheet, as Figure 5.7 shows. The first reactor predicts the formation of chloroprene (5.10a) and 1,4-dichlorobutane (5.10b). On the other hand, the second reactor is required for simulating the complete conversion of chlorine and the by-production of 1,1,2-trichloroethane ((5.10c) and (5.10d)) and trichloroethylene (5.10e):

$$C_2H_2 + \mathrm{VCM} \longrightarrow C_4H_5Cl \tag{5.10a}$$

$$2\ \mathrm{EDC} \longrightarrow C_4H_8Cl_2 \tag{5.10b}$$

$$\mathrm{VCM} + Cl_2 \longrightarrow C_2H_3Cl_3 \tag{5.10c}$$

$$\mathrm{EDC} + Cl_2 \longrightarrow C_2H_3Cl_3 + HCl \tag{5.10d}$$

$$C_2H_2 + 2\ Cl_2 \longrightarrow C_2HCl \tag{5.10e}$$

Table 5.6 shows the inputs of the two conversion reactors. The value of selectivity S required for 1,4-dichlorobutane production is calculated through the following correlation (Dimian and Bildea, 2008):

$$S = 0.989 + 0.0506X - 0.0652X^2 \quad \text{for} \quad 0.4 < X < 0.65 \tag{5.11}$$

where variable X is the EDC conversion in the tubular reactor and is fixed at 51%.

5.3.2 Results

The first simulation is performed by supplying an initial flow rate of 73000 kg/h pure 1,2-dichloroethane at a reaction temperature of 530°C and 18 bar. Table 5.7

Table 5.7: Simulation results in terms of outlet mass fraction. Expected values from Dimian and Bildea (2008).

Component	**Results** $[kg/kg]$	**Expected** $[kg/kg]$	**Rel Error** [%]
1,2-dichloroethane	0.49890	0.48923	2.0
vinyl chloride	0.31478	0.32110	2.0
hydrogen chloride	0.18461	0.18812	1.9
acetylene	0.00010	0.00007	41.1
chloroprene	0.00040	0.00032	25.6
1,1,2-trichloroethane	0.00047	0.00040	18.8
1,4-dichlorobutane	0.00064	0.00063	1.8
trichloroethylene	0.00010	0.00014	27.3

summarises results of the simulation comparing the two outlet compositions. The relative error for the main component is around 2%, while the lower error is for the dichlorobutane, confirming reliability of the kinetic model and of correlation (5.11). On the other hand, the relative error for other impurities is larger but this does not affect the whole plant simulation: in fact, in absolute terms the error for those component ranges between 30 and 80 ppm by wt. Furthermore, the tube length at which 51% conversion is achieved is equal to 280 m, while in the case study used as reference it is 250 m (12.2% relative error).

The unit as described is implemented in the flow-sheet: inlet temperature and pressure are controlled by a pump and a heater before the reactor in order to feed the purified 1,2-dichloroethane at 530°C and 18 bar. The actual flow-rate is higher with respect to the one used for the test: a proper scale-up is required but, in order to realise it, more accurate specifications on heat transfer system are needed. Therefore, also in the flow-sheet the length of the reactor is adjusted in order to reach the desired conversion, and it is the only design variable that has been modified: however, the mass balance results are still consistent with the available data. Figure 5.8 shows the tubular reactor composition profile for main components involved.

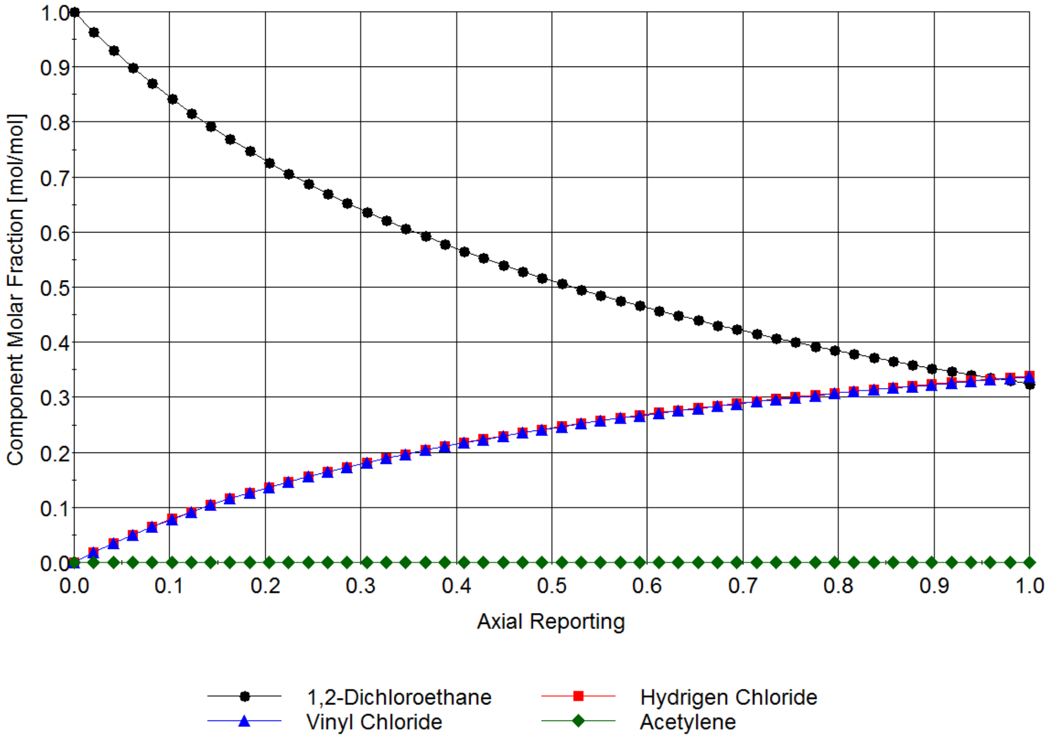

Figure 5.8: Component molar fraction profile along the reactor. Outlet composition is almost equimolar for main component HCl, VCM and EDC.

Chapter 6

Separation units ùmodelling

In this chapter modelling of quench section and distillation trains for vinyl chloride and 1,2-dichloroethane purification are described in detail and simulation results are reported. The flow-sheet structure is presented starting from the simplified initial scheme up to the final configuration, discussing also the order for recycle closure.

6.1 Quench

The quench section immediately follows the pyrolysis reactor since it has to cool down quickly the effluent in order to avoid undesired side reactions. On the other hand, cooling allows heavy components to condense achieving a first separation of the product stream. In real practice, coke and tars are removed basically filtering the liquid at the bottom of the quench tower: if an high-detailed model for the cracking were used, taking into account coking phenomena, the quench section would include a solid removal system. However, the quench section is essential in order to represent properly the feed condition for the downstream distillation column which is required for hydrogen chloride recovery. The scheme shown in Figure 6.1 represents the real configuration reported previously in Figure 2.10*b* where the furnace effluent is quenched with a liquid stream obtained by a downstream flash. The same flash unit supplies a vapour stream and a liquid stream to the distillation column for hydrogen chloride recovery. Pyrolysis outlet pressure is slightly lower than 18 bar since smooth pipe pressure drop correlation is used but the quench section is assumed to operate at lower pressure. Thus a valve reduces the value to 11 bar, which is the same operative pressure of the HCl recovery column. The stream, obtained by mixing the pyrolysis effluent and part of the liquid coming from the downstream flash, is cooled down to 315.15 K and the adiabatic flash splits vapour and liquid phase. High flow-rates of liquid are usually applied in order to quench effluents, therefore the split fraction specification for the splitter unit is specified as 0.9. A recycle breaker unit is required in order to supply proper initial guesses during initialisation procedure.

After modelling the quench section, a simplified flow-sheet can be implemented and considered as a starting point for the whole plant model (see Figure B.1 in Appendix B). The flow-sheet at this point is made up with three reactor units modelled as described in the previous chapter and a quench section: all separation steps are described by component splitters in order to close all recycle streams and achieve purity specifications. This scheme is useful for the identification of the two main recycle streams involved in the process and, above all, for a general comprehension of interactions

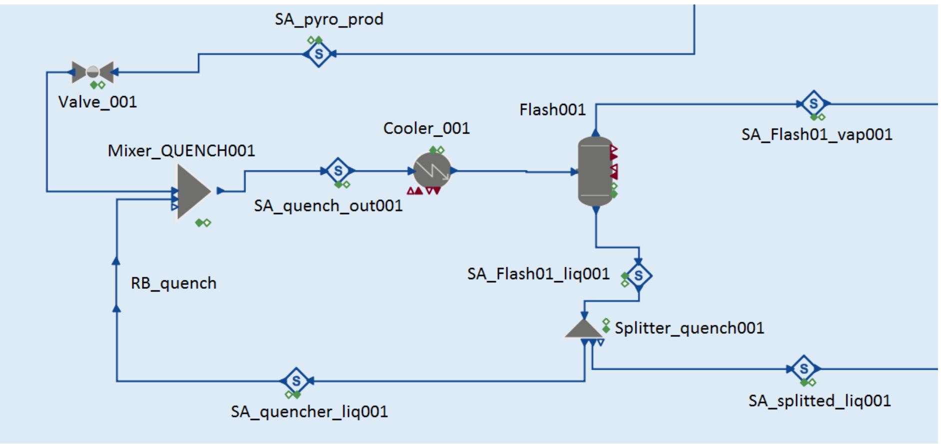

Figure 6.1: Quench section, detail of flow-sheet. Effluent from the pyrolysis is mixed with the liquid coming from the downstream flash and cooled.

between units. For instance, once initialisation with open recycles breakers has been completed, it is required to close these units sequentially since convergence problems may be caused by infeasible specifications in combination with recycles loops. At this level, with a simplified system, to establish a proper sequence or at least a guide line for the recycle breakers closure is essential for obtaining more easily a solution when complexity will increase due to rigorous distillation models and smaller recycle loops.

6.1.1 Results

Simulation results are compared to values reported by Best (1996) in terms of weight fraction of the three main components involved in this section of the plant: 1,2-dichloroethane, vinyl chloride and hydrogen chloride. It is clear that a pre-fractionation step before distillation column leads to a rough separation between the lightest (HCl) and the heaviest component (EDC). This is helpful to the HCl column since the vapour feed contains just a small amount of 1,2-dichloroethane and hydrogen chloride content in the liquid stream is limited. Table 6.1 reports results of the simulation compared with reference values. Evaluation is based on the streams that are actually fed to the column: the liquid stream coming from the flash unit is mixed with the recycle coming from the product column, whereas the vapour stream is directly supplied to the feed tray. Maximum absolute errors for the simulation are -2.66 and +2.48 in mass fraction percentage for hydrogen chloride respectively in the vapour and liquid phase. The prediction can be considered accurate, but at the same time it is clear that the recovery of HCl in the vapour stream should be higher.

6.2 1,2-Dichloroethane purification

The purification of 1,2-dichloroethane is essential since all impurities are vented in this section. However, chlorination reactors outlets are mixed and pre-treated before the distillation train. Two component splitters are exploited in order to dry and remove very light components. The first component splitter simulates a caustic soda washing and drying, hence it is assumed that the entire amount of water, with unconverted chlorine and hydrogen chloride, leaves the process. Dry EDC is then supplied to the

Table 6.1: Composition of vapour and liquid stream fed to the HCl column. Comparison between values obtained from simulation and US patent by Best (1996).

Component	**Reference** [%wt]	**Simulation** [%wt]	**Delta** [%wt]
	Vapour stream		
1,2-dichloroethane	1.96	2.70	+0.74
vinyl chloride	30.24	32.13	+1.89
hydrogen chloride	67.80	65.14	-2.66
	Liquid stream		
1,2-dichloroethane	53.96	52.69	-1.27
vinyl chloride	37.42	36.00	-1.42
hydrogen chloride	8.61	11.09	+2.48

following component splitter which simulates the degasser unit for the recovery of very light components from the main stream: since oxychlorination process is oxygen-based, this unit allows to recycle unconverted ethylene and oxygen back to the reactor. Only 10% of the gas stream is actually vented. Pre-treatments are performed at 1.2 bar and 365 K. Finally, the EDC stream coming from chlorination is mixed with the recycle stream coming from the vinyl chloride purification section and sent to the first light distillation column (Light1). Figure 6.2 shows the modelling of distillation section according to alternative B, previously discussed in section 2.6.1. The distillate stream of the first distillation column is sent to a chlorination reactor for chemical conversion of residual trichloroethylene, then EDC loss is reduced from the additional light column (Light2). Light impurities are vented and EDC with new heavy species are recycled back to the beginning of the section. Accumulation problems of TRI in the first light column were not spotted and purity specification can be achieved easily with the supplied operative specifications. Typically this problem is solved by recycling a side stream rich in EDC and TRI from column Light1 to the direct chlorination reactor in order to convert the impurity to higher chlorinated components that are easier to remove (see Figure 2.12), but in this case it is not required. Chlorination of trichloroethylene is performed in the additional reactor placed between columns Light1 and Light2. Heavies are removed in two columns: the first (Heavy1) allows to achieve the purity specification for EDC, whereas the second (Heavy2) limits its loss. Table 6.2 summarises design specifications for each column. Main columns Light1 and Heavy1 simply operate at the same pressure 1.2 bar, without requiring any intermediate compression, whereas Light2 and Heavy2 columns operate respectively at 1.1 and 0.2 bar according to Groenendijk (2000).

Each unit is modelled as a rigorous distillation column where mass and energy balances are performed for each tray assuming equilibrium. Set of equations is referred as the MESH equations since material balance (M), phase equilibrium relation (E), mole fraction summation (S) and energy balance (H) are calculated. In the condenser and the reboiler units it is also assumed that the vapour-liquid equilibrium is achieved: in fact, they are taken into account as ideal stages. Furthermore, pressure is assumed to be constant among the entire column. For higher detailed modelling of these units, pressure drop and Murphy efficiency correlations can be very easily implemented but further information from real practice are required.

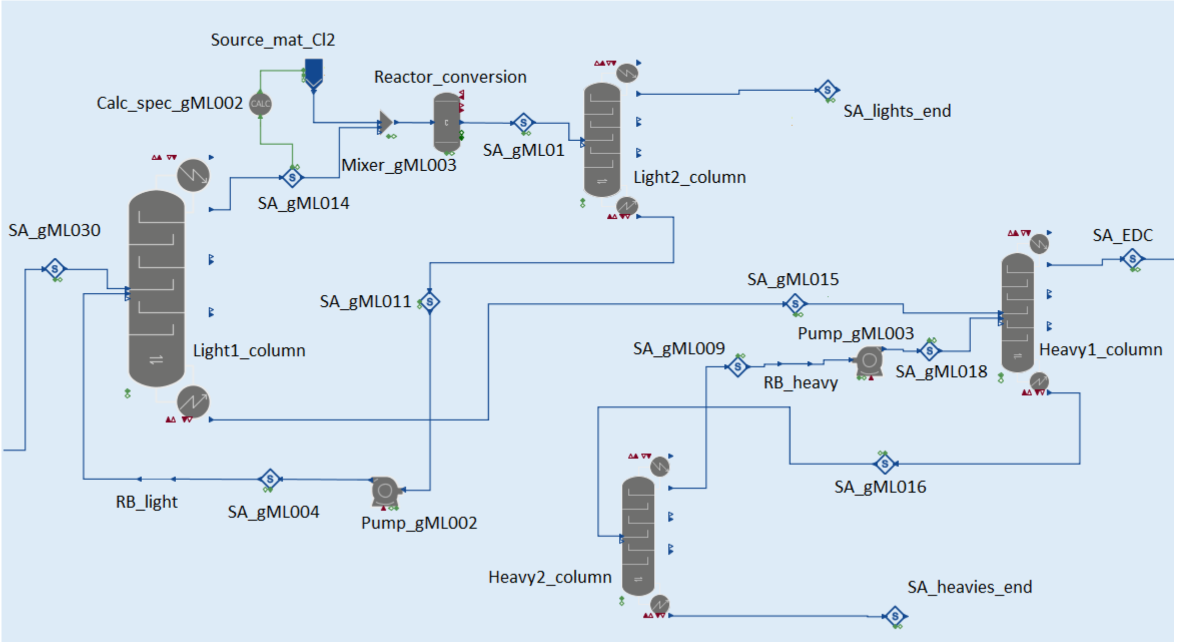
Source_mat_Cl2
Reactor_conversion
Calc_spec_gML002
CALC
Mixer_gML003
SA_gML01
Light2_column
SA_lights_end
SA_gML014
SA_gML030
Light1_column
SA_gML011
SA_gML015
SA_EDC
Pump_gML003
SA_gML009
RB_heavy
SA_gML018
Heavy1_column
SA_gML016
RB_light
SA_gML004
Pump_gML002
Heavy2_column
SA_heavies_end

Figure 6.2: 1,2-Dichloroethane purification section, detail of flow-sheet. Configuration with chlorination reactor and recycle of new heavies back to first light column.

Table 6.2: Distillation columns design specifications for 1,2-dichloroethane purification section.

Parameter	**Light 1**	**Light 2**	**Heavy 1**	**Heavy 2**
Pressure [bar]	1.2	1.1	1.2	0.2
Ideal stages	47	10	6	13
Feed stage(s)	30	5	3	6
	(L2 res) 15		(H2 dist) 5	
Condenser type	Total	Total	Total	Total

Table 6.3: Distillation columns operation specifications for 1,2-dichloroethane purification section.

Variable		**Light 1**	**Light 2**	**Heavy 1**	**Heavy 2**
Reflux ratio	$[mol/mol]$	20	20	7.0	1.0
Recovery	$Stream$	Dist	Res	Res	Dist
	$Component$	EDC	EDC	TCE	EDC
	$Value$ [%]	7.00	95.00	95.00	99.00

In order to convert TRI into heavier component a simple conversion reactor is used. A source unit supplies a pure chlorine flow-rate at 1.2 and 362 K (distillate conditions) and trichloroethylene is converted to hexachloro-1,3-butadiene (C_4Cl_6, Nbp=210°C) by the following reaction:

$$\mathrm{ClHC{=}CCl_2 + 0.5\ Cl_2 \longrightarrow 0.5\ Cl_2C{=}CCl{-}ClC{=}CCl_2 + HCl} \tag{6.1}$$

According to case study by Groenendijk (2000), trichloroethylene conversion is specified to be 57%. Chlorine is fed in stoichiometric amount exploiting a calculator unit.

6.2.1 Results

Due to their design configurations, each column has to be supplied by two independent operation specifications: reflux ratio and recovery ratio for a key component are used for each column since typically this set of variables allows to achieve a more stable simulation. Table 6.3 summarises all specifications supplied to each column for the simulation. Light columns operate at high reflux ratio but the value can be increased up to 25. Because of the high selectivity in chlorination steps and cracking furnace, feed stream composition is higher than 99% in 1,2-dichloroethane and only a small amount of impurities has to be removed. As a consequence, top and bottom temperatures are typically very close and the profile is very flat, especially for Light1 and Heavy1 column. It is rather more important to check the composition profile and the recovery or the loss ratio for 1,2-dichloroethane. Figure 6.3 displays the liquid mass fraction profile for main light impurities (CLP and TRI) and main heavies impurities (TCE and DCB) in column Light1: it is already possible to observe that the heavies recovery is total but a very small amount of chloroprene and trichloroethylene still remains at the bottom. Table 6.4 confirms the observation by reporting the recovery ratio for the main components. The residue stream contains 82 ppm and 26 ppm by weight of chloroprene and trichloroethylene respectively: their amount is clearly below the threshold values (100 and 600 ppm by wt) suggested by Groenendijk (2000). After conversion, the reactor outlet is sent to column Light2 in order to reduce EDC loss. The combination of two light columns with the specified recovery leads to limit the overall EDC loss to 0.37% and at the same time to ensure that chloroprene composition in the distillate does not exceed 8%wt, thus avoiding polymerisation issues (Figure 6.4). Moreover, Light1 column temperature profile is very flat and all stages operate at about 89°C; top and bottom temperature for Light2 column are not so close and their values are respectively 58.5° and 86.3°.

EDC 99.15% pure is sent to the first heavy column, which performs the finishing purification before the cracking furnace. The operative specification is based on 1,1,2-

Table 6.4: Recovery ratio simulation results for light and heavy columns main components.

		Recovery Ratio [%*mol*]			
Stream	Component	Light 1	Light 2	Heavy1	Heavy2
Residue	EDC	93.00	95.00	27.70	1.00
	TCE	100.00	–	95.00	98.04
	DCB	100.00	–	99.82	100.00
	HCB	100.00	100.00	100.00	100.00
Distillate	CLP	81.94	70.48	100.00	–
	TRI	82.84	45.86	98.65	0.00

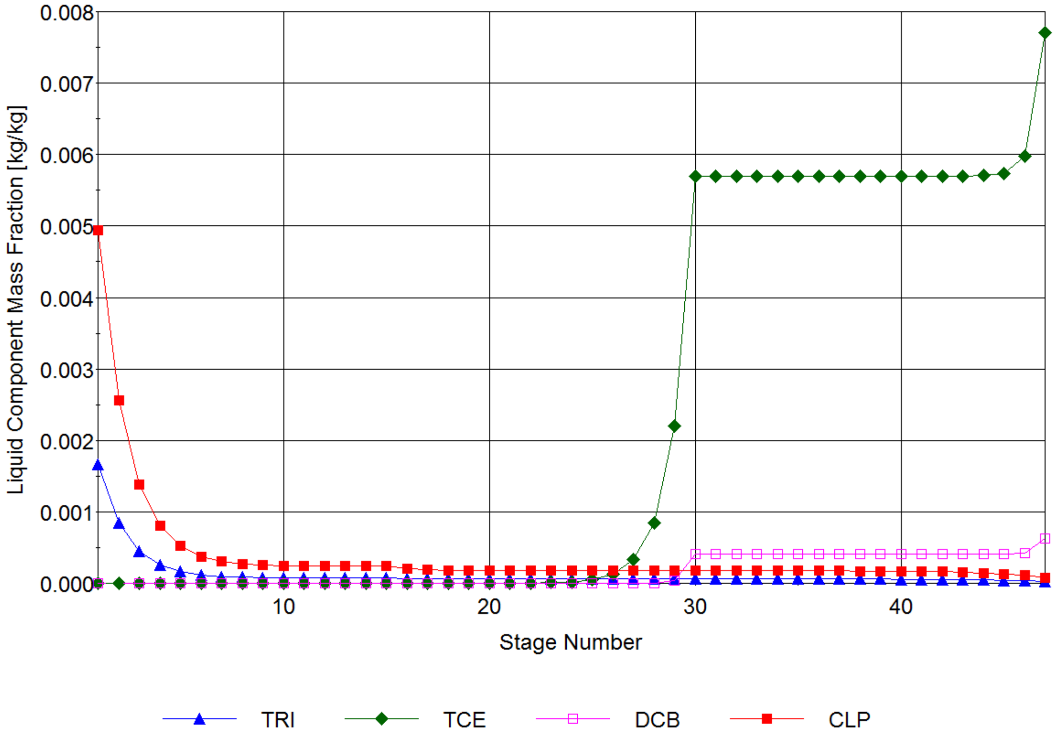

Figure 6.3: Light1 column liquid composition profile for main light and heavy impurities.

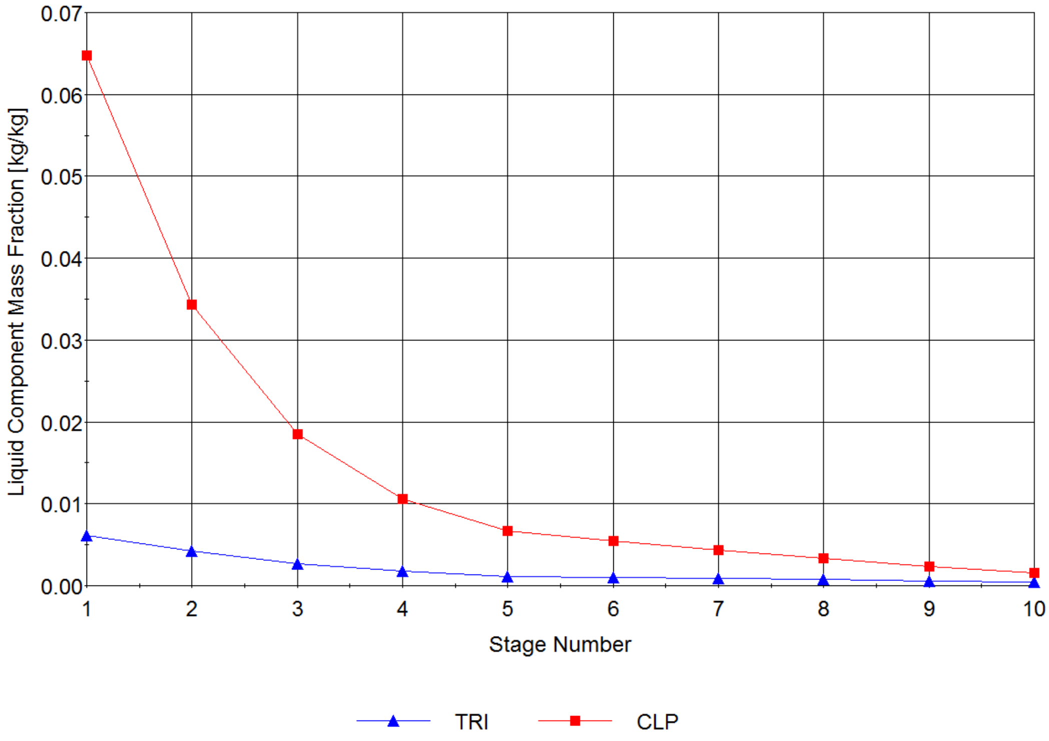

Figure 6.4: Light2 column liquid composition profile for main light impurities.

trichloroethane since it is the main impurity that has to be removed from the stream. Figure 6.5 shows the liquid composition profile for heavy impurities in the first heavy column: the separation is easy and only few stages are required. 99.95%wt pure 1,2-dichloroethane is achieved as top liquid distillate and only 397 ppm by weight of TCE are sent to the pyrolysis reactor: a typical value of 1,1,2-trichloroethane allowed to be fed to the furnace is about 500 ppm by wt (Benyahia, 2005). Hexachloro-1,3-butadiene and 1,4-dichlorobutane are almost totally removed, as Table 6.4 highlights, but 27.7% of EDC would be lost without the additional column. Heavy2 column operates below atmospheric pressure performing a very efficient separation between EDC and TCE. The vented mixture is rich in 1,1,2-trichloroethane (62.01%wt) and 1,2-dichloroethane is at 32.12%wt (Figure 6.6). EDC loss in heavy section is hence reduced from 27.7% to 0.38% and overall TCE removal achieved is 94.91%. Furthermore, it is possible to note that the entire amount of chloroprene entering the heavy section is fed to the furnace, while trichloroethylene, because of the azeotrope, is partially dragged by EDC (1.35%) and a small amount leaves the process at the heavies end: 28 ppm by weight of TRI can be found in the impurity outlet stream. As said above, the temperature profile of column Heavy1 is flat and about 89°C. On the other hand, top and bottom temperatures for Heavy2 column are respectively 39.0°C and 52.7°C.

6.3 Vinyl chloride purification

After quanch, pyrolysis effluent is sent to purification section where the main by-product HCl and unconverted 1,2-dichloroethane are recovered before the finishing column for polymer grade vinyl chloride. By ensuring a high selective operation for the

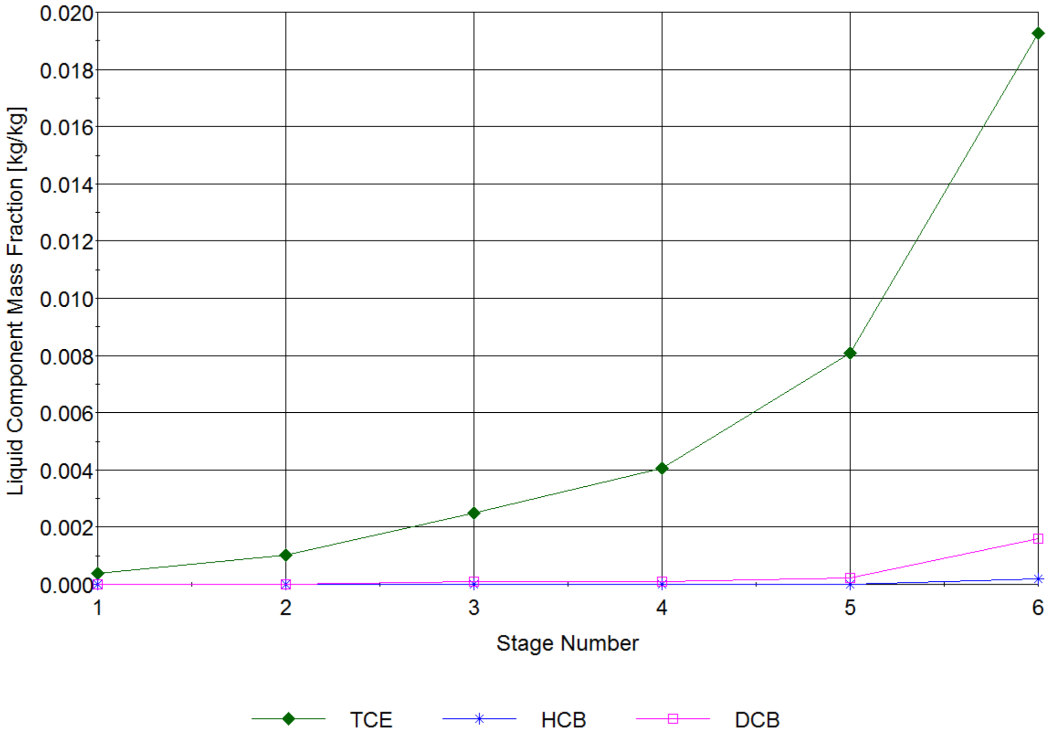

Figure 6.5: Heavy1 column liquid composition profile for main heavy impurities.

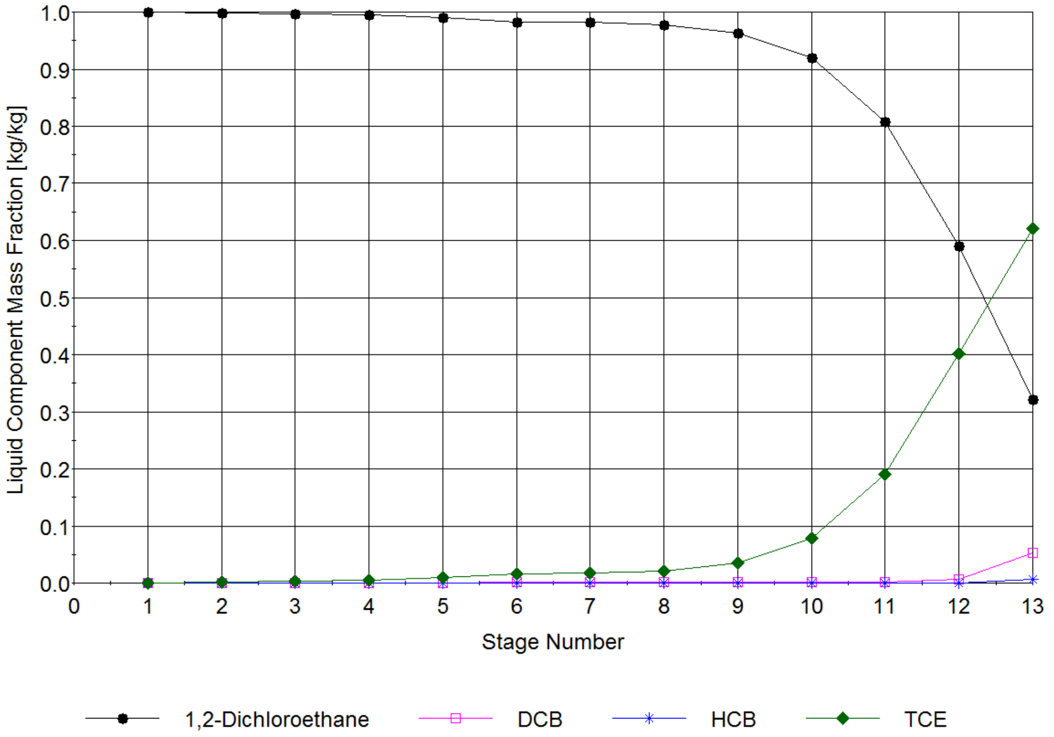

Figure 6.6: Heavy2 column liquid composition profile for main heavy impurities and 1,2-dichloroethane.

cracking process, the vinyl chloride purification modelling can be focused just on the three components: hydrogen chloride, 1,2-dichloroethane and vinyl chloride. However, as discussed in Chapter 4, in this case the prediction accuracy must be verified with further analysis and additional data. Since the critical temperature of HCl is 51.5°C, mixtures containing this component at higher temperature cannot be properly predicted applying mixing rules but they must be validated with additional data. As said before, the NRTL model applies the Antoine equation in order to estimate the vapour pressure and to predict the vapour-liquid equilibrium, but above $T_{c,HCl}$ values of this pure property are extrapolated and accuracy is not guaranteed any more. Furthermore, due to some significant differences between Antoine prediction and experimental data for pure hydrogen chloride and vinyl chloride, interaction parameters for this binary mixtures may be affected by error. As a consequence, the VCM purification train cannot be completely modelled with rigorous distillation columns.

Figure 6.7 shows the detail of the final flow-sheet where this section is modelled with two rigorous distillation columns and one component splitter. Table 6.5 summarises design specifications for the simulation of the HCl recovery column and the VCM finishing column. The EDC column is simulated by a component splitter beacuse a rigorous column can not reach convergence: most of the stages operate above $T_{c,HCl}$ and the errors on pure vapour pressure for VCM and HCl affect the equilibrium calculation, as discussed in section 4.2.1. The HCl recovery column is a 42 ideal stages column operating at 11.0 bar with a partial condenser. It is simultaneously fed by the vapour stream coming directly form the quench and by a liquid stream: the latter is obtained by mixing the quench outlet and the recycle flow-rate from the VCM finishing column. Due to the advantage of this feed configuration (see section 6.1.1), the HCl column feed design is realised according to the case study by Simulation Sciences inc. (1992), whereas all remaining specifications are referred to Bezzo et al. (2004). Distillate is exclusively in vapour phase and the liquid is totally refluxed back to the first tray. Since almost pure hydrogen chloride is drawn as distillate, higher pressure operation is required to increase top temperature up to -30°C. Bottom temperature is above $T_{c,HCl}$ (about 100°C), hence HCl column prediction cannot be considered accurate and it requires additional data. Combined with binary interaction parameters, this may cause convergence problems and errors.

The following part of the distillation train operates at 5.0 bar. The component splitter performs the complete separation between vinyl chloride (with residual hydrogen chloride) and 1,2-dichloroethane with impurities that are going to be removed in the EDC distillation section. As reported by Bezzo et al. (2004) the second distillation column operates at about 30°C at the top and 150°C at the bottom, hence it is clear that almost all trays operate above $T_{c,HCl}$. The stream containing vinyl chloride and residual hydrogen chloride is sent to the top tray of the finishing column. The last unit is a rigorous distillation column with 30 ideal stages and total condenser. At the bottom monomer grade vinyl chloride is achieved and the liquid distillate, containing HCl and residual VCM, is recycled back to the first column.

6.3.1 Results

According to design specifications, respectively for HCl column and VCM column, three and two degrees of freedom are determined and assigned. Table 6.6 displays operation specifications supplied to distillation column models. HCl column has a

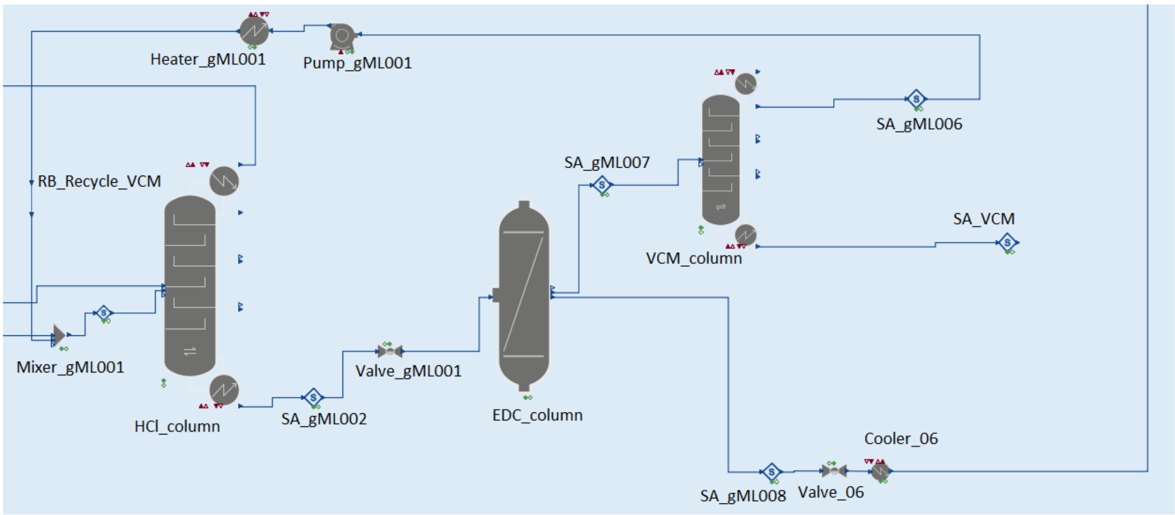
Heater_gML001
Pump_gML001
SA_gML006
SA_gML007
RB_Recycle_VCM
SA_VCM
VCM_column
Mixer_gML001
Valve_gML001
HCl_column
SA_gML002
EDC_column
Cooler_06
SA_gML008
Valve_06

Figure 6.7: Vinyl chloride purification section, detail of flow-sheet.

Table 6.5: Distillation columns design specifications for vinyl chloride purification section. Rigorous distillation column models are used for simulates HCl and VCM columns.

Parameter	**HCl column**	**VCM column**
Pressure [*bar*]	11.0	5.0
Ideal stages	42	30
Feed stage(s)	(vap) 18	2
	(liq) 22	–
Condenser type	Partial	Total

Table 6.6: Operation specification of distillation columns for vinyl chloride purification section.

Variable		**HCl column**	**VCM column**
Specification 1		Top vapour recovery HCl	Reflux ratio
	value	0.996	7.0
	u.o.m.	mol/mol	mol/mol
Specification 2		Top vapour purity VCM	Bottom purity VCM
	value	10.0	99.999
	u.o.m.	ppm by mol	%wt
Specification 3		Top liquid flowrate	–
	value	0.0	–
	u.o.m.	kmol/hr	–

partial condenser but the distillate is exclusively in vapour phase, therefore the distillate liquid flow-rate is set to zero, satisfying one degree of freedom. At the same time it is known by the case study used as reference that a small amount of VCM is lost at the top and HCl is not completely removed. During typical steady state operation, in the distillate stream about 20 ppm by weight of VCM are still present and HCl in the residue is about 60 ppm by weight. In order to improve stability of calculation, top vapour purity for VCM and recovery ratio for HCl are specified. Furthermore, due to how model equations are implemented, specifications are in mole basis since it further improves stability. It must be pointed out that the specification on VCM is achieved: 10.0 ppm by mole specification leads to 17.1 ppm by weight. However, HCl recovery is not high enough and 869 ppm by weight are still present: in industrial practice, 100 ppm is considered the threshold value for plant stable operation. The reflux ratio, defined as refluxed liquid over vapour phase distillate, is estimated as 1.74 from the simulation. Figure 6.8 shows the composition profile of the main components for HCl column: few stages above the vapour feed are required in order to remove 1,2-dichloroethane from the liquid stream. The upper part is almost totally dedicated to the removal of VCM from HCl, whereas the bototm is focus on the recovery of HCl from vinyl chloride and EDC. However, the complete removal of hydrogen chloride in the stripping section is hard to achieve without loosing higher amount of product. The EDC component splitter separates completely 1,2-dichloroethane and other heavy components from vinyl chloride and hydrogen chloride, sending the former to the EDC purification section and the latter to the VCM column. Vinyl chloride at 99.8% is sent to the finishing column. VCM column specifications are vinyl chloride composition, specified as 99.999%wt, and the reflux ratio on molar base, which is equal to 7.0 since this value allows to achieve the desired product purity. Figure 6.9 shows that HCl amount in the product, however, is still 10 ppm by weight even if 0.5 ppm is the maximum allowed value, but first, in order to properly simulate this unit, the prediction at the bottom of the HCl recovery column must be adjusted. The temperature profile, displayed in Figure 6.10, is nearly flat: 30 ideal stages are required but from the first tray to the bottom the temperature increase is only 1°C, clearly pointing out that the complete separation of HCl from VCM is hard to achieve.

It must be clear that the final flow-sheet simulation has been performed with all sets of binary interaction parameters that have been regressed except for the mixture

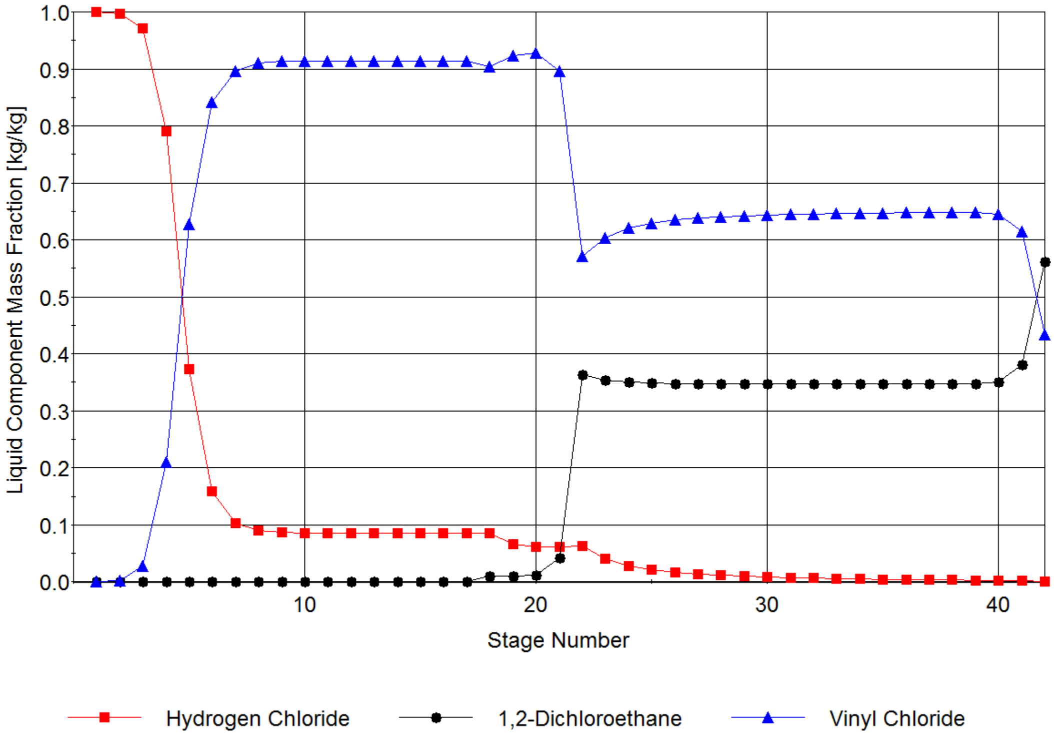

Figure 6.8: HCl column liquid mass fraction profile for main components.

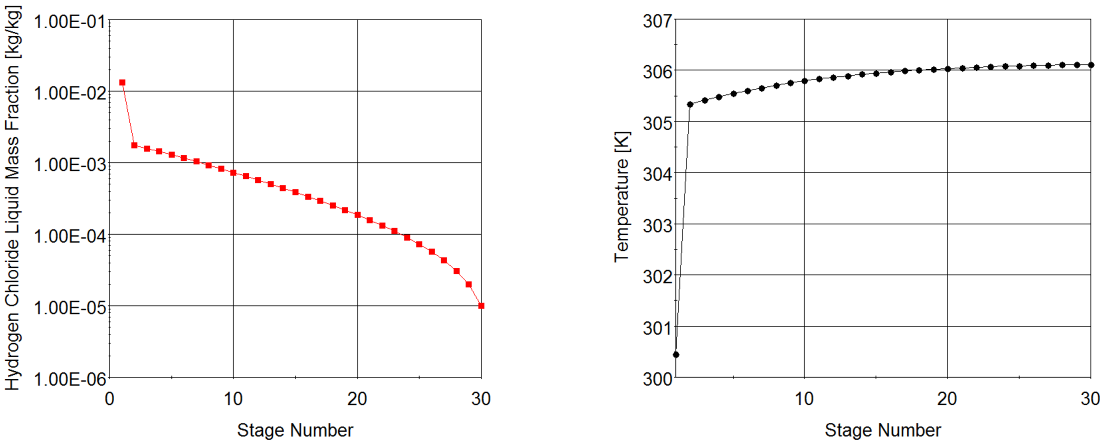

Figure 6.9: VCM finishing column liquid mass fraction profile for hydrogen chloride.

Figure 6.10: VCM finishing column temperature profile.

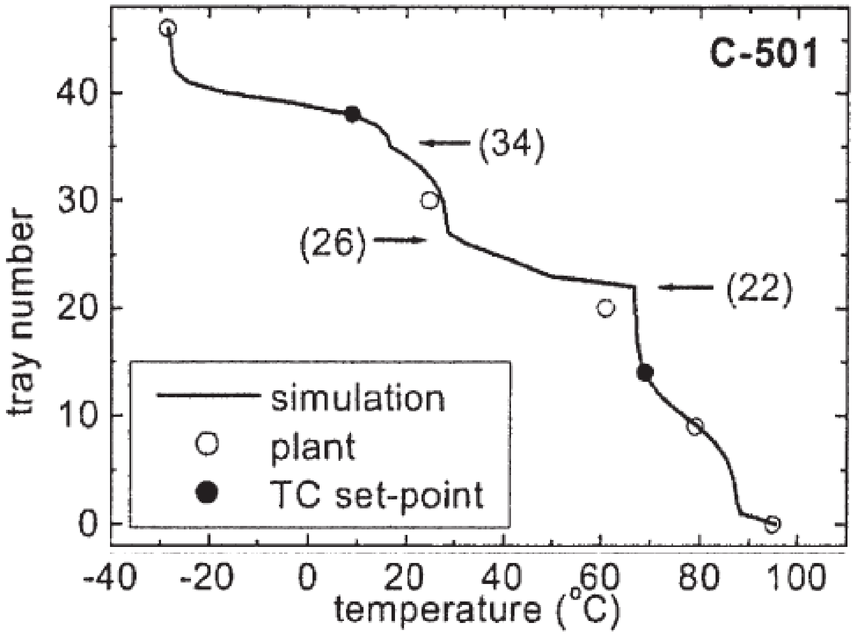

Figure 6.11: HCl column reference temperature profile. (Bezzo et al., 2004)

VCM+HCl, because in this way the VCM purification results are closer to actual practice.

In fact, when the VCM+HCl binary mixture information are added two problems occur: first of all, the estimated concentration of vinyl chloride at the top cannot be different from 0 ppm, since the order of magnitude of this variable is now estimated about 10^{-15} kg/kg. Moreover, HCl recovery must be decreased to 95% in order to achieve convergence: as a consequence HCl concentration in the residue is very high, around 1.14%wt, clearly above the threshold value. Results are verified according to purity values of VCM and HCl but also on temperature profile, comparing them to the reference case study. Figure 6.11 shows the expected temperature profile for HCl column, whereas Figure 6.12 displays temperature profiles obtained from simulations. It can be observed that temperature profile obtained from the simulation with the chosen set is more similar to the reference one. Performing the calculation with the full set of BIPs major differences can be observed especially in the upper part, where most of the trays are at about -30°C. Top temperature (-29.1°C) does not change from one to the other simulation. Bottom temperature, whereas, is slightly different because of the HCl recovery that can be achieved: it is estimated as 92.6°C for the chosen set (HCl recovery 99.6%) and 89.9°C with the full BIPs set (HCl recovery 95.0%).

Since the SRK prediction for pure hydrogen chloride can be considered more accurate, further tests using the equation of state have been performed, both with and without binary interaction parameters. In any case, simulation results are not close to the real case since the distillate is completely free from VCM and temperature profile, reported in Figure 6.12, is different from the reference case. Even if SRK equation of state is applied, results are different from the expected ones. This may suggest that the main task to be carried out for the validation may be to achieve an accurate mixture prediction above $T_{c,HCl}$ rather than adjust the pure component vapour phase prediction.

Furthermore, analysis of the equilibrium prediction with the full set of BIPs and

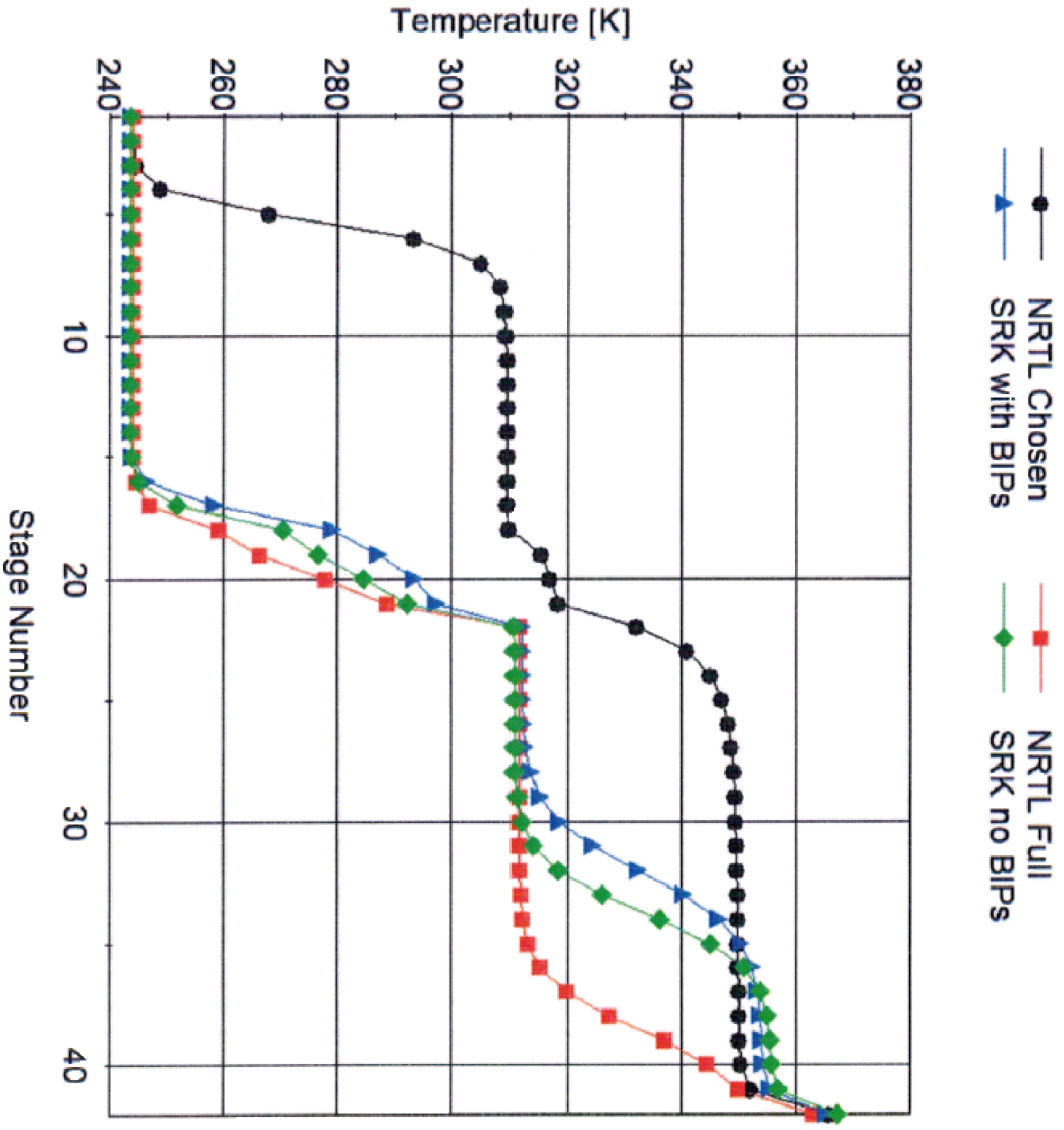

Figure 6.12: HCl column temperature profiles obtained from simulations based on NRTL model with full set of regressed BIPs (full), the same set without VCM+HCl parameters (chosen), and SRK model.

the chosen set of BIPs have been performed directly using Multiflash$^{\text{TM}}$ software and comparing numerical values for composition in the operative range: three flash calculation at constant pressure and temperature have been performed in order to check the prediction at the top, at the bottom, and between the two feed streams. Input values for flash calculations are supplied according to temperature and composition from simulation results: particularly stages 2, 20 and 41 are used as reference. Table 6.7 summarises the result of this analysis, showing that no meaningful differences between the two prediction were found at the top and at the bottom. On the other hand, the thermodynamic model with the full set of BIPs does not predict any vapour phase at 277.5 K (stage 20). Binary interaction parameters for the mixture VCM+HCl have an effect on the vapour-liquid equilibrium calculation and as a consequence they affect the HCl column solution. However, the prediction departs from the expected result instead to get closer to it. This behaviour may be due to the error on the pure vapour pressure prediction from the Antoine equation.

6.4 Recycle structure

After addition of both purification sections, the final flow-sheet configuration is therefore achieved as reported in Figure B.2 in Appendix B. It is good practice to verify the material balance closure even if no warnings or error messages are displayed: the Bal_gML unit is a very simple model which allows to perform this check. From the simulation it reports that the total mass balance error is $-7.32 \cdot 10^{-6}$ kg/s, operating with the default tolerance of $1.0 \cdot 10^{-5}$ kg/s.

In order to simulate properly the plant, however, the initialisation procedure must be completed: MIP is expensive from a computational point of view since it takes about 18.2 minutes to converge for the present case. However, once it is completed, a faster and more stable simulation can be achieved staring from the variable set that can be saved. Convergence of the simulation with open recycles is guaranteed since recycle breaker initial guesses are specified exactly as the values of source units that allow to obtain convergence simulating individually each section. However, due to the flow-sheet complexity, in order to complete calculations during MIPs it is convenient to supply a proper order of closure of recycle breakers and adjusters: during iteration steps failure usually occurs on detailed models as distillation columns or reactors, because of inconsistency with their specifications. As a consequence, it is convenient to specify the order of closure of recycle breaker units and all other loops involved in the simulation. The overall number of recycle breaker units is 9 while 7 are actually material recycle streams. Two of them are used in order to isolate distillation sections from the rest of the plant during MIP, since these units are more sensitive to input changes. The recycle breaker between the two conversion rectors (RB_pyro) is exploited in order to isolate the VCM distillation section from the pyrolysis reactor, whereas the recycle breaker RB_001, placed before the component splitter for very light components removal, is used to isolate the EDC purification train. In addition to the material recycle breakers, three loops have to be closed since EDC conversion in cracking, HCl conversion in oxychlorination and solvent flow-rate in direct chlorination are controlled by three adjusters. The unit named adjuster works as a controller, moving the variable values from initial guesses to user specifications, and it is treated like a recycle stream by the solver. The full sequence is presented below:

Table 6.7: Flash calculations comparison between NRTL model with full set of regressed binary interaction parameters and chosen set of BIPs. Three mixture are analysed according to condition at the top, the middle and the bottom of HCl recovery column.

	Full		**Chosen**		**Delta**	
Comp	Vapour $[mol/mol]$	Liquid $[mol/mol]$	Vapour $[mol/mol]$	Liquid $[mol/mol]$	Vapour $[mol/mol]$	Liquid $[mol/mol]$
Top			$T = 244.4$ K; $P = 11$ bar			
HCl	9.99E-01	9.89E-01	9.99E-01	9.89E-01	4.70E-05	4.30E-05
C2H2	4.20E-04	4.08E-04	4.20E-04	4.07E-04	-1.10E-07	1.53E-06
VCM	6.24E-04	1.05E-02	6.70E-04	1.05E-02	-4.62E-05	-4.45E-05
Total	8.94E-01	1.06E-01	8.98E-01	1.02E-01	-4.67E-03	4.67E-03
Middle			$T = 277.5$ K; $P = 11$ bar			
HCl	–	1.01E-01	4.08E-01	9.88E-02	-4.08E-01	2.10E-03
C2H2	–	4.42E-05	1.69E-04	4.34E-05	-1.69E-04	8.54E-07
VCM	–	8.92E-01	5.92E-01	8.94E-01	-5.92E-01	-2.06E-03
EDC	–	6.75E-03	1.47E-04	6.80E-03	-1.47E-01	-4.53E-05
TCE	–	2.89E-06	3.36E-08	2.91E-06	-3.36E-08	-1.96E-08
CLP	–	1.70E-05	1.35E-06	1.71E-05	-1.35E-06	-1.07E-07
TRI	–	2.87E-07	7.80E-09	2.89E-07	-7.80E-09	-1.91E-09
DCB	–	4.25E-07	1.04E-09	4.28E-07	-1.04E-09	-2.90E-09
Total	–	1.00E-00	6.81E-03	9.93E-01	-6.81E-03	6.81E-03
Bottom			$T = 352.2$ K; $P = 11$ bar			
HCl	8.24E-03	3.44E-03	7.35E-03	3.45E-03	8.98E-04	-7.62E-06
VCM	9.58E-01	7.15E-01	9.59E-01	7.15E-01	-9.84E-04	-3.72E-04
EDC	3.33E-02	2.81E-01	3.32E-02	2.81E-01	8.61E-05	3.78E-04
TCE	2.26E-05	3.43E-04	2.26E-05	3.43E-04	-1.62E-08	4.90E-07
CLP	4.20E-05	2.35E-04	4.20E-05	2.35E-04	-1.91E-08	2.95E-07
TRI	3.02E-06	5.29E-05	3.02E-06	5.28E-05	-8.20E-11	7.62E-08
DCB	2.47E-06	2.50E-04	2.47E-06	2.50E-04	-6.87E-10	3.79E-07
Total	1.84E-03	9.98E-01	3.17E-04	1.00E-00	1.53E-03	-1.53E-03

- Adj_conversion_pyro;
- RB_quench;
- RB_recycle_VCM;
- RB_HCl;
- Adj_conversion_oxy;
- RB_lights;
- RB_heavies;
- RB_001;
- RB_EDC;
- RB_pyro;
- Adj_DC_holdup;
- RB_oxy_ethylene.

RB_pyro and RB_001 are closed in the final part of the sequence when their output are closer to the solution and, as a consequence, are more stable. The sequence starts at pyrolysis reactor adjusting the length in order to achieve the desired conversion. Later the quench recycle and the VCM recycle from the finishing column are closed. Once hydrogen chloride recycle has been closed it is possible to achieve the desired conversion in the oxychlorination reactor. RB_001 is left open while the two recycles in the EDC distillation section are closed. Hence, at first the EDC distillation section is connected with other unit operations closing RB_001 and the recycle of 1,2-dichloroethane from the VCM purification train. Now RB_pyro can be closed connecting the cracking furnace to the vinyl chloride purification section. The last step is to adjust the solvent flow-rate for direct chlorination reactor and to close the ethylene recycle for oxychlorination.

Conclusions

The objective of the thesis has been the development of a reliable model to simulate the performance of a vinyl chloride plant based on the balanced process, since it is the most widely used and most convenient route. Since a reliable thermodynamic model is essential to properly simulate the behaviour of the mixtures involved, two main tasks have been accomplished: at first the software Multiflash^{TM} has been used for the regression of interaction parameters for main binary mixtures that are present in the process. Then, by using the gPROMS$^{®}$ ProcessBuilder software the whole plant has been accurately modelled.

A proper thermodynamic model has been selected according to the specific features of the 15 chemical species considered in the process: the NRTL activity model allows to properly describe an highly interacting system of components as the one involved in the balanced process. However, it is combined with the Redlich-Kwong equation of state in order to properly predict the vapour-liquid equilibrium at relatively high pressure, since part of the plant (pyrolysis and HCl recovery column) operates at 11 bar. Seven binary mixtures have been regressed from experimental vapour-liquid or solubility data in order to validate the selected thermodynamic model. The regression results for EDC+TRI, EDC+TCE and EDC+Cl_2 binary mixtures are very accurate and the relative error on vapour pressure and saturation temperature is below 1%. Also the binary mixtures involving EDC and ethylene is accurately predicted since the maximum relative error on the vapour pressure is about 3%. The reliability of these results is further demonstrated by the simulation results since the direct chlorination reactor and the EDC purification section outlets are close to the expected values in terms of composition.

However, it has been highlighted that, a high definition can not be guaranteed for the a vapour-liquid equilibrium involving vinyl chloride or hydrogen chloride. The main reasons are two: first of all, the HCl critical temperature is 51.5°C while HCl and EDC recovery columns operate above this value. The pure vapour pressure value, required by the NRTL model, is obtained by the Antoine model but it is valid only below this physical limit (i.e. the HCl critical temperature) and the prediction can not represent the real behaviour of the mixture in these conditions. Furthermore, the VLE calculation accuracy is highly affected by the pure vapour pressure prediction and it has been stated by comparison with reliable experimental data that the available Antoine model does not properly estimate the value of P^{sat} for HCl and VCM. Since the value for pure vapour pressure is required for the VLE calculation, these errors clearly affect the binary interaction parameters regression for the EDC+VCM, EDC+HCl and VCM+HCl mixtures.

By taking into account the HCl recovery column temperature profile as reference, further tests have been performed using the Soave-Redlich-Kwong equation of state, since this model does not require the application of the Antoine equation. It has been observed that the result does not differ significantly from the ones achieved with the NRTL equation of state. Therefore it is suggested to consider as first task to improve the prediction accuracy of HCl above its critical point rather than adjust the Antoine equation parameters.

Because of the issues in the thermodynamic representation, simulation results are only partially accurate: only the amount of VCM at the distillate of the HCl recovery column is properly represented and is close to the value suggested by references. The other units in the VCM purification section, that are placed downstream from the HCl recovery column, are affected by the wrong prediction of the bottom stream. On the other hand, the remaining parts of the plant, where liquid-vapour equilibrium calculations for HCl and VCM with EDC are not required, are accurately predicted.

The oxychlorination and pyrolysis reactor units are not affected by binary interaction parameters because the reactions take place in gas phase, but it has been verified that also the direct chlorination reactor is not affected by them. Tubular reactors have been used in order to simulate oxychlorination and pyrolysis reactors, whereas a vapour-liquid equilibrium reactor is exploited to represent the boiling condition of the liquid mixture in direct chlorination process. Molecular kinetic models have been implemented in order to simulate the reaction mechanisms involving for each unit main side reactions. Results are accurate in terms of conversion and selectivity for the chlorination reactors, while it has been verified that the prediction of the pyrolysis outlet is accurate in terms of composition.

To conclude, a complete and reliable model representing the entire VCM manufacture process has been developed and validated with thermodynamic data, but further work is required in order to obtain a reliable representation of all units in the process flow-sheet. As discussed above, additional data are required for a proper prediction of systems involving HCl above its critical temperature. Then a correction of the Antoine equation for HCl and VCM vapour pressure can be useful in order to improve the accuracy on binary interaction parameters regression for mixtures involving these two chemical species. Furthermore, the flow-sheet may be improved by adding high detailed models for reactor units: for instance a radical mechanism may be used to simulate the EDC cracking furnace or a fluidised-bed model may be implemented to represent the solid phase real behaviour in the oxychlorination process. Besides, major advantages can be achieved by designing an optimal heat integration network in order to reduce the energy consumption and operative costs.

Appendix A

Codes

A basic initialisation code for the regression of binary interaction parameters using Excel® interface for Multiflash™ is reported below:

```
puredata DIPPR;

model MRK RKS RK;
bipset NRTLBIP3 3;
model MNRTLVLEMRK NRTL VLE MRK NRTLBIP3;

pd GAS gas MRK;
pd LIQUID1 liquid MNRTLVLEMRK;
pd LIQUID2 liquid MNRTLVLEMRK;

components
''component 1'' ''component 2'';

unit amount mol temperature K pressure Pa;

bipset NRTLBIP3 3 quadratic activity none;
''component 1'' ''component 2''
a12
b12
c12
a21
b21
c21
alpha12;
```

Kinetic model for oxychlorination process: key parameters and equations.

```
PARAMETER
-----------------------------------
# USER-DEFINED parameters
-----------------------------------
k0     AS ARRAY(Reactions_kinetic)     OF REAL #Pre-exp factors
Ea     AS ARRAY(Reactions_kinetic)     OF REAL #Activation energies
F      AS ARRAY(Reactions_kinetic)     OF REAL #Exp for Pa_to_bar
Cl_exp AS ARRAY(Reactions_kinetic)     OF REAL #Exp for Cl2 pp
Ka     AS ARRAY(components_adsorption) OF REAL #Adsorption const
Cc     AS                                 REAL #CuCl2 conc on cat



UNIT
UP     AS universal_parameters_gML
UCF    AS unit_conversion_factors_gML



SET
# Reaction names
Reaction_irreversible  :=[ 'oxy', 'sideCl', 'sideTCE', 'sideCO2'];

# Reaction stoichiometry
S(,'oxy')     := [-0.5, 1, -2, 0, -1, 0, 0,  1, 0, 0, 0, 0, 0, 0];
S(,'sideCl')  := [  -1, 2, -4, 2,  0, 0, 0,  0, 0, 0, 0, 0, 0, 0];
S(,'sideTCE') := [-0.5, 1, -1, 0,  0, 0, 0, -1, 1, 0, 0, 0, 0, 0];
S(,'sideCO2') := [  -3, 2,  0, 0, -1, 0, 0,  0, 0, 0, 0, 0, 0, 2];

use_rate_per_volume  :=1; #kmol/h/m3-cat
use_partial_pressure :=1; #bar

component_adsorption :=['ETHYLENE'];

k0('oxy')       :=269;              # 1/s
k0('sideCl')    :=0.28;             # kmol/m3/s
k0('sideTCE')   :=1.4E+5;           # kmol/m3/s/Pa^1.5
k0('sideCO2')   :=164438438.33;     # kmol/m3/s/bar^2.5

Ea('oxy')       :=37800;            # J/mol
Ea('sideCl')    :=14594.8;          # K, it's Ea/R
Ea('sideTCE')   :=128040;           # J/mol
Ea('sideCO2')   :=112000;           # J/mol

F('sideTCE')    :=1.5;
F('sideCO2')    :=2.5;

Cl_exp('oxy')        :=0;
Cl_exp('sideCl')     :=-1;
Cl_exp('sideTCE')    :=0.5;
Cl_exp('sideCO2')    :=0.5;

Ka              :=0.63;             # m3/mol
Cc              :=993;              # mol/m3



EQUATION
CASE kinetic_reaction_switch OF
    WHEN reactions_on:
```

```
# USER-DEFINED rate law
#------------------------------
(1/reac_rate_scale) * R('oxy')
    = (1/reac_rate_scale) * alpha  # Used for initialisation
# NUMERATOR
    * Kinetic_parameter('oxy')/ucf.s_to_hr
    * adsorption_constants('ETHYLENE') * Cc * x('ETHYLENE')
# DENOMINATOR
    / (UP.gas_constant*T /ucf.mol_to_kmol*ucf.Pa_to_bar
    + adsorption_constants('ETHYLENE')/UCF.mol_to_kmol
    * x('ETHYLENE'));

# Side Reactions
# Chlorine production
(1/reac_rate_scale) * R('sideCl')
        = (1/reac_rate_scale) * alpha  # Used for initialisation
        * Kinetic_parameter('sideCl')/ucf.s_to_hr
        * x('OXYGEN')* MAX(x('CHLORINE'),1e-11)^Cl_exp('sideCl');

# Trichloroethane production
(1/reac_rate_scale) * R('sideTCE')
        = (1/reac_rate_scale) * alpha  # Used for initialisation
        * Kinetic_parameter('sideTCE')/ucf.s_to_hr
        /(ucf.Pa_to_bar^F('sideTCE'))* x('1,2-DICHLOROETHANE')
        * MAX(x('CHLORINE'),1e-10)^Cl_exp('sideTCE');

# Carbon dioxide production by ethylene combustion
(1/reac_rate_scale) * R('sideCO2')
        = (1/reac_rate_scale) * alpha  # Used for initialisation
        * Kinetic_parameter('sideCO2')/ucf.s_to_hr
        * x('ETHYLENE')* x('OXYGEN')
        * MAX(x('CHLORINE'),1e-10)^Cl_exp('sideCO2');


# USER-DEFINED equation for kinetic constants
# ---------------------------------------------------
LogK('oxy')     = LOG(k0('oxy'))-Ea('oxy')/up.gas_constant/T;
LogK('sideCl')  = LOG(k0('sideCl'))+11.73-Ea('sideCl')/T;

FOR j IN Reactions_kinetic - 'oxy' - 'sideCl' DO
    LogK(j) = LOG(k0(j))-Ea(j)/up.gas_constant/T;
END # FOR j IN Reactions_kinetic DO

FOR j IN Reactions_kinetic DO
    (1/pre_exp_fact_scale) * Kinetic_parameter(j)
    = (1/pre_exp_fact_scale) * EXP(LogK(j)) ;
END  # FOR j IN Reactions_kinetic DO


# USER-DEFINED equation for adsorption constants
# ----------------------------------------------
logKads('ETHYLENE') = LOG(Ka('ETHYLENE'));
(1/pre_exp_fact_scale) * adsorption_constants('ETHYLENE')
    = (1/pre_exp_fact_scale) * EXP(logKads('ETHYLENE')) ;
```

Appendix B

Flow-sheet

A simplified process flow-sheet, with only reactor units and component splitters, is at first reported in Figure B.1. Then the final flow-sheet configuration, with rigorous distillation column models, is displayed Figure B.2.

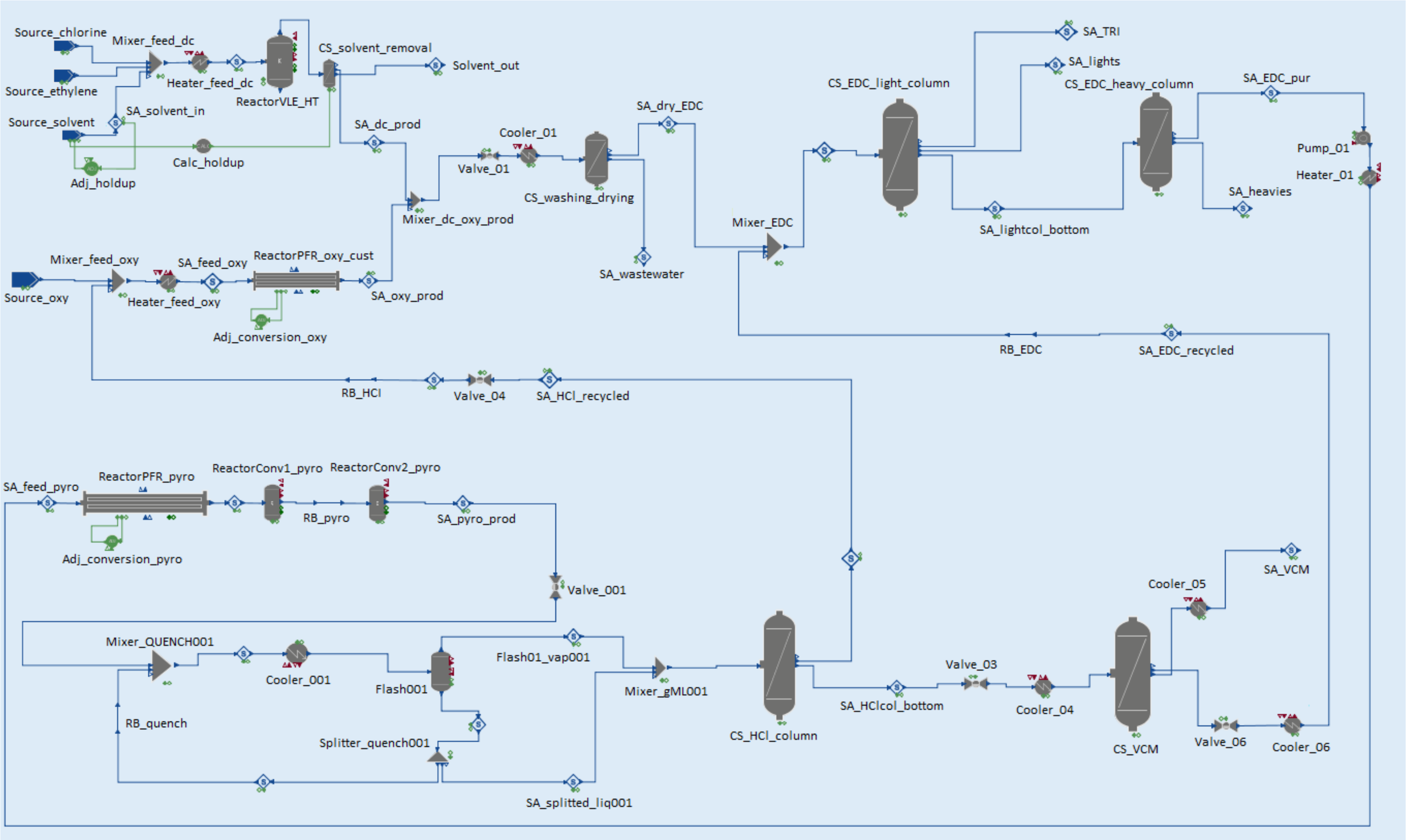
Source_chlorine
Mixer_feed_dc
Source_ethylene
Heater_feed_dc
ReactorVLE_HT
CS_solvent_removal
Solvent_out
Source_solvent
SA_solvent_in
Calc_holdup
Adj_holdup
SA_dc_prod
Cooler_01
Valve_01
CS_washing_drying
SA_dry_EDC
Mixer_dc_oxy_prod
SA_wastewater
Mixer_feed_oxy
SA_feed_oxy
ReactorPFR_oxy_cust
Source_oxy
Heater_feed_oxy
SA_oxy_prod
Adj_conversion_oxy
RB_HCl
Valve_04
SA_HCl_recycled
CS_EDC_light_column
SA_TRI
SA_lights
CS_EDC_heavy_column
SA_EDC_pur
Pump_01
Heater_01
SA_heavies
Mixer_EDC
SA_lightcol_bottom
RB_EDC
SA_EDC_recycled
SA_feed_pyro
ReactorPFR_pyro
ReactorConv1_pyro
ReactorConv2_pyro
RB_pyro
SA_pyro_prod
Adj_conversion_pyro
Valve_001
Mixer_QUENCH001
Cooler_001
Flash001
Flash01_vap001
Mixer_gML001
RB_quench
Splitter_quench001
SA_splitted_liq001
CS_HCl_column
SA_HClcol_bottom
Valve_03
Cooler_04
CS_VCM
Cooler_05
SA_VCM
Valve_06
Cooler_06

Figure B.1: Simplified flow-sheet with quench section and component splitter replacing rigorous distillation columns. Closure of hydrogen chloride and 1,2-dichloroethane recycle streams.

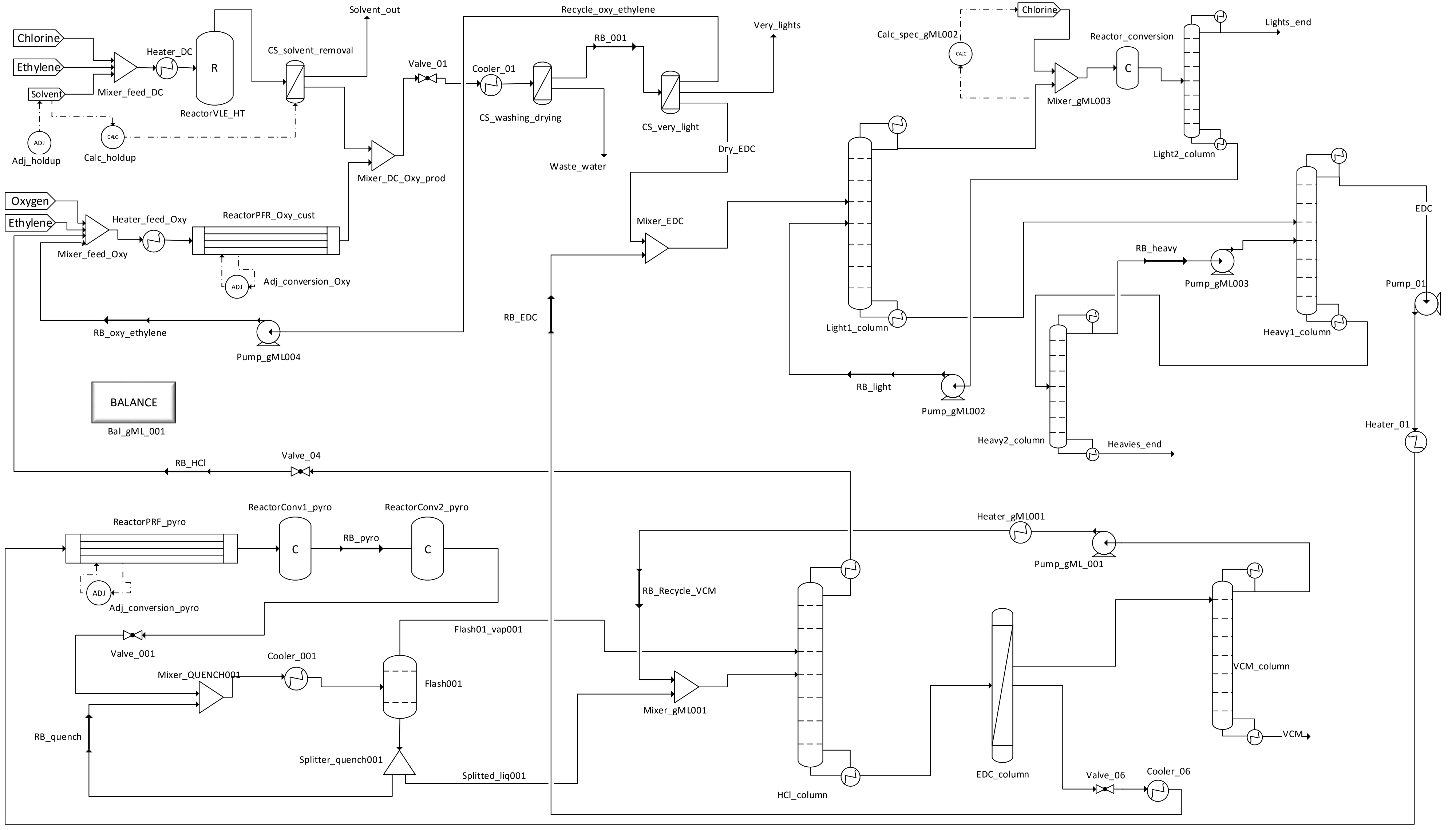
Chlorine
Ethylene
Solvent
Mixer_feed_DC
Heater_DC
R
ReactorVLE_HT
ADJ
Adj_holdup
CALC
Calc_holdup
CS_solvent_removal
Solvent_out
Valve_01
Mixer_DC_Oxy_prod
Oxygen
Ethylene
Mixer_feed_Oxy
Heater_feed_Oxy
ReactorPFR_Oxy_cust
ADJ
Adj_conversion_Oxy
RB_oxy_ethylene
Pump_gML004
BALANCE
Bal_gML_001
Recycle_oxy_ethylene
Cooler_01
CS_washing_drying
RB_001
Waste_water
CS_very_light
Very_lights
Dry_EDC
Mixer_EDC
RB_EDC
Calc_spec_gML002
CALC
Chlorine
Reactor_conversion
C
Mixer_gML003
Light2_column
Lights_end
Light1_column
RB_light
Pump_gML002
RB_heavy
Pump_gML003
Heavy1_column
Heavy2_column
Heavies_end
EDC
Pump_01
Heater_01
RB_HCl
Valve_04
ReactorPRF_pyro
ADJ
Adj_conversion_pyro
ReactorConv1_pyro
C
RB_pyro
ReactorConv2_pyro
C
Valve_001
Mixer_QUENCH001
Cooler_001
Flash001
Flash01_vap001
RB_quench
Splitter_quench001
Splitted_liq001
RB_Recycle_VCM
Mixer_gML001
HCl_column
Heater_gML001
Pump_gML_001
EDC_column
Valve_06
Cooler_06
VCM_column
VCM

Figure B.2: Representation of the final flow-sheet with rigorous distillation column models for EDC and VCM purification section and additional unit for mass balance checking.

Acknowledgements

By spending six months at Process Systems Enterprise Ltd. I grew up both professionally and humanly and I will be always grateful to people who gave me this opportunity. Therefore, I would like to express my deep gratitude to my supervisor Prof. F. Bezzo for the constant and accurate technical support during the entire period required to develop the project, for the patience and the time spent for correcting this study. In the same way, I am very grateful to Prof. C. Pantelides for giving me the possibility to work on this project and for providing precious suggestions.

I am particularly indebted to Dr. S. Spatenka for supervising the project and for his guidance: I am grateful for his help and the interest shown despite the distance. A special thanks must be reserved to Eng. F. Calado for the technical and the moral support. I have been very lucky to work with expert engineer always willing to help me.

Finally I would like to thank all the interns who shared with me this important life and work experience and all the people that I have met during my staying in this great company.

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