STELLINGEN

behorende bij het proefschrift

Process Development of Thermal Hydrodechlorination

door

Antoon ten Kate

(Delft, 4 oktober 1993)

1. Gezien de relatieve frequentie waarin de stellingen worden gelezen, zou men beter kunnen spreken van het proefschrift behorende bij de stellingen dan het gebruikelijke omgekeerde.

2. De kwaliteit van de zomer wordt mede bepaald door de vraag of de mooie dagen in het weekend vallen of juist daarbuiten.

3. Ouderbijdrage gaat verder dan financiële steun.

4. De wet van Murphy luidt dat als iets mis kan gaan, het ook mis gaat, en wel op het meest desastreuze moment. Statistisch gezien is deze wet onjuist, en zij zegt dan ook meer over de menselijke perceptie.

5. Een stoplicht staat altijd op rood.

6. De vergaande vooruitgang in de elektronica kenmerkt zich door verkleining van de elektronische schakelingen en apparatuur en het vergroten van de bijgaande emballage.

7. De gebruikelijke wiskundige weergave van een kubus is vanuit een oogpunt van perspektief onjuist.

8. De moeite die men zich getroost om competitievervalsing tegen te gaan en sportlieden onder zoveel mogelijk gelijke omstandigheden hun wedstrijd te laten afwikkelen, staat in contrast met tijdmeting op 0.01 s of zelfs op 0.001 s zoals bij bobsleeën. Het is beter om in een aantal runs de wedstrijd te beslissen.
   (Albertville, Olympische Winterspelen 1992)

9. De volwassenheid van turnen blijkt omgekeerd evenredig met de leeftijd van haar topbeoefenaarsters.
   (Barcelona, Olympische Zomerspelen 1992)

10. De WAO is verziekt.

11. Of van vervuilingen sprake is, hangt niet alleen af van het type stof, maar met name van de concentratie. Om te spreken met Paracelsus vervuilingen bestaan niet, het gaat om de concentraties.

(Paracelsus -16^{de} eeuw-)

Niet alleen van belang is dus vermindering van afval als totaal, maar ook per deelgroep: dit is te bereiken door verscheidenheid van produkten aan te bieden, leidende tot minder afval per soort en tevens tot minder grondstof gebruik per soort.

12. Chloor is groen. *(χλωρος: fris groen -Grieks-)*

13. Dioxinen zijn dodelijker voor chemische processen dan voor de mens.

14. De vermelding in Kirk-Othmer dat fosgeen een katalytische werking bezit bij de produktie van $SiCl_4$ uit vast SiC en gasvormig HCl, is niet in overeenstemming met de oorspronkelijke literatuur en berust op een *kapitale* verschrijving. Bedoeld wordt cobaltchloride ($CoCl_2$) in plaats van fosgeen ($COCl_2$).

    M. Grayson, D. Eckroth, *Kirk-Othmer, Encyclopedia of Chemical Technology*, 3^{rd} ed., vol **12**, New York (1980), 1007.

    G. Wiebke, G. Kratel, J. Kral, G. Stohr, *German Patent 2.319.995*, April 19 (1973).

15. Een 3^{de} geldstroom projekt ontleent zijn naam aan het geld dat zij van derden krijgt en aan andere derden betaalt.

16. Zonder technisch personeel was geen stelling gemaakt.

(dit proefschrift)

Introduction

As a supplement to the thesis of ir. Antoon J.B. ten Kate, we would like to present the current state of the art. Based on the experimental experiences and theoretical advances at Leiden University and Delft Technical University, we have built a demonstration pilot plant which is suited to treat 600 ton/year of hazardous halogenated liquid waste. As the development continued the demonstration unit built differs from the one described in the thesis; therefore we would like to inform about the present state. One of the main differences is the transportability of the pilot plant!

The transportable demonstration unit

A key feature of the demonstration pilot plant is simplicity. The main objective is to demonstrate the process of thermal hydrodehalogenation, rather than to pursue complete optimalisation. The simplicity also facilitates adaptation of the plant when other halogenated waste than chlorinated liquids need to be treated.

To accomplish simplicity the following changes has been conducted.

- Hydrogen is supplied from gas cylinders. The capacity of the plant is that low that a reformer is not essential.
- Hydrogen chloride produced is neutralised. The proven technology of HCl recovery can be implemented later on.
- The pressure is not increased but maintained at atmospheric level.
- The capacity of the plant is 600 ton/year (100 l/h).
- Heat is supplied by partial oxidation of hydrogen. The suppletion of air may not only generate heat, but also may accelerate dechlorination (by forming radicals) and decrease soot formation.

The new design

The flowsheet resembles the flowsheet presented in figure 6.1 of the thesis. The halogenated hydrocarbon (HHC) is pumped to the reactor and sprayed with hydrogen into the hot reactor. The reactor is heated using a burner in which hydrogen is combusted with stoichiometric amounts of air. The hot reaction gas flows downwards through the reactor tube. At the end of the tube the gas is quenched by a cold liquid. The cold liquid is sprayed in such a way that a shield of liquid droplets is formed through which the reactor gas has to flow. The liquid contains sodium hydroxide (NaOH), keeping the pH high to assure maximum collection of hydrogen halogenide (HX) and neutralising the hydrogen halogenide dissolved. Rather harmless sodium halogenide salt (NaX) is formed. After leaving the quench the gas is submitted to a second washing step with fresh sodium hydroxide solution to assure complete removal of HX. The cleaned gas is combusted in an incinerator.

The liquid leaving the quench is recycled for reuse as spray. In the recycle it is freed from solid contaminants in a filter and cooled in a heat exchanger. A small part is purged and collected in a storage vessel. The liquid is refreshed by the fresh sodium hydroxide solution supplied in the second washer.

The reactor is an empty tube. At its top a nozzle and burner of a special design are installed. The construction material is aluminium oxide (Al_2O_3) for its chemical inertness and temperature resistance. The reactor tube is placed concentrically within the surrounding quench vessel.

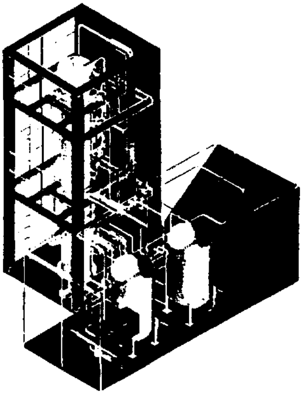

Figure 1 CAD-CAM designed lay-out of transportable demonstration plant.

The liquid holdup in the quench vessel is well below the exit of the reactor tube to keep aluminium oxide from thermoshocks it can not withstand. For the same reason the reactor tube is surrounded by a protective metal shield, sheltering it against the liquid sprays.

Most recent results

Since april 1993 the pilot plant has been operated. Tests with chlorobenzene show that the dechlorination levels aimed at can be achieved. Soot formation is still present, but does not interfere with the process. Compared to the observed masses at Delft Technical University, a large decrease of the soot formation has been realised.

The demonstration plant can be transported. Therefore, demonstration on site is possible! In principle, any kind of liquid or liquified halogenated waste can be treated.

Acknowledges

We would like to thank prof. dr. R. Louw and coworkers at Gorlaeus laboratories of Leiden University and prof. ir. C.M. van den Bleek and his coworkers for their kind cooperation.

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Process Development
of
Thermal HydroDechlorination

Process Development of Thermal HydroDechlorination

Proefschrift

ter verkrijging van de graad van doctor
aan de Technische Universiteit Delft,
op gezag van de Rector Magnificus,
prof. ir. K.F. Wakker
in het openbaar te verdedigen
ten overstaan van een commissie
aangewezen door het College van Dekanen
op maandag 4 oktober 1993
te 16:00 uur

door

Antoon Jacob Berend ten Kate

geboren te 's Gravenhage
Scheikundig Ingenieur

Dit proefschrift is goedgekeurd door de promotoren:

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Voor Merel
en mijn ouders

Contents

1 **Introduction**: chlorinated and other halogenated compounds; manufacturing, use, hazards and waste treatment.

4 **Mechanism of thermal hydrodechlorination**: dechlorination, soot and tar formation of chlorobenzene.

5 **Why does SiC corrode?** experimental observations, theory and modelling.

6 **Design of an industrial plant to treat chlorinated waste**: flowsheet, apparatus choices, economics.

7 **Final discussion**: future outlook and promising features.

Notation

symbol	denotation	units	use in equations
A	area	m^2	2.4; 2.37; 2.40; 2.42; 4.34; 5.6
A_{active}	active wall surface area	m^2	3.1
c	B.E.T. constant (expressing heat of adsorption)	-	3.6
c	concentration	mol/m^3	4.37; 4.39; 5.6-14
c_p	heat capacity at constant pressure	J/mol K	
c_v	heat capacity at constant volume	J/mol K	
C	split ratio constant	(mol/s)/(mol/s)	2.3-4; 2.41-42
$C^*(t)$	split ratio constant, as a result of fouling varying with time	(mol/s)/(mol/s)	2.44-47; 2.49
C_d	drag coefficient	-	2.4; 2.38; 2.40; 2.42
C_i	reactant concentration in phase i	mol/m^3	2.17-35
C_{soot}	carbon quantity of soot produced	mol	3.1
C_{feed}	carbon quantity fed	mol	3.1
$\mathbb{D}$	diffusion coefficient	m^2/s	2.25; 5.6; 5.9-10; 5.13; 5.17-18
d_b	bubble size (diameter)	(c)m	2.1
f	overshoot		footnote 4.1
g	standard acceleration of free fall	9.81 m^2/s	2.25
ΔG_r	Gibbs energy function change of reaction	kJ/mol	4.54
h	height	m	2.1
ΔH_{ads}	heat of adsorption	kJ/mol	3.6
ΔH_j	negative reaction heat concerning reaction j	kJ/mol	4.40
ΔH_{liq}	heat of condensation	kJ/mol	3.6
$-\Delta H_r$	heat of reaction	kJ/mol	2.2; 2.10-15; 5.5
ΔH_{vap}	heat of vaporisation	kJ/mol	3.6
k	constant of transport rate through film layer	m/s	5.18
k	reaction rate constant:		
	• first order	s^{-1}	2.20; 3.1
	• second order	$m^3/mol\ s$	4.3
	• any order	$(m^3/mol)^{q-1}/s$	4.38
k_{eff}	pseudo first order reaction rate constant	s^{-1}	1.30; 4.2-5; 4.43
k_{jx}	rate constant of reaction j in 'x-ward' direction	$(m^3/mol)^{q-1}/s$	4.37
$k_{principal}$	rate constant of principal reaction	$m^3/mol\ s$	4.43
k_1	forward reaction rate constant	$(m^3/mol)^3/s$	5.11-13
k_{-1}	backward reaction rate constant	$(m^3/mol)^2/s$	5.11-13; 5.16
K	equilibrium constant	$(mol/m^3)^{\Delta n}$	4.10; 4.26-27; 4.38; 4.54; 5.3; 5.12-15
K_{ij}	interchange coefficient between phases i and j in fluidised bed	s^{-1}	2.17-35

L_f	bed height at given fluidisation conditions	m	2.20; 2.29
M	molar weight	(k)g/mol	2.37-38
Δn	stoichiometric change of reaction	-	
N_r	number of reactions	-	4.36
N_s	number of species	-	4.37
P	pressure	N/m^2 (atm)	2.3; 2.37-41; 2.44; 2.47-49; 4.39; 6.1
ΔP	pressure difference or drop	N/m^2 (atm)	2.3; 2.37-41; 2.44; 2.47-49;
P_1	pressure before capillary	N/m^2	2.39
P_2	pressure in narrowest passage of capillary	N/m^2	2.39
q	order of reaction	-	
Q	heat demand of reaction system	J/s	4.40
r	reaction rate	mol/m^3 s	4.2
r	radius	(c)m	5.6-8
r	inner tube radius	cm	4.5
R	inner tube radius	m	5.7-18
R	gas-law constant	8.314 J/mol K	3.6; 4.4-7; 4.26; 4.39; 4.54
$\mathbb{R}_i$	reaction rate for compound i	mol/m^3 s	4.34; 4.36
$\mathbb{R}_j$	overall rate of reaction j	mol/m^3 s	4.40
$\mathbb{R}_{jx}$	rate of reaction j in 'x-ward' direction	mol/m^3 s	4.36-37
rate	reaction rate	mol/m^3 s	5.10-11; 5.13
S	split ratio	(mol/s)/(mol/s)	2.3; 2.36; 2.40-43; 2.47-49
S	surface area	m^2	4.44
Sh	Sherwood number	-	5.18
t	time (of measurement)	s	2.44-47; 2.49
T	temperature	K	1.30; 2.37-42; 3.6; 4.4-7; 4.26; 4.39; 4.54; 5.3; 5.15-17
u_i	gas velocity in phase i of fluidised bed model	m/s	2.17-35
u_{mf}	minimum fluidisation velocity	m/s	2.1
u_o	superficial gas velocity	m/s	2.1
V	volume	m^3	4.44; 6.1
$V_{reactor}$	reactor volume	m^3	3.1
x	distance (along axis of tubular reactor)	m	4.34-35; 4.40; 5.9
x_{Cl}	molar chlorine fraction	mol/mol	2.6-7
$Y_{C.soot}$	soot production (yield)	C%	2.12
Y_{soot}	soot production (yield)	wt%	2.11
α	ratio of volume of clouds and wakes with respect to volume of bubbles	m^3/m^3	2.22-23
β_i	ratio of gas volume in phase i with respect to volume of bubbles	m^3/m^3	2.17-35
δ	thickness of film layer	m	5.7-18
δ	ratio of volume of bubbles compared to reactor volume	m^3/m^3	2.23-24
ϵ_{mf}	voidage at minimum fluidisation	m^3/m^3	2.22-23
ϵ_{void}	porosity of material	m^3/m^3	3.5

κ	compressibility coefficient	-	2.4; 2.38-40; 2.42
ν_{ij}	stoichiometric factor of species i in reaction j	-	4.56
$\nu_{h(j.x)}$	reaction order concerning species h in reaction j in the 'x-ward' direction	-	4.37
ξ	conversion	mol%	2.5; 2.20; 2.35; 2.43; 2.51
ρ	density	kg/m^3	3.5
σ	correction factor for change of system pressure due to addition of reference stream [1]	-	2.47-50
τ	residence time	s	3.1
ϕ_i	molar flow i	mol/s	2.36; 2.40; 2.44; 2.47; 2.49-50
$\phi_{m.i}$	mass flow through orifice or critical capillary	kg/s	2.37
ϕ_{mol}	molar flow	mol/s	2.5; 2.43; 2.51; 4.34-35; 4.39; 5.6; 5.9; 5.14
ϕ_{moleq}	flow expressed in terms of molequivalents	'moleq.'/s	2.5-7; 2.43; 2.51
ϕ_v	volumetric flow	m^3/s	2.24; 4.39; 5.14

subscripts

b	bubble phase of fluidised bed	2.17-35
bulk	in bulk (gas) phase	4.5-6; 5.7-11
c	critical capillary	2.4; 2.38; 2.40
c	cloud phase of fluidised bed	2.17-35
e	emulsion phase of fluidised bed	2.17-35
feed	concerning feed	2.5; 2.7-9; 2.43; 2.51; 4.35
gas	in gas phase	3.1
L_f	at top of fluidised bed	2.32; 2.34
main	concerning main stream, i.e. effluent leaving reactor	2.36; 2.40; 2.44-45; 2.50-51
o	orifice	2.4; 2.37; 2.40
O.C.R.	determined by 'Organic Chlorine Remainder' method	2.10
product	concerning product	2.6; 2.8; 2.10
ref	while reference stream is added	2.45; 2.47-50
reference	concerning reference stream	2.45; 2.47; 2.49-50
$SiCl_4$	silicon tetrachloride	5.6-18
split	concerning split stream	2.5; 2.42; 2.44-45; 2.47; 2.49-50
tit.	determined by titration	2.5; 2.43; 2.51
titration	concerning stream through titration unit	2.36; 2.40
wall	at wall	3.1; 4.5; 4.7; 5.7-11
x	index indicating forward or backward reaction	4.37

---

[1] definition given in equation 2.48

Chapter 1

Introduction

chlorinated and other halogenated compounds;
manufacturing, use, hazards and waste treatment.

---

§ 1.1 Introduction.

In the discussion about chlorine all opinions seem to agree at one point: without it the world definitely would be different. However, where industry emphasizes the benefits of chlorine and its derivatives during manufacturing and use, environmentalists focus on the drawbacks of these compounds afterwards. In fact, the properties that make chlorinated compounds so attractive during their economic lifetime are closely related to, if not similar to, the properties causing the environmental problems. Proper management of the 'chlorine chain' should therefore include adequate recycling and destruction methods for chlorinated waste in order to prevent spill to the environment.

A very promising method for proper chlorinated waste treatment is thermal hydrodechlorination. This process turns chlorinated waste into HCl, that might be recycled, and into organics which can be used as a fuel. The objective of the study underlying this thesis is scaling up thermal hydrodechlorination to a waste destruction process at industrial scale.

In this chapter an introduction to chlorinated compounds will be given, including manufacturing, use, hazards (toxicology), present waste treatment and possible alternatives. The chapter ends with an introduction to thermal hydrodechlorination.

§ 1.2 Present applications and manufacturing methods of chlorinated compounds. [3,11,19,27]

The assertion from the industrial point of view that the world would look different without chlorine can be substantiated by the numerous applications of chlorinated compounds. Shortly listed, chlorinated hydrocarbons are used [11,27]

- as solvents,
- as intermediates in chemical processing,
- as synthetics and plasticizers (PVC, synthetic rubber),
- as flame retarding agents or as raw material for them,
- as agricultural chemicals (insecticides),
- in production of medicines.

The large number of applications is due to the extraordinary properties of these chemicals. Generally speaking an increase in the chlorine content results in a higher chemical reactivity, a decreased flammability and an improved solubility for a large number of organic and inorganic materials, with a noteworthy exception for water. Furthermore, the presence of chlorine in an organic molecule increases density and viscosity, while specific heat and dielectric constant are reduced. In several chemical processes chlorine is used as a facile leaving group for the introduction of another functional group. [11,19,23]

The wide range of applications as a result of these special features is demonstrated by table 1.1, that lists the most important chlorinated organics and their major industrial applications.

In the Netherlands, a large fraction of the chlorine production is used in manufacturing chlorinated hydrocarbons. A report published in september 1990 [6] estimates the total chlorine production in the Netherlands at that time to be 644 kton/year; the amount of chlorine used in chlorinated hydrocarbons was estimated to be at least 392 kton/year (60 wt% of the complete chlorine production) [6,19]. Estimating the average chlorine content of the chlorinated hydrocarbons to be 40 wt% [25] one can calculate that approximately 1000 kton/year chlorinated hydrocarbons must have been produced in the Netherlands during that period.

In 1976 the U.S. demand for chlorinated hydrocarbons was circa 9 Mton, with an average chlorine content of about 70 wt%. In the USA 46.5 wt% of the 1974 chlorine production was used in the production of chlorinated hydrocarbon derivatives. [19] In 1980, in West-Germany 3 Mton chlorine was produced, 80% to 90% of which was used in manufacturing chlorinated hydrocarbons [3]. From these figures, the total chlorinated hydrocarbon production in Germany during that period is estimated to be 6.4 Mton.

The synthesis paths used in commercial manufacturing can be reduced to five basic chemical pathways. [3,11] Three of them do not effect the C-C bond and are real chlorination processes in the sense that they actively add chlorine to the organic material:

- substitution (paragraph 1.2.1),
- addition (paragraph 1.2.2),
- displacement (paragraph 1.2.3).

The two others change the chlorine contents of the organics partly by interference with the C-C bond:

- elimination (paragraph 1.2.4),
- pyrolysis (paragraph 1.2.5).

In the paragraphs mentioned the pathways will be elucidated.

§ 1.2.1 Substitution chlorination.

'Substitution chlorination' is the replacement of a hydrogen atom in a hydrocarbon by a chlorine atom. Two pathways exist: a radical mechanism and a mechanism based on electrophilic attack.

The radical mechanism starts with the dissociation of chlorine into radicals by thermal or photochemical means. Once the radicals are formed, the reaction is continued by a number of propagating steps, as illustrated by reaction equations 1.2 and 1.3. First, the chlorine radical reacts with a hydrocarbon molecule producing molecular hydrogen chloride and a hydrocarbon radical. In a second step, the hydrocarbon radical reacts with molecular chlorine, producing molecular chlorinated hydrocarbon and a chlorine radical, which can initiate a new chain.

chain initiation

$$Cl_2 \xrightleftharpoons{heat/light} Cl\cdot \tag{1.1}$$

chain propagation

$$RH + Cl\cdot \longrightarrow R\cdot + HCl \tag{1.2}$$

$$R\cdot + Cl_2 \longrightarrow RCl + Cl\cdot \tag{1.3}$$

chain termination

$$R\cdot + Cl\cdot \longrightarrow RCl \tag{1.4}$$

$$2Cl\cdot \longrightarrow Cl_2 \tag{1.5}$$

$$2R\cdot \longrightarrow R\text{-}R \tag{1.6}$$

Radical based substitution chlorination is a commercially important chlorination process. The process temperature requires close control due to the highly exothermic reaction; this is commonly done by cooling or dilution. In the production of chloromethanes the reaction temperature is typically kept at about 500 °C.

Substitution chlorination of a certain feedstock yields all possible chlorinated derivatives, e.g. from methane mono-, di-, tri- and tetra-chloromethane are produced.

Table 1.1 Commercial applications of chlorinated hydrocarbons. [1,6,9]

intermediate	end product	applications
chlorinated C_1-C_2 hydrocarbons (circa 25% of total chlorinated hydrocarbon production)		
methylene chloride		• metal degreaser/cleaner, solvent, paint remover.
chloroform	• CFC's, halones • polytetrafluoroethene (PTFE, teflon)	• propellant, refrigerant, extinguishant, blowing agent. • pan coatings, tube and vessel coatings, seals, implants, bearings, lubricants.
carbon tetrachloride	• thermal outcrop • CFC 11, CFC 12	• thermal ore extraction. • see chloroform.
trichloroethene		• metal degreaser, spot remover, dry cleaning.
1,1,1-trichloroethane		• solvent, metal degreaser, dry cleaning.
perchloroethene	 • CFC 113, CFC 114	• dry cleaning, solvent, metal degreaser, extraction agent. • degreaser, solvent, refrigerant, blowing agent, propellant.
dichloroethane (ethylene dichloride: EDC)	• vinylchloride monomer (VCM) • ethenediamine	• see above • fungicides, paper and textile chemicals, detergent manufacturing, polyurethane production.
methylchloride	 • other chlorinated hydrocarbons • silanes, silicone oils, silicone rubbers • methylcellulose	• solvent • phosgene, chlorinated C_1-hydrocarbons, benzyl chloride. • paint, isolation, damping liquid in hydraulic systems, plastic surgery, sealing kit, hoses, lubricants, pills, balsams, cosmetics. • filler, thickener and dispersive agents in paint, paper, textile, glues, pills, balsams.
vinyl chloride/PVC (circa 45% of total chlorinated hydrocarbon production)		
vinylchloride (VC)	• polyvinylchloride (PVC)	• cables, isolation material, tubes, rainproof clothing, toys, window frames, wallpaper, floor covering, sewers, domestic gloves, infusion bags, packing material, etc.

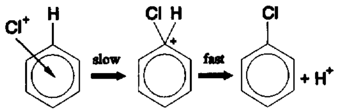
other chlorinated hydrocarbons (circa 30% of total chlorinated hydrocarbon production)		
allylchloride, epichlorohydrine	• epoxyresins	• paint, electrical isolation, laminate in electronics, adhesives, composite in air planes, glues, powder coating.
linear chlorinated derivatives	• chloroprene • chlorinated paraffins • poly-olefins	• seals, hoses. • engine oil, retardants. • coating of underwater cables.
cyclic chlorinated derivatives	• chlorinated aromatics (chlorobenzenes, chlorotoluene, chlorocyclopentadiene)	• pesticides.
oxidated products: • propene-oxide	• polypropyleneglycol, polyether, polyols. • carboxymethyl-cellulose.	• polyurethanes (car industry, footwear, packing material, construction, textile, furniture industry). • thickener in food, cosmetics, oil industry, adsorbents in napkins and wallpaper paste.
• chloroacetic acid	• iminodiacetic acid.	• polymers, ion exchangers, pharmaca.
• chlorophenols		• pesticides.
phosgene	• isocyanates • polycarbonates	• polyurethanes (see propene-oxide). • artificial glass in construction and decoration, domestic apparatus, hypodermics, CD's, car industry (e.g. bumpers, dashboards, back lights).
hexachloro-cyclopentadiene		• basis for flame retarding adducts, key intermediate in manufacturing of insecticides.
terephtaloyldichloride	• aramide/twaron polymer	• hoisting cable, conveyer belt strengthener, fire resistant clothing, aircraft components, brake blocks, sports equipment.

Oxygen has a negative effect by slowing down the reaction. This is due to inhibition of the initial radical producing steps. Sometimes oxygen is deliberately added to suppress the polychloro formation.

Electrophilic chlorine substitution is especially important for aromatic compounds. The aromatic character is conserved. Typical catalysts of the reaction are ferric chloride, $FeCl_3$, and aluminium chloride, $AlCl_3$.

The mechanism of electrophilic chlorine substitution is exemplified by reaction equations 1.7 to 1.9. Under influence of the ferric chloride catalyst chlorine is polarized, potentially leading to cleavage of the Cl-Cl bond. The Cl^+-cation thus produced easily reacts with the π-electrons of the aromatic ring. The so formed benzenonium ion quickly produces chlorobenzene by loosing a proton to the base in the reaction mixture. [16]

$$:\ddot{\underset{\cdot\cdot}{Cl}}-\ddot{\underset{\cdot\cdot}{Cl}}: + FeCl_3 \rightleftharpoons \underset{polarized}{:\ddot{\underset{\cdot\cdot}{Cl}}-\ddot{\underset{\cdot\cdot}{Cl}}:---FeCl_3} \rightleftharpoons \underset{cleaved}{:\ddot{\underset{\cdot\cdot}{Cl}}^{+} + FeCl_4^{-}} \qquad (1.7)$$



(1.8)

$$H^+ + FeCl_4^- \rightleftharpoons FeCl_3 + HCl \qquad (1.9)$$

External sources producing chlorine radicals, such as light, should be avoided. If too much chlorine radicals are present, addition of chlorine will exceed its substitution, resulting into a completely different product [11]. A commercially important electrophilic chlorine substitution process is the production of chlorobenzene from benzene, taking place at 40 °C in the presence of ferric chloride. [19]

§ 1.2.2 Addition chlorination.

Chlorine addition occurs on unsaturated hydrocarbons. Elementary chlorine supplied by hydrogen chloride (HCl), chlorine (Cl_2), or hypochlorous acid (HOCl) is added to the carbon atoms surrounding the double or triple bond. The chlorine atoms show a preference to which carbon of the C-C bond they attache. This preference depends on the process conditions and the chlorination medium applied. By addition the C-C bond becomes more saturated.

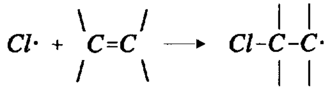
Analogue to substitution two types of addition can be distinguished: a radical mechanism and an electrophilic mechanism. [16]

The radical addition mechanism is exemplified by reaction equations 1.10 to 1.14. In the initial step radicals are formed from molecular chlorine by light induced dissociation. The first step of the propagation chain comprises the attack of these chlorine radicals on the unsaturated hydrocarbon bond. A chlorinated hydrocarbon radical is formed. In the second propagation step these chlorohydrocarbonaceous radicals react with molecular chlorine producing the desired chlorinated hydrocarbon and a chlorine radical. This radical restarts the propagation chain. [11,19]

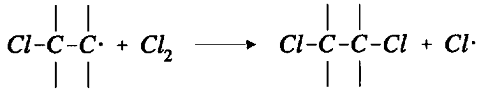
chain initiation

$$Cl_2 \xleftrightarrow{heat/light} Cl\cdot \tag{1.10}$$

chain propagation

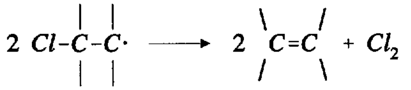


$$Cl\cdot + \mathrm{>C=C<} \longrightarrow Cl-\underset{|}{\overset{|}{C}}-\underset{|}{\overset{|}{C}}\cdot \tag{1.11}$$

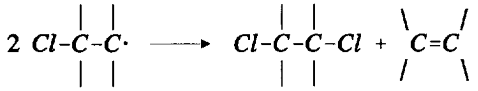


$$Cl-\underset{|}{\overset{|}{C}}-\underset{|}{\overset{|}{C}}\cdot + Cl_2 \longrightarrow Cl-\underset{|}{\overset{|}{C}}-\underset{|}{\overset{|}{C}}-Cl + Cl\cdot \tag{1.12}$$

chain termination



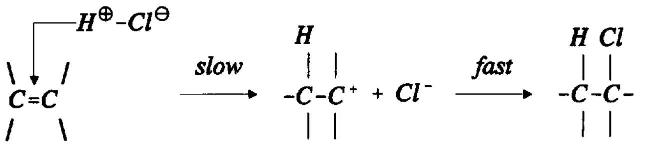
$$2\ Cl-\underset{|}{\overset{|}{C}}-\underset{|}{\overset{|}{C}}\cdot \longrightarrow 2\ \mathrm{>C=C<} + Cl_2 \tag{1.13}$$



$$2\ Cl-\underset{|}{\overset{|}{C}}-\underset{|}{\overset{|}{C}}\cdot \longrightarrow Cl-\underset{|}{\overset{|}{C}}-\underset{|}{\overset{|}{C}}-Cl + \mathrm{>C=C<} \tag{1.14}$$

A commercially important application of the radical chlorine addition is the production of 1,2-dichloroethane from ethene. This reaction is carried out at 40-50 °C in the presence of a ferric chloride catalyst. The introduction of 5% air to the chlorine feedstock prevents subsequent chlorine substitution yielding 1,1,2-trichloroethane.

Electrophilic addition is especially important in the case of chlorination with HCl or HOCl. The π-electrons in the C-C double or triple bond are attractive to electrophiles like H^+-ions. Reaction equation 1.15 exemplifies the mechanism. Hydrogen chloride contains a highly polar H-Cl bond that easily can lose H^+ to the π-electrons of the unsaturated bond. The so formed carbocation quickly reacts with the negative chloride ion to yield the desired chlorohydrocarbon. Since the first step is an attack by an electrophile, the addition is called electrophilic. [16]



(1.15)

For both reaction mechanisms the final product distribution depends on the stability of the intermediates and in case of electrophilic addition on the polarity of the chlorine feedstock in particular.

The electrophilic addition reaction can be catalyzed by metal chlorides such as ferric chloride ($FeCl_3$), aluminium chloride ($AlCl_3$), antimony pentachloride ($SbCl_5$) and cupric chloride ($CuCl_2$). Light and the reactor walls influence the reaction. The chlorination is inhibited by oxygen.

A commercial application of the electrophilic addition chlorination is the production of 1,1-dichloroethane from vinylchloride. At 50 °C in the presence of ferric chloride hydrogen chloride is attached to vinylchloride. The chlorine atom from hydrogen chloride attaches to the already chlorinated carbon atom from vinylchloride, corresponding with Markovnikov's rule. [19]

A special addition process is oxychlorination. In oxychlorination the chlorine feedstock is hydrogen chloride. In the presence of oxygen or air hydrogen chloride is converted to chlorine over a $CuCl_2$ catalyst (see 1.16).

$$2HCl + \frac{1}{2}O_2 \longrightarrow Cl_2 + H_2O \qquad (CuCl_2;\ 270\ ^{\circ}C) \qquad \textbf{(1.16)}$$

A commercially important application of oxychlorination is the production of 1,2-dichloroethane from ethene. Typical reaction temperatures are 230-315 °C.

§ 1.2.3 Displacement chlorination.

Displacement resembles substitution as far as an exchange is involved. However, in displacement a functional group instead of a hydrogen atom is replaced by the chlorine atom. This functional group can be such as a hydroxyl group, but as well a halogen atom like bromine or iodine. The reaction is acid catalyzed. An example of displacement is the synthesis of chloromethane from the reaction between HCl and methanol. Commercially the opposite reaction, displacement of chlorine by a functional group, is more common. [11,19]

§ 1.2.4 Elimination.

The opposite of addition is elimination. HCl is driven from a molecule, producing an unsaturated hydrocarbon. A commercially very important application is the production of vinylchloride from 1,2-dichloroethane. Most vinylchloride produced by industry is made by this thermal, noncatalytic cracking process. The reaction is carried out at 350-515 °C in the vapour phase. Chlorine and oxygen and similar reagents greatly accelerate the reaction; unsaturated hydrocarbons and alcohols retard or even inhibit it.

The mechanism of elimination is radical based, as will be exemplified by the dehydrochlorination of 1,2-dichloroethane (see equations 1.17 to 1.18). A chlorine radical abstracts a hydrogen atom from the saturated 1,2-dichloroethane. By this reaction molecular hydrogen chloride and a hydrocarbonaceous radical are formed. The radical regains a stable form splitting off a chlorine radical. The remaining skeleton is vinylchloride. The chlorine radical restarts the elimination chain.

$$Cl\text{-}CH_2\text{-}CH_2\text{-}Cl + Cl\cdot \longrightarrow Cl\text{-}CH_2\text{-}\dot{C}H\text{-}Cl + HCl \qquad (1.17)$$

$$Cl\text{-}CH_2\text{-}\dot{C}H\text{-}Cl \longrightarrow CH_2\text{=}CH\text{-}Cl + Cl\cdot \qquad (1.18)$$

§ 1.2.5 Chlorinolysis (pyrolytic chlorination).

Pyrolysis includes the alteration of the carbon structure of hydrocarbons when severe conditions are applied like elevated temperatures while excluding oxygen. In excess chlorine the hydrocarbon feedstock is also chlorinated, leading to chlorinated derivatives of a shorter carbon chain length. This special type of pyrolysis is called chlorinolysis.

A typical commercial application of chlorinolysis is the production of carbon tetrachloride and tetrachloroethene. The hydrocarbon feedstock may include hydrocarbons up to C_3 and any partially chlorinated derivatives. The overall reaction to the products aimed at are illustrated by reaction equations 1.19 to 1.21. Typical reaction temperatures are 600-900 °C. No catalyst is applied.

1,2-dichloroethane feedstock

$$ClCH_2\text{-}CH_2Cl + 4\ Cl_2 \longrightarrow CCl_4 + \tfrac{1}{2}\,Cl_2C\text{=}CCl_2 + 4\ HCl \qquad (1.19)$$

propane feedstock

$$C_3H_8 + 8\ Cl_2 \longrightarrow CCl_4 + Cl_2C\text{=}CCl_2 + 8\ HCl \qquad (1.20)$$

The production of carbon tetrachloride and tetrachloroethene is affected by the following equilibrium:

$$2CCl_4 \rightleftharpoons Cl_2C{=}CCl_2 + 2Cl_2 \qquad (1.21)$$

By this equilibrium the ratio in which the two species are produced, can be controlled. The practical flexibility of this ratio is an advantage of chlorinolysis. Another advantage is the possible utilization of waste as hydrocarbon feed to the reactor.

Essential in the process is the recycling of unreacted chlorine to the reactor, and the utilization of the large amounts of hydrogen chloride that are formed as byproduct.

§ 1.2.6 Byproducts of chlorination processes.

Most chlorination processes produce hydrogen chloride as a major byproduct. Integration with hydrogen chloride processing activities is therefore commonly encountered. Hydrogen chloride can be used in several applications, such as: [3]

- oxychlorination,
- chlorine addition to unsaturated hydrocarbons (hydrochlorination),
- chlorine displacement of the hydroxyl group in methanol, forming chloromethane,
- production of pure chlorine, Cl_2,
- preparation of hydrochloric acid by absorption in water.

Other byproducts are undesired chlorinated hydrocarbons. Frequently, these chlorinated byproducts can not be used and should be regarded as waste. [3]

§ 1.3 General toxicology and hazards of chlorinated compounds.

'A different world without chlorine' is also justifiable from an environmental viewpoint as the chlorinated organics have a strong impact on living organisms and the environment as a whole.

Several chlorinated hydrocarbons are effective as central nervous system stimulants. It is proposed that the chlorinated hydrocarbons stimulate nerve centres and potentiate the action of acetylcholine, a substance that plays an important role in transferring the stimulation pulse from a nerve to a muscle [7]. Spastic behaviour may result. The acute poisoning by chlorinated hydrocarbons reflects that of strychnine. [12]

A generalisation for all toxicological effects of chlorinated hydrocarbons can hardly be made. Nevertheless, based on toxic effects two groups may be distinghuished: [17]

-1- solvents.

This toxicological class of chlorinated hydrocarbons is typified by carbon tetrachloride. Besides their central nervous system effects, they poison liver and kidney.

-2- insecticides.

This toxicological class of chlorinated hydrocarbons is typified by DDT and congeners. They show strong effects on the central nervous system, causing loss of muscle control, effectuating spasm, breathing problems, etcetera.

Though members of the toxicological class of solvents may show similar toxic effects, the degree in which they act may differ considerably and can not be predicted from their molecular structure. This difficulty in generalisation can be demonstrated by the hepatotoxic potency (potential to cause liver diseases) of seven chlorinated aliphatics. Table 1.2 lists the compounds in order of increasing potency. [12]

Table 1.2 Seven chlorinated aliphatics in order of increasing hepatotoxic potency. [12]

substance	structure formula	Cl/C	H/C
1,1,1-dichloroethane	$C_2H_3Cl_3$	1.5	1.5
tetrachloroethene	C_2Cl_4	2	0.0
trichloroethene	C_2HCl_3	1.5	0.5
tetrachloroethane	$C_2H_2Cl_4$	2	1.0
1,1,2-trichloroethane	$C_2H_3Cl_3$	1.5	1.5
chloroform	$CHCl_3$	3	0.5
carbon tetrachloride	CCl_4	4	0.0

The poor correlation between toxic effects and molecular structure is strongly emphasized by the different TLV-values[1] of two very related compounds, the isomers 1,1,1-dichloroethane and 1,1,2-dichloroethane, which are respectively 350 ppm and 10 ppm. [19]

Notwithstanding these generalising difficulties, it can be stated that in general the chlorinated solvents cause liver and kidney disease, are known or suspect to be carcinogenic[2] and/or mutagenic[3] and cause central nervous system depression. [1,2,6,11,12,19,23]

---

[1] TLV = Threshold Limit Value.

[2] carcinogenic: causing cancer.

[3] mutagenic: causing alterations, especially concerning descending generations.

Typical members of the toxicological class of insecticides are DDT, hexachlorobenzene, lindane, aldrin, dieldrin, isodrin and the soil fumigant DD. In general, they show the following toxicological effects: [12,17]

- nausea (sickness) and vomiting,
- spasm,
- paralysis of tongue, lips, face and hands,
- respiratory disorder (like lack of breath and coughing),
- depression of the central nervous system (e.g. disturbance of equilibrium, dizziness, confusion, anorexia, and weight loss).

Another distinction from a toxicological point of view is between aliphatic and aromatic chlorinated hydrocarbons.

- Aliphatic chlorinated hydrocarbons are quite toxic; a lot of them are known or suspect to be carcinogens of the liver, lung, skin and blood-forming tissues. When the substitution grade of chlorine (or generally of halogen) increases, the anaesthetic action and the range of systemic effects rise. In general, unsaturated chlorinated aliphatics are more narcotic, but less toxic than saturated ones. For the saturated chlorinated aliphatics the narcotic effect is proportional to the number of chlorine atoms. This kind of correlation does not hold for toxicity. [23]

- The toxicity of aromatic chlorinated hydrocarbons is difficult to predict. The toxicity is usually not greater, and is frequently less, than that of corresponding nonchlorinated aromatics. An exception to this rule has to be made for naphthalene and biphenyls. [23]

Toxicity is just one aspect of the environmental hazards imposed by chlorinated hydrocarbons. Their damaging effect is aggravated by other properties. [1,6,11,19]

- Chlorinated products are very persistent to the environment, i.e. they are hardly broken down by biological means. Especially highly chlorinated compounds are nearly nondegradable.
- Due to their persistence chlorinated organics accumulate in the environment. This accumulation does not only take place at the site of deposit, but also in food chains.

Due to these harmful properties risk assessments concerning these chlorinated hydrocarbons frequently recommend low tolerable levels. MAC-values of a lot of chlorinated hydrocarbons are set at ppm-level, e.g. phosgene at 0.1 ppm and 1,3-dichloropropene (a component of the DD mixture) at 1 ppm.

Environmental concern has grown during past decades. Some chlorinated hydrocarbons have become very notorious in the public opinion: [6]

- polychlorobiphenyls (PCB's),
- polyvinylchloride (PVC),
- polychlorodibenzodioxins and -furans (PCDD/F),
- chlorofluorocarbons (CFC's), derived from chlorinated hydrocarbons by fluorination.

The notoriety of a certain substance is not always purely based on reason, but sometimes strongly influenced by the fear for the unknown.

The environmental problem concerning chlorinated hydrocarbons is partly due to the dualistic character of some of their properties. At one hand the properties of chlorinated hydrocarbons are very favourable during use, on the other hand the same kind of properties may cause the environmental drawbacks. Next table illustrates this kind of dualistic character of properties.

Table 1.3 *Two sides to every property...*

useful property	environmental drawback
good solvent for organic substances.	easily dissolving and accumulating in adipose (fatty) tissue.
durability (especially for highly chlorinated polymers like PVC and CFC's).	long term load to environment due to nondegradability.
excellent intermediate in chemical processing.	catalysis of cellular conversions, a potential cause for mutagenic and carcinogenic effects.

The life of a chlorinated hydrocarbon can be divided in three phases; before, during and after use. Every phase is related to its own kind of environmental problems.

- Before use, during manufacturing, the biggest hazards include exposure of personnel to the chlorohydrocarbons, unwanted emission to the environment, and danger from misoperation.

  The industrial hazards can not be predicted on toxicological data alone. Other factors should also be considered like vapour pressure, partition distribution between blood and tissues, and rate and route of absorption. [12]

  The biggest hazards in industrial use of commercial volatile chlorinated solvents are excessive vapour inhalation and central nervous system depression [19]. Extensive ventilation prevent these problems [11]. Concerning nonvolatile chlorinated hydrocarbons absorption through the skin is the most troublesome danger: serious damage to vital organs like the liver may result. Protective wear is used, such as rubber gloves, e.g. made of neoprene (itself a product of the chlorinated hydrocarbon industry!). [11]

  An other serious hazard occurs when the chlorinated hydrocarbons are subject to burning. Besides carbon monoxide (CO), chlorinated products are formed, like hydrochloric acid, phosgene ($COCl_2$) and chlorinated dibenzodioxins and -furans. Phosgene particularly arises from highly chlorinated compounds, while hydrogen chloride is formed if a sufficient large hydrogen fraction is available [11,23]. Also chlorinated dibenzodioxins and -furans may be formed in the fire. Though at much smaller concentrations they cause considerable danger due to their high toxicity.

Other process dangers include the violent reaction of chlorinated hydrocarbons with aluminium (Al), liquid oxygen, and the alkalimetals potassium (K) and sodium (Na). Low-chlorinated aliphatics are highly flammable, peroxidizable, reactive to divalent light metals forming dangerous reactive products and can be subject to violent polymerization. Chlorinated aromatics can easily react with oxidizing materials. [23] The explosive character of some chlorination processes and chlorinated compounds form another hazard. [11,23]

- Most chlorination processes have a large exothermic heat of reaction, which may lead to run-away situations. The potential of explosion emphasizes the necessity of a proper temperature control.
- Halogenated (fluorinated, chlorinated or brominated) acetylenes are unstable and should be treated as explosives. Especially if in contact with caustic material (like NaOH) the danger of explosion is founded.

- Also during use chlorinated compounds may cause a burden to the environment. Some chlorinated compounds are used directly in the environment, causing a direct pollution. Pesticides, herbicides and fungicides used for agricultural purposes cause pollution of soil and surface water. Though these agricultural additives are primarily meant to protect animals or plants, they deteriorate others. E.g. insecticides, which are little selective in general, are not only active on insects, but also on other organisms like animals and man. The problem is worsened because of the bad degradability of the compounds and the resulting accumulation in the environment.

  But also when chlorinated hydrocarbons are not directly used in the environment, some deterioration may occur. Solvents evaporate and cause air pollution or are spilled causing pollution of soil and surface water. [6]

- After their use an adequate waste handling is essential. Chlorinated hydrocarbons should not be dumped, contaminating soil, water or air. Too many times contamination of soil with PCB's or PVC has been reported, increasing their public notoriety [21]. Good treatment of the compounds involves a separation of the chlorine from the carbon structure. The remaining carbon structure is environmentally more acceptable and the chlorine can be reused or is neutralised as a salt. Common treatment nowadays is incineration, which nevertheless requires close control because of the danger of formation of products of incomplete combustion (PIC's). Examples of these are the toxic and very persistent chlorinated dibenzodioxins and -furans. These products of incomplete combustion eventually contaminate air and food, accumulating in the food chain. [6] This emphasizes the need for a proper method to treat chlorinated hydrocarbon waste.

§ 1.4 Policy concerning chlorinated and other halogenated compounds.

Policy makers stand in between industry and environmentalists. A good policy has to be made maintaining or increasing welfare while saving the environment. The chlorine based chemical industry provides a lot of products with unrivalled properties. These properties enhance the efficiency of several processes, and thus save the environment. However, on the other hand the chlorinated products themselves are very awkward to the environment, contributing to a number of issues concerning environmental deterioration.

To be able to properly balance the industrial advantages and the environmental drawbacks a dinstinction has to be made between open and closed applications. In open applications the final product contains chlorine and as such the chlorine leaves the factory with the product. The producer loses control over what happens afterwards to the chlorine. Only if proper waste collection is managed the producer can prevent outflow of the chlorine to the environment. On the contrary, in closed applications the chlorine does not leave the industrial sites. The end products do not contain chlorine. In closed applications chlorine is commonly used for its property as an excellent reaction intermediate. Preventing pollution by chlorinated substances is, of course, much easier in these closed applications.

Chlorine related processes or products are not troublesome themselves as long as the environment is not charged with the chlorinated compounds. Closed applications are far more acceptable from this point of view than open applications. From this perspective the Dutch government has set up its policy. The keyword is 'integrated substance chain management' [28]. The substance should be controlled during its whole lifetime. Spill to the environment may not occur. In practice, several alternatives that all can fulfil the same need, must be considered weighing environmental and economical aspects. The impact on the environment can be deduced from the effect on the most important environmental issues as defined in the National Environmental Policy Plan. This practice should result in close control of the products, with highly reduced or no spill to the environment, a kind of overall closed application.

Some products do not fit in the practice of integrated substance chain management. E.g. agricultural pesticides can hardly be collected after use. For these kind of substances alternatives will have to be found with less negative environmental impact. In this perspective CFC's are banned. CFC's give raise to environmental deterioration by ozone depletion and global warming. Several applications of CFC's lead to direct emission into the environment. Capturing CFC's from the environment is nearly unfeasible.

Governmental actions should not be restricted to forcing the industrial emissions below acceptable limits, but also to changing the public attitude. The modern western society is a consumer society. People are used to have their products delivered in disposable packaging. Instead of throwing away, this packaging should be collected and reused or recycled. The case of plastics is a good example. Plastics, e.g. PVC, are durable products, which are hardly broken down by environmental means. In fact, plastics are extremely suitable for manifold use. People should be incited to alter their consuming attitude. They should learn to reuse those materials, especially since durability is one of their most prominent properties. [1]

Besides environmental and commercial aspects directly related to chlorine containing products, the chlorine issue is complicated by the connection of base and chlorine production. Chlorine is commonly produced by electrolysis of an aqueous sodium chloride salt (NaCl) solution. At the positive anode the chlorine gas evolves, while at the negative cathode hydrogen gas and hydroxyl ions are produced. As illustrated by the reactions taking place at the electrodes (see equations 1.22 to 1.24) chlorine and caustic soda are produced in stoichiometric quantities.

$$\textit{anode} \qquad 2Cl^- \rightarrow Cl_2 + 2e^- \tag{1.22}$$

$$\textit{kathode} \qquad 2H_2O + 2e^- \rightarrow H_2 + 2OH^- \tag{1.23}$$

$$\textit{overall} \quad (2Na^+) + 2Cl^- + 2H_2O \rightarrow (2Na^+) + Cl_2 + H_2 + 2OH^- \tag{1.24}$$

If the use of chlorine is decreased alternative production processes for base have to be established. In the USA, at the moment the request for base already exceeds the request for chlorine gas. [9]

§ 1.5 Chlorinated waste treatment. [24,25]

A prominent link in the substance chain is the treatment of waste. Two types of treatment could be distinguished:

- treatment based on recycling,
- treatment based on destruction.

Obviously, the recycling option offers the best opportunities from an environmental point of view. But depending on composition and physical structure of the waste this treatment is not always applicable. Then destructive treatment offers the last remedy converting harmful waste into environmentally acceptable species that do not disturb the natural equilibrium.

The waste mainly arises [24]

- during production, e.g. manufacturing halogenated hydrocarbons or synthetics,
- during use, e.g. as (metal) degreasers, paint removers, solvents, or in dry cleaning and pharmaceutical and pesticide industry.

An inventory of the halogenated waste streams in the Netherlands is given in table 1.5.

In 1988, 65000 ton halogenated waste was produced in the Netherlands. Part of this waste stream, 35000 ton (53 wt%), was incinerated, 6000 ton (10 wt%) was dumped and 24000 ton (37 wt%) was recycled or found some other profitable use. [24] The same kind of figure holds for Germany, as illustrated in table 1.4. Keeping in mind the restricted accuracy of the data, the table roughly indicates that about 5 wt% of the chlorinated hydrocarbons produced becomes waste and typically 40 wt% of this waste is reused or recycled (often via regeneration to HCl).

***Table 1.4** Estimates of halogenated hydrocarbon streams. Numbers are indicative, not precise.* [3,21,24]

area	production (10^6 ton)	waste (10^3 ton)	recycled (10^3 ton)
Germany (FRG)	6.4 (1980)	150-200 (1976) (3.1 wt% [(1)])	80 (1976) (40 wt% [(2)])
Netherlands (1988)	1.0	65 (6.5 wt% [(1)])	24 (37 wt% [(2)])

(1) *percentage of production.*
(2) *percentage of waste.*

Methods for treatment of the highly halogenated waste can be divided into two categories:

- ***physical treatments***, mainly achieving separation of reusable components:
  a. distillation (paragraph 1.5.1)
  b. liquid-liquid extraction (paragraph 1.5.2)

- ***chemical treatment***, mainly transforming the waste into less harmful compounds, sometimes with recovery of heat and products (and so with an opportunity of recycling):
  c. incineration (paragraph 1.5.3)
  d. pyrolysis (paragraph 1.5.4)
  e. wet air oxidation (paragraph 1.5.5)
  f. ozonisation (paragraph 1.5.6)
  g. gasification (paragraph 1.5.7)
  h. catalytic dehalogenation (paragraph 1.5.8)
  i. thermal dehalogenation (paragraph 1.6)

The state of the methods ranges from idea to practical application, i.e. from very small to full scale. The several methods will be discussed into more detail in the indicated paragraphs. A summary of the main characteristics of these waste treatment processes is given in table 1.6.

Treatment methods for low-halogenated waste will not be discussed as these kind of waste requests a totally different approach. Low-halogenated waste streams are for instance flue-gases and waste water streams. Low-halogenated waste treatment includes membrane, adsorption, electrochemical and biological technologies.

Table 1.5 An inventory of halogenated waste streams in the Netherlands. [24]

class	components	waste stream [ton/year]	fraction [wt%] (1)	other main constituents
liquid waste				
solvents	dichloromethane, 1,1,1-trichloroethane, trichloroethene, Freon 113 (2), tetrachloroethene, dichloroethane.	> 3000	varies, 20-80	water, oil, hydrocarbons
(metal) degreasers	1,1,1-trichloroethane, tetrachloroethene, dichloromethane, trichloroethene.	1600	30-70	halogen free organics
oil waste	dichloromethane, 1,1,1-trichloroethane, trichloroethene.	> 2000	< 10	oil
watery waste	dichloromethane, dichloropropene, dichloroethene, pesticides.	> 3800	< 5	water
distillation residues	dichloromethane, 1,1,1-trichloroethane, trichloroethene, Freon 113 (2), tetrachloroethene	> 1000	10-40	oils, not halogenated hydrocarbons
other liquid waste (3)	dibromoethane, dichloroethene, bromochloroethane, dichloromethane	122	> 80	pollutants (solids)
	dichloromethane	752	2-5	halogen free solvents, water
	waste from vinylchloride production, agricultural and fine chemicals production.	> > 10000	60/70 (4)	---

class	components	waste stream (ton/year)	fraction (wt%) (1)	other main constituents
paste-like and solid waste				
'per'slurry (waste from dry cleaning)	tetrachloroethene (per)	1200	25-35	solid dust: dirt, fats, filter powder
paint removal	dichloromethane	2000 (5)	35-60	solids, thickener
other pastes and solids (3)	PVC, liquid and solid halogenated aromatics (6), chlorinated alkanes.	> 1100	60	water, solids

(1) *average fraction of halogenated compounds in waste stream.*

(2) *Freon 113 = trichloro-trifluoroethane.*

(3) *these waste streams particularly come from production processes of halogenated hydrocarbons and synthetics.*

(4) *fraction elementary chlorine.*

(5) *1800 ton/year of these 2000 ton/year are directly emitted into the air!*

(6) *e.g. tetrabromobisphenol A, tribromophenol.*

Table 1.6 Options for halogenated waste treatment. [24,25]

process	state of the art	waste class (1)	type of process	x_{Cl} (2)	potential emission	costs (3)
distillation	full scale	1, 1a.	profitable: reuse of solvents	no limit	residues, water, off-gases	450-550
steam stripping	full scale	1a.	profitable: reuse of solvents	10	residues, water, off-gases	200
liquid-liquid extraction	little practical application	1, 1a.	profitable: reuse of solvents	no limit	little (extractant in treated water)	20
liquid injection incinerator	full scale	1, 1a, 2, 3, 4, 5.	destruction (recovery heat and HCl possible)	60-80	fumes, waste water	unknown
rotary kiln incinerator (AVR)	full scale	1, 1a, 2, 3, 4, 6.	destruction (recovery heat and HCl possible)	4-5	fumes, waste water	>150 <3000
fluidised bed combustor	not (yet) in practice	1, 1a, 2, 3, 4, 5?	destruction (recovery heat and HCl possible)	unknown	fumes, waste water	unknown
cement-furnace	idea	1, 1a, 2, 3, 4.	destruction, intrinsic use of waste as fuel	3-5	unknown	unknown
blast-furnace	idea	1, 1a, 2, 3, 4, 5?	destruction	30	unknown	300-450
pyrolysis	full scale	1, 1a, 2, 3, 4, 5, 6.	destruction (heat recovery possible)	70	fumes, slags, fly-ash, waste water	unknown
wet air oxidation	no practical application	2.	destruction (released heat used in process)	4	acid gases and hydrocarbons in off-gases, pollutants in treated stream	50-250

UV/ozonisation	yet no practical application	3.	destruction	1	see wet air oxidation, plus excess ozone.	200
gasification (Shell)	idea based on proven technology	1, 1a, 2, 3, 4, 5.	profitable: production syngas	10-40	waste water, off-gases	500-750
catalytic hydro-dehalogenation (KTI)	full scale	1, 1a, 2, 3, 4.	profitable: reuse of HX and hydrocarbons.	5-10	residues, off-gases, salt solutions	300-400
catalytic hydro-dehalogenation (UOP)	pilot plant	1, 1a, 2, 3, 4, 5.	profitable: reuse of HCl and hydrocarbons.	60	residues, off-gases, salt solutions	300-400
thermal hydro-dehalogenation (THD)	lab / pilot plant	1, 1a, 2, 3, 4, 5.	profitable: reuse of HCl and hydrocarbons	70	waste water, off-gases	150-700

(1) *waste classes:*

1. solvents (1,1,1-trichloroethane, dichloromethane, trichloroethene, tetrachloroethene).
1a. like class 1, but maximum chlorine fraction 10 wt%.
2. solved or suspended organic compounds in watery wastes (mainly non-aromatics).
3. like class 2, but including aromatic compounds.
4. all types of liquid halogenated hydrocarbon waste (maximum chlorine fraction 5-10 wt%).
5. like class 4, but maximum chlorine fraction 60 wt%.
6. solid halogenated hydrocarbon waste.

(2) *maximum chlorine content [wt%].*

(3) *costs given are only rough estimates [fl/ton].*

§ 1.5.1 Distillation (physical treatment).

Distillation is frequently applied as a halogenated waste treatment. As all physical technologies, distillation is not destructive, aiming at recovering the reusable components.

The distillation efficiency largely depends on the difference in volatility. Therefore the application of distillation is commonly restricted to halogenated solvents with a relative low molecular mass and correlated high volatility. Some types of distillation can be distinguished:
- batch distillation,
- thin film evaporation,
- rectification,
- fractionation,
- steam stripping.

Which type of distillation offers the best opportunities depends on the type of waste and the requirements that need to be met. Items involved include:
- the purity required,
- the composition of the waste,
- the amount of residue,
- the volatility of the halogenated compounds,
- the decomposition of the halogenated compounds,
- the existence of azeotropes.

The remaining residue is commonly disposed off by incineration.

Advantages of distillation include:
- the ultimate aim of distillation is reuse,
- distillation is a relative simple technology,
- the economically attraction of recovering,
- the very limited emissions (to water and air).

A disadvantage of distillation is compounds with about the same volatility are separated with difficulty.

§ 1.5.2 Liquid-liquid extraction (physical treatment).

Liquid-liquid extraction is another physical treatment. The treatment can be used for toxic, biological nondegradable organics, as long as the halogenated hydrocarbon concentration is high enough to render an economically feasible process. Extraction usually separates organic compounds from water/organic mixtures, but in principle also extraction from organic/organic mixtures is possible. Liquid-liquid extraction is in the stage of development. Therefore, in spite of the range of possible applications, the practice of liquid-liquid extraction in waste treatment is yet relatively restricted.

Liquid-liquid extraction has the following advantages.
- The halogenated compounds are recovered by a non-thermal physical method. No danger of thermal decomposition or chemical interaction exists.
- Components with equal boiling points can be separated.

On the other hand the following disadvantages exist.

- Both the extracted waste stream and the extraction liquid will be contaminated with remaining organic compounds. Treatment afterwards is essential.
- The technology itself may be cheap, but the overall price is raised by the essential treatment afterwards.

§ 1.5.3 Incineration (chemical treatment).

At the moment most halogenated waste is treated by incineration. However, incineration seems not a logical way to destruct halogenated compounds as some of them are known for their flame retarding or even flame extinguishing properties. The large oxidation stability of the halogenated hydrocarbons requires really elevated temperatures in order to reach complete destruction. Due to this fact and the lower heat of combustion the incineration of the halogenated waste is relatively expensive. For this reason incineration is only applied if the recovery of the halogenated compounds is economically nonprofitable.

The overall reaction is given by reaction equation 1.25. Besides the combustion products carbon dioxide (CO_2), water (H_2O) and hydrochloric acid (HCl), byproducts can be formed, such as chlorine (Cl_2) and not completely oxidated chlorinated hydrocarbons, e.g. polychorodibenzodioxins and -furans.

$$C_xH_yCl_z + [x+\tfrac{1}{4}(y-z)]\,O_2 \longrightarrow x\,CO_2 + \tfrac{1}{2}(y-z)\,H_2O + z\,HCl \qquad \textbf{(1.25)}$$

Suppression of byproduct formation is essential. Especially formation of chlorine should be reduced for its toxicity and the low efficiency of conventional methods to collect chlorine. According to the Deacon reaction chlorine is produced from hydrogen chloride and the excess oxygen that is supplied during incineration.

$$2\,HCl + \tfrac{1}{2}O_2 \rightleftarrows Cl_2 + H_2O \qquad \textbf{(1.26)}$$

Due to its exothermal nature the Deacon reaction is shifted to the left as temperature increases. In practice, some extra fuel can be supplied decreasing the amount of available oxygen and increasing temperature. However, the elevation of temperature should be kept below the limit of formation of nitrogen oxides (NO_x). Typical incineration temperatures are 1250-1650 °C if the produced HCl is to be recovered, and 1000-1300 °C in case of no HCl recovery. Another way to limit the chlorine production is addition of steam.

Very notorious byproducts are polychlorodibenzodioxins and -furans (PCDD/F). These compounds, frequently shortly referred to as 'dioxins', are not only one of the most toxic substances produced by man, but are very persistent to the environment as well. This 'unique' combination has given dioxins their notorious name [6].

According to the present knowledge the formation of dioxins is caused by a set of conditions:

- the presence of (chlorinated) aromatic oxidation products in the off-gases (due to incomplete oxidation; e.g. in domestic waste incineration caused by a too low temperature as a result of liquid from fruit),
- the presence of hydrogen chloride (HCl) in the off-gases,
- the presence of fly-ash in the off-gases,
- excess oxygen in the off-gases,
- slow cooling of the off-gases in the temperature region of 200-400 °C because of heat recovery and off-gas cleaning.

In practice, in order to decrease the dioxin formation, at least one of these conditions should be avoided. In the chemical waste incineration practice this include:

- removal of solids and metals from the waste before incineration,
- improvement of the oxidation process (e.g. less dead spaces in the reactor),
- removal of the fly-ash before the temperature is decreased to 400 °C or alternatively poisoning the catalytic property of the fly ash,
- the critical temperature range, 400-200 °C, should be passed as quick as possible.

As an end-of-pipe solution the dioxins produced can be collected. At temperatures below 40 °C dioxins preferably stick to particles. Injection of particles in the off-gases and recollection afterwards has proven to be a rather effective mean to catch dioxins.

The halogen fraction of the waste is normally limited to about 10 wt%, with an exception for liquid injection incineration (see table 1.6). Higher halogenated hydrocarbons are less susceptible to combustion. An increase of the halogen content causes a decrease of the heat of combustion. Sometimes, the halogen fraction is artificially lowered by addition of some fuel.

Other reasons for the restriction of the halogene content are imposed by the treatment of the reactor off-gas and the prevention of formation of undesired halogenated products.

Characteristics that determine whether or not the halogenated waste can be incinerated include:

- heat of combustion (related to halogen content and moisture),
- state of aggregation,
- ash content,
- viscosity.

The emissions of an incinerator are restricted by legislation. Table 1.7 lists the actual emissions and tolerable emissions according to the Dutch legislation.

Table 1.7 Emissions from incineration. [10,13,24]

component	measured (1) [mg/Nm^3]	RV'89 (2) [mg/Nm^3]
total solids/dust	4000 - 10000	5
hydrogen chloride (HCl)	400 - 2000	10
hydrogen fluoride (HF)	3 - 20	1
sulfurdioxide (SO_2)	100 - 800	40
nitrogen oxides (NO_x)	300 - 500	70
heavy metals (3)	10 - 20	1.0
mercury (Hg)	0.2 - 1.0	0.05
cadmium (Cd)	0.2 - 0.5	0.05
carbon monoxide (CO)	30 - 2000	50
organic substances (as C)	1 - 10	10
polychlorodibenzodioxins and -furans (PCDD/F):	measured (1) [ng/Nm^3]	RV'89 (2) [ng/Nm^3]
• total	200 - 2000	
• TEQ (4)	5 - 100	0.1

(1) *actual measured emissions from waste incinerators.*

(2) *tolerated maximum emission according to RV'89 (directive for incineration by dutch government; 'richtlijnen verbranden 1989'* [13]*)*

(3) *Sb, Pb, Cr, Cu, Mn, Sn, As, Co, Ni, Se, Te, V.*

(4) *toxicity equivalent quantity (the amount of 2,3,7,8-TCDD with the same toxicological effect).*

The incineration practice is worked out in various ways:

- combustion at sea,
- liquid injection incineration (AKZO),
- rotary kiln incineration (AVR-Chemie),
- fluidised bed combustion,
- incineration in cement-furnaces,
- incineration in blast-furnaces (John Brown Engineers & Constructors B.V.).

Table 1.6 lists the main features of the incineration practices. Combustion at sea used the buffering capacity of the seas. About 80 gram HCl per 1 cubic metre can be dissolved in the alkaline seawater without a remarkable change of pH. This actually meant a direct disposal of the hydrogen chloride in an environmentally acceptable way. However, the complete off-gas, including its hazardous components, was brought into direct contact with the environment. Related hereto and to supposed difficulties in maintaining the required high degrees of destruction and dangers dealing with the transport of the hazardous waste to the final destruction location at sea, the incineration at sea has been banned since 1990. [3,24]

At present most liquid halogenated waste is treated by incineration, while the solid waste is dumped in landfills. The policy of the Dutch government is to reduce this dumping to zero before the year 2000. Therefore technologies should be expanded to treat solid halogenated waste as well.

Advantages of incineration include the following items.

- Though basically a destruction method, incineration offers the possibility to recov heat and elementary chlorine.
- Incineration is a proven technology.

Disadvantages include the following items.

- The halogen fraction of the intake is commonly limited.
- Incineration causes emissions of environmentally harmful species, such as products of incomplete combustion (PIC's), sulfurdioxide (SO_2), nitrogen oxides (NO_x) and large amounts of carbon dioxide (CO_2).
- The social risk of dioxin formation.
- The environmental requirements and end-of-pipe solutions result in huge aftertreatment systems, increasing the costs of destruction.
- In case of (co)incineration in cement- or blast-furnaces, the quality of the chief product will remain the principal objective, which may hamper the destruction efficiency of the halogenated waste.

§ 1.5.4 Pyrolysis (chemical treatment).

Pyrolysis means thermal destruction under exclusion of oxygen. As a result oxidation steps do not occur. Pyrolysis of halogenated waste takes place at elevated temperatures lower then required for incineration. Dioxins and related compounds are broken down. Pyrolysis is a commercially applied method of halogenated waste treatment in the USA.

A plant for waste pyrolysis typically exists of three parts:

- a pyrolysis furnace (indirectly heated to 540-870 °C),
- an afterburner for the volatile waste components and the products of pyrolysis (T=900-1200 °C),
- an unit for heat recovery.

The waste is fed to the indirectly heated pyrolysis furnace by a conveyer belt. Volatile components and pyrolysis products (like e.g. HCl) leave the furnace in the gaseous phase. Inerts, like metals and other inorganic substances, remain solid or paste-like. They are removed from the pyrolysis furnace by the conveyer belt.

Pyrolysis is very appropriate to treat waste like the following:

- high viscosity waste that can not be sprayed into liquid injection incineration chambers,
- materials with a low melting point (though care has to be taken for fouling of heat exchangers and for the difficult removal of the residue),
- waste with a high ash content (however, extra gas cleaning is required),
- waste containing toxic components having a high vapour pressure at the incineration temperature.

Advantages of pyrolysis include the following items.

- Metals and salts do not melt (for the pyrolysis reactor temperature is chosen below their melting point).
- There is little or no turbulence in the furnace. As a result there will be little or no solid particles in the off-gases.
- NO_x is not produced; more than that it is broken down to nitrogen and water under these reductive conditions.
- The emission of acid gases, like HCl and SO_x, is reduced to 10-50% by the alkaline components in the waste.
- Metals and salts in the pyrolytic residue are hardly leached out because of their physical and chemical immobility.
- The reductive conditions and the small amount of solids in the off-gases effectively exclude the formation of dioxins.

Disadvantages of pyrolysis include the following items.

- The waste treatment is based on destruction.
- Tar (and soot) are formed.
- The system does not seem very appropriate for liquid waste treatment.
- Readdition of the produced HCl to unsaturated bonds is likely to occur. Treatment afterwards by incineration is essential.
- In such afterburning systems the formation of dioxins is rather probable again.

§ 1.5.5 Wet air oxidation (chemical treatment).

Wet air oxidation concerns the oxidation of dissolved and suspended organic contaminants in watery waste. Relatively elevated temperatures (175-320 °C) and elevated pressures (20-200 bar) are required to enlarge the solubility of oxygen (O_2) and thus the reaction rate. An average conversion of 80% is reached. The remaining organics include small molecular biological degradable components, like acetic acid and formic acid. However, halogenated aromatics (chlorobenzene, PCB's, dioxins, pesticides) are resistant to the above mentioned conditions. Their destruction requires higher pressures and temperatures.

Wet air oxidation is appropriate for diluted waste and as such it is no alternative for incineration.

Wet air oxidation presents the following advantages.

- The method is excellent for waste, the toxicity of which prohibits biological treatment and which is too diluted for other treatments to be economically feasible.
- If the heat of combustion of the waste is large enough, the treatment operates without suppletion of external fuel.
- The oxidation products remain in the water phase, not resulting in any emission of NO_x, SO_2 or particles.

Disadvantages of the technology are the following items.

- The destruction efficiency largely depends on the chemical composition of the organic contaminants and is rather sensitive to metals and the like.
- Both gaseous and liquid discharge contain contaminants which frequently require some aftertreatment.

§ 1.5.6 UV/Ozonisation (chemical treatment).

Chemicals as ozone (O_3), hydrogen peroxide (H_2O_2) and potassium permanganate (K_2MnO_4) are strong oxidants. They are frequently applied to treat industrial liquid waste streams containing phenols, cyanides and sulfurised organic substances. Since ozone as such is not really effective in the treatment of halogenated compounds, ultraviolet radiation is added to supply extra energy to break down the organic structures. Though ozonisation has been applied at industrial scale to treat the types of waste metioned above, the combination with ultraviolet radiation to treat halogenated waste is still in development.

As ozone readily reacts with all kinds of organic functional groups, pretreatment is usually applied to limit the ozone consumption. Ozonisation can particularly be used in the treatment of low concentrated waste.

UV/Ozonisation has the following advantages.
- UV/Ozonisation seems very promising as a pretreatment method, e.g. before biological treatment.
- The ozonisation technology appears to be relatively simple.
- Only limited emissions seem to be released by the process.

On the other hand, ozonisation has some disadvantages as well.
- Ozonisation is a rather unselective process.
- Whenever the waste contains oxidation resistant hydrocarbons, it can not be treated by UV/ozonisation.

§ 1.5.7 Gasification (chemical treatment).

There is little or no experience with treatment of halogenated waste by gasification, though gasification itself is a more or less proven technology. Gasification is the process of converting a liquid oil into a gaseous syngas, which prominently is a mixture of carbon monoxide (CO) and hydrogen (H_2). The oil reacts with oxygen and steam at temperatures of 1300-1500 °C and pressures of 10-100 bar. Different types of oil can be converted, ranging from light oil to asphalt. Shell and Texaco own the patents of rather similar gasification processes.

In general, the idea to treat halogenated waste under gasification process conditions exhibits good prospects, though some remarks have to be made.
- The technology can only handle organic waste streams; the tolerable water content of the feed is very limited.
- With increasing halogen content the heat yield declines; therefore the tolerable halogen content is limited.

The advantages of gasification include the following items.
- Within the limits of the halogen and water content, the process shows a large flexibility towards the composition of the feed.
- Based on the reductive process conditions dioxin formation is not expected.
- Gasification is a more or less proven technology with respect to nonhalogenated feedstocks.

Disadvantages are listed below.

- The lack of experience with gasification of halogenated waste include some risks with respect to:
  - the maximum tolerable halogen content of the waste,
  - the effect of halogens in the process (related with chemistry and corrosion),
  - the unknown composition of the waste water produced and the amount of not precipitated heavy metals,
  - the unknown composition of the produced off-gas, especially concerning the halogenated byproducts that have dangerous properties at low concentrations, such as dioxins,
  - the operation of the soot recovery installation, which may need to be altered because of the huge salt content of the watery soot sludge.
- A large waste water stream is produced due to the enormous amounts of base required for neutralisation of the formed HCl and precipitation of heavy metals.

§ 1.5.8 Catalytic hydrodehalogenation (chemical treatment).

In catalytic hydrodehalogenation the halogen content is selectively removed from the halogenated waste by processing in a reductive hydrogen atmosphere. Typical temperatures and pressures of the catalyzed reaction are respectively 250-300 °C and 50-60 bar. The technology is applicable for liquid waste streams, like spent oil and other waste oils, that are contaminated with halogenated, especially chlorinated, hydrocarbons. The process can be divided in three steps:

-1- pretreatment; separation of any water phase in the waste, followed by separation of metals that would poison the catalyst. The halogenated hydrocarbons are separated from the metals by 'evaporating' methods like flashing or distillation.

-2- hydrodehalogenation treatment; conversion of the waste to halogen free hydrocarbons and hydrogen halogenide HX in the main reactor.

-3- aftertreatment; neutralisation or recovery of the produced HX.

In the Netherlands two companies are active in the development of catalytic hydrodehalogenation; KTI and UOP. Their processes are quite similar with an exception for the tolerable level of waste halogen content.

Advantages of catalytic hydrodehalogenation comprise the following items.

- The process gives no rise to environmentally unacceptable emissions to air, water or soil.
- Catalytic hydrodehalogenation is in principle a recycle process: useful products are formed (hydrogen chloride and 'clean' hydrocarbons).
- The technology can be implemented as part of an integrated process system.
- The process is flexible towards the composition and physical structure of the waste as long as the tolerable halogen content is not exceeded.

Disadvantages are listed below.

- The process can only handle waste that can be pumped; this requires extra unit operations in the case of solid waste like PVC.
- The pretreatment has to satisfy stringent requirements to prevent catalyst poisoning by metals.
- The tolerable halogen content should never be exceeded.

§ 1.6 Thermal hydrodehalogenation (chemical treatment).

In thermal hydrodehalogenation the halogenated waste is destructed in a reductive hydrogen atmosphere at elevated temperatures of 600-900 °C. No catalyst is applied. The chemistry of thermal hydrodehalogenation is based on hydrogenolysis: hetero-atoms and functional groups are split off from the organic structures and replaced by hydrogen atoms.

$$RX + H_2 \longrightarrow RH + HX \tag{1.27}$$

In comparison to pyrolysis the suppletion of hydrogen has some positive effects on the dehalogenation. [14]

- The dehalogenation rate is accelerated.
- All halogenated substances can be converted.[4]
- At circa 900 °C the maximum, thermodynamic, dehalogenation level for all chlorinated hydrocarbons is reached within 1-10 s.
- The soot formation is reduced.

The required hydrogen may be supplied as syngas because carbon monoxide (CO), water (H_2O) and carbon dioxide (CO_2) behave like inerts. The organic chlorine is nearly completely converted into inorganic hydrogen chloride (HCl); the reaction equilibrium restricts the conversion only at the last permillages. E.g. in threefold excess of hydrogen a hydrodehalogenation conversion up to 99.96 mol% is attainable for chlorobenzene at 900 °C.

Besides to dechlorination the organic structures are subject to some reorganisation. Preferably small organic structures are formed:

- aliphatic compounds particularly produce C_1 and C_2 molecules,
- aromatic compounds particularly produce benzene.

On the other hand also some larger structures are formed resulting in solid products. However, in comparison to pyrolysis the soot and tar production is rather limited due to the suppletion of hydrogen.

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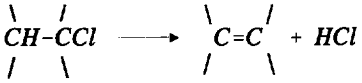
[4] In pyrolysis the major route for dechlorination is elimination of HCl from the organic skeleton. The chlorinated hydrocarbons having a H-donor at the neighbouring C atom of the C-Cl bond are dechlorinated according to:



$$\mathrm{CH{-}CCl} \longrightarrow \mathrm{C{=}C} + \mathrm{HCl}$$

Chlorinated hydrocarbons having no H-donor at the neighbouring C atom can not undergo this type of reaction. In pyrolysis these compounds, like the chlorinated benzenes, ethenes and methanes, are dechlorinated with difficulty. Under more severe conditions, e.g. by elevating the temperature, these recalcitrant compounds finally break down. However, under those conditions HCl is not the only chlorine containing product: a range of chlorinated organics is formed. E.g. polychlorobiphenyls (PCB's) may be formed from chlorobenzene. Also a huge quantity of soot and tar is formed. The hydrogen addition suppresses the formation of these products. [14]

The chemical mechanism behind thermal hydrodehalogenation is of a radical type (see reaction equations 1.28 to 1.29). It is proposed that a hydrogen radical attacks the halogenated hydrocarbon leading to an activated complex. This complex will fall apart for instance into a hydrocarbon molecule and a halogen radical. The halogen radical reacts with a hydrogen molecule producing molecular hydrogen halogenide and another hydrogen radical, which can restart the dehalogenation chain. [22] More information about the mechanism will be discussed in chapter 4.

$$H\cdot + RX \longrightarrow RH + X\cdot \qquad \textbf{(1.28)}$$

$$X\cdot + H_2 \longrightarrow HX + H\cdot \qquad \textbf{(1.29)}$$

The dehalogenation rate depends on temperature and composition of the halogenated mixture. Every halogenated hydrocarbon is related to a specific 'floor' temperature, which at least is required for a sufficient dehalogenation. Some chlorinated compounds are already dehalogenated at 600 °C, while others like chlorobenzene need temperatures up to 900 °C. Unfortunately the easily dehalogenated compounds give raise to an enlarged soot and tar formation at temperatures higher than strictly required for dehalogenation. Processing a chlorinated waste mixture requires 900 °C in order to convert all chlorinated compounds. As a result soot formation should always be taken into account.

Monochlorobenzene features an excellent model substrate from a chemical point of view for its difficult dehalogenation. Labscale investigations at Leiden University predict a pseudo first order dehalogenation rate in excess hydrogen, following approximately: [22]

$$k_{eff}\,(chlorobenzene) = 7.943\ 10^{10} \exp(-\frac{28900}{T})\ \ s^{-1} \qquad \textbf{(1.30)}$$

It is stated that nearly all other chlorinated hydrocarbons are hydrodechlorinated more rapidly than chlorobenzene.

In the presence of active coal the hydrodehalogenation rate is speeded up. E.g. the temperature required to dechlorinate chlorobenzene is lowered to 600 °C. However, the consumption of active coal is rather high, in the order of 1 kg active coal per 1 kg chlorobenzene [14]. Therefore application of this active coal induced activation seems to be limited to low concentrated waste treatment or guard bed uses.

Thermal hydrodehalogenation possesses several advantages.

- The chlorine product, which is HCl, can be reused. Light hydrocarbons and benzene are the main hydrocarbon products, which at least can be used as a fuel.
- In contrast with incineration dry HCl is produced in the reactor due to the reductive reaction conditions.
- Emissions to the environment seem to be limited.
- Due to the reductive atmosphere dioxin formation is not expected.
- The technology is extremely suitable to treat highly halogenated waste.
- The technology is flexible to composition and physical structure of the waste. The technology offers the potency to treat all kinds of waste.
- Integration into other processes is possible.

A disadvantage of thermal dehalogenation is the state of the art. Process experience is only available in small labscale units. For this reason a project was started to develop thermal dehalogenation to a process at industrial scale. The development of the reactor and its directly connected units forms the backbone of this thesis.

§ 1.7 Other than chlorine containing halogenated compounds.

Most information given in relation to chlorinated compounds can be extended to other halogenated compounds. Chlorinated compounds are the most important and most frequently occurring halogenated compounds. For this reason these compounds have been focused on during the project, and in this chapter up till now. In this paragraph some information about other than solely chlorinated compounds will be given. To some extent the picture drawn for chlorinated compounds holds for all halogenated compounds, as will be shown.

Halogens are the elements in the seventh column of the periodic system. In sequence of increasing molecular weight the following halogens exist: fluor (F), chlorine (Cl), bromine (Br), iodine (I) and astatine (At). [8] Besides chlorine, also fluorine and bromine are frequently encountered in organic material.

§ 1.7.1 Fluorinated hydrocarbons.

Fluorinated hydrocarbons are denser and more volatile than their corresponding hydrocarbons. They have low refractive indices, low dielectric constants, low solubilities, low surface tensions, and viscosities comparable to the analogue hydrocarbons. [11]

Especially the saturated highly fluorinated hydrocarbons are very stable due to their chemical inertness. They are nonflammable, can be heated up to 260-316 °C and are physiological harmless. [5,11,20]

These fluorinated monomers were once used in aerosol packaging till their environmentally harmful properties concerning ozone depletion and global warming were recognized. However, they are still used as refrigerants, solvents, blowing agents, fire extinguishers, lubricants and hydraulic fluids. More and more often fluorine is used in the synthesis of narcotics; in inhalation anaesthetics, in drugs for cancer chemotherapy, in steroids, in analgesic agents (e.g. analogues of aspirin with even stronger effect) and in antibiotics. [5,11,20]

On the contrary, the unsaturated fluorinated hydrocarbons are rather reactive. They are frequently used as a feedstock for the production of fluorinated polymers [5]. Examples of these polymers are polytretafluoroethene (PTFE=teflon), polymers of chlorotrifluoroethene, fluorinated ethene-propene polymers, polyvinylidene fluoride, hexafluoropropene. Of these especially PTFE is very famous for its excellent properties. The polymers are known as thermoplastic substances, resistant to chemicals and oxidation. They are noncombustible, have a broad useful temperature range (up to 285 °C), have a high dielectric constant and are resistant to moisture, weathering, ozone and ultraviolet radiation. [11]

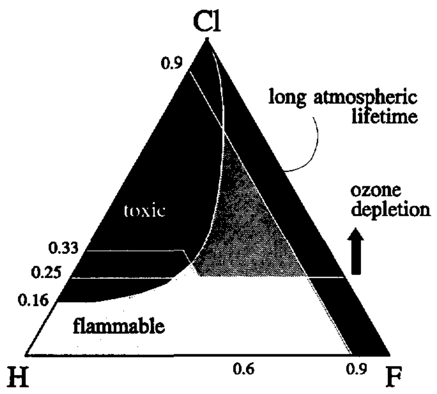


Figure 1.1 Schematic presentation of properties of halogenated hydrocarbons. [15,26]

The polymers find a widespread use in high temperature wire and cable insulation, other electrical equipment, chemical processing equipment, coatings for cooking utensils, piping and gaskets. [11,20]

Environmental drawbacks especially involve the chlorinated fluorocarbons. These compounds, e.g. CFC-11 and CFC-12, have excellent refrigerating properties, seemed harmless when introduced, but happened to deplete ozone in the stratosphere and to contribute to global warming. As result of these environmentally unacceptable features these chlorinated fluorocarbons have been banned. An overview of important properties of chlorinated fluorocarbons is given by the triangular figure 1.1. [15,26]

It must be emphasized that ozone depletion is effectuated by chlorinated fluorocarbons, but not by solely fluorinated hydrocarbons, as also can be deduced from the triangular figure 1.1. [11]

§ 1.7.2 Brominated hydrocarbons.

Brominated hydrocarbons exhibit some excellent features as intermediates in chemical processing in comparison to corresponding chlorinated hydrocarbons. Reactions in which the brominated hydrocarbon intermediates are involved are relatively faster, have a higher yield and require a less elevated temperature and pressure. Sometimes these features compensate the higher price of bromine. [4]

The main application of brominated hydrocarbons is as endproduct, such as: [11]

- antiknock agent (dibromomethane),
- fumigant (bromomethane, dibromomethane),
- flame extinguishant (chlorobromomethane, bromotrifluoromethane),
- flame retardant, extensively used in synthetic polymers and foams (tetrabromobisphenol A, tetrabromophtalic anhydride, decabromodiphenyl ether, vinyl bromide).

In the USA in 1976 69% of all bromine was used as 1,2-dibromoethane, making it the most frequently applied brominated hydrocarbon. The major application of 1,2-dibromoethane was its use in combination with lead alkyls as anti knock agent in gasoline. [4,18]

§ 1.8 Purposes of investigation.

In cooperation with Royal Schelde and Leiden University a project has been set up to develop thermal hydrodehalogenation to a destruction process at industrial scale. Starting point were the experiences at labscale [22].

During the project the development has been focused on liquid chlorinated hydrocarbons. Model substrates have been chlorobenzene and DD[5]. The objective involved the development of the reactor and its integration with other units.

A bench scale pilot plant has been designed and erected (chapter 2). Experimental experiences in this plant (chapter 3) has led to recommendations for a plant at larger scale. A design for a plant at industrial scale has been made (chapter 6).

Besides the bench scale pilot plant a smaller installation has been developed especially to investigate soot and tar formation. This small installation is suited to investigate sooting attitudes of chlorinated hydrocarbons and the sooting activity of construction materials (chapters 2 and 3).

A computer model is set up to predict sooting tendencies. The model correlates the dechlorination and the soot formation tendency in the hydrodechlorination of chlorobenzene (chapter 4).

In the indicated chapters the mentioned aspects of the process development will be discussed.

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Chapter 2

Experimental apparatus and installations

design, construction and flowsheet

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§ 2.1 Introduction: purposes of installations.

The objective of the present study is to develop the process of thermal hydrodechlorination from small labscale to industrial scale. Investigation of possible bottlenecks is required and plausible solutions need to be given. As a tool to reach this objective two installations have been constructed:

- ***the mini pilot plant installation (1 kg/h).***
  Its scale is in between labscale (about 1-10 g/h) and desired industrial scale (about 1-10 ton/h). In this installation the main topics of investigation have been the configuration of reactor and essential unit operations for pretreatment of the feed and aftertreatment of the reactor effluent.

- ***the bench scale installation (30 g/h).***
  In this installation the investigations have been focused on soot and tar production. The major objectives of research have been a better quantification of the soot and tar production. The effects of process conditions (H_2/Cl ratio, residence time, temperature) and construction materials are investigated.

In the forthcoming paragraphs these installations will be discussed.

Paragraph 2.2 covers the mini pilot plant. After discussion of the flowsheet (paragraph 2.2.1) the configuration and design of the reactor is reported (paragraph 2.2.2). Next the analysis (paragraph 2.2.3) and the design of other apparatus is covered. Finally, safety measures are discussed in paragraph 2.2.5. Methods involved in the design of the pilot plant and the determination of the split ratio are presented in appendices 2.A and 2.B, respectively.

Paragraph 2.3 covers the bench scale installation. Recommendations for this installation which has to measure soot formation in thermal hydrodechlorination, are obtained by studying existing methods which are used to predict soot formation in fluid coking (paragraph 2.3.1). The flowsheet of the designed installation is discussed in paragraph 2.3.2 and comments on the analysis used are given in paragraph 2.3.3.

Paragraph 2.4 gives information on the chemical and physical properties of the model substances used in this study.

§ 2.2 Mini pilot plant installation.

§ 2.2.1 Flowsheet of the mini pilot plant installation.

Basically the pilot plant installation is divided in four distinct sections, as shown in figure 2.1:

- the feed section,
- the reactor section,
- the treatment section,
- the analysis section.

The central item of the installation is the reactor. It is fed by a mixture of chlorinated hydrocarbon and hydrogen. The H_2-gas is supplied from gas cylinders and has a purity of 99.95%. The required flow rate of about 1 Nm^3/h is regulated by a flow controller. Originally, a gas preheater was used. Later the gas preheater was removed as in practice, the temperature of the gas at the entrance of the reactor was completely determined by the reactor wall temperature.

The chlorinated hydrocarbon feed is pumped through a preheater to the reactor. The flow rate of the liquid feed is obtained by weighing a measuring vessel placed upon an electronic balance. The measuring vessel can be filled from the storage vessel, using gravitation. By the combination of the relatively small measuring vessel and storage vessel, a system is realised which not only measures accurately but also has a large storage volume.

In the preheater the chlorinated hydrocarbons can be evaporated before they enter the reactor. Feeding the chlorinated hydrocarbons as a gas improves the mixing of the chlorinated hydrocarbon with the H_2 gas. However, not all chlorinated hydrocarbons can be evaporated in the preheater as some of them already coke at boiling temperature, e.g. DD[1].

In the installation several chlorinated hydrocarbons have been processed, of which monochlorobenzene (of technical quality) has been the main model substance. At standard conditions about 1 kg/h of monochlorobenzene is fed to the installation.

During start-up and shut-down 'neutral' substances are fed to the reactor system. Then N_2-gas (99.998% purity) and hexane or water are used. They are fed via the same routes as the standard substances.

The chlorinated hydrocarbons are fed into the reactor via an injection system, of which the performance has been improved during the study. Finally, the original system was replaced by an 'air blast' nozzle to increase the mixing of liquid chlorinated hydrocarbons and H_2 gas.

As stated before, the core of the installation is the reactor. It can be operated as a fluidised bed reactor or as an (empty) tubular reactor. The reactor is heated electrically to the operation temperature of 600 - 900 °C. The operation pressure is 'atmospheric', typically 1.2 atm. The inner diameter of the reactor is 95 mm, its length 1400 mm. At standard conditions (900 °C, 1 atm.) the residence time in the reactor is 8 s.

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[1] DD = mixture of dichloropropane and -propenes.

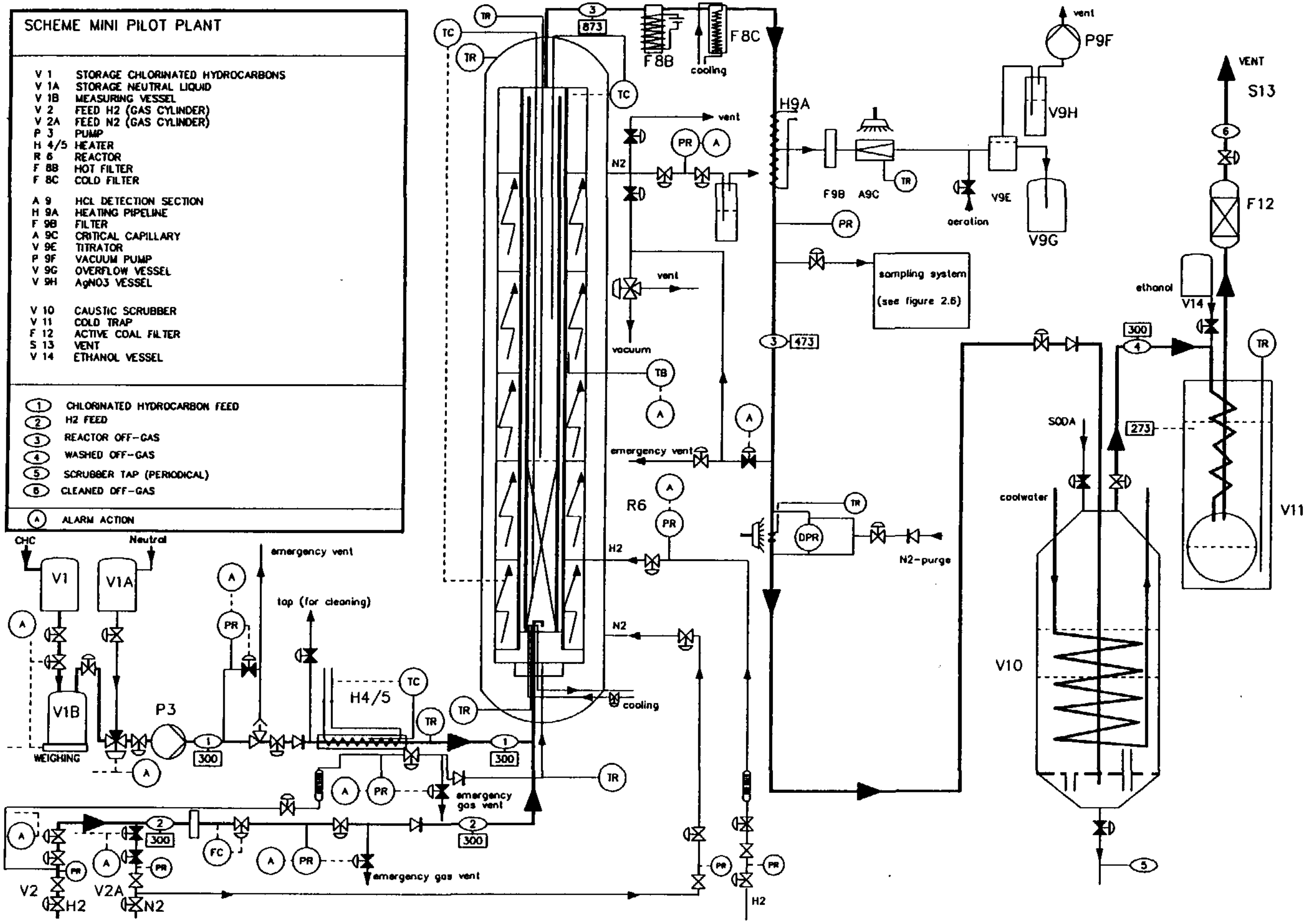

Figure 2.1 Flowsheet of mini pilot plant.

Extraordinary construction material and safety precautions resulted in a somewhat complicated construction of the reactor. To withstand the severe process conditions ceramic silicon carbide (SiC) has been chosen for the inner reactor wall. The ceramic tube is placed in a nickel alloy housing. In this way, construction problems related with the difficult tooling of the ceramic material are solved. To prevent accumulation of reaction medium in the space between the SiC-tube and the Nimonic housing, this so called annular space is purged with a small stream of H_2 gas. For safety reasons, the reactor is embodied in a N_2 containing box.

More detailed information about the reactor is given in paragraph 2.2.2.

Directly after the reactor, physically at the top of it, soot and tar are separated from the exhaust gases. After attempts with a cyclone were unsuccessful, two glass lined filters have been installed. The first filter is kept at an elevated temperature of 300 °C, and is called the hot filter. Here, soot is caught. The second filter, the cold filter, is cooled to temperatures of about 20 - 50 °C. In this filter most of the tar is caught. More information about the cyclone and filters is given in paragraph 2.2.4

After leaving reactor and filter section the exhaust gas is transported to the rest of the treatment section. The main operation consists of washing the exhaust gas in a caustic soda scrubber. Hydrogen chloride (HCl) dissolves in the water solution and is neutralised. Some hydrocarbon products condense in the scrubber and form a liquid phase which does not mix with the water phase. More detailed information about the scrubber is given in paragraph 2.2.4.

After the scrubber a cold trap, cooled by ice, is installed to condense hydrocarbons with a low boiling point. Here, always some water is caught from the gas leaving the caustic soda scrubber. Via an active carbon filter, which functions as a last security measure, the exhaust gas is blown off.

Analytical information to determine the levels of chemical conversion is obtained as follows:

- The production of soot and tar can be evaluated from the amounts caught in the filters and observed in the reactor.

- The dechlorination level is determined by two alternative ways:

  1) **on-line titration of the produced HCl.**
  Because the HCl-stream is too large to be measured as a whole, a well defined split stream is analysed. As HCl is the only desired chlorine containing product, the HCl titration is a clear indication of the dechlorination level.

  2) **off-line GC-analysis of the product gas.**
  Once in an experiment the residual amount of chlorinated hydrocarbons is measured cumulatively for a certain period of time (usually half an hour). This is a direct measure of the dechlorination level.

More detailed information about the analysis section of the mini pilot plant is given in paragraph 2.2.3.

§ 2.2.2 Reactor.

The objective of the present study is to develop the process of thermal hydrodechlorination from small labscale to industrial scale. As a tool to reach this objective the mini pilot plant has been constructed. The main considerations and major criteria applied during the design are the following.

- The development is focused on the treatment of liquid chlorinated hydrocarbons.
- The scale of the new installation (about 1 kg/h) is chosen halfway labscale (about 1-10 g/h) and desired industrial scale (about 1-10 ton/h).
- The design is based on the experimental experiences at labscale as reported by Louw and Manion [31].
- At atmospheric pressure the required reaction temperature is 600 - 900 °C, the exact temperature depending on the chlorinated hydrocarbon being processed. Typical residence times are 2 - 10 s.
- The dechlorination rate of monochlorobenzene and chloromethane are known. In comparison with other chlorinated hydrocarbons the dechlorination rate of these compounds is supposed to be the slowest on a per chlorine basis.
- Little information was available about the nature and quantity of soot and tar formation, other than that their formation will depend on the molecular stability of the chlorinated hydrocarbons and the amount of H_2 available. From labscale experiments a threefold amount of H_2 molecules per amount of Cl atoms is advised. Soot and tar formation will increase if unstable molecules like hexachlorobutadiene and tetrachloroethene are used.
- Louw [33] showed at labscale that active carbon activates the dechlorination process substantially, while the active carbon loses its activity after treatment of a relatively limited amount of chlorinated hydrocarbons (about 1 kg active carbon is deactivated per 1 kg chlorobenzene).
- For simplicity, the mini pilot plant will not recycle mass or heat.
- The fluidised bed material will only be refreshed periodically.

From the little information on the soot formation one can expect problems when processing a mixture of a stable chlorinated hydrocarbon, like chlorobenzene, which requires elevated temperatures, and a unstable chlorinated hydrocarbon, like hexachlorobutadiene, which gives raise to large soot formation already at lower temperatures. Then, excessive soot formation is to be expected. To solve the problem at a larger scale a two step processing may be adequate: a first step at relatively moderate temperatures to process the unstable chlorinated hydrocarbon with limited soot formation and a second step at elevated temperatures to convert the stable chlorinated hydrocarbon. However, this will only be attractive if in the second reactor no or a very limited amount of soot is produced.

The rapid loss of catalytic activity limits the useful application of active carbon at industrial scale. An example of such industrial application could be the use of active carbon in a third reactor to dechlorinate unconverted 'last ends'. Another example may be the treatment of waste streams with small concentrations of chlorinated hydrocarbons. These applications are beyond the scope of the present study aiming at an industrial process that is unsensitive towards deactivating contaminants in the waste.

Considering the available information a fluidised bed reactor was chosen.

- Due to the large solid mass moving around the reactor possesses excellent heat control. The circulating particles enable reaction heat to be used for heating the feed to the required reaction temperature. Hot spots are unlikely to occur.

- The bed material was thought to collect the produced soot and tar. This would simplify the treatment of the solid byproducts. The coked bed material could be sent to a separate combustion unit where the soot and tar are burnt off.

- When using a fluidised bed the extension of the process to the treatment of solid waste might be easier.

Of course, the fluidised bed can also be operated as an (empty) tubular reactor. The reactor flow always is upwards, i.e. from bottom up.

The design of the reactor is based on kinetic data of thermal hydrodechlorination of chlorobenzene [31]. These kinetics have been combined with hydrodynamic fluidised bed models to predict the conversion in the reactor. In most fluidised beds the bed material is involved in the reaction as reactant or catalyst. The majority of fluidised bed models is developed for this kind of system. Here, the bed material is considered not reactive at all: thermal hydrodechlorination solely occurs in the gas phase. Therefore, some common fluidised bed models have been adapted to describe gas phase reaction instead of gas-solid reaction for which they were originally meant. [6,15,16,19,20,26,28,42,43,44]

Four models have been used to estimate the chemical conversion.

- ***ideal plug flow model ('tube').***
  This model is the simplest, predicting the highest conversion. It is an one-phase model; only the gas phase is considered. The effect of the chemically inert solids is restricted to occupation of space.

- ***adapted Van Deemter model.***
  This model is a two-phase model. A bubble phase and an emulsion phase are distinguished in the bed. The emulsion phase contains the solids, and some gas. Therefore, the chemical conversion in the emulsion phase must be combined with the conversion of the bubble phase.

- ***adapted Kunii and Levenspiel model***
  This model is a further extension of the second model. The gas bubbles are surrounded by clouds and wakes, through which the gas must be transported before reaching the emulsion phase. The clouds and wakes form a third phase in the system.

- ***ideal CSTR-model ('tank').***
  This model is again a simple model. It is taken into account mainly as a reference.

In appendix 2.A the derivations of the adapted van Deemter model and the adapted Kunii and Levenspiel model are given.

Based on these models the configuration presented in table 2.1 has been designed. The conversion in the designed reactor predicted by the four different models is presented in figure 2.2.

Table 2.1 Designed reactor configuration.

standard conditions: temperature [°C] pressure [atm] H_2/Cl ratio [mol/moleq.]	 600 - 900 1 3
reactor dimensions: diameter [mm] length [mm]	 95 1400
residence time: in fluidised bed [s] in freeboard [s]	 2-3 5
residence time in empty tube [s]	8
fluidised bed: material mass [kg] height [mm]	 sand 5 400
flow pattern in empty tube	laminar, upstream
attainable dechlorination level at standard conditions [mol%]	99.96

With a diameter below 30 cm fluidisation behaviour may strongly be affected by the wall [18,20]. However, since the chemical reaction occurs in the gas phase, it is expected that the wall effect will not play a major role in the scaling-up. For practical reasons a diameter of about 10 cm is chosen.

The bed material is thought to collect all soot and tar. A periodical refreshment of the bed material must limit the collected fraction carbon on the bed material. Assuming that about 2 wt% of the chlorinated hydrocarbon feed will be converted to soot, the bed mass will grow about 0.4 wt% every hour. After operation of one working-day (8 hours) the fraction of collected soot on the bed material amounts to about 3.2 wt%, which is tolerable.

Sand is used as bed material for several reasons:
- it has good fluidisation properties,
- it is inert towards dechlorination,
- it is readily available,
- it is easy to handle.

The fluidisation properties of the applied sand have been measured and are given in table 2.2. Values predicted by the empirical relations of Wen and Yu [13,22] and Goroshko [11,22] correspond to the measured minimum fluidisation velocity within acceptable limits.

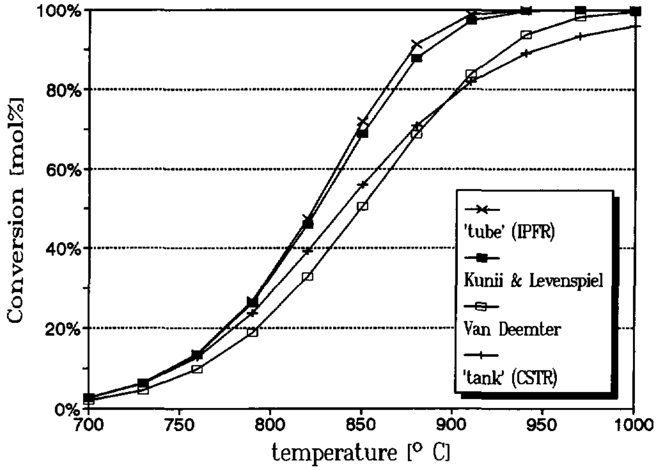

Figure 2.2 Comparison of conversion prediction of the four design models.

Table 2.2 Fluidisation properties of the sand applied.

minimum fluidisation velocity (u_{mf}) [m/s] • measurement: • prediction by empirical relations: Wen and Yu [13,22] Goroshko [11,22]	0.038 0.0389 0.0355
voidage at minimum fluidisation (ϵ_{mf}) [m^3/m^3]	0.383
density [kg/m^3]	2520
particle size (mean particle diameter) [μm]	218
Geldart class of particle	B

The Geldart classification of particles indicates what kind of fluidisation behaviour may be expected for a certain solid. A Geldart B solid shows the following behaviour: [27]

- As soon as the gas velocity exceeds the minimum fluidisation velocity (u_{mf}), bubbles are formed in the bed.
- At larger gas velocities these bubbles grow and coalesce as they rise through the bed. The bubble size, which is still rather small at the distributor, increases roughly linearly with the distance above the distributor and the excess gas velocity. In formula

$$d_b \propto h\,(u_o - u_{mf}) \tag{2.1}$$

- The bubble size is roughly independent of the mean particle size of the solids.
- The vigorous bubbling promotes gross circulation of solids in the bed.

As shown by the general reaction equation below, thermal hydrodechlorination is an exothermic reaction (e.g. the reaction enthalpy of the dechlorination of chlorobenzene is $-\Delta H_{r,298}$ = 64.0 kJ/mol):

$$RCl + H_2 \longrightarrow RH + HCl + (-\Delta H_r) \tag{2.2}$$

However, the heat required for the feed to reach the reaction temperature is much larger than the heat produced by the reaction. As a result the reactor as a whole becomes heat demanding. Some alternatives to supply the required heat have been considered:

- external heating of the bed material. This requires circulation of bed material.
- heat exchange by internals in the bed. These internals may not hamper the fluidisation. A proper choice for the construction material will be difficult.
- heat exchange through the wall. This adds another requirement to the construction material. Besides its resistance against the process conditions it should also have rather good heat transport properties.
- heat suppletion by a second reaction. This reaction may not have a negative influence on the main dechlorination reaction.

In the end, heat exchange through the wall was chosen for the pilot plant. At larger scale heat suppletion by a second reaction may be more favourable. E.g. partial oxidation of excess H_2 seems promising. This alternative will be discussed in chapter 6, covering the design of a plant at industrial scale.

The severe process conditions require extraordinary construction materials. Since no metals or alloys, except exotic ones like platina and gold, are guaranteed to withstand the severe process conditions of a hydrogen and hydrogen chloride gas containing mixture at elevated temperatures (up to 900 °C), a ceramic construction material has been chosen. Another reason was the suspicion that metals would activate soot formation, while ceramics were believed to be inert. As ceramic material silicon carbide (SiC) has been chosen, because of its good heat transport properties, and also for reasons of availability in the required size. The inner diameter of the reactor is 95 mm, the length of the SiC-tube is 1400 mm.

Table 2.3 shows the favourable properties of silicon carbide, such as: [14,39]

- high chemical stability,
- high thermal stability,
- strength at elevated temperatures,
- low thermal expansion,
- high thermal shock resistance,
- high temperature for abrasion,
- thermal conductivity comparable to that of aluminium alloys,
- high hardness.

***Table 2.3** Properties of silicon carbide (SiC).* [2,7,38,39]

property	general SiC	AnnaNox (1)
melting point [°C]	decomposes 2200 - 2700	
limit of application [°C]	1650	1600 (ox.) 1700 (red.)
hardness [kg/mm^2] Moh's scale	1700 - 2370 9.0 - 13 (2)	
density [10^3 kg/m^3]	3.0 - 3.2	2.60
specific heat [J/kg °C] (25 - 1000 °C)	840	1000
linear coefficient of expansion [10^{-6} m/m °C] (25 - 800 °C)	4.5	4.8
thermal conductivity [W/m K] (at 1100 °C)	12.6	23
electrical conductivity [$\Omega^{-2}m^{-1}$] (at 25 °C)	~ 100	
thermal shock resistance	good	extremely good
dielectric constant	about 10.0 (3)	
crushing strength at 25 °C [kg/mm^2]	340	300
bending strength [kg/mm^2]	60	80
chemical stability	stable to H_2, N_2 and CO. Slow oxidation in air above 1000 °C. High resistance to coal ash, acid and neutral slags. Attacked by basic slags at high temperature.	

(1) AnnaNox is the applied SiC (delivered by Annawerk, Rödental, Germany)

(2) The Moh's hardness of 13 which some forms of SiC exhibit, make SiC the hardest available material after diamond (15) and boron carbide (14).

(3) value relative to permittivity of vacuum.

As a result of its strength, mechanical manipulation of the ceramic material is very difficult. Leaktight construction is nearly impossible. For this reason the implemented SiC-tube has been surrounded by a Nimonic housing. The Nimonic housing provides a leaktight enclosure. Nimonic is a high quality nickel alloy, with rather good prospects to withstand the process conditions. Some properties of the applied Nimonic PK 33 are given in table 2.4.

Table 2.4 Properties of Nimonic PK 33. [5,23]

composition					
Ni	Remainder	Al	1.7-2.5	C	< 0.07
Cr	16.0-20.0	Fe	< 1.0	Zr	< 0.06
Co	12.0-16.0	Mn	< 0.5	S	< 0.015
Mo	5.0-9.0	Si	< 0.5	B	< 0.005
Ti	1.5-3.0	Cu	< 0.2		

physical properties		
density [10^3 kg/m^3]	8.21	
melting range [°C]	1300-1345	
hot-working:		
maximum preheating temperature [°C]	1170	
minimum working temperature [°C]	950	
specific heat [J/kg °C]	419	
coefficient of expansion [10^{-6} m/m °C]	15.1	(20-800 °C)
	16.1	(20-900 °C)
thermal conductivity [W/m K]	10.97	(20 °C)
	24.41	(900 °C)
electrical resistivity [10^{-6} Ωm]	1.26	
mechanical properties		
rupture strength [MPa]	600	(650 °C)
	300	(760 °C)
	100	(870 °C)
corrosion		
weight loss after exposure for 100 hours in air [mg/cm^2]	0.13	(700 °C)
	0.26	(800 °C)
	0.79	(900 °C)
	2.42	(1000 °C)
weight loss after 1000 hours of cycle in air (1) [mg/cm^2]	123	(1000 °C)

(1) repetitive cycles of 20 min at temperature and 10 min at room temperature.

For reasons of safety the reactor is surrounded by a N$_2$-box. The box is filled with N$_2$ at a pressure somewhat higher than the reactor. In case of leakage this overpressure will prevent the reaction medium to leave the reactor. Instead, N$_2$ will flow from the box into the reactor, preventing emission of hydrogen and toxic chlorinated hydrocarbons.

Within the N$_2$-box also the electrical heaters of the reactor are placed.

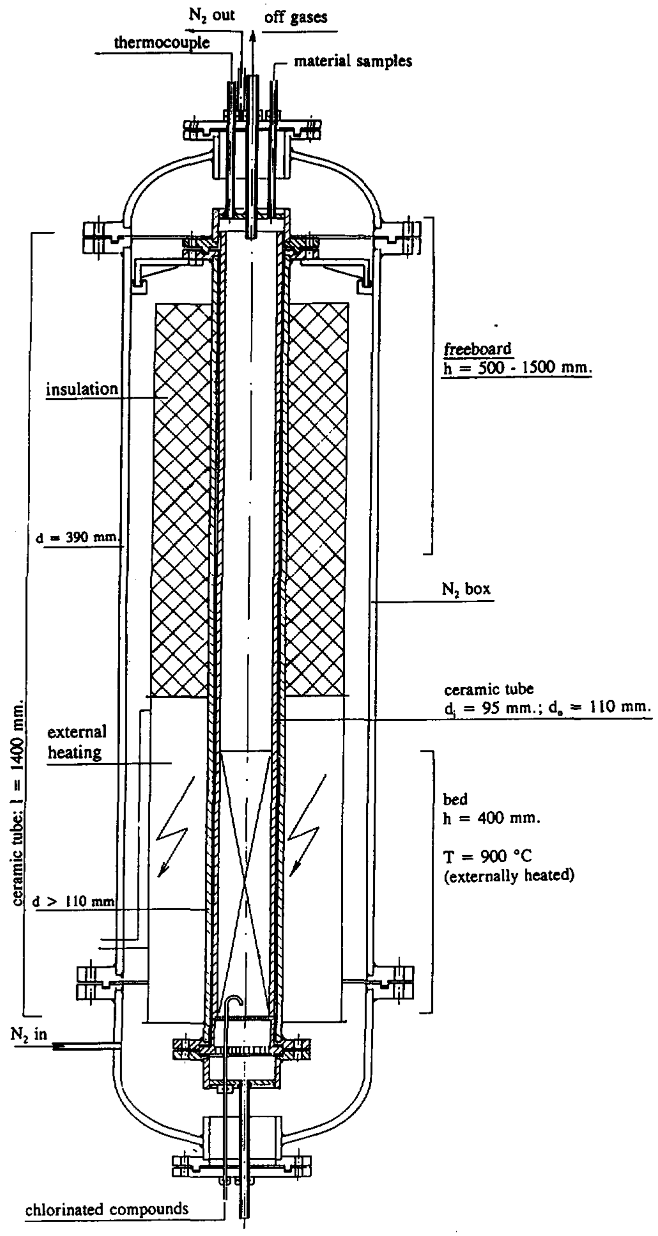

Figure 2.3 Mini pilot reactor design and construction.

As shown in tables 2.3 and 2.4, the thermal expansion coefficients of SiC and Nimonic differ, complicating the mechanical design. When heated to elevated temperatures the SiC-tube and the Nimonic housing will inevitably deviate; at operation temperature a gap between the construction materials unavoidably occurs. This space between the SiC-tube and the surrounding Nimonic housing is called the annular space. At room temperature the annular space is kept as small as possible to enable assemblage. A small stream of H_2 gas is purged in the annular space to prevent accumulation of reaction medium.

The Nimonic housing and the surrounding N_2-box also expand differently. However, this is mainly due to a difference in temperature. A flexible connection at the top of the construction prevents occurrence of tensile forces. The observed larger expansion of the Nimonic housing in comparison to the N_2-box is about 1 cm.

The reactor is fed with hydrogen gas and chlorinated hydrocarbons. For a good reactor performance the reactants must be properly mixed. Moreover, the chlorinated hydrocarbon feed, which is a liquid at room temperature, must be evaporated. Evaporation before the reactor simplifies the input into the reactor. The reactor feeds are both gaseous, by which the required proper mixing of the reactants is facilitated. However, some chlorinated hydrocarbons tend to coke at temperatures as low as their boiling point. Without any precaution those chlorinated hydrocarbons, such as DD, can not be evaporated before the reactor. To reduce soot formation, the evaporation can best take place in the presence of hydrogen. In fact, the better the heterogeneous system of chlorinated hydrocarbon liquid and gaseous hydrogen is mixed, the smaller the soot formation will be.

The mixing quality of gas and liquid is increased by a larger exchange surface between the two phases. Two principally different alternatives are

- to bubble hydrogen gas through the chlorinated hydrocarbon liquid,
- to spray chlorinated hydrocarbon liquid into the hydrogen gas.

The final goal is to have a gaseous reaction medium at elevated temperatures. Heat must be supplied and since the heat capacity of hydrogen gas is too small, external heating is required. Due to this external heating hot surfaces will be present. To prevent any pyrolytic areas at the surfaces, H_2 is the best choice for the continuous phase in the evaporation system. Consequently, the best procedure to evaporate is to spray the liquid chlorinated hydrocarbons into a hot region filled with hydrogen gas. Then, from a practical point of view, the evaporation can best be carried out in the reactor.

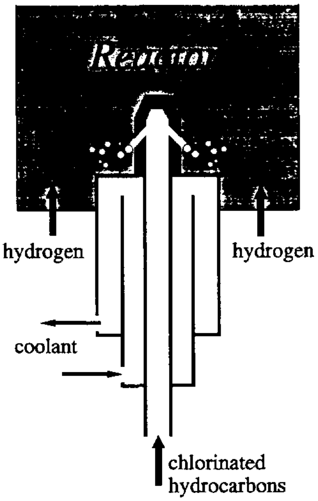

Figure 2.4 Injection system.

At the start of the present study information about soot formation lacked. Also, the best method to inject the liquid feed in the fluidised bed, was not known. For this reason a simple injection system has been developed and implemented (see figure 2.4). The liquid chlorinated hydrocarbons are fed into the reactor through a tube with an inner diameter of 4 mm. At the top of the injection system the tube is connected to four small channels, each having an inner diameter of 2 mm (as such the total flow area is kept constant). These channels point downwards with an angle of 45°.

To prevent evaporation and subsequent soot formation in the injection tube itself, the system is equipped with a cooling jacket. The temperature of the injection system can be controlled by the flow rate of coolant through this jacket. First water was used as coolant, but a better temperature control was realised with nitrogen.

Obviously, the extent to which the feed streams are mixed, affects the amount of soot production. To improve mixing the original injection system was later replaced by a gas driven nozzle. This air blast nozzle produces very small droplets of chlorinated hydrocarbon, which are swept away by the hydrogen gas stream. Hydrogen and chlorinated hydrocarbon are already contacted within the nozzle.

§ 2.2.3 Analysis.

The basis of thermal hydrodechlorination is the replacement of C-Cl bonds by H-Cl bonds. Every Cl leaving a carbon and joining a hydrogen atom contributes to the dechlorination level. In fact, the only chlorine containing product of successful dechlorination is hydrogen chloride, HCl.

The best detection of the dechlorination level would be the measurement of the number of C-Cl bonds in the medium before and after reaction. However, a method for accurate measurement of C-Cl bonds in an atmosphere of H_2, hydrocarbons and in particular HCl is not available. Therefore, two alternative analyses are carried out in the mini pilot plant:

-1- on-line titration of the produced HCl. Measurement of HCl, being the only desired chlorine containing product, is a direct measurement of the dechlorination level.

-2- off-line GC-analysis of the product gas. Summation of all measured quantities of still chlorinated hydrocarbons gives the level of unsuccessful dechlorination.

As the titration method measures the amount of H-Cl bonds formed, it is an excellent way to measure broken C-Cl bonds. However, since the conversion approaches unity the accuracy of the method is less than that of GC-analysis.

Titration of the complete HCl flow is unfeasible because of the large volumes involved. Instead, a small portion of the complete gas stream is split off and sent to a titration system (see figure 2.5). The ratio between the complete gas stream and this split stream is called the split ratio. It is controlled by combining a critical capillary in the split stream and an orifice plate in the main stream.

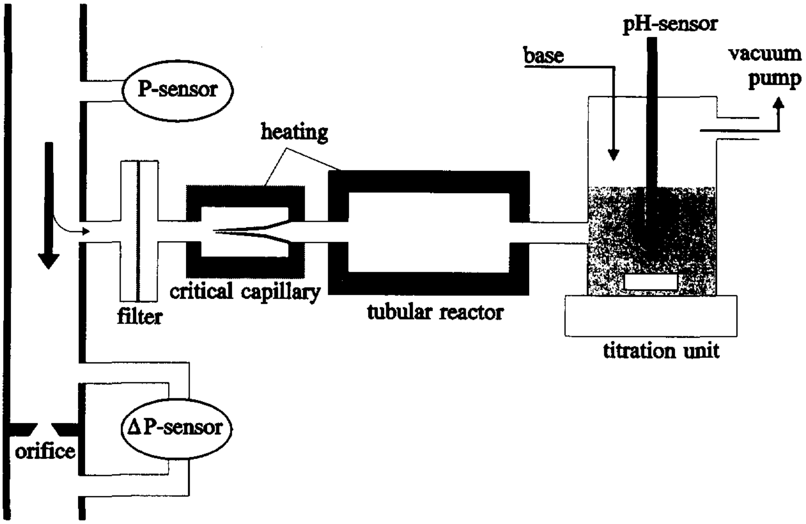

Figure 2.5 Configuration of split system.

The split ratio is set by the system pressure and the pressure drop over the orifice, as long as the orifice and the critical capillary are well temperature controlled:

$$S = C\sqrt{\frac{\Delta P}{P}} \tag{2.3}$$

$$C = C(T_o,T_c,\kappa) = \frac{C_{d_o}\,A_o}{C_{d_c}\,A_c}\left(\frac{T_o}{T_c}\right)^{-\frac{1}{2}}\kappa^{-\frac{1}{2}}\left(\frac{\kappa+1}{2}\right)^{\frac{\kappa+1}{2(\kappa-1)}} \tag{2.4}$$

According to the formulas the gas composition has only a very small influence on the split ratio. This is caused by the similarity of transport phenomena occurring in orifice and capillary [4]. The derivation of the split ratio formula is given in appendix 2.B.

In practice the split system includes

- a filter before the critical capillary to collect small particles that may block the narrow passage,
- external heating of the capillary and the orifice to prevent condensation of heavier hydrocarbons,
- a vacuum pump realising the required pressure drop over the capillary (note that pH control is not influenced by subatmospheric conditions),
- purging of the device that measures the pressure drop over the orifice plate, to prevent corrosion of its delicate membrane.

The required ratio constant C has been determined by calibration with H_2 and N_2. In practice, this split and titration system offered a fairly good method for the on-line analysis of the dechlorination level. The split ratio used was typically about 300 - 400.

Another method to determine the split ratio constant is the 'HCl reference method'. Addition of a known stream of HCl to the reactor off gas causes a change in the titration signal. This change not only reveals the desired constant but also gives information about the degree of fouling of the critical capillary and the orifice plate. The 'HCl reference method' is discussed in appendix 2.B.

If the split ratio is known, the dechlorination conversion can be determined from the titration signal:

$$\xi_{tit.} = \frac{S * \phi_{mol}(HCl)\,|_{split}}{\phi_{moleq.Cl}\,|_{feed}} \qquad (2.5)$$

As the equation points out, the determination depends on:

- the molar equivalent input of chlorine in the feed (which is influenced by pump rate, reading of the balance and composition of the chlorinated hydrocarbon feedstock),
- the split ratio (which is influenced by system pressure and pressure drop over the orifice),
- the HCl titration (which is influenced by the signal of the pH-unit and molarity of the NaOH titer).

Another method to measure the dechlorination conversion is GC-analysis. By GC-analysis the quantity of unconverted 'last ends' is determined. From a view of accuracy the measurement of the small remainder by GC-analysis is more attractive than the measurement of the bulk product by titration.

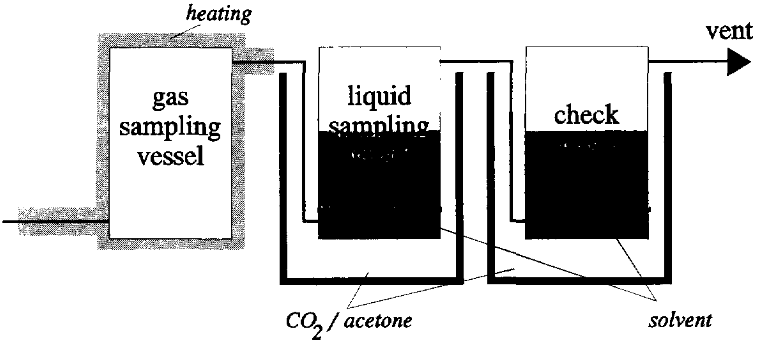

Figure 2.6 Sampling system.

To obtain a sample for GC-analysis a sampling system has been designed. The sampling system takes a well defined sample of the complete gas flow from the reactor. The sampling system consists of three vessels in series (see figure 2.6):

-1- The first vessel is an empty gas tube, thermostrated at 200 °C. In the vessel a gas phase sample is taken, particularly for analysis of light components like C_1 and C_2 hydrocarbons.

-2- In the second vessel the gaseous effluent stream is led through a solvent at low temperature ($T \approx -40$ °C). The gas/liquid contact is enlarged by distributing the gas through a quartz grid. The vessel is cooled by solid CO_2 dissolved in acetone in a surrounding dewar vessel. In the liquid heavier components like benzene and not yet dechlorinated chlorobenzene accumulate.

-3- The third vessel, which is an exact copy of the second, is used to check the sampling efficiency of the second vessel.

Readdition of HCl to unsaturated hydrocarbons may occur. However, examination of the dechlorination levels indicates that this readdition is none or very limited.

In relation to the development of the sample system the following remarks need to be made:

- After removing the cooling of the second and third vessel the pressure in these vessels raises due to increasing vapour pressures. To prevent this built-up during the warming up to room temperature the vessels are vented via washbottles filled with toluene.

- The volume of the liquid sample vessel is a compromise. A large quantity of liquid results in a better gas/liquid contact. However, it also requests a long sample time to reach optimal concentrations with respect to detection limits. Moreover, more expensive solvent of high quality is needed.

- The choice of applied solvent is mainly set by the required large quantity of high quality. Acetone seemed very promising from a point of physical properties (such as boiling point and related retention time in GC-analysis) and availability in the required quality. However, acetone forms dimers under influence of HCl. In GC-analysis the dimerisation product interferes with benzene and chlorobenzene, the main components of the liquid sample. Eventually, n-hexane has been chosen for its combination of physical properties (boiling point lower than benzene, but high enough to prevent excessive evaporation at room temperature) and chemical stability.

The GC data give information about the dechlorination level. Most straightforward is to identify all chlorinated hydrocarbons that appear in the sample, and subsequently sum up all their C-Cl bonds. This demands an enormous effort. Louw [30] proposes an estimation method, which is called the 'estimated organic chlorine remainder'. The method is based on the following observations:

- During thermal hydrodechlorination the hydrocarbon structure is altered as well. The smallest species are most stable. As a consequence, they are the main constituents of a typical reaction product.

- Chlorobenzene (the smallest chloroaromatic) and chloromethane (the smallest chloroaliphatic) are the most difficult species to dechlorinate, not only from a point of thermodynamics but also from a kinetical point of view.

Louw's method estimates the dechlorination level from the fractions of benzene and chlorobenzene in the sample. Consider the fraction of benzene and chlorobenzene in the reaction product. According to the above mentioned observations, the relative ratio of C-Cl bonds in this fraction is always higher than that in the complete reaction product. In other words, the relative ratio of C-Cl bonds found in the considered fraction provides an (over)estimation of the actual ratio.

$$x_{Cl.product} = \frac{\phi_{moleq.}(C{-}Cl)\,|_{product}}{\phi_{moleq.}(C{-}Cl)\,|_{product} + \phi_{moleq.}(C{-}H)\,|_{product}} \tag{2.6}$$

$$\approx \left. \frac{1*\phi_{mol}(C_6H_5Cl)}{1*\phi_{mol}(C_6H_5Cl) + [\ 5*\phi_{mol}(C_6H_5Cl) + 6*\phi_{mol}(C_6H_6)\ ]} \right|_{product}$$

$$= \frac{1}{6} \left. \frac{\phi_{mol}(C_6H_5Cl)}{\phi_{mol}(C_6H_5Cl) + \phi_{mol}(C_6H_6)} \right|_{product}$$

The ratio of C-Cl bonds in the feed is expressed by:

$$x_{Cl.product} = \frac{\phi_{moleq.}(C{-}Cl)\,|_{feed}}{\phi_{moleq.}(C{-}Cl)\,|_{feed} + \phi_{moleq.}(C{-}H)\,|_{feed}} \tag{2.7}$$

The dechlorination conversion, which is an measure for the fraction of unbroken C-Cl bonds, can be calculated from the quotient of the above determined ratios:

$$\xi_{O.C.R.} = 1 - \frac{x_{Cl.product}}{x_{Cl.feed}} \tag{2.8}$$

If pure chlorobenzene is fed, the ratio of C-Cl bonds in the feed is given by:

$$x_{Cl.feed} = \left. \frac{1*\phi_{mol}(C_6H_5Cl)}{1*\phi_{mol}(C_6H_5Cl) + 5*\phi_{mol}(C_6H_5Cl)} \right|_{feed} = \frac{1}{6} \tag{2.9}$$

in which case the formula for the dechlorination conversion according to 'estimated organic chlorine remainder' simplifies to:

$$\xi_{O.C.R.} = 1 - \left. \frac{\phi_{mol}(C_6H_5Cl)}{\phi_{mol}(C_6H_5Cl) + \phi_{mol}(C_6H_6)} \right|_{product} \tag{2.10}$$

The ratio of molar flows is determined by taking the ratio of respective concentrations, measured in the GC sample.

According to Louw this method gives a conservative estimation of the actual conversion: [30]

- As benzene is more volatile than chlorobenzene, its sampling efficiency will be lower. In other words, the actual molar flow ratio will be smaller than the calculated one based on measured concentrations.
- The volatile, nonaromatic hydrocarbon fraction of the dechlorination product (methane, ethane, ethene) contains definitely less chlorine.
- Liquid products other than (chloro)benzene, which appear in much smaller quantities than benzene, have at maximum the same chlorine content as given by the φ_{Cl}/φ_H ratio.

The approximation is permitted as long as the conversion is almost complete, i.e. near to the equilibrium. In this case the conversion based on the 'estimated organic chlorine remainder' of the aromatic fraction and the aliphatic fraction should be high and roughly the same (see also paragraph 4.4). However, exact limits for which the estimation is permitted, are not available. [30]

The soot and tar production is determined by weighing the observed amounts. Soot is collected in the hot filter, but particularly in the reactor, even behind the SiC-tube! Tar is determined by the collected mass in the second filter. The tar and soot production is also indicated by the detected polyaromatic compounds in GC-analysis.

The soot production is represented by the quotient of collected mass of soot divided by the mass of chlorinated hydrocarbons fed:

$$Y_{soot} = \frac{m(soot)}{m(feed)} \tag{2.11}$$

The soot production is thus represented by the quotient of the carbon quantity in the collected soot mass divided by the total mass of the chlorinated hydrocarbon feed. A more accurate representation of the soot production would be the comparison of carbon quantities.

$$Y_{C.soot} = \frac{m_C(soot)}{m_C(feed)} \tag{2.12}$$

Then, additional information is required about the composition of the soot and the chlorinated hydrocarbon feedstock.

In the top of the reactor samples of construction material can be hanged to investigate their sooting tendency. It should be noted that most of the soot obtained on the samples is not due to local soot formation but to soot collection on the material. The samples happened to give more information about the deposit activity than sooting activity of the construction materials.

§ 2.2.4 Design of other apparatus.

To separate the solid products from the reactor off gas two types of collecting devices have been installed:

- a cyclone,
- two filters.

The design of the cyclone is based on the design rules given by D. Leith [29]. In the design the standard dimension ratios for a general purpose cyclone as proposed by Lapple [20] are followed. The data used in the cyclone design are summarised in table 2.5.

Table 2.5 Data necessary for cyclone design and their design values.

particle size distribution	d_p = 25 μm (1)
inlet dust loading	0.01 kg/kg
particle density	2250 kg/m^3 (2)
gas flow rate	1.8 m^3/h
gas temperature	about 200 °C

(1) d_p: the mean particle size of a soot sample from the pipelines after the reactor as measured by a Coulter Counter.

(2) for the particle density the density of graphite is taken. [41]

The construction material has to fulfil requirements on corrosion and abrasiveness [29]. First, a cyclone was constructed using glass. An obvious advantage is its transparency, however it could not be heated. Heating improves the performance of the cyclone. Therefore, a cyclone made of hastelloy was implemented.

Higher soot and tar collection efficiency has been realised using a filter system. Cylindrical cartridge filters of woven glass fibre collecting solids with particle sizes down to 2 μm are installed:

- The first filter collects soot. It is kept at 300 °C to prevent condensation of tarry products.
- The second filter collects tar. It is cooled to about 20 - 40 °C using a cryostat. At the low temperature heavier hydrocarbons are condensed or even solidified, enabling capture by the filter.

Both woven glass fibre filters are surrounded by housings of stainless steel.

Several constructions have been used to connect the reactor and the filters. Especially the connection between the reactor and the first filter appears to be important as this connection is an notorious location for soot deposition. Finally, the best connection has been realised by placing the first filter on top of the reactor:

- The passage between reactor and filter is short and wide, reducing the chance of obstruction,
- Construction problems related with thermal expansion of the reactor have been overcome.

Further treatment of the reactor off gas is taken care of by the scrubber. Different functions can be distinguished:

- solution of hydrogen chloride (HCl),
- neutralisation of the dissolved HCl,
- (partial) condensation of organic products,
- catching soot and tar.

Another function, determination of the dechlorination level by measurement of the HCl quantity, was not feasible due to the large flow of HCl.

The solution and neutralisation of hydrogen chloride are expressed by the following equations.[2]

solution and dissociation (acidification): (-ΔH$_r$ = +73.4 kJ/mol)

$$HCl_{(g)} \rightarrow H^+_{(aq)} + Cl^-_{(aq)} \qquad \textbf{(2.13)}$$

neutralisation (reaction with caustic soda): (-ΔH$_r$ = +27.1 kJ/mol)

$$CO_3{}^{2-}{}_{(aq)} + 2\ H^+_{(aq)} \rightarrow H_2CO_3{}_{(aq)} \qquad \textbf{(2.14)}$$

evaporation of CO_2: (-ΔH$_r$ = -19.9 kJ/mol)

$$H_2CO_3{}_{(aq)} \rightarrow H_2O + CO_2{}_{(g)} \qquad \textbf{(2.15)}$$

If the scrubber was not cooled, its temperature would rise because of the heat released by the solution and neutralisation reactions (together contributing for about 290 J/s at design conditions) and the heat of the incoming gas stream (contributing for about 65 J/s at design conditions). At design conditions the adiabatic temperature rise would be about 10 °C/h. The temperature rise is undesired for several reasons:

- less HCl dissolves,
- less organic species will condense,
- boronsilicate glass (the construction material) is corroded by warm bases.

For this reason the scrubber has been cooled by an internal cooling spiral.

The scrubber has been designed for batch wise operation. At standard conditions about 6.5 kg caustic soda in 30 litre water is used. The dimensions of the vessel are 85 cm in height and 30 cm inner diameter.

The gas enters the scrubber through a teflon distribution plate. The holes in the plate are 2 mm. There is always liquid under and above the plate. The liquid holdups under and above the plate need to be mixed. By implementing a long downcomer pipe and a small riser pipe the natural flow streams in the vessel are manipulated, resulting in a circulation flow between the upper and lower liquid compartment (see figure 2.7). Since the downcomer pipe is filled with liquid only, while above the riser a mixture of liquid and gas is present, a pressure

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[2] Reaction enthalpies at 18 °C, 1 atm. [40]

difference exists between the pipes. This provides the driving force for the circulating flow. The same principle is used in air lift systems, e.g. air lift fermenters [20].

The requirement to mix is demonstrated by early experiments in which the liquid below the distribution plate was already acid while the liquid above was still alkaline. Also another phenomenon was envisaged in the compartment below the plate: caustic soda precipitated as a white fluffy powder.

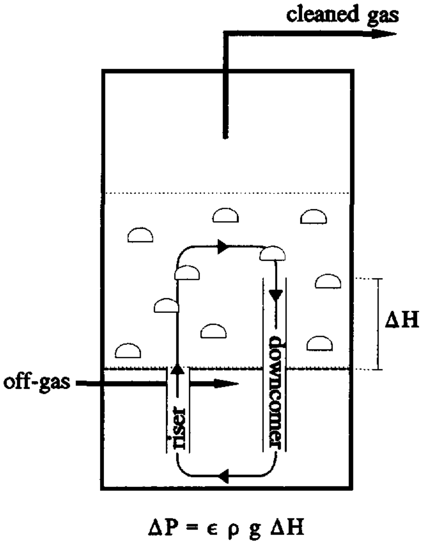

Figure 2.7 Mixing system in scrubber.

§ 2.2.5 Safety measures.

The hazards connected with chlorinated hydrocarbons emphasize the need for safe operation. A general summary of hazards connected with chlorinated hydrocarbons is given in paragraph 1.3, whereas a detailed description of the hazards connected with the model substances used in this study is given in paragraph 2.4.

The dangerous properties which require special precaution include the following.

- The chlorinated hydrocarbons are toxic as demonstrated by their low MAC-values (e.g. MAC for 1,3-dichloropropene is 1 ppm),
- Especially the low chlorinated hydrocarbons are rather flammable,
- When exposed to a burning flame (very) toxic compounds are formed (e.g. dioxins!).

Besides the hazards concerned with chlorinated hydrocarbons, H_2 gas and the produced HCl exhibit some dangerous properties:

- H_2 gas is flammable and susceptible to explosion (explosion limits in air are 4 - 76 vol%; autoignition temperature is 585 °C [8]),
- HCl is a toxic, aggressive and corrosive gas.

For reasons of safety the reactor is surrounded by a N_2-box. In case of a leak in the reactor wall, N_2 will flow into the reactor instead of reaction medium out of it. This prevents uncontrolled burning of a H_2 rich gas with chlorine and hydrocarbons.

The installation as a whole has been placed in an isolated, well ventilated cell, which originally has been designed as a high pressure box. During operation no one is permitted to be inside this box.

Operating conditions are controlled as follows. The reactor temperature is regulated by electric heating. The system pressure depends on the pressure drop over the various parts of the installation, and as such on the flow rate and the fouling grade. The flow rate of the chlorinated hydrocarbons is set by the pump rate; the H_2 is regulated by a gas flow rate controller.

Security measures, which lead to shut down, are taken if an operation condition exceeds certain security limits. The security limit for the temperature is set at 1000 °C. It is determined by a thermocouple in the reactor and a thermocouple outside the reactor wall. The pressure in the reactor may not deviate too much from atmospheric pressure (normally a pressure up to 0.4 bar is tolerated) but it certainly may not exceed the pressure in the N_2-box. Pressure release from the reactor itself is rather difficult; for this reason pressure relieves have been installed in the feed pipelines before the reactor and in the effluent pipeline after the reactor.

Before every experiment the installation is checked to be leaktight. Start-up and shut-down are always carried out with neutral substances which are relatively harmless and have limited dangerous implications. As neutral gas N_2 is chosen, as neutral liquid n-hexane or water.

§ 2.3 Bench scale installation.

§ 2.3.1 Introduction and comparison with existing test methods.

To investigate the effect of several process parameters on soot and tar formation the mini pilot plant installation, being rather large and requiring great effort to operate, has been down-scaled to a bench scale installation. During the development of the bench scale installation experimental experiences from the mini pilot plant were taken into account. This resulted in the installation as described in the next paragraph 2.3.2.

Initially, translation has been considered of the Conradson carbon test or the Ramsbottom carbon test. These tests are proven methods to investigate soot formation in fluid coking [3,24]. However, the major differences between the process conditions as shown in table 2.6 prohibit a successful translation. Among others, the large discrepancy with respect to the difference between operation temperature and boiling temperature of the feedstock reveals a serious problem.

Table 2.6 *Major differences between process conditions of thermal hydrodechlorination and fluid coking.*

condition	THD	FC
operation temperature [°C]	600 - 900	550
boiling temperature [°C]	~ 100	> 350
reaction atmosphere	hydrogen	oxygen

THD: thermal hydrodechlorination.
FC: fluid coking (Ramsbottom carbon test).

The comparison, as described above, finally leads to the general conclusion that batch-wise testing of the sooting tendency as in the Ramsbottom carbon test, is unfeasible for thermal hydrodechlorination. To treat large enough quantities of chlorinated hydrocarbons in order to produce accurately measurable amounts of soot, a continuous process is required. From this starting point the bench scale installation has been developed.

§ 2.3.2 Flowsheet of the bench scale installation.

The flowsheet of the installation is presented in figure 2.8.

Chlorinated hydrocarbons are fed from a storage system, in which the flow rate can be measured. The storage system consists of two burets: one having a large diameter, and a second one having a small diameter. The small one is used to measure the flow rate at certain moments, the large one for the average value.

The flow rate of the chlorinated hydrocarbon feed is set by a HPLC pump. They are pumped to a double-walled vaporisation chamber. The temperature in the chamber is kept close to the boiling point of the feed by thermostatic controlled oil heating. Also H_2 is fed to the vaporisation chamber. This promotes the evaporation and prevents soot formation. The latter is important when less stable chlorinated hydrocarbons are fed, like dichloropropene, which already forms soot at its boiling point.

The vaporisation chamber is placed directly on top of the reactor. A weir prevents liquid to flow into the reactor, only a gaseous mixture enters the reactor. The quartz reactor is electrically heated. Along its axis a quartz tube with thermocouples is placed to record the axial temperature profile. A support at the exit of the reactor enables several samples of construction material to be standing in the reactor.

Directly below the reactor a quench is placed, which is filled with water before each experiment. Here, most of the reactor off gas is captured.

- The dechlorination product HCl dissolves.
- A large fraction of the hydrocarbon product condenses and forms a second liquid phase.
- Soot and tar fall down from the reactor and remain in the quench. Tar tends to solve in the hydrocarbon liquid phase.

The HCl-holdup is measured by conductivity and by titration. The conductivity provides an on-line measurement of the HCl concentration, but is sometimes disturbed by tarry products contaminating the sensor. Titration is carried out periodically by taking samples from the water layer in the quench.

For an accurate analysis by conductivity the temperature of the quench needs to be thermostrated. The double-walled quench is cooled to about 3 °C by melting ice-water flowing between its walls.

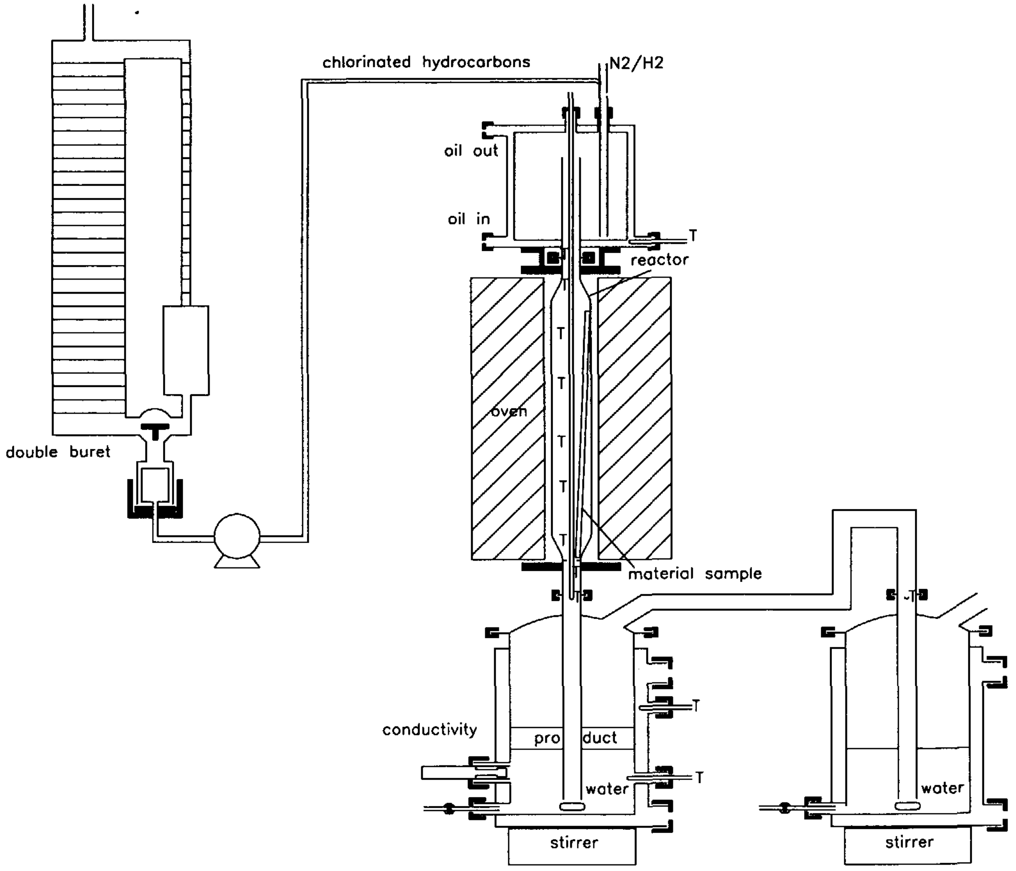

Figure 2.8 Flowsheet of bench scale installation.

Only excess H_2 and light hydrocarbons leave the quench and pass on to the second quench. The second quench is identical to the first one and functions as a guard or check quench. During most experiments no changes in the water of the second quench have been detected, demonstrating a nearly 100% efficiency of the first quench.

Part of the gas leaving the second quench is sampled in a special gas flask for off-line (GC/)MS-analysis. For this purpose a known stream of N_2 is added as an internal standard.

The hydrocarbon liquid phase formed in the first quench is analysed by GC-analysis. More information about this and the other analyses is given in the next paragraph.

§ 2.3.3 Analysis.

The dechlorination is measured by two methods:

- During operation the HCl built-up in the first quench is measured. The actual HCl holdup is determined by
    - titration of small samples from the water phase taken periodically,
    - measuring the conductivity of the water phase.

- After the experiment the hydrocarbon phase of the first quench is analysed by GC. This gives information about the dechlorination level.
    - The conversion is indicated by the quantity of chlorobenzene found divided by the quantity fed. Depending on the capture efficiency of the quench, this indication overestimates the actual dechlorination.
    - According to the 'estimated organic chlorine remainder' method the ratio of chlorobenzene and benzene concentrations gives a conservative estimation of the dechlorination (see paragraph 2.2.3).

  The actual dechlorination level will lie in between these estimations.

The soot production is determined by weighing the amount of soot particles and filaments obtained in the reactor and in the quench. The tar production is determined by GC-analysis of the dissolved tarry compounds in the hydrocarbon phase of the quench. This includes polyaromatic hydrocarbons (PAHs) from biphenyl and naphthalene up to triphenylene.

For each experiment an overall mass balance of the complete installation is calculated, including next items:
- registered flow rates of H_2 and of chlorinated hydrocarbons;
- fraction product remaining in the quench by above mentioned analyses;
- registered flow rate and composition of emitted gas.

§ 2.4 Chlorinated hydrocarbon model substances.

In the present study several chlorinated hydrocarbon model substances have been used. In decreasing order of use, the following liquids have been tested:

- (mono)chlorobenzene, as the liquid chlorinated hydrocarbon that is dechlorinated with most difficulty [31],
- DD, a mixture mainly consisting of 1,3-dichloropropene and 1,2-dichloropropane, being an actual waste stream,
- a mixture of chloroform, methylchloroform and chlorobenzene, called the Cl-cocktail,
- a mixture of chlorobenzene and methanol, to verify experimentally that no dioxin formation occurs in thermal hydrodechlorination.

The quality of gases and frequently applied chlorinated hydrocarbons is given in table 2.7. Information about physical properties, toxicity and flammability of the chlorinated hydrocarbons is presented in tables 2.8 to 2.11.

***Table 2.7** Quality of the main chemicals used in this study.* [1,36]

liquid	chlorinated hydrocarbons	fraction [mol%]
MCB	monochlorobenzene	99.7
DD	1,2-dichloropropane	28.16
	1,3-dichloropropene (Z)	28.39
	1,3-dichloropropene (E)	22.75
	3,3-dichloropropene	7.48
	2,3-dichloropropene	4.87
	chloropropene	3.00
	1,1,3-trichloropropene	0.87
	3,3,3-trichloropropene	0.86
	1,5-hexadiene	0.21
	remainder	3.41
Cl-cocktail	monochlorobenzene	49.9
	chloroform	25.0
	methylchloroform	25.1
gas	**purity [wt%]**	**contaminants**
H_2	99.95	<200 ppm N_2 <5 ppm H_2O <5 ppm O_2
N_2	99.998	<5 ppm H_2O <5 ppm O_2

***Table 2.8** Chlorinated model substances.* [8,34,35]

species	synonyms [CAS-number]	structure
chlorobenzene	phenyl chloride [108-90-7]	C_6H_5Cl
1,2-dichloropropane	propylene dichloride [78-87-5]	$CH_3CHClCH_2Cl$
1,3-dichloropropene	1,3-dichloropropylene [542-75-6]	$CHCl=CHCH_2Cl$
chloroform	trichloromethane [67-66-3]	$CHCl_3$
methylchloroform	trichloroethane (1,1,1- or α-) [71-55-6]	CH_3CCl_3
benzene	benzol, coal naphtha, phenyl hydride [71-43-2]	C_6H_6

***Table 2.10** Threshold values of the chlorinated model substances.* [8,12,32,34,35]

species	MAC (1) [ppm]	MAC (1) [mg/m^3]	TLV-TWA (1) [ppm]	LD$_{50}$ (1) [mg/kg]	odour threshold [ppm]
chlorobenzene	75	350	75	2910	60
1,2-dichloropropane	75	350	75	1900	50
1,3-dichloropropene	1	5	1	250	(2)
chloroform	10	50		800	200-300
methylchloroform	200	1080		10300	100
benzene	10	30	10	3400	180

(1) *MAC:* *Maximum Acceptable Concentration (dutch standard)*
TLV-TWA: *Threshold Limit Value - Time Weighted Average (american standard)*
LD$_{50}$: *Lethal Dose (oral rat).*

(2) *odour threshold is below the concentration causing injury from single exposure, but probably above the concentration causing injury from prolonged exposure.*

Table 2.9 Flammability of the chlorinated model substances. [8,34,35]

species	flash point [°C]	autoignition point [°C]	explosion limits [vol%]
chlorobenzene	28.9	590	1.3 - 11
1,2-dichloropropane	16.0	557	3.4 - 14.5
1,3-dichloropropene	28.3		5.3 - 14.5
chloroform	--		
methylchloroform	--	537	
benzene	-11.1	555	1.2 - 8

Table 2.11 *Physical data of the chlorinated model substances:* [8,34,35]

M molecular weight [g/mol]
T_m melting point [°C]
T_b boiling point [°C]
ρ_l liquid density [10^3 kg/m^3] (1)
ρ_g vapour density (relative to air) (1)
p^* vapour pressure at 20 °C [mbar]

species	M	T_m	T_b	ρ_l	ρ_g	p^*
chlorobenzene	112.5	-44	132	1.1	3.9	12
1,2-dichloropropane	112.0	-100	96	1.2	3.9	56
1,3-dichloropropene	111.0	-84	104	1.2	3.8	40
chloroform	119.4	-63	61	1.5	4.1	200
methylchloroform	133.4	-32	74	1.3	4.6	133
benzene	78.1	6	80	0.88	2.7	100

(1) *The relative density of the saturated vapour/air mixture can be calculated from the vapour density and pressure according to:*

$$\rho_{g,sat} = 1 + \frac{p^*_{mbar}}{1000}(\rho_g - 1) \qquad \textbf{(2.16)}$$

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Appendix 2.A Fluidised bed models for gas phase reaction.

Two commonly accepted models for fluidised beds are adapted to describe a gas phase reaction instead of gas/solid catalysed reaction:

- the three-phase Kunii and Levenspiel model [26,27],
- the two-phase Van Deemter model [15,27].

The model for a fluidised bed reactor as proposed by Kunii and Levenspiel [26] is based on the following assumptions (see figure 2.9):

- The bed consists of three regions: bubble, cloud and emulsion, in which the wake is considered to be part of the cloud.
- The gas velocities in cloud/wake and emulsion phase can be neglected in comparison to the gas velocity in the bubble phase.
- The cloud/wake phase is a kind of intermediate phase in between the bubble and the emulsion phase; gas passes from the bubble phase into the emulsion phase via the cloud and wake phase.
- The rate of interchange between the phases can be described with first order exchange rate coefficients.

The notation used by Kunii and Levenspiel will be maintained:

C_b, C_c, C_e: Reactant concentration in bubble, cloud/wake and emulsion phase, respectively.

K_{bc}, K_{ce}: Interchange coefficients between bubble and cloud/wake phases and between cloud/wake and emulsion phases, respectively.

Unlike the original Kunii and Levenspiel model the reaction is taking place in the gas phase only.

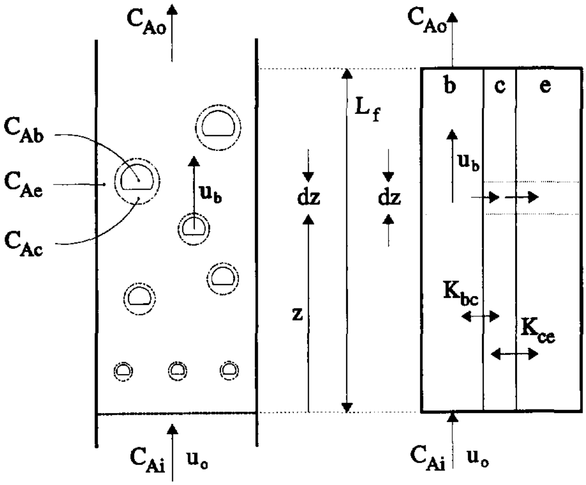

Figure 2.9 Kunii and Levenspiel fluidised bed model. [25,26]

For each phase a molar balances has been set up over a small slice, at a certain height in the bed. Following the assumption by Kunii and Levenspiel the gas velocities in the emulsion phase and cloud/wake phase are neglected, which obviously simplifies the set of equations.

bubble phase:

$$-u_b\frac{\partial C_b}{\partial x} = \beta_b k C_b + K_{bc}(C_b-C_c) \tag{2.17}$$

cloud/wake phase:

$$-u_c\frac{\partial C_c}{\partial x} = \beta_c k C_c + K_{bc}(C_c-C_b) + K_{ce}(C_c-C_e) \approx 0 \tag{2.18}$$

emulsion phase:

$$-u_e\frac{\partial C_e}{\partial x} = \beta_e k C_e + K_{ce}(C_e-C_c) \approx 0 \tag{2.19}$$

Combining and integrating these equations results in:

$$\xi = 1 - \exp(-K_f)$$

$$K_f = \frac{L_f k}{u_b} \left[\beta_b + \frac{1}{\dfrac{k}{(K_{bc})_b} + \dfrac{1}{\beta_c + \dfrac{1}{\dfrac{k}{(K_{ce})_b} + \dfrac{1}{\beta_e}}}} \right] \tag{2.20}$$

The formula is similar to the original Kunii and Levenspiel equation, derived for gas/solid catalysed reactions [26]. The difference between the original model and the adapted version is caused by the difference in reaction phase. In the original Kunii and Levenspiel model the reaction occurs on the solids, while in the adapted version it takes place in the gas phase. As shown in equation 2.20, all parameters related to solid volumes are replaced by alike parameters based on gas phase volumes. As such the β-parameters are the gas phase equivalents of the γ-parameters in the original Kunii and Levenspiel model.

$$\beta_b = \frac{\textit{gasvolume in bubbles}}{\textit{volume of bubbles}} \tag{2.21}$$

$$= 0.99 - 0.999 \approx 1$$

$$\beta_c = \frac{\textit{gasvolume in clouds and wakes}}{\textit{volume of bubbles}}$$

$$= \varepsilon_{mf} \left(\frac{3u_{mf}}{\varepsilon_{mf} u_{br} - u_{mf}} + \alpha \right) \tag{2.22}$$

$$\beta_e = \frac{\textit{gasvolume in emulsion}}{\textit{volume of bubbles}}$$

$$= \varepsilon_{mf} \left(\frac{1-\delta}{\delta} - \frac{3u_{mf}}{\varepsilon_{mf} u_{br} - u_{mf}} - \alpha \right) \tag{2.23}$$

In these equations α represents the volume of clouds and wakes relative to the bubble volume.

It is assumed that almost all gas flows through the bubble phase. This assumption leads to the following equation:

$$\frac{\phi_v}{\phi_{v.b}} = \frac{u_o}{u_b\, \delta} = 1 \tag{2.24}$$

According to Kunii and Levenspiel [27] the interchange coefficients can be calculated using the following expressions:

$$K_{bc} = 4.5\left(\frac{u_{mf}}{d_b}\right) + 5.85\left(\frac{\mathbb{D}^{1/2} g^{1/4}}{d_b^{5/4}}\right) \tag{2.25}$$

$$K_{ce} = 6.77\left(\frac{\mathbb{D}\,\varepsilon_{mf}\,u_{br}}{d_b^3}\right)^{1/2} \tag{2.26}$$

Above model has been used to design the mini pilot plant reactor. As stated, the model is applicable for fluidised beds in which the gas flow through the solid phase can be neglected[3]. Probably for this reason, Kunii and Levenspiel in a recent version of their book [27] restrict the application of their model to fluidised beds using a fine Geldart A powder. However, the sand used in the mini pilot plant is a Geldart B solid. The effect of this discrepancy on the accuracy of the model prediction is not known.

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[3] The concentration gradients in the cloud and wake phase and the emulsion phase follow the concentration gradient in the bubble phase. From the given expressions the gradients can be calculated, showing that under design conditions these gradients are too large to be neglected.

$$\left(\frac{\partial C_c}{\partial x}\right)/\left(\frac{\partial C_b}{\partial x}\right) = \frac{K_{bc}\,(K_{ce} + k\beta_e)}{(K_{bc} + k\beta_c)(K_{ce} + k\beta_e) + k\beta_e K_{ce}}$$

$$\approx 1.0 \quad (600\ ^\circ C)$$

$$\approx 0.85 \quad (900\ ^\circ C)$$

$$\left(\frac{\partial C_e}{\partial x}\right)/\left(\frac{\partial C_b}{\partial x}\right) = \frac{K_{bc}\,K_{ce}}{(K_{bc} + k\beta_c)(K_{ce} + k\beta_e) + k\beta_e K_{ce}}$$

$$\approx 1.0 \quad (600\ ^\circ C)$$

$$\approx 0.65 \quad (900\ ^\circ C)$$

Neglecting the differential terms in the equations for the cloud and wake phase and the emulsion phase is only permitted if the respective gas velocities are very small.

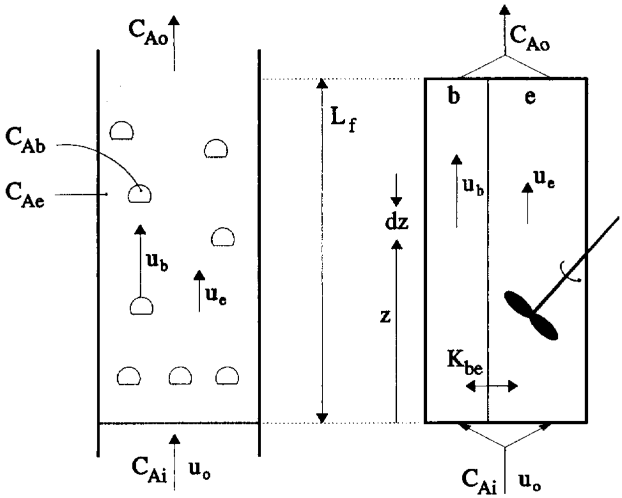

Figure 2.10 Van Deemter fluidised bed model. [14,26]

The second fluidised bed model that has been adapted, is the Van Deemter model [15]. The model is based on the following assumptions (see figure 2.10):

- The bed consists of two phases, namely the bubble and the emulsion phase.
- The gas velocity in the emulsion phase is assumed to be equal to the minimum fluidisation velocity.
- The flow pattern of the bubble phase is assumed to be ideal plug flow; the emulsion phase is assumed to be ideally mixed.
- The interchange rate between the phases can be described by a first order exchange rate coefficient.

The notation used in the Kunii and Levenspiel model is maintained. The interchange coefficient K_{be} between bubble phase and emulsion phase can approximated by the bulk flow term of K_{bc} in the above mentioned model of Kunii and Levenspiel: [27]

$$K_{be} \cong 4.5 \left(\frac{u_{mf}}{d_b}\right) \tag{2.27}$$

For both phases a molar balance is set up. For the bubble phase it is set up over a small slice, at a certain height in the bed:

$$-\delta u_b \frac{\partial C_b}{\partial x} = \beta_b \delta k C_b + \delta K_{be}(C_b - C_e) \tag{2.28}$$

For the emulsion phase it is set up over the complete bed height:

$$-(1-\delta)u_e\left(\frac{C_e-C_o}{L_f}\right) = \beta_e(1-\delta)kC_e + \delta K_{be}\left(C_e-\frac{\int_O^{L_f}C_b dx}{L_f}\right) \tag{2.29}$$

The fed gas flow is split up over the bubble phase and the emulsion phase:

$$u_o = u_b\delta + u_{mf}(1-\delta) \tag{2.30}$$

From this equation an expression for the volume fraction of bubbles in the reactor (δ) can be derived:

$$\delta = \frac{u_o - u_{mf}}{u_b - u_{mf}} \tag{2.31}$$

At the top of the bed the gas streams leaving the bubble and emulsion phases are mixed. This leads to an expression for the effluent concentration:

$$C_{L_f} = \frac{u_b\delta\, C_{b.L_f} + u_{mf}(1-\delta)C_e}{u_B\delta + u_{mf}(1-\delta)} \tag{2.32}$$

Solving all equations, an expression is derived for the overall conversion:

$$\xi = 1 - \frac{[\frac{v_b}{1+r_b}(1-\exp\Delta) + v_e][\frac{v_b}{1+r_b} + v_e] + [\frac{r_b}{1+r_b}v_e + \theta]v_b\exp\Delta}{[\frac{r_b}{(1+R_b)^2}(1-\exp\Delta) + v_e] + \theta} \tag{2.33}$$

In here, the following dimensionless groups are used:

$$\begin{aligned} v_b &= \frac{u_b\delta}{u_o} \\ v_e &= \frac{u_{mf}(1-\delta)}{u_o} \\ r_b &= \frac{\beta_b k}{k_{be}} \\ \Delta &= -\frac{K_{be} + \beta_b k}{u_b}L_f \\ \theta &= [\frac{K_{be}}{K_{be}+\beta_b k}\delta\beta_b + (1-\delta)\beta_e]\frac{kL_f}{u_o} \end{aligned} \tag{2.34}$$

A similar model is developed by Kunii and Levenspiel [27], except that they assume ideal plug flow in the emulsion phase. It is interesting that this two-phase model is proposed particularly for Geldart B fluidised systems.

Also the adapted Van Deemter model has been used to design the mini pilot plant reactor.

In case of no exchange between the phases (interchange coefficients set equal to zero) and no gas flow through the emulsion phase, both adapted models reduce to the simple model of ideal plug flow through the bubble phase:

$$\xi = 1 - \exp(-\beta_b \delta \frac{k L_f}{u_o}) \tag{2.35}$$

This simple plug flow model predicts maximum conversion.

Appendix 2.B Methods to determine the split ratio.

Appendix 2.B.1 Determination using a calibrated split ratio constant.

In order to measure the amount of HCl produced by titration, a small portion of the gas leaving the reactor is split off. The proportion between the complete gas stream and this split stream is called the split ratio. It is set by combining a critical capillary in the split stream and an orifice in the main stream.

The split ratio is the quotient of gas flow through the orifice plate divided by the gas flow through the capillary:[4,5]

$$S = \frac{\phi_{main} - \phi_{titration}}{\phi_{titration}} \tag{2.36}$$

The gas flow through the orifice (units of mass per time) is given by: [4,20,37]

$$\phi_{m_o} = C_{d_o} A_o \sqrt{\frac{M}{R T_o} P \Delta P} \tag{2.37}$$

---

[4] Note that the split ratio is defined as the gas stream that is not analysed in the titration system divided by the gas stream which is analysed. The gas stream leaving the reactor is the sum of these streams.

[5] Assuming ideal gas behaviour the value of the split ratio is irrespective of the units used (mass, volume or moles).

The gas flow through the capillary (units of mass per time) is given by: [4,20,37]

$$\phi_{m_c} = C_{d_c} A_c\, P \sqrt{\frac{M}{RT_c}} * f(\kappa)$$

$$f(\kappa) = \kappa^{0.5} * \left(\frac{2}{\kappa+1}\right)^{\frac{\kappa+1}{2(\kappa-1)}} \qquad (2.38)$$

The equation for the critical capillary can be derived from the equation for an orifice assuming critical conditions in the narrowest passage of the capillary, i.e. the critical pressure ratio is reached. Under those conditions the pressure P_2 in the narrowest passage of the critical capillary and the pressure P_1 before the capillary are correlated: [37]

$$\frac{P_2}{P_1} = \left(\frac{2}{\kappa+1}\right)^{\frac{\kappa}{\kappa-1}} \qquad (2.39)$$

A larger pressure difference by further decrease of pressure P_2 does not result in an increased gas flow. The gas velocity is equal to the sonic speed under the prevailing conditions in the narrowest passage; the flow through the capillary is at its maximum. [9,37]

Dividing equation 2.37 by equation 2.38 gives the split ratio:

$$S = \frac{\phi_{main} - \phi_{titration}}{\phi_{titration}} = \frac{C_{d_o} A_o}{C_{d_c} A_c} \sqrt{\frac{T_c * \Delta P}{T_o * P}} * \frac{1}{f(\kappa)}$$

$$f(\kappa) = \kappa^{0.5} * \left(\frac{2}{\kappa+1}\right)^{\frac{\kappa+1}{2(\kappa-1)}} \qquad (2.40)$$

Due to the basic similarity of the transport phenomena occurring in orifice and capillary, the split ratio is nearly independent of gas composition. The gas composition has only a small influence on the split ratio via the drag coefficients (C_d) and the compressibility coefficient (κ). [4]

The following simplified form of equation 2.40 clearly shows that as long as the orifice and the critical capillary are well temperature controlled, the split ratio solely depends on the system pressure and the pressure drop over the orifice:

$$S = C\sqrt{\frac{\Delta P}{P}} \tag{2.41}$$

$$C = C(T_o,T_c,\kappa) = \frac{C_{d_o}A_o}{C_{d_c}A_c}\left(\frac{T_o}{T_c}\kappa\right)^{-\frac{1}{2}}\left(\frac{\kappa+1}{2}\right)^{\frac{\kappa+1}{2(\kappa-1)}} \tag{2.42}$$

The split ratio constant must be known to calculate the split ratio from the system pressure and the pressure drop over the orifice. The split ratio constant has been determined by calibration using known H_2 and N_2 gas streams. Results are presented in figure 2.11. The data follow theory. The split ratio is proportional to the square root of the quotient of the pressure drop over the orifice divided by the system pressure. The split ratio constant is independent of gas composition. Also its temperature dependence follows theory.

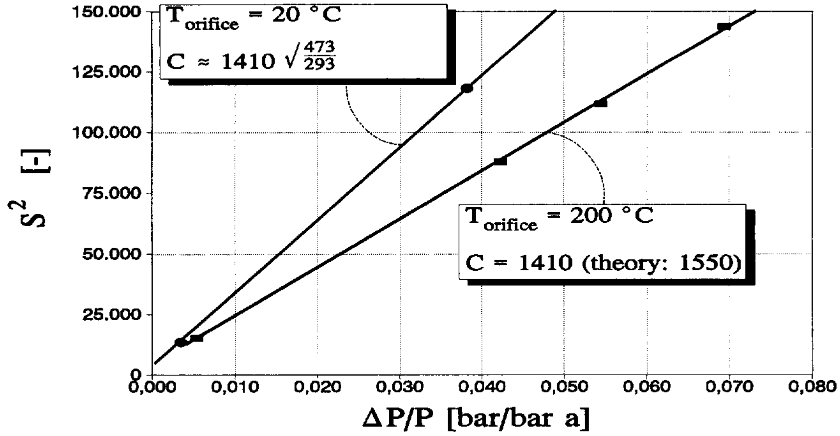

Figure 2.11 Calibration results of split ratio.

As the split ratio is known, the dechlorination conversion can be determined from the titration signal:

$$\xi_{tit.} = \frac{S * \Phi_{mol}(HCl)\big|_{split}}{\Phi_{moleq.Cl}\big|_{feed}} \tag{2.43}$$

In the mini pilot plant system the observed split ratio was typically 300 - 400.

Appendix 2.B.2 Determination using a HCl reference stream.

In practice it showed that, notwithstanding the precautions taken in practice, the determination of the dechlorination conversion was still sometimes tormented with partly or complete obstruction of the capillary and contamination of the orifice. It appeared that, except for complete obstruction of the capillary, the theoretical relation between split ratio and pressures was still holding under these conditions, however with a different ratio constant. The split ratio constant was no more given by the calibrated value.

From this point of view an extension to the split system has been designed. The extension consists of a kind of calibration during operation. Addition of a known stream of HCl to the reactor off-gases causes a change in the titration signal. This change gives information about the actual split ratio.

The essential equation is derived as follows. Due to fouling of the critical capillary and the orifice, the split ratio constant changes as time proceeds. The split ratio constant is now expressed as $C^*(t)$, in which t indicates the time dependency of the constant.

The reactor off gas stream (ϕ_{main}) and the split stream (ϕ_{split}) are correlated according to the split ratio constant at the time of measurement t_1:

$$\phi_{main} = \left[C^*(t_1) \sqrt{\frac{\Delta P}{P}} + 1 \right] \phi_{split} \tag{2.44}$$

By adding a known flow of HCl ($\phi_{reference}$) to the reactor off gas stream, the total gas flow increases. The split stream will change accordingly. The altered split stream ($\phi_{split\,|\,ref}$) is correlated with the complete gas stream according to the split ratio constant at the time of measurement t_2:

$$\phi_{main} + \phi_{reference} = \left[C^*(t_2) \sqrt{\frac{\Delta P_{|\,ref}}{P_{|\,ref}}} + 1 \right] \phi_{split\,|\,ref} \tag{2.45}$$

In a short period of time the fouling in the system does not really change. If the measurements are taken quickly after each other, the split ratio will be nearly unchanged and it can be considered constant within this interval of time:

$$C^*(t_{1-2}) = C^*(t_1) = C^*(t_2) \tag{2.46}$$

From equations 2.44 to 2.46 it can be derived that

$$S^*(t) = C^*(t) \sqrt{\frac{\Delta P}{P}} = \frac{\phi_{reference}}{\sigma.\phi_{split\,|\,ref} - \phi_{split}} - \frac{\phi_{split\,|\,ref} - \phi_{split}}{\sigma.\phi_{split\,|\,ref} - \phi_{split}} \tag{2.47}$$

with

$$\sigma = \sqrt{\frac{\Delta P_{|ref}}{\Delta P}\frac{P}{P_{|ref}}} \tag{2.48}$$

The reference flow is much larger than the change it causes in the split stream. For this reason the last term in equation 2.47 can be neglected, giving a rather simple formula for the split ratio:

$$S^*(t) = C^*(t)\sqrt{\frac{\Delta P}{P}} \approx \frac{\phi_{reference}}{\sigma.\phi_{split_{|ref}} - \phi_{split}} \tag{2.49}$$

This leads to the final equation which correlates the flow rate of HCl in the reactor off gases to the measured titration signals and the known flow of added HCl:

$$\phi_{main} \approx \frac{\phi_{split}}{\sigma.\phi_{split_{|ref}} - \phi_{split}} * \phi_{reference} \tag{2.50}$$

Then, the dechlorination conversion can be determined as follows:

$$\xi_{tit.} = \frac{\phi_{mol}(HCl)\,|_{main}}{\phi_{moleq.Cl}\,|_{feed}} \tag{2.51}$$

Applying this method, the extent of fouling during operation is measured as well. The fouling is indicated by the time dependency of the split ratio constant $C^*(t)$ as calculated by equation 2.49.

Because twice a titration signal has to be measured, the accuracy of this 'HCl reference method' is less than that of the original method based on off-line calibration, in which only once a titration signal need to be measured. However, the 'HCl reference method' is less sensitive to fouling. Therefore application of the 'HCl reference method' is particularly attractive in systems susceptible to fouling.

The 'HCl reference method' requires a rather large additional stream of HCl. Applying a system with a critical capillary the flow rate of the additional HCl can easily be controlled by regulation the pressure before that capillary.

The 'HCl reference method' has not yet been tested in practice.

Chapter 3

Experimental observations

how to operate the process

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§ 3.1 Introduction.

§ 3.1.1 Contents of chapter.

In this chapter the experimental observations from both bench scale and mini pilot plant installation are discussed. The chapter is divided in four parts:

- ***experimental observations in the bench scale installation.***
  In the bench scale installation close control of process conditions is realised. No reactive wall surfaces are present as the reactor is constructed from quartz glass. Therefore, the installation is very suitable to investigate the gas phase process. The influence of process conditions like residence time and excess H_2 in terms of the H_2/Cl ratio is explored.

  In addition, material samples can be implemented, offering the opportunity to investigate their influence on the process. Wall effects by SiC and Hastelloy are examined. The bench scale installation has proven to be useful for this kind of material research.

- ***experimental observations in the mini pilot plant installation.***
  In the mini pilot plant more soot is formed than in the bench scale installation. Also the kind of soot differs: powder soot is observed in the mini pilot plant and filament soot in the bench scale plant. These phenomena are probably due to the presence of reactive surfaces in the mini pilot plant, a hypothesis confirmed by material research experiments in the bench scale installation. Therefore, the experimental observations in the mini pilot plant merely focus on operational factors involved in the technical realisation of the process. Topics of investigation have been:
  - optimal reactor configuration,
  - optimalisation of the injection system,
  - location of soot deposition,
  - verification of the non-formation of dioxins,
  - acquisition of know-how, such as managing the corrosion by the chlorinated hydrocarbons and the hydrogen chloride produced.

- ***analysis of the soot and tar produced.***
  The soot produced is analyzed for its chemical composition and some physical and transport related properties. Comparison of the soot formed under different circumstances, reveals further support for the observed trends. Some important transport properties are validated.

The tar composition is analyzed. The major PAHs (polyaromatic hydrocarbons) that contribute to the tar are identified. In the experimental installations a similar fingerprint is obtained concerning the PAH composition of the tar produced.

- ***conclusions.***
  In the successive paragraphs conclusions are presented. The most important conclusions are summarised in the final paragraph 3.5.

An exceptional phenomenon in the mini pilot plant, the occurrence of a reaction band, is covered in chapter 5.

§ 3.1.2 Terminology used to appoint solid products.

In thermal hydrodechlorination solid byproducts are formed. According to their nature and physical appearance different types of solid products can be distinguished. Tar and soot are formed, which differ by colour, solvability, physical structure and chemical composition. The terminology used to appoint the various solid products is listed in table 3.1.

Table 3.1 *Terminology to appoint different types of solid products formed in thermal hydrodechlorination.*

main group	subdivision	characteristics
tar	sublimation tar	solid; seems to be deposited by sublimation; yellow, crystalline structure.
	brown tar	very viscous liquid or solidified material; brown; sticky.
	black tar	solid; black.
soot	filament soot	solid; black; thin rigid slices, with a shiny and a dark side; tend to break when bent.
	powder soot	solid; black; graphite-like, powdery; tendency to disperse.
The main difference between soot and tar is the solvability of tar in organic solvents like acetone and chlorobenzene.		

This terminology is mainly based on visual, and thus practical, features. In paragraph 3.4 the chemical composition and some physical parameters of the soot and tar will be discussed. In paragraph 3.4.3 photographs of the soot are presented.

§ 3.2 Experimental observations in the bench scale installation.

§ 3.2.1 Performance characteristics of the bench scale installation.

The heat input from the electrical heating and the heat loss to the environment impose a temperature profile on the reactor. The profile obtained in the reactor is shown in figure 3.1. It does not change during the experiments and is reproducible for all experiments.

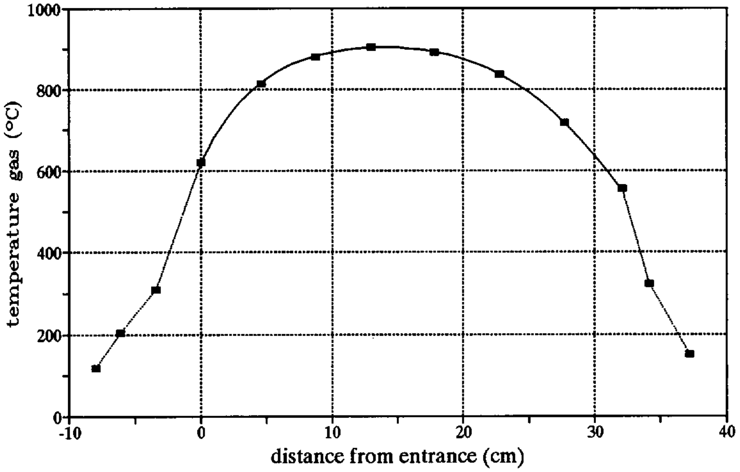

Figure 3.1 *Temperature profile of bench scale installation.*

The main products of thermal hydrodechlorination typically accumulate at the following locations.

- hydrogen chloride (HCl) dissolves in the water of the quench,
- benzene condenses in the quench and forms an organic phase on top of the water phase,
- some tar condenses in the downcomer between reactor and quench; most tar condenses in the quench and dissolves in the organic layer.
- soot is mainly deposited on the reactor wall; it is retrieved from the reactor afterwards.

In the bench scale installation generally filament soot is obtained. However, under certain conditions, e.g. if certain soot promoting materials like metals are present, powder soot is observed.

Typical balances for the bench scale installation are given in tables 3.2 and 3.3. They originate from experiments with chlorobenzene at a residence time of 24 s and a H_2/Cl ratio of 1.4. As shown the balances are almost complete.

Table 3.2 Chlorine balance bench scale installation.

input (1)	output (1)			balance [mol%]
MCB	HCl	MCB	CBP	
480.9	468.5	0.9	1.1	-2.2%

(1) *quantity [mmol] of chlorinated compounds*
MCB: monochlorobenzene;
CBP: chlorobiphenyl;
HCl: hydrogen chloride.

Table 3.3 Overall mass balance of bench scale installation.

input [g]	MCB	H_2O	solvent	H_2		total
	54.1	400.9	62.5	2.2		519.7
output [g]	soot	H_2O	org. layer	H_2	benzene	total
	2.7	389.4	115.1	2.3	0.8	509.5
balance [wt%]						-2.0%

The determination of the mass of tar produced in the system is hampered with inaccuracy which stems from the following difficulties.

- The separation of the organic layer is not precise.
- The method applied in the determination of the tar fraction in the organic layer is sensitive to errors. The method gives an indication of the relative proportions of the tar components rather than an absolute validation.

The measured dechlorination levels are lower than expected from chemical kinetics [12] assuming an ideal plug flow in the reactor. This discrepancy may be caused by several reasons. Two remarks need to be made here:

- This installation is not meant for a kinetic study of dechlorination rate as nearly complete dechlorination is pursued. Errors in the analysis of the dechlorination degree introduce large deviations from the expected 'true' value. The dechlorination level is too high for a proper kinetic study.
- The assumption of ideal plug flow in the reactor is incorrect. The Reynolds number is typically about 40 [1], indicating laminar flow. Although ideally laminar flow would effectuate a nearly equal degree of conversion in comparison to ideal plug flow, inhomogeneous distribution of reactants will not be adjusted causing inefficient use of reactor volume. Bypass effects in the reactor have not been examined.

Table 3.4 Standard operation conditions in the bench scale installation.

general description	actual value
feed	chlorobenzene
$T_{\text{set point}}$	900 °C
residence time	8 s
$(H_2/Cl)_{\text{at entrance}}$	3 mol/mol
pressure	atmospheric

It needs to be emphasized that the purpose of the installation is to have a closer look at the soot and tar production, and not to investigate dechlorination rates. Emphasis is given to the production of solid products.

Most of the experiments in the bench scale installation have been performed with chlorobenzene. Standard operation conditions are listed in table 3.4.

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[1] Reynolds number in case the residence time is 8 s; at larger residence times the Reynolds number is lower.

§ 3.2.2 Experimental investigation of the influence of process conditions on the formation of soot and tar.

In this study some process conditions have been examined for their influence on soot and tar formation, namely:

- the residence time,
- the excess of hydrogen, expressed as the ratio of molecular hydrogen to elementary chlorine in the feed (H_2/Cl).

The experimental results are discussed in this paragraph. The effect on the composition of the tar is discussed in paragraph 3.4.4.

The influence of temperature on soot and tar formation has not been investigated here, because in practice the actual temperature is almost fixed by the required dechlorination grade. As the bench scale installation is not fit for pressurised operation, neither the effect of pressure on soot and tar formation has been investigated.

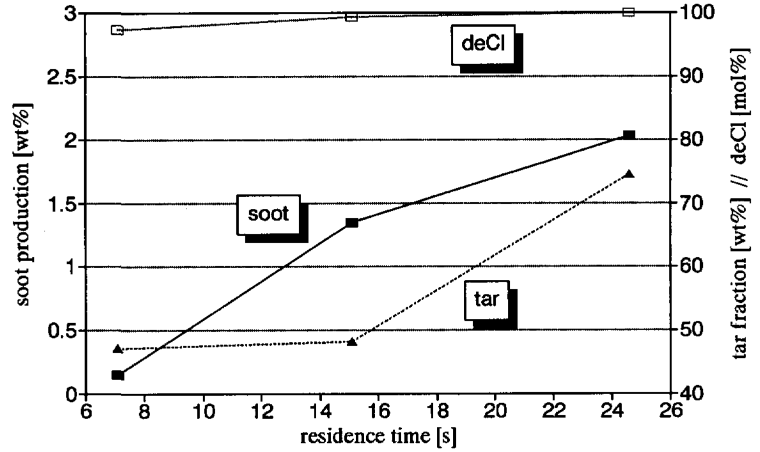

Figure 3.2 Influence of residence time on dechlorination and soot and tar formation.

The residence time obviously effects dechlorination and formation of soot and tar. In accordance with the expectation longer residence times result in higher conversion grades, i.e. more soot is formed and the dechlorination level increases (see figure 3.2). Observation of the effects on tar formation is hampered by the inaccuracy of the measurements. The trend observed for dechlorination and soot formation shows the importance of a properly chosen residence time.

- The residence time has to be sufficiently long to reach the desired degree of dechlorination,

- but not too long in order to prevent aggravated soot and tar formation.

By changing the ratio in which hydrogen and chlorinated hydrocarbons are fed, the effect of hydrogen on the soot and tar formation is investigated. Experimental results are represented in figures 3.3 and 3.4. Hydrogen clearly has a reducing influence on soot formation. Under pyrolytic conditions, as shown in figure 3.3, up to 50 wt% of soot may be formed at a residence time of about 24 s. Suppletion of excess hydrogen ($H_2/Cl=2.7$) under similar conditions, results in a diminished soot production of 3.2 wt%.

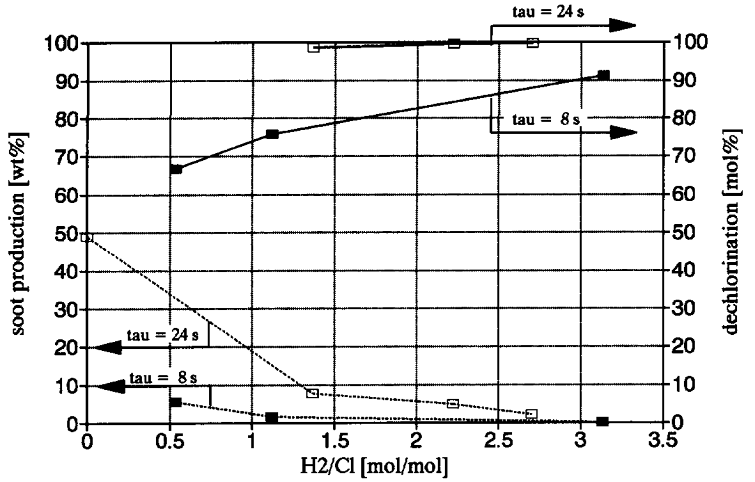

Figure 3.3 *Influence of H_2/Cl ratio on soot formation and dechlorination.*

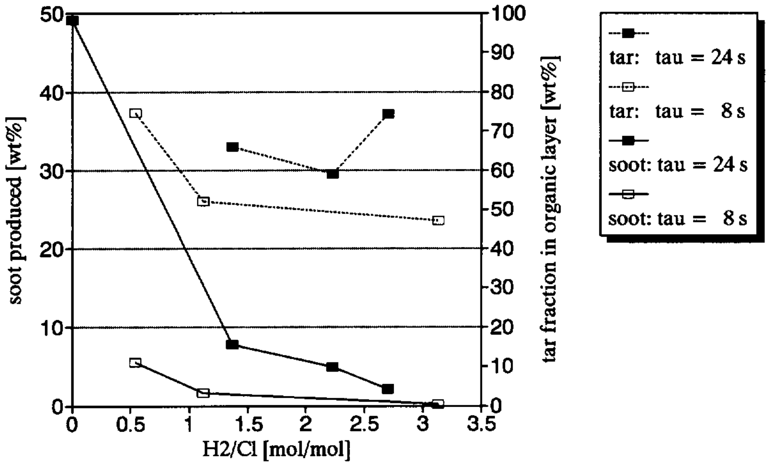

Figure 3.4 *Influence of H_2/Cl ratio on soot and tar formation.*

As shown in the figures the dechlorination increases. Concluding:

- Hydrogen accelerates the rate of dechlorination.
- Hydrogen diminishes the rate of soot and tar formation.

A hydrogen excess improves the efficiency and selectivity of the process. From a chemical point of view a large excess is recommended.

The favourable effect of hydrogen is also demonstrated in table 3.5. The table shows that chlorobenzene remains nearly unconverted at 600 °C under pyrolytic conditions. At 900 °C the dechlorination is almost complete; however, it is accompanied with severe soot formation. Suppletion of hydrogen reduces the soot formation.

***Table 3.5** Soot production during dechlorination of several compounds under various conditions.*

chlorinated species	T_{set} [°C]	residence time [s]	H_2/Cl (N_2/Cl)	soot [wt%]
DD	618	72.2	0 (1.11)	21.7
dichloropropane	604	52.1	0 (0.19)	1.5
chlorobenzene	610	72.2	0 (1.24)	0.0
chlorobenzene	908	28.0	0 (0.84)	49.1
chlorobenzene	930	12.8	4.02 (0)	1.7

The table shows also that DD, a mixture of dichloropropane and -propenes, is already reactive at 600 °C. Under pyrolytic conditions the decomposition is accompanied by a huge formation of soot. In comparison with DD, pure dichloropropane exposes less activity. This indicates that the observed decomposition of DD is due to the unsaturated aliphatic dichloropropenes.

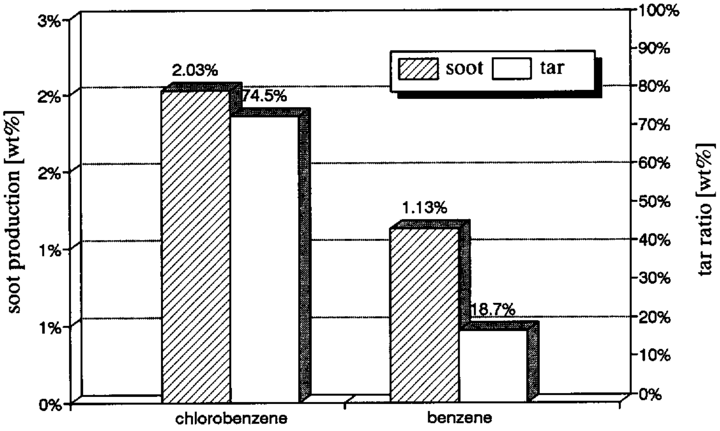

***Figure 3.5** Comparison of soot and tar formation from benzene and chlorobenzene.*

In a comparative experiment benzene has been submitted to conditions identical to those of thermal hydrodechlorination of chlorobenzene. The experimental results (see figure 3.5) indicate that chlorobenzene is less stable and exhibits an larger tendency to soot formation than benzene itself. This observation endorses the general observation that the reactivity is increased by the presence of molecular chlorine [1,2,6].

Soot production may be affected by the wall surface. Some construction materials are investigated for their soot promoting potential.

- A hastelloy sample from a thermocouple that was used in the mini pilot plant effectuated tremendous soot formation (see figure 3.6). Especially powder soot is formed. Dechlorination increased as well. This indicates that a large fraction of the soot produced in the mini pilot plant is caused by soot promoting activities of metals present in the thermocouples. However, the precise quantity is hard to determine. Assuming first order kinetics for the conversion of chlorinated hydrocarbons into soot and ideal plug flow in the reactor, an expression can be obtained for the reactor soot production:

$$\frac{C_{soot}}{C_{feed}} = 1 - \exp\left[-\left(k_{gas} + k_{wall} \frac{A_{active}}{V_{reactor}} \right) \tau \right] \tag{3.1}$$

Using this equation a preliminary estimation of the metal induced soot production in the mini pilot plant can be made. Neglecting gas phase soot formation in the bench scale installation, it is estimated that the thermocouples of the mini pilot plant cause a soot production of about 1.1 wt% of the chlorobenzene feed.

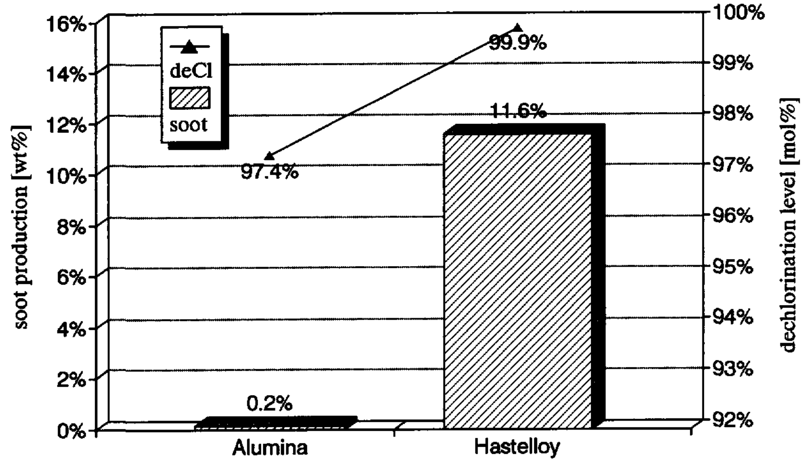

Figure 3.6 *Influence of hastelloy surface on soot formation and dechlorination.*

- The influence of nonmetallic materials like alumina (Al_2O_3) quartz glass (SiO_2) and silicon carbide (SiC) normally is limited. However, experiments in the bench scale installation have demonstrated that silicon carbide can be activated, leading to extra soot production and corrosion effects. This matter is discussed in chapter 5.

§ 3.2.3 Quench research.

In the bench scale installation experience is gained in quenching the product stream of thermal hydrodechlorination.

The gas leaving the bench scale reactor is cooled in the downcomer and in the quench. Due to the low volumetric flow rate most heat is lost in the first part of the downcomer. Here the contribution of the quench water to the heat withdrawal is limited.

From the downcomer the gas is blown into the (stagnant) liquid of the immersion quench. The HCl fraction of the gas dissolves in the water layer of the liquid. As indicated by measurements in the second quench, no detectable amount of HCl leaves the first quench. This proves that the absorption of HCl in the immersion quench is efficient.

Typically the temperature of the quench is kept below 5 °C. At this temperature the vapour pressure of the most important organic products are low, e.g. that of benzene is less than 50 mbar [9]. Consequently, organic products like benzene condense and form an organic layer. Tarry products dissolve in this organic layer. Inspection of the second quench indicates that no or only a very limited amount of tar is emitted from the first quench. The collection efficiency of the quench appears to be sufficient.

The following observations are made for the transport of solid or solidifying soot particles and tar droplets. After the reactor the particles and droplets are dragged by the gas and pass through the liquid. The solids seem incapable to depart from the gas bubbles. Above the liquid surface the gas velocity diminishes. The gas flow becomes too low to entrain the solids, which fall back on the liquid surface. The tar droplets dissolve in the organic layer. The soot particles first float on the liquid surface. After absorption of some liquid they sink. If only a water layer is present, the particles sink to the bottom of the vessel. If an organic layer is present as well, the particles remain in the organic (upper) phase. In that case the particles seem to float on the interface between the organic and water layer.

The observed 'sinking' phenomenon is in accordance with the measured density of the soot particles, as discussed in paragraph 3.4.3. The apparent density of the soot is typically 600 kg/m^3, i.e. lower than the densities of water (1000 kg/m^3) and benzene (900 kg/m^3). However, the true density of the soot is higher, typically about 2000 kg/m^3. The density of the soot that has just fallen back on the liquid surface, is presumably the apparent density. The fresh particles float on the surface. At the surface the particles adsorb liquid. When their pores are filled with enough liquid to make their average density exceed the liquid density, the particles start to sink. As observed the descent finishes at the bottom of the quench or at the interphase surface. The average density of the soot particle that has adsorbed benzene, is probably lower than the density of water, for which reason they do not sink below the interface.

It has to be noted that in the bench scale installation the quench is of the immersion type, i.e. the gas stream is blown through a stagnant liquid holdup. However, for reasons of safe operation a scrubber type of quench is proposed for a larger installation (see chapter 6). The information retrieved in the immersion quench needs to be translated to such type.

In the design of the quench the following important issues are involved.

- ***The cooling efficiency.***
  From the bench scale experience no information is available with respect to the cooling efficiency.

- ***The efficiency of HCl absorption.***
  The HCl absorption efficiency of the immersion quench used is sufficient. This efficiency is determined mainly by the area between gas and liquid phase. Which phase is continuous and which disperse, is of minor importance. The gas bubbles in the immersion quench of the bench scale installation have a relatively small surface area, and consequently a relatively small exchange area. By spraying liquid into a gas stream a larger exchange area will be realised.

- ***The efficiency of soot and tar collection.***
  The bench scale experiments indicate that most of the tar and soot is captured in the freeboard above the liquid of the quench. Obviously the gas velocity in the gas bubble is too high for relaxation, while the gas velocity in the freeboard is low enough. Calculation of the size of the soot particle that is yet elutriated at the specific gas velocities, confirms this view.

***Table 3.6** (theoretical) Size of particle just elutriated at typical gas velocities in bench scale installation.*

rising bubble:	
velocity [mm/s] (1)	215
just elutriated soot particle size [μm]	40
gas stream in freeboard:	
velocity [mm/s]	0.2-1
just elutriated soot particle size [μm]	1.2-2.7

(1) rising velocity of gas bubble in water [10].

As long as the gas velocity in the scrubber quench is kept below the freeboard velocity, a satisfactory capture of soot particles can be realised. Phenomena like vapour condensation on soot particles and collision with water droplets will increase the capture efficiency of the scrubber quench.

§ 3.3 Experimental observations in the mini pilot plant installation.

§ 3.3.1 Characteristics of the installation performance.

The temperature profile of the electrically heated reactor has been monitored with five thermocouples. As could be expected, the influence of the gas stream on this profile is negligible.

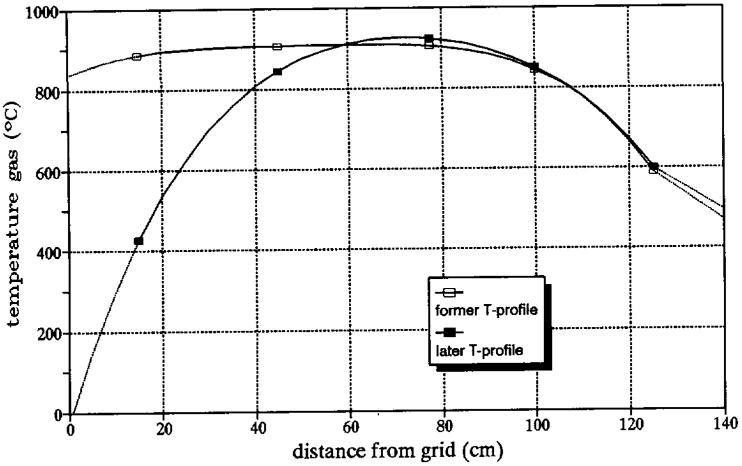

Figure 3.7 Temperature profile of mini pilot plant.

During the experiments two temperature profiles have been imposed (see figure 3.7). During the early experiments the profile is relatively 'wide'; over a relatively large section of the reactor the temperature is maintained at the required elevated level. In later experiments the temperature profile becomes 'sharpened' to fulfil certain heating conditions at the injection point. For optimal operation the injection nozzle should not be heated above the boiling temperature of the chlorinated hydrocarbon feed. In order to diminish the heat flux to the nozzle, the temperature in the lower part of the reactor is decreased (by rearrangement of the heating elements). As shown in the figure, the upper part of the temperature profile remains unchanged.

Usually the dechlorination level is monitored by measuring the HCl produced via the split titration system. Sometimes, the 'organic chlorine remainder' is also determined, using off-line GC analysis (see paragraph 2.2.3). The dechlorination grades according to both analytical methods are compared in table 3.7. In general the discrepancy is remarkably small, considering:

- the accuracy of sampling and analysis,
- the adsorption of HCl on soot and tar products in the tubing to the titration system, which will create an apparent 'loss' of HCl.

Only in case of experiment E the discrepancy is larger. In this experiment the reaction temperature has been 600 °C, resulting in incomplete dechlorination. In this case, the validity of the method to interpret the GC data, the 'organic chlorine remainder' method, is questionable (see paragraph 2.2.3).

Table 3.7 Comparison of several dechlorination measurements.

Experiment (1)	dechlorination level [mol%]		
	titration (2)	GC analysis (3)	scrubber
A	98.9		92.9 (4)
B	96	99.96	
C	95 (6)	97.4	97.4 (4)
D	82		79.6 (4) 83.5 (5)
E	67	84.3	

(1) *process conditions:*

(A) feed: MCB; T = 900 °C; τ = 9 s; $H_2/Cl = 5.0$
(B) feed: MCB; T = 900 °C; τ = 9 s; $H_2/Cl = 4.9$
(C) feed: MCB; T = 900 °C; τ = 12 s; $H_2/Cl = 4.8$
(D) feed: DD; T = 900 °C; τ = 10 s; $H_2/Cl = 3.9$
(E) feed: DD; T = 600 °C; τ = 9 s; $H_2/Cl = 4.2$
MCB: monochlorobenzene
DD: dichloropropane and -propene mixture

(2) *dechlorination level according to HCl split flow.*
(3) *dechlorination level according to organic chlorine remainder.*
(4) *determined via titration of Cl^- ion content.*
(5) *determined via titration of caustic soda content.*
(6) *assumed split ratio: S=330.*

Table 3.7 also shows dechlorination levels under the name of scrubber. During normal operation the complete gas stream, except the small split stream, is washed in the scrubber. After shutdown of the experiment the scrubber will contain all HCl produced. Measurement of the Cl^- content of the scrubber must indicate the same dechlorination level as the split titration system does. As shown, the discrepancy between both dechlorination levels is indeed within a range of acceptable accuracy.

Table 3.8 summarises the differences between the three methods used to measure the dechlorination grade.

A C-balance can be set up using the GC analysis data and element analysis on the soot produced. Table 3.9 presents the overall picture for a chlorobenzene experiment. The balance is closed within 10%. Taking into account the error sensitive steps involved, especially in the sampling stage, this margin is more than acceptable.

***Table 3.8** Comparison of the methods applied in the mini pilot plant to determine the dechlorination level.*

characteristics	methods		
	split titration	GC analysis	scrubber
on/off-line	on-line.	off-line.	off-line.
sampling	small fraction of complete gas stream dissolved in water.	complete gas stream (in gas bottle or solvent).	complete gas stream dissolved in water; sample from this water solution.
type of analysis	titration.	GC.	titration.
object of measurement	H^+ content	(chlorinated) hydrocarbon content	Cl^- content
conversion calculus	HCl according to H^+ content compared with Cl feed	comparison of chlorobenzene and benzene fractions according to 'organic chlorine remainder' method	HCl according to Cl^- content compared with Cl feed

Table 3.9 *C-balance of mini pilot plant installation.*
(process conditions: $T = 900$ °C; $\tau = 12$ s; $H_2/Cl = 4.8$)

specification		feed	products		
		chlorobenzene	benzene	tar (3)	soot
mass	[g]	7254	3626 (1)	259.0	639.3 (2)
C fraction	[moleq./g]	0.0533	0.0769	0.0779 (3)	0.0805 (4)
C quantity	[moleq.]	386.9	278.8	20.2	51.5
total C quantity	[moleq.]	386.9	350.5		

(1) 2294 gram condensed in cold filter, 1332 gram exhausted as vapour.

(2) 597.4 gram in reactor, 21.1 gram in annular space, 20.8 gram in first filter.

(3) tar production is determined by summation of all identified PAH fractions. The average C fraction, calculated from measured mass and C quantity, nearly matches the C fraction of pure biphenyl.

(4) calculated from measured C mass fraction (96.7 wt%) and atomic mass (12.011 g/moleq. [9]).

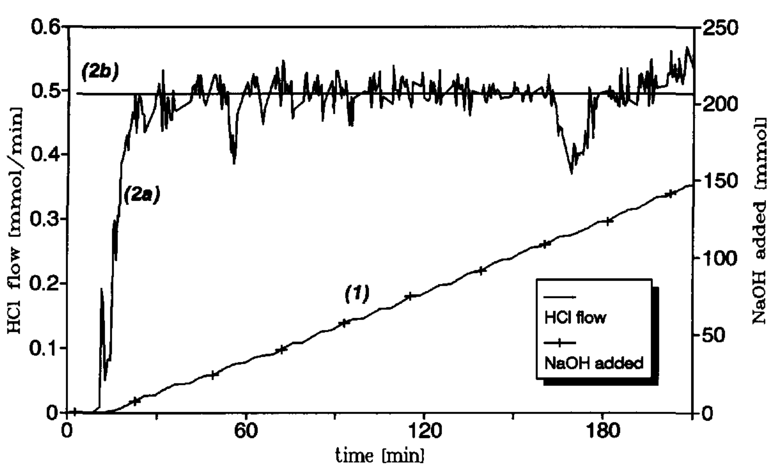

Figure 3.8 *Typical titration plot.*
(1) measured NaOH supply.
(2a) HCl molar flow (determined by derivation).
(2b) average HCl molar flow.

A typical titration plot is offered in figure 3.8. The acid HCl exhaust stream is neutralised by a 0.25 M caustic NaOH solution. The quantity of NaOH required to maintain the pH at 9.75[2] is measured and converted into molar flow by calculating the time derivative of this signal. The signal obtained is influenced and disturbed by:

- hydrodynamic time response of the titration vessel (mixing),
- time response of the pH-stat control system (the pH swings around its setpoint, as the NaOH solution is supplied in discrete steps),
- the imperfect derivation of the signal.

The figure shows larger deviations at the end of the experiment which are probably caused by contamination of the mini pilot installation, especially in the critical capillary.

As demonstrated by experiments in the bench scale installation, and underlined with further evidence by the analysis of the soot formed, the production of soot and tar in the mini pilot plant reactor is strongly influenced by the presence of thermocouples and SiC wall. Therefore, the experiments in the mini pilot plant focus on items which are involved in the technical realisation of the process, such as the type of reactor and the best method to feed the chlorinated hydrocarbons.

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[2] This pH has been chosen to promote dissolution of HCl and to have a not too vigorous pH response at small concentration changes.

§ 3.3.2 Influence of reactor configuration on performance.

The soot formation in a fluidised bed and in an empty tube are compared in table 3.10.

***Table 3.10** Soot quantities at different reactor configurations.*

configuration	reactor soot [wt%]	annular soot [wt%]	exhausted soot [wt%]
feed = DD; T = 900 °C.			
5 kg fluid bed	no data available		0.5 - 1.0
1 kg fluid bed			5 - 10
empty tube			0.5 - 1.0
feed = chlorobenzene.			
5 kg fluid bed (600 °C)	none	none	none
5 kg fluid bed (900 °C)	4.6	5.7	0.6
empty tube (900 °C)	0.5-1.5	0.5-1.5	0.5-2.0

The DD experiments have been carried out during the early stage of the study. At that time measurement of the soot quantity within the reactor and annular space was too inaccurate. Based on the experience from these experiments the soot sampling method has been improved, so the above mentioned quantities could be measured during the experiments with chlorobenzene.

The DD experiments show a large influence of the bed mass on the exhausted soot quantity. Even though the soot deposit on the bed material is unknown in case of the 1 kg bed operation, the soot formation must have been abundant. Just the exhausted soot quantity (5-10 wt%) exceeds the complete soot production of the 5 kg bed (3.5 to 4.4 wt% on the bed material[3] and less than 1 wt% emitted).

The influence of the bed mass is not straightforward. The aggravated soot formation of the 1 kg bed in comparison to the 5 kg bed can not be extrapolated to smaller beds, as shown by the empty tube (0 kg bed) experiments. It is felt that alteration of the operation due to different bed masses has been accompanied by yet unrevealed changes in other process parameters. Especially, interactive effects on the injection system are suspected to play a role. The influence of the injection will be discussed in next paragraph.

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[3] see table 3.11

The emitted soot fraction in the 5 kg fluidised bed is of the same order as that in empty tube operation. The decrease in soot emission aimed at in the fluid bed operation, shows to be negligible. Moreover, during the fluid bed operation much soot is produced in the reactor and the annular space. As will be discussed in next paragraph, lumps are formed if the soot deposition exceeds a certain 'saturation' level. These lumps deteriorate the operation of the fluidised bed and finally lead to a complete obstruction of the reactor.

After all, the experiments in the mini pilot plant show that using a fluidised bed does not give the benefits assumed in advance.

- The fluidised bed operation leads to an increased soot formation.
- In a fluidised bed lumps of soot and bed material are formed, causing malfunctioning of the reactor and creating the danger of obstruction.

In practice the operation of the fluidised bed happened to be difficult.

The results given in table 3.10 concerning experiments with chlorobenzene at 600 °C, should be interpreted as reference data. They show that chlorobenzene is not converted at 600 °C. Negligible dechlorination[4] and soot formation are expected and observed, indicating no catalytic effects in the reactor at that temperature.

§ 3.3.3 Soot deposition.

Following the practical definition of soot and tar as given in paragraph 3.1.2:

- soot is found in the reactor, the annular space and the first filter,
- tar is found in the second filter and subsequent units of the installation, especially in the scrubber and the cold trap.

In the mini pilot plant installation mainly 'powder soot' is observed. The small particles may stick together, forming rather huge lumps of soot. The formation of these lumps depends on the quantity of soot production and the reactor configuration (and therefore on process conditions). The soot lumps cannot be blown out of the reactor and are found in the reactor or the annular space. They have never been observed in the first filter.

The 'filament soot', a soot type obtained in the bench scale installation, is almost not noticed in the mini pilot plant installation. Only some very small pieces are found. They commonly have lost their shiny appearance due to accumulation of powder soot on their surface.

In fluid bed operation the quantity of soot produced is far more difficult to measure. Relative to the bed mass only little soot is formed. Moreover, the bed material can only be retrieved from the reactor by a vacuum cleaner or by disassembling the reactor. As the soot mass is determined from the difference of bed mass before and after operation large errors are involved.

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[4] actually 2.8 mol% dechlorination was observed.

The amount of soot produced can also be calculated by burning off the soot from the contaminated bed material. However, it is difficult or almost impossible to take a representative sample of the bed material as it sticks together, creating lumps. The soot fraction of the lumps and that of loose sand differ, as shown in table 3.11. In order to calculate the overall soot production, the amount of lumps in the bed needs to be known. However, this amount is hardly measurable. In fact, the only practical method seems to determine this amount is the reverse calculation, i.e. calculating the amount of lumps from the overall soot fraction.

The lumps seem to originate from excessive soot in the bed. Comparison of sets A and B as given in table 3.11, shows that lumps are not yet created if a limited amount of soot is present. The lumps are obtained by accumulation of soot on the bed material. Assuming that the lumps are only created after the sand is 'saturated' with soot, a tentative estimation for the 'saturation' fraction would be about 3 wt%.

Table 3.11 *Soot accumulation on bed material in fluidised bed.*

set (1)	soot fraction on bed material [wt%]			portion of lumps [wt%] (4)	remaining soot in bed [wt%] (5)
	lumps (2)	loose sand (2)	overall (3)		
A	none observed	1.2	n.a. (60)	0	4.4
B	19.6	3.0	7.7 (420)	28.6	3.5

(1) *process conditions: DD fed into 5 kg fluidised bed at 900 °C.*
A: set of experiments in which 1364 gram DD is fed.
B: set of experiments in which 11856 gram DD is fed,

(2) *soot fraction (mass of soot/mass of bed) determined by burning.*

(3) *soot fraction (mass of soot/mass of bed) determined by weighing. Between brackets the actual weights are given in grams:*
- set A: weight not measurable; calculated assuming overall soot fraction to be equal to the soot fraction on the loose sand.
- set B: measured weight.

(4) *the calculated fraction of lumps in the bed mass (mass of soot in lumps/mass of soot in bed).*

(5) *soot production estimated from overall soot fraction in the bed (mass of soot/mass of DD fed).*

The measurement of the soot in an empty reactor is easier. The soot is sampled and weighed after disassembling the reactor. Depending on operating and process conditions different amounts are found, ranging from 0.5 wt% to more than 10 wt%. If monochlorobenzene is fed, at standard conditions the soot mass obtained inside the reactor is about 2 to 5 wt% of the feed.

Usually the soot quantity in the annular space is of the same order as inside the reactor. The operating conditions determine which of the two is largest. At the end of this paragraph the origin of annular soot is discussed.

Emitted soot is captured by a cyclone or by a hot filter. In the early experiments a cyclone was used to collect the soot. However, its efficiency was rather low. Moreover, the small amount of soot that was collected, tended to block the passage, at least realising pressure buildup. Better results are obtained using a filter system, consisting of first a hot filter ($T \approx 200$ °C) and second a cold filter ($T < 40$ °C). In the hot filter soot is collected, in the cold filter tar. In the hot filter almost all emitted soot is collected, realising two targets:

- accurate measurement of the emitted quantity of soot,
- preventing contamination of the installation behind.

At standard conditions the mass of emitted soot is about 1 wt% of the chlorinated hydrocarbon feed in case DD is fed, and about 0.5-2.0 wt% if chlorobenzene is fed.

The cold filter collects tar to prevent obstructions in the rest of the installation. Not all tar is collected, as demonstrated by the presence of naphthalene or biphenyl like crystalline deposits in the scrubber and the cold trap. Its purpose is operational, not analytical. The quantity collected in the filter depends on several factors:

- the fraction of tar in the exhaust gases,
- the temperature of the filter,
- the residence time of the exhaust gases in the cold filter,
- the presence of a solvent in the filter case.

The quantity of collected tar is not only determined by the quantity of the tar produced, but also by the tendency of the tarry products to condensate in the filter. Because the temperature control of the filter has been too poor for reproducible condensation conditions, the collected quantity may only be interpreted as a slight indication of the tar production. Typically 2 to 5 wt% of tarry products are observed in the filter.

It should be noted that, in order to obtain reproducible data from the collected tar quantities, the conditions in the filter should not only be well controlled during operation, but also in the period between shutdown and sampling (to prevent uncontrolled evaporation).

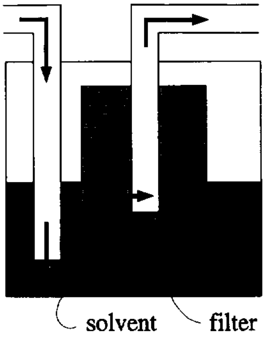


Figure 3.9 *Modified cold filter.*

During the last experiments a modified filter has been used, improving the collecting efficiency of the second filter. In the filter house a liquid is added through which the exhaust gases are forced to flow (see figure 3.9). The liquid not only acts as a solvent, but also improves cooling. In this situation most of the tarry components remain in the filter. As demonstrated by GC analysis about 90 wt% of the benzene produced is collected in the filter.

It is important to collect soot and tar directly behind the reactor, otherwise it will definitely block the transport lines. The obstruction usually occurs at the first spot where the temperature is below 200 °C. The tar acts as a kind of adhesive, sticking the soot particles together; the soot particles occupy space creating pressure drop and, finally, complete obstruction. If the cold spot has a curvation, the tendency to obstruct increases.

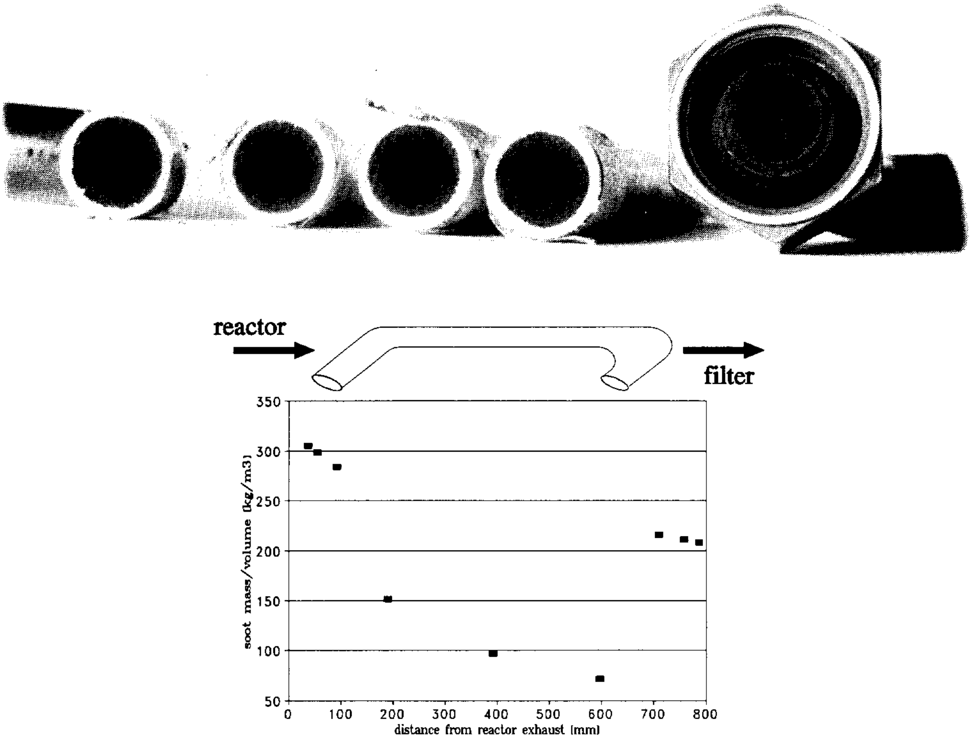


Figure 3.10 *Obstruction of effluent pipe by soot deposit.*
Feed: about 4 mmol/s DD, 15 mmol/s H_2.
$T_{reactor}$ = *900 °C;* T_{pipe} = *270 °C.*
$D_{i.pipe}$ = *10 mm;* $v_{gas.pipe}$ = *10.8 m/s.*

An example of obstruction by soot and tar is given in figure 3.10. The example originates from an experiment in which DD has been treated with a relative small excess of H_2 ($H_2/Cl \approx 2$). Severe soot formation was encountered, leading to the shown obstruction of the connection pipe between reactor and hot filter.

A profile is constructed showing the soot deposition along the distance from the reactor. The figure reveals that soot deposition is extreme in curvatures and declines smoothly in straight pipes. As shown by the photograph the first part of the pipe is completely obstructed by soot. The density of the obstructing soot is 300 kg/m^3, giving a first approximation of the bulk density (see also paragraph 3.4.3).

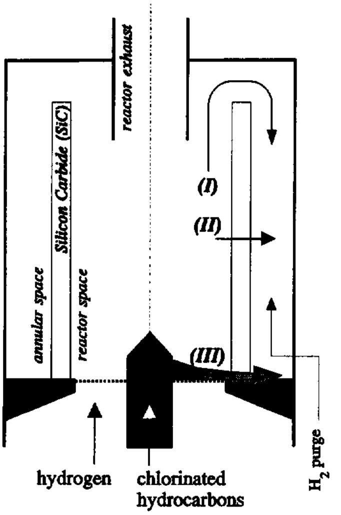


Figure 3.11 *Schematic representation of possible routes of transport across the SiC tube, involved in the formation of annular soot.*
route I: *blowover of reactor soot.*
route II: *gas transport of chlorinated hydrocarbons.*
route III: *liquid transport of chlorinated hydrocarbons.*

Soot is also found in the annular space between the SiC tube and the Nimonic housing. This annular soot may be formed in the annular space itself, but can also originate from soot formed in the reactor. As shown in figure 3.11 soot may be blown from the reactor space into the annular space. However, next soot deposition was observed after an experiment with a new SiC tube which was coated with white Al_2O_3. In the middle the tube had turned black by soot and remained white at top and bottom. The white section at the top corresponds with the metal pipe inserted in the SiC tube to lead the gas flow to the reactor exhaust. Neither was soot observed between this insertion pipe and the SiC tube. Based on these observations, it is unlikely to assume that the annular soot originates from soot formed in the reactor.

Moreover, analysis demonstrates that annular soot has a larger fraction of metals than reactor soot. In general, the occurrence of metals indicates formation by metal catalysis [8]. The larger metal fraction of the annular soot not only explains the accelerated formation, but also implies that the formation took place at the metal wall, i.e. within the annular space.

This requires transport of (chlorinated) hydrocarbons into the annular space. Taking into account the relatively large porosity of the SiC applied the (chlorinated) hydrocarbons probably penetrate through the SiC wall, either in gas phase or in liquid phase. Tests with water showed that the applied SiC is permeable to both. Some experimental observations indicate that this transport occurs in liquid phase.

- Gas phase penetration of the chlorinated hydrocarbons and successive soot production should diminish by an increased H_2 purge flow. However, in practice an increased H_2 flow through the annular space showed no noticeable effect on the annular soot formation.

- Installation of the spraying nozzle effectuates a decrease of the annular soot production. When very volatile chlorinated hydrocarbons are fed, like DD and the Cl-cocktail, the annular soot fraction even completely disappears. If liquid penetration is assumed, the effect of spraying can be explained by a better evaporation of the chlorinated hydrocarbons. Less chlorinated hydrocarbons will reach the SiC surface in liquid state; the liquid flow penetrating the SiC wall diminishes. In case chlorobenzene is fed, some liquid droplets still reach the wall, realising a limited penetration and successive soot production. However, in case of DD or the Cl-cocktail the chlorinated hydrocarbon feed is completely evaporated and no liquid penetration can occur. No annular soot is formed.

§ 3.3.4 Influence of feed on performance.

The way that the chlorinated hydrocarbons are fed, obviously effects the quality of operation. As discussed in previous paragraphs H_2 is supplied in excess to the chlorinated hydrocarbons. By this operation the dechlorination is accelerated and the soot formation decreased. The abundance of H_2 at 'macroscopic' level is only effective if the reactants are also properly mixed at 'microscopic' level. The initial contact between H_2 and chlorinated hydrocarbons is very important. Good mixing eliminates the existence of pyrolytic areas where a limited availability of H_2 implies aggravated soot formation.

The temperature of the feed system needs to be controlled accurately, especially if chlorinated hydrocarbons are fed which tend to form soot at their boiling point. The strong temperature increase requires efficient 'microscopic' mixing of H_2 and chlorinated hydrocarbon: no pyrolytic areas should exist.

- If the injection system is too hot the chlorinated hydrocarbons may coke in the internals of the feed system, where no H_2 is available yet. Especially if a spraying nozzle with a narrow aperture is used, such soot formation can result in a complete obstruction.

- If the injection system is too cool the chlorinated hydrocarbons do not evaporate completely. Injected liquid accumulates in the neighbourhood or on the nozzle itself. Especially if the nozzle is cooled, the surface of the nozzle will be a favourable spot for accumulation. Where liquid accumulates a poor contact exists between H_2 and chlorinated hydrocarbons. The resulting pyrolytic conditions cause an aggravated soot formation.

Depending on the type of chlorinated hydrocarbons fed, a different quality of temperature control is required. E.g. chlorobenzene requires less accurate temperature control than DD. The required quality of temperature control is determined mainly by the tendency of the chlorinated hydrocarbon feed to form soot at its boiling point, but also by the volatility of the feed.

During the incorporation of the spraying nozzle in the mini pilot plant these aspects were considered. Initially, the temperature of the nozzle happened to exceed the tolerable level. In contrary to the former injection system a cooling jacket around the spraying nozzle was not feasible. Instead the decrease in the nozzle temperature was achieved by the following.

- The electrical heating system was moved upwards. As shown in figure 3.7 the temperature at the injection point considerably decreased, while at some distance from the grid the temperature remained identical to the former profile. The temperature profile was somewhat 'sharpened'.
- To have the nozzle sufficiently cooled the liquid flow through the nozzle was increased.

These alterations, of course, restricted the range of operation, but could be realised without actually changing the hardware configuration.

Also during startup a flow through the nozzle is required, in order to have a sufficient low temperature when the chlorinated hydrocarbon feed is started. Otherwise, immediate obstruction may occur in the spraying channel. Water seems to be a good choice for the cooling medium during startup. Water does not cause any soot formation and possesses excellent heat transport properties (relatively high c_p and ΔH_{vap}). However, water vapour condenses in the cold filter. In this water HCl dissolves, leading to corrosion and disturbing the split titration system. Startup with another coolant does not have these problems, but will cause some additional soot formation. In some experiments the startup has been carried out with water, in others with hexane.

By implementing the nozzle the following results are effectuated.

- All kinds of liquids can be fed. The disturbances observed when the chlorinated hydrocarbons were still fed with the former injection system, do not take place anymore. E.g. DD can be fed without obstruction of the injection point, even under conditions of severe soot formation. However, good temperature control is required.

- As discussed in paragraph 3.3.3 the amount of soot in the annular space is reduced. This indicates a better introduction of the chlorinated hydrocarbons inside the reactor.

- Under normal conditions the soot formation is somewhat suppressed, especially with easily sooting species like DD. However, if the spray from the nozzle spouts onto the reactor thermocouples, extraordinary high soot formation may be realised. This was once observed after a new spraying nozzle was incorporated.

§ 3.3.5 Secondary effects on process operation.

As elucidated by the experiments in the bench scale installation, some reactive surfaces are present in the mini pilot plant, namely

- the silicon carbide wall,
- the hastelloy thermocouples,
- the nimonic housing.

Frequently at 50 cm from the top of the reactor a band of soot is observed; sometimes accompanied by a band of corrosion on the nickel alloy thermocouples. This phenomenon is caused by the instability of SiC, as will be discussed in chapter 5.

The thermocouples in the reactor have some reactive influence. The quantitative contribution of the thermocouples to the overall soot formation is unknown. On beforehand the influence of thermocouples was supposed to be negligible as only a small surface area is present. However, based on bench scale experiments, now the thermocouples are believed to be responsible for about 1.1 wt% soot of the total of 2 to 5 wt% soot normally observed, i.e. 50% to 20% relative. Also the different types of soot observed in both installations, supply supplementary evidence for the influence of the metal surfaces. In the bench scale installation (where no metal is exposed) filament soot is observed, rich in carbon; in the mini pilot plant installation powder soot is found, containing metals. Testing the thermocouple in the bench scale plant resulted in a heavy production of powder soot, as discussed in paragraph 3.2.2.

The strong influence of metal is also demonstrated by a mini pilot plant experiment without SiC tube in the reactor. The SiC tube is expected to effect the soot formation in several ways:

- SiC activates soot formation locally leading to the formation of 'humps' of soot. Without SiC these humps are not observed.
- The SiC tube covers the nickel containing nimonic housing. Without the SiC tube an increased soot formation is expected due to the metal activity.
- The SiC tube acts like a heat shield in the pilot plant. Without SiC the reaction medium is in contact with hotter surfaces, probably resulting in an aggravated soot formation.

Table 3.12 *Soot quantities in mini pilot plant reactor with and without SiC tube. feed = chlorobenzene; empty tube; T = 900 °C.*

configuration	reactor soot [wt%]	annular soot [wt%]	exhausted soot [wt%]
with SiC	0.5-1.5	0.5-1.5	0.5-2.0
without SiC	11.5		0.4

As shown in table 3.12, the experiment without the SiC tube indeed results in an enormous soot formation. This leads to two important conclusions.

- Some metals activate the soot formation. Before using a metal surface in the thermal hydrodechlorination process, the actual soot promoting properties of the considered metal have to be investigated. For this purpose the bench scale installation is very suitable.

- The annular soot is formed by metal activity. From the observed soot fraction a first estimation can be made for the flow of chlorinated hydrocarbons into the annular space. The flow must be larger than 1 wt% (assuming 100% conversion of chlorinated hydrocarbons into soot) and smaller than 9 wt% (assuming 11.5% soot formation as observed in the experiment without SiC).

The effect of the H_2 flow through the mini pilot reactor has been investigated. Besides to a probable increase of dechlorination, an enlarged H_2 flow is expected to lower soot formation. This expectation is based on the following effects.

- The residence time is shortened.
- The ratio H_2/Cl is increased effectuating better reducing circumstances.
- By the increase in the H_2 flow the total gas flow is increased. The drag force by which the gas can blow out the soot particles from the reactor, is increased. Nuclei leading to soot formation are blown out, effectuating less soot formation.

Table 3.13 *Soot quantities at different feed ratios of H_2 and chlorinated hydrocarbon. feed = chlorobenzene; empty tube; T = 900 °C.*

flow		residence time [s]	reactor soot [wt%]	annular soot [wt%]	exhausted soot [wt%]
MCB [kg/h]	H_2 [Nl/min]				
0.58	11	12.9	0.8	2.9	0.8
1.1	20	7.0	0.5-1.5	0.5-1.5	0.5-2.0
1.1	32	4.7	1.85	1.69	

Shaded: *experimental standard conditions.*

As shown in table 3.13 the effect of H_2 flow and residence time is small or absent under the circumstances applied in the mini pilot plant, especially on the total of soot observed inside the reactor. In contrast to the observations in the bench scale installation, the variation in residence time and H_2/Cl ratio shows only a restricted effect on the soot formation. This difference is probably due to the metals present in the pilot installation.

It should be noted that the H_2/Cl ratio has been varied between 4.5 and 7.7. A more stringent decrease of the H_2/Cl ratio leads to more soot formation, as demonstrated by the bench scale experiments. The experiment with DD presented in table 3.14 supports this observation. An enormous soot formation occurs when DD is processed with a H_2/Cl ratio of about 1.9.

As indicated by the table, soot formation depends on the type of chlorinated hydrocarbon waste. Unsaturated hydrocarbons with increasing chlorine content are less stable and form soot more easily. The soot formation does not only differ in terms of quantity, but also with respect to composition and structure of the soot (see paragraph 3.4).

Not directly shown by the tables are operational requirements concerned with the storage and transport of the chlorinated hydrocarbons. Most chlorinated hydrocarbons have excellent properties as a solvent. High quality synthetics, like Teflon and Kevlar, need to be chosen for flexible tubing and connections. Frequently Viton is also applicable, but e.g. in chlorobenzene Viton swells a bit, leading to malfunctioning or complete break down of the apparatus.

Table 3.14 Soot quantities with different feeds (empty tube; T = 900 °C).

feed	residence time [s]	H_2/Cl ratio [mol/mol]	reactor soot [wt%]	annular soot [wt%]	exhausted soot [wt%]
chlorobenzene	7.0	4.9-5.2	0.5-1.5	0.5-1.5	0.5-2.0
DD	6.0	1.9	3.9	0.1	7.2
DD	8.1	4.0	(1)	(1)	0.8
DD+benzene(2)	5.7	3.3	4.0	0	0.4
Cl-cocktail (3)	5.1	2.8	2.3	0	0.6

The soot fraction is defined as the mass of soot divided by the total mass of chlorinated and nonchlorinated hydrocarbons fed.

(1) *small unmeasurable quantity.*

(2) *DD: 60.5 wt% (51.7 mol%); benzene: 39.5 wt% (48.3 mol%).*

(3) *composition given in table 2.7.*

Of all chlorinated hydrocarbons applied, especially the processing of DD demands a lot of attention. The quality of the mixture appears to deteriorate in time. Frequently a small layer of some deposit is found on gaskets and valves. Malfunctioning and complete break down of the apparatus involved may follow. The mixture seems to be susceptible to polymerisation. After addition of an inhibitor (the epoxy resin 'edanol') the effect of deterioration was limited.

§ 3.3.6 Dioxin formation.

Experiments have been carried out to investigate the possibility of dioxin formation under conditions of thermal hydrodechlorination. The experiments are performed in the mini pilot plant installation and in a smaller installation at the Gorlaeus laboratory [16]. The operational conditions during these experiments are listed in table 3.15.

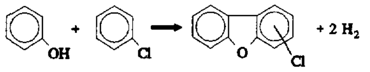
Table 3.15 Experimental conditions to verify non-formation of PCDD/F (dioxins).

	mini pilot	labscale [16]	
O-carrier	methanol	methanol	phenol
ratio chlorobenzene/O-carrier [mol/mol]	2.15, 2.01	2	9
residence time [s]	6.1	2.1	2.7
$T_{set\text{-}point}$ [°C]	900	920	920
T_{max} [°C]	910	940	940

To investigate the possibility of dioxin formation oxygen has to be introduced in the reaction system. Therefore hydrocarbons containing atomic oxygen, like methanol and phenol, have been added to the chlorinated feed. Under the conditions of thermal hydrodechlorination methanol will decompose mainly to carbon monoxide and hydrogen gas, according to

$$CH_3OH \longrightarrow CO + 2H_2 \qquad \textbf{(3.2)}$$

However, the oxygen atom from methanol may also be used in the formation of the dioxin skeleton. If phenol is added, the formation of chlorinated members of the dioxin family seems even more straightforward, as shown by the following reaction equation:



(3.4)

In labscale experiments at the Gorlaeus laboratory, experiments with both methanol and phenol have been performed. In the mini pilot plant installation only experiments with methanol have been carried out.

The hydrocarbon product formed during these experiments has been analyzed for its dioxin content by external research laboratories, specialised in dioxin analysis[5]. The analysis of dioxins appeared to be bothered by the presence of the poly aromatic hydrocarbons (PAH's). In case of the sample from the mini pilot plant the separation of dioxins and PAH's has been taken care of by an additional sulfonation step during the cleanup of the sample [14]. While PAH's are susceptible to sulfonation, dioxins are not. After sulfonation PAH's and dioxins are easily separated. In case of the labscale experiment the separation of PAH's and dioxins is realised by an additional cleanup step over a large aluminium oxide column (the so called Hagenmaier cleanup) [16]. For the rest, the cleanup and analysis of the samples have been carried out according to the standard procedure (see figure 3.12).

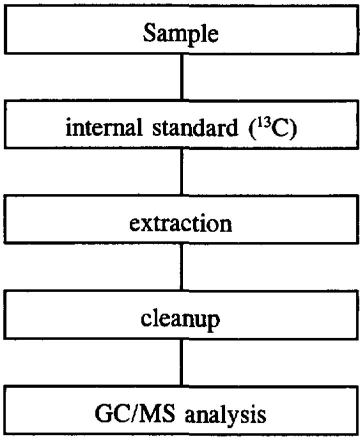


Figure 3.12 *Standard procedure dioxin analysis.* [11,14,16]

Besides the dioxins the dechlorination level and the PAH production are measured as well. The results are summarised in table 3.16. The table shows large differences between the methanol experiment on labscale and that in the mini pilot plant. The reason behind these differences is not known. About the same degree of carbon recovery is obtained for both experiments. Roughly equal dechlorination levels are realised. Comparison of the methanol experiment and the phenol experiment at labscale reveals substantial differences as well.

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[5] the mini pilot plant sample is analyzed by TNO-Environment and Energy, Delft; the labscale samples are analyzed by Tauw Infra Consult B.V., Deventer.

***Table 3.16** GC analysis of product from experiments to verify non-formation of 'PCDD/F' (dioxins).* [15,16]

	mini pilot	labscale [16]	
O-carrier	methanol	methanol	phenol
'gaseous' products (C_1-C_2) (1,2)			
carbon monoxide	0.33	25.58	7.11
carbon dioxide	1.31	0.16	0.54
methane	19.25	0.90	8.57
ethane	n.d. (4)	0.02	0.28
ethene	n.d. (4)	0.13	1.10
ethyne	n.d. (4)	0.02	0.05
'liquid' products (aromatic compounds) (1,3)			
benzene	82.04	78.66	82.39
naphthalene	0.04	0.14	1.33
biphenyl	0.29	2.72	3.93
chlorobenzene	0.02	0.94	0.94
dechlorination (mol%) (5)	99.9	98.8	98.9
C recovery (%)	86.2	89.9	96.9

(1) *quantity of the species detected, expressed in comparison to the chlorobenzene molar feed [mol%].*

(2) *gas sample taken at end of experiment.*

(3) *liquid sample collected during complete experiment.*

(4) *not detected (< 1.2 ppm).*

(5) *conversion according to method of 'organic chlorine remainder'.*

Analysis of the methanol/monochlorobenzene mixture used as feed for the methanol experiment at labscale, revealed a small fraction of highly chlorinated dibenzodioxins and -furans. In the liquid product retrieved from the experiment no dioxins were observed. The experiment not only shows that at process conditions applied dioxins are not formed, but even that dioxins are destructed! A similar observation is made for the labscale experiment in which phenol is added.

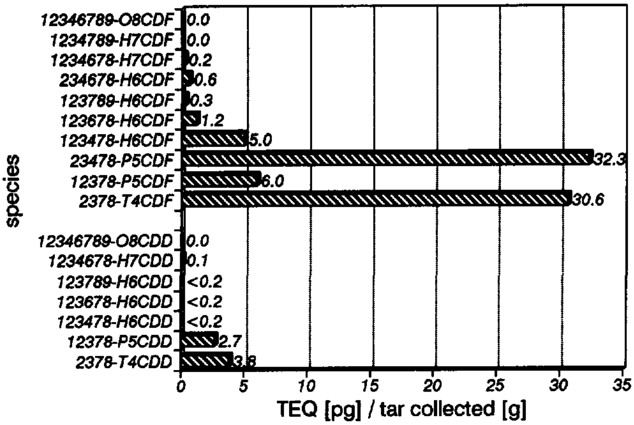

Figure 3.13 *PCDD/F-analysis of product from experiment in mini pilot plant to verify non-formation of dioxins.*
Observed PCDD/F per 1 gram tar: 82.9 pg TEQ (668.5 pg 'dirty 17').

However, after operation with the methanol/monochlorobenzene mixture in the mini pilot plant, members of the so called dirty seventeen have been observed. Some of the most hazardous dioxins and furans were found in the retrieved sample. In figure 3.13 the observed 'fingerprint' of dioxins is presented. Some comments on the outcome of this experiment need to be given:

- In contrary to the theoretical expectation and the experiments at labscale dioxins are observed.
- It is remarkable that highly chlorinated species are present at concentrations of the same order as the lower chlorinated species. Due to the dechlorination conditions one would expect a similar ratio between the chlorinated members of the dioxin family as there is for the chlorinated benzenes.
- The dioxins observed consist mainly of chlorinated dibenzofurans. Tetra- and pentachlorodibenzofurans contribute for 75% of the total TEQ value. TEQ represents a measure of the toxicological hazard.

The different results obtained in the two installations create an obscure picture. Under the well established conditions of the labscale experiment dioxins are destructed. This seems to prove that dioxin and its related compounds are chemically unstable under conditions of thermal hydrodechlorination. But at a similar experiment in the larger mini pilot plant, some dioxins are detected. Their origin is obscure.

- It is unlikely that the exhausted dioxins originate from dioxins in the feed. In the feed a small fraction of only seven (hepta) and eight (octa) times chlorinated dibenzodioxins and -furans is observed. The 'fingerprint' of these dioxins does not match the 'fingerprint' of the dioxins found in the filter. Therefore, ineffective destruction of fed dioxins is not a plausible cause.

- The operation of the two experimental installations is different. Besides the inherent differences of the flow pattern in the reactors, the operation conditions are slightly different, as is expressed by table 3.15. The reaction media are subjected to different residence times and temperature profiles. Moreover, different startup and shutdown procedures are applied. From the experimental data it is hard to deduce what difference finally caused the dioxins observed.
  - Different process conditions, such as residence time and temperature, lead to a different product composition. Maybe lower temperature and longer residence time give raise to the exhaust of dioxins.
  - Different startup and shutdown procedures are used. The labscale installation is flushed with hydrogen for about 24 hours before the experiment [16]. In the larger mini pilot plant nitrogen is passed through during startup and shutdown. The nitrogen used contains a small fraction of oxygen[6], which might react with carbon deposits in the reactor. Taking into account that on the carbon deposit some chlorine containing species are adsorbed, the elements required to form dioxins are all available. The question is whether their (low) concentrations can give raise to the observed quantity of dioxins at the temperature of concern.

Concluding, the following can be stated. In the small labscale installation a more conditioned operation is effectuated. At the conditions applied no dioxins are formed; fed dioxins are even destructed. However, a similar experiment at the larger scale mini pilot installation gave raise to dioxins. It is obscure whether these dioxins are formed during operation as the result of slightly different operation conditions, or whether they are formed during the startup and/or shutdown stage. Both plausible explanations indicate that at conditions differing from the well established labscale situation dioxins may be formed. The way the process is carried out seems to have a great impact on this matter. To prevent dioxin formation in plants of even larger scale, the operation procedure has to be evaluated. At the moment it is unclear to what extent the conditions may be varied away from the strict conditions applied in the labscale experiment.

§ 3.4 Analysis of the soot and tar produced.

§ 3.4.1 Analytical methods to determine the chemical composition of the soot.

Typically, the composition of soot is determined in two steps:
-1- determination of the carbon (C) and hydrogen (H) fraction by CH-element analysis.
-2- determination of the chlorine (Cl) and metal (M) fraction using mainly X-ray fluorescence (XRF) and thermogravimetric analysis (TGA).

The CH-element analysis is a rather straightforward method. The sample is combusted and the H_2O and CO_2 produced are measured. The method gives rather accurate results (about 1 wt%).

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[6] N_2 technical quality: $O_2 < 5$ ppm.

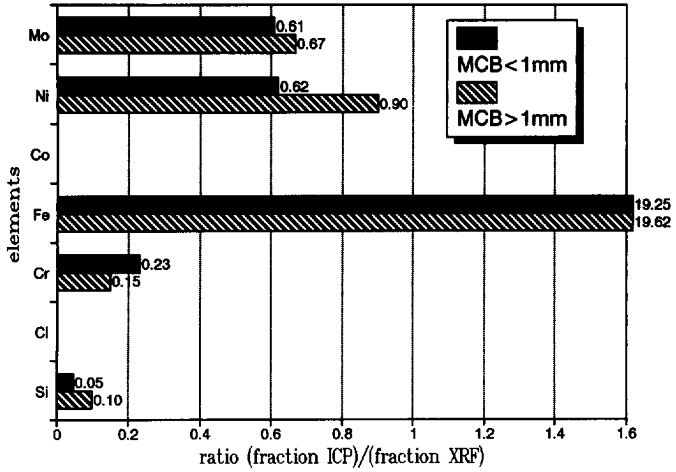

Figure 3.14 *Comparison of XRF and ICP analysis to determine soot composition.*

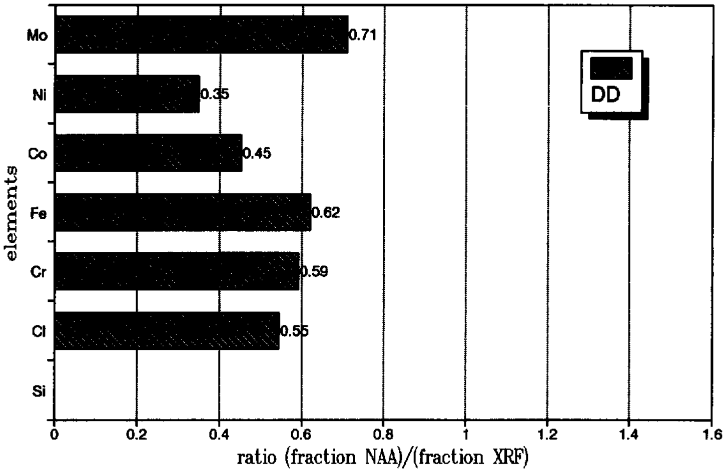

Figure 3.15 *Comparison of XRF and NAA analysis to determine soot composition.*

Determination of the chlorine and metal fraction is complicated. Available analytical methods mainly give semi-quantitative results. In this study XRF has been compared with NAA[7] and ICP[8]. While XRF and NAA suffers from rather strong matrix effects, ICP does not. However, since ICP requires a liquid sample, the soot needs to be dissolved. If the contaminants on the soot dissolve differently, this might introduce errors in the analysis of

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[7] NAA = Neutron activation analysis

[8] ICP = Inductive Coupled Plasm

the actual composition. As shown in figure 3.14 the ICP results do not correspond with the XRF results. E.g. while the Fe fraction according to ICP is about 20 times larger than that according to XRF, the Si fraction is about 20 times smaller. The NAA and XRF results correspond in a much better way. The fingerprints of the contaminant fractions are comparable. Figure 3.15 shows the quotient of the detected values according to NAA analysis divided by those according to XRF analysis. This quotient appears to be comparable for all contaminants, with a value about 0.5. For practical reasons XRF analysis has been chosen as the standard method to determine the metal and chlorine composition of the soot.

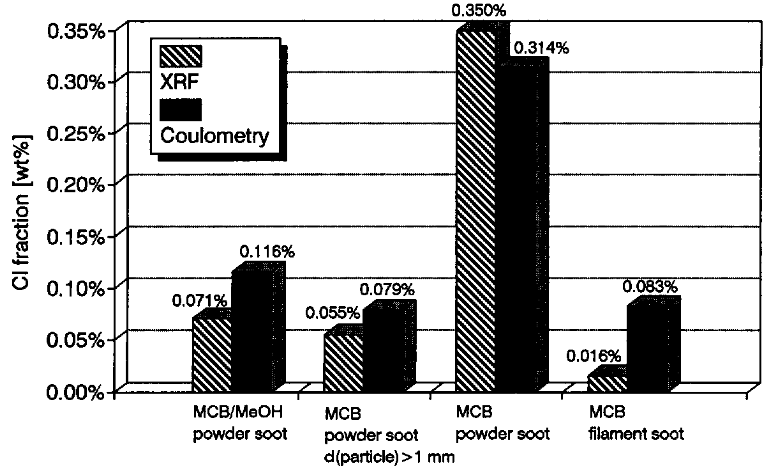

Figure 3.16 Comparison of XRF and coulometric analysis to determine the chlorine content of soot.

At the end of this study, coulometric detection of the chlorine fraction in the soot became feasible. The coulometric analysis comprises combustion of the soot sample and coulometric titration of the HCl produced. In figure 3.16 some analytical results according to this coulometric analysis and XRF analysis are compared. As revealed by the figure the absolute values differ to some extent, certainly for the chlorobenzene filament soot; however taking into account the semi quantitative character of the analytical methods employed the results are acceptable.

Thermogravimetric analysis (TGA) is another analytical method to typify the soot. TGA indicates the quantity of substances adsorbed on the particles and the combustible part of the soot. TGA samples of about 80 mg are heated according to a specific temperature program:

$$\boxed{T_{room} \xrightarrow{10^\circ C/min} 120^\circ C \xrightarrow{15min\ isotherm} 120^\circ C \xrightarrow{50^\circ C/min} 865^\circ C}$$

During the temperature program the soot is heated in a N_2 stream at a standard flow rate of 3.6 l/h. After a temperature of 850 °C is reached and the mass of the sample reaches a constant value, the gas stream is switched to air, at the same flow rate. The soot is combusted. A typical TGA-plot is given in figure 3.17.

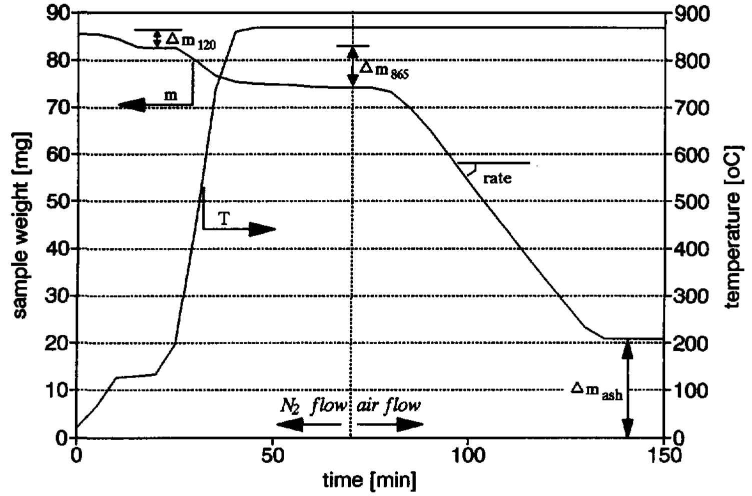

Figure 3.17 Typical result of thermogravimetric analysis (TGA).

The observed TGA weight loss during the temperature program is due to desorption of absorbed material.

- The TGA weight loss till 120 °C is an indication of the water content. Since no water is available in the reactor, the water must have been absorbed after operation. This means that the observed water content is indicative for the hygroscopic property of the soot.
- The TG weight loss achieved between 120 °C and 865 °C is due to desorption of organic material. These volatiles contribute to the so called SOF, the soluble organic fraction [3,13]. The SOF is condensed on the soot during and after operation. Normally the SOF contains potential soot precursors. The SOF may include PAH's. If PAH's are absorbed, the soot constitute a toxicological hazard. [7]

After the desorption program is finished, the sample is combusted. The combustion rate may be used as a characterisation of the soot. The remaining ash consists of the noncombustibles of the soot.

The ash fraction and the metal fraction according to XRF analysis can be compared with the fraction that has not been identified as C or H in the element analysis. As presented in figure 3.18, the ash fraction is complementary to the detected C and H fraction.

The metal fraction according to XRF analysis gives a poorer fit. At low concentrations XRF and element analysis reveal the same trend. With an apparently constant value, the XRF results are lower than the data according to element analysis. However, at higher concentrations (approx. 15 wt%) the XRF results deviate. At these concentrations the trend given by XRF does not compare anymore with the trend according to other techniques.

The differences probably result from the strong influence of the soot matrix in XRF analysis. The XRF results are semi quantitative. Since the influence of the soot matrix is presumably equal for all metal fractions, the XRF data can be well interpreted in a relative sense.

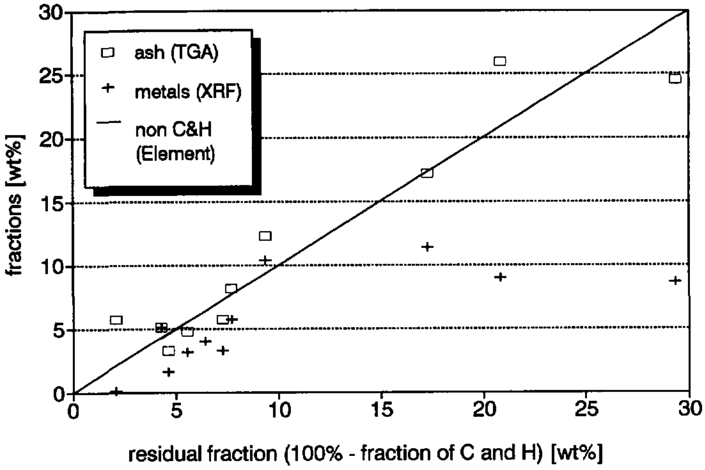

Figure 3.18 *Comparison of analytic methods to determine chlorine and metal fraction of soot.*

According to these observations the analytical results are interpreted as follows.

- The ash remainder detected in TGA is taken as total metal fraction of the soot.
- The metal fractions according to XRF are compared among themselves, indicating the relative contribution of each metal to the total metal fraction.

§ 3.4.2 (Trends in) The chemical composition of the soot produced.

The composition of thermal hydrodechlorination soot has been investigated for a set of samples. The samples originate from different process conditions and different locations. The samples that have been investigated, are listed in table 3.17. The feedstock sequence given in the table, is in order of increasing chlorine content (see e.g. figure 3.21). The analytical results presented in tables 3.18 to 3.20 and figures 3.19 to 3.21, are average values[9].

The overall composition of the soot is given in weight fractions by table 3.18; in figure 3.19 the composition is shown on a molar base. Carbon is the main constituent of the soot, contributing for 80 to 95 mol%. The hydrogen contribution is much smaller and seems less sensitive to operating conditions. The hydrogen fraction is typically in between 5 and 10 mol%. The ash remainder observed at TGA, which is to be interpreted as the metal fraction, is the smallest molar fraction of importance. Depending on the process conditions at which the soot is formed, the ash remainder is 1 to 8 mol%. The chlorine content appears to be negligible, as will be discussed later.

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[9] average with respect to the number of analysed samples of the considered type.

Table 3.17 Types of soot investigated for their composition.

A	filament soot retrieved from bench scale reactor.
a1	feedstock = chlorobenzene
B	powder soot retrieved from mini pilot reactor.
b0 b1 b2 b3 b4	feedstock = mixture of chlorobenzene and methanol. feedstock = chlorobenzene. feedstock = mixture of DD and benzene. feedstock = Cl cocktail. feedstock = DD.
C	powder soot retrieved from annular space in mini pilot reactor.
c0 c1	feedstock = mixture of chlorobenzene and methanol. feedstock = chlorobenzene.
D	powder soot retrieved from mini pilot reactor with nimonic wall
d1	feedstock = chlorobenzene.

The molar weight of the metal fraction, which is required to convert weight into molar fractions, is calculated from the XRF data. As discussed in the previous paragraph XRF data present a fairly good indication of the relative presence of metals in the soot. From these relative data the average molar mass of the overall metal fraction can be calculated. Table 3.19 gives the metal weight fractions according to XRF, and the average molar mass calculated from these. The XRF weight fractions are also shown in figure 3.20.

The main metal contaminants are nickel (Ni), chromium (Cr) and iron (Fe). The metals are probably present as carbides or as pure metal particles, as will be discussed later.

Under thermal hydrodechlorination conditions metals are known soot promoters. This metal activity results in the presence of metals in the soot produced [8]. As discussed in previous paragraphs 3.2.2 and 3.3.5), the metal activity has been observed in thermal hydrodechlorination as well. E.g. table 3.10 shows extreme soot formation if the mini pilot reactor is operated without SiC tube, i.e. with the nimonic housing as actual reactor wall. This increase in soot formation is attributed to the activity of the metals in the nimonic wall. The increase of the total metal fraction present in the soot, as demonstrated in table 3.19 and figure 3.20, supplies additional evidence for the metal activity. Clearly, the soot formed during operation without SiC tube (d1) contains a larger fraction of metals than the soot produced under standard operation with SiC tube (b1). The metal activity is even perceptible by comparison of the metal fraction in reactor soot and annular soot (b0/1 versus c0/1). Soot retrieved from the annular space, where an abundant metal surface is present, is contaminated with a metal fraction which is, at least, twice as large.

No relationship is found between the observed composition of the metal fraction and the type of chlorinated hydrocarbon processed.

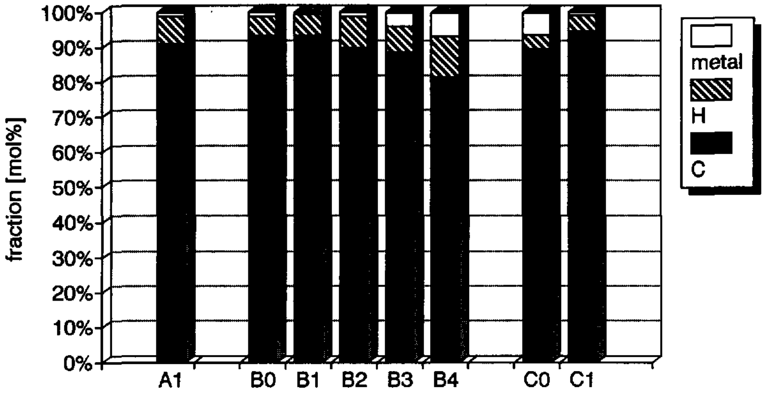

Figure 3.19 *Soot composition (C, H and metal fraction) [mol%].*

Table 3.18 Composition of soot: C, H and ash (metal) fractions [wt%].

feedstock	C [(1)]	H [(1)]	ash (metal)	sum
filament soot				
(A1) MCB	97.20	0.71	5.70	103.61
powder soot collected in reactor				
(B0) MCB/MeOH	92.27	0.46	5.70	98.43
(B1) MCB	94.83	0.52	3.30	98.65
(B2) DD+benzene	92.77	0.79	6.44	100.00
(B3) Cl cocktail	82.11	0.58	17.20	99.89
(B4) DD	69.78	0.84	24.50	95.12
powder soot collected in annular space				
(C0) MCB/MeOH	78.85	0.30	25.90	105.05
(C1) MCB	95.33	0.39	5.10	100.82

(1) C and H fraction according to element analysis; metal fractions estimated by ash content according to TGA.

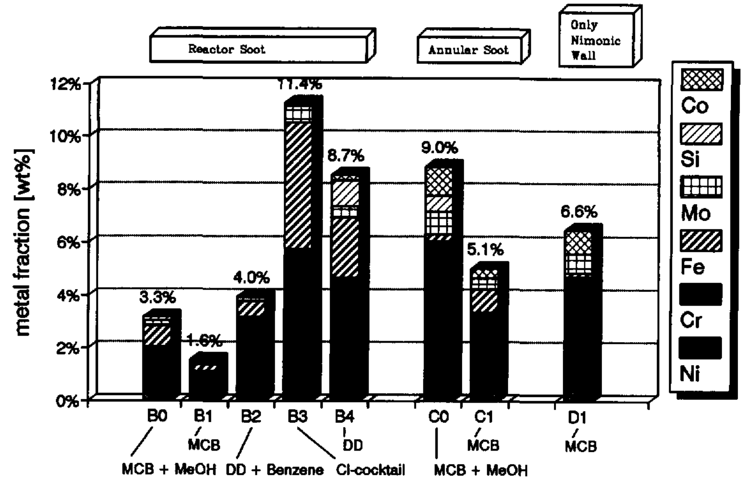

Figure 3.20 *Weight fraction of metals present in the soot according to XRF analysis (see table 3.19). [wt%]*

Table 3.19 *Composition of soot: metal fractions according to XRF analysis.*

feedstock	Ni [wt%]	Cr [wt%]	Fe [wt%]	Mo [wt%]	Si [wt%]	Co [wt%]	M.avg [g/mol]
powder soot collected in reactor							
(B0) MCB/MeOH	1.5	0.6	0.8	0.2	0.2	0.0	54.9
(B1) MCB	0.8	0.4	0.3	0.1	0.1	0.0	56.1
(B2) DD+benzene	2.3	0.9	0.6	0.2	0.0	0.0	56.9
(B3) Cl cocktail	2.5	3.3	4.8	0.6	0.1	0.0	55.9
(B4) DD	2.9	1.8	2.3	0.4	1.0	0.2	51.2
powder soot collected in annular space							
(C0) MCB/MeOH	5.1	1.0	0.3	0.9	0.6	1.1	55.9
(C1) MCB	2.4	1.0	0.9	0.4	0.0	0.4	58.4
powder soot retrieved from mini pilot reactor with nimonic wall only							
(D1) MCB	4.2	0.5	0.2	0.7	0.0	0.9	60.3

Table 3.20 Composition of soot; thermogravimetric analysis (TGA).

feedstock	$\Delta m_{130\,°C}$ (1) [wt%]	$\Delta m_{865\,°C}$ (2) [wt%]	rate of combustion [mg/min]	ash remainder (3) [wt%]
filament soot				
(A1) MCB	0.3	1.0	1.1	5.7
powder soot collected in reactor				
(B0) MCB/MeOH	0.0	1.3	1.5	5.7
(B1) MCB	0.4	3.3	1.4	3.3
(B2) DD+benzene	0.5	4.1	1.5	6.4
(B3) Cl cocktail	0.4	7.2	1.5	17.2
(B4) DD	3.3	10.2	1.1	24.5
powder soot collected in annular space				
(C0) MCB/MeOH	0.2	3.1	1.8	25.9
(C1) MCB	0.5	2.3	1.8	5.1

(1) $\Delta m_{130\,°C}$: *indication of absorbed water fraction.*
(2) $\Delta m_{865\,°C}$: *indication of soluble organic fraction (SOF).*
(3) *ash:* *indication of metal fraction.*

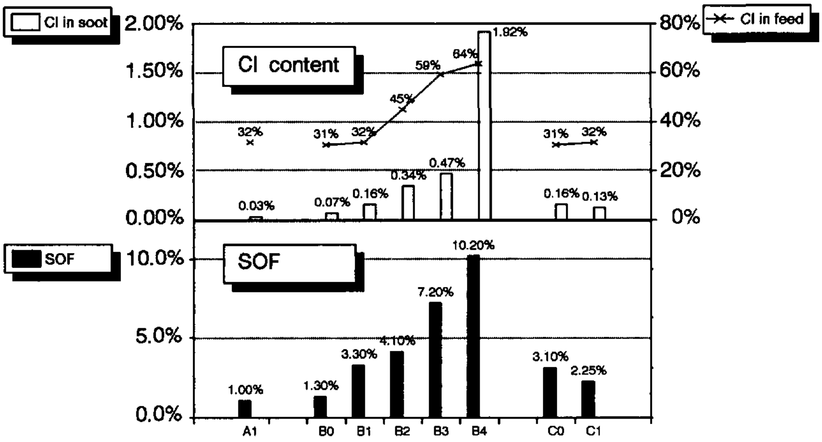

Figure 3.21 *Chlorine content and soluble organic fraction (SOF) of soot, in comparison with chlorine content of feed. [wt%]*

XRF analysis also gives information on the chlorine content of the soot. The results are presented in figure 3.21. The chlorine content of the soot apparently follows the chlorine content of the chlorinated hydrocarbon feedstock. DD produces soot with a higher chlorine content than chlorobenzene. However, chlorine appears to be a minor, nearly negligible, constituent of the soot. The observed chlorine fraction does not exceed 1 mol% (2.5 wt%) and is in general below 0.2 mol% (0.5 wt%).

Due to the limited presence, it is difficult to determine whether the chlorine is chemically or physically bonded. Efforts to get an indication, e.g. by washing to determine physically bonded HCl, did not give satisfactory results. Some HCl was detected in the 'wash water', but to which extent the chlorine had been removed from the soot, could not be determined. Errors involved in the analysis exceeded the small actual chlorine fraction.

The small chlorine fraction indicates that the observed metals are not present in the form of chloride salts. In all observations the chlorine fraction is smaller than 15 mol% of the metal fraction. Also different trends are observed if the metal fraction and the chlorine content are set against the chlorinated hydrocarbon feedstock (displayed in figures 3.20 and 3.21). Presumably, the metals are present in a pure metallic form or as carbides.

The results of thermogravimetric analysis (TGA) are presented in table 3.20. The weight loss at 120 °C, probably due to desorption of water, is normally rather low (<0.5 wt%). Only the soot produced from DD exhibits a relatively large water fraction (3.3 wt%).

The weight loss encountered between 120 °C and 865 °C is due to desorption of the soluble organic fraction (SOF). As depicted in figure 3.21, the SOF follows a similar trend as the chlorine content of the soot. Apparently, just as the chlorine content of the soot, the SOF is related to the chlorine fraction of the chlorinated hydrocarbon feed. This leads to the hypothesis that the observed chlorine content of the soot is effectuated by chlorinated species in the SOF attached to the soot. This would imply that the observed chlorine is physically bonded. Unfortunately, the desorbed fraction could not be analyzed in order to confirm the hypothesis.

§ 3.4.3 Physical properties of the soot produced.

The physical properties of the soot investigated are density, particle size and surface area. Also the physical appearance of the soot is examined, using magnifying techniques such as electron microscopy.

density

Using He pycnometry, the true density is measured for a set of soot samples (see table 3.21). The true density is the weight per volume of solid material. The apparent density is the weight per volume occupied by solid material and pores. The true density and the apparent density are related by the porosity of the material (ϵ_{void}) according to:

$$\frac{\rho_{true}}{\rho_{apparent}} = 1 - \epsilon_{void} \qquad (3.5)$$

Using Hg porosimetry, the porosity of a sample of soot from chlorobenzene is measured. The results are presented in table 3.21.

***Table 3.21** Density and porosity of soot produced in mini pilot plant at thermal hydrodechlorination of chlorobenzene, and of activated carbon.*

sample	true density (1) [10^3 kg/m^3]	porosity (2) [%]	apparent density (1) [10^3 kg/m^3]
reactor soot (d_p < 1 mm)	2.122	72.9	0.57
reactor soot (d_p > 1 mm)	2.068	65.9	0.71
annular soot	1.913	71.6	0.54
activated carbon (3)	2.1	39	1.28

(1) *Determined by He pycnometry.*

(2) *Determined by Hg porosimetry.*

(3) *Data from literature [4]; apparent density is calculated.*

***Table 3.22** Density of soot produced at thermal hydrodechlorination.*

sample	density [10^3 kg/m^3]
filament soot	
(A1) MCB	1.933
powder soot from reactor	
(B1) MCB	2.106
(B2) DD+benzene	2.094
(B4) DD	2.322
powder soot from annular space	
(C1) MCB	1.913

The porosity measurements reveals a voidage about 70 vol%, which is larger than the porosity of activated carbon. Apparently the soot consists of a rather void material. SEM analysis confirms this impression, as will be discussed later on.

The true density of the soot is about 2.1 10^3 kg/m^3, which is typical for materials mainly existing of a carbon skeleton. The density varies with the chlorinated hydrocarbon feed, that produced the soot. However, the deviation is small (~10%). Any dependency of the true density on the type of feed has not been revealed.

The bulk density as estimated from the complete obstruction of the exhaust pipe (0.3 10^3 kg/m^3; see paragraph 3.3.3) is of the same order as the measured apparent density.

particle size

The particle size of a set of powder soot samples from the pilot plant reactor is determined by sieve analysis. Two fractions can be distinguished:

- a fraction of small rather regular particles (d_p < 2500 μm),
- a fraction of irregular lumps (d_p > 2500 μm).

After brushing the lumps break to particles. The lumps are just cohesive clusters of the small particles. It is believed that the lumps are created if a too large quantity of soot remains in the reactor. After an ordinary process operation in the mini pilot plant, typically 45 wt% of the soot is observed as lumps (see figure 3.22).

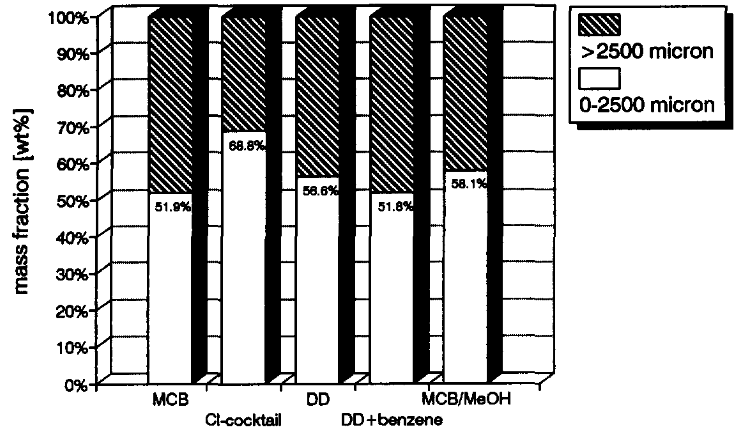

Figure 3.22 *Particle size distribution: fraction of particles (d_p < 2500 µm) versus fraction of lumps (d_p > 2500 µm).*

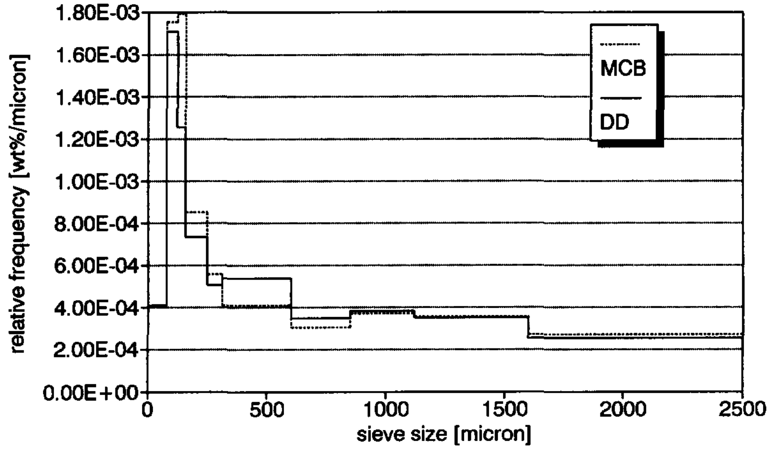

Figure 3.23 *Size distribution of soot particles smaller than 2500 µm.*

Within the fraction of small particles a high relative frequency is observed of particles with a size smaller than 500 µm (see e.g. figure 3.23). The mean and median particle size of this fraction are given in table 3.23 for various soot samples.

Table 3.23 Mean and median particle size of soot according to sieve analysis.

series	particle size [μm]		ratio
	mean	median	
B0	669.4	291.4	2.30
B1	991.8	774.4	1.28
B2	838.1	474.6	1.77
B3	711.1	346.0	2.06
B4	980.0	738.7	1.33

A limited fraction of the soot is emitted from the mini pilot reactor. The emitted soot consists of very fine particles. The particle size distribution of this soot from experiments with DD has been monitored using a Coulter Counter. The Coulter Counter is very suitable to analyze such small particles. Because the analytical method requires suspension of the sample, the soot has been suspended in a 1% NaCl water solution. The analysis showed a rather smooth Gaussian like particle size distribution with a mean particle size of about 30 μm. This value is remarkably close to the calculated value of 35 μm that is yet elutriated by the H_2 gas stream in the mini pilot plant reactor.

surface

The internal surface of the soot is explored using adsorption techniques. Nitrogen adsorption isotherms are measured for powder soot samples produced from chlorobenzene. The adsorption isotherms are interpreted according to the B.E.T. equation and the t-method. The analytical results are presented in table 3.24. For comparison the values for activated carbon are added to the table. Figure 3.24 shows the adsorption isotherms according to the t-method.

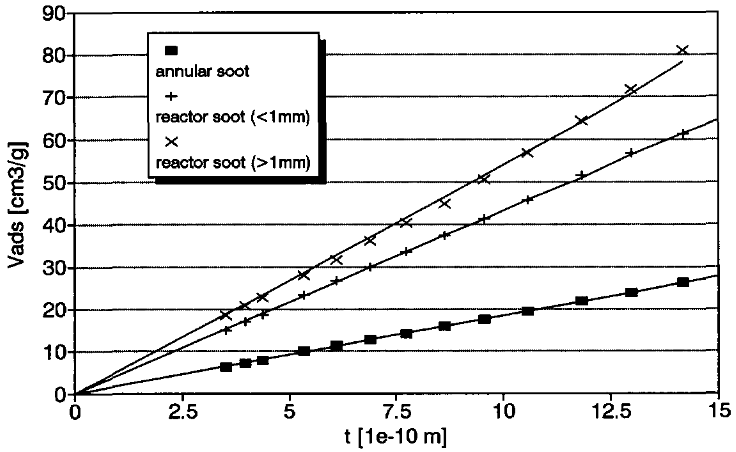

Figure 3.24 *T-method representation of adsorption isotherms, to determine internal surface of powder soot.*

Table 3.24 Internal surface ⁽¹⁾ of soot ⁽²⁾ and activated carbon.

sample	c [-]	ΔH_{ads} ⁽³⁾ [kJ/mol]	V_m [Nml N_2/g]	S_{BET} [m^2/g]	S_t [m^2/g]
reactor soot (d_p < 1 mm)	88.15	-8.46	15.25	67.77	66.45
reactor soot (d_p > 1 mm)	112.57	-8.61	18.32	81.44	81.44
annular soot	77.27	-8.37	6.51	28.91	28.62
activated carbon ⁽⁴⁾	≥ 400	≤ -9.43	≥ 90	≥ 400	

⁽¹⁾ *measurement by adsorption isotherm of N_2 (T = 77 K).*

⁽²⁾ *powder soot produced from chlorobenzene in mini pilot plant.*

⁽³⁾ *ΔH_{ads} is the heat of adsorption related to c:* [18]

$$c \approx \exp\left(\frac{\Delta H_{liq} - \Delta H_{ads}}{R\,T}\right) \tag{3.6}$$

$\Delta H_{liq} = -\Delta H_{vap}(N_2) = -5.590$ kJ/mol at boiling point [9].

⁽⁴⁾ *data retrieved from literature* [4].

Table 3.25 Types of pores. [4]

type of pores	pore width [nm]
micropores	< 2.0
mesopores	2.0 - 50
macropores	> 50

The S-t curves of the soot are straight lines, which typify the soot as a common t-substance. The S-t curve intersects the origin, indicating that soot does not posses micropores. As indicated by the value of the parameter c in the B.E.T. equation the heat of (physical) adsorption for the soot is much lower than that for activated carbon. This means that the adsorption is weaker. The heat of adsorption is in the order of that of the common t-substance silica (c=130). Also the internal surface of the soot is much lower than that of activated carbon.

Obviously the soot does not have the adsorption characteristics of activated carbon. If one intends to use the soot as activated carbon, the soot has to be reprocessed. Though the soot may not be an adsorption material as efficient as activated carbon, some gases are still adsorbed. Considering the origin of the soot, the soot is plausibly contaminated with chlorinated and nonchlorinated hydrocarbons. The existence of this adsorbed fraction on the soot has also been indicated before by TG analysis, as described in paragraph 3.4.2.

physical appearance

Filament soot is a hard vitreous black material. Figure 3.25 depicts a photograph of it. One side is shiny, the other dark. The shiny side is originally attached to the reactor wall, the dark side focused the reactor space.

Scanning Electron Microscopy (SEM) reveals the following information (see figures 3.26 and 3.27). Typical microscopic dimensions are given in table 3.26.

- The filaments have a sharp edge. Examination of the edge exposes a dense material, without cavities.
- One side of the filament is flat, with a few pits on it. The flatness gives the surface its shiny appearance. The other side is covered by domes giving it its dark appearance. Presumably the domes are placed opposite to the pits.

Table 3.26 Microscopic dimensions of filament soot.

Filament thickness	3-6 μm
Dome dimension	4-6 μm

The reason for the existence of the domes is unclear. Mechanisms to explain the existence of the domes are speculative.

1) Droplets of precursor material formed in the reactor space collide on the wall surface. On the wall the precursors are further converted into soot. The domes are the remainder of the former droplet shape.
2) The domes may be the result of a kind of 'frozen' boiling phenomenon. The domes are created by gas evolving from precursor material already deposited on the wall. The pits observed at opposite flat side and craters observed on other samples supports the hypothesis.

The dense structure of the material as observed on the edge of the filaments seems to indicate that the last steps involved in the soot formation take place in the liquid phase.

Powder soot is a soft black powdery material. Figure 3.28 depicts a photograph. SEM analysis reveals the following information (see figures 3.29-31).

- Powder soot exists of clusters, which look like balls of wool. The clusters are constructed from elementary fibres and elementary particles. Though different chlorinated feedstocks produce soot of different density (and porosity), according to the microscopic analysis, the basic structures (fibre and clusters) are similar.

The large voidage which was demonstrated by Hg porosimetry, is also revealed by the SEM photographs. Typical microscopic dimensions are given in table 3.27.

Table 3.27 microscopic dimensions of powder soot.

elementary fibre	1100 nm
elementary particle	200-400 nm

The exposed structure of the powder soot does not look like oil soot, but has a great resemblance with gas black coke [5]. Powder soot seems to originate from reactions in which gaseous species are involved. These reactions are probably catalysed, as indicated by the Transmission Electron Microscopic (TEM) photograph depicted in figure 3.32. This photograph shows the presence of crystallite structures in the soot, which according to micro-analysis (TEM-EDS) contain nickel (Ni), chromium (Cr) and cobalt (Co).

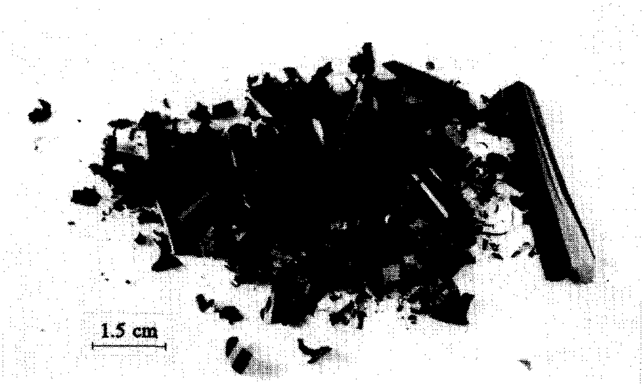

Figure 3.25 *Filament soot; normal view.*

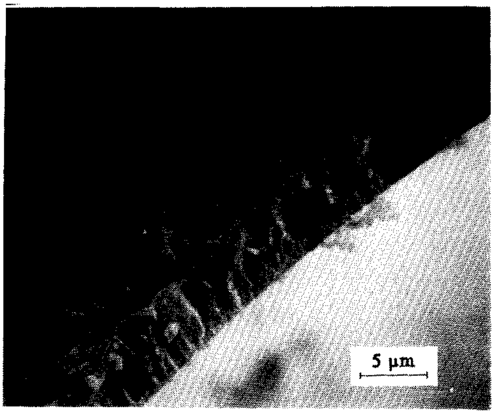

Figure 3.26 *Filament soot; edge of slice (lamella).*

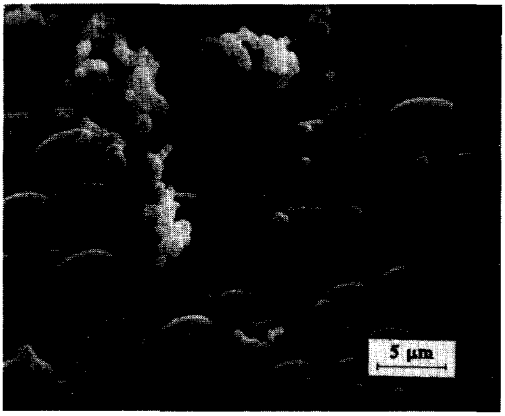

Figure 3.27 *Filament soot; surface of slice.*

Figure 3.28 Powder soot; normal view.

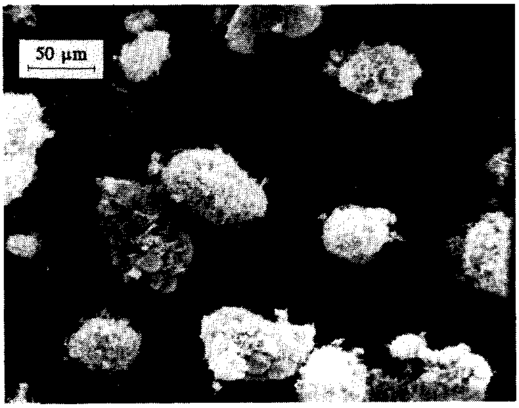

Figure 3.29 Powder soot; soot clusters.

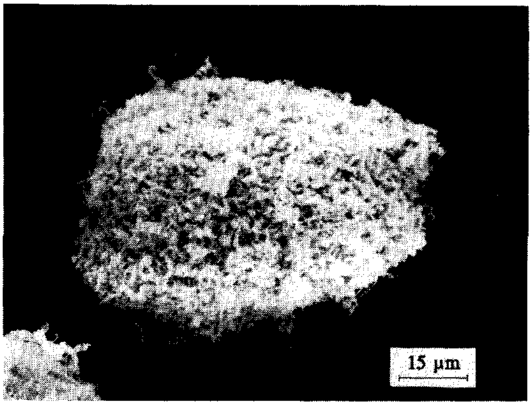

Figure 3.30 Powder soot; view of one cluster.

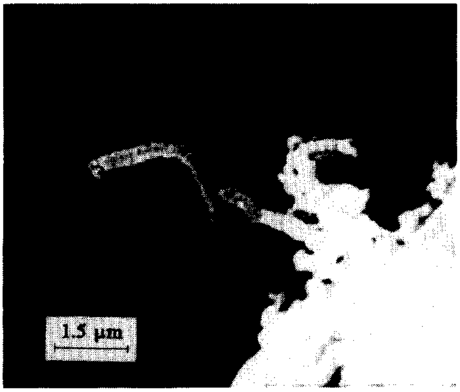

Figure 3.31 *Powder soot; elementary fibre.*

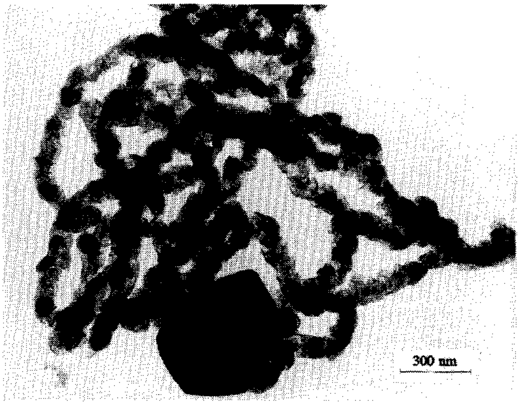

Figure 3.32 *Powder soot; TEM photo.*

§ 3.4.4 (Trends in) The chemical composition of the tar produced.

Tar is collected in the organic layer of the quench in the bench scale installation and in the cold second filter of the mini pilot plant. The tar collection efficiency of the second filter is best if a solvent is added to the filter system. The composition of the tar samples, collected as solutions of tar in organic solvents, is determined by GC analysis. Referring to the definitions given in paragraph 3.1.2, all types of tar (sublimation tar, brown tar and black tar) are included in these samples of dissolved tar.

The composition of tar produced in thermal hydrodechlorination of chlorobenzene is determined. Typical compositions are represented in table 3.28 and figure 3.34. Chemical structures of the aromatic compounds observed in the reactor off-gas are given in figure 3.33. The most important component of tar is biphenyl, contributing for about 80 wt% of the tar. Other significant contributors are terphenyl (~5 wt%), triphenylene (~4 wt%) and naphthalene (~4 wt%). Apparently, the formation of polyphenyl compounds is a major step in the production of tar and the subsequent soot production.

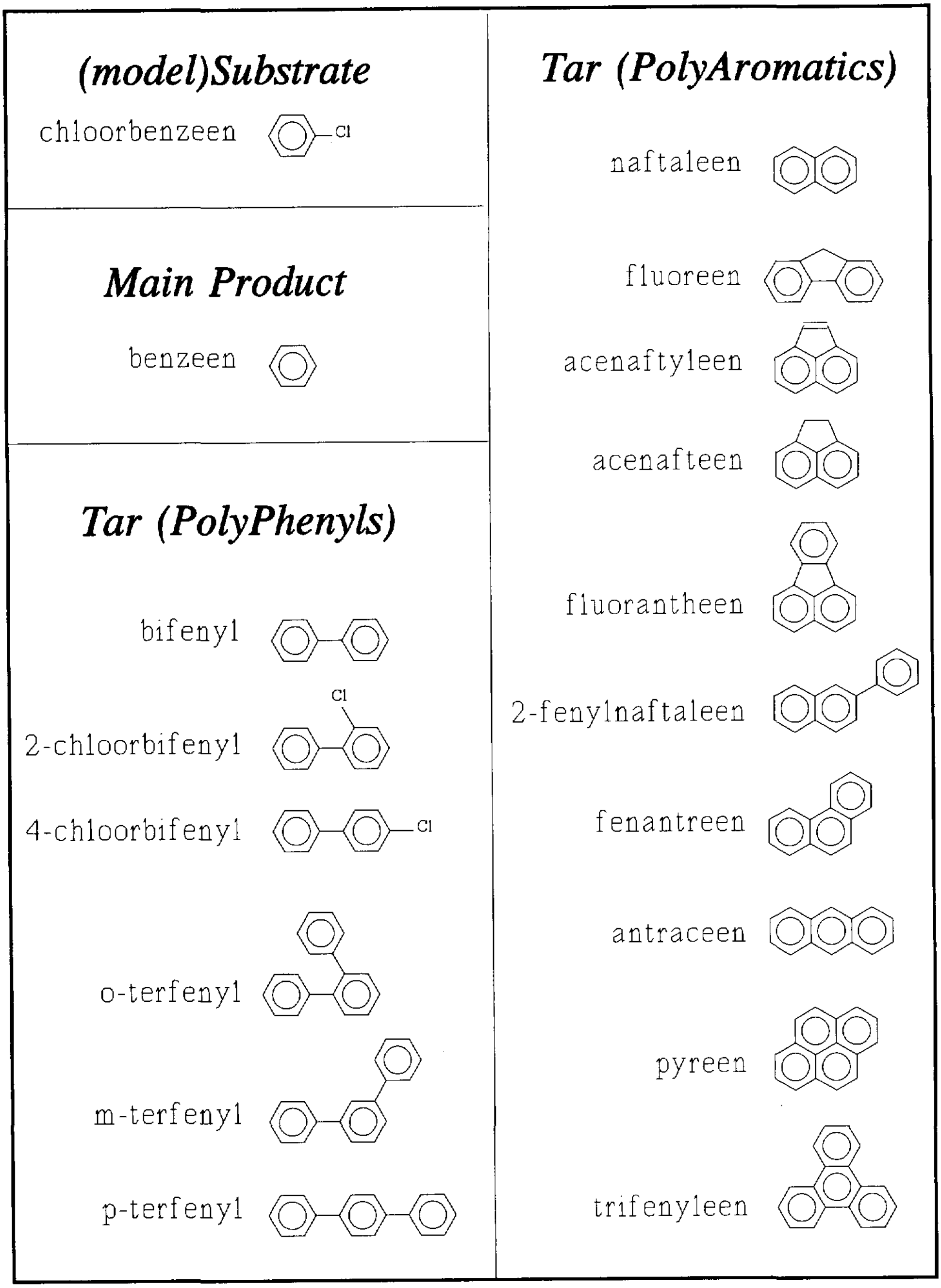

Figure 3.33 *Chemical structure of aromatic species observed in product stream of thermal hydrodechlorination of chlorobenzene.*

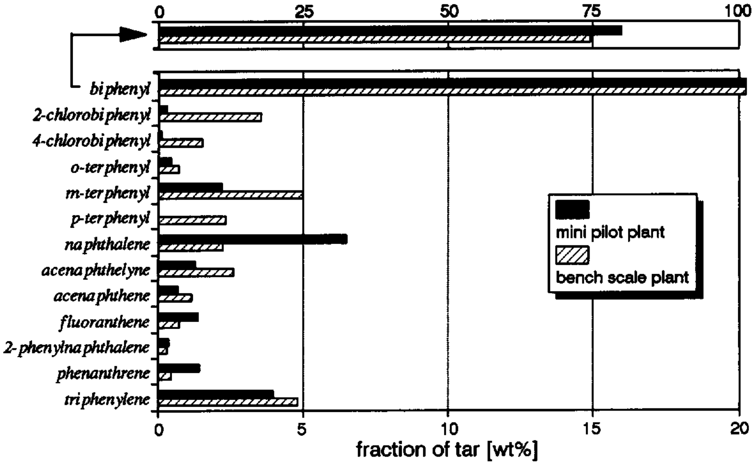

Figure 3.34 *Composition of tar produced at thermal hydrodechlorination of chlorobenzene in bench scale and mini pilot installation.*

Table 3.28 Composition of tar [wt%].

tar component	Mini pilot plant	Bench scale plant	
		standard	hastelloy
polyphenyls			
biphenyl	79.89	74.50	83.31
2-chlorobiphenyl	0.28	3.56	0.02
4-chlorobiphenyl	0.12	1.52	0.02
o-terphenyl	0.46	0.71	0.64
m-terphenyl	2.19	4.97	3.76
p-terphenyl	0.00	2.33	1.88
polyaromatics			
naphthalene	6.48	2.23	3.38
fluorene	0.44	0.13	0.17
acenaphthelyne	1.27	2.58	0.94
acenaphthene	0.67	1.15	0.10
fluoranthene	1.38	0.73	0.66
2-phenylnaphthalene	0.37	0.32	0.35
phenanthrene	1.41	0.46	0.65
anthracene	0.00	0.00	0.00
pyrene	1.07	0.00	0.07
triphenylene	3.96	4.82	4.06

In table 3.28 and figure 3.34 the composition of tar collected in the mini pilot plant and the bench scale plant are compared. In the mini pilot plant apparently more naphthalene and phenanthrene are formed, while in the bench scale installation relatively more terphenyl and triphenylene are produced. The difference is probably due to metal activity in the mini pilot plant, which activity is absent in the bench scale installation. This postulate is confirmed by the results of an experiment in which a hastelloy bar is placed within the bench scale installation. As for the composition, the tar produced in this experiment ranges between the tar produced in the mini pilot plant and that produced in the bench scale installation at standard conditions.

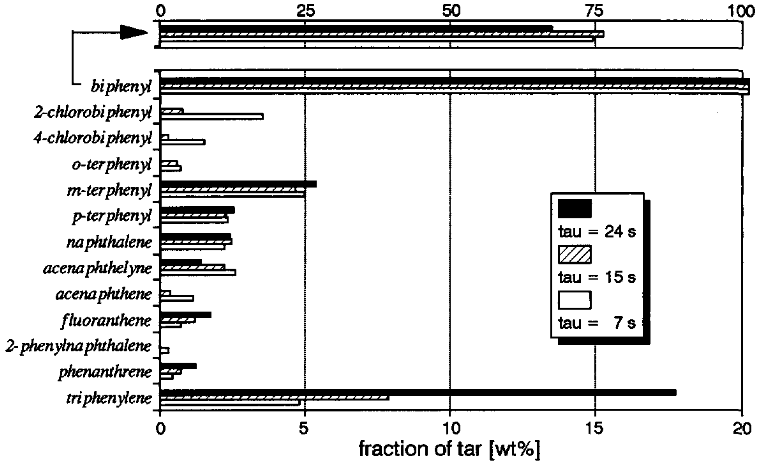

Figure 3.35 Effect of residence time on tar composition.

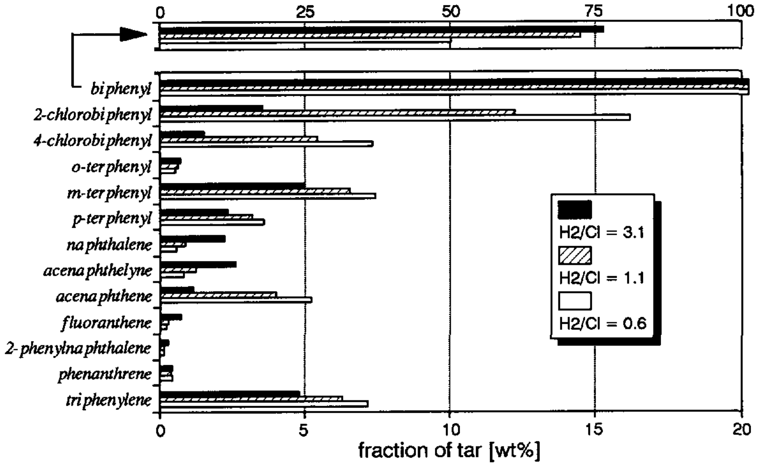

Figure 3.36 Effect of H_2/Cl ratio on tar composition (residence time ≈ 8 s.).

Other construction materials, such as alumina (Al_2O_3), quartz glass (SiO_2) and silicon carbide (SiC), including its activated form, appear to have negligible effect on the tar composition.

The only chlorinated hydrocarbons detected in the tar are chlorobiphenyls. In accordance with the expectations the proportion of chlorobiphenyls in the tar decreases with an increase of the overall dechlorination level. The chlorine content of the tar is small, never exceeding 5 wt%, commonly below 1 wt% of the tar mass if a satisfactory dechlorination level is reached. The chlorobiphenyl content accompanies the decrease in soot and tar formation when active metals are present.

The effect of process conditions on tar composition has been examined. Bench scale experiments, previously discussed in paragraph 3.2.2, indicate the following.

- Longer residence times effectuate an increase in dechlorination and soot and tar production. The tar composition seems unaffected, except the fraction of triphenylene which increases at larger residence times. The fraction of chlorobiphenyls decreases in line with the overall dechlorination level.

- An increase of the H_2/Cl ratio results in accelerated dechlorination and reduced soot and tar formation. The tar composition seems unaffected at longer residence times (24 s), but at shorter residence times (8 s) a dependency of the tar composition on the H_2/Cl ratio is noticed. An increase of the H_2/Cl ratio leads to less terphenyl, less triphenylene and, in accordance with the enlarged dechlorination level, less chlorobiphenyl. At the other hand the fractions of biphenyl and naphthalene are higher.

The results are also depicted in figures 3.35 and 3.36.

§ 3.5 Conclusions.

In two installations the process of thermal hydrodechlorination has been investigated. Over both installations fairly good mass balances can be set up. The dechlorination in both installations reaches the level of >99.9 mol% aimed at. The scale up of thermal hydrodechlorination renders no problem with respect to the dechlorination grade. However, thermal hydrodechlorination is always accompanied by soot and tar production. Soot and tar not only evoke some technological problems, but constitute a toxicological hazard as well.

The soot formation depends on several factors:

1) the type of chlorinated hydrocarbon processed, the availability of hydrogen (expressed as the ratio H_2/Cl), the initial contact between the chlorinated hydrocarbons and hydrogen, the temperature of the injection system, the wall material and the reactor configuration,
2) applied process conditions: temperature, residence time and pressure.

In principal the process conditions are set by the required degree of dechlorination. To have a sufficient dechlorination rate for all chlorinated hydrocarbons a temperature of 900 °C is demanded at atmospheric pressure. At that temperature, the residence time needed in an ideal plug flow reactor is in the order of 1-10 s.

It is shown by experiments that longer residence times result in aggravated soot and tar formation. The residence time should be sufficiently long to obtain the desired dechlorination level, but may not be too long to prohibit abundant production of soot and tar.

By variation of the H_2/Cl ratio it is demonstrated that hydrogen has a positive effect on the dechlorination rate and diminishes the soot and tar production. Excessive use of hydrogen improves the process in a sense of efficiency and selectivity. From a chemical point of view it is recommended to use hydrogen in abundance, at least with $H_2/Cl = 3$.

Experimental results lead to the following comments concerning the operation of the process.

- A comparison is made between a fluidised bed and an empty tube as reactor configuration. The use of an empty tube is recommended based on the undermentioned experiences.
  - Operation in a fluidised bed leads to more soot.
  - The exhaust of soot is identical for both configurations. The expectation that the fluidised bed would demonstrate a decreased emission of soot proved to be incorrect.
  - In fluidised bed lumps of soot and bed material are formed during operation, leading to malfunctioning and the potential danger of complete obstruction of the reactor.

  Evidently, the reactor in the empty tube configuration can best be operated with a gas stream from top to bottom. In the mini pilot reactor the flow is upwards, as the reactor was originally designed as a fluidised bed. To invert the direction in this installation appeared to be impractical.
- It is important to create a good initial contact between hydrogen and chlorinated hydrocarbons. Spraying offers good prospects. The temperature control of the nozzle is important, especially if easily sooting species are treated.
- With respect to the choice of a proper construction material the following comments can be made.
  - Metals like nickel (Ni), chromium (Cr) and cobalt (Co) are soot promoters. These metals are typically the major constituents of high quality alloys like hastelloy and nimonic. In the reactor none of these alloys or other materials containing the mentioned metals should be used.
  - The use of silicon carbide as reactor wall is not advised. As will be shown in chapter 5, SiC can become an active soot promoter.

With respect to quenching the thermal hydrodechlorination product, some experience is gained from the immersion quench of the bench scale installation.

- The produced HCl dissolves in the water layer of the quench. Benzene, the main hydrocarbon product if chlorobenzene is processed, condenses in the quench and forms an organic layer. Tarry byproducts dissolve in this organic layer, giving it a brown non-transparent appearance.
- In the bench scale installation the soot mainly remains in the reactor. If the filament soot does not stick to the reactor wall, it is still unable to leave the reactor through its narrow exit. The small soot particles that are blown out, first pass the quench liquid in the gas bubbles, by which they are entrained. In the freeboard above the liquid the particles relax and fall down on the liquid surface. After adsorption of some liquid the solids start to sink to the bottom of the vessel or, if two liquid phases are present, to the interphase area between the water and organic layer.

The immersion quench demonstrates a satisfactory efficiency to catch hydrogen chloride, produced organic products and soot and tar. For reasons of safety a scrubber type of quench is recommended for a larger scale installation. It is believed that in such type of quench similar or even better results will be achieved.

Concerning dioxins controversial results have been obtained. On one hand, in well conditioned labscale experiments (RUL) the dioxin destruction potency of thermal hydrodechlorination has been proved. On the other hand, in the mini pilot installation, which is operated under less well established conditions, some dioxins have been observed. The origin of these dioxins is obscure. Probably the dioxins are formed during startup or shutdown, demonstrating the essence of a proper operation procedure. However, other possible causes for the observed dioxins can not yet be excluded. A more detailed investigation in the larger scale plant, presently under construction at Royal Schelde, is therefore recommended.

In this study two types of soot have been observed: filament soot and powder soot. Definition and description of these soot types are given in paragraphs 3.1.2 and 3.4.3, respectively.

- Powder soot seems produced mainly by metal activity. The composition of powder soot is typically as follows:
  - 80-95 mol% C,
  - 5-10 mol% H,
  - <1 mol% Cl,
  - 1-8 mol% ash remainder.

  Filament soot contains a larger fraction of C and H, and a smaller metal fraction.

  The chlorine is probably present as adsorbed hydrogen chloride or yet unconverted chlorinated hydrocarbons. The chlorine content as well as the soluble organic fraction (SOF) follow the chlorine content of the feed.

- Some physical properties of powder soot have been determined.
  - The true density of powder soot is 2.1 10^3 kg/m^3; its apparent density is in the range of 0.5-0.7 10^3 kg/m^3. The true density of filament soot is comparable with that of powder soot.
  - Powder soot is a rather void material as indicated by its porosity of about 70 vol%.
  - The soot mass consists of lumps and smaller powdery particles. If the lumps are brushed they break apart into the smaller particles, which are believed to be the basic soot particles. Typically 45 wt% of the powder soot mass consists of lumps ($d_p > 2500$ μm).
  - The internal surface area of powder soot, typically in the order of 10-100 m^2/g, is much smaller than that of activated carbon. Also the heat of adsorption is much smaller. Though in comparison with activated carbon the soot may be a poor adsorbent, the soot still exhibits an ample ability to adsorb. Up to 10 wt% can be adsorbed, as indicated by the detected SOF.

The major components of the tar produced from chlorobenzene are the following species:

- biphenyl (80 wt%),
- terphenyl, triphenylene, naphthalene (about 5 wt% each).

Monochlorobiphenyls are the only chlorine containing hydrocarbons detected in the tar. The chlorine content due to the chlorinated biphenyls is commonly below 1 wt% of the tar.

A remarkable phenomenon is encountered concerning the activity of certain metals in thermal hydrodechlorination. As previously discussed, metals like nickel, chromium and cobalt promote soot formation. After placing a hastelloy bar in the bench scale installation indeed enormous soot production is observed. However, also an increase in dechlorination level is noticed. Both the quantity of chlorobenzene in the off gas and the fraction of chlorobiphenyls in the tar diminish. Apparently, the active metals do not only effect soot production, but dechlorination as well. Unfortunately the promotion of soot formation is much stronger than the enhancement of dechlorination.

Chapter 4 considers the mechanism of gas phase thermal hydrodechlorination of chlorobenzene. As will be discussed in that chapter, the reactions leading to the formation of soot also result in the separation of chlorine from the hydrocarbon structures. In other words, soot formation is accompanied by dechlorination. The above mentioned observation fits into this picture: with respect to dechlorination the reactions leading to soot compete with the *hydro*dechlorination reactions effected by hydrogen.

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Chapter 4

Mechanism of thermal hydrodechlorination

dechlorination, soot and tar formation of chlorobenzene

§ 4.1 Introduction.

In this chapter the mechanism is discussed of the dechlorination and the soot and tar formation of chlorobenzene in thermal hydrodechlorination. Chlorobenzene is chosen as model substance as its treatment requires the most severe thermal hydrodechlorination conditions. For the same reason chlorobenzene is one of the major model substances used in the experimentations (see previous chapters). The developed model describes thermal hydrodechlorination of chlorobenzene in a wall-less tubular reactor. The final model is given in the appendix 4.A.

After the chemical mechanism is revealed, answers may be given to questions like the following. How are the reactions initiated; are walls needed to start the reactions? What is the heat demand of the medium at every location in the reactor; are there endothermic spots that may cause extinction of the reaction? To what extent are dechlorination and soot and tar formation coupled; do conditions exist, in which no soot formation occurs? In this chapter this kind of questions is answered.

In paragraph 4.2 the background of dechlorination is discussed. Paragraph 4.3 focuses on the formation of soot and tar. At the end of both paragraphs the implementation of relevant matter into the calculation model is discussed. The complete model is presented in appendix 4.A. Paragraph 4.2.5 elucidates possible wall effects. Interesting results of the model calculations are presented in paragraph 4.4. The chapter closes with a final discussion in paragraph 4.5.

§ 4.2 Dechlorination of chlorobenzene: rate and mechanism.

§ 4.2.1 Overall dechlorination rate.

The overall thermal hydrodechlorination rate of chlorobenzene follows pseudo first order kinetics, if excess hydrogen is available [38,46].

$$C_6H_5Cl + H_2 \longrightarrow C_6H_6 + HCl \tag{4.1}$$

$$r_{deCl} \approx k_{eff}\,[C_6H_5Cl] \quad mol/m^3\,s \tag{4.2}$$

$$k_{eff} = k\,[H_2] \quad s^{-1} \tag{4.3}$$

In literature, two expression are found for the pseudo first order rate constant.

- Manion [38] gives an expression for conditions in which hydrogen is supplied in a ratio of about 3 H_2 molecules per chlorine atom.

$$k_{eff} = 7.94 \cdot 10^{10} \exp(-\frac{240}{RT}) \quad s^{-1} \tag{4.4}$$

- Ritter [46] used very small chlorobenzene fractions in his experiments, typically in the order of 0.0037 ($H_2/Cl \approx 270$). His expression therefore applies to very diluted conditions. The contribution of bulk gas and wall reactions are distinguished.

$$k_{eff} = k_{bulk} + k_{wall} \cdot (\frac{1}{r}) \tag{4.5}$$

$$k_{bulk} = 1.13 \cdot 10^{10} \exp(-\frac{225}{RT}) \quad s^{-1} \tag{4.6}$$

$$k_{wall} = 1.45 \cdot 10^{11} \exp(-\frac{260}{RT}) \quad cm/s \tag{4.7}$$

The expressions are compared for the tube size as used by Manion (r = 0.2 cm). As shown by table 4.1 the dechlorination rate is lower under the relatively concentrated conditions applied by Manion. This can only in part be explained by the difference in hydrogen concentration. Under 'concentrated' conditions the hydrogen fraction is about 75 vol%, under 'diluted' conditions it is nearly 100 vol%.

***Table 4.1** Comparison of dechlorination rates at 900 °C.*

condition	rate [s^{-1}]
'concentrated' [Manion]	1.63
'diluted' [Ritter]	2.99
ratio [Ritter/Manion]	1.84

As will be discussed later, the rate determinating step in thermal hydrodechlorination is the attack of a hydrogen radical on a chlorinated hydrocarbon.

$$H\cdot + RCl \longrightarrow products \tag{4.8}$$

Consequently, the pseudo first order rate constant is proportional to the hydrogen radical concentration.

Following the assumption postulated by Manion [38] that in his reactor the hydrogen dissociation is in equilibrium, the hydrogen radical concentration is proportional to the square root of the concentration of molecular hydrogen (see equation 4.10).

$$H_2 \overset{K}{\rightleftarrows} 2\,H\cdot \tag{4.9}$$

$$[H\cdot] = \sqrt{K\,[H_2]} \tag{4.10}$$

According to this relationship, the rate constants would differ a factor of 1.15. Apparently, other factors have some influence as well. Probably different construction materials are used by Manion and Ritter, provoking dissimilar wall activities.

According to Ritter [46], 64% of the overall dechlorination is contributed by wall effects. However, Manion [38] concludes that in his system wall effects are presumably negligible. Obviously, the wall influence is strongly affected by other process parameters, e.g. the type of construction material.

For a better evaluation of wall effects, it is essential to understand the nature of the gas phase reactions first. Gas phase thermal hydrodechlorination of chlorobenzene proceeds according to the following general mechanism.

initiation:

$$RCl \longrightarrow R\cdot + Cl\cdot \tag{4.11}$$

propagation:

$$H\cdot + RCl \longrightarrow RH + Cl\cdot \tag{4.12}$$

$$Cl\cdot + H_2 \longrightarrow HCl + H\cdot \tag{4.13}$$

termination:

$$H\cdot + R\cdot \longrightarrow RH \tag{4.14}$$

Initially, dissociation of chlorobenzene produces radicals. These radicals set up a chain of propagating steps, resulting in an accelerated dechlorination. The total amount of radicals is controlled by competition between the initiating dissociation and the radical associating termination.

The separate steps of the mechanism are discussed below.

§ 4.2.2 Initiation and termination of radical reactions.

Hydrogen radicals are required in the propagation. Manion [38] assumes that the hydrogen dissociation is in equilibrium. However, the gas phase kinetics are far too slow to establish equilibrium [1,2,37]. Therefore, other reactions are involved that regulate the H· radical concentration. Dissociation of chlorobenzene (reaction 4.11) is expected to initiate the production of radicals. Consecutive reactions with molecular hydrogen produce the required hydrogen radicals. This view is confirmed by Ritter [46].

The chlorobenzene dissociation is a dechlorination step. However, in comparison to the propagation chain its rate is negligible slow. Only during the short moments of initiation it has a tangible contribution to the momentary dechlorination rate (see e.g. figure 4.2 on page 143).

It should also be emphasised that this first step is a pyrolytic one! Apparently, before entering the stage where hydrogen induced reactions accelerate dechlorination and reduce soot production, the reaction medium passes through a pyrolytic stage. Obviously, nuclei for soot and tar formation are generated in this initial stage.

The termination reaction eliminates radicals by association into molecules. Initiation and termination steps control the magnitude of the radical pool. Due to this buffering action the actual H· radical concentration is close to the value it would have if the hydrogen dissociation would be in equilibrium.

Possible catalysing effects by reaction chains are found to play a minor or no role in the establishment of the hydrogen dissociation equilibrium.

- If Cl_2 is present, it can catalyse the recombination of hydrogen radicals to molecules according to the following reaction chain [56]:

$$H\cdot + Cl_2 \longrightarrow HCl + Cl\cdot \tag{4.15}$$

$$H\cdot + HCl \longrightarrow H_2 + Cl\cdot \tag{4.16}$$

$$2\ Cl\cdot \longrightarrow Cl_2 \tag{4.17}$$

+

$$2\ H\cdot \longrightarrow H_2 \tag{4.18}$$

The first step of this could also take place via

$$\begin{array}{lcll}
H\cdot + RCl & \longrightarrow & HCl + R\cdot & \quad (4.19) \\
R\cdot + Cl_2 & \longrightarrow & RCl + Cl\cdot & \quad (4.20) \\
\hline
 & & & + \\
H\cdot + Cl_2 & \longrightarrow & HCl + Cl\cdot & \quad (4.21)
\end{array}$$

However, in the hydrogen rich atmosphere applied the Cl_2 concentration appears to be far too low to bring about any considerable effect.

- Hydrogen dissociation may also be catalysed by the following reaction chain involving hydrocarbon molecules and radicals.

$$\begin{array}{lcll}
H\cdot + RH & \longrightarrow & R\cdot + H_2 & \quad (4.22) \\
H\cdot + R\cdot & \longrightarrow & RH & \quad (4.23) \\
\hline
 & & & + \\
2\ H\cdot & \longrightarrow & H_2 & \quad (4.24)
\end{array}$$

  This kind of sequences does not have a considerable impact either, as under the H_2 rich conditions applied most hydrocarbon species are susceptible to the reverse reaction of reaction equation 4.22. This is confirmed by model calculations, as will be discussed later on.

Concluding, the hydrogen dissociation equilibrium is not completely established in a wall less reactor. The $H\cdot$ radical concentration exceeds equilibrium, albeit the overshoot is restricted. The overshoot results in an accelerated dechlorination. Yet, the assumption of equilibrated hydrogen dissociation may offer a first, conservative estimation of the actual $H\cdot$ radical concentration.

A major effect of wall reactions certainly is the establishment of the hydrogen dissociation equilibrium [38,46]. With a larger wall surface available, the radical concentration will get closer to the equilibrium value. Though the equilibrium assumption postulated by Manion [38] is not applicable to all reactor systems, it may be correct for his reactor with its relatively large S/V ratio.

§ 4.2.3 Propagation mechanism of dechlorination chain.

Figure 4.1 shows a schematic representation of the propagation chain. The represented cycle clearly demonstrates the importance of the radicals as reaction carriers.

The first step is a H· radical attacking the chlorobenzene molecule. The H· radical displaces the Cl atom on the hydrocarbon molecule in an addition/elimination sequence. Molecular benzene and a Cl· radical are produced. In the second step, the Cl· radical reacts with the H_2 bath gas forming HCl and a reactive H· radical, which continues the dechlorination chain. As long as molecular hydrogen and chlorobenzene are present the reaction chain carries on. The overall reaction is the conversion of hydrogen and chlorobenzene into benzene and hydrogen chloride. The radical activity in the cycle catalyses the overall reaction. For this reason the dechlorination rate of thermal hydrodechlorination exceeds that of pyrolysis. [38,45]

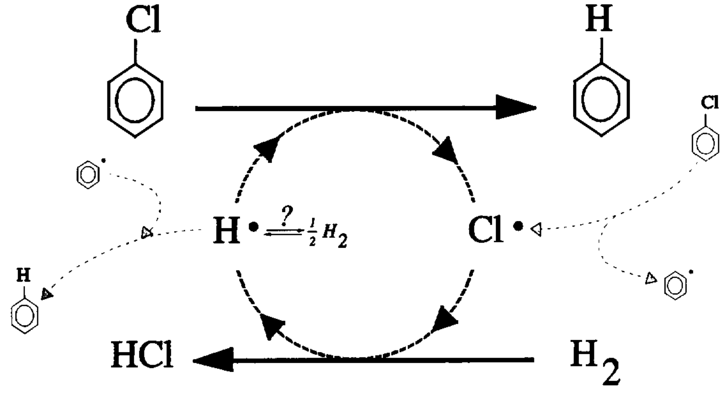


Figure 4.1 Schematic representation of dechlorination mechanism of chlorobenzene.

The reaction between chlorine radicals and molecular hydrogen is very fast. Under conditions of thermal hydrodechlorination the reaction is expected to be near equilibrium. This expectation is confirmed by the model calculations, to be discussed in paragraph 4.2.4.

$$Cl\cdot + H_2 \overset{K}{\rightleftharpoons} HCl + H\cdot \tag{4.25}$$

The equilibrium constant of the mentioned reaction is given by [52]

$$K = 1.86 \exp\left(-\frac{4.1}{RT}\right) \tag{4.26}$$

This constant is approximately 1 within the temperature range 1000 to 2000 K. Therefore, the ratio of Cl· to H· radicals is proportional to the ratio of produced hydrogen chloride to yet unconverted hydrogen. [26]

$$\frac{[Cl\cdot]}{[H\cdot]} \propto \frac{1}{K}\,\frac{[HCl]}{[H_2]} \approx \frac{[HCl]}{[H_2]} \qquad (4.27)$$

Clearly, with proceeding dechlorination, the relative proportion of Cl· radicals increases.

Besides the pathway of displacement shown, H· radicals may also effectuate dechlorination by abstracting Cl atoms.

$$H\cdot + RCl \longrightarrow HCl + R\cdot \qquad (4.28)$$

Nevertheless, displacement (reaction 4.12) is identified as the main reaction route.

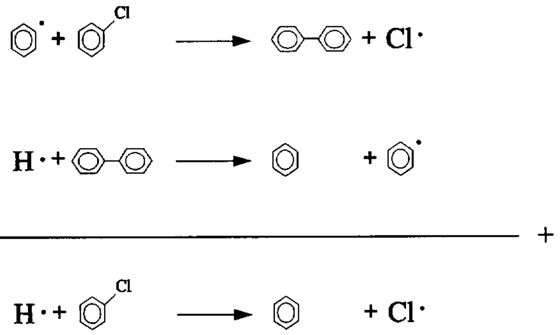
1) According to the literature [38,14,46] at the temperatures of concern the abstraction rate is lower than that of displacement.
2) Moreover, the phenyl radical will react further, mainly with H_2, but also with HCl.

$$R\cdot + H_2 \longrightarrow RH + H\cdot \qquad (4.29)$$

$$R\cdot + HCl \longrightarrow RH + Cl\cdot \qquad (4.30)$$

Abstraction (reaction 4.18) followed by this reaction with HCl (reaction 4.30) leads to identical products as by displacement (reaction 4.12). In this view, the abstraction route can be interpreted as a kind of catalysed pathway.

Under concentrated conditions also another catalysed pathway is identified. Phenyl radicals may react with chlorobenzene molecules, producing biphenyl and Cl· radicals. By subsequent attack of a H· radical biphenyl dissociates into benzene and a phenyl radical. Overall the sequence produces identical species as displacement.



(4.31)

(4.32)

(4.33)

Dechlorination of heavier chlorinated polyphenyls, like biphenyl and terphenyl, takes place in similar reaction chains as those discussed for chlorobenzene.

§ 4.2.4 Dechlorination and hydrodynamical submodel of calculation model.

A computer model has been developed to describe gas phase thermal hydrodechlorination of chlorobenzene. In this paragraph the hydrodynamical part of the model and the dechlorination part of the incorporated reaction mechanism are presented. In paragraph 4.3.4, the incorporated soot and tar formation steps are presented. The complete reaction mechanism is given in appendix 4.A, comprising all reactions involved with their rate equations and other relevant data.

In the model ideal plug flow is assumed. A mass balance over a thin slice reveals the well known fundamental differential equation for plug flow:

$$\frac{d\phi_{mol.i}}{dx} = - \mathbb{R}_i * A \tag{4.34}$$

Boundary conditions are given by the molar flows fed.

$$\phi_{mol.i}\,(x=0) = \phi_{mol.i}\Big|_{feed} \tag{4.35}$$

The overall conversion rate for each species is found by summing the reactions in which the species is involved. Each reaction rate is composed of a forward and a backward part.

$$\mathbb{R}_i = \Sigma_{j=1}^{N_r}\ \nu_{i.j} * (\mathbb{R}_{j.forward} - \mathbb{R}_{j.backward}) \tag{4.36}$$

The calculation of the forward and backward rate is identical. The corresponding rate constant is multiplied with the concentration of the relevant reactants.

$$\mathbb{R}_{j.x} = k_{j.x}\ \Pi_{h=1}^{N_s}\ c^{\nu_{h.(j.x)}} \tag{4.37}$$

The forward and backward rate constants are coupled by the thermodynamical equilibrium constant.

$$\frac{k_{forward}}{k_{backward}} = K_{equilibrium} \tag{4.38}$$

Concentrations are determined from the molar flows, assuming ideal gas behaviour.

$$c_i = \frac{\Phi_{mol.i}}{\Phi_v} = \frac{\Phi_{mol.i}}{\Sigma\Phi_{mol.i}\frac{RT}{p}} \qquad \textbf{(4.39)}$$

The heat demand of the reaction system is:

$$\frac{dQ}{dx} = \Sigma_{j=1}^{N_r}\,(\mathbb{R}_j \cdot \Delta H_j) * A \qquad \textbf{(4.40)}$$

The primary dechlorination reactions of the reaction mechanism are summarised in table 4.2. The listed reactions, which only involve molecular hydrogen, hydrogen chloride, chlorobenzene and benzene, and their related radicals, have been discussed in the previous paragraphs. Kinetical terms are obtained from the NIST Chemical Kinetics database [37], thermodynamical data are acquired from the NIST thermodynamical database [52].

***Table 4.2** Primary dechlorination steps of radical reaction mechanism of thermal hydrodechlorination of chlorobenzene (notation explained in table 4.8).*

	primary species (feed and main products): dissociation						
1	H_2	+	M	⇄	2H·	+	M
2	HCl	+	M	⇄	H·	+	Cl· +M
3	ϕ_{Cl}			⇄	ϕ·	+	Cl·
4	ϕ			⇄	ϕ·	+	H·
	primary species: reaction with H· and Cl·						
5	H·	+	ϕ_{Cl}	⇄	ϕ	+	Cl·
6	H·	+	ϕ_{Cl}	⇄	HCl	+	ϕ·
7	H·	+	ϕ	⇄	H_2	+	ϕ·
8	Cl·	+	H_2	⇄	HCl	+	H·
9	Cl·	+	ϕ	⇄	HCl	+	ϕ·

Nevertheless, other reactions also play a role in dechlorination. An example is the mentioned catalysed dechlorination pathway via biphenyl. The example shows the necessity to extend the model with soot and tar formation steps, not only to understand the soot and tar formation, but also to properly describe the dechlorination. In the next paragraphs the soot and tar formation will be assessed, after which the required extension is implemented into the model.

To validate the calculation model, it should be compared to gas phase kinetics according to literature or experimental experience. Therefore, with respect to dechlorination rate the model is compared to data offered by Ritter [46]. This source supplies information about homogeneous gas phase dechlorination, without taking into account the contribution of wall surfaces.

Because of the interactions between dechlorination and soot and tar formation, the model can only be properly validated after all aspects have incorporated. For this reason the validation of the model is not discussed here, but will be discussed in paragraph 4.3.4.

In anticipation of this validation, some results of the calculation model are presented here to elucidate some of the statements made in this section.

- The calculations confirm the expectation that the initial production of radicals is effected by the dissociation of chlorobenzene (reaction 4.11). Consecutive reactions with molecular hydrogen produce the hydrogen radicals. Radical production by gas phase dissociation of molecular hydrogen (reaction 4.9) appears negligible. Model calculations indicate that the production of hydrogen radicals via chlorobenzene dissociation is 10^4 times faster than the production by hydrogen dissociation. Only at very diluted conditions, when the chlorobenzene concentration becomes too low to play a dominant role in radical production, the hydrogen dissociation gains some significance. Ritter [46] confirms this view.

  The magnitude of the radical pool is determined by the relative rates of initiation and termination steps. Model calculations indeed show the buffering action by the initiation and termination reactions. Under concentrated conditions ($H_2/Cl \approx 3$) the H· radical overshoot[1] is rather large with a maximum of 4.2. Under more diluted conditions the overshoot decreases.

- Figure 4.2 presents the rates of the various primary dechlorination reactions. The figure concerns the treatment of chlorobenzene under 'concentrated' conditions.

  The most important dechlorination pathway is the displacement of the Cl atom by a H· radical (reaction 5 in the figure). Cl abstraction (reaction 6 in the figure) is always a factor 0.43 slower.

  As presented in reaction equations 4.31 to 4.33 a catalysed dechlorination chain via biphenyl exists. As shown in the figure (reaction 13), the relative contribution of this chain may be as much as 75% of the displacement reaction. In more diluted systems, the contribution diminishes as the concentration of phenyl radicals strongly decreases. The similar catalysing sequence involving the chlorophenyl radical (reaction 17) reaches a relative contribution of 55% at maximum.

  The figure also clearly shows the initiation by chlorobenzene dissociation.

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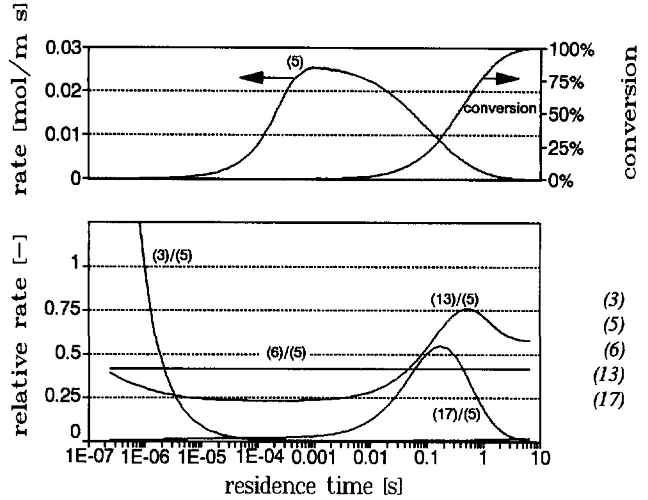
[1] Overshoot (f) is defined as the actual concentration relative to the concentration if hydrogen dissociation would be in equilibrium.

$$f = \frac{[H\cdot]}{\sqrt{K\,[H_2]}}$$



(3) $\phi_{Cl} \Rightarrow \phi\cdot + Cl\cdot$
(5) $H\cdot + \phi_{Cl} \Rightarrow \phi + Cl\cdot$
(6) $H\cdot + \phi_{Cl} \Rightarrow HCl + \phi\cdot$
(13) $\phi\cdot + \phi_{Cl} \Rightarrow \phi\text{-}\phi + Cl\cdot$
(17) $\phi_{Cl}\cdot + \phi_{Cl} \Rightarrow \phi\text{-}\phi_{Cl} + Cl\cdot$

Figure 4.2 *Reaction rates of principal dechlorination steps (reaction numbers refer to tables 4.9 on pages 170 to 175).*

Besides this thermal hydrodechlorination model for chlorobenzene, a model has been composed to describe the gas phase dechlorination of chloromethane. This model only comprises 9 equations, analogue to those presented here for chlorobenzene. Calculations with this chloromethane model confirm the mechanism as proposed for chlorobenzene. Again, the radical production is induced by dissociation of the chlorinated hydrocarbon. Once more, the contribution of the hydrogen dissociation appears very much restricted.

§ 4.2.5 Wall effect on dechlorination rate.

What influences does the wall have on the overall dechlorination rate? Heterogeneous catalysis accelerates hydrogen dissociation and will impose equilibrium.

$$H_2 \overset{wall}{\longleftrightarrow} 2\ H\cdot \qquad \textbf{(4.41)}$$

By imposing the equilibrium the quantity of active (H·) radicals decreases and the dechlorination slows down. However, also the principal dechlorination reactions are affected.

$$H\cdot + RCl \xrightarrow{wall} Products \tag{4.42}$$

According to Manion and Ritter, these reactions follow pseudo first order kinetics, the constant of which may be split in a bulk gas and a wall term.

$$k_{eff} = k_{principal} * [H\cdot] \tag{4.43}$$

$$k_{principal} = k_{bulk} + k_{wall}\cdot\left(\frac{S}{V}\right) \tag{4.44}$$

Evaluation of these equations indicate an ambiguous wall effect. On one hand, the wall effectuates a decrease of the H· radical concentration, on the other $k_{principal}$ is increased.

- If the radical pool is large, the associative wall effect is dominant. An increased wall surface leads to delayed dechlorination.
- If the radical pool is already close to equilibrium, as under diluted conditions, the increase of $k_{principal}$ is dominant. The wall has an accelerating effect on the dechlorination rate. This situation is reported by Ritter [46].

Apparently, the final wall effect depends on the chlorinated hydrocarbon fraction.

The existence of this ambiguous wall effect is also demonstrated by other observations of Ritter [42]. The dechlorination rate of dichlorobenzene, contrary to that of monochlorobenzene, decreases with increasing wall surface. The probable cause of the opposite effect is the larger tendency to produce (H·) radicals.

- The decomposition of dichlorobenzene is faster, as result of lower strength of the C-Cl bonds.
- Dichlorobenzene offers more Cl-sites per molecule that can be abstracted.

As result the associative wall effect will prevail, realising a decelerating effect on the dechlorination rate.

From these reflections the following can be concluded with respect to scaling up. In larger reactors, relatively less wall surface is present, and the reaction rate is predominantly determined by homogeneous gas phase kinetics. For small tubes, of the kind in which Manion did his experiments, the assumption of equilibrated hydrogen dissociation may be valid. However, for reactors with a smaller S/V ratio (a larger diameter) the H· radical concentration surpasses equilibrium. In those reactors, under concentrated conditions, an accelerated dechlorination rate is encountered. Besides that, since the radical pool is more abundant, more reactants that can form soot are present. Soot formation presumably increases.

The developed radical model, in complete form given in appendix 4.A, describes dechlorination in a reactor without walls or with a small S/V ratio, so in principle the industrial situation.

§ 4.3 Soot and tar formation.

§ 4.3.1 Soot formation in general.

Literature [18,29,42,45,49] puts forward that formation of soot takes place according to a general pathway, irrespective of the exact process conditions. In incineration, pyrolysis as well as hydrogenolysis, four steps can be distinguished:

1) production of precursor molecules (which react rapidly to give larger species),
2) chemical growth (that results in the formation of numerous small particles with a size smaller than 2 nm),
3) particle growth by surface reactions as well as by physical condensation, coagulation and agglomeration,
4) competing particle degradation, e.g. in case of incineration by oxidation.

The implementation of these steps depends on the actual process condition. E.g. in flames particle growth is mainly achieved by acetylene addition. It is stated that in flames nearly all fuels initially break down to acetylene. The conditions of thermal hydrodechlorination (hydrogenolysis) are too mild to accomplish this kind of degradation. Here, other compounds play a role in particle growth.

Though most of the soot mass is provided by surface growth reactions (step 3), it is believed that particle inception (steps 1 and 2) controls the amount of soot ultimately produced. These first two steps in soot formation are homogeneous gas phase reactions. These earliest chemical steps are the critical bottlenecks and thus rate limiting. In view of this, the prediction of soot production by solely the gas phase reactions provides a lower limit estimate of the soot yield. [18,29,42,45,49]

Literature [26,49] states that polycyclic aromatic hydrocarbons (PAHs) are important precursors of soot.

1) On atomic level the structure of soot resembles that of PAHs (i.e. both have a benzenoid network of sp^2 carbons). As a result, the difference between soot and PAHs is not due to their chemical structure, but related to their different molecular weight and geometrical structure. [33]
2) In flames the concentration of PAHs peaks just before the zone where soot nucleation takes place.
3) Thermodynamics indicate that polycyclic aromatic molecules are very stable if abundant hydrogen is present ([H2] / [C2H2] > > 1) [51]. In thermal hydrodechlorination PAHs will act as intermediates in soot growth.

The significance of aromatics and polyphenyls in soot growth is due to two reasons: [6,50]

1) the formation of related aryl radicals that can react with other hydrocarbons.
2) the ability of aromatics to undergo substitution reactions, e.g. internal substitution reactions which are important for stabilizing the growing network (see e.g. equation 4.53).

Aromatics are relatively stable compounds, the related aryl radicals are the active species in growth. Normally equilibrium is assumed:

$$ArH + H\cdot \rightleftharpoons Ar\cdot + H_2 \quad \textbf{(4.45)}$$

As result of the equilibria, the concentrations of the aromatic molecules and their corresponding aryl radicals are directly related. While the aromatic molecules behave as thermodynamic stable 'sinks' in the growth sequence, the aryl radicals act as the reactive agents. As such, the H· radical is an activator in soot formation. [26]

The activating property of H· radicals is due to their potential to abstract H atoms from hydrocarbons, which is much stronger than that of hydrocarbon radicals: reaction 4.46 is much faster than reaction 4.47 [29]

$$H\cdot + R_xH \longrightarrow H_2 + R_x\cdot \quad \textbf{(4.46)}$$

$$R_y\cdot + R_xH \longrightarrow R_yH + R_x\cdot \quad \textbf{(4.47)}$$

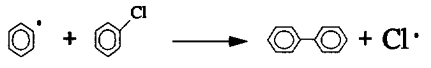
With respect to this, an overshoot of H· radicals increases reactivity, and thus soot formation [21,23]. However, H· radicals can also displace phenyl groups, leading to degradation of the hydrocarbon structure (see e.g. equation 4.32). With respect to these early steps of soot growth, the H· radical has an ambiguous effect.

Besides the type of bath gas, one of the major discrepancies between combustion and hydrogenolysis is the applied temperature. Due to the high temperatures in combustion (chloro)benzene molecules rapidly degrade into smaller species. The mass growth is primarily effectuated by the nonaromatic species like C_2H_2, C_4H_4 and C_4H_2 [6]. The aromatic structure only provides the foundation upon which larger aromatic structures are built by addition of these nonaromatic species. The concentration of (chloro)benzene molecules and phenyl radicals is too low for direct phenyl polymerisation. [24]

The conditions applied in hydrogenolysis are less severe. Hydrocarbon structures are primarily preserved. In thermal hydrodechlorination, the major pathway to soot formation is phenyl polymerisation, particularly if chlorobenzene is treated.

§ 4.3.2 Phenyl polymerisation.

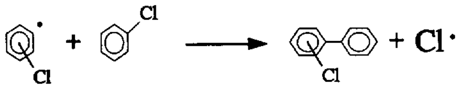
The reaction between chlorobenzene and a phenyl radical is the major pathway to biphenyl.



(4.48)

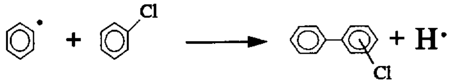
As discussed before, this reaction is part of a dechlorination catalysing chain, as biphenyl is susceptible to degradation by H· radicals (see reaction equation 4.32).

In fact, further growth can only be achieved by subsequent polyphenylation of chlorinated biphenyls. Chlorobiphenyls are chiefly formed from chlorobenzene by displacement of the Cl atom by a chlorophenyl radical.



(4.49)

To a smaller extent chlorobiphenyls are formed by H displacement, as follows.

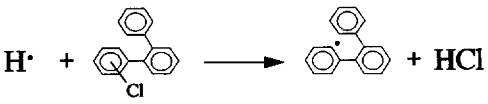


(4.50)

Chlorobiphenyls are susceptible to dechlorination in a similar pathway as chlorobenzene. They also may react further to terphenyl, in a reaction sequence comparable to their own formation. In view of growth the formation of chlorobiphenyls is a very important step.

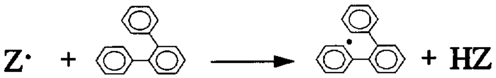
Terphenyls gain stability by internal substitution. The stabilisation occurs in a two step reaction sequence.

- The first step is the formation of a terphenylyl radical, chiefly formed by Cl abstraction by H· radicals:



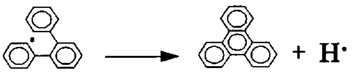
(4.51)

Production of terphenylyl radicals by H abstraction is much slower.



(Z = Cl, H) (4.52)

- The second step involves the actual stabilisation by ring closure. Triphenylene is formed.



(4.53)

By the internal substitution the stability of the molecules is increased. For this reason, terphenyls are important intermediates in the soot and tar formation.

§ 4.3.3 Naphthalene formation.

Phenyl polymerisation is the major pathway to form soot nuclei from chlorobenzene. Nevertheless, the mechanism is incapable to explain the formation of condensed PAHs like naphthalene. A number of alternative reaction routes potentially leading to naphthalene is proposed in literature. In this paragraph the alternatives are discussed.

In assessing the routes on their feasibility, useful information is obtained by interpreting the thermodynamical data presented in table 4.3.

- The Gibbs energy function change of reaction (ΔG_r) is an indication of the likelihood of the reaction to occur at the temperature of concern. The position of the chemical equilibrium and this energy function are correlated by

  $$RT \ln K = -\Delta G_r \qquad (4.54)$$

  The equilibrium constant K is the quotient of product concentrations divided by reactant concentrations when the reaction has reached equilibrium. With a larger K the equilibrium shifts to the right; i.e. the more positive $-\Delta G_r$ is, the more likely the reaction takes place.

- In case of an endothermic reaction, the reaction enthalpy (ΔH_r) might be taken as an indication of the energetic barrier that reactants have to pass. In other words, in the endothermic case the reaction enthalpy may supply a first rough estimate of the activation energy.

Table 4.3 Thermodynamical data of possible naphthalene formation routes.

reaction		ΔH_r (1)	ΔS_r (1)	$-\Delta G_r$ (1)
acetylene formation	(4.55)	420.5	253.1	-123.6
acetylene addition	(4.56)	-416.7	-241.8	133.0
cyclopentadiene formation	(4.57)	-25.5	45.9	79.3
radicalisation	(4.59)	-105.4	?	105.4
'dimerisation'	(4.60)	-109.2	47.6	165.0
benzyn formation	(4.61a)	398.3	?	
production adduct	(4.61b)	-254.4	?	
degradation adduct	(4.61c)	68.6	?	
deficient phenylation	(4.65)	3.8	11.3	9.5

(1) ΔH_r, $-\Delta G_r$(900 °C) in kJ/mol; ΔS_r in J/mol K.

Four alternative routes to naphthalene will be discussed.

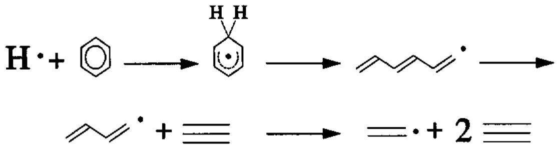
- ***naphthalene formation via acetylene addition.***

Naphthalene can be formed by addition of acetylene to (chloro)benzene. This mechanism has been demonstrated for pyrolytic and oxidative conditions. It has been proven that in incineration all fuels initially degrade to the same essential species, which has been postulated to be acetylene. [29] The acetylene builds into soot particles.

For these process conditions it is stated that whatever fuel is treated, reaction pathways relax to the acetylene addition mechanism. The molecular structure of the fuel influences the growth process only at its early stages: [21]

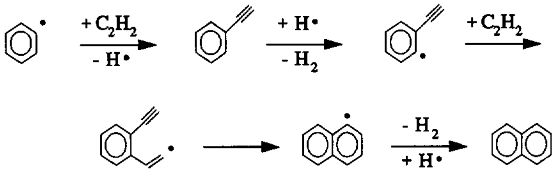
- by providing more efficient reaction partners for the formation of aromatic molecules,
- by affecting the generation of hydrogen atoms,
- by the easiness of acetylene formation.

Under conditions of thermal hydrodechlorination acetylene may be formed from (chloro)benzene as follows. [46]



(4.55)

Consecutive addition steps produces naphthalene. [18]

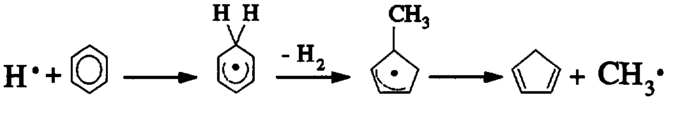


(4.56)

The mechanism comprises a rather long and complicated pathway. The required initial degradation and subsequent growth give an ambivalent impression. As shown in table 4.3 the acetylene formation is thermodynamically very unattractive.

Though this mechanism is known to be important in oxidative (combustion) and pyrolytic systems, its significance in thermal hydrodechlorination appears to be restricted. Acetylene is only produced in limited quantities as result of the relative lower temperatures (<900 °C versus >1400 °C) and the stabilising effect of H_2 on the hydrocarbon radicals [46].

- ***naphthalene formation via cyclopentadiene 'dimerisation'.***
  By gasification reactions (chloro)benzene can degrade into cyclopentadiene, a substance susceptible to dimerisation even at relative mild conditions [11,34]. Cyclopentadiene can be formed from (chloro)benzene according to the following reaction chain. [35]

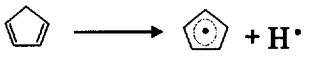


(4.57)

The produced methyl radical is stabilised by H_2.

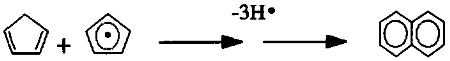
$$CH_3\cdot + H_2 \longrightarrow CH_4 + H\cdot \qquad (4.58)$$

By H abstraction cyclopentadiene is converted in its related radical. Due to resonance structures this radical possesses extravagant stability. For this reason the cyclopentadienyl radical is found in relative high concentrations and it can act as an important intermediate. [34]



(4.59)

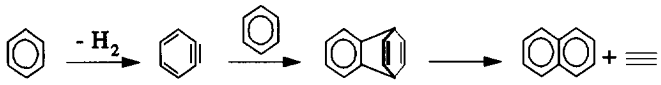
It is proposed that these compounds react, and via a sequence of steps forming naphthalene. [34,38]



(4.60)

As shown in table 4.3, with respect to thermodynamics the sequence is attractive. However, 'it is a long way...', as said by Klinkenberg [34]. Also to get from cyclopentadiene to naphthalene 4 H atoms have to be removed. This dehydrogenation seems rather ambivalent in the hydrogen atmosphere.

- ***naphthalene formation via a Diels-Alder mechanism.***
  Another, rather striking, reaction route is proposed by Bruinsma [9]. Via a sequence of growth by a Diels-Alder mechanism, and subsequent degradation of the intermediate adduct, naphthalene may be formed.



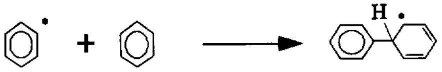
(4.61)

Though the mechanism is elegant, its relevance is questionable. The formation of benzyn is rather tentative. Available thermodynamical data point out that the formation of the Diels-Alder adduct is unattractive. And, at the elevated temperatures of concern a radical mechanism is more likely.

- ***naphthalene formation via deficient phenylation.***

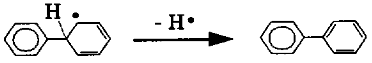
Here, we want to propose another pathway. The proposed pathway is a phenyl radical reacting with molecular (chloro)benzene, but without forming biphenyl. This pathway of deficient (poly)phenylation is somewhat analogous to that of the gasification of (chloro)benzene to acetylene, which is shown in reaction equation 4.55. But contrary to the gasification into acetylene, this reaction can thermodynamically occur (see table 4.3).

The first step is the addition of a phenyl radical to a (chloro)benzene molecule. The adduct 6-phenyl-2,4-cyclohexadien-1-yl is formed.



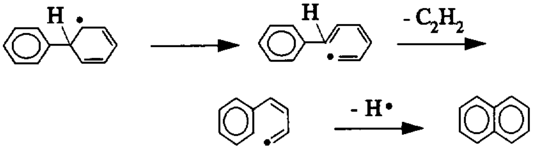
(4.62)

In normal phenylation the adduct decays by elimination of the H atom on the neighbour carbon of the added phenyl group.



(4.63)

However, decay may also take place by scission of the neighbouring C-C bond. Via a sequence of consecutive reaction steps, in which a C_2-group is eliminated, naphthalene is formed. An example of such a reaction chain is given.



(4.64)

Deficient phenylation offers a uncomplicated pathway to naphthalene formation. The mechanism shows strong analogies with the mechanisms of phenyl polymerisation and gasification to acetylene, which both are well accepted in literature [24,29,46]. For thermodynamical reasons, the naphthalene formation has been modelled according to the following overall reaction.

(4.65)

§ 4.3.4 Soot and tar formation submodel of calculation model.

The calculation model concerning thermal hydrodechlorination of chlorobenzene, of which the basis is presented in paragraph 4.2.4, is extended with soot and tar formation. Table 4.4 lists the additionally implemented reactions. The complete reaction mechanism is summarised in appendix 4.A.

Table 4.4 Primary soot and tar formation steps of radical reaction mechanism of thermal hydrodechlorination of chlorobenzene (notation explained in table 4.8).

	chlorophenyl radical ($\phi_{Cl}\cdot$): formation from primary species						
10	ϕ_{Cl}			⇄	$\phi_{Cl}\cdot$	+	$H\cdot$
11	$H\cdot$	+	ϕ_{Cl}	⇄	H_2	+	$\phi_{Cl}\cdot$
12	$Cl\cdot$	+	ϕ_{Cl}	⇄	HCl	+	$\phi_{Cl}\cdot$
	biphenyl (ϕ-ϕ): propagative formation						
13	$\phi\cdot$	+	ϕ_{Cl}	⇄	ϕ-ϕ	+	$Cl\cdot$
14	$\phi\cdot$	+	ϕ_{Cl}	⇄	ϕ-ϕ_{Cl}	+	$H\cdot$
15	$\phi\cdot$	+	ϕ	⇄	ϕ-ϕ	+	$H\cdot$
16	$\phi_{Cl}\cdot$	+	ϕ	⇄	ϕ-ϕ_{Cl}	+	$H\cdot$
17	$\phi_{Cl}\cdot$	+	ϕ_{Cl}	⇄	ϕ-ϕ_{Cl}	+	$Cl\cdot$
	phenyl radicals: termination						
18	$2\phi\cdot$			⇄	ϕ-ϕ		
19	$\phi\cdot$	+	$\phi_{Cl}\cdot$	⇄	ϕ-ϕ_{Cl}		
	biphenyl: dechlorination						
20	$H\cdot$	+	ϕ-ϕ_{Cl}	⇄	HCl	+	ϕ-$\phi\cdot$
21	$H\cdot$	+	ϕ-ϕ_{Cl}	⇄	ϕ-ϕ	+	$Cl\cdot$
	biphenyl: radicalisation						
22	$H\cdot$	+	ϕ-ϕ	⇄	H_2	+	ϕ-$\phi\cdot$
23	$Cl\cdot$	+	ϕ-ϕ	⇄	HCl	+	ϕ-$\phi\cdot$
24	$H\cdot$	+	ϕ-ϕ_{Cl}	⇄	H_2	+	ϕ-$\phi_{Cl}\cdot$
25	$Cl\cdot$	+	ϕ-ϕ_{Cl}	⇄	HCl	+	ϕ-$\phi_{Cl}\cdot$
	terphenyl (ϕ-ϕ-ϕ): propagative formation						
26	$\phi\cdot$	+	ϕ-ϕ	⇄	ϕ-ϕ-ϕ	+	$H\cdot$
27	$\phi\cdot$	+	ϕ-ϕ_{Cl}	⇄	ϕ-ϕ-ϕ	+	$Cl\cdot$
28	$\phi\cdot$	+	ϕ-ϕ_{Cl}	⇄	ϕ-ϕ-ϕ_{Cl}	+	$H\cdot$
29	$\phi_{Cl}\cdot$	+	ϕ-ϕ	⇄	ϕ-ϕ-ϕ_{Cl}	+	$H\cdot$
30	$\phi_{Cl}\cdot$	+	ϕ-ϕ_{Cl}	⇄	ϕ-ϕ-ϕ_{Cl}	+	$Cl\cdot$
	terphenyl: dechlorination						
31	$H\cdot$	+	ϕ-ϕ-ϕ_{Cl}	⇄	HCl	+	ϕ-ϕ-$\phi\cdot$
32	$H\cdot$	+	ϕ-ϕ-ϕ_{Cl}	⇄	ϕ-ϕ-ϕ	+	$Cl\cdot$

	terphenyl: radicalisation						
33	$H\cdot$	+	ϕ-ϕ-ϕ	$\rightleftarrows$	H_2	+	ϕ-ϕ-$\phi\cdot$
34	$Cl\cdot$	+	ϕ-ϕ-ϕ	$\rightleftarrows$	HCl	+	ϕ-ϕ-$\phi\cdot$
35	$H\cdot$	+	ϕ-ϕ-ϕ_{Cl}	$\rightleftarrows$	H_2	+	ϕ-ϕ-$\phi_{Cl}\cdot$
36	$Cl\cdot$	+	ϕ-ϕ-ϕ_{Cl}	$\rightleftarrows$	HCl	+	ϕ-ϕ-$\phi_{Cl}\cdot$
	triphenylene: formation						
37	ϕ-ϕ-$\phi\cdot$			$\rightleftarrows$	$(\phi)\phi_3$	+	$H\cdot$
38	ϕ-ϕ-$\phi_{Cl}\cdot$			$\rightleftarrows$	$(\phi)\phi_3$	+	$Cl\cdot$
	acetylene: formation						
39	$H\cdot$	+	ϕ	$\rightleftarrows$	n-$C_6H_7\cdot$		
40	n-$C_6H_7\cdot$			$\rightleftarrows$	C_2H_2	+	n-$C_4H_5\cdot$
41	n-$C_4H_5\cdot$			$\rightleftarrows$	C_2H_2	+	$C_2H_3\cdot$
42	$C_2H_3\cdot$			$\rightleftarrows$	C_2H_2	+	$H\cdot$
43	$C_2H_3\cdot$	+	$H\cdot$	$\rightleftarrows$	C_2H_2	+	H_2
44	$C_2H_3\cdot$	+	H_2	$\rightleftarrows$	C_2H_4	+	$H\cdot$
45	$\phi\cdot$	+	C_2H_2	$\rightleftarrows$	ϕ-C_2H	+	$H\cdot$
	naphthalene: formation by deficient polyphenylation						
46	$\phi\cdot$	+	ϕ	$\rightleftarrows$	$\phi\phi$	+	$C_2H_3\cdot$
	naphthalene: formation by acetylene growth						
47	ϕ-$C_4H_4\cdot$			$\rightleftarrows$	$\phi\phi$	+	$H\cdot$
48	ϕ-$C_4H_4\cdot$			$\rightleftarrows$	C_2H_2	+	ϕ-$C_2H_2\cdot$
49	ϕ-$C_2H_2\cdot$			$\rightleftarrows$	C_2H_2	+	$\phi\cdot$
50	ϕ-$C_2H_2\cdot$			$\rightleftarrows$	ϕ-C_2H	+	$H\cdot$

Major assumptions and simplifications made in the model derivation are listed below.

- The model does not consider compounds with 2 or more Cl atoms per molecule.
- No distinction is made with respect to position in the molecule (e.g. the precise location of the Cl atom in chlorobiphenyl).
- Chlorinated triphenylene is not considered.
- Growth by polyphenylyl radicals, such as the (chloro)biphenylyl radical, is not incorporated. The concentration of these radicals is presumably too low to have a noticeable effect. Also abstraction by polyphenylyl radicals is neglected as their abstraction potential is small compared with Cl· and H· radicals [29].

The kinetic data are obtained from Ritter [42,26] and Frenklach [24]. Ritter supplies the kinetics of phenyl polymerisation, while Frenklach supplies the kinetics concerning the formation of naphthalene and acetylene. The thermodynamical data are acquired from the NIST thermodynamical database [52].

The model is compared with literature data for validation.

- Ritter [46] reports that he had to multiply the gas phase hydrogen recombination rate with a factor of about 1000 in order to fit his model with experimental data. He explains the required increase by wall effects. However, Ritter has chosen rather slow kinetics for the benzene dissociation. If his rate is replaced by that according to the NIST Chemical Kinetics database [37], a normal hydrogen recombination rate is sufficient to fit his experimental data. With the corrected kinetics the H· radical overshoot remains of the same order.

- As discussed in paragraph 4.2.4., the overall bulk rate according to Ritter [46] is used to compare the model results with actual dechlorination data. This source supplies information about homogeneous gas phase dechlorination, eliminating the contribution of wall surfaces. In order to get a proper fit, reactions concerning the attack of H· radicals on molecular chlorobenzene needed to be altered. After division of the literature values [37,38] by 1.7 satisfactory results are obtained (see figure 4.3).

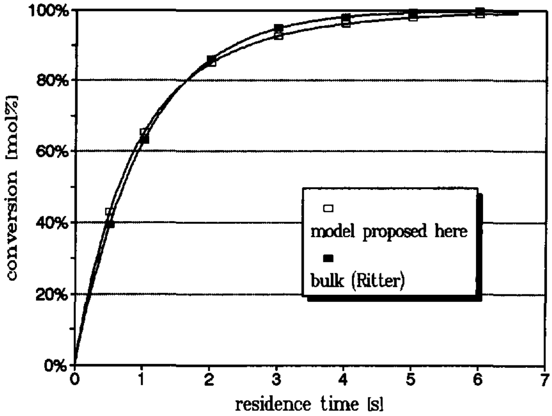


Figure 4.3 *Comparison of conversion according to model presented (diluted conditions, 900 °C) and bulk gas kinetics (Ritter [46]).*

The required adaptation may be explained as follows. The original literature values have been derived under the assumption of hydrogen dissociation equilibrium. However, in reality the H· radical concentration exceeds the equilibrium. A lower concentration is assumed than actual present, leading to overestimation of the kinetical rate constants.

In this view, competitive rate experiments give better estimations for the rate constants. Using this kind of experiments, Cui [14] determined the reaction rate constant of H· radicals abstracting Cl atoms from chlorobenzene (reaction 6 in tables 4.9). His rate constant is indeed smaller than that proposed by others. Though the difference is restricted to a factor of 1.3 at 900 °C, the result is indicative. At this point further investigation is recommended.

- Accurate data concerning soot and tar formation are not available. For this reason, a proper validation of the model with respect to soot and tar formation is not possible. Nevertheless, as will be discussed in paragraph 4.4, the model predictions are in the same order of the soot and tar masses observed in the bench scale installation.

§ 4.3.5 The effect of Cl on soot formation.

Soot and tar formation in chlorine containing systems is more pronounced than in analogue systems without chlorine [26,33,44,45,54]. This higher soot propensity is due to a set of properties.

- C-Cl bonds are weaker than corresponding C-H bonds. The dissociation rate of chlorinated hydrocarbons exceeds that of the nonchlorinated analogues (see e.g. table 4.6). The initial production of radicals is much higher. [26,33,44,45,54]

- Aromatic hydrocarbons, which behave like stable 'sinks' in soot formation, are (re)activated by H abstraction. A Cl· radical abstracts a H atom with more ease than the H· radical [23,26,33,44,45].

  Moreover, the produced HCl is a rather reactive molecule, which, contrary to H_2, can not be regarded as a stable 'sink'. A kind of catalysing sequence may be set up, effectuating that even a small concentration of Cl· radicals may have a manifest effect. [29]

$$Cl\cdot + RH \longrightarrow R\cdot + HCl \tag{4.66}$$

$$H\cdot + HCl \rightleftarrows Cl\cdot + H_2 \tag{4.67}$$

$$\underline{\hspace{10cm}}\ +$$

$$H\cdot + RH \longrightarrow R\cdot + H_2 \tag{4.68}$$

- The elimination of a Cl atom is favoured over the elimination of a H atom. Therefore, growth is much faster if chlorine is displaced (reaction 4.69 is more attractive than reaction 4.70).

$$R_x\cdot + R_yCl \longrightarrow R_xR_y + Cl\cdot \tag{4.69}$$

$$R_x\cdot + R_yH \longrightarrow R_xR_y + H\cdot \tag{4.70}$$

In fact, a kind of catalysis of soot formation is effected at the expense of Cl. Remind that at the entrance of the reactor both the concentrations of chlorinated hydrocarbons and hydrocarbon radicals are high. At the entrance extravagant soot formation occurs.

The Cl favoured soot formation has remarkable consequences.

a) As mass growth is accompanied by Cl elimination, it effectuates dechlorination. In fact, a catalytic chain is realised if the mass growth is succeeded by degradation (see paragraph 4.2.3).

b) The presence of Cl unmistakably stimulates soot formation. Nevertheless, since soot formation is effected at the expense of Cl, the formed soot will contain no or only a small proportion of Cl!

Soot formation and dechlorination are coupled. Their relationship is illustrated by the following phenomena.

- The initial step for both events is (pyrolytic) dissociation.
- A side-effect of soot formation is catalysis of dechlorination (see reaction equations 4.31 to 4.33).

The relationship is also indicated by the bench scale experiment with hastelloy (see paragraph 3.4.3). Hastelloy does not only promote soot formation, but it accelerates dechlorination, as well.

§ 4.4 Results of model calculations.

The model calculates the molar flow of 26 species (see appendix 4.A). The molar flow of the most important molecules are presented in figure 4.4, that of relevant radicals in figure 4.5. At maximum 7 C-mol% of the produced hydrocarbon is converted into PAHs. Biphenyl is the most important PAH, contributing for at least 70% of the C present in PAHs.

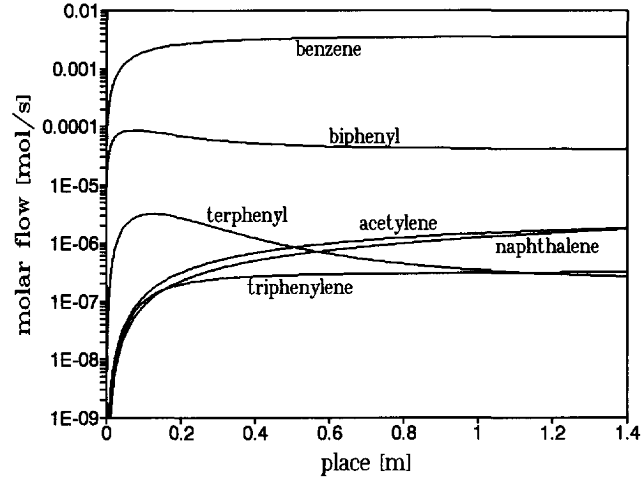


Figure 4.4 *Molar flows of most important hydrocarbons (concentrated conditions, 900 °C).*

In the radical profiles, roughly two reaction bands can be distinguished.

- First, the initial radical production is clearly recognised. Phenyl and Cl· radicals, the products of dissociation of molecular chlorobenzene, and H· radicals, the radical product of the reaction of the previous radicals with hydrogen, are indisputably important during this stage of initiation. The dissociation competes with association to molecular benzene. The radical pool passes through a maximum at the moment initiation and termination equalise.

  Especially Cl· radicals tend to be 'stabilised' by reaction with hydrogen, keeping their fraction relatively low. As discussed before, this stabilising reaction is almost continuously in equilibrium. According to the equilibrium, the Cl· concentration is proportional to the HCl concentration and H· concentration (see equation 4.27). Initially

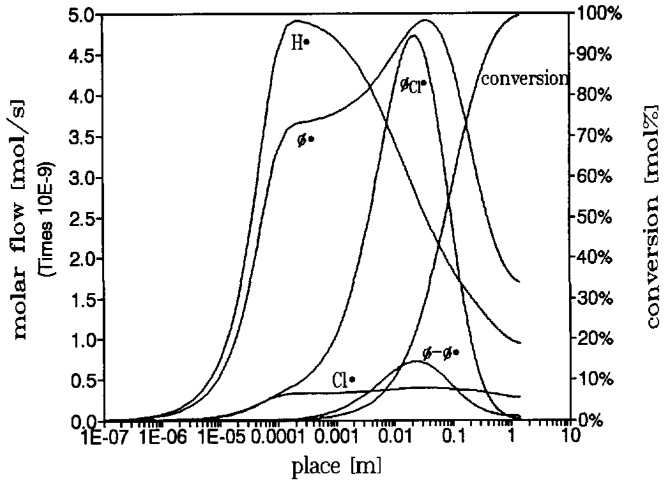


Figure 4.5 *Molar flows of most important radicals (concentrated conditions, 900 °C).*

little HCl is present, and the equilibrium is capable to 'buffer' the produced Cl· radicals. The HCl concentration start to increase only after the H· concentration already passed its maximum. Therefore the maximum flow of Cl· radicals is delayed in comparison with the maximum of H· radicals.

- After radicals are formed, other reactions take over. The general type of these reactions is the conversion of a radical and a molecule into respectively the corresponding molecule and radical. H· induced dissociation of larger polyphenyls that are formed in the meanwhile, give raise to chlorophenyl and biphenylyl radicals in particular. In a similar way a further increase of the phenyl radical concentration is effectuated.

  This second reaction band indicates the activity of polyphenyl production and accompanying degradation.

Figure 4.6 presents the heat demand of the reactions. Initially, some heat is required for the endothermic production of radicals. After this short initiation period, the main exothermic dechlorination takes over. Then, the reaction system produces heat. The initial heat demand is so small it causes only a restricted temperature fall. No additional heat is required to initiate the chemical processes.

According to model calculations, the hydrogen dissociation is not completely in equilibrium. Under concentrated conditions at 900 °C an H· overshoot of 4.2 is encountered. This is in accordance with the observations by Ritter [42]. Nevertheless, since the overshoot is rather limited, the assumption of equilibrium renders a fairly good estimation of the actual H· radical concentration. In a real reactor the walls also contribute to establish the equilibrium. Then, the concentration is even closer to equilibrium. Whether equilibrium, as assumed by Manion [38], is actually reached, depends on the surface area of the wall and its activity.

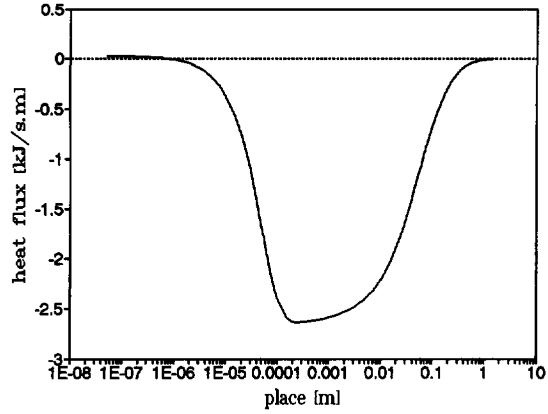


Figure 4.6 *Heat demand of reaction system (concentrated conditions, 900 °C).*

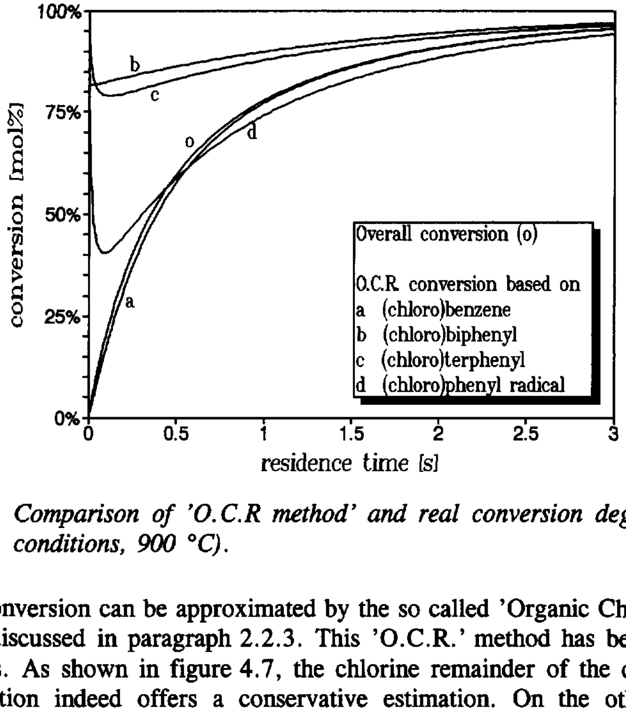


Figure 4.7 *Comparison of 'O.C.R method' and real conversion degree (concentrated conditions, 900 °C).*

The actual conversion can be approximated by the so called 'Organic Chlorine Remainder' method, as discussed in paragraph 2.2.3. This 'O.C.R.' method has been applied on the model results. As shown in figure 4.7, the chlorine remainder of the chlorobenzene and benzene fraction indeed offers a conservative estimation. On the other hand, at low conversion degrees the chlorine remainder of (chlorinated) biphenyls or terphenyls gives a poor indication. At high degrees the method supplies a sufficient approximation of the actual conversion.

Model calculations also indicate that no readdition occurs of inorganic chlorine (Cl· or HCl) to organic species.

Until now only isothermal operation has been discussed. In reality the temperature changes throughout the reactor. The effect of the temperature profile on the reactor performance is investigated for the mini pilot plant. Basically, similar trends are observed as in isothermal operation.

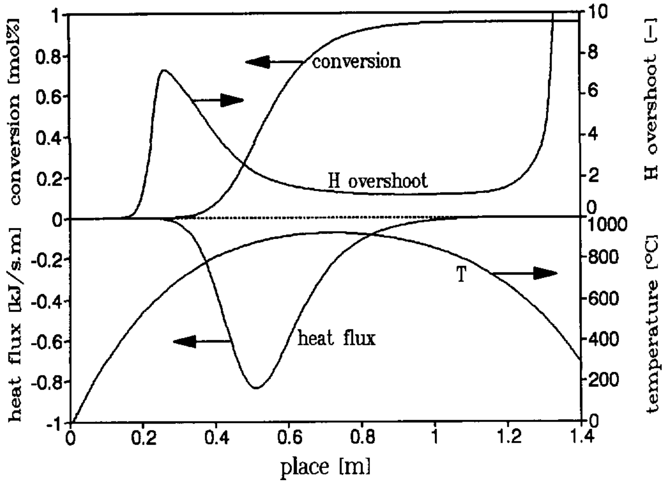


Figure 4.8 *Nonisothermal operation (concentrated conditions).*

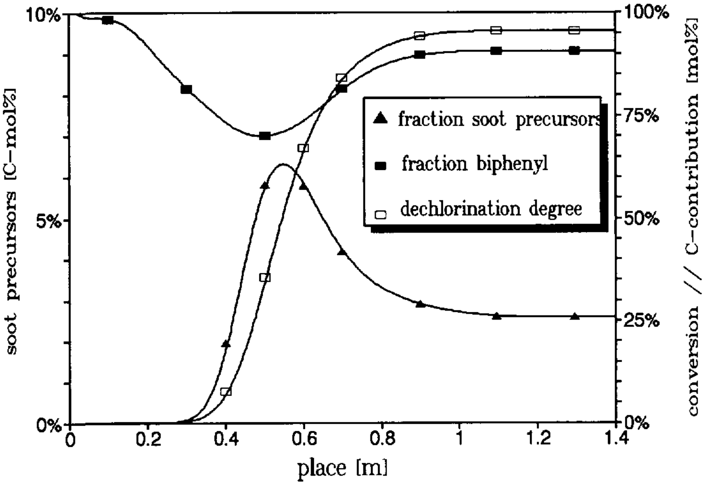


Figure 4.9 *Simulated dechlorination and soot production in mini pilot reactor (temperature profile shown in figure 4.8).*

- Statements, such as that the 'O.C.R.' method is applicable and that no readdition of inorganic chlorine occurs, are, generally, still valid.

- The operation gives a smoother impression (see figure 4.8). Radicals are produced in a lower temperature region (T < 900 °C) preceding the actual dechlorination. Because of the lower temperature, a more gentle dissociation is observed. The radical concentrations are generally beyond the level observed at isothermal operation. The radical molar flow profiles merely follow the temperature profile. Due to the smooth initiation, the endothermic start is too small to notice.

  Apparently, the H· radical overshoot is larger with its maximum about 7.25 at 0.26 m. However, the magnitude of overshoot is mainly a result of the low equilibrium concentration at low temperatures. The overshoot is merely positioned before the temperature of interest. At T ≈ 900 °C, the majority of radicals is already produced and the dissociation appears to be near equilibrium (overshoot < 2).

- The soot and tar precursors are formed in a similar way as in isothermal operation. PAHs contribute at maximum for 6.3 C% of all nonchlorinated hydrocarbons produced. At the end of the reactor 2.6 C% is accumulated in PAHs. Biphenyl is the most important PAH, contributing for at least 70 C% of the carbon present in PAHs.

The model is used to investigate the effect of dilution. As figure 4.10 presents, a decline of the dechlorination rate is calculated. This decline is caused by a decrease of the radical pool, as result of the smaller fraction of chlorinated hydrocarbons in the feed.

- With a smaller fraction of chlorinated hydrocarbons in the feed, the initial production of H· radicals is smaller, are depicted in figure 4.11. Only after a while, when the radical pool approaches equilibrium, the H· radical concentration of the more diluted systems surpass that of the more concentrated ones.

- With a smaller fraction of chlorinated hydrocarbons in the feed, the concentration of phenyl and alike radicals is lower. As result, the catalytic dechlorination route via these radicals is less pronounced.

The dilution effect alters if hydrogen dissociation equilibrium is imposed. In this case, the H· radical concentration strictly follows the concentration of molecular hydrogen. As a side-effect the complete radical pool is tempered; i.e. the concentrations of other radicals like the phenyl radical, are less abundant. Then dilution, meaning an increase of molecular hydrogen, effectuates an increased H· radical concentration throughout the reactor. The overall dechlorination rate is accelerated.

The hydrogen dissociation may be imposed by wall effects. This leads to the following postulate. In small reactors with a relative high S/V ratio, dilution results in accelerated dechlorination, in accordance with the measurements of Manion and Ritter [38,46]. On the other hand, in bigger reactors a decline is expected. To validate this hypothesis additional experimental and modelling research would be required.

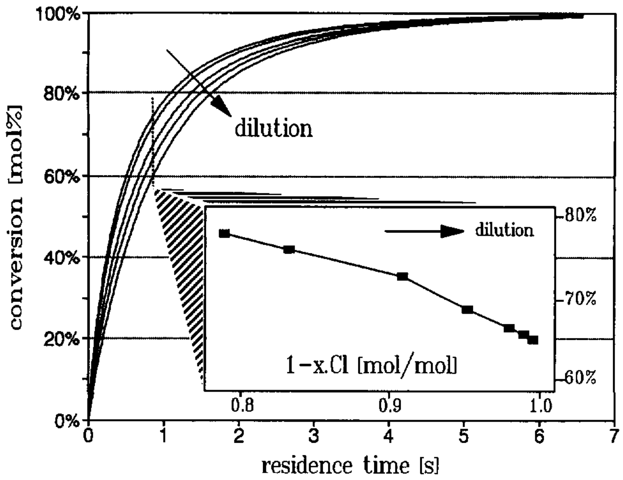


Figure 4.10 Effect of dilution on conversion (900 °C). (see table 4.5)

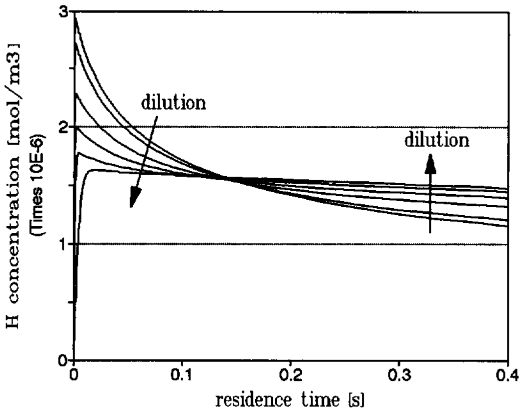


Figure 4.11 Effect of dilution on H· radical concentration (900 °C). (see table 4.5)

for all:

$$\frac{[H\cdot]_{0.4\,s}}{[H\cdot]_{exit}} \approx 2$$

Table 4.5 dilution series (depicted in figures 4.10 and 4.11).

H_2/Cl	$x(H_2)$ = 1 - x(Cl)	remark
3.8	79.1 %	'concentrated' conditions
5	83.3 %	
10	90.9 %	
20	95.2 %	
50	98.0 %	
100	99.0 %	
269.3	99.6 %	'diluted' conditions

The model provides limited information about gasification, mainly as coincidental event during mass growth. Acetylene is mainly produced from vinyl radicals.

$$C_2H_3\cdot \longrightarrow C_2H_2 + H\cdot \qquad (4.71)$$

The majority of the vinyl radicals is produced as byproduct during naphthalene formation (reaction 4.65). The remainder is produced by direct gasification of (chloro)benzene effected by H· radicals (reaction 4.55). Under isothermal, concentrated conditions about 60% of the acetylene yield is formed as byproduct of deficient phenylation.

Remarkably the model calculations indicate an overproduction of acetylene with respect to ethene. Even in the hydrogen rich atmosphere, vinyl radicals would dissociate more rapidly than that they would abstract H atoms from hydrogen (reaction 4.71 versus reaction 4.72).

$$C_2H_3\cdot + H_2 \longrightarrow C_2H_4 + H\cdot \qquad (4.72)$$

But, as said, the model does not primarily focus on gasification phenomena. At this moment gasification is only incorporated in the model as a side-effect of soot and tar formation. Therefore, one needs to be careful in the interpretation of the present results with respect to gasification. For a proper evaluation, the model should be extended.

§ 4.5 Final discussion.

A computer model is developed to describe thermal hydrodechlorination of chlorobenzene. Literature data are reviewed, and adapted where necessary.

In the radical mechanism underlying thermal hydrodechlorination, the most important type of radical reaction is the desubstitution of a functional group from the hydrocarbon by a H· radical. Particularly, displacement by an addition/elimination sequence appears to have a large contribution to the overall conversion. Functional groups like Cl atoms and phenyl groups are eliminated. In such a way, H· radicals accelerate the dechlorination rate and reduce the quantity of tar and soot precursors.

Split off Cl or phenyl radicals need to be stabilised. Normally, they gain stability by adopting a H atom. The predominant source for this H atoms is molecular hydrogen. When a H atom is abstracted from H_2, a H· radical is produced, which can proceed the chain.

Dechlorination can also occur by a catalysing chain in which phenyl radicals are involved. Therefore, the general dechlorination sequence is best represented by

1) Cl displacement:

$$Y\cdot + RCl \longrightarrow RY + Cl\cdot \qquad Y = H,\ \phi \qquad (4.73)$$

2) H abstraction by the Cl· radical formed:

$$Cl\cdot + ZH \longrightarrow HCl + Z\cdot \qquad Z = H,\ \phi,\ C_nH_m \qquad (4.74)$$

The formed Z· radical can restart the chain.

The H· radicals are initially produced by partial (homolytic) dissociation of the chlorinated hydrocarbon feed. The radical pool is regulated by this dissociation and terminating association of H· and hydrocarbon radicals. Gas phase dissociation of H_2 is too slow to impose equilibrium. An overshoot of H· radicals is observed, with a maximum typically in the order of 5.

The overall dechlorination rate follows pseudo first order kinetics, if excess hydrogen is present [38,46]. Nevertheless, the pseudo first order constant is effected to some extent by the initial fractions of chlorinated hydrocarbons and hydrogen. At large changes of these fractions the effect becomes manifest.

- A large increase of the H_2 concentration causes a noticeable shift of the dissociation equilibrium to the side of H· radicals.
- A much smaller chlorinated hydrocarbon fraction diminishes the potential for the initial production of radicals.

In this way the difference in the overall rates given by Manion [38] and Ritter [46] can be explained.

Wall surfaces certainly effect the dechlorination rate. Yet, contrary effects are noticed; on one hand the primary dechlorination steps are accelerated, on the other the H_2 dissociation equilibrium is imposed. Depending on the process conditions and its surface type and area, the wall induces acceleration or decline of the overall dechlorination rate. In view of this, the opposite wall effect observed by Ritter [42,46] for chlorobenzene and dichlorobenzene can be understood.

The initial step in soot growth is the gas phase production of PAHs. Their production is not only a matter of concern because PAHs are important intermediates in soot growth, but also because they are identified to be carcinogenic and mutagenic. They adsorb on the surface of soot particles and may be transported in this way to the human lungs where they remain in contact with the long tissue for a long period of time. In this way PAHs may constitute a toxicological danger. [26]

The main pathway from chlorobenzene to PAHs is phenyl polymerisation. Biphenyl, which is the main tar component, and terphenyl, triphenylene, and so on, are formed in this way. Phenyl polymerisation is especially favourable if a Cl atom is eliminated. This does not only mean that, in comparison to their nonchlorinated analogues, chlorinated hydrocarbons are more sensible to soot formation, but also that the soot formed contains no or very limited amounts of chlorine!

Another consequence of the favourable Cl elimination is the existence of a catalysed dechlorination path. The net effect of phenyl polymerisation and subsequent reduction of formed polyphenyls (e.g. by H· radicals), is dechlorination!

Phenyl polymerisation can not explain the formation of condensed aromatics like naphthalene. The origin of these compounds is yet not completely understood. The formation route via deficient phenylation is proposed.

Hydrocarbon (R·) radicals play an active role in soot formation. The presence of R· radicals comprises soot and tar production. To diminish soot and tar formation, the R· concentration must be reduced. Reduction is achieved by reaction with molecular hydrogen. This stabilisation (equation 4.75) competes with growth reactions (equation 4.76).

$$R\cdot + H_2 \rightleftharpoons RH + H\cdot \tag{4.75}$$

$$R\cdot + R \longrightarrow RR\cdot \xrightarrow{(n-2)R} (R)_n\cdot \longrightarrow soot \tag{4.76}$$

The reaction with hydrogen is near equilibrium. According to the equilibrium, H_2 reduces while H· promotes soot formation.

H· radicals are also known to accelerate the dechlorination rate. Again, a kind of competition exists.

$$H\cdot + RCl \longrightarrow RH + Cl\cdot \tag{4.77}$$

$$H\cdot + RY \xrightarrow{-HY} R\cdot \xrightarrow{(n-1)R} (R)_n\cdot \longrightarrow soot \tag{4.78}$$

Under conditions of thermal hydrodechlorination the net effect of hydrogen is reduction of the soot formation, and acceleration of the dechlorination rate.

The mechanism demonstrates that dechlorination and soot formation are correlated. At thermal hydrodechlorination soot formation is inevitable. Though by adding more H_2 the amount of soot is reduced, the soot production never is completely inhibited.

Model calculations prove the applicability of the 'Organic Chlorine Remainder' (O.C.R.) method. They also indicate, that the initial heat demand of the radicals formation is small. Extinction because of a large initial temperature decrease, is not expected. No readdition of inorganic Cl is observed. In general, nonisothermal operation seems to give smoother results than isothermal operation. This is mainly due to the (virtual) sharp temperature increase at the reactor entrance in the latter case.

In literature an interesting opportunity is found for process improvement. Ritter [43,44,45] reports that addition of 1-5 vol% oxygen to the hydrogen bath gas allows the operation temperature to decrease more than 200 °C. The product composition remains similar, except for an increased methane production and the formation of carbon monoxide. The possibility of dioxin formation is theoretically assessed, but no experimental data are presented.

***Table 4.6** Thermodynamics of H· radical producing reactions.* [52]

reaction	ΔH_r (1)	ΔS_r (1)	$-\Delta G_r$ (1)
hydrogen dissociation	436.0	98.7	-320.2
benzene dissociation	464.0	135.7	-304.8
chlorobenzene dissociation	395.8	142.2	-229.0
H abstraction by oxygen	228.4	6.5	-220.8

(1) ΔH_r, $-\Delta G_r$(900 °C) in kJ/mol; ΔS_r in J/mol K.

The accelerating effect by oxygen addition is explained by an increase of the radical pool. Equation 4.79, presented in table 4.7, shows the reaction molecular hydrogen and oxygen undergo, producing a H· radical. Finally 2 H· radicals per oxygen molecule may be produced by this and subsequent reactions. The initial reaction in which oxygen abstracts a H atom from hydrogen, is less endothermic than the dissociation of (chlorinated) hydrocarbons or hydrogen (see table 4.6). Taking the endothermic reaction enthalpy as an indication of the energetic barrier that must be passed during initiation, the radical production obviously is much easier if oxygen is available.

***Table 4.7** Thermodynamics of H· radicals producing partial oxidation producing H· radicals.* [24,45,52]

reaction		ΔH_r (1)	ΔS_r (1)	$-\Delta G_r$ (1)
$H_2 + O_2 \longrightarrow HO_2\cdot + H\cdot$	(4.79)	228.4	6.5	-220.8
$HO_2\cdot + H\cdot \longrightarrow 2\ OH\cdot$	(4.80)	-150.6	25.1	180.0
$OH\cdot + H_2 \longrightarrow H_2O + H\cdot$	(4.81)	-62.8	-10.9	50.0
$O_2 + 3\ H_2 \longrightarrow 2\ H_2O + 2\ H\cdot$	(4.82)	-47.7	9.9	59.3

(1) ΔH_r, $-\Delta G_r$(900 °C) in kJ/mol; ΔS_r in J/mol K.

The question arises whether this observation is restricted to diluted systems as investigated by Ritter, or whether it can be extrapolated to more concentrated systems, as well. In diluted systems the available dissociation potential is little and the oxygen suppletion can substantially add to the radical production. In concentrated systems, a considerable radical production is already provided by the much larger chlorinated hydrocarbon fraction. It is unclear whether in this case the oxygen suppletion still adds to the radical production in a substantial way. Further investigation on this matter is recommended.

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Appendix 4.A Complete calculation model of thermal hydrodechlorination of chlorobenzene.

In tables 4.9a and 4.9b the calculation model is presented, which has been used to describe the radical mechanism underlying thermal hydrodechlorination of chlorobenzene. The model embodies 26 species, which are listed in table 4.8. The model includes dechlorination steps according to Manion [38] and Ritter [46] (see paragraph 4.2.4), and production of soot precursors via phenyl polymerisation and deficient phenylation (see paragraph 4.3.4). The radical reactions taken into account have been discussed in the previous paragraphs.

The kinetical data concerning the primary dechlorination steps are mainly obtained from the NIST Chemical Kinetics database [37]. The kinetics concerning phenyl polymerisation are chiefly rendered from Ritter [42,46], while the kinetics concerning naphthalene production are given by Frenklach [24]. The thermodynamical data are acquired from the NIST thermodynamical database [52].

The model has been validated using data offered by Ritter [46].

The reactor is modelled as an ideal plug flow reactor. The equations used are presented in paragraph 4.2.4. The differential equations are integrated using the RRGRK package [28], that uses a Gibbs-Runge-Kutta integration method.

The model offers the possibility to simulate nonisothermal operation. Temperature influences the kinetical and thermodynamical values and the molar gas volume. Real reactors usually are operated at nonisothermal conditions. However, isothermal simulation leads to results which are interpreted with more ease, offering the opportunity to gain a better insight of the mechanism.

Table 4.8 *Species incorporated in the calculation model.*
M = collision body, i.e. any species
ϕ : symbolises 1 aromatic ring

molecules	radicals
H_2 = hydrogen	$H\cdot$ = hydrogen radical
HCl = hydrogen chloride	$\phi\cdot$ = phenyl radical
ϕ = benzene	$Cl\cdot$ = chloride radical
ϕ_{Cl} = chlorobenzene	$\phi_{Cl}\cdot$ = chlorophenyl radical
ϕ-ϕ = biphenyl	ϕ-$\phi\cdot$ = biphenylyl radical
ϕ-ϕ_{Cl} = chlorobiphenyl	ϕ-$\phi_{Cl}\cdot$ = chlorobiphenylyl radical
ϕ-ϕ-ϕ = terphenyl	ϕ-ϕ-$\phi\cdot$ = terphenylyl radical
ϕ-ϕ-ϕ_{Cl} = chloroterphenyl	ϕ-ϕ-$\phi_{Cl}\cdot$ = chloroterphenylyl radical
$(\phi)\phi_3$ = triphenylene	$C_6H_7\cdot$ = hexatrienyl radical
C_2H_2 = acetylene	$C_4H_5\cdot$ = butadienyl radical
C_2H_4 = ethene	$C_2H_3\cdot$ = vinyl radical
ϕC_2H = phenylacetylene	$\phi C_4H_4\cdot$ = phenyl-butadienyl radical
$\phi\phi$ = naphtalene	$\phi C_2H_2\cdot$ = phenyl-vinyl radical

***Table 4.9a** Complete radical reaction mechanism of thermal hydrodechlorination of chlorobenzene (notation explained in table 4.8).*

	primary species (feed and main products): dissociation						
1	H_2	+	M	$\rightleftarrows$	$2H\cdot$	+	M
2	HCl	+	M	$\rightleftarrows$	$H\cdot$	+	$Cl\cdot$ +M
3	ϕ_{Cl}			$\rightleftarrows$	$\phi\cdot$	+	$Cl\cdot$
4	ϕ			$\rightleftarrows$	$\phi\cdot$	+	$H\cdot$
	primary species: reaction with H· and Cl·						
5	$H\cdot$	+	ϕ_{Cl}	$\rightleftarrows$	ϕ	+	$Cl\cdot$
6	$H\cdot$	+	ϕ_{Cl}	$\rightleftarrows$	HCl	+	$\phi\cdot$
7	$H\cdot$	+	ϕ	$\rightleftarrows$	H_2	+	$\phi\cdot$
8	$Cl\cdot$	+	H_2	$\rightleftarrows$	HCl	+	$H\cdot$
9	$Cl\cdot$	+	ϕ	$\rightleftarrows$	HCl	+	$\phi\cdot$
	chlorophenyl radical ($\phi_{Cl}\cdot$): formation from primary species						
10	ϕ_{Cl}			$\rightleftarrows$	$\phi_{Cl}\cdot$	+	$H\cdot$
11	$H\cdot$	+	ϕ_{Cl}	$\rightleftarrows$	H_2	+	$\phi_{Cl}\cdot$
12	$Cl\cdot$	+	ϕ_{Cl}	$\rightleftarrows$	HCl	+	$\phi_{Cl}\cdot$
	biphenyl (ϕ-ϕ): propagative formation						
13	$\phi\cdot$	+	ϕ_{Cl}	$\rightleftarrows$	ϕ-ϕ	+	$Cl\cdot$
14	$\phi\cdot$	+	ϕ_{Cl}	$\rightleftarrows$	ϕ-ϕ_{Cl}	+	$H\cdot$
15	$\phi\cdot$	+	ϕ	$\rightleftarrows$	ϕ-ϕ	+	$H\cdot$
16	$\phi_{Cl}\cdot$	+	ϕ	$\rightleftarrows$	ϕ-ϕ_{Cl}	+	$H\cdot$
17	$\phi_{Cl}\cdot$	+	ϕ_{Cl}	$\rightleftarrows$	ϕ-ϕ_{Cl}	+	$Cl\cdot$
	phenyl radicals: termination						
18	$2\phi\cdot$			$\rightleftarrows$	ϕ-ϕ		
19	$\phi\cdot$	+	$\phi_{Cl}\cdot$	$\rightleftarrows$	ϕ-ϕ_{Cl}		
	biphenyl: dechlorination						
20	$H\cdot$	+	ϕ-ϕ_{Cl}	$\rightleftarrows$	HCl	+	ϕ-$\phi\cdot$
21	$H\cdot$	+	ϕ-ϕ_{Cl}	$\rightleftarrows$	ϕ-ϕ	+	$Cl\cdot$
	biphenyl: radicalisation						
22	$H\cdot$	+	ϕ-ϕ	$\rightleftarrows$	H_2	+	ϕ-$\phi\cdot$
23	$Cl\cdot$	+	ϕ-ϕ	$\rightleftarrows$	HCl	+	ϕ-$\phi\cdot$
24	$H\cdot$	+	ϕ-ϕ_{Cl}	$\rightleftarrows$	H_2	+	ϕ-$\phi_{Cl}\cdot$
25	$Cl\cdot$	+	ϕ-ϕ_{Cl}	$\rightleftarrows$	HCl	+	ϕ-$\phi_{Cl}\cdot$

	terphenyl (ϕ-ϕ-ϕ): propagative formation						
26	$\phi\cdot$	+	ϕ-ϕ	$\rightleftarrows$	ϕ-ϕ-ϕ	+	$H\cdot$
27	$\phi\cdot$	+	ϕ-ϕ_{Cl}	$\rightleftarrows$	ϕ-ϕ-ϕ	+	$Cl\cdot$
28	$\phi\cdot$	+	ϕ-ϕ_{Cl}	$\rightleftarrows$	ϕ-ϕ-ϕ_{Cl}	+	$H\cdot$
29	$\phi_{Cl}\cdot$	+	ϕ-ϕ	$\rightleftarrows$	ϕ-ϕ-ϕ_{Cl}	+	$H\cdot$
30	$\phi_{Cl}\cdot$	+	ϕ-ϕ_{Cl}	$\rightleftarrows$	ϕ-ϕ-ϕ_{Cl}	+	$Cl\cdot$
	terphenyl: dechlorination						
31	$H\cdot$	+	ϕ-ϕ-ϕ_{Cl}	$\rightleftarrows$	HCl	+	ϕ-ϕ-$\phi\cdot$
32	$H\cdot$	+	ϕ-ϕ-ϕ_{Cl}	$\rightleftarrows$	ϕ-ϕ-ϕ	+	$Cl\cdot$
	terphenyl: radicalisation						
33	$H\cdot$	+	ϕ-ϕ-ϕ	$\rightleftarrows$	H_2	+	ϕ-ϕ-$\phi\cdot$
34	$Cl\cdot$	+	ϕ-ϕ-ϕ	$\rightleftarrows$	HCl	+	ϕ-ϕ-$\phi\cdot$
35	$H\cdot$	+	ϕ-ϕ-ϕ_{Cl}	$\rightleftarrows$	H_2	+	ϕ-ϕ-$\phi_{Cl}\cdot$
36	$Cl\cdot$	+	ϕ-ϕ-ϕ_{Cl}	$\rightleftarrows$	HCl	+	ϕ-ϕ-$\phi_{Cl}\cdot$
	triphenylene: formation						
37	ϕ-ϕ-$\phi\cdot$			$\rightleftarrows$	$(\phi)\phi_3$	+	$H\cdot$
38	ϕ-ϕ-$\phi_{Cl}\cdot$			$\rightleftarrows$	$(\phi)\phi_3$	+	$Cl\cdot$
	acetylene: formation						
39	$H\cdot$	+	ϕ	$\rightleftarrows$	$n\text{-}C_6H_7\cdot$		
40	$n\text{-}C_6H_7\cdot$			$\rightleftarrows$	C_2H_2	+	$n\text{-}C_4H_5\cdot$
41	$n\text{-}C_4H_5\cdot$			$\rightleftarrows$	C_2H_2	+	$C_2H_3\cdot$
42	$C_2H_3\cdot$			$\rightleftarrows$	C_2H_2	+	$H\cdot$
43	$C_2H_3\cdot$	+	$H\cdot$	$\rightleftarrows$	C_2H_2	+	H_2
44	$C_2H_3\cdot$	+	H_2	$\rightleftarrows$	C_2H_4	+	$H\cdot$
45	$\phi\cdot$	+	C_2H_2	$\rightleftarrows$	ϕ-C_2H	+	$H\cdot$
	naphthalene: formation by deficient polyphenylation						
46	$\phi\cdot$	+	ϕ	$\rightleftarrows$	$\phi\phi$	+	$C_2H_3\cdot$
	naphthalene: formation by acetylene growth						
47	ϕ-$C_4H_4\cdot$			$\rightleftarrows$	$\phi\phi$	+	$H\cdot$
48	ϕ-$C_4H_4\cdot$			$\rightleftarrows$	C_2H_2	+	ϕ-$C_2H_2\cdot$
49	ϕ-$C_2H_2\cdot$			$\rightleftarrows$	C_2H_2	+	$\phi\cdot$
50	ϕ-$C_2H_2\cdot$			$\rightleftarrows$	ϕ-C_2H	+	$H\cdot$

Table 4.9b Numerical data of radical reaction mechanism of thermal hydrodechlorination of chlorobenzene.

nr	ln(k) [(1)]			q	$\ln(K_c)$ [(1)]		Δn	ΔH_r [(1)] [kJ/mol]	source [(2)]	$\tau = 1$ s [(3)]	
	$\ln(k_0)$	E_a/R	p		A	B				rate	type
1	21.06	51.03	0	2	13.52	51.59	1	428.9	a,f	-1.0e-10	-0.34
2	17.60	41.20	0	2	12.60	50.89	1	423.1	a,f	-5.6e-09	-0.45
3	31.16	43.00	0	1	18.63	46.66	1	388.0	a,f	1.5e-05	1.00
4	33.04	48.10	0	1	17.70	54.79	1	455.5	a,f	-1.5e-05	-0.63
5	15.43	2.60	0	2	0.69	-8.29	0	-68.9	a,e,f	1.6e-03	1.00
6	17.50	5.53	0	2	5.66	-4.48	0	-37.3	a,e,f	6.8e-04	1.00
7	14.92	4.08	0	2	4.60	3.47	0	28.8	a,f	-8.0e-04	-0.28
8	16.66	2.25	0	2	0.62	0.50	0	4.1	a,f	3.3e-03	0.06
9	16.21	6.29	0	2	5.10	3.90	0	32.4	b,f	-9.2e-05	-0.25
10	37.10	55.61	0	1	18.82	55.63	1	462.5	b,f	-2.1e-07	-0.46
11	16.81	9.36	0	2	4.97	3.81	0	31.6	b,f	-1.2e-05	-0.21
12	16.12	6.29	0	2	5.85	4.48	0	37.3	b,f	-7.3e-06	-0.09
13	13.94	2.26	-0.12	2	-5.60	-9.70	0	-80.6	b,f	1.2e-03	1.00
14	26.95	16.76	-10.65	2	-6.31	-1.72	0	-14.3	b,f	4.4e-06	0.01
15	12.89	2.01	0	2	-6.22	-1.36	0	-11.3	b,f	-1.4e-03	-0.28
16	22.00	10.05	-5.48	2	-6.72	-2.09	0	-17.3	b,f	-3.2e-04	-0.08
17	13.87	2.23	-0.13	2	-6.02	-10.38	0	-86.3	b,f	3.0e-04	1.00

18	14.41	2.63	0	2	-24.05	-56.25	-1	-467.7	b,f	3.4e-09	0.40
19	12.35	1.53	0	2	-25.14	-57.35	-1	-476.8	b,f	3.3e-10	0.46
20	16.12	5.69	0	2	7.41	-3.44	0	-28.6	b,d,f	4.4e-06	1.00
21	16.52	3.77	0	2	1.11	-7.61	0	-63.3	b,d,f	3.4e-05	1.00
22	16.81	9.36	0	2	5.29	3.47	0	28.8	b,d,f	-2.2e-06	-0.36
23	16.21	6.29	0	2	6.21	4.17	0	34.6	b,d,f	-2.3e-06	-0.24
24	16.81	9.36	0	2	4.30	4.12	0	34.2	b,d,f	-9.3e-09	-0.01
25	16.12	6.29	0	2	4.45	4.17	0	34.7	b,d,f	9.3e-09	0.01
26	34.22	25.85	-17.91	2	-6.71	-1.13	0	-9.4	b,f	-3.1e-05	-0.68
27	13.98	2.36	-0.29	2	-5.47	-8.66	0	-72.0	b,f	1.9e-05	0.99
28	31.34	24.08	-17.34	2	-6.54	-1.72	0	-14.3	b,f	-1.7e-06	-0.68
29	35.00	26.48	-18.29	2	-7.60	-2.76	0	-23.0	b,f	-8.4e-06	-0.65
30	13.98	2.33	-0.26	2	-6.33	-10.32	0	-85.8	b,f	5.3e-06	0.99
31	16.12	5.69	0	2	7.41	-3.44	0	-28.6	b,d,f	3.3e-07	1.00
32	16.52	3.77	0	2	1.23	-6.88	0	-57.2	b,d,f	2.5e-06	1.00
33	16.81	9.36	0	2	5.30	2.76	0	23.0	b,d,f	7.3e-08	1.00
34	16.21	6.29	0	2	6.22	3.47	0	28.8	b,d,f	1.3e-07	1.00
35	16.81	9.36	0	2	4.30	4.12	0	34.2	b,d,f	2.9e-08	1.00
36	16.12	6.29	0	2	4.45	4.17	0	34.7	b,d,f	4.8e-08	1.00

37	27.85	4.46	-2.06	1	2.93	-5.73	1	-47.7	b,d,f	5.4e-07	0.04
38	28.90	4.71	-2.18	1	5.30	-13.82	1	-114.9	b,d,f	7.6e-08	0.99
39	24.12	15.70	-1.87	2	-3.90	10.94	-1	91.0	b,c,f,g	2.6e-07	0.00
40	33.94	20.63	0	1	18.60	20.40	1	169.6	b,c,f,g	2.6e-07	1.00
41	33.45	19.88	0	2	17.34	18.32	1	152.3	c,f,g	2.6e-07	0.19
42	32.71	19.12	0	1	11.26	20.93	1	174.0	c,f	1.6e-06	0.00
43	16.81	0.00	0	2	-2.27	-30.66	0	-254.9	c,f	9.2e-09	0.34
44	15.14	22.19	0	1	-3.69	0.70	0	5.8	c,f	1.5e-10	1.00
45	10.33	-3.90	0	2	-6.48	-3.90	0	-32.4	c,f	6.6e-08	0.01
46	4.51	2.93	0	2	1.41	0.48	0	4.0	d,e,f	1.4e-06	1.00
47	27.85	4.46	-2.06	1	5.76	-6.93	1	-57.6	b,d,f,g	2.7e-08	0.07
48	35.05	20.02	0	1	18.93	18.46	1	153.4	c,d,f,g	-2.7e-08	-0.95
49	32.71	19.12	0	1	17.50	23.81	1	198.0	c,d,f,g	-1.2e-07	0.00
50	27.74	19.78	0	1	10.92	19.78	1	164.5	c,f,g	9.5e-08	0.02

(1)

$$k = k_0\, (T^*)^p \exp(-\frac{E_A/R}{T^*}) \qquad [\ k\text{: } (\frac{m^3}{mol})^{q-1} s^{-1}\ ]$$

$$\ln(K_c) = \frac{\Delta S_r}{R} - \frac{\Delta H_r}{R}\frac{1}{T^*} = A - \frac{B}{T^*} \qquad [\ K_c\text{: } (\frac{m^3}{mol})^{-\Delta n}\ ]$$

$$T^* = \frac{T}{1000} \qquad [\ T^*\text{: } 10^3 K\ ]$$

q	order of forward reaction.
Δn	stoichiometric change of reaction.

(2)

kinetics

a	NIST Chemical Kinetics database [37].
b	Ritter [42,46].
c	Frenklach [24].
d	estimated (by analogy).
e	optimised (this work).

thermodynamics

f	NIST thermodynamical database [52].
g	estimated (by analogy).

(3)

reaction classification (after $\tau = 1$ s under 'concentrated' conditions)

rate:	overall rate (forward minus backward) [(mol/s) / m]
type:	indicating (ir)reversibility or equilibration of reaction;

$$type \doteq \frac{r_{forward} - r_{backward}}{r_{forward} + r_{backward}}$$

$$\begin{array}{lll} type & \approx & 1\text{: } \textit{irreversible to the right} \\ type & \approx & 0\text{: } \textit{equilibrated} \\ type & \approx & -1\text{: } \textit{irreversible to the left} \end{array}$$

Chapter 5

Why does SiC corrode?

experimental observations, theory and modelling

§ 5.1 Summary.

Near the exit of the mini pilot plant reactor frequently a band has been observed, showing exceptional soot formation and severe nickel alloy corrosion. The plausible cause for the band occurrence is the instability of silicon carbide (SiC) under the conditions of thermal hydrodechlorination in the presence of nickel chloride salts. Subsequent reactions lead to the formation of the hump of soot and the severe corrosion of nickel alloys.

The hypothesis of instable SiC is confirmed by experimental evidence from the bench scale installation, information from literature and a computer model predicting the observed peaks.

§ 5.2 Experimental observations.

In the mini pilot plant reactor frequently 'bands' have been observed. Typically, the band occurred at a distance of about 110 cm from the grid. The local temperature can be estimated from the temperature profile and was usually about 700 °C to 800 °C.

The band manifested itself in two different ways:
- a ring of soot was formed on the SiC tube,
- corrosion of nickel alloy thermocouples obviously took place, sometimes resulting in the complete disappearance of the metal surface.

To explain the appearance of the band, the behaviour of the silicon carbide wall material in thermal hydrodechlorination has been investigated in the bench scale installation. A set of experiments has been carried out.

- A slice of the SiC wall from the mini pilot plant reactor has been placed within the bench scale reactor. Subjected to the process conditions of thermal hydrodechlorination, a huge hump of soot appeared at about 23 cm from the entrance of the reactor. The overall soot production considerably increased. From the temperature profile the local temperature is estimated to be about 750 °C to 850 °C.

  The hump was located at just one side of the SiC slice. Actually, this side had already served as wall surface in the mini pilot plant reactor. At the side of the saw-cuts, with newly generated surfaces, no soot was observed!

- A slice of 'fresh' unused SiC has been tested under the same conditions. No hump of soot appeared. The observed soot production was limited, but a little bit larger than if no SiC was present.

- The same slice as in the first experiment has been placed within the bench scale reactor. This time, the process conditions of thermal hydrodechlorination were simulated; 37 wt% hydrochloric acid was supplied instead of chlorobenzene. No actual humps were formed, but two corrosion zones were observed. Additionally to the zone observed before at the exit of the reactor, a second band appeared at the entrance (at about 4 cm from the top, the local temperature being about 800 °C). The corrosion zones only appeared at the SiC surface which already had been wall surface in the mini pilot plant reactor.

Table 5.1 *Experiments in bench scale installation in relation to silicon carbide SiC corrosion.*

experiment description	soot production (1)
standard thermal hydrodechlorination conditions.	0.19
SiC, retrieved from the mini pilot plant reactor.	1.03 - 2.72
'fresh' SiC.	0.69
SiC, retrieved from the mini pilot plant reactor; thermal hydrodechlorination simulated by feeding 37 wt% hydrochloric acid (HCl).	0.01
quartz grid	1.12
Al_2O_3	0.16

(1) The soot production is defined as the observed soot mass divided by the fed mass of chlorinated substance.

- Additional experiments were carried out with relatively porous materials, like a quartz grid material and ceramic Al_2O_3. These experiments were performed to investigate the effect of surface structure upon the formation of soot, and in particular the hump of soot. In both cases no hump of soot was observed. No increase in the soot production was noticed with ceramic Al_2O_3, in the case of the quartz grid a relatively large increase was observed.

Additional information is obtained by XRF analysis, indicating the surface composition of the SiC specimen. The results are given in table 5.2. It should be emphasized that the results are indicative, due to the physical structure of the analysed specimen and the incapability of the analytic method to measure the carbide fraction.

Table 5.2 *XRF analysis of the SiC specimen (1). Due to the physical structure of the specimen and the impossibility to measure the carbide fraction (2), the analytical results are indicative.*

specimen	Si	Co	Ni	Cl
'fresh' SiC				
• unused	68.9	<(3)	<	0.12
• after subjection to thermal hydrodechlorination.	69.3	<	0.011(4)	0.11
SiC from mini pilot plant reactor:				
• original wall surface	66.5	0.11	0.41	0.51
• surface of saw-cut	68.5	<	<	0.20

(1) The composition data are given in wt%.

(2) The carbide content is estimated to be 29.95 wt%, according to literature [13].

(3) below detection limit.

(4) in the order of the noise level.

§ 5.3 Explication of the band occurrence.

The occurrence of the band is attributed to the reaction of silicon carbide, SiC, with the dechlorination product hydrogen chloride, HCl.

$$SiC_{(s)} + 4HCl_{(g)} \rightleftarrows SiCl_{4_{(g)}} + 2H_{2_{(g)}} + C_{(s)} \qquad (5.1)$$

Other silanes than $SiCl_4$ may be formed from SiC as well, as indicated by the following overall reaction equation.

$$SiC_{(s)} + p\ HCl_{(g)} \rightleftarrows SiCl_pH_{4-p\,(g)} + (p-2)\ H_{2_{(g)}} + C_{(s)} \qquad (5.2)$$

From a thermodynamical point of view, $SiCl_4$ is most probably formed, as illustrated in figure 5.1. The figure also shows that the equilibria shift to the left if the temperature is increased.

By the reaction silicon carbide is corroded and carbon is formed. However, it can not explain the measured increase of mass; by the reaction the solid state mass is decreased. However, the carbon produced forms a nucleus for further soot growth by subsequent reactions with chlorinated hydrocarbons, effectuating an overall increase of mass.

The question remains why the SiC corrosion occurs that locally. On the basis of figure 5.2 this will be explained.

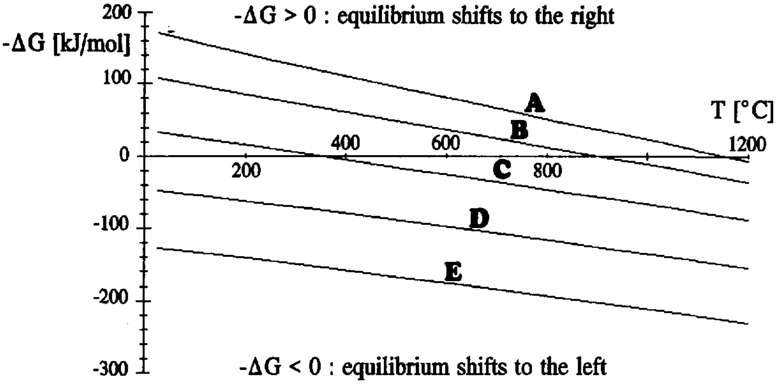

Figure 5.1 *Gibbs free energy change for SiC corrosion reactions (see equation 5.2).* [1,5]
A: p=4; B: p=3; C: p=2; D: p=1; E: p=0.

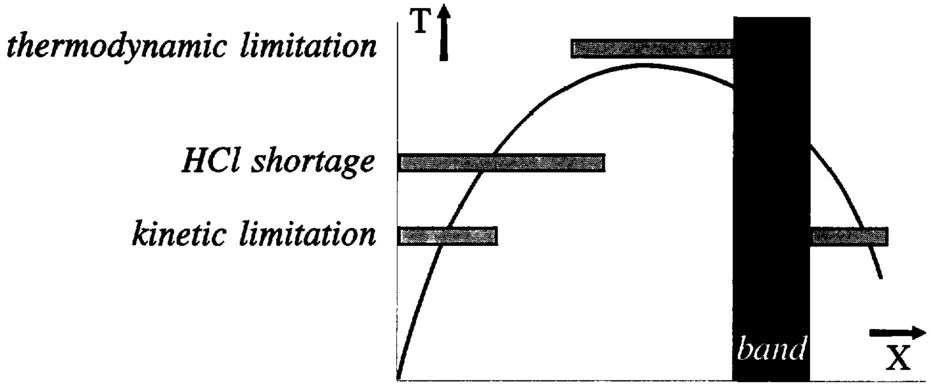

Figure 5.2 *Schematic explanation of local occurrence of SiC corrosion front.*

Due to the exothermal nature of the reaction, the equilibrium constant of the reaction 5.2 decreases with an increase of temperature. [1,5]

$$K_{eq.} = 1.722 \cdot 10^{-9} \exp(\frac{25270}{T}) \quad mol/m^3 \qquad \textbf{(5.3)}$$

Thus, lower temperatures are enhancing from a thermodynamical point of view, as they shift the equilibrium constant to the left. On the other hand, at higher temperatures the kinetical rate increases. As a result, a maximum exists for the overall corrosion rate as a function of temperature.

In the reactor a temperature profile exists. From the elevated temperatures in the middle of the reactor the temperature decreases, passes through an optimum according to the corrosion reaction and diminishes to a level at which no reaction occurs. The temperature optimum causes a local acceleration of the corrosion, effectuating a local excessive soot production by which the hump of soot is formed.

At the entrance side of the reactor a similar optimal temperature is encountered. However at this spot no or a too limited amount of HCl has yet been produced. At this spot the corrosion reaction can not take place. If HCl is deliberately added, as in the simulation experiment with hydrochloric acid, all ingredients are already present at the entrance, resulting in corrosion at that spot as well.

§ 5.4 SiC corrosion model.

A model has been developed to describe the local acceleration of the SiC corrosion reaction. Basis of the corrosion model is the overall hydrodechlorination model, which describes the dechlorination of chlorobenzene in a non-isothermal plug flow reactor, using the overall dechlorination rate according to Manion [8] (see paragraph 4.2). The original model, which only takes into account homogeneous gas phase reaction, is extended with the gas solid reaction occurring at the wall of the reactor tube according to:

$$SiC_{(s)} + 4HCl_{(g)} \longrightarrow SiCl_{4_{(g)}} + 2H_{2_{(g)}} + C_{(s)} \tag{5.4}$$

As shown by its heat of reaction, the reaction is exothermal.

$$-\Delta H_r = 210\ kJ/mol \tag{5.5}$$

Gaseous reactants and products are being transported to and from the wall. This transport is assumed to be diffusion controlled, taking place in the film layer covering the wall. A schematic representation of the model is given in figure 5.3.

To simplify the model only the diffusion limitation for the product silicon tetrachloride ($SiCl_4$) is regarded. This simplification is permissible for the following reasons.

- The corrosion reaction is rather small in comparison to the main hydrodechlorination reaction. The concentration of $SiCl_4$ produced will be small relative to concentration of the bulk species H_2 and HCl. The relative concentration change in the film layer will be far more pronounced for $SiCl_4$ than for the bulk species.

- As for H_2, besides its appearance in bulk concentration, its large diffusion coefficient contributes to an even smaller concentration gradient in the film layer.

The wall concentrations of H_2 and HCl are approximated by their bulk concentrations.

In the model steady state conditions are assumed.

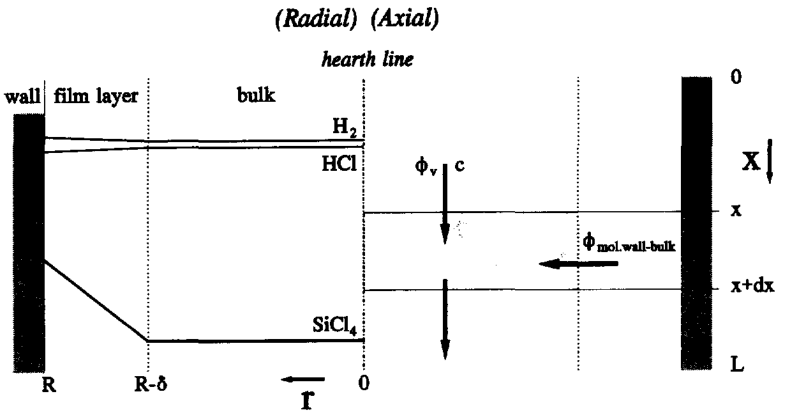

Figure 5.3 Schematic representation of the SiC corrosion model.

For $SiCl_4$ no reaction occurs in the film layer. Setting up a mass balance over a thin slice of the film layer leads to an expression for the molar flow.

$$-\mathbb{D}_{SiCl_4}\left(A\frac{\partial c}{\partial r}\right)\Big|_{r+dr} = -\mathbb{D}_{SiCl_4}\left(A\frac{\partial c}{\partial r}\right)\Big|_{r} = \Phi_{mol.SiCl_4} \tag{5.6}$$

The concentration of $SiCl_4$ at the begin and end of the layer respectively are the concentration at the wall and the concentration in the bulk.

$$\begin{aligned} r = R &: \quad c_{SiCl_4} = c_{wall} \\ r = R-\delta &: \quad c_{SiCl_4} = c_{bulk} \end{aligned} \tag{5.7}$$

From these equations a differential equation for the $SiCl_4$ concentration in the film layer is derived.

$$r\frac{\partial c}{\partial r} = constant = \frac{c_{wall}-c_{bulk}}{\ln(\frac{R}{R-\delta})} \tag{5.8}$$

This leads to a new expression for the molar flow through the film layer.

$$\Phi_{mol.SiCl_4}\Big|_{wall-bulk} = 2\pi\mathbb{D}_{SiCl_4}\Delta x\,\frac{c_{wall}-c_{bulk}}{\ln(\frac{R}{R-\delta})} \tag{5.9}$$

At the wall surface the corrosion reaction takes place. In the steady state all $SiCl_4$ produced is transported through the film layer; the production rate and the molar flow through the film layer are equal, leading to the following expression:

$$rate = \mathbb{D}_{SiCl_4} \frac{c_{wall} - c_{bulk}}{R \ln(\frac{R}{R-\delta})} \tag{5.10}$$

The kinetics of the $SiCl_4$ production are unknown. Following the stoichiometric factors, next equation is assumed.

$$rate = k_1 \, c^4_{HCl.wall} - k_{-1} \, c_{SiCl_{4.wall}} \, c^2_{H_{2.wall}} \tag{5.11}$$

By doing so, the forward and backward reaction rate constants are directly related by the thermodynamical equilibrium constant:

$$K_{eq.} = \frac{k_1}{k_{-1}} \tag{5.12}$$

Combining these equations, while assuming that the wall concentration of H_2 and HCl are equal to their bulk concentration, an expression is derived for the production rate of $SiCl_4$ in which no wall concentrations appear.

$$rate = \frac{k_{-1} \, (K_{eq.} \, c^4_{HCl} - c_{SiCl_4} \, c^2_{H_2})}{1 + k_{-1} \, c^2_{H_2} \, \frac{R}{\mathbb{D}_{SiCl_4}} \, \ln(\frac{R}{R-\delta})} \tag{5.13}$$

Through the film layer the $SiCl_4$ produced is transported into the bulk stream of the plug flow reactor. The bulk concentration of $SiCl_4$ changes accordingly. The actual change is expressed by the mass balance over a thin slice of the bulk stream, leading to the following expression:

$$\frac{\partial}{\partial x}(\phi_v \, c_{SiCl_4}) = \phi_{mol.SiCl_4} \big|_{wall \longrightarrow bulk} \tag{5.14}$$

The above mentioned equation are implemented in the overall thermal hydrodechlorination computer program. The required model parameters are validated as follows.

- The equilibrium constant of the equation is calculated from thermodynamical properties.

$$K_{eq.} = 1.722 \cdot 10^{-9} \exp(\frac{25270}{T}) \quad mol/m^3 \tag{5.15}$$

- The kinetical factors are unknown. In the model they have been varied, assuming an Arrhenius type of expression. The best results have been obtained assuming the following kinetical function for the backward reaction:

$$k_{-1} = 10^{13} \exp(-\frac{45000}{T}) \quad m^7/mol^2s \tag{5.16}$$

- The diffusion coefficient of $SiCl_4$ in the reaction medium can be calculated using following estimation: [2,10]

$$\mathbb{D}_{SiCl_4} = 1.575 \cdot 10^{-8}\, T - 0.6893 \cdot 10^{-5} \quad m^2/s \tag{5.17}$$

- The thickness of a film layer in the reactor is estimated using the expression appropriate for the laminar flow in the reactor pipe: [6]

$$Sh = \frac{kd}{\mathbb{D}} = \frac{d}{\delta} = 3.66 \tag{5.18}$$

With the kinetical factors properly chosen, the model is capable to predict the observed peaks (see figures 5.4 and 5.5):

- the single peak which occurred under conditions of thermal hydrodechlorination in the mini pilot plant reactor and the bench scale reactor,

- the double peak which was observed in the bench scale reactor when hydrochloric acid was fed instead of chlorobenzene.

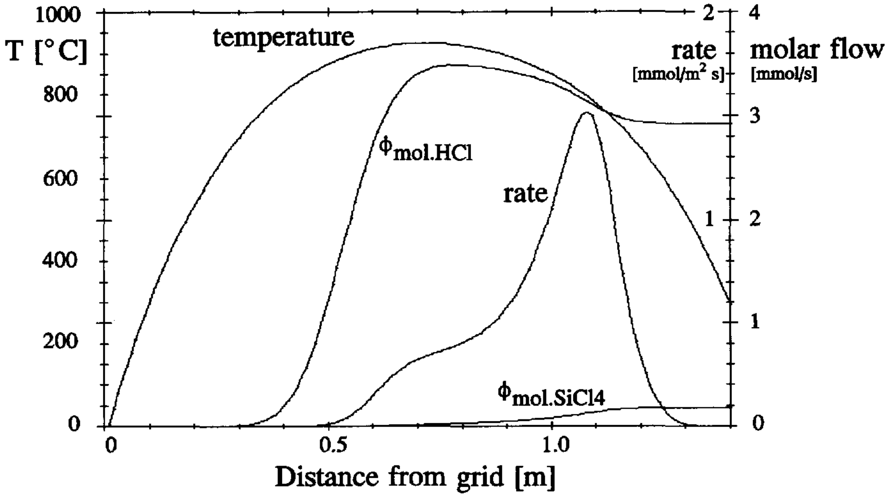

Figure 5.4 *Calculated axial profiles through mini pilot reactor (chlorobenzene fed). Rate: production rate of $SiCl_4$ [mmol/m²s].*

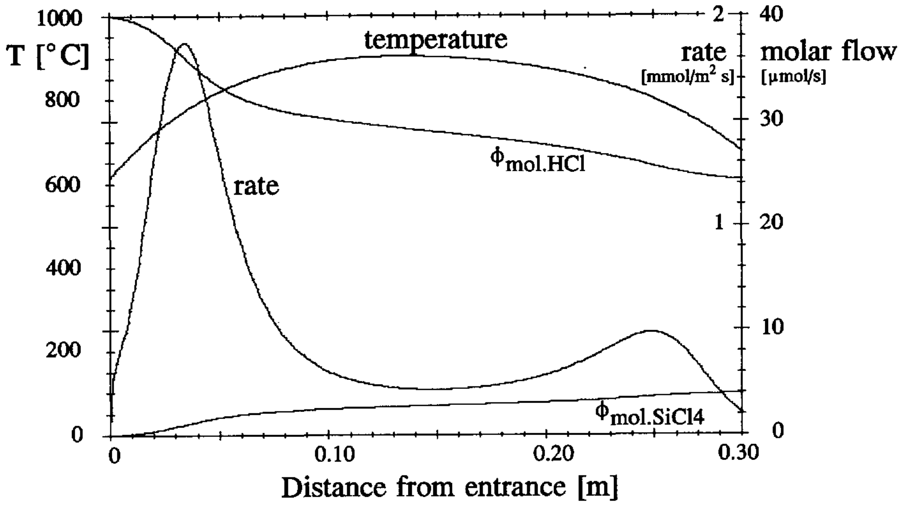

Figure 5.5 *Calculated profiles through bench scale reactor with hydrochloric acid fed. Rate: production rate of $SiCl_4$ [mmol/m²s].*

§ 5.5 Catalytic nickel influence on the SiC corrosion.

Not all SiC specimen produce a hump of soot (see table 5.1). Whereas, after being exposed in the bench scale installation, the mini pilot plant SiC showed the hump of soot, the 'fresh' SiC did not. Analysis of the surface elucidates another difference: the mini pilot plant SiC is contaminated with Ni and Co, while the 'fresh' SiC carries none of these elements. Probably, nickel and cobalt are deposited on the former wall surface as chloride salts. These salts originate from corrosion of the Nimonic housing and the Hastelloy thermocouples by the thermal hydrodechlorination product HCl.

The nickel and cobalt chloride salts apparently possess catalytic properties, accelerating SiC corrosion. This view is confirmed by the German patent [3,14], covering the production of $SiCl_4$ by reaction of SiC and HCl. The invention of the patent is enclosed in the addition of nickel and/or cobalt chloride salts as catalysts! As stated by the patent the production of $SiCl_4$ from SiC and HCl is thermodynamically attractive. However, without any Ni or Co chloride catalyst present the reaction rate is far too slow. Over a Ni or Co chloride catalyst the conversion can be almost complete (up to 99.5 wt%). Appropriate conditions need to be chosen including temperature and molar ratio of the reactants. According to the patent the temperature must be in between 600 °C and 900 °C; the typical temperature of examples given in the patent is 700 °C.

The patent makes a remark about a strange phenomenon. The normally rather volatile Ni and Co chloride salts, certainly at temperatures about 700 °C, lose this pronounced transport activity in contact with SiC; they tend to remain on the SiC surface.

The required presence of the catalytic chloride salts also explains why the mini pilot plant SiC has its soot hump only attached to the former wall surface side, and not to the sides of the saw-cut. As clarified by the XRF analysis the surface of the saw-cut contains only a very limited amount of Ni and Co salts.

§ 5.6 Explication of nickel alloy corrosion.

As stated, the SiC corrosion resulted in two band phenomena:

- abundant local soot formation, provoked by the formation of soot nuclei,
- severe local nickel alloy corrosion.

The second phenomenon is probably caused by a subsequent reaction of the $SiCl_4$ produced with Ni. Two different types of reaction are possible, each leading to a different set of products:

- formation of nickel chloride salts ($NiCl_x$),
- formation of nickel silicide compounds (Ni_ySi).

Suppose the corrosion is caused by the first type of reaction, e.g.

$$SiCl_4 + Ni + H_2 \longrightarrow Si + NiCl_2 + 2HCl \tag{5.19}$$

Summation of this reaction and the reaction in which $SiCl_4$ is produced, leads to the next overall reaction:

$$SiC + Ni + 2HCl \longrightarrow Si + C + NiCl_2 + H_2 \tag{5.20}$$

This overall reaction can be interpreted as the summation of nickel corrosion by HCl accompanied by SiC dissociation. Because the SiC dissociation is unfavourable at the temperature of concern, the overall reaction is less attractive than solely the corrosion of Ni by HCl. From this point of view, it unlikely that the catalysed chlorination mechanism causes the observed accelerated corrosion.

The nickel corrosion is probably due to the formation of rather stable Ni Si compounds. According to thermodynamics the formation of Ni Si compounds becomes attractive at the temperatures of concern. The overall reaction is depicted below.

$$SiCl_4 + qNi + 2H_2 \longrightarrow Ni_qSi + 4HCl \tag{5.21}$$

Figure 5.6 presents the Gibbs free energy change of some Ni corrosion reactions. Thermodynamically, the formation of Ni_3Si is the most favourable of all Ni Si compounds.

Obviously, Si and Ni have some particular interaction. This is also demonstrated by other studies:

- Ni/SiC catalysts exhibit unusual chemisorption behaviour, [12]
- in joining SiC ceramics with metals extraordinary behaviour is observed in case nickel is joined, [5]
- nickel chloride salts normally demonstrate a large volatility, but in the presence of SiC their transport activity is suppressed. [14]

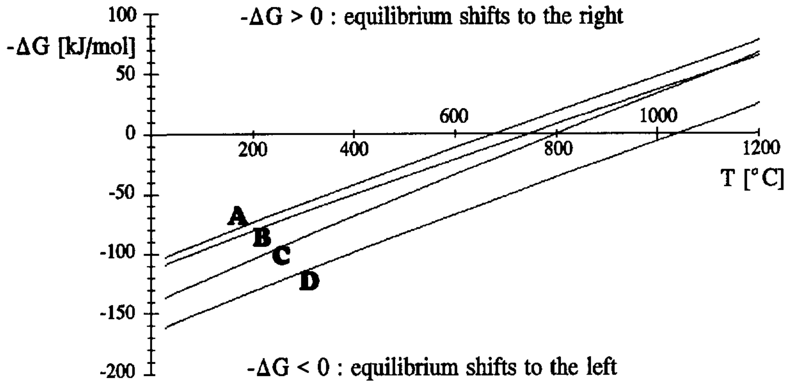

Figure 5.6 *Gibbs free energy change for nickel corrosion reactions with $SiCl_4$ (see equation 5.21).* [1,5] *A: q=3; B: q=2; C: q=1.5; D: q=1.*

By the corrosion some Cl is bonded into an inorganic compound other than HCl. This may lead to a wrong (conservative) indication of the dechlorination level if it is determined by HCl titration. However, the following should be noted.

- The chlorine of that fraction of the $SiCl_4$, which is involved in the corrosion of nickel alloys, is recovered as HCl as demonstrated by reaction equation 5.21.

- The remainder of the $SiCl_4$ is sampled in the water of the titration system. $SiCl_4$ dissolves and is converted into SiO_2 according to the following equation:

$$SiCl_4 + 2H_2O \longrightarrow SiO_2 + 4HCl \qquad \textbf{(5.22)}$$

  As can be seen, by the reaction HCl is reproduced.

Therefore, the effect of SiC corrosion on measuring the dechlorination measurement by titration is very limited and can be neglected.

§ 5.7 Conclusions.

The strange band phenomena observed in the mini pilot reactor are due to corrosion of silicon carbide. Silicon carbide happens to react with hydrogen chloride, resulting in activated zones for soot production and forming chlorinated silanes that aggressively attack nickel alloys. The reaction with HCl has a noticeable effect only if a nickel containing activator or alike is present.

In the mini pilot reactor a combination of high quality nickel alloy and high quality ceramic has been chosen to solve problems related with corrosion and construction. As stated, this 'unique' combination resulted in the unexpected and unfortunate behaviour (see figure 5.7). It is uncertain whether this behaviour also is provoked by metal contaminants of the feed.

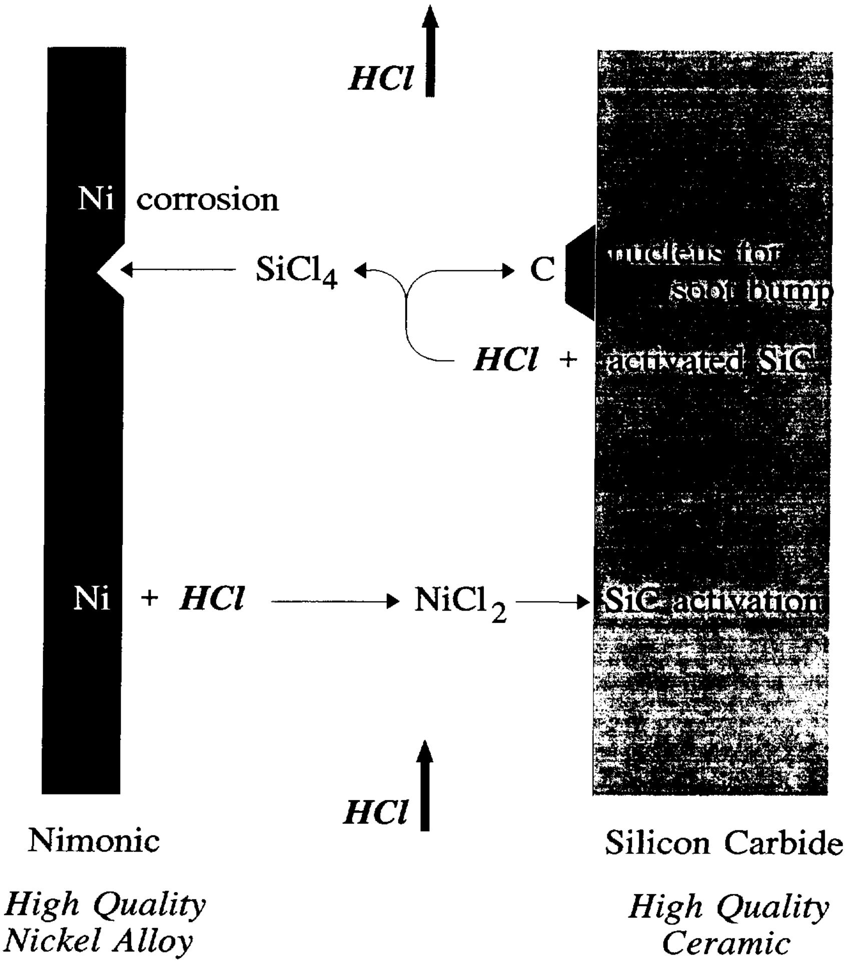

Figure 5.7 *Reactions taking place effectuating band phenomena.*

The final conclusion is to avoid silicon carbide in the reactor.

At this place it is interesting to notify a remarkable spin off of the present research study. As demonstrated, nickel largely affects the HCl induced conversion rate of SiC into C. In thermal hydrodechlorination, this has the rather dramatic consequence that SiC can not be used as construction material. However, the catalytic nickel effect happens to be very useful in another study. This study [9] investigates the possibility to increase the strength of active coal, e.g. to allow application at elevated temperatures in oxidative conditions. The objective is met by converting the active coal into 'active SiC', in which the catalytic properties of nickel have proven to be very useful.

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Chapter 6

Design of an industrial plant to treat chlorinated waste

flowsheet, apparatus choices, economics

§ 6.1 Introduction.

Under auspices of the Royal Schelde (RS) an industrial plant has been designed to treat 22.000 ton/year chlorinated waste. The purpose of the plant is to convert the waste in clean hydrocarbons and hydrogen chloride (HCl). The hydrocarbon product can at least be used as a fuel, HCl is upgraded to concentrated (33 wt%) hydrochloric acid. An alternative is the production of anhydrous hydrogen chloride, having a higher economical value. In the designs the results of this study and those at labscale [37,38] are implemented.

The work has been carried out by various project teams. Based on our experimental experiences, we contributed to the design with advise, particularly with respect to reactor and quench. The design is licensed by Royal Schelde.

In the forthcoming paragraphs some design considerations and an impression of both plants will be given.

§ 6.2 Elementary process choices.

§ 6.2.1 Basic assumptions.

The main objective of the design is to create a reliable installation. Sometimes choices can be made between new or recently developed technologies which have prosperous economical and environmental features, and older technologies which comprise proven and reliable unit operations. To ensure reliability the RS design preferentially uses this kind of proven technologies.

Principal assumptions that underlay the industrial plant design, are following. [11]

- The design is based on a model waste, consisting of equal parts of dichloropropane and -propene, trichloropropane and chlorobenzene.
- The plant is designed to treat 0.85 kg/s waste (22.000 ton in 300 days of continuous operation).
- Rate kinetics are applied according to Manion [33]; soot formation is taken to be 1-2 wt% of the feed.
- Fuel gas and 33 wt% concentrated hydrochloric acid are the products aimed at.

The model waste is chosen since it comprises

- a considerable chlorine content (58 wt%),
- a significant aromatic fraction (25 mol%),
- and a mixture of notoriously soot producing substances (unsaturated aliphatics and aromatics).

***Table 6.1** Properties of the design model waste. Model waste consists of equal parts of dichloropropane (DCP^{ane}), dichloropropene (DCP^{ene}), trichloropropane (TCP^{ane}) and chlorobenzene (MCB).* [12]

species	DCP^{ane}	DCP^{ene}	TCP^{ane}	MCB	Model Waste
molar weight [g/mol]	113	111	147.4	112.5	121
Cl content [wt%]	63	64	72	32	58
aromatic fraction [mol%]	0	0	0	100	25
density [10^3 kg/m^3]	1.16	1.19	1.39	1.11	1.18
boiling point [°C]	370	350	429	405	389

The isolation of HCl from the reactor flue gases into concentrated hydrochloric acid seems relatively simple and straightforward. An alternative is the production of anhydrous hydrogen chloride. Especially if in the neighbourhood a HCl consuming industry exists, like oxychlorination plants, the production of anhydrous hydrogen chloride improves the economical benefit of the process. Therefore the decision which is the best chlorine product, depends on the actual location. For reasons of flexibility and simplicity, the RS design aims at the production of hydrochloric acid. Both the RS design and the alternative will be discussed in this chapter.

Other basic choices that were needed in the plant design, are discussed in the next paragraph. Options to collect and remove soot and tar are discussed in the paragraph next to that (6.2.3).

§ 6.2.2 General process choices.

General process choices are discussed below.

- High dechlorination levels are required. A conversion degree near thermodynamical equilibrium is aimed at. Higher temperatures increase the reaction rate, but also shift the exothermic equilibrium to the left. A consideration of temperature level and required reactor volume against obtainable conversion degree has to be made.

  In this respect the implementation of a recycle stream seems promising. It requires a lower conversion per reactor pass. Nevertheless, the recycle demands the separation of products and yet unconverted substances. In this case the separation is complicated because of the complexity of the mixture and diversity of product groups (hydrogen and chlorinated hydrocarbons versus hydrogen chloride and hydrocarbons). No proven technology is known to achieve this separation in a simple step. Conceivably, adsorption on active coal offers good prospects, but before actual implementation further investigation is needed to verify usefulness and reliability of this technique [26]. Therefore, the RS design does not consider a recycle and aims at a high dechlorination level per reactor pass.

- Some hydrogen sources are considered: [11]
  - 'pure' hydrogen gas (> 90 vol% H_2),
  - steam reformer gas (≈ 50 vol% H_2),
  - catalytic reformer gas (≈ 80 vol% H_2),
  - coal/oil gasification gas (20-50 vol% H_2).

  Besides H_2, these gases chiefly consist of CO, CO_2 and CH_4. These species do not interfere with the dechlorination chemistry [33].

The actual choice depends on the location site, e.g. whether hydrogen is available from a neighbouring plant. Another aspect to be considered is invoked by the heat requirements of the plant. As will be discussed below, the chlorinated waste is heated to reaction temperature by the hydrogen gas. Therefore, the heat content of the gas must be large enough to fulfil this requirement or the excess H_2 should be large enough to allow partial oxidation. The heat content of the gas is determined by its heat capacity and temperature. In this respect the presence of chemically inert contaminants like CO, CO_2 and CH_4, is favourable since they considerably add to the heat capacity of the gas.

In the RS design, a steam reformer is used to produce hydrogen gas, because of its high hydrogen content and satisfactory heat content.

Also the synthesis gas from oil gasification might be considered. An advantage of syngas is that its heat content usually is higher than that of the reformer gas [11,38]. Also, the gasification process comprises the opportunity of a closed loop with respect to soot and tar handling. In that case all soot and tar are to be collected in oil, after which the contaminated oil has to be recycled to the gasification unit [22]. Yet, too little is known about the soot and tar collection in oil for a reliable design based on this recycling principle.

Another point of consideration is the possibility of a hydrogen recycle. The recycle of unused hydrogen decreases the overall hydrogen demand. Implementation of a recycle is especially attractive, as a larger excess of hydrogen is used. A larger hydrogen excess results in more reductive reaction conditions, effectuating reduced soot formation. Depending on the wall influence, the dechlorination rate is slightly accelerated or declined (see paragraph 4.5). The required hydrogen separation may be realised by pressure swing adsorption (PSA) or membrane technology [40].

The unused hydrogen may be recycled to the hydrogen generation unit instead of to the thermal hydrodechlorination (THD) reactor. The gas heat content contributes to the heat requirements of the generator. Less fuel is needed if the same temperature is employed; or, if the additional heat is used to increase the temperature, the endothermic equilibrium is shifted to the right, i.e to the production side of hydrogen. Nevertheless, exploring calculations indicate only small effects, unless CO and CO_2 are removed from the recycle. [11]

In the RS design the hydrogen recycle remains optional.

- The chlorinated waste must be heated to reaction temperature. After the reaction medium has reached the reaction temperature, the heat required to initiate the chemical reaction, i.e. the production of initial radicals, is negligible small (see chapter 4). In the empty tube reactor configuration the reaction heat produced by the exothermic dechlorination can not be used to heat the feed. Therefore, the heat must be supplied by an external source. After exploration of various methods two options remain to supply the demanded heat.

  1) The synthesis gas contains sufficient heat to bring the mixture to reaction temperature. The method offers a simple solution to the heating problem, which is favourable from an exergetical viewpoint. However, a drawback of the method is the entanglement of heat and mass flows, declining the flexibility of the overall system. Because of its simplicity, this option has been chosen in the RS design. If necessary, the system flexibility is enlarged by warming the waste to a temperature just below the boiling point before it is injected.

  2) The flexibility is largely improved if the heat is generated in situ. In this view, heat production by partial oxidation of the excess hydrogen is attractive. However, this method requires stringent safety demands due to explosion risk and the risk of the formation of undesired products. If added oxygen reacts with chlorinated hydrocarbons instead of with hydrogen, so called PICs, like dioxins, may be formed. A proper mixing of oxygen and hydrogen is required.

     An additional advantage of oxygen suppletion may be an accelerated dechlorination rate. According to the experimental observations by Ritter [41,42,43] addition of small amounts of oxygen increases the dechlorination rate. Nevertheless, as discussed in chapter 4, the extent of acceleration presumably depends on the initial chlorinated hydrocarbon concentration. Under the relatively concentrated conditions of concern ($H_2/Cl \approx 3$) the effect of oxygen addition is uncertain.

     In the RS design, the option of oxygen suppletion is not incorporated for reasons of safety and simplicity.

- The gases that leave the reactor, need to be quenched for a set of reasons.
  - Rechlorination must be prevented. Since addition of HCl to unsaturated bonds favourable occurs at temperatures between 300 °C and 500 °C[1], the gases leaving the reaction zone must quickly pass this temperature region [37].
  - The use of a heat exchanger is troubled with the potential danger of obstruction and malfunctioning due to soot, tar and metal salt deposit. Also the choice of construction material is difficult because of the elevated temperatures, large temperature differences and the aggressive media (hydrogen and hydrogen chloride -in gas phase and as water solution-).

Heat recuperation certainly benefits the economics of the process. However, at this stage of development the use of a sophisticated heat exchanger is beyond scope. Systems based on high temperature cyclones [36] or systems like the Shell Waste Heat Boiler used in oil gasification plants [5,8,28,51] reveal promising features with respect to heat recuperation.

- At the entrance of the reactor heat is supplied to bring the chlorinated waste to reaction temperature; in the quench directly after the reactor, heat is quickly removed from the reaction medium. In the construction of reactor and quench measures must be taken to prevent the risk of heat extinction. If too much heat is removed, the reactor temperature decreases leading to insufficient dechlorination.

- Based on a comparison with similar processes, like (hydro-) gasification and hydroalkylation, a positive effect of pressure is expected. Theoretically two major advantages are foreseen.

  - At higher pressures a smaller reaction volume is sufficient. The gas is compressed and the chemical kinetics are increased. As the dechlorination rate is about proportional to the square root of the pressure (assuming equilibrated hydrogen dissociation), the overall volume reduction follows

$$V \propto p^{-1.5} \tag{6.1}$$

  - At higher pressures the soot and tar formation is reduced. This can be seen, for example, in the next equation.

$$C_{(s)} + 2\ H_{2(g)} \rightleftarrows 1\ CH_{4(g)} \tag{6.2}$$

  At higher pressures the equilibrium shifts to the right, from solid carbon to gaseous methane.

On the other hand, the construction of pressurised apparatus is more difficult, so extended safety precautions need to be taken.

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[1] For the incineration off gases, in which O_2 and fly ash are present, this is the favourable temperature for dioxins formation. [29,30]

Due to the promising expectations of pressure, the RS plant was originally designed under pressure. During the design period, the results became available of pressurised labscale experiments, that were carried out at the Gorlaeus Laboratory to confirm the theoretical expectations [32,38]. Compared to the atmospheric experiences similar temperature and residence time appear to be needed. Relatively more lighter compounds (C_1 and C_2) are formed. Conform expectations, the aliphatic product fraction is more saturated; only small amounts of or no acetylene is found. On the other hand, also more polycyclic aromatics, like naphthalene, happened to be produced. Soot and tar still are observed. These experimental observation put question marks to the usefulness of an elevated pressure. Therefore, the RS demonstration unit, under construction in spring 1993, is operated under atmospheric conditions.

The credit of pressure actually depends on the subsequent parts of the installation, e.g. if the produced HCl is used for vinylchloride manufacturing, which process operates at an elevated pressure.

§ 6.2.3 Process choices concerning soot collection and removal.

Soot and tar which are emitted from the reactor, need to be collected. First, some options of collection before the quench have been considered.

- *Separation by mechanical means.*
  Filters and cyclones separate solids larger then 1 μm from gas flows with an efficiency of about 90-95% [4]. However, their application does not seem fruitful in this process. Experimental experience with cyclones indicate an prominent chance of obstruction. The softness of the soot and stickiness of the tar deteriorate the cyclone operation. Filters have a better prospect, as demonstrated in the experimental pilot plant. Nevertheless, filters need periodical cleaning, which may require complete shut-down regarding the location of the filters. Also the elevated temperature involves some problems, like choice of construction material and the liquid aggregation state of tar.

- *Separation by electrostatic filters.*
  Electrostatic filters are used in incineration processes [4,8]. The system is capable to collect particles as small as 0.1 μm, and has a very high efficiency of about 99.9%. The power consumption is relatively small [4]. However, its application in the process of concern does not seem fruitful, either, as the operation temperature may not exceed 350 °C. At higher temperatures the collection efficiency drops and deposit and corrosion by metal chlorides may occur [4]. Also, the collection efficiency is very sensible to the condition of the particles, i.e. their conductivity, electrical charge and related properties like moisture content. Besides that, the safety requirements involved in the high voltage operation are unattractive. [3,4]

In general, soot collection at elevated temperatures is difficult. Also, at higher temperatures tar may be still gaseous or liquid. Therefore gas/solid or gas/liquid separation of soot and tar before the quench does not seem feasible.

Part of the soot and tar will remain in the quench. Then, the best option is to collect all soot and tar in there. Various options have been reviewed.

- ***Washing with water (solution).***
  The soot particles and solid or liquid tar droplets can be separated from the gas stream by washing with water or a water solution like hydrochloric acid. Basically two ways can be distinguished in which the reactor off gas stream and the washing liquid contact.

  - **Disperse gas phase, continuous liquid phase.**
    The reactor effluent gas bubbles trough the water phase, like in the bench scale immersion quench (see chapter 3). The surface of the gas bubbles forms the exchange area between liquid and gas phase. The exchange area is determined by the number and size of gas bubbles.

    According to experiences in the bench scale installation the soot and tar collection efficiency during the transport through the water phase, is low. Similar inefficiency is experienced in the immersion quench of the Akzo incinerator (see paragraph 6.4.2). If during misoperation any soot is formed in the combustion chamber, it is not captured in the immersion quench, but it is emitted as black smoke from the exhaust pipe [34].

  - **Continuous gas phase, disperse liquid phase.**
    In this case, the liquid is sprayed into the gas stream. The surface of the liquid droplets determines the exchange area.

    A liquid spray is an efficient way to separate soot from gas streams. E.g. sprayers are used as soot collectors in the Shell Gasification Process (SGP) [18,28]. Not only the solids are hit by the liquid droplets, but also they serve as nuclei for condensation of water vapour. This phenomenon increases the collection efficiency [18,28]. In the SGP process, the usual 3 wt% soot in the gas is typically reduced to less then 1 ppm after scrubbing [28].

- ***Use of gravity.***
  Bench scale experiments indicate that the soot particles relax in the freeboard of the quench (see paragraph 3.2.3). Apparently, the velocity of upward streaming gas has to drop below a certain value before relaxation occurs. An upward gas flow does not carry soot particles if its velocity is below a critical value, which is known as the elutriation velocity. Under that condition, the soot particles will tend to fall down, realising simple separation from the gas stream. The velocity of a gas bubble in the quench liquid apparently exceeds the elutriation value.

  This method of separation, especially in combination with countercurrent spraying, offers very promising prospects.

- ***Washing with oil.***
  Instead of water or a water solution, oil or an other hydrophobic hydrocarbon may be used as a spray. Soot and tar more easily suspend and dissolve in these organic liquids, as indicated by the bench scale experiments (see paragraph 3.2.3).

  Using an organic liquid as quench medium does not seem favourable, mainly due to the presence of HCl, as will be discussed later on (see paragraph 6.4.2). However, addition of small amounts of hydrocarbons to the quench water may increase the soot collection efficiency.

After consideration of the various options, in the RS design the soot is collected by countercurrent scrubbing with hydrochloric acid, making advantage of gravity.

After collection the suspended soot and tar need to be separated from the water. According to bench scale experiences the soot mainly floats on the water surface. Only a limited fraction sinks. Therefore, most soot can be removed by skimming off the upper layer of the liquid, which contains the floating soot. The small fraction of descended soot can be removed periodically from the bottom of the quench.

An organic layer may be formed as result of the addition of oil to the spray liquid or the condensation of hydrocarbon product in the gas. The existence of such a layer may facilitate the soot and tar removal. Bench scale experiments indicate that if an organic layer is present, all tar dissolves in that phase, and that all soot, floating or sinking, remains in it. Both tar and soot are easily removed by tapping the immiscible organic layer from the water layer.

The addition of this kind of organic liquids is a proved method in soot removal systems. E.g. in the Shell Pelletizer System [22,54] an oil is added to agglomerate the small soot particles into larger pellets, which afterwards are separated with more ease. In general, the organic liquid has to wet the solid material and be immiscible with the carrier liquid of the suspension [54]. High aromaticity and large surface tension of the liquid promise good separation efficiencies [35]. The pH degree has a large influence on the liquid/solid interaction, and therefore interferes with the separation efficiency. E.g. the Shell Pelletizer is very pH sensible; unfortunately, its efficiency in acid environments appears rather low. [35]

The addition of an organic liquid to improve the soot and tar collection and removal deserves further investigation. The possibility has not been incorporated in the RS design.

The removed soot needs aftertreatment. This is due to contamination of the soot.

- The soot is contaminated with chlorine. The chlorine is not molecularly bonded, but is present via adsorbed hydrogen chloride and/or chlorinated hydrocarbons (see paragraph 3.4.2). This means that the soot can be cleaned from chlorine by washing or similar unit operations.
- The soot is also contaminated with PAHs, albeit that the soluble organic fraction (SOF) is small (see paragraph 3.4.2). Removal of PAHs is not always necessary, e.g. when the soot is burnt it is not essential. However, when the soot is used, one should always consider the presence of the toxic PAHs.

§ 6.3 Flowsheet of designed industrial plant.

§ 6.3.1 Flowsheet of the RS plant producing saturated hydrochloric acid. [11,23,38]

A schematic representation of the RS industrial thermal hydrodechlorination plant is given in figure 6.1. The plant converts the chlorinated waste into useful products, viz. concentrated hydrochloric acid and a hydrocarbon/hydrogen gas stream that at least can be used as a fuel gas.

In the forthcoming paragraph the flowsheet of the plant will be discussed. The central part of the plant is its reactor, which takes care of the chemical fission of chlorine from the hydrocarbon skeleton. The aftertreatment section accomplishes the definite physical separation.

By steam reforming of natural gas a hot hydrogen containing gas is produced. The gas is led to the reactor. Steam, carbon monoxide and other components of the gas do not interfere with the dechlorination reaction, and may be considered as inerts. The heat of the gas is used to bring the chlorinated waste to reaction temperature. Additional heat, to improve the flexibility of the system, can be generated by partial oxidation of excess hydrogen.

The liquid chlorinated hydrocarbon waste first undergoes some pretreatment before it is sent to the reactor. First, the feed is led through a homogenisation tank to suppress variations in the Cl input. Then, the waste passes a filter to remove solids that might obstruct the sprayer nozzle.

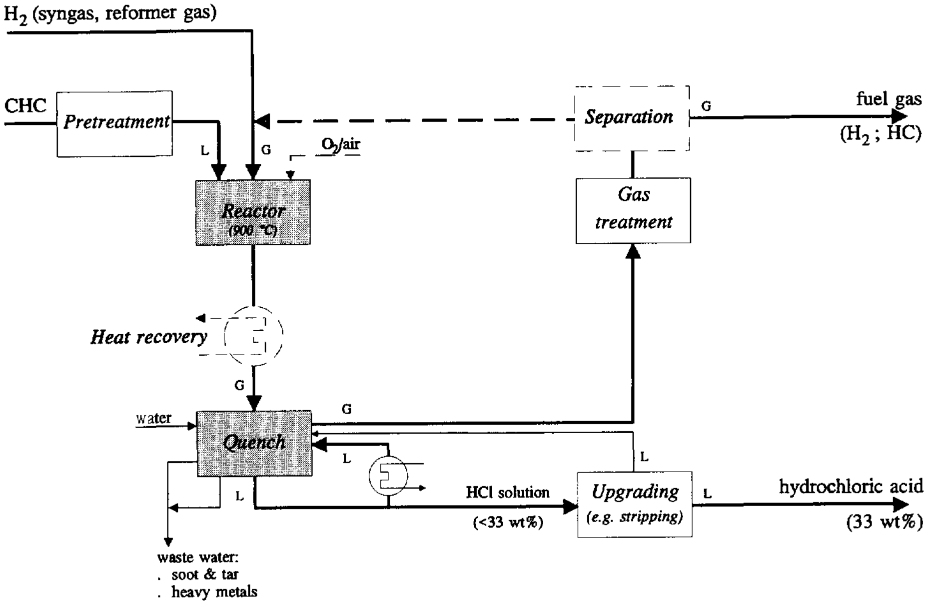

Figure 6.1 *Schematic representation of the RS industrial thermal hydrodechlorination plant producing hydrochloric acid.* [11,23,38]

The pretreated waste is introduced in the reactor by a spraying nozzle. The nozzle is cooled to prevent early soot formation. The waste is evaporated and brought to the reaction temperature of about 900 °C by the heat of the hydrogen gas. Sufficient residence time is provided to reach the maximum conversion of thermodynamical equilibrium. The reactor off gases are directly introduced into the quench. The option of heat recuperation has not been incorporated for reasons of simplicity and proven feasibility.

In the designed quench the reactor gases are quickly cooled by direct contacting with a hydrochloric acid stream. In the RS design, the quench is a scrubber quench. HCl from the reactor gases is absorbed in the not too concentrated hydrochloric acid quench medium. The quench liquid contains nearly all HCl, only a limited amount is emitted via the quench flue gases. A small part of the quench liquid is upgraded to the final product, 33 wt% hydrochloric acid [37], e.g. by stripping [44]. The largest part is recycled via a cooler. By this cooler the quench temperature is externally controlled.

In the quench soot and tar are collected by spraying and gravitational relaxation. Most soot and tar float on the surface of the liquid holdup at the bottom of the quench, a very limited part sinks to the bottom of the vessel. The floating and descended soot and tar are tapped from the quench and transported to an aftertreatment unit.

The gas stream leaving the quench, passes through a treatment section. Among others this section includes an alkaline scrubber to remove the last traces of HCl. The gas remainder consists of nonchlorinated organics and hydrogen, that at least can be used as fuel gas.

A H_2 recycle is considered. Especially if a large excess of H_2 is used, a H_2 recycle becomes attractive. To relieve the separation requirements the recycle stream may include light hydrocarbons, which do not deteriorate the conversion efficiency as long as they are present in only small amounts. For the ease of simplicity and proven feasibility the H_2 recycle has not been implemented in the RS design.

§ 6.3.2 Flowsheet of alternative plant producing anhydrous hydrogen chloride. [7,34,45,47]

An alternative to the RS design is the production of anhydrous hydrogen chloride. The alternative is based on comparable systems, which exist for combustion installations, like the Akzo incinerator [7,34,47]. A big difference with incinerator systems is the presence of condensable organics. The patented design by S.I.R. [45] considers the production of hydrochloric acid from a gas stream contaminated with these organics.

The alternative plant primarily consists of proven technologies, however it also is more complicated. For reasons of simplicity the RS design does not comprise this alternative flowsheet.

The basic difference between the RS design and this alternative, is the place where HCl is collected. As shown in figure 6.2, the flowsheets are similar up to the quench. In the alternative design the reactor gases are quenched with nearly saturated hydrochloric acid instead of a less concentrated solution. As a result, most HCl leaves the quench in the gas phase. In the alternative design the main functions of the quench are to quickly cool the reactor gases and to collect process contaminants like soot, tar and heavy metals.

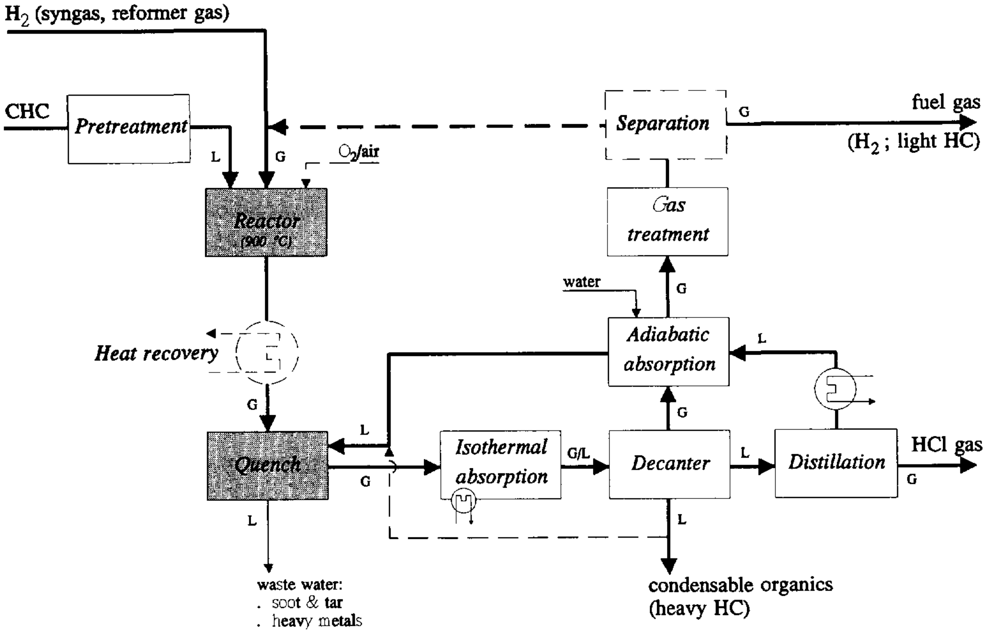

Figure 6.2 *Schematic representation of an alternative industrial thermal hydrodechlorination plant producing anhydrous hydrogen chloride.* [7,34,45,47]

The quench is operated at boiling point of the quench medium. The quench medium is introduced as a liquid, and mainly leaves the quench in vapour phase. The latent evaporation heat is used to cool the reactor gases. Since the quench is operated at boiling point, the immersion type is the most logical choice.

In the liquid holdup of the immersion quench the soot, tar and heavy metals are collected. To prevent outrageous builtup of these contaminants, a small part of the quench liquid is drained.

The quench flue gases are sent to an absorption unit, consisting of isothermal and adiabatic adsorption, a decanter unit and distillation. First, the gases enter the isothermal adsorption unit, followed by the buffering/decanter vessel. In the decanter condensable organics like aromatics are separated. The liquid water stream from the decanter is sent to the distillation unit, where it is converted into the desired anhydrous HCl. The decanter gas is sent to the adiabatic absorber. There the gas is washed with the liquid that leaves the distillation unit as bottom stream and fresh water. The liquid product of the adiabatic absorber is sent back to the quench. The gas product is treated like the flue gas of the hydrochloric acid plant, as described above.

The decanted organics may be added to the liquid quench stream leaving the adiabatic absorber. The presence of liquid organics in the quench unit may improve the soot and tar collection.

§ 6.3.3 Short remarks concerning safety and contamination.

In the RS design a lot of attention has been paid to safety aspects, because of the dangerous substances and process conditions involved. A summary of potential hazards may elucidate these safety requirements:

- the toxicity of the waste (chlorinated hydrocarbons) and products (hydrogen chloride),
- the exothermic character of the process,
- the flammability related with the chlorinated hydrocarbons and hydrogen and the high operation temperature,
- the explosion risk involved in the process or after leak of hydrogen and (chlorinated) hydrocarbons to the environment,
- the chance of uncontrolled combustion after leak to open air, potentially leading to undesired species like Cl_2 and PICs, e.g. phosgene or dioxins,
- the production of contaminated soot and tar (PAHs, heavy metals),
- the occurrence of strong acids and bases in the process.

If the process is operated under pressure, additional measures are undertaken. The actual measures are beyond the scope of this thesis. This was done in a separate study [11,14].

In an early stage of the process development, a kind of 'HAZOP' (hazard and operability) study has been carried out [11,14]. A number of plausible disasters was put forward by this study:

- HCl discharge,
- dioxin discharge (after leakage to the environment and subsequent uncontrolled burn),
- chlorinated hydrocarbon discharge,
- a too high reactor temperature,
- explosion or fire after breakage and/or leakage,
- underpressure due to condensation and solvation.

Most frequent causes leading to the disasters, were found to be

- leakage and breakage,
- obstruction,
- fall-out and malfunctioning of valves, pumps, compressors and control loops.

More information can be found in the separate study [11,14].

The study also led to preliminary start-up and shut-down procedures. The rates of these procedures appear both to be determined by: [11,14]

- the speed of heating resp. cooling, which are restricted to prevent large temperature shocks,
- the chlorine fraction in the system.

Details are given by the mentioned study [11,14].

Heavy metals and contaminants in the feed need to be considered: where can they damage the process and to what extent, and where can they be isolated. Following short summary is given as elucidation. [7]

- Fluorides may harm the construction material.
- Heavy metals are plausibly converted into chloride salts and dissolved in hydrochloric acid. They can be disposed of as part of this solution. Attention must be paid that their concentration in the neutralised drain does not exceed the tolerable levels.

- Sulphur, phosphor and bromine may interfere with the HCl treatment and upgrading. If e.g. HCl is to be used as a feedstock in vinylchloride (VC) production, these contaminants constitute a serious hazard.
- Metals, like iron (Fe), are known to form eutectica with the masonry that is commonly applied in kilns. This does not only imply destruction of the kiln wall, but also leads to deposit and subsequent obstruction in the following parts of the installation.

The aftertreatment section is designed for a certain product quality, based on a certain feedstock. Of course, the process operation is restricted within a certain variation. This restrictions lead to additional requirements, like an upper and lower boundary to the chlorine content of the feed. The flexibility and sensitivity to contaminants is part of subsequent research in the Royal Schelde demonstration plant, which is under construction in spring 1993.

§ 6.4 Apparatus choices.

§ 6.4.1 Reactor configuration.

Based on the experimental experiences the reactor is configured as a downstream empty tube. Because of the downwards configuration solid material like soot is carried away with the gas flow, and does not fall back on the waste insertion point.

The actual construction is designed by the Royal Schelde. A schematic representation is offered in figure 6.3. As shown, in the design the reactor and quench are integrated. The actual reactor is a ceramic tube, hanged in between the quench and the dome-like outerpart of the reactor tube, which is called the H_2-dome.

This H_2-dome is implemented for constructional reasons, as will be discussed later. Here, H_2 is introduced. From the H_2-dome the hot hydrogen gas streams along the sprayer nozzle through which the chlorinated waste is introduced into the reactor. To prevent early decomposition of the waste within the nozzle, the sprayer system is cooled. The optimal sprayer configuration is part of the present research program by Royal Schelde. In this respect a coiled sprayer as used in the Akzo incinerator features promising properties. [34]

Two important design aspects are incorporated in the final configuration of the reactor/quench combination: [52]

- the realisation of a proper homogeneous (plug) flow,
- the minimalisation of (thermal) tension.

The construction of a suspended ceramic reactor is chosen for some reasons.

- Leakage of a hot medium containing chlorinated hydrocarbons to the environment is prevented.
- The pressure drop over the ceramic wall is very limited, even at pressurised operation. In this way the problem is solved, which is related with the small tensile strength of the ceramic. [38]

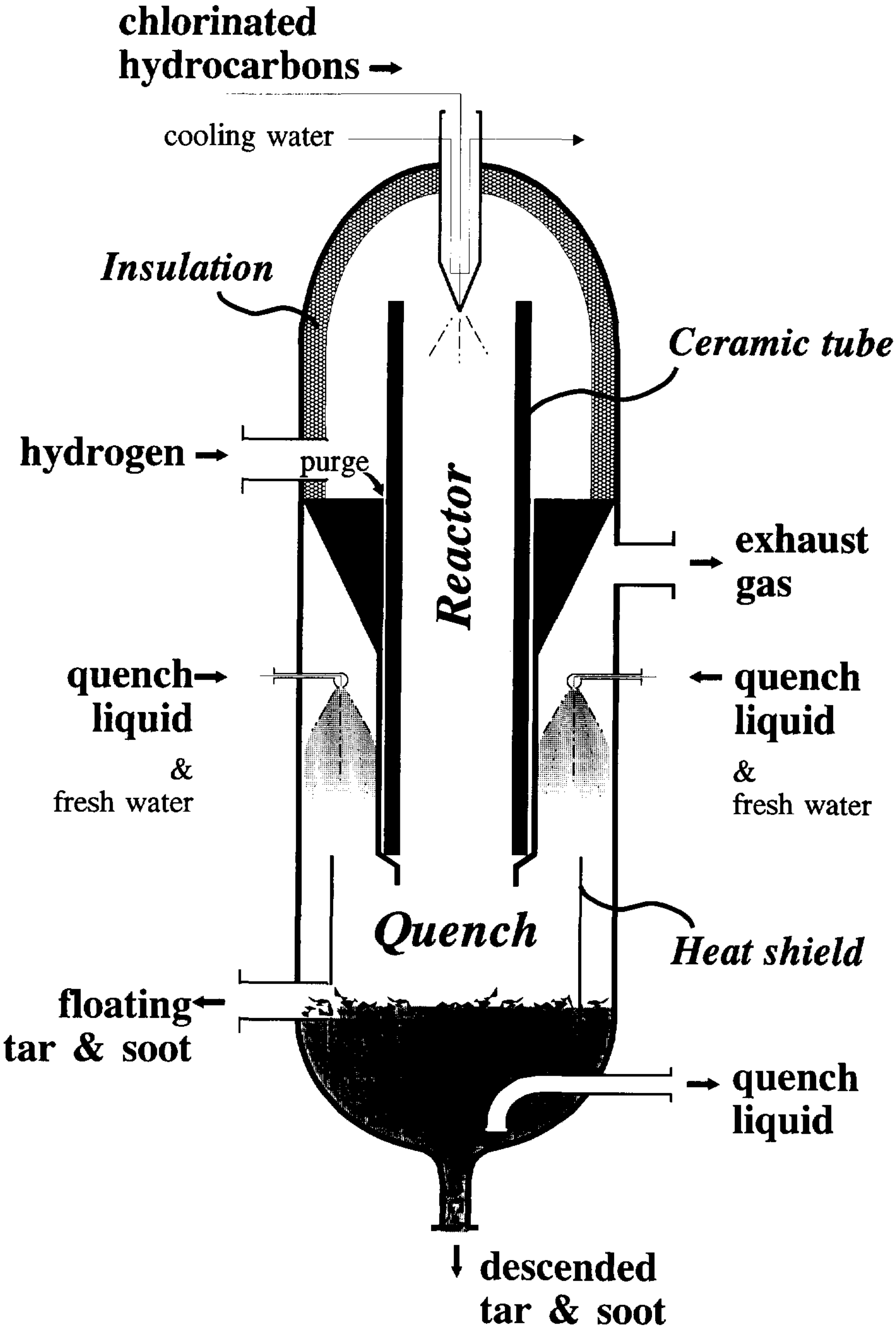

Figure 6.3 *Schematic representation of reactor/quench construction according to RS design.*

The reactor wall has to withstand an elevated temperature of 900 °C and a corrosive medium containing hydrogen and hydrogen chloride. The ceramic aluminiumoxide (Al_2O_3) fulfils most requirements:

- it is chemically inert;
- it does not catalyse soot formation;
- it is heat resistant;
- it has a poor heat conduction, which is favourable in this configuration! [25]

Against these positive features, it also exhibits some drawbacks.

- Aluminiumoxide has a poor thermal and mechanical shock resistance. [25]
- If contaminations like fluorides are present, the material is susceptible to degradation. [19,27]

The poor shock resistance is a problem especially at the exhaust side of the reactor. Therefore the reactor exhaust is made of Hastelloy X [25]. This nickel alloy reveals some excellent properties;

- it is resistant to elevated temperatures and thermal shocks,
- the material is relatively easy to work.

The resistance of the material against acid conditions is fairly good [10,39]. The Hastelloy X exhaust pipe is a part of the metal construction which supports the ceramic tube. Non metal materials like graphite are also considered. They have a better resistance [34,39,44], but they are more difficult to work with. The alternative option to use graphite will be discussed in paragraph 6.4.2.

The wall of the H_2-dome forms the outer wall at the top of the reactor. The wall is constructed of 10CrMo910 which is resistant to hydrogen embrittlement, and is applicable to 500 °C. The alloy is covered with isolating pouring concrete having a high Al_2O_3 content. [25]

At pressurised operation, the H_2-dome and quench vessel may function as a pressure vessel for the reactor.

§ 6.4.2 Quench configuration.

The elementary requirements of the designed quench are the following.

- The quench must quickly cool the reactor gases.
- It should collect most or all soot and tar.
- It has to be fail safe.

Besides noncondensable inerts (H_2, CO, CO_2, N_2), low boiling hydrocarbons (CH_4, C_2H_4, C_2H_6) and soot and tar, the reactor off gases contain water, hydrogen chloride and benzene. It is logical to select one of these as the quench liquid. A fourth option is to choose a high boiling organic substance, at the dewpoint of which all HCl and H_2O are still in the gas phase. Use of this kind of oil may facilitate further treatment. [13]

Comparison of the various systems at boiling point may indicate the best option. In all cases, the liquid quench phase contains soot and heavy hydrocarbons among which tar, and the metal contamination. The noncondensable gases and light hydrocarbons always remain in the gas phase. The options differ in the distribution of water, hydrogen chloride and benzene over gas and liquid phases. [13]

- If benzene is applied as quench medium, hydrogen chloride divides over gas and liquid phases. This is unfavourable to further processing. Also, circulation of large quantities of benzene is adverse with respect to safety.

- Quenching with oil has the advantage that water and hydrogen chloride remain in the gas phase, which is attractive to further processing. However, the use of oil introduces a new substance in the process, which means that additional processing steps are required. E.g. the oil will have to be regenerated, as it is contaminated with soot, tar and metals during use.

- If water is used as quench medium most hydrogen chloride dissolves in the liquid phase. Calculations indicate that with the water quantity required to cool the gases, hydrochloric acid is prepared with a hydrogen chloride concentration above the azeotrope. This means that further processing to a more concentrated acid or anhydrous hydrogen chloride is feasible without difficult extraction or similar steps to pass the azeotrope. The quench gas phase contains benzene and a small remainder of hydrogen chloride.

- Quenching with concentrated hydrochloric acid effectuates that most hydrogen chloride remains in the gas phase, and that it perfectly can be separated from soot, tar and metals. Subsequent separation of hydrogen chloride from the cleaned gas can be realised with ease.

From this comparison it may be concluded, that, if the quench is operated at the boiling point of the quench medium, the use of superazeotropic hydrochloric acid offers the most attractive option. [13]

If the quench is operated below boiling point, the comparison changes a bit. Benzene and oil remain unattractive as quench media for the reasons mentioned. And hydrochloric acid is still attractive. But, the situation for water improves, as more hydrogen chloride dissolves because of the lower temperature. Instead of being distributed over two phases, HCl is more effectively collected in one single phase. However, the temperature should not be diminished too far below dewpoint to prevent condensation of benzene.

In the RS design diluted hydrochloric acid is chosen as quench medium. The quench is operated below boiling point. HCl is nearly completely collected in the liquid phase. The choice of quench medium does not impose restriction on the type of quench. [38]

In the alternative design aiming at the production of anhydrous hydrogen chloride, the reactor gases are quenched with very concentrated hydrochloric acid. The quench is operated at boiling point. Because of this, the quench should be an immersion quench.

The RS design is simpler and seems to offer a better feasibility at this stage of development, certainly with respect to soot collection.

The substances present in the quench form a complex physical system. In the appendix 6.A information about the gas/liquid system of hydrogen chloride (HCl) - water (H_2O) - benzene (C_6H_6) is given. The behaviour of benzene is typical for that of other (poly)cyclic hydrocarbons. Some characteristic properties of the gas/liquid system should be mentioned, here.

- Hydrogen chloride and water form constant boiling mixtures. At atmospheric condition, the maximum temperature azeotrope of 20.4 wt% HCl is reached at 108.6 °C. [6]
- Water and benzene are immiscible and form a so called heteroazeotrope. Under atmospheric pressure the heteroazeotrope occurs at 68 °C, 72 mol% benzene.
- Notwithstanding the maximum temperature azeotrope of the HCl-H_2O subsystem, the boiling temperature of the quench mixture is lower than that of pure water, because of the occurrence of the heteroazeotrope and the presence of noncondensables. A decrease of 10-15 °C is observed in comparable quenches. [44]

Principally two types of quench can be distinguished. The basic difference concerns the way the reactor off gas stream and the washing liquid are contacted.

- In the immersion quench gas is plunged into the liquid holdup. The gas phase is disperse as it flows as bubbles through the continuous liquid phase.
- In the scrubber quench the liquid is sprayed into the gas stream. Here, the disperse phase is liquid and the gas phase is continuous.

The immersion quench is used in the bench scale installation. The Akzo incinerator, or more generally the Nittetu process, gives an example of its industrial application. [7,34,44,47] These industrial processes and the process of concern are similar with respect to the hot reactor off gases, containing a considerable hydrogen chloride fraction, that both need to be cooled quickly.

The Nittetu immersion quench comprises a special design, see figure 6.4. The hot gases are purged into the cool liquid via holes in the downcomer from the reactor. The special design of holes and weirs effectuate a vigorously swirling mixture of gas and liquid. Excellent interphase exchange is realised due to the turbulence. The gases are quickly cooled to the boiling point of the quench liquid. The rising gas effectuates a liquid circulation around the weirs. [34,44]

The choice of material is difficult for two reasons: high temperature and the presence of aggressive hydrochloric acid. The Nittetu design includes a special solution to these. The downcomer is constructed of graphite of a relatively porous quality. The turbulent bubble bath wets the graphite tube and keeps it cool. Due to its porosity (about 20%) the tube actually adsorbs the liquid. So to speak, the graphite tube 'boils'. [34,44]

The choice of graphite is due to its excellent thermal shock resistance and stability towards hydrochloric acid. Though in oxidative atmospheres a temperature restriction of 300 °C exists since at that temperature graphite start to burn, under reductive conditions such restrictions do not seem to exist. Besides that, the special cooling system keeps the temperature at the boiling point of the quench medium, which normally is far below 300 °C. [34,44]

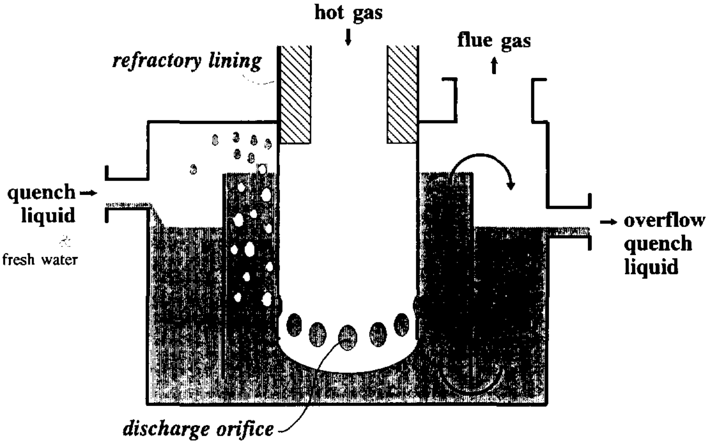

Figure 6.4 *Schematic representation of Nittetu immersion quench.* [34,44]

Unfortunately, the soot collection efficiency of the immersion quench appears rather poor. This was already shown in the bench scale installation, where the exhausted particles come to rest only in the freeboard above the quench liquid. It is also confirmed by experiences in the Akzo incinerator after misoperation. If soot is produced in the furnace, the plume of smoke at the exhaust pipe becomes black. The soot is hardly collected in the quench. [34]

The immersion quench is intrinsically safe with respect to fall out of quench medium supply. If for any reason the supply of quench liquid is stopped, the liquid volume contained by the quench delays the moment of cooling loss.

On the other hand, the compression due to the dissolvement of hydrogen chloride and the condensation of gaseous compounds may lead to a momentary reversed flow. Instead of gas out of the hot reactor, cool quench medium is transported into it, which might have dramatic consequences. The danger of reversed flow is especially a threat at pressurised operation.

To prevent this kind of reversed flow, the gas velocity in the Akzo incinerator is always kept above a critical value. Implosions due to compression only take place outside the downcomer. At all times a gas flow is maintained through the downcomer, even at shutdown. [34]

In the scrubber quench the quench liquid is sprayed countercurrently into the gas stream. One of the main advantages of the scrubber quench is an improved soot collection. Another advantage is that the danger of reversed flow does not exist. Though the scrubber quench lacks the intrinsic safety related with fall out of the quench medium supply, fail safe operation can easily be guaranteed by simple safety measures.

Though the immersion quench presents the benefit of proven technology and relative simplicity, the scrubber quench has been chosen in the RS design, mainly for its soot collection potential and safe operation.

The physical realisation is presented schematically in figure 6.3. As mentioned earlier, the quench and reactor are completely integrated in the design. The gases leave the reactor downwards, are turned around, and flow upwards through the actual quench. In the quench the gases are countercurrently washed by a spray of hydrochloric acid drops. Soot and other particles are separated from the gas stream and accumulate on the liquid reservoir at the bottom.

- Some of the solids leaving the reactor simply are not carried away with the turning gas stream, and continue to fall down to the liquid reservoir at the bottom.
- Others, that are carried away, are dragged by the liquid spray and purged to fall downwards with the liquid droplets.

Of course, the way the quench medium is sprayed, has a strong influence on the overall quench performance. The spray must meet some objectives.

- The complete annular quench volume surrounding the reactor must be covered by the cold spray. No tunnels or bypass of hot gas may exist.
- All wall surfaces need to be wetted.
- A screen of droplets should be formed at the bottom of the downcomer. When the film layer on the outside wall of the downcomer reaches the bottom, it breaks and forms such screen. The gas stream leaving the reactor first penetrates this droplet screen, before the actual countercurrent washing in the annular volume starts.

A relatively small stream of fresh water is injected above the huge hydrochloric acid stream. The fresh water removes last traces of hydrogen chloride in the gas to achieve optimal HCl removal.

The scrubber quench can be compared with the reflux subsystem of a distillation tower. The dimensions of the quench are based on a design method proposed by Fair [15,24]. The nature of this method is empirical. The quench volume is determinated by

- heat transfer,
- mass transfer,
- soot capture.

Here, the design results are shortly summarised. The upward gas velocity and downward liquid velocity may not differ too much to prevent a disturbed flow pattern, such as flooding or entrainment. The design velocity difference is taken half the empirically determined tolerable maximum, which is 1.4 m/s for this system [24]. The gas is cooled from about 1000 °C (900 °C at the reactor entrance plus the temperature rise due to the exothermic reaction) to about 70 °C. Though the gas liquid streams are not perfectly countercurrent, the logarithmic temperature difference provides a fairly good approximation for design purposes [15]. If the quench medium is heated from 60 °C to 70 °C, the logarithmic temperature difference is about 200 °C. Design calculations [24] indicate that in comparison to heat transfer the mass transfer is rate limiting. Departing from 135 m^2/m^3 liquid surface per quench volume, about 5* times longer contact time is required for the mass transfer [24]. The mentioned liquid surface ratio is realised with nozzles having a orifice diameter of 8.35 mm. The spray droplets may not be too fine to prevent entrainment at relatively low gas rates [15]. Based on analogy with similar processes the soot collection of the designed sprayer system is expected to be very near to 100% [9].

Concerning the construction material the following can be stated.

- In the RS design the quench wall is made of H II steal with Hastelloy B2 cladding. The Hastelloy B2 has good resistance characteristics with respect to the aggressive hydrochloric acid. To decline the costs a cladding is used.
- Alternative to the RS design, which proposes to use Hastelloy X at the end of the reactor downcomer, a graphite construction may be used, similar to the Nittetu process. [34,44]
- Heat shields are implemented in the quench to prevent contact between the hot reactor gases and the outer quench wall. Since heat resistance is of no concern anymore, the choice of construction material for the outer wall is facilitated.
- Special requirements are demanded for the spray nozzles to prevent wear and subsequent ineffective atomization.

§ 6.5 **Process economics.** [37,52]

A global estimation of the costs is carried out by the Royal Schelde [37,52]. The estimation is based on the following. [37,52]

- The capacity of the installation is 22.000 ton/year.
- The average chlorine content of the waste is 60 wt%.
- The hydrogen containing gas is produced in a steam reformer, which is considered as an integral part of the thermal hydrodechlorination plant.
- The production of soot (which needs further treatment) is 1-2 wt% of the chlorinated hydrocarbon feed at maximum.
- The produced fuel gas has an intrinsic value of fl 0.26/Nm^3.
- The produced 33 wt% hydrochloric acid has an intrinsic value of fl 30,=/ton.
- The economical life is 10 years.
- The interest rate is 8%.
- The plant is located at an industrial site, where basic utilities are present, such as steam, electricity, etcetera.

The investments are estimated to be Mfl 44 - 50,=. In this estimation costs are included concerning engineering, interest over the building costs, supervision of assembly and start of operation. In the determination of the processing costs, the investments are set on fl 45 million. [37,52]

Table 6.2 presents the composition of the processing costs. As shown, the costs are predominantly governed by the fixed costs (circa 65%). Since the net variable costs are low, the factory results are nearly insensible to variations in the prices of raw material. Therefore a rather stable price of treatment may be expected. [11,37,52]

Table 6.2 *Composition of processing costs.* [37,52]

fixed costs, including assurances	fl	350,=/ton
semi variable costs (incl. pay and maintenance)	fl	125,=/ton
price of raw material minus profits	fl	50,=/ton
overall processing costs	fl	525,=/ton

Comparison of the processing costs with that of other treatments reveals the following.

- AVR bases the processing costs on the composition and caloric value of the waste. Above the minimal cost price involved in the combustion of liquid waste, surcharges are paid with increasing content of chlorine, fluorine, sulphur, volatile metals, etcetera. The minimum price is fl 100,=/ton, but the costs can rise to fl 2000,=/ton - fl 3000,=/ ton, e.g. for PCB containing waste. [47] For waste containing 60 wt% Cl, the price typically is between fl 500,=/ton and fl 1000,=/ton [11].

- In the Akzo incinerator the treatment of waste with a high Cl content is charged with a price between fl 800,=/ton and fl 1200,=/ton. [47]

This comparison indicates that the calculated costs of the thermal hydrodechlorination plant are at least competitive.

§ 6.6 Conclusion.

Based on the experimental experiences of this study and those at labscale [37,38] and preferentially applying proven technologies, a plant has been designed under auspices of the Royal Schelde (RS), which treats 22.000 ton/year of chlorinated waste by thermal hydrodechlorination. After treatment valuable products remain: concentrated hydrochloric acid and a gas containing hydrocarbons and hydrogen, which at least can be used as a fuel gas. An economical evaluation indicates a cost price of about fl 525,=/ton for 60 wt% Cl waste. This price is competitive to that of incineration.

An alternative plant producing anhydrous hydrogen chloride is presented as well. Depending on the plant location, the production of anhydrous hydrogen chloride may improve the economical result. For reasons of simplicity and flexibility with regard to location, the Royal Schelde design does not comprise this alternative option.

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Appendix 6.A Hydrogen chloride (HCl) - water (H_2O) - benzene (C_6H_6) gas/liquid system.

Hydrogen chloride (HCl) dissolves extremely well in water (H_2O). HCl and H_2O form constant boiling mixtures. At atmospheric pressure, the maximum temperature azeotrope is found at 108.6 °C, the azeotropic HCl fraction being 20.4 wt% [6]. At a higher pressure the azeotrope shifts to a higher temperature and a smaller HCl fraction. The HCl-H_2O gas/liquid system is depicted in figure 6.5. [6,17,20,53]

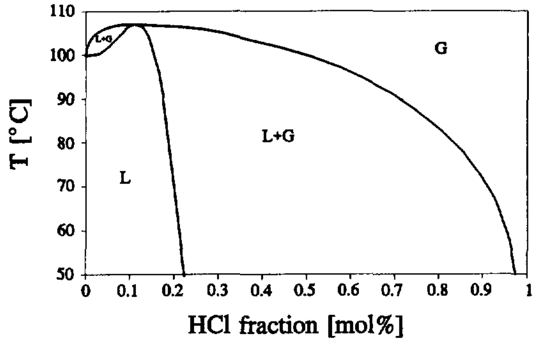

Figure 6.5 *HCl-H_2O gas/liquid system.* [6,17,53]

p [atm]	b.p. [°C]	HCl [mol%]
0.066	48.7	13.1
0.33	81.2	12.1
0.65	97.6	11.5
1.0	108.6	11.2
1.3	116.2	10.8
5 (1)	152.8	9.7
10 (1)	176.8	8.4
20 (1)	202.7	7.2

Table 6.3 *Properties of HCl-H_2O azeotropes.* [6,17,20,53]
(1) *extrapolated value.*

The coexisting gas phase of subazeotropic hydrochloric acid is H_2O richer than the liquid phase; it is impossible to extract anhydrous HCl from such acid. To prepare anhydrous HCl via distillation, the HCl concentration of the hydrochloric acid must be above the azeotrope. [6]

The HCl gas phase, that is in coexistence with concentrated hydrochloric acid, contains a very small H_2O fraction. Conversely, it means that the water content of the HCl gas has to be very small in order to prevent condensation. Though dry HCl gas is not corrosive, solutions in polar solvents like water form more or less strong acids and behave aggressively. In other words, condensation may lead to severe corrosion. A typical value below which the H_2O fraction must be to prevent condensation, is 870 vol-ppm at 10 °C (atmospheric pressure). [6]

Benzene (C_6H_6) and water are immiscible liquids. The dissolvement in each other is negligibly small: at atmospheric conditions the dissolved water fraction in benzene never exceeds 1.5 mol%, the dissolved benzene fraction is always smaller than 0.1 mol% [46]. The immiscible liquids form a so called heteroazeotrope [1]. Due to the presence of the other liquid phase, the boiling point of the mixture is lower than that of the respective pure liquids. The binary gas/liquid system for benzene and water is shown in figure 6.6.

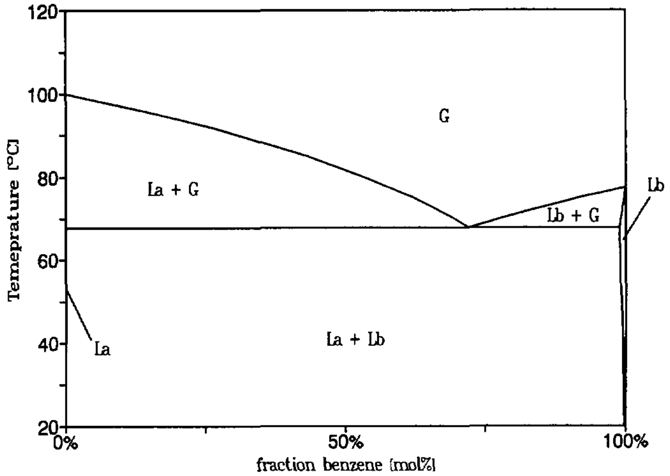

Figure 6.6 *Benzene-water gas/liquid system (p = 1 atm).* [2,17,21,46]
L_a: water (aqua) liquid phase; L_b: benzene liquid phase; G: gas phase.

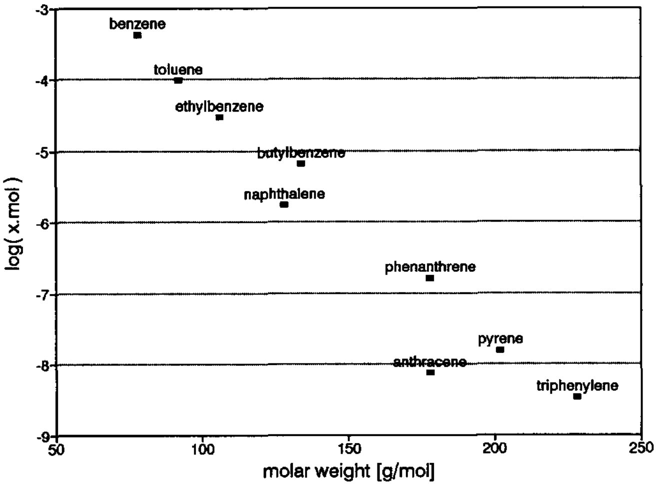

Figure 6.7 *Solubility of (poly)cyclic hydrocarbons in water.* [48]
x_{mol}: mol fraction of (poly)cyclic hydrocarbon dissolved.

The benzene/water system provides a clear indication for all organic/water systems. As shown in figure 6.7, the water solubility, c.q. miscibility, of other cyclic hydrocarbons is even worse than that of benzene. If the hydrocarbons condense, they form a second liquid phase besides the water phase.

All these physical phenomena affect the boiling point of the $HCl-H_2O-C_6H_6$ system. The actual temperature at which the mixture boils is determined by

- the maximum temperature azeotrope of the $HCl-H_2O$ subsystem,
- the minimum temperature heteroazeotrope of the $H_2O-C_6H_6$ subsystem,
- the presence of noncondensable gases like H_2.

Overall, the boiling point is expected to be lower than 100 °C, the boiling point of pure water at 1 atmosphere. In the Nittetu incinerator system the liquid in the quench boils 10-15°C below the atmospheric boiling point. This is only due to the effect of partial pressure of the noncondensing gases in the exhaust gases of the incinerator (CO_2 and N_2) [44]. In the thermal hydrodechlorination the reactor off gases contain an appreciable proportion of condensable organics, probably leading to a smaller decrease of the effective boiling point of the quench medium.

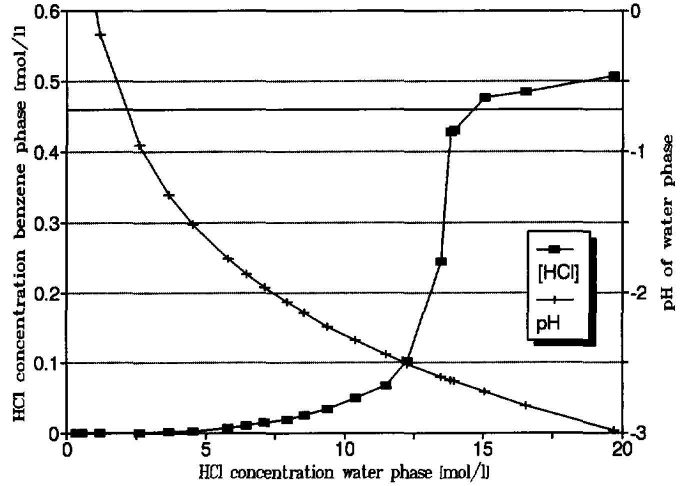

Figure 6.8 *HCl distribution over coexisting liquid phases of water and benzene (20 °C).* [31,49,50]

HCl does not only dissolve in water, but also in benzene, albeit in a restricted quantity. Figure 6.8 indicates the distribution of HCl over coexisting liquid phases of water and benzene. The figure shows that the favourable dissolvement of HCl in water is very pronounced at relatively low concentrations. At high concentrations a sharp increase of the HCl content of the benzene phase is noticed, until a kind of upper limit is reached. Remarkably, the upper limit exceeds the saturated concentration of pure benzene, which is 0.46 mol/l. [31,49,50]

The HCl fraction in the organic layer must be kept as low as possible.

- HCl may induce acid catalysed reactions. [16,38]
- HCl may lead to unwanted products in further treatment of the organics, e.g. in combustion.

The purity requirements of commercial anhydrous HCl gas depends on its use. Normally only traces [ppm] of H_2O are tolerated. Commercial concentrated hydrochloric acid has to meet the purity requirements summarised in table 6.4. Besides the mentioned requirements, the presence of Cl_2 has a deteriorating effect on the commercial benefit. [6]

***Table 6.4** Purity requirements of commercial concentrated hydrochloric acid.* [6]

HCl content	> 30 wt%
SO_4^{2-}	< 0.5 wt%
Fe^{3+}	< 0.002 wt%
organic Cl	< 0.02 g/l

Chapter 7

Final discussion

future outlook and promising features

§ 7.1 Introduction.

This chapter summarises the most important results of this study and comments the future outlook of thermal hydrodechlorination. In the first paragraph the present state of development is shortly recalled. Recommendations for future development and promising alternatives are mentioned. In the next paragraph (paragraph 7.3) the functionality of thermal hydrodechlorination is evaluated with respect to the environment. The environmental burden is assessed by evaluation of the (chlorinated) substance chain. Paragraph 7.4 compares the process of thermal hydrodechlorination to that of incineration and catalytic hydrodechlorination. Finally, in the last paragraph, the future outlook of thermal hydrodechlorination is discussed.

§ 7.2 State of the art.

Thermal hydrodechlorination is proven at labscale (~ 1 g/h) and pilot plant scale (~ 1 kg/h) as a valuable method to dechlorinate waste. Process development has led to the construction of a demonstration unit in spring 1993 by Royal Schelde. The labscale experiments are covered by the work of Manion [4]; the pilot plant experiences are discussed in this thesis. The investigations have shown the following.

- High dechlorination levels are easily obtained. Within residence times of 1-10 s, thermodynamic equilibrium is reached, which is typically above 99.9 mol% conversion. An easy method to monitor the dechlorination is the 'Organic Chlorine Remainder' (O.C.R.) method (see chapters 3 and 4), which gives a conservative estimate of the actual dechlorination level.

- The major drawback of thermal hydrodechlorination is the formation of soot and tar. The production of these compounds is inherently coupled to thermal hydrodechlorination (see chapters 3 and 4). The presence of soot and tar cause technological problems in transportation and separation. The occurrence of tar (PAHs) constitutes a possible toxicological hazard, in particular if the tar is adsorbed on the soot particles. The characterisation of soot and tar is discussed in paragraph 3.4 of this thesis. The recommended treatment of soot and tar is proposed in chapter 6.

Some experience is gained with construction materials (chapters 3 and 5). The bench scale installation, described in chapter 2, is suitable to investigate construction materials, in particular with respect to their soot promoting properties. Our experiences reveal the following.

- Metals like nickel and cobalt increase the dechlorination rate, but also increase soot formation. Unfortunately, the increase of soot formation is the most serious one. Therefore, metals like the two mentioned can not be used as reactor wall material.

- Ceramic materials give the best prospects. However, unexpected interaction with traces of metal salts may affect the stability of ceramic material under conditions of thermal hydrodechlorination, as has been noticed for silicon carbide (see chapter 5). A simple test in the bench scale installation is advised to evaluate the stability of the optional construction materials, to exclude unpleasant surprises.

Based on the experience obtained by the experiments, Royal Schelde (RS) designed an industrial plant capable to treat 22.000 ton/year 60 wt% Cl waste, producing fuel gas and 33 wt% concentrated hydrochloric acid. The investment of the plant is estimated to be fl 45 million, the cost price to be fl 525,=/ton waste. The flexibility of the plant with respect to variation in the chlorine content of the waste is predominantly determinated by the after treatment section.

Alternatively, anhydrous hydrogen chloride may be produced. The production of this chloride compound may be more favourable economically, but also requires a more complicated installation (see chapter 6). For reasons of simplicity the RS design aims at the production of hydrochloric acid.

Royal Schelde has constructed a demonstration unit, which will be in operation in spring 1993. Objectives of this installation are to prove thermal hydrodechlorination at industrial scale and to investigate some not yet completely understood aspects of the system. Among others in the demonstration unit attention will be paid to topics like

- input of chlorinated waste,
- continuous collection and proper treatment of soot and tar,
- operability and efficiency of the designed quench.

The present study indicates that spraying is an appropriate method to introduce the waste into the reactor. After being sprayed, the chlorinated hydrocarbons evaporate within the reactor volume. Instable chlorinated hydrocarbons, which tend to form soot even at their boiling point, do not directly decompose into soot because of the immediate presence of hydrogen. In future the way of spraying should be optimised. Also, alternative methods need to be considered for chlorinated, or more general halogenated, waste which is sprayed with difficulty. A vaporisation chamber before the reactor may be adequate for such compounds.

In the demonstration unit attention needs to be given to the topic of dioxins. The hypothesis of non-formation, or even complete destruction, of dioxins (see chapter 3) must be verified.

Interesting future development may involve the following issues:

- feasibility of heat recovery from the hot reactor off gases (see chapter 6),
- treatment of halogenated waste other than the liquid chlorinated hydrocarbons, such as solid PVC or Br containing flame extinguishants,
- catalysing effects by suppletion of oxygen (see chapter 4).

The suppletion of oxygen renders various interesting prospects.

- By partial oxidation of the hydrogen bath gas, the flexibility of heat housekeeping is increased.
- According to Ritter [5,6,7] small amounts of oxygen accelerate the dechlorination rate considerably. It is unknown whether this is restricted to the 'diluted' condition Ritter used ($Cl/H_2 \approx 300$), or whether it can be extended to the more concentrated conditions applied in this study ($Cl/H_2 \approx 3$, see chapter 4).

§ 7.3 Substance chain assessment of thermal hydrodechlorination.

The use of a chemical substance effectuates a certain impact on the environment. The definitive environmental burden is determined by the total of emissions during all stages of production, use and waste treatment. The best situation is obtained if the substance is brought under full control, so that the emission to the environment is diminished and the risks for external safety are reduced [9].

In order to assess the environmental impact a substance chain can be set up [9]. All stages are reviewed and the total burden is determined. This paragraph covers the substance chain of chlorinated hydrocarbons from production to waste treatment by thermal hydrodechlorination. For simplicity, the assessment only considers perfect chemical conversions; formation of byproducts or inefficiencies are ignored. In this way, a first indication of the environmental impact is acquired.

First, complete reuse of the hydrocarbon compounds is assumed in this paragraph. After that, a substance chain is set up without recycle. As the feasibility to recycle the hydrocarbon product stream of thermal hydrodechlorination has not been demonstrated at the moment, the latter case is a more realistic approach of the actual environmental impact. To assess the impact of thermal hydrodechlorination, this case is compared to the substance chain involving incineration.

The production of chlorinated hydrocarbons frequently involves two steps:

1. the production of chlorine gas, normally by electrolysis of a watery sodium chloride solution (equation 7.1),
2. the chlorination by a substitution reaction of the chlorine gas and hydrocarbons (equation 7.2).

After their use the chlorinated hydrocarbons are treated by thermal hydrodechlorination (equation 7.3). Undesired byproducts formed in the production stage, are treated in the same way. Assuming all products can be recycled, the overall conversion simplifies to the transition of the aqueous sodium chloride solution into the base sodium hydroxide and the acid hydrogen chloride. After neutralisation of these, a perfect recycle without emission of any substances to the environment would be established!

$$2\ NaCl + 2\ H_2O \xrightarrow{electrolysis} 2\ NaOH + Cl_2 + H_2 \qquad (7.1)$$

$$Cl_2 + RH \xrightarrow{chlorination} RCl + HCl \qquad (7.2)$$

$$H_2 + RCl \xrightarrow{THD} RH + HCl \qquad (7.3)$$

$$\overline{\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad} +$$

$$2\ NaCl + 2\ H_2O \longrightarrow 2\ NaOH + 2\ HCl \qquad (7.4)$$

As said before, this simple assessment only offers a first indication of the environmental aspects. For instance energy requirements and spillage of the chlorinated products during their manufacture, use and treatment are not considered, nor the fact that processes are never 100% efficient.

When treated by incineration, the hydrocarbon part of the chlorinated waste would be converted into CO_2 and H_2O. Then, the substance chain can not be closed. More raw material must be used and more 'endproducts' are emitted into the environment. Reminding the limitations of the assessment, the overall transition already gives an indication of the environmental benefit of thermal hydrodechlorination.

The production of chlorinated hydrocarbons may also take place in one single step by in situ generation of Cl_2. An example is oxychlorination, for which a similar assessment is set up.

$$RH + HCl + \frac{1}{2} O_2 \xrightarrow{oxychlorination} RCl + H_2O \qquad (7.5)$$

$$H_2 + RCl \xrightarrow{THD} RH + HCl \qquad (7.6)$$

$$\overline{\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad} \; +$$

$$H_2 + \frac{1}{2} O_2 \xrightarrow{\qquad} H_2O \qquad (7.7)$$

Again, a nice and simple overall transition appears. The overall conversion simplifies to the combustion of hydrogen. According to the overall transition only H_2O is emitted. Also much heat is generated as the overall transition is a very exothermic reaction. This demonstrates the importance of a good heat recovery.

According to the overall transition, the integral process system uses hydrogen. The supply of hydrogen involves the use of external sources of raw material and heat, which should be considered in the assessment as well.

So far, the assessment concerns a system in which all processes are completely and perfectly integrated. All products that can be reused, are recycled with 100% efficiency. However, it is questionable whether the organic stream produced in thermal hydrodechlorination can really be used as feedstock for (oxy)chlorination, since it does not consist of a simple and well defined hydrocarbon mixture. In general the feed of thermal hydrodechlorination is a waste, of which the composition is obscure, complex and not very well defined. Moreover, soot and tar formation alter the hydrocarbon composition. Therefore, in case of thermal hydrodechlorination it is better to assess the situation in which the hydrocarbon product is used as feedstock for hydrogen. The hydrocarbon recycle regarded is more applicable to systems like catalytic hydrodechlorination.

Consider the system in which chlorinated hydrocarbons are produced by oxychlorination and the chlorinated waste is treated by thermal hydrodechlorination (THD). Part of the hydrocarbon exhaust stream is used to produce synthesis gas which contains all hydrogen required in the thermal hydrodechlorination step.

The precise composition of synthesis gas depends on the feed and process conditions applied. The Shell Gasification Process has been taking as example for the syngas production. The main products are CO and H_2, typically produced in about equal amounts, in particular if heavy feedstocks are treated [1]. This leads to the reaction equation for gasification as denoted in equation 7.10.

$$\begin{array}{lr}
C_nH_m + p\ HCl + \frac{p}{2}\ O_2 \xrightarrow{oxychlorination} C_nH_{m-p}Cl_p + p\ H_2O & (7.8) \\[2em]
p\ H_2 + C_nH_{m-p}Cl_p \xrightarrow{THD} C_nH_m + p\ HCl & (7.9) \\[2em]
\frac{p}{n}\ C_nH_m + \frac{mp}{4n}\ O_2 + (p-\frac{mp}{2n})\ H_2O \xrightarrow{gasification} p\ CO + pH_2 & (7.10) \\[1em]
\hline
 & + \\[1em]
\frac{p}{n}\ C_nH_m + \frac{p}{2}(1+\frac{m}{2n})\ O_2 \longrightarrow p\ CO + \frac{mp}{2n}H_2O & (7.11)
\end{array}$$

The overall transition shows the following.

- The chlorine loop is closed.
- The production of 1 molar quantity of chlorinated hydrocarbon ($C_nH_{m-p}Cl_p$) involves the conversion of $^p/_n$ molar quantity of its nonchlorinated analogue (C_nH_m). The remainder can be used for different purposes.

This integral process system may be compared with an integral system in which the chlorinated waste is destructed by incineration. Equations 7.12 to 7.14 denote this chain, which is based on the following assumptions.

1. The chlorine content of the waste is assumed to allow incineration without suppletion of an additional fuel.
2. The only chlorine product is HCl: i.e. the Deacon equilibrium is favourably positioned; no or negligible Cl_2 is formed.
3. The hydrogen content of HCl is completely delivered by the chlorinated hydrocarbon feedstock.

$$C_nH_m + p\ HCl + \frac{p}{2}\ O_2 \xrightarrow{oxychlorination} C_nH_{m-p}Cl_p + p\ H_2O \qquad (7.12)$$

$$C_nH_{m-p}Cl_p + (n+\frac{m}{4}-\frac{p}{2})\ O_2 \xrightarrow{incineration} n\ CO_2 + (\frac{m}{2}-p)\ H_2O + p\ HCl \qquad (7.13)$$

$$\underline{\hspace{14cm}}\ +$$

$$C_nH_m + (m+\frac{n}{4})\ O_2 \longrightarrow n\ CO_2 + \frac{m}{2}H_2O \qquad (7.14)$$

The overall transition of this 'incineration system' shows the following.

- Again, the chlorine loop is closed.
- The production of 1 molar quantity of chlorinated hydrocarbon ($C_nH_{m-p}Cl_p$) involves the conversion of 1 molar quantity of its nonchlorinated analogue (C_nH_m).

Comparison of the overall transitions of the 'thermal hydrodechlorination system' and the 'incineration system' reveals that thermal hydrodechlorination is especially attractive

- if the waste has a very high chlorine content (as it can not be combusted properly),
- if the waste has a rather low chlorine content (as a considerable amount of fuel gas or synthesis gas remains).

§ 7.4 General comparison of thermal hydrodechlorination to other chlorinated hydrocarbon waste treatments.

In this paragraph thermal hydrodechlorination is compared with two alternative treatments: incineration, nowadays the main method to treat chlorinated waste, and catalytic hydrodechlorination, a promising alternative, similar to thermal hydrodechlorination. Table 7.1 summarises the three processes.

- ***Thermal hydrodechlorination versus incineration.***

  The basic difference between thermal hydrodechlorination and incineration is that in incineration the chlorinated hydrocarbon molecule is destructed completely. In thermal hydrodechlorination the C-Cl bond is attacked specifically and a valuable organic product remains.

  Both treatments present the option to recycle HCl. In thermal hydrodechlorination it is also possible to 'recycle' the caloric heat of the hydrocarbon product.

Table 7.1 Comparison of thermal hydrodechlorination to incineration and catalytic hydrodechlorination. [3,8]

Incineration	Thermal HydroDechlorination	Catalytic HydroDechlorination
Oxidation process: excess O_2.	Reduction process: excess H_2.	Reduction process: excess H_2.
Elevated combustion temperatures: $T \geq 1300$ °C.	Less vigorous reaction temperature: $T = 700 - 900$ °C.	Mild reaction temperature: $T = 250 - 300$ °C.
Atmospheric pressure.	Atmospheric pressure.	Pressure: 50 - 60 bar.
No catalyst.	No catalyst.	Catalyst.
Restricted Cl content of waste (< 60 wt%) (related with caloric value of waste)	No restriction on Cl content of waste.	Restriction on Cl content depends on type of catalyst (<10 wt%; <60 wt%).
Cl content is released by destruction of hydrocarbon skeleton. (breakage of C-Cl bond consumes heat)	Cl content is released by selective breakage of C-Cl bond. (breakage of C-Cl bond produces heat)	Cl content is released by selective breakage of C-Cl bond. (breakage of C-Cl bond produces heat)
Cl-product: $HCl + Cl_2$.	Cl-product: HCl.	Cl-product: HCl.
'wet HCl': H_2O present • formed from hydrocarbons, • to limit Cl_2 formation (Deacon reaction).	'dry HCl': • no H_2O formation from hydrocarbons, • Cl_2 formation already unattractive.	'dry HCl': • no H_2O formation from hydrocarbons, • Cl_2 formation already unattractive.
Destruction of hydrocarbon skeleton without energy 'reuse'.	Slight alteration of hydrocarbons: fuel or synthesis gas remain.	Hydrocarbons nearly completely unaltered; directly reusable!
Minor soot formation.	Some soot and tar formation.	No or negligible soot formation.
Potential formation of PICs like dioxins.	Potentially no dioxin formation.	No dioxin formation.
Widely used process.	Proven at mini pilot scale; demonstration unit under construction.	< 10 wt% Cl: proven at industrial scale; < 60 wt% Cl: development stage.
costs (60 wt% Cl): ~ fl 1000,=/ ton.	est. costs (60 wt% Cl): ~ fl 525,=/ ton.	est. costs (~10 wt% Cl): ~ fl 350,=/ton.

Incineration leads to the production of HCl and Cl_2. The ratio HCl/Cl_2 is predominantly set by the Deacon equilibrium.

$$2\ HCl + \frac{1}{2} O_2 \rightleftarrows Cl_2 + H_2O \tag{7.15}$$

In the oxygen rich off gas of the incinerator (typically 11 vol% O_2), the quantity of steam determines which proportion of the Cl mass is present as Cl_2. As Cl_2 is hazardous and difficult to collect, it is an undesired product. Steam is present as incineration product, binding the hydrogen released from the original hydrocarbons. Moreover, normally a considerable amount of additional steam is supplied. Therefore, incineration always leads to the production of 'wet' HCl.

In thermal hydrodechlorination the only inorganic chlorine compound produced is HCl. The proportion of Cl_2 is negligible as it reacts vigorously with hydrogen, present in excess.

$$Cl_2 + H_2 \longrightarrow 2\ HCl \tag{7.16}$$

Oxygen containing groups in the chlorinated waste, like hydroxyl groups, are converted more readily to CO than to H_2O. Therefore, thermal hydrodechlorination can produce 'dry HCl', in principle.

In incineration the formation of PICs (products of incomplete combustion) is a well known hazard. Under less controlled conditions dioxins can be formed in reactor and after treatment section. In thermal hydrodechlorination the formation is already very unlikely from a chemical viewpoint.

The estimated cost price of thermal hydrodechlorination is competitive with the actual cost price of incineration, in fact even somewhat cheaper.

Thermal hydrodechlorination is capable to treat all kinds of chlorinated hydrocarbon waste, and can, in principle, be extended to halogenated waste in general. Even substances that are incinerated with difficulty can be treated by thermal hydrodechlorination successfully, like flame retarding and extinguishing species.

To complete the survey, thermal hydrodechlorination is a process in development, while incineration is a widely used process.

- ***Thermal versus catalytic hydrodechlorination.***
  The basic difference between thermal and catalytic hydrodechlorination is the use of a catalyst. As a result, in catalytic hydrodechlorination milder conditions are sufficient, effectuating less alteration of the hydrocarbon structures: the product has a higher (economical) value. On the other hand, restrictions are imposed on the waste to prevent catalyst poisoning. This limits the application of catalytic hydrodechlorination. The cost prices of catalytic and thermal hydrodechlorination are competitive.

§ 7.5 Future outlook.

Evaluation of environmental and economical aspects, as discussed in the previous paragraphs, indicates that thermal hydrodechlorination is more attractive than incineration in the following cases:

- ***treatment of chlorinated hydrocarbon waste having a high chlorine content.*** The caloric value of chlorinated hydrocarbons decreases with their chlorine content. Chlorinated hydrocarbons having a large chlorine content possess flame retarding or even extinguishing properties. Whereas they are combusted with difficulty, they are easily dechlorinated by thermal hydrodechlorination.

- ***treatment of chlorinated hydrocarbon waste having a rather low chlorine content.*** Whereas in incineration the hydrocarbon structure is completely destructed, it is mainly conserved in thermal hydrodechlorination. The conservation gains benefit as the 'hydrocarbon' content gets larger, i.e. with a lower chlorine content (see paragraph 7.3).

In principle, thermal hydrodechlorination can be extended to treat any kind of halogenated waste. Under process conditions of about 900 °C and excess hydrogen, residence times in the order of 1-10 s are sufficient to reach thermodynamic equilibrium, which is always close to complete dehalogenation. Not only chlorine, or in general halogens, but also other functional groups can be removed under conditions of thermal hydrodechlorination. The benefits cited above for treating chlorinated waste counts for all kinds of these wastes.

Comparison of thermal hydrodechlorination to catalytic hydrodechlorination reveals the following. Catalytic hydrodechlorination is the more dedicated process: it treats rather well defined wastes and converts them into a useful chlorine containing product and a useful hydrocarbon product. Since the hydrocarbon feedstock is much better defined and less reorganisation of the organic structures occurs, the hydrocarbon product has a higher value than the rather undefined fuel gas produced at thermal hydrodechlorination. On the other hand, the catalytic process is sensitive to contaminants in the waste that cause catalyst poisoning. The catalytic process demonstrates a high selectivity towards dechlorination, however only a select group of wastes can be treated.

Thermal hydrodechlorination is developed to demonstration scale. The major problem is the formation of soot and tar. In particular, the tar constitutes a technological and health related problem. Catalytic hydrodechlorination is a dedicated process and, depending on the type of waste, the current state of the art ranges from paper study to demonstration scale. Incineration is a proven technology.

Thermal hydrodechlorination can be used to treat any kind of chlorinated waste, whatever its chlorine content may be. In fact, the acceptable range of chlorine content is determined by the after treatment section.

Thermal hydrodechlorination exhibits the best prospects if it is integrated. Three streams are suitable for integration (see figure 7.1):

- the hydrogen (H_2) supply,
- the hydrogen chloride (HCl) product,
- the product containing clean hydrocarbons and unconverted hydrogen.

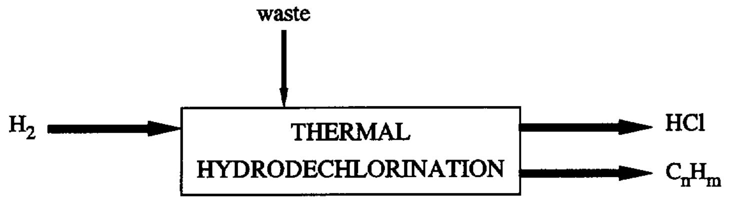

Figure 7.1 *The major substance streams which enter and leave the thermal hydrodechlorination process. These streams are suitable for integration.*

For environmental reasons, integration of the HCl stream is very attractive as a reuse of chlorine is effectuated. Integration with an oxychlorination plant or the like, is strongly recommended.

The produced hydrocarbons can be used as H_2-source. However, if the chlorinated waste has a high chlorine content, all 'fuel' is needed to produce the required H_2, and the advantage of producing a fuel gas is lost.

If a cheap external source of hydrogen is available, the attractiveness of thermal hydrodechlorination over incineration increases. In that case the complete hydrocarbon product with its caloric value remains. The process is improved in an economical as well as an environmental way.

An economic evaluation [2] of the process shows that large scale operation is much more attractive than small scale operation. Synergy which evolves from integration with other processes, could not be taken into account in this evaluation. According to the evaluation, a central treatment point is advised if thermal hydrodechlorination is applied to destruct the chlorinated waste. It should be noted that the feasibility of integration with neighbouring plants becomes rather restricted in such case.

The general conclusion is following. One of the primary objectives of the study is that thermal hydrodechlorination can be used as a 'total treatment' method processing any kind of chlorinated or halogenated waste. From a chemical viewpoint, this objective is feasible. Technological problems related with soot and tar formation exist, but can be solved.

Thermal hydrodechlorination competes with other technologies like catalytic hydrodechlorination and incineration.

- Catalytic hydrodechlorination is a dedicated technology for treating specified wastes. The ultimate hydrocarbon product may have a larger value than the one produced by thermal hydrodechlorination. Hence, in case of a well defined waste catalytic hydrodechlorination may be more appropriate. However, catalytic hydrodechlorination is sensitive to contaminants destroying catalytic activity.

- At present, incineration is the commonly applied industrial treatment method. It consists mainly of proven technology. Incineration can be used to treat chlorinated waste with chlorine fractions up to 60 wt%. The caloric value of the chlorinated waste and the tolerable HCl concentration which the after treatment section can handle, determine the actual limit to the chlorine fraction of the waste. Problems involve the formation of undesirable byproducts at misoperation and in the postreactor zone. Species like PICs and dioxins may be formed. Still, under normal operation incineration is a sound method to treat chlorinated waste.

Though at the moment incineration may be the most appropriate method to treat undefined chlorinated waste, thermal hydrodechlorination offers better prospects: any kind of chlorinated, or more generally halogenated, waste can be treated, a reusable Cl product is produced and a useful hydrocarbon product remains. Thermal hydrodechlorination needs further development, among others to solve the problems related with soot and tar.

In particular, thermal hydrodechlorination is suited to treat waste which can not be handled by dedicated technologies like catalytic hydrodechlorination and the robust technology of incineration. Further development of thermal hydrodechlorination should at least focus on the treatment of these wastes.

The process development presented in this thesis is continued by Royal Schelde. A demonstration unit with a capacity of 600 ton/year has been constructed. The plant not only is a tool for further investigations, but also will be used for demonstration purposes. As the designed construction is transportable, the process can be demonstrated on location!

§ 7.6 Literature references.

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Summary

Chlorinated substances possess various attractive properties. To be able to use them at present and in the future, it is essential to have a proper method to treat the inevitable waste. Such a method is thermal hydrodechlorination, actually a very promising treatment method for halogenated waste in general. During the past years the development of this process has been conducted, thereby focusing on chlorinated liquid waste. These research activities underlay this thesis.

When the development started, experience with thermal hydrodechlorination was only available from small laboratory scale experiments performed at the Gorlaeus Laboratory of the Leiden University. This information is accumulated in the thesis by J.A. Manion. [1]

The main problems to develop the process appeared to be the following.

- The dechlorination reaction is accompanied by the formation of an appreciable quantity of soot and tar.
- The dechlorination is an exothermal reaction, but overall the reactor demands heat. More heat is involved in bringing the reaction medium to the required temperature than is produced by the reaction.
- The rather severe reaction conditions (elevated temperature of 900 °C, hydrogen and hydrogen chloride) result in a difficult choice of construction material.

To get answers to the unknown two installations have been raised.

- ***a mini pilot plant (1 kg/h)***
  The investigation with this plant focused on the optimalisation of the industrial reactor and the essential unit operations for the pretreatment of the feed and the aftertreatment of the reactor effluent.

- ***bench scale installation (30 g/h)***
  In this installation in particular soot and tar production have been investigated. It also offers an excellent tool to investigate construction materials for their behaviour and soot promoting properties.

The design considerations and lay out of the installations are discussed in chapter 2.

The soot formation depends on various factors:

- the type of chlorinated hydrocarbon processed, the availability of hydrogen, the initial contact between chlorinated hydrocarbon and hydrogen, the temperature of the injection system, the wall material and the reactor configuration,
- the applied process conditions: temperature, residence time and probably also pressure.

The combination of residence time and temperature is set by the required dechlorination degree. At 900 °C residence times in the order of 1-10 s are sufficient. Dechlorination levels higher than 99.9% are achieved. The maximum of the dechlorination level is determined by thermodynamical equilibrium.

Longer residence times or higher temperatures result in aggravated soot formation. So, unnecessary deviation should be prevented. A larger excess of hydrogen decreases soot formation, but also has a negative effect on the economical feasibility of the process. From a chemical viewpoint $H_2/Cl = 3$ seems attractive.

Two ways of operating the mini pilot plant reactor have been compared: operation as a fluidised bed versus that as empty tube. On beforehand the fluidised bed operation seemed most promising.

- By the circulating bed material at least part of the reaction heat can be used to bring the feed to the reaction temperature.
- Soot and tar deposit on the bed material. This offers an excellent method to deal with these solid byproducts, especially if all soot and tar are collected in this way.
- The extension to solid waste treatment is straightforward.

Unfortunately, the fluidised bed operation appeared less attractive.

- In the fluidised bed more soot is formed than in the empty tube under similar conditions.
- The fluidised bed does not achieve complete soot collection. Actually, about equal amounts of soot are still emitted.
- Lumps of soot and bed material are formed which entirely deteriorate the reactor operation.

These observations are discussed in detail in chapter 3.

Another important facet is the choice of construction material. Metals like nickel, chromium and cobalt are distinct soot promotors. They also accelerate dechlorination, but the promotion of soot formation is far more abundant. High temperature alloys containing these elements (which frequently is the case) should therefore not be used. The best choice is to use ceramic construction material. However, even in the selection of ceramics one has to be careful as shown by our experience with silicon carbide (SiC). As discussed in chapter 5 SiC exhibits an unexpected instability towards HCl if nickel or cobalt is present. For a proper choice of material one should always verify the behaviour and soot promoting properties of the material. An installation like the bench scale installation is suited for this kind of verification.

Two types of soot have been encountered: filament soot and powder soot. The definition and description of these soot types are given in chapter 3. A typical soot composition is as follows:

- 80-95 mol% C,
- 5-10 mol% H,
- < 1 mol% Cl,
- 1-8 mol% ash remainder.

Most probably the chlorine is present as adsorbed HCl or yet unconverted chlorinated hydrocarbons.

A reaction model is developed to describe thermal hydrodechlorination of chlorobenzene (chapter 4). The model shows that dechlorination and soot formation are closely linked. Actually, it shows that soot is an inevitable byproduct of thermal hydrodechlorination. The initial steps of dechlorination are exactly the same as those of soot formation. Furthermore, soot formation is a kind of dechlorination as it preferentially occurs at the expense of molecularly bonded Cl. So, chlorine is not only eliminated by desubstitution by a hydrogen atom, but also by addition of a hydrocarbon group. This also means that

- chlorinated hydrocarbons have a higher tendency to form soot than their nonchlorinated analogues,
- the soot formed contains no or only a limited amount of molecularly bonded chlorine.

If these steps of soot growth are followed by degrading steps, a catalysing reaction chain results that accelerates dechlorination.

Besides on temperature and reactant concentrations, the reaction rate depends on the rate of initial radical production. The initial radicals are produced by dissociation of the chlorinated hydrocarbons; the gas phase dissociation of molecular hydrogen is too slow. The radical production is so abundant that the concentration of $H\cdot$ radicals exceeds equilibrium.

The precise contribution of wall effects is unclear. On one hand the wall will accelerate the principal dechlorination reactions, on the other it may impose hydrogen dissociation equilibrium, decelerating dechlorination. The final wall effect depends on type and area of its surface and process conditions.

Ritter [2] reports an accelerating effect by suppletion of small amounts of oxygen to the reaction medium. By adding 1-5 vol% O_2 the reaction temperature may decrease 200 °C maintaining the high conversion level. However according to the model calculations it is not certain that the acceleration takes place under all conditions. Further investigation of this interesting option is recommended.

Based on the experiences mentioned above and those obtained at labscale, a plant has been designed under auspices of the Royal Schelde, which treats 22.000 ton/year of chlorinated waste. In the design, which is discussed in chapter 6, preferentially proven technologies are used. The process produces concentrated hydrochloric acid and a gas containing hydrocarbons and hydrogen, which at least can be used as a fuel gas. An economical evaluation indicates a cost price of about fl 525,=/ton for waste containing 60 wt% chlorine. Also presented is an alternative plant producing anhydrous hydrogen chloride. This alteration may improve the economical feasibility, however it also decreases flexibility.

At present, the process development has reached the demonstration stage. A demonstration plant has been built by Royal Schelde. Since april 1993 it is in operation, proving the process at even larger scale. The plant can be transported, enabling demonstration on location! In the handout by Royal Schelde enclosed to this thesis the present state of development is pointed out.

At the end of the thesis (chapter 7) the main conclusions are recapitulated while forecasting the future. In this outlook, among others, the environmental impact of thermal hydrodechlorination is assessed.

Literature references

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Samenvatting

Gechloreerde stoffen hebben verscheidene aantrekkelijke eigenschappen. Om deze stoffen nu en in de toekomst te kunnen gebruiken, is het van belang om onvermijdelijke afval op een goede manier te verwerken. Thermisch hydrodechloreren is een dergelijke methode, feitelijk in ruimere zin toepasbaar op alle soort halogeen houdend afval. In afgelopen jaren is het proces ontwikkeld, waarbij in eerste instantie gericht werd op de verwerking van vloeibaar gechloreerd afval. De resultaten van dit werk vormen de basis voor dit proefschrift.

Toen gestart werd met het ontwikkelingswerk, was de enige kennis van thermisch hydrodechloreren de experimentele ervaring op labschaal zoals opgedaan aan het Gorlaeus laboratorium van de Rijks Universiteit Leiden. Deze ervaring staat vermeld in het proefschrift van J.A. Manion. [1]

De belangrijkste vraagstukken bij de ontwikkeling waren de volgende:

- Als nevenprodukt van de dechlorering wordt een aanzienlijke hoeveelheid roet en teer gevormd.
- Hoewel de dechlorering een exotherme reaktie is, is de reaktor als geheel warmtebehoevend. Er is meer warmte benodigd om het reaktiemedium op de vereiste temperatuur te krijgen dan er vrijkomt bij de reaktie.
- De strenge proces kondities stellen hoge eisen aan het konstruktiemateriaal (hoge temperatuur van 900 °C, waterstof en waterstofchloride gas).

Ten behoeve van het ontwikkelingswerk zijn twee installaties gebouwd.

- ***een mini pilot plant (1 kg/h)***
  In deze installatie is met name aandacht geschonken aan de optimalisatie van reaktor en aanverwante unit operations betreffende voorverwerking van de voeding en naverwerking van de produkten uit de reaktor.

- ***een bench scale installatie (30 g/h)***
  In deze installatie zijn roet- en teervorming onderzocht. De installatie is uitstekend geschikt om het gedrag van konstruktiematerialen en hun roet promotende eigenschappen te onderzoeken.

Het ontwerp van de installaties is besproken in hoofdstuk 2.

De roetvorming hangt van verschillende factoren af:

- het type chloorkoolwaterstof, de hoeveelheid waterstof, het initiële kontakt tussen chloorkoolwaterstof en waterstof, de temperatuur van het injektiesysteem, het wandmateriaal en de reaktor configuratie,
- de toegepaste proceskondities: temperatuur, verblijftijd en druk.

Door de vereiste dechloreringsgraad zijn temperatuur en verblijftijd vastgelegd. Bij 900 °C is een verblijftijd tussen 1 en 10 s voldoende om de vereiste dechloreringsgraad van groter dan 99.9% te bewerkstelligen. De maximale dechloreringsgraad is thermodynamisch bepaald.

Langere verblijftijden of hogere temperaturen leiden tot een vergrote roetvorming. Derhalve dient een onnodige verlenging of verhoging voorkomen te worden. Een grotere overmaat waterstof verlaagt de roetvorming, maar maakt het proces ook economisch onaantrekkelijker. Vanuit een chemisch standpunt is een overmaat van $H_2/Cl = 3$ attractief.

Een vergelijk is gemaakt tussen twee operatiewijzen van de mini pilot plant reaktor: als fluïde bed en als lege buis. Vantevoren leek de fluïde bed operatie de meest aantrekkelijke.

- De circulerende deeltjes voeren tenminste een gedeelte van de reaktiewarmte terug naar de voeding. Deze terugvoer vermindert de totale energiebehoefte van de reaktor.
- Roet en teer slaan neer op het bed materiaal. Dit levert een voortreffelijke manier om met de vaste bijprodukten om te gaan, met name als alle roet en teer op deze wijze worden afgevangen.
- Deze operatie is zeer eenvoudig uit te breiden naar de verwerking van vast afval.

In praktijk bleek de fluïde bed operatie evenwel niet zo aantrekkelijk.

- In fluïde bed operatie wordt meer roet gevormd dan zonder.
- Het bed materiaal vangt niet alle roet en teer af. Sterker nog, de roetuitstoot blijkt ongeveer gelijk te blijven.
- Er worden klonten van roet en bed materiaal gevormd die de reaktor operatie geheel verstoren.

Deze waarnemingen worden gedetailleerd besproken in hoofdstuk 3.

Een ander belangrijk punt is de materiaalkeuze. Metalen zoals nikkel, chroom en cobalt zijn beruchte roet promotors. Zij versnellen weliswaar ook de dechlorering, maar de versnelling van roetvorming is veel groter. Hoge temperatuur legeringen die deze elementen bevatten (hetgeen dikwijls het geval is) kunnen derhalve niet worden toegepast. De beste keuze is om keramisch materiaal te gebruiken. Maar ook in de keuze hiervan dient voorzichtigheid betracht te worden, als gedemonstreerd door onze ervaring met silicium carbide (SiC). Als besproken in hoofdstuk 5 is SiC tegen de verwachting in instabiel ten opzichte van HCl als nikkel of cobalt aanwezig is. Om tot een goede keuze te kunnen komen zal men altijd het gedrag en de roet promotende eigenschappen van het potentiële konstruktiemateriaal moeten nagaan. Een opstelling zoals de bench scale installatie is hiervoor uitermate geschikt.

Twee soorten roet zijn waargenomen: flinter (filament) en poeder (powder) roet. De definitie en omschrijving van deze roetsoorten zijn gegeven in hoofdstuk 3. Het roet is typisch als volgt samengesteld:

- 80-95 mol% C,
- 5-10 mol% H,
- < 1 mol% Cl,
- 1-8 mol% asrest.

Het chloor is meest waarschijnlijk aanwezig als geadsorbeerd HCl of nog niet afgebroken chloorkoolwaterstoffen.

Een reaktiemodel is opgezet om de thermische hydrodechlorering van chloorbenzeen te beschrijven (hoofdstuk 4). Door het model wordt de nauwe onderlinge samenhang tussen dechlorering en roetvorming aangetoond. Roetvorming is een niet te voorkomen bijprodukt. De initiële stappen van dechlorering en roetvorming zijn precies dezelfde. Verder kan roetvorming worden opgevat als een soort dechlorering aangezien roetvormingsstappen met name optreden ten koste van moleculair gebonden chloor, dat wil zeggen door chloor af te splitsen. Dit betekent tevens dat

- chloorkoolwaterstoffen een grotere neiging vertonen tot roetvorming dan hun ongechloreerde tegenhangers,
- het gevormde roet nauwelijks of geen moleculair gebonden chloor bevat.

Als de roetvormingsstappen gevolgd worden door degraderende stappen ontstaat een katalyserende reaktieketen die de dechlorering versnelt.

Naast temperatuur en reactantconcentraties hangt de reaktiesnelheid af van de snelheid waarmee de initiële radicalen worden aangemaakt. De initiële radicalen ontstaan door de dissociatie van de gechloreerde koolwaterstof; de gas fase dissociatie van moleculaire waterstof is veel te langzaam. De produktie van radicalen is zo groot dat de concentratie van H· radicalen de evenwichtswaarde ruim overschrijdt.

De exakte bijdrage van wandeffecten is onduidelijk. Aan de ene kant worden de primaire dechloreringsreakties versneld, aan de andere kant wordt het waterstof dissociatie evenwicht opgedrongen hetgeen leidt tot een verlaging van de dechloreringssnelheid. De uiteindelijke uitkomst hangt af van het type materiaal, het aangeboden oppervlak en de proceskondities.

Ritter [2] maakt melding van een versnellend effect door kleine hoeveelheden zuurstof aan het reaktiemengsel toe te voegen. Door 1-5 vol% O_2 toe te voegen kan de reaktietemperatuur 200 °C zakken onder behoud van het hoge dechloreringsniveau. In navolging van de modelberekeningen is het evenwel twijfelachtig of deze vinding in alle situaties versnellend werkt. Nader onderzoek naar deze interessante optie wordt aanbevolen.

Gebaseerd op de bovenbeschreven ervaringen en die verkregen op labschaal, is een plant ontworpen onder auspiciën van de Koninklijke Schelde Groep, die 22.000 ton/jaar chloorhoudend afval verwerkt. Het ontwerp, zoals besproken in hoofdstuk 6, gaat hierbij voornamelijk uit van bestaande technologieën. De plant produceert geconcentreerd zoutzuur en koolwaterstof en waterstof houdend gas, dat tenminste als 'fuel gas' gebruikt kan worden. Een economische evaluatie toont aan dat een kostprijs gewettigd is rond fl 525,=/ton van 60 massa% chloor houdend afval. Daarnaast is een alternatieve plant gepresenteerd die waterstof chloride gas produceert. Deze verandering verbetert de economie van het proces, maar verlaagt de flexibiliteit.

Op dit moment is de procesontwikkeling beland op het niveau van demonstratie. Een demonstratie plant is gebouwd door de Koninklijke Schelde Groep. Sinds april 1993 is deze in operatie. De plant is verplaatsbaar, zodat op lokatie het proces op deze tamelijk grote schaal bewezen kan worden. In de handout van de Koninklijke Schelde Groep, die aan dit proefschrift is toegevoegd, is de huidige stand van zaken toegelicht.

Aan het eind van het proefschrift, in hoofdstuk 7, zijn de belangrijkste conclusies gerecapituleerd en is het toekomstbeeld geschetst. In deze schets is onder meer het effect van thermisch hydrodechloreren op het milieu in ogenschouw genomen.

Literatuur referenties

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Dankwoord

Het procesontwikkelingswerk van thermische hydrodechlorering begon in de mooie, maar ook hete zomer van 1988. Het was dezelfde zomer waarin de dioxine kwestie de voorpagina van de nederlandse kranten haalde, waaruit eens te meer bleek hoe belangrijk een goede wijze van behandelen van chloorhoudend afval is. De resultaten van het ontwikkelingswerk zijn in dit proefschrift vervat. Het werk had niet verricht kunnen worden zonder de inspanning van velen. Op deze plaats wil ik graag de mensen en instanties bedanken die het onderzoek mogelijk hebben gemaakt en ervoor gezorgd hebben dat het tot een goed einde is gebracht.

Het onderzoek is uitgevoerd in een samenwerkingsverband met de Rijks Universiteit Leiden en de Koninklijke Schelde Groep, daarbij gesponsord door NOVEM namens het ministerie van VROM. De samenwerking was boeiend en leerzaam. Als chemisch procestechnoloog je web te spannen tussen zuiver chemie en werktuigbouwkunde is fantastisch.

In het bijzonder wil ik Peter Mulder bedanken voor zijn assistentie bij het ontrafelen van het reaktiemechanisme. Wouter van der Meer wil ik bedanken voor de plezierige uren bij de Schelde, die niet alleen plezierig waren, maar ook hebben geleid tot de ontwerpen van de installaties op demonstratie en industriële schaal.

Buitengewoon erkentelijk ben ik ook voor het stipendium verleend door de toen nog Zout en Basischemicaliën geheten divisie van Akzo. Dit heeft met name het interessante en nuttige modelwerk mogelijk gemaakt.

Ten behoeve van het procesontwikkelingswerk zijn twee installaties gebouwd. Bij de realisatie daarvan zijn zeer velen betrokken geweest. De ondersteunende technici onder leiding van Dolf Pruisken hebben voortreffelijk werk afgeleverd. Niet alleen was daarbij tijdsdruk een tegenspeler, maar ook door bezuinigingsmaatregelen gedwongen terugloop in bezetting. Het is bewonderingswaardig dat het ondersteunend personeel, met name in die tijd, zo goed en zonder enige wanklank jegens de jonge onderzoeker zijn taken heeft verricht. Bedankt, ik heb veel van jullie geleerd.

Ondanks dat zeer vele betrokken zijn geweest bij de technische ondersteuning, wil ik drie man in het bijzonder noemen: Kees Koeleman, John van Leeuwen en Leon Roessen. Gedurende langere perioden waren zij aan de mini pilot plant gelieerd. Zonder hen was het onmogelijk geweest deze installatie in bedrijf te krijgen en te houden. Enorm bedankt.

Naast de technische ondersteuning, heeft het projekt niet kunnen gedijen zonder de onontbeerlijke ondersteuning op andere vlakken, zoals

- ***analyse.***
  De soms ongewone bepalingen leiden vaak tot boeiende discussies met de analisten onder leiding van Louk Peffer. Altijd werd wel een oplossing, vaak in letterlijke zin, gevonden. Het verkennen van het onbekende terrein, met ieders inbreng vanuit zijn gezichtsveld en achtergrond, heeft geresulteerd in een boeiende samenwerking.
- ***reproduktie.***
  Een projekt bestaat niet zonder rapportages, en hoewel met de huidige programmatuur al veel kan worden voorbereid op de PC, moet tenslotte alles worden uitgeprint, eventuele foto's gemaakt worden, en na het knip- en plakwerk alles worden vermenigvuldigd. Bedankt, Jan Smit, Theo Hunnego, Fred Hammers en Hans van der Aardweg.

Ook dit boekje is in eerste instantie uitgeprint. De scherpe letterkwaliteit is mede mogelijk gemaakt door de gastvrijheid van Eduard van Raalte. Bij zijn automatiseringsbedrijf Orcim Automation zijn tekst en figuren uitgeprint.

Evenmin was veel mogelijk geweest zonder de enthousiaste inbreng van afstudeerders. Zij hebben bijgedragen aan het ontwerp van de installaties, het uitvoeren van experimenten, het interpreteren van de resultaten en het uitzetten van het optimale ontwikkelingspad. Bedankt, Joost Pollmann, Mark Bierens, Roeland Krap, Edwin Berends, Martin Heyne, Marga Overgaag, Richard Jansen, Michiel de Groot, Luuk Delahaye, Tom Reitsma, Erik Prins en Jeroen Goossens.

Hiernaast hebben andere studenten en tweede fase studenten (TWAIO's) ook hun bijdrage geleverd aan de procesontwikkeling middels voorontwerpen en reaktorkundig modelleerwerk.

Mijn kamergenoten, waarvan ik er door verhuizingen heel wat heb gehad, en andere leden van de research groep onder leiding van Cock van den Bleek, wil ik bedanken voor de gezelligheid en het zo nu en dan dienen als klinkend klankbord, vooral op die momenten dat alles roetzwart voor ogen werd. In het bijzonder wil ik Jaap Struijk noemen, met name voor zijn chemisch intellect bij het opzetten van het reaktiemodel. Rob Moene en ik hebben beide kunnen profiteren van een nuttige kruisbestuiving, toen onze nogal verscheiden onderzoeken in de omzetting van SiC in C (of omgekeerd) plots een sterke parallel vertoonden.

Het gehele werk had nooit verricht kunnen worden zonder de inspanningen van mijn promotoren. Ieder op zijn eigen vlak en eigen manier heeft een stimulerende invloed gehad op de voltooiing van het werk. Alle met hun wetenschappelijke inbreng, Cock met zijn vaak ingenieuze ideeën en inspirerende enthousiasme als een nieuw en goed idee geboren was, de kritische noten en tot overdenken prikkelende opmerkingen, maar bovenal de bruikbare en goede suggesties van Albert en de wijsheid en de enthousiasmerende positieve visie van prof. P.J. van den Berg, zowel wat betreft zakelijke als persoonlijke aangelegenheden. Ik dank jullie drieën zeer.

Een zeer belangrijke bijdrage is geleverd door Thom van Velzen. Zonder zijn hand- en spandiensten, was niet mogelijk geweest wat in de afgelopen jaren is verwezenlijkt. Thom assisteerde bij de mini pilot plant opstelling, hielp bij het modificeren, het in gereedheid brengen van de opstelling en het uitvoeren van de experimenten. Maar ook zorgde hij voor een goede sfeer, niet alleen tijdens de koffiepauzes gehouden op zijn kamer. Ik weet dat een ieder die met hem heeft gewerkt in het HKW-projekt dezelfde erkentelijkheid voelt voor zijn onbaatzuchtige en tomeloze inzet. Thom, bedankt.

Promoveren doe je niet alleen. De stimulans van vrienden en familie is van enorm belang. Mijn ouders wil ik in het bijzonder danken. Hun bijdrage is onbetaalbaar. Zij hebben de ruimte en de prikkel gegeven, reeds vanaf heel vroeger. Zonder hen was deze promotie niet mogelijk geweest.

Maar meer dan wie dan ook heb jij, Merel, in het promotiewerk gedeeld. Als klankbord en als stimulans, opbeurend als het in mijn ogen tegenzat, zorgend voor voldoende relativering. Je was een welwillend oor voor zaken die mij niet duidelijk waren, waarvan niet verwacht kon worden dat jij het dan wel zou weten, maar waar je altijd een richting wist aan te geven die mij duidelijkheid verschafte. Zeker in de laatste fase was weinig tijd besteedbaar aan andere zaken, maar ook dat gaf geen probleem. Je staat altijd klaar. Promoveren doe je niet alleen. Wat dat betreft hebben de Duitsers gelijk als zij spreken van 'Frau Doctor'. Lieve Merel, dank je wel.

Curriculum vitae

Antoon Jacob Berend ten Kate werd 4 december 1963 te 's Gravenhage geboren.

Na de middelbare school aan het 1ste Vrijzinnig christelijk Lyceum te Den Haag tussen 1976 en 1982 te hebben doorlopen, vatte hij de studie Scheikundige Technologie van de Technische Universiteit Delft aan. Het propaedeuse diploma werd in de zomer van 1983 cum laude behaald. Het doctoraal diploma volgde op 19 januari 1988. Het afstudeerwerk dat hieraan mede ten grondslag lag, werd uitgevoerd binnen de vakgroep Chemische Technologie. Het betrof een computer simulatie van een ideaal geroerde tank, waarin ten gevolge van een sterk exotherme reaktie meerdere stationaire toestanden kunnen optreden. Uiteindelijk doel was om een zodanige regeling op te zetten dat de reactor in een voorheen instabiel stationair werkpunt gehouden kan worden.

In de zomer van 1988 werd een aanvang gemaakt met het promotieonderzoek, waarvan het resultaat in dit proefschrift is verwoord. Het onderzoek is verricht binnen de vakgroep Chemische Procestechnologie van de Technische Universiteit Delft, in het kader van een samenwerkingsverband met de Rijks Universiteit Leiden en de Koninklijke Schelde Groep. Doel van het onderzoek was de procesontwikkeling naar industriële schaal van thermische hydrodechlorering.

Sedert 1 juni 1993 is hij als Pooltechnoloog in dienst van Akzo Nederland BV, en in die funktie werkzaam bij het Process Development Department van het Research Centre in Deventer van de Akzo Chemicals BV.

Naast bovengenoemde professionele aktiviteiten is hij een fervent hockeyer en skiër.