

## EXPERIMENTAL ASSESSMENT OF TWO-STAGE COMBUSTION OF HIGH PVC SOLID WASTE WITH HCl RECOVERY

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LOAY SAEED

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## Abstract

Energy recovery from solid wastes is, to a large extent, limited by over-large fractions of PVC (polyvinyl chloride) and other organic chlorine compounds, which can cause problems in the operation of an incinerator, combustor or gasifier. However, PVC behaves differently from most other plastic materials. At temperatures in the range 200-400°C, PVC decomposes into HCl (hydrogen chloride) and a cokes/char-like residue. This residue can then be burned at higher temperatures as any other chlorine-free solid waste-derived fuel.

In this work, a laboratory-scale test facility for two-stage combustion of high-PVC solid waste was built and put into operation at Helsinki University of Technology. The facility (40 kW fuel input) contains two fluidized beds: a bubbling fluidized bed (BFB), operating with nitrogen at ~350°C, and a circulating fluidized bed combustor (CFBC), operating at 800-850°C. Most of the chlorine can be removed (recovered) as HCl from the BFB, which leaves a small percentage to be removed from the flue gases after the CFBC. At the same time, this reduces the HCl corrosion problems, with a low risk of formation of chlorinated species such as dioxin and furans.

The design work was based on process optimization calculations for a 40 MW<sub>thermal</sub> plant design case using a process simulation program (PROSIM). The design case was scaled down from 40 MW to 40 kW thermal fuel input. A new module for the pyrolysis reactor was built to be used in the simulation of the two-stage combustion process. The simulation work showed a process thermal efficiency of approx. 36 % compared to 33%, depending on pyrolysis temperature and the PVC content in the solid waste, for a conventional waste incineration plant. The design of the test facility was also based on kinetic data on the de-hydrochlorination of typical PVC, on combustion of chars from PVC and wood, and on information from the literature.

Two types of PVC (bottle-grade PVC and sewage pipe PVC) were used as a fuel in a two-stage combustion test facility. The results from both tests were very promising. The chlorine content in the chars taken from the BFB for the bottle-grade PVC was below 0.1 %-wt (from 50.93%-wt in the PVC), at chlorine-to-carbon mass ratio < 0.001 kg Cl / kg C. This means that a char (which is forwarded to the CFBC) in Class I (less than 0.15%-wt Cl) of the Finnish classification of solid recovered fuel (SRF) can be produced using this process. The char chlorine content for the sewage pipe PVC was about 5%-wt (from 53.54%-wt in the PVC) at chlorine-to-carbon mass ratio < 0.06 kg Cl / kg C. Also, the char sample analysis of sewage pipe PVC 2 for the determination of polychlorinated toxic compounds showed very small amounts of PCDD (0.78 ng/g, 0.155 ng TEQ/g) and PCDF (2.51 ng/g, 0.35 ng TEQ/g).

The result shows that the process has the potential to remove most of the chlorine from a fuel input that contains large amounts of PVC chlorine, i.e., amounts that are problematic for other thermal processes. This despite the use of a cheap perforated distributor plate in both reactors (BFB and CFBC), which may have affected the bed material mixing (especially in the BFB) and the quality of the char that was forwarded to the CFBC. The results also show that the total amount of chlorine released with the CFBC flue gases as HCl was less than 6.5% of the Cl input with the PVC.

The test results show new information about the behavior of different types of PVC in a two-stage combustion process. They confirm that the optimal temperature range for operating the BFB during pyrolysis, 340-350°C, is the optimum temperature range in which to release most of the chlorine from the PVC. It also shows the stabilizer effects of different PVC types on degradation during pyrolysis in the BFB reactor, which affects the quality of the char forwarded to the CFBC.

Many tests to examine the PVC behavior when mixed and pyrolyzed or co-pyrolyzed with other fuels like wood (Finnish pine) and Polish coal were performed in this work. The results show that there is an interaction in PVC/wood pine mixtures that affects the degradation of both fuels. A similar interaction also occurs with the PVC/Polish coal mixture.

**Keywords:** Fluidized bed, HCl, polyvinyl chloride, pyrolysis, solid waste, stabilizers

## Preface

A large part of the work described here was part of the Finnish national research program “Waste to REF and Energy” (Jätteiden energiakäyttö), 1998-2001, funded by the Finnish Technology Agency “Tekes”, the Finnish Plastics Industries Federation, Foster Wheeler Energia Oy and Borealis Polymers Oy. It received support also from Fortum Foundation (formerly Imatran Voiman säätiö), Ekokem Oy (support funding / apurahoitus 1999) and Helsinki University of Technology. These all are acknowledged for supporting this work.

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# Contents

<b>Abstract.....</b>	<b>3</b>
<b>Preface.....</b>	<b>4</b>
<b>Contents .....</b>	<b>5</b>
Abbreviations and Symbols .....	7
Abbreviations .....	7
Symbols.....	7
Greek letter.....	8
Subscripts.....	9
<b>1. Introduction.....</b>	<b>10</b>
1.1 PVC: Background and overview .....	10
1.2 PVC thermal degradation.....	10
1.3 PVC waste recycling.....	12
1.4 Problem description .....	14
1.5 Objectives of the research work.....	14
1.6 Outline of the thesis .....	15
<b>2. Literature review of thermal processes for high-PVC waste treatment.....</b>	<b>18</b>
2.1 Process for HCl recovery form plastics .....	18
2.2 West Virginia University Process.....	19
2.3 Process for converting plastic waste into electric power .....	19
2.4 Thermospliting recycling process for HCl recovery from PVC waste.....	20
2.5 BSL incineration process .....	21
2.6 Linde gasification process.....	22
2.7 Akzo Nobel steam gasification process .....	23
2.8 Process for PVC incineration.....	24
2.9 Process for steam gasification of PVC waste .....	24
2.10 Gasification process of waste containing PVC.....	25
2.11 Conclusion .....	26
<b>3. Theoretical design work using a process simulation program (PROSIM).....</b>	<b>29</b>
3.1 PVC pyrolysis .....	29
3.2 Pyrolysis module.....	30
3.3 Design of two-stage combustion power plant with HCl recovery .....	30
3.3.1 Process description (design case).....	30
3.3.2 Analysis result for changing pyrolysis reactor temperature .....	33
3.4 Design of conventional solid waste incineration plant .....	34
3.4.1 Process description.....	34
3.5 Comparison between two-stage combustion plant with HCl recovery and conventional solid waste incineration plant.....	34
3.5.1 Technical comparison .....	34
3.5.2 Environmental comparison .....	38

3.5.3 Summary of the main finding from the theoretical design work .....	38
<b>4. Test facility design description and experimental procedure .....</b>	<b>40</b>
4.1 Kinetic calculation .....	40
4.2 Test facility description .....	41
4.2.1 Reactors .....	41
4.2.2 Non-mechanical valves (seal pot) .....	43
4.2.3 Gaseous products and gas analysis .....	43
4.3 Pressure drop around the test facility .....	43
4.4 Measurement equipments and accuracy .....	45
4.4.1 Temperature measurements .....	46
4.4.2 Pressure and flow rate measurements .....	47
4.4.3 pH measurements .....	48
4.4.4 Gas analyzer .....	48
4.4.5 Calibration gases .....	50
4.5 Fuel types used and test procedure .....	50
4.5.1 Fuel types used for the tests .....	50
4.5.2 Pyrolysis tests .....	52
4.5.3 Two-stage combustion tests .....	53
<b>5. Test results and discussion .....</b>	<b>54</b>
5.1 Bottle-grade PVC pyrolysis .....	54
5.2 PVC waste No.1 (sewage pipe) pyrolysis .....	56
5.3 PVC waste No.2 (sewage pipe) pyrolysis .....	59
5.4 Comparison of PVC types .....	61
5.4.1 FT-IR spectrometer gas analysis results .....	62
5.4.2 Char samples analysis .....	62
5.5 Pyrolysis test with 100% wood (Finnish pine) .....	63
5.6 Pyrolysis test with 100% Polish coal .....	65
5.7 Pyrolysis test with 20% bottle-grade PVC + 80% wood (Finnish pine) .....	66
5.8 Pyrolysis test with 20% bottle-grade PVC + 80% Polish coal .....	69
5.9 Two-stage combustion test with 100% bottle-grade PVC .....	71
5.10 Two-stage combustion test with 100% PVC waste as a fuel .....	75
5.11 Dioxins/Furans (PCDD/Fs) .....	78
<b>6. Conclusion .....</b>	<b>80</b>
6.1. Theoretical work .....	80
6.2. Experimental work .....	80
6.3 Contribution of the work .....	82
6.4 Recommendations and future work .....	83
<b>References .....</b>	<b>85</b>

## Abbreviations and Symbols

### Abbreviations

BFB	Bubbling fluidized bed
CFBC	Circulating fluidized bed combustor
CIP	Conventional incineration plant
ESP	Electrostatic precipitator
FT-IR	Fourier transform infrared
GC/MSD	Gas chromatograph/ mass selective detector
HCl	Hydrogen chloride
HDPE	High density polyethylene
I-TEQ	International toxic equivalency quotient
LHV	Lower heating value
LDPE	Low density polyethylene
MSW	Municipal solid waste
NDIR	Non-dispersive infrared photometer
PVC	Polyvinyl chloride
PCBs	Polychlorinated biphenyls
PCDD	Polychlorinated dibenzo-p-dioxins
PCDF	Polychlorinated dibenzo-furans
PE	Polyethylene
PAH	Polycyclic aromatic hydrocarbon
PP	Polypropylene
PS	Polystyrene
PUF	Polyurethane foam
PROSIM	Process Simulation Program
RDF	Refuse-derived fuel
SRF	Solid recovered fuel
t	tonne (1000 kg)
TCD	Thermal conductivity detector
VCM	Vinyl chloride monomer

### Symbols

$C_0$	initial concentration (kg/m <sup>3</sup> )
$c_p$	specific heat (kJ/kg.K)
$d$	circular diameter (m)
$D_e$	diameter of the flue gases exit pipe (m)
$E$	Specific energy (kJ/kg)
$E_a$	kinetics activation energy (J/mol)
$g$	gravity acceleration (m/s <sup>2</sup> )
$H$	height of the cyclone inlet duct (m)
$H$	riser height (m)



$H_v$	pressure drop in the cyclone (kPa)
$h$	specific enthalpy (kJ/kg)
$h^\circ$	enthalpy of formation (kJ/mole)
$k$	chemical reaction rate coefficient (1/s)
$K$	constant that depends on cyclone configuration and operations ( $K=12-18$ )
$L_{sp}$	height of the solid in the stand pipe (m)
$m$	actual mass (kg)
$m_0$	initial mass (kg)
$m_\infty$	final mass (kg)
$m^\circ$	mass flow rate (kg/s)
$M$	molecular weight (g/mole)
$N$	reaction rate order (-)
$N$	number of moles (-)
$P$	power (MW)
$p$	pressure (bar) or (kPa)
$\Delta p_b$	pressure drop across the bed (kPa)
$\Delta p_d$	pressure drop across the distributor (kPa)
$\Delta p_{cy}$	pressure drop across the cyclone (kPa)
$\Delta p_r$	pressure drop in the riser (kPa)
$\Delta p_{sp}$	pressure drop in the stand pipe (kPa)
$R$	ideal gas constant (= 8.314 J/mol. K)
$t$	time (s)
$T$	temperature ( $^\circ\text{C}$ )
$U_o$	superficial gas velocity (m/s)
$U_{mf}$	minimum fluidization velocity (m/s)
$U_t$	terminal settling velocity (m/s)
$V_i$	gas inlet velocity in the cyclone (m/s)
$W$	mass fraction (%)
$W_c$	width of the cyclone inlet duct (m)
$x$	conversion ratio of PVC (-)
$Z$	height of the riser (m)

### Greek letter

$\eta$	thermal efficiency (%)
$\gamma$	stoichiometric ratio (-)
$\alpha_{FB}$	degree of conversion (-)
$\rho_g$	gas density ( $\text{kg/m}^3$ )
$\rho_s$	solid density ( $\text{kg/m}^3$ )
$\varepsilon$	voidage (-)
$\varepsilon_{mf}$	voidage under minimum fluidization (-)
$\varepsilon_o$	overall voidage (-)

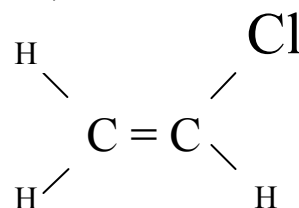
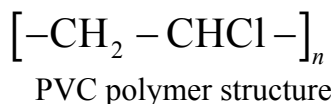
## Subscripts

<i>b</i>	bed
<i>B</i>	blower
<i>d</i>	distributor
<i>e</i>	exit
<i>cy</i>	cyclone
FB	fluidised bed
<i>i</i>	inlet
<i>m</i>	number of Hydrogen atoms
<i>g</i>	gas
<i>mf</i>	minimum fluidization
<i>n</i>	number of carbon atoms
<i>p</i>	pump
<i>py</i>	refer to pyrolysis
<i>r</i>	riser
<i>s</i>	solid
<i>sp</i>	stand pipe
<i>st</i>	steam turbine
<i>t</i>	terminal
<i>w</i>	refer to water
<i>o</i>	initial state
<i>o</i>	overall

# 1. Introduction

## 1.1 PVC: Background and overview

Polyvinyl chloride (PVC) is a synthetic polymer material (or resin), which is built up by the repetitive addition of the monomer vinyl chloride (VCM) with the formula  $[-CH_2-CHCl-]_n$ . PVC has thus the same chain structure as polyethylene except for the presence of chlorine. Pure PVC is a rigid material that is mechanically tough, has a fair degree of weather resistance, is water and chemical resistant, electrically insulating, but relatively unstable to heat and ultraviolet light (EU, 2000; Summers, 1997).



Polyvinyl chloride (PVC) is ranked second behind polyethylene in terms of worldwide polymer consumption because it has a good chemical resistance and can be used in different applications such as building and construction, packing, wires and cables, transport, furniture etc. (Scheirs, 1998). World production of PVC today is at more than 20 million tonnes per year (up from 3 million tonnes in 1965), which corresponds to about one fifth of the total plastics production. Production is mainly located in the US, Western Europe and Asia (EU, 2000). The production of PVC may exceed 30 million tonnes by 2010. The main applications of PVC in Europe are in the building sector, which accounts for 57% of all uses; PVC is also used in many other applications such as household appliances (18%), packaging (9%), electric and electronic equipment (7%), automotive equipment (7%), furniture (1%) and other applications (1%) (Plinke et al., 2000).

## 1.2 PVC thermal degradation

Many researchers have investigated PVC degradation (Baum and Wartman, 1958; Stromberg et al., 1959; Ballistreri et al., 1980; Hirschler, 1985 and Wypych, 1985) but the mechanisms that occur during thermal degradation are not yet fully understood. PVC behaves differently from other commodity plastic materials such as polyethylene (PE), polypropylene (PP) and polystyrene (PS). At temperatures in the range 200-400°C, PVC decomposes into HCl plus some hydrocarbons and a cokes-like residue (Shigaki et al., 1973; Cullis and Hirschler, 1981; Bockhorn et al., 1999; Bockhorn et al., 1996; Zevenhoven et al., 1997). This is apparently due to relatively low activation energy for thermal degradation (Brandrup, 1996). Williams (1998) noticed that the thermal degradation of PVC begins at around 150°C because the C-Cl bond in the PVC structure

has a low bond dissociation energy (339 kJ/mol) compared to (414 kJ/mol) for the C-H bond and (611 kJ/mol) for a C = C bond, and on heating it has a tendency to break first.

Pyrolysis tests on PVC showed that 90% or more of the chlorine was released as HCl at a temperature between 350 and 400°C (Oudhuis et al., 1991; Wu et al., 1994; Zevenhoven et al., 2002). If the pyrolysis temperature rises above 400°C, there will be a second stage of degradation that will further break down the hydrocarbon intermediates produced after dehydrochlorination. Figure 1.1 illustrates PVC decomposition over the temperature range 50-900°C.

In general, PVC degradation during pyrolysis below 400°C follows two steps. The first corresponds to hydrochlorination and polyene chain formation, while the second to the degradation of the polyene chain (Wu et al., 1994). Later, however, several researchers suggested that this first step of PVC decomposition during the pyrolysis reaction includes two parallel processes. The first is the conversion of PVC to HCl and an intermediate residue; the second is the decomposition of the intermediate residue into a polyene chain and some volatiles. The second step is the decomposition of the polyene into volatile (gaseous) aromatics and solid residue (see, for example, (Marcilla and Beltrán, 1995)).

Many additives are added to PVC during processing before its use in different applications. These additives include stabilizers, plasticizers, lubricants, colorant, filler, impact modifier, flame-retardants, antistatic agents and blowing agents (Møller et al., 1995). The main function of a heat stabilizer is to prevent degradation during processing. Part of it will be lost during that and sometimes during the application period also. The effects of additives and stabilizers on the pyrolysis kinetics of waste PVC (e.g., waste PVC pipe) seem to be particularly significant, especially during the first degradation reaction stage (Kim, 2001). They have in common the ability to react with HCl when this is liberated from the polymer. Another task is to replace labile chlorine atoms, which may initiate the dehydrochlorination of more stable groups, and thus to enhance the heat stability (Braun, 2002).

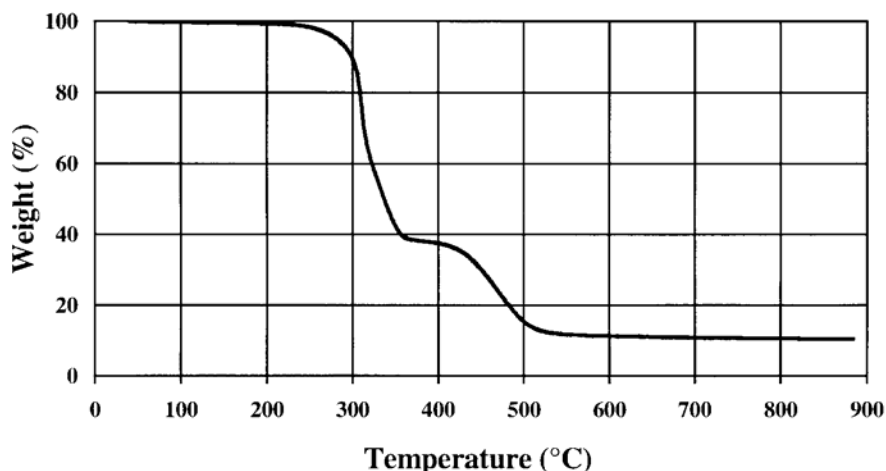


Fig.1.1 Variation in residual weight (%) with temperature (°C) for pyrolysis of a typical PVC sample in nitrogen, heating rate 20°C/min (Zevenhoven et al., 2002)

Stabilizers are often composed of salts of metals like lead, barium, calcium, cadmium, or organo-tin compounds. The amount of formulated lead compound stabilizers sold in the European Union in 1998 was about (112000 tonnes), which represents 70% of the total stabilizers used in PVC production. The rest contains 9% mixed metal solid stabilizers (e.g., Ca/Zn systems), 9.4% organo-tin compound stabilizers and 11.3% liquid stabilizers (Ba/Zn or Ca/Zn) (Donnelly, 1999). Stabilizers form the most important categories of additives; those containing heavy metals such as lead and cadmium, in particular, need to be assessed scientifically in terms of their hazardous characteristics and the risks they pose to human health and the environment. They should be handled with care. Furthermore, landfilling with PVC waste may become undesirable because landfills and their long-term behavior imply uncertainty and risk (Mersiowsky, 2002).

Some heat stabilizers could actually act as a degradation accelerator if there is not sufficient mixing of the stabilizer and PVC (Gökçel et al., 1999). Also, some stabilizers such as Ca/Zn, if added (typically 1%-wt) to a pure PVC resin, increase the maximum dehydrochlorination rate (Stipanelov et al., 2000). These stabilizers are more expensive and less effective than lead-based stabilizers, but, because of their (relative) physiological harmlessness, these newer types are used in food packaging materials, children's toys and bottle seals (Gould et al., 1984).

### **1.3 PVC waste recycling**

According to the statistics mentioned in Section 1.2, the PVC waste amounts will increase significantly and the disposal of these wastes, which include municipal and industrial wastes, is now recognized to be a major environmental problem. Around half of the chlorine in the municipal solid waste (MSW) comes from PVC, which also means that around half the HCl in the combustion gases comes from MSW incinerators (Shibai et al., 2001).

There are many options for dealing with PVC waste (and solid wastes with large fractions of PVC) and for each there are advantages and disadvantages. The option of landfilling with PVC waste has been exercised for many years, but is becoming undesirable because of land wastage and seepage of toxic decomposition products out of landfill areas (McGhee, 1995). Besides that, landfills and their long-term behavior imply uncertainty and risk because of the fate of the PVC products and their additives like stabilizers and plasticizers (Mersiowsky, 2002)<sup>1</sup>.

The second option is the incineration of PVC waste, which, is in most cases too expensive because of the technical problems related mainly to corrosion effects and the often-unacceptable emissions such as HCl, dioxins and furans. The third option is the recycling of the PVC.

There are four recycling types. The first is primary recycling, which includes the processing of PVC waste into the same or similar types of products from which it was generated (Leidner, 1981) using standard plastics processing methods.

The second is the secondary recycling or mechanical recycling, which utilizes the PVC waste unsuitable for direct reprocessing using standard plastic processing. The

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<sup>1</sup> Several recent publications address the fate of PVC in landfills; their conclusions appear to correlate with the activities of those acknowledged in these publications.

disadvantage of this type of recycling is high cost as well as low demand for the recycling products.

The third is the tertiary, or chemical, recycling, where the PVC waste is converted into short-chain chemicals for reuse in polymerization or other chemical processes. Four different process technologies are currently considered for chemical recycling: cracking, gasification, hydrogenation and pyrolysis (Braun, 2002). A reasonably economical process can be used, some revenues from the products would also be possible, and the net cost of disposal might be significantly reduced (Scott et al., 1990). The pyrolysis of waste PVC is likely to be one of the most promising ways of recycling because it is environmentally friendly, economically viable and can treat a large quantity of waste PVC in a technically stable manner (Kim, 2001).

The fourth type is the quaternary recycling, or energy recovery recycling. PVC waste has an average heating value (21 MW/kg), which can be compared to other fuels as in Table 1.1.

Table 1.1 Proximate and ultimate analysis of different types of fuel (dry %-wt)

Fuel type	Proximate analysis						Ultimate analysis					
	FC	Vol	Ash	MC	LHV	HHV	C	H	N	S	O*	Cl
Bituminous coal (Poland) [1]	53	35.9	11.1	3	27.4	28.4	70.6	4.3	1.2	1.3	11.8	0.07
Coal Illinois #6 [2]	46.4	39.21	16.8			23.5	61	4.1	1.2	3.6	14.6	0.04
Peat [3]	23.2	72.1	2.35	27.9		24.1	57.8	6.1	1.79	0.19	31.5	
Wood [3]	12.6	85.8	0.45	6.15		19.1	48.9	6	0.17	0.06	43.8	
Sewage sludge (dried) [4]	8.5	74.7	17.9	5.2	15.8		40.5	5.8	1.7	0.5	37.2	0.3
Car tyre scrap (Nokia/Slite)[1]	30.6	69.4	6.35	0.66	35.5		79.6	7.0	0.43	1.54	5	0.06
RDF [4]	8.9	73.4	17.7	3.2	19.1		48.4	7.0	0.84	0.12	25.2	1.0
LDPE [3]		99.9	<0.05	0.10	46.0		85.7	14.3			0.16	
HDPE [3]		99.9	<0.05	0.16	43.1		85.6	14.2			0.30	
PP [3]		99.9	<0.05	0.13	46.5		85.5	14.3			0.19	
PS (white) [3]		97.0	2.89	0.11	40.6		88.9	8.3			0.16	
PUF [4]		1.8	0.3	1.80	27.0		63.2	6.7	6.6	0.01	13.5	9.6
PVC [3]	7.5	92.3	<0.05	0.18		21.2	40.1	5.1			0.65	53.8
Black Liquor solids [2]	15.6	55.78	40.2		9		29.2	4.4	0.14	4.9	31.1	0.06
Orimulsion (dried) [2]	4.9	93.7	1.4		39.7		82.8	10.1	0.7	3.7	1.5	0.07

\*[1] Kääntee et al., 2004, [2] Zevenhoven and Hupa, 1998, [3] Zevenhoven et al., 1997, [4] Zevenhoven et al., 2000a; FC: Fixed carbon; Vol: volatiles; MC: moisture content as received; RDF: refuse-derived fuel; LDPE: low density polyethylene; HDPE: high density polyethylene; PP: polypropylene; PS: polystyrene; PUF: polyurethane foam; PVC: polyvinyl chloride

In general, PVC wastes can be converted into energy via two main processes: thermal conversion and liquefaction. Thermal conversion processes (gasification, combustion and pyrolysis) offer the best means to heat and power generation from solid waste fuels and, at the same time, provide an attractive method of disposal and volume reduction (Juniper, 1997). The research work in this thesis lies in the area of the fourth type of recycling.

#### **1.4 Problem description**

Energy recovery from the combustion of solid wastes with high concentrations of chlorine is complicated from both technical and environmental viewpoints. The presence of HCl with other aggressive gases in the flue gases will increase the risk of boiler corrosion if the temperature of the steam rises above 400°C; besides that, there is the additional potential risk of dioxin and furan formation. In general, waste-derived fuels should contain less than 2% by weight of chlorine in order to avoid problems with the operation of the incinerator, combustor or gasifier. In Finland, more than 90% of the chlorine found in the dry fraction of household waste (when newsprint, paper, metal, glass and biowaste are collected separately) is related to PVC (Hietanen, 2000).

In Finland, a classification for solid recovered fuels (SRF) is suggested, which, for chlorine, defines Class I as having less than 0.15%-wt Cl, Class II less than 0.5%-wt Cl, and Class III less than 1.5%-wt Cl. Sources for chlorine in waste are mainly polyvinyl chloride, PVC (~55%-wt Cl), sodium chloride, NaCl (~61%-wt Cl), chlorine in bleached paper and various organic solvents. Hence, for a Class SRF, the mass fraction of PVC is limited to less than 0.2%-wt, which would enforce dilution of a high-PVC waste with a chlorine free fraction. This makes high-PVC containing wastes uninteresting from a waste-to-energy perspective.

Not much has been published in the literature prior to this work on the behavior of 100% PVC waste in a bubbling fluidized bed or circulating fluidized bed in a laboratory scale test facility or a full-scale plant; for this reason, similarities and differences between our work and other processes were difficult to predict (see Chapter 2).

#### **1.5 Objectives of the research work**

The motivation for the research is based on an idea (Zevenhoven, 2000) for a two-stage combustion process, which can deal with solid wastes that contain problematically large fractions of PVC. In this process, the first reactor is a bubbling fluidized bed (BFB) pyrolyser and the second a circulating fluidized bed combustor (CFBC). High-PVC solid waste is fed to the BFB, where it is heated up to about 350°C to release (most of) the chlorine as hydrogen chloride (HCl). In order to avoid any risk of dioxin and furan formation, the gas used for the fluidization in this first reactor is nitrogen (N<sub>2</sub>). The gases from the BFB contain mainly N<sub>2</sub>, HCl, H<sub>2</sub>O and small amounts of other gases. The solid residue is combusted in the CFBC at around 800-850°C with little environmental hazard or corrosion problems. Figure 1.2 shows the simplified scheme of the process.

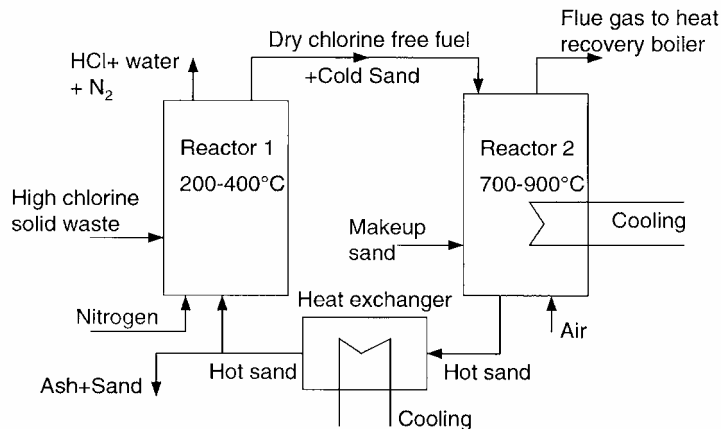


Fig. 1.2 Simple process schematic for two-stage combustion of high-PVC solid waste

The objective of this thesis is to assess whether the process shown in Fig. 1.2 is able to deal with high-PVC solid waste, and to investigate the behavior of PVC waste only, and of PVC waste mixed with other fuel like wood (pine) and Polish coal. For this purpose, a test facility was built at Helsinki University of Technology/Otaniemi based on kinetic data on de-hydrochlorination for a typical PVC, combustion of chars from PVC and wood, process optimization calculations for a 40 MW<sub>thermal</sub> plant design case (scaled down from 40 MW to 40 kW thermal fuel input), and on information about BFBs and CFBCs from the literature. Several experimental tests were carried out using different types of PVC waste in the first reactor (BFB) only. In addition to that, two tests were performed using two types of PVC waste in a two-stage combustion process operation, and some pyrolysis tests were performed using PVC mixed with other fuel like wood (Finnish pine) and Polish coal.

## 1.6 Outline of the thesis

This thesis is divided into six chapters. The introduction is included in Chapter 1, while a literature review of other thermal processes for waste PVC prior to this work is presented in Chapter 2. The theoretical design work relating to two-stage combustion (design case) using a process simulation program (PROSIM) is presented in Chapter 3. The test facility design description and experimental procedure of all the tests are presented in Chapter 4, along with the description of the measurement equipment. The results of the tests, together with a discussion of them, can be found in Chapter 5. Finally, Chapter 6 presents the conclusions reached from this work and recommendations for further work in the future.

In addition to the summarized part, most of the work in this thesis is presented in the following publications, which are attached here as appendices:

- I. Ron Zevenhoven, Loay Saeed, Carl-Johan Fogelholm, "Optimization of two-stage Combustion Process for High- PVC Solid Wastes with HCl Recovery", ECOS 2000, Enschede, the Netherlands, July 2000, part 4, pp.1959-1970.



- II. Loay Saeed, Ron Zevenhoven, 2000 “Comparison between Two-Stage Waste Combustion with HCl Recovery and Conventional Incineration Plants”. *Energy Sources*, 24 (1), 2002, pp.41-57.
- III. Loay Saeed, Ron Zevenhoven, 2002 “Experimental Study on Two-Stage Combustion of High-PVC Solid Waste”. *Proc. of R'02 Recovery Recycling Re-integration*, Palexpo-Geneva (Switzerland) February 2002 (CD-ROM).
- IV. Loay Saeed, Antti Tohka, Matti Haapala, Ron Zevenhoven, “Two-stage combustion of PVC-containing wastes with HCl recovery: an experimental assessment”, *Energy Sources*, 2004, *in press*.
- V. Loay Saeed, Antti Tohka, Matti Haapala, Ron Zevenhoven, “Pyrolysis and Combustion of PVC-containing fuels in a two-stage fluidized bed process: PVC, PVC-wood and PVC-coal mixtures”, *Fuel Processing Technology*, 2004, *in press*.
- VI. Loay Saeed, Antti Tohka, Matti Haapala, Ron Zevenhoven, “Slow pyrolysis of different PVC types in a bubbling fluidized bed: stabilizer effects”, *Journal of Analytical and Applied pyrolysis*, 2004, *in press*.

The disputant is the leading author of five publications (II-VI). Discussion with the co-authors has helped in building the pyrolysis module used in the simulation and the kinetic calculations of PVC degradation in a BFB pyrolysis reactor. In addition, Zevenhoven gave valuable advice and comments during the design and construction of the test facility. He also contributed comments on all the papers. The co-author Haapala was responsible for checking the FT-IR gas analyzer and its calibration for all gases considered. He also checked some of the results after they were analyzed by the disputant in publication (IV-VI). Tohka helped with the part of publication (IV-VI) relating to experimentation.

In Paper I, the idea of the two-stage combustion process was used to design a 40 MW fuel input plant using a process simulation program (PROSIM). In this paper, simulation results are presented for various process temperatures and waste-derived fuels with varying amounts of (wet) PVC mixed with (wet) wood. The process has a predicted thermal efficiency of approx. 36%, depending on pyrolysis temperature and the PVC content of the solid waste. Paper I, was written by Zevenhoven, but the disputant made all the simulation calculations related to the process. Prof. Fogelholm contributed several comments on this paper.

Paper II presents a comparison between a two-stage waste combustion process that makes use of the properties of PVC and a conventional solid waste incineration plant of 40 MW fuel input. The comparison was made from the perspective of plant performance and environmental impact, mainly considering HCl emission. The disputant carried out all the simulation calculation and wrote most of the paper.

In Paper III, the description and the design parameters of the two-stage combustion test facility are presented. Some simulation calculations are carried out in this paper. Also, different PVC waste type quality is discussed. The disputant is the leading author of this paper.

In paper IV, several test results using pure bottle-grade PVC, with wood and with Polish coal are presented. The main part in this paper concentrates on the first stage of decomposition of PVC in the bubbling fluidized bed. The result shows that there is an interaction in PVC/wood pine mixture, which affects the degradation of both fuels. A similar interaction occurred with the PVC/Polish coal mixture. Results from the two-stage combustion test using 100% pure bottle-grade PVC are also presented. The chemical analysis shows that the chlorine content is below 0.1%-wt at the chlorine-to-carbon mass ratio  $< 0.001 \text{ kg Cl/kg C}$ . The disputant acted as the leading author of this paper.

In paper V, the design of the test facility rig is presented. The design of rig is based on a kinetic decomposition calculation for PVC, design procedures found in the literature and on the earlier simulation calculations of the process. Zevenhoven carried out the kinetics decomposition calculation for PVC and actively commented on the paper. Results from the pyrolysis/de-hydrochlorination of the PVC and char combustion test using a waste PVC sewage pipe are presented. This paper was mainly written by the disputant.

Paper VI was also mainly written by the disputant. The paper shows the effects of stabilizers on the thermal degradation of PVC in a bubbling fluidized bed. Three types of PVC were used in the tests: pure rigid bottle-grade PVC and two types of rigid PVC (sewage piping) waste. The results from the tests and char analysis shows that the weight fraction and the type of the stabilizer, especially lead-based compound, have a major effect by slowing PVC degradation, especially during the first degradation stage, when compared to a more pure PVC which contains only a small amount of tin based compound.

## 2. Literature review of thermal processes for high-PVC waste treatment

Processes that deal with high-PVC waste have been suggested since more than thirty years ago. There are many processes that deal with plastic solid waste, but, in this review, we will concentrate on all processes that deal with some form of energy recovery for mainly high-PVC solid waste. Most of these processes aim to recover in usable form as much of the chlorine present in PVC as possible.

### 2.1 Process for HCl recovery form plastics

Shigaki et al. (1973) introduced a process (Fig. 2.1) for the disposal of scrap vinyl polymers containing hydrogen and chlorine. The scrap polymer is crushed first in a crusher (4) and then fed into a rotary kiln (7) through a screw conveyor (6). The rotary kiln is heated by air, which is circulated through a heat exchanger (9). The temperature in the rotary kiln is maintained at 280°C to cause the partial decomposition of the scrap. The chlorine is separated from the scrap and recovered in the structure (14). Crushed and partially decomposed polymer is sequentially discharged onto the grate of furnace (15), which is subjected to a current of air that is substantially in excess of that required for the complete combustion of the scrap material. A water spray unit (19) is mounted after the furnace to control the temperature of the hot gases, which are then passed through an air heat exchanger (9). Cyclone (20) is mounted after the air heat exchanger to remove the fine solid particles and the fly ash that arise from the combustion. The gases are then discharged to the ambient atmosphere through a chimney (22). No data concerning the performance of the process is available.

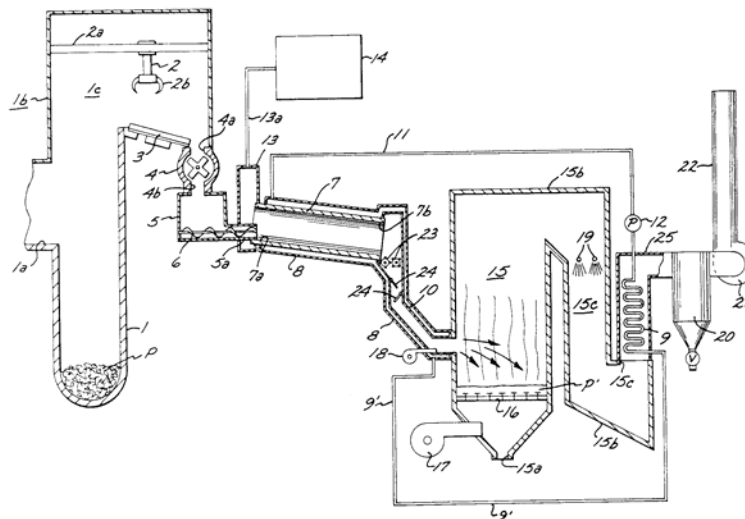


Fig. 2.1 Schematic of Hydrogen chloride recovery incinerator for plastics containing hydrogen and chlorine (Shigaki et al., 1973)

## 2.2 West Virginia University Process

Researchers at West Virginia University proposed a flow diagram of a high-PVC solid waste pyrolysis system (Fig. 2.2). Two fluidized beds are used, one for combustion and the other for pyrolysis. Sand is circulated between these two beds, transferring combustion heat to the pyrolysis bed and char to the combustion bed. No air is present in the pyrolysis bed, resulting in a higher calorific value of the produced gas. A portion of the pyrolysis gas is used as the fluidizing gas in the pyrolysis chamber. Preheated air is used to fluidize the combustion bed and for combustion of the char (Leidner, 1981). No data are available about the performance of the process.

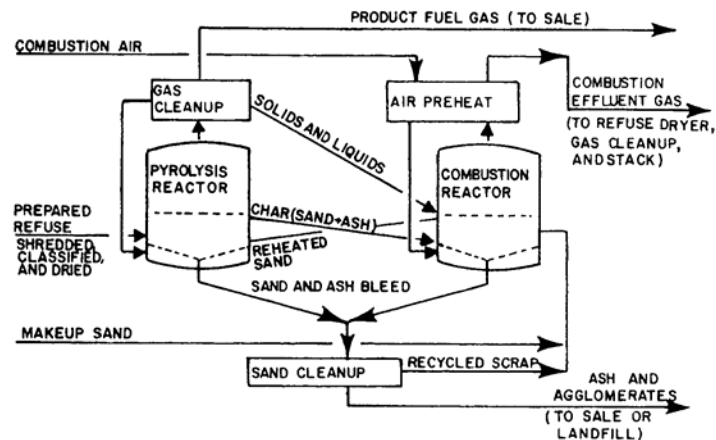


Fig. 2.2 Schematic of West Virginia University's pyrolysis process (Huang & Dalton, 1975)

## 2.3 Process for converting plastic waste into electric power

Dummersdorf et al. (1994) introduced a pyrolysis process for converting plastic waste into electric power (Fig. 2.3). The plastic waste (unpurified and unsorted plastics of any composition) is first size-reduced to a certain fragment size in a shredder stage. After temporary storage in (1), they are fed to a transport screw (2) in which the polymer material is further size-reduced, melted and compressed and delivered in the form of one or more strands to a plasma pyrolysis reactor (3). Here, the plastic waste is subjected to plasma chemical/pyrolytic/gasifying degradation in an electrically generated plasma in a reducing atmosphere at temperatures above 1500 K. The hot plasma pyrolysis gas is then cooled in a quenching stage (4), to stabilize hydrocarbons and, after gas purification, is fed to a combined gas and steam turbine process. The gas purification stage adjoins the waste-heat stage (5) to generate steam and the gas cooler (6) to cool the plasma pyrolysis gas before it enters the gas purification stage and to reheat it after it has left the gas purification stage. This stage essentially comprises an acidic absorption stage (7) and an alkaline absorption stage (8) and is used, above all, to remove heavy metals in the form of soluble compounds and HCl, HF, HCN and H<sub>2</sub>S from the plasma pyrolysis gas. Additional equipment may also be used in the gas purification stage (for example, an adsorption

stage), depending on the composition of the plasma pyrolysis gases. After leaving the gas purification stage, the plasma pyrolysis gas is compressed to a pressure above 10 bar in the compression stage (9) and is delivered to the heat exchanger (6) for reheating to medium temperatures. The plasma pyrolysis gas is then used to generate power in a gas turbine (10), of which the waste gases may be used to generate steam in another waste heat generator (11). The steam thus generated is then converted into additional power in a steam turbine (12). No data concerning the performance of the process is available.

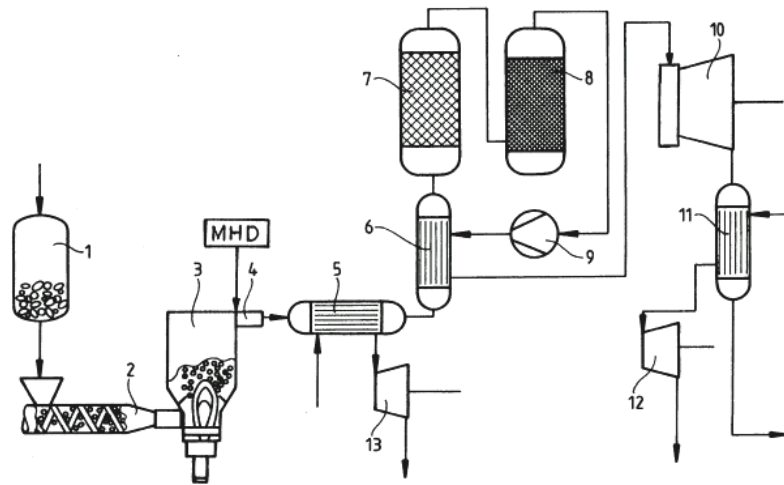


Fig. 2.3 Process for converting plastic waste into power (MHD: Megneto Hydro Dynamic) (Dummersdorf et al., 1994)

#### 2.4 Thermosplitting recycling process for HCl recovery from PVC waste

Wacker Chemie GmbH in Germany developed several processes for the direct recovery of HCl. Thermosplitting is a process for decomposition of PVC involving mono-combustion in a rotary kiln to produce HCl (Fig. 2.4). This process was developed to handle the increasing amounts of PVC waste expected to be generated in the future, as well as PVC products that are difficult to recycle, such as composite materials (e.g., tarpaulins and cable sheathing). A study by Wacker Chemie GmbH has shown that with a throughput of 250 000 tn of PVC waste, approximately 90000 tn of HCl will be produced, as well as a surplus of energy.

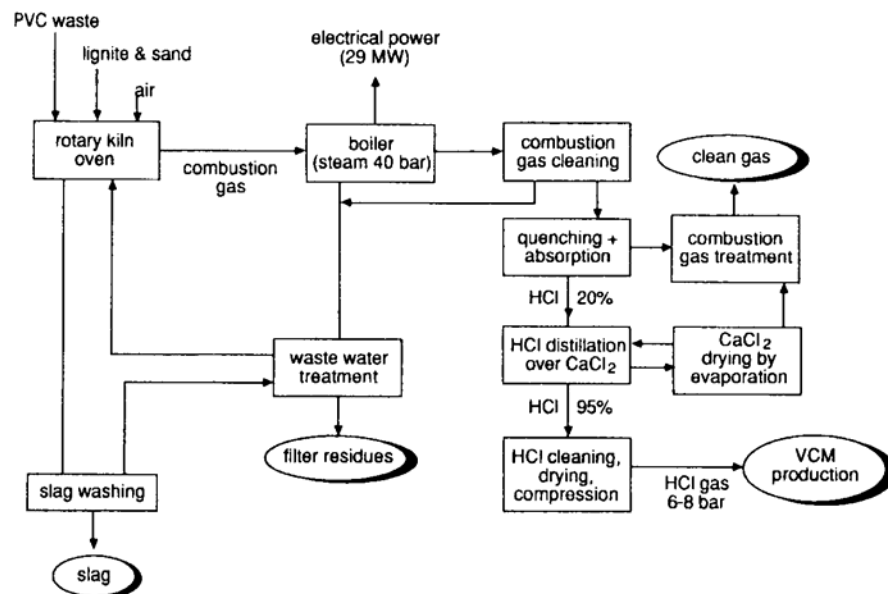


Fig. 2.4 Schematic of the thermosplitting recycling process for the direct recovery of HCl from waste PVC (From Wacker Chemie GmbH, Schkopau, Germany) (Scheirs, 1998)

By-products of the process are 54000 tn of slag and 20000 tn of wet-filtration residue, which must be disposed of under toxic waste regulations since it contains heavy-metal stabilizers (Scheirs, 1998).

For a thermosplitting plant to be cost-effective, a minimum volume of 80000 t/y of PVC waste is necessary. A recycling plant based on this process has been built for Buna GmbH (at Schkopau, Germany); this was scheduled for operation in 1998.

## 2.5 BSL incineration process

BSL Olefinverbund GmbH in Schkopau built a plant containing fluid and solid waste streams for the processing of chlorine. The process includes pretreatment of the waste, thermal treatment and energy recovery, flue gas purification, purification of the HCl and wastewater treatment. Figure 2.5 shows the schematic representation of the process principles (Tukker et al., 1999).

The waste is incinerated in the rotary kiln and a post-combustion chamber directly after the rotary kiln at temperatures of 900 to 1200°C. During this treatment, HCl is released and recovered. Based on the heat capacity of the waste, halogen content, and potential slag formation, an optimal mixture of wastes is determined. In this way, a continuous production of high-quality HCl can be assured. Also, the formation of dioxins and furans can be diminished in this way. The flue gas from the post-combustion is cooled from 1200 to 230-300°C. The steam produced from this process is added to the steam network of the BSL Schkopau site. In the next step of the process, the flue gas purification, the HCl is absorbed from the flue gas by water. Other impurities are removed from the gas. The raw HCl is then purified to a useful feedstock.

Solid waste streams are slag and filter residues. The slag is inert and can be used as a filler in mines. The filter residues can be partly fed to the rotary kiln and reprocessed into slag. Another part of the filter residue has to be landfilled (as chemical waste).

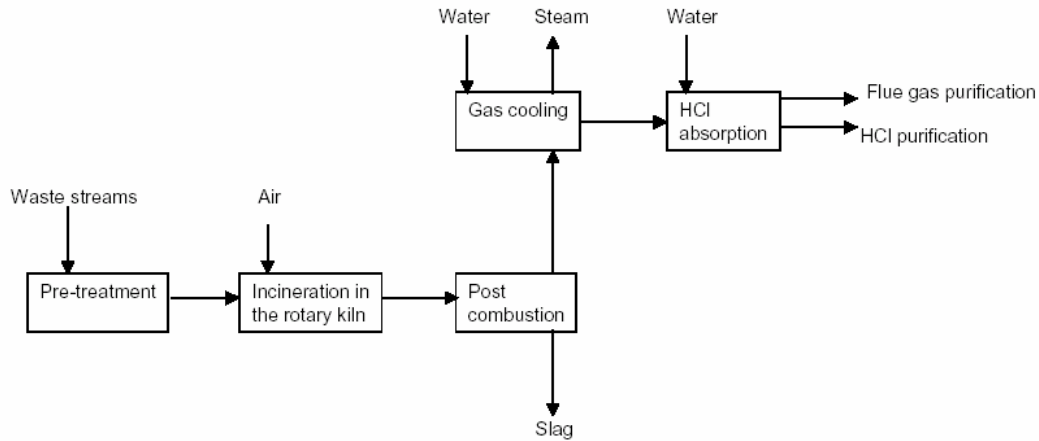


Fig 2.5 Schematic of the BSL incineration process (Tukker et al., 1999).

## 2.6 Linde gasification process

With this process, waste streams with very high PVC content can be recycled; the process can deal with all kinds of PVC, both hard and softened types. The plastic waste as delivered passes a conditioning process in which it is precrushed and separated from steel and nonferrous metals before entering the reactor (Fig. 2.6). A pressurized reactor filled with slag is operated at up to 1400-1600 °C. The slag mainly consists of silicates. PVC, sand, oxygen and steam are fed into the reactor according to the process conditions. The process is exothermic. Resulting products in the reducing atmosphere are a synthesis gas (CO / H<sub>2</sub>) containing HCl and a slag. It is likely that this slag contains most of the metal stabilizers present in the PVC-formulation. HCl is absorbed with water from the synthesis gas. The resulting hydrochloric acid has to be purified from metal chlorides and other chlorinated compounds. Pure HCl gas is produced by distillation of the hydrochloric acid. The HCl-free synthesis gas can be used as feed for chemical processes or as a fuel gas (Tukker et al., 1999).

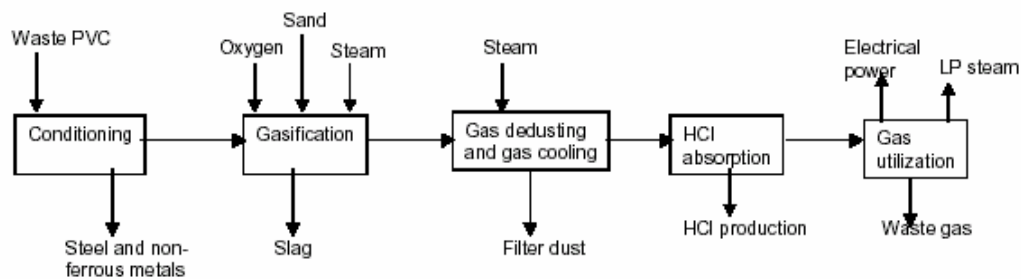


Fig. 2.6 Schematic of the Linde KCA gasification process (Tukker et al., 1999)

In the Linde gasification process, from an input of some 3 t/hr PVC waste, an output of 3500-4000 m<sup>3</sup> combustible gas is achieved. HCl production depends on the waste feed and varies around 700 m<sup>3</sup>/hr. Linde KCA expects no dioxins or furans to be generated under optimum process conditions.

## 2.7 Akzo Nobel steam gasification process

Akzo Nobel Chemicals in Holland developed a process of circulating fluidized bed for gasification of PVC waste (Jaspers, 1999). The process consists of two physically separated reactors at atmospheric pressure; a gasification reactor in which PVC-rich plastic waste is converted at 700-900 °C with steam into product gas (fuel gas and HCl) and residual char, and a combustion reactor that burns the residual char to provide the heat for gasification (Fig. 2.7).

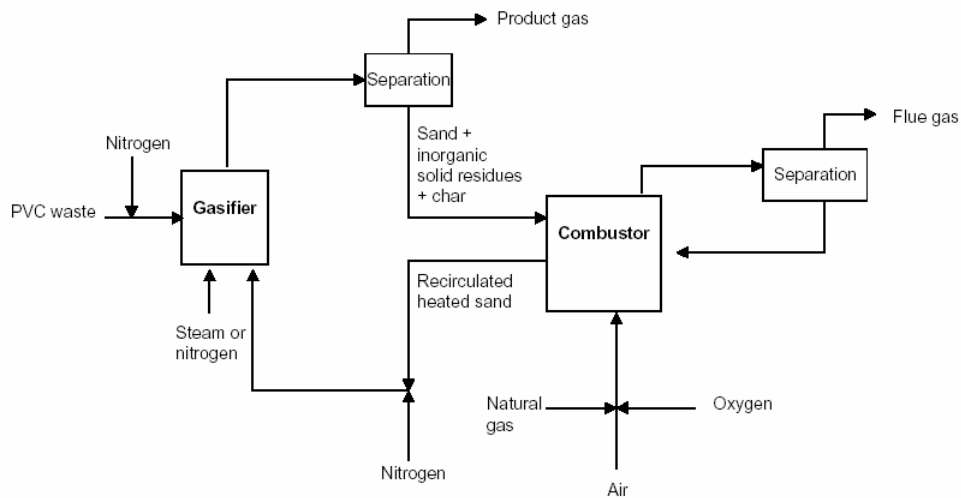


Fig. 2.7 Schematic drawing of the Akzo Nobel circulating fluid bed process for gasification of PVC waste (Jaspers, 1999)

Circulating sand between the gasifier and the combustor transfers heat between the two reactors. Both reactors are of the riser type with very short residence times. This type of reactor allows for a high PVC waste throughput. The atmosphere in the gasifier is reducing, avoiding the formation of dioxins/furans. Depending on the formation of tars, a partial oxidation may be required to convert these tars into gaseous products. This product stream consisting of fuel gas and HCl is quenched to recover HCl. HCl is purified to specification for VCM production by oxy-chlorination. Additives in the waste stream, mainly consisting of chalk and metal stabilizers, are separated from the flue gas or, as a bleed, from the circulating sand. No data are available about the performance of this process.



## 2.8 Process for PVC incineration

During the 1970s, Takuma Boiler Mfg. Co. in Japan built a large incinerator especially for the incineration of PVC (Fig. 2.8). HCl is produced in the rotary kiln by heating PVC waste. After HCl is vaporized from the resin, the carbonized plastic is burned in the incinerator with a low risk of corrosion. Since the volume of gas containing HCl is small, the disposal problems are minimized. HCl gas may be passed through a cyclone followed by a gas cooler, and then reacted with gas to produce ammonium chloride, which can then be collected by a cyclone (Leidner, 1981). No data are available about the performance of the process.

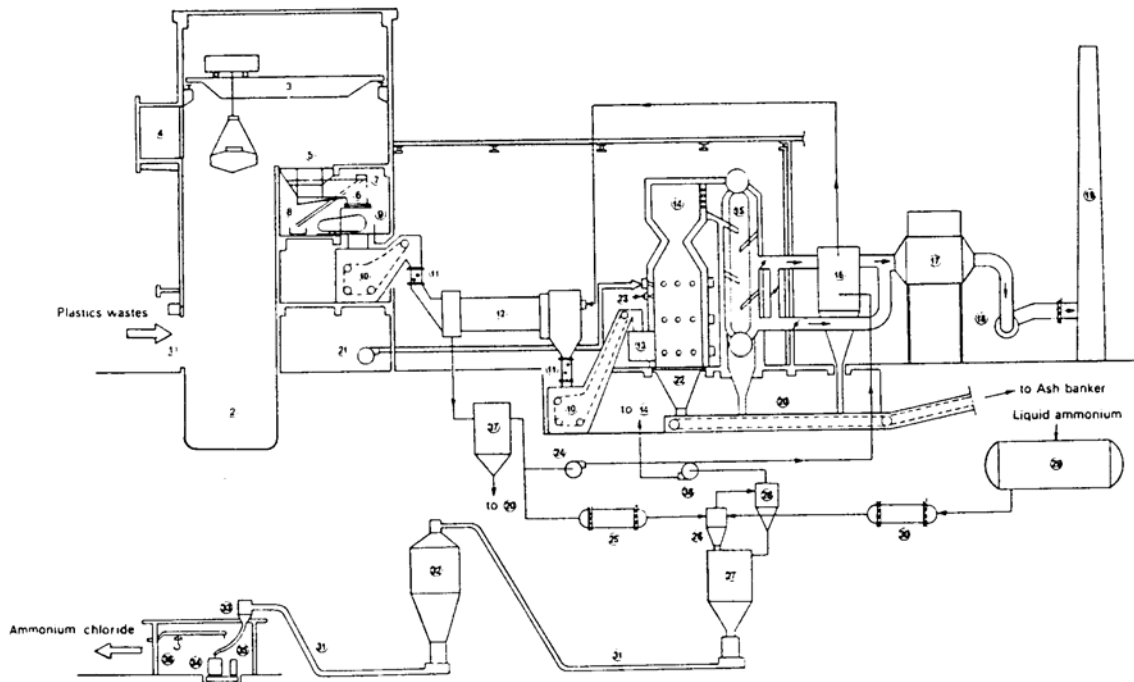


Fig. 2.8 Polymer waste disposal plant: (1) open/close fan; (2) deposition well; (3) feed crane; (4) crane-operating room; (5) hopper; [6] vibrating feeder; (7) metal collector; (8) conveyor for collected metal; (9) crusher; (10) fixed-quantity feeder; (11) gas seal feeder; (12) pretreatment unit (rotary kiln); (13) spreader; (14) incinerator; (15) boiler; (16) circulating gas heater; (17) dust collector; (18) air induction fan; (19) smoke stack; (20); flight conveyor for ash; (21) push-in fan; (22) open/ close-type ash-dispensing bed; (23) auxiliary burner; (24) gas-circulating fan; (25) gas cooler; (26) reactor; (27) ammonium chloride separator; (28) gas filter; (29) ammonium storage; (30) ammonium carburetor; (31) conveyor for ammonium chloride; (32) ammonium chloride storage; (33) feed chute; (34) container bag; (35) weight scale; (36) discharge hoist; (37) multicyclone; (38) surplus gas fan (Leidner, 1981).

## 2.9 Process for steam gasification of PVC waste

Slapak et al. (2000) introduce a process for PVC recycling using steam gasification in a bubbling fluidized bed at about 977°C (Fig 2.9). PVC waste is pretreated in a hammer mill or shredder to obtain a small feed size ( $\pm 1$ cm), which is fed to the reactor by a screw conveyor. Steam enters at the bottom of the reactor through an inclined perforated plate or

pipe distributor. The gas stream leaving the reactor contains entrained alumina bed material fines and char as well as solid and liquid inorganic compounds such as CaO and CaCl<sub>2</sub>. The solids are subsequently separated from the gas stream by a cyclone and bag filter. Due to the maximum permitted temperature for the bag filter, the gas stream is cooled down to 200°C with water that is to be recirculated to the reactor. The product gas stream is scrubbed with water. Syngas leaves the scrubber at the top and the HCl-solution leaves the scrubber at the bottom. The syngas has a relatively low heating value (LHV) of 8.6 MJ/Nm<sup>3</sup>. The flow rate is 4.1 Nm<sup>3</sup>/s. Make-up and recycle CaCl<sub>2</sub> are added to the HCl solution up to 40 wt % CaCl<sub>2</sub>. The next step is extractive distillation. At the top of the column, 100 wt % HCl gas is recovered, dried and compressed to 7 bar, suitable for an oxychlorination process. At the bottom, a 40 wt % CaCl<sub>2</sub> solution leaves the column. This solution enters an evaporator to concentrate the CaCl<sub>2</sub> solution before it is recirculated into the process. The steam leaving the evaporator contains a small amount of hydrochloric acid. This steam is recirculated to the reactor.

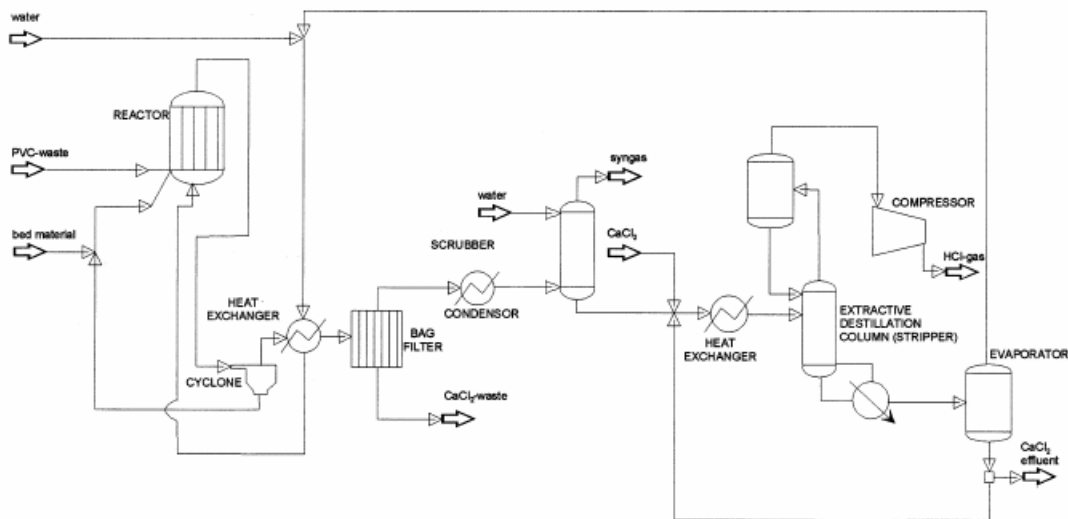


Fig.2.9 Design of the process for steam gasification of PVC waste (Slapak et al., 2000)

## 2.10 Gasification process of waste containing PVC

Borgianni et al. (2002), introduced a process for gasification of wastes containing PVC. The feasibility of this process is examined in a bench scale two-stage reactor system (see Fig. 2.10). The first stage is constructed from a 50 mm (inner diameter) by 500 mm length quartz tube equipped with a quartz fritte on the bottom side, working at 600°C. The second stage is a 30 mm (inner diameter) by 700 mm length quartz tube filled with 4 mm diameter alumina spheres, working at 1000°C to avoid the presence of tar in the exhaust syngas. Each stage reaches the desired working temperature by means of electrical heaters. A blend of refuse-derived fuel (RDF), 10% of PVC and alkaline compounds (Na<sub>2</sub>CO<sub>3</sub>), is used in the tests. The addition of the alkaline compounds has a positive effect on the amount of unreacted materials in the residue. The alkaline substance acts as a catalyst,

increasing the reaction rate in the coke gasification. The blend is immediately pyrolyzed after it is introduced into the reactor. Due to gravity, char goes to the bottom of stage one (E in Fig. 2.10) and meets the gasifying mixture consisting of steam and oxygen, introduced through the quartz frit at the bottom of stage one. The mixture, which mainly consists of hydrogen, carbon monoxide, carbon dioxide, gaseous hydrocarbons, volatile and non-volatile substances, flows up to stage two. During this stage, tar, liquid and heavy hydrocarbon trapped in the package increase their residence time, allowing for complete gasification and reforming.

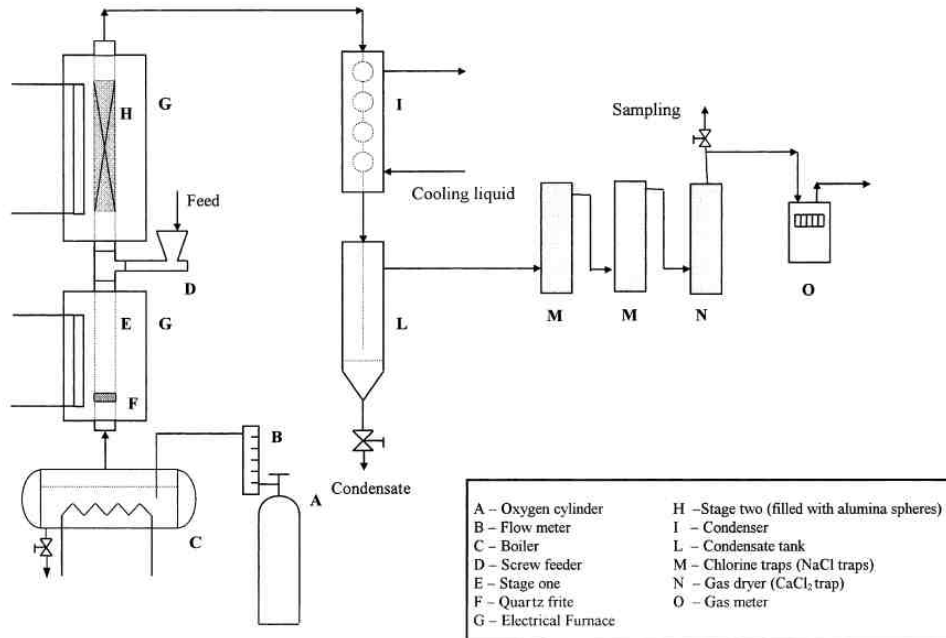


Fig. 2.10 Schematic diagram of the bench scale gasification unit (Borgianni et al., 2002)

## 2.11 Conclusion

Most of the information about the processes described above is taken from the literature, where one often finds just a description of the process with very little data about the performance or operation. It will therefore be difficult to discuss and comment on the weakness and the strength of each one.

Shigaki (1973) claims in the patent that there is no toxic chlorinated compound found in the flue gas from the chimney. The patent does not give any information about the pyrolysis medium gas used in the first stage (Is air or nitrogen used inside the rotary kiln?) where the temperature is very low (280°C) and there is a possibility of toxic chlorinated compounds being formed if the medium gas is air.

The description of the West Virginia University process does not give any operational data, nor does it give any comments about the difficulties that might be associated with the sand moving between both fluidized bed reactors and with the removal of ash and other inert materials from the sand.

Operational data is not available rather for the process introduced by Dummersdorf et al. (1994); it is the same with other processes introduced in this chapter from Wacker Chemie GmbH, Linde KCA Akzo Nobel chemicals and Takuma Boiler Mfg Co.

Slapak et al. (2000) do not give any experimental data about the process. The experimental data that is presented concerns the reactor (BFB) only. All the other data was simulated using Aspen Plus software. Also, the PVC used in the reactor was virgin PVC, not the kind used in the simulation. Therefore, it would be difficult to comment on the performance of the process.

Borgianni et al. (2002) introduced a process for handling PVC waste (up to 20% of the fuel). The bench scale was rather small, but the operational data shows that the content of the chlorine in the syngas (NaCl + HCl) was very small and under the limits allowed by Italian law. The dioxins and NO<sub>x</sub> emission are also claimed to be well under the low limits, although no specific data are given.

The idea of the process introduced in this thesis was presented through a simulation calculation and supported with experimental work after building a lab-scale test facility. The results show that solid waste containing a high PVC fraction can be handled outstandingly well using the process. The amount of chlorine in the char transferred from the BFB to the CFBC was rather small, taking into account that we used 100% PVC (as input fuel). Furthermore, the amounts of polychlorinated compounds (like PCDD/F) were very small in the char taken from the BFB bed. The sand is circulated smoothly from the BFB to the CFBC with the gravity and overflow, returned from the CFBC to the sand cooler after the cyclone, and then to the BFB by gravity and the fluidization of the sand in the sand cooler. There would normally be an ash disposal tube at the bottom of the CFBC, but the amount of fuel handled in this case was not large enough to warrant it.

However, a superior process is the one that can deal with high-PVC containing waste and at the same time deal with different types of waste and other fuel. Also, the operational cost of the process should be acceptable with low emissions and no dioxin or furan formation. In addition, the disposal of unavoidable waste products from the process should comply with environmental regulations.

The previously reported energy recovery processes that deal with high PVC solid waste are summarized in Table 2.1.

Table 2.1 List of processes that deal with high-PVC solid waste

Process Developer	Process type	Stages type	Pressure bar	Temp. °C		Medium gas	Products and energy carrier	Scale status	Bed material	Max. input Cl %	Country
				1 <sup>st</sup> St.	2 <sup>nd</sup> St.						
Shigaki et al., 1973	Pyrolysis + combustion	Rotary kiln + grate furnace	Atmospheric	280	DNA	Air	RHFG + HCl	DNA	-	DNA	Japan
West Virginia University, 1975	Pyrolysis + combustion	BFB+ CFBC	DNA	760	1000	Nitrogen & air	Fuel gas + RHFG	Lab. scale	Sand	DNA	USA
Dummersdorf et al., 1994	Pyrolysis + combustion	Plasma reactor + Gas turbine	Atmospheric	>1200	-	DNA	Electricity	-	-	DNA	Germany
Wacker Chemie GmbH	Combustion	Rotary kiln	DNA	DNA	-	Air	Electricity + HCl	-	Sand	DNA	Germany
Wacker Chemie GmbH	Combustion	Rotary kiln + combustor	DNA	900-1200	1200	Air	HCl+ Steam+ Inert slag	Large scale	-	High	Germany
Linde KCA,	Gasification	Gasifier	Pressurized	1400-1600		Oxygen & steam	Electricity + HCl	Pilot oper. in 2000	Sand	High	Germany
Akzo Nobel Chemicals, 1999	Gasification + combustion	CFB + CFBC	Atmospheric	700-900	-	Nitrogen & steam	Fuel gas + RHFG + HCl	Lab. and pilot	Sand	High	Holland
Takuma Boiler Mfg Co.	Pyrolysis + combustion	Rotary kiln + incinerator	Atmospheric	-	-	-	RHFG	Large scale	-	DNA	Japan
Slapak et al. 2000	Gasification	BFB	Atmospheric	977		Steam	Fuel gas + HCl	Lab scale	alumina	20	Holland
Borgianni et al., 2002	Pyrolysis + gasification	Two gasifiers	Atmospheric	600	1000	Oxygen & steam	Fuel gas	Lab scale	quartz frite alumina	10	Italy
The work in this thesis	Pyrolysis + combustion	BFB + CFBC	Atmospheric	200-400	800	Nitrogen & air	HCl + RHFG	Lab. scale	Sand	High	Finland

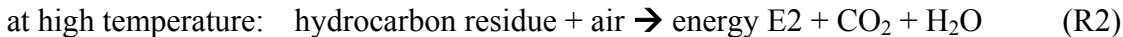
Pyro : Pyrolysis; Com.: combustion; Gasifi. : Gasification; atmo. : atmospheric pressure; RK: Rotary kiln; GF: grate furnace; IN: Incinerator; PR: Plasma reactor; GT: Gas turbine; Elec.: Electricity; FG: Fuel gas; RHFG: recovered heat from flue gases; Press. : Pressurized; DNA: Data not available

### 3. Theoretical design work using a process simulation program (PROSIM)

(See also publication I, II and III)

The main theoretical work, supporting the later design work of the test facility, involved the use of the Process Simulation Program (PROSIM) software for integrated energy system analysis and efficiency optimization. This was developed and used at Helsinki University of Technology for optimizing the mass and energy balances of processes (Giglmayr et al., 2001).

The variables that are optimized are most importantly the temperature in the first reactor and the amount of PVC in the solid waste (Saeed, 2000). It is noted that the processes in reactor 1 are endothermic, i.e., they need heat, which is provided by the hot sand. In short, the two-stage process involves the following chemistry:



In a parallel study, the pyrolysis of PVC and PVC-containing fuels was analyzed (Zevenhoven et al., 2002) giving input data for the PROSIM calculation. This gave information on the degree of HCl release for the PVC with increasing temperature and the calorific value (LHV) of chars from PVC.

#### 3.1 PVC pyrolysis

The temperature window in which a typical PVC is decomposed into a chlorine-free char was analyzed in a set of experiments where PVC was pyrolyzed in nitrogen at temperatures in the range 250-400°C. In addition, the pyrolysis of PVC/wood (and also PVC/polyethylene) mixtures was studied in the same temperature range. In these tests, the presence of carbonaceous decomposition products in the pyrolysis off-gas was detected by oxidation with air (at 900°C) followed by measurement of CO + CO<sub>2</sub> (Zevenhoven et al., 2002). Table 3.1 gives the composition of the PVC and wood (Finnish pine) samples that were used in those tests, as well as in the process simulations discussed below.

The results of the chemical analysis of the residues from PVC pyrolysis in nitrogen show that at 250°C the decomposition of the PVC has already started, showing a maximum rate at ~300°C. At 350°C, the amount of Cl in the solid residue is less than 0.1%: the PVC has released ~99.5% of its chlorine. The corresponding net calorific value for these residues is given in Fig. 3.2, showing a trend that levels off at 38.2 MJ/kg. (see publication I and II)

Table 3.1 Properties of PVC and wood (pine) samples (dry) used in the test and process simulations

dry	PVC	Pine wood
C %-wt	40.1	48.9
H %-wt	5.1	6.0
Cl %-wt	53.8	-
O %-wt	-	43.8
N %-wt	-	0.17
S %-wt	-	0.06
Ash %-wt	-	0.5
LHV MJ/kg	20.1	17.8

Pyrolysis experiments with PVC/wood (and PVC/PE) mixtures in nitrogen at 250-400°C show a slow pyrolysis of wood into carbon-containing gases at about the same rate as the secondary decomposition of the PVC, i.e., the further decomposition of the hydrocarbon residue from PVC de-hydrochlorination into volatile hydrocarbons (Zevenhoven et al., 2002).

### 3.2 Pyrolysis module

A new pyrolysis module had to be implemented into the PROSIM software for simulating the process considered in this work. This new module calculates the heat needed to heat up and dry the incoming waste-derived fuel, decompose the PVC and, from the heat that is needed, calculate the mass flow rate of the returned hot sand. The details are given in publication II.

### 3.3 Design of two-stage combustion power plant with HCl recovery

#### 3.3.1 Process description (design case)

The process scheme is shown in Fig. 3.1. The input fuel contains 80% wet wood + 20% wet PVC. First the wood is dried in dryer (2) (assuming for the design case that wood contains 15% water) and then fed with the wet PVC (assuming 5% water) into the pyrolysis reactor (1). Thermal input for the pyrolysis reactions comes from recycled hot sand from the FBC (fluidized bed combustor). A flow of nitrogen of 4 kg/s is used to fluidize the bed in the pyrolysis reactor (this gives a fluidization velocity of 1-2 m/s in a bubbling fluidized bed, for example). For simplicity, the separation of water + HCl from the product gas is not included in the discussion here. The FBC is modeled as a burner (3) plus a hot bed (4) with a fluidized boiler (5). The low-chlorine char from the PVC, plus the wood, are burned in the FBC, followed by heat recovery in a superheater (6), economizer (7) and air preheater (8).

Electric power is generated using a steam turbine (10+11+12+13+14) where the first stage is a regulation stage followed by three stage groups with bleeding of steam for the

feedwater tank, the feedwater heater and final expansion in the last stages. The isentropic efficiency for the turbine is assumed 0.86. Two feedwater heaters instead of one gives increased efficiency. The first feedwater pressure is 1.17 bar, while pressure for the second is 0.24 bar. Table 3.2 gives the specifications for the design case; the effect of varying process parameters and waste-fuel input will be discussed in the following sections.

Table 3.2 Two-stage combustion of high PVC waste power plant (design case) versus the conventional incineration plant (design case)

	Two-stage Combustion (Section 3.3)	Conventional incineration plant (Section 3.4)
Pyrolysis reactor:		Combustor:
Fuel input, kg/s (20%PVC+80%Wood)	0.5 kg PVC +2 kg Wood	0.5 kg PVC+2 kg wood
Chlorine in fuel to be burned %-wt	10.76 <sup>1</sup> /0.029 <sup>2</sup>	10.76
PVC conversion %	99.8%	-
Pyrolysis reactor temperature	350°C	-
Sand input temperature	410°C	-
Water content in the PVC	5%	5%
Water content in the wood	15%	15%
LHV of PVC	20.1 MJ/kg	20.1 MJ/kg
LHV of wood	17.8 MJ/kg	17.8 MJ/kg
LHV of CnHm <sup>3</sup>	38.2 MJ/kg	-
Fluidized bed reactor:		
Combustion efficiency	0.98	0.98
Fluidized bed temperature	800°C	~1300°C <sup>4</sup>
Air factor, stoichiometry	1.1	1.1
Steam cycle:		
ST <sup>5</sup> isentropic efficiency	0.86	0.86
Condenser pressure	0.03 bar	0.03 bar
First feed water heater pressure	1.17 bar	1.17 bar
Second feed water heater	0.240 bar	0.240 bar
Deaerator pressure	3 bar	3 bar
Superheater temperature	510°C	510°C
Steam pressure	78 bar	78 bar
Steam mass flow rate	12.60 kg/s	12.30 kg/s
Net plant output	14.173 MW	13.43 MW
Thermal efficiency (LHV)	36.8%	33.4%
Flue gases mass flow rate	15.63 kg/s	16.44 kg/s
HCl recovered	0.276 kg HCl/s	None
HCl emissions (no gas cleaning)		
at 2% O <sub>2</sub>	43 mg/m <sup>3</sup> <sub>STP</sub> dry	20718 mg/m <sup>3</sup> <sub>STP</sub> dry
at 11% O <sub>2</sub>	23 mg/m <sup>3</sup> <sub>STP</sub> dry	10904 mg/m <sup>3</sup> <sub>STP</sub> dry
Minimum stack temperature	150°C	230°C

<sup>1</sup> Chlorine in fuel in pyrolysis reactor, <sup>2</sup> Chlorine in fuel to be burned in FBC, <sup>3</sup> Residue from PVC after decomposition to be burned in the second reactor, <sup>4</sup> Combustor temperature, <sup>5</sup> Steam Turbine



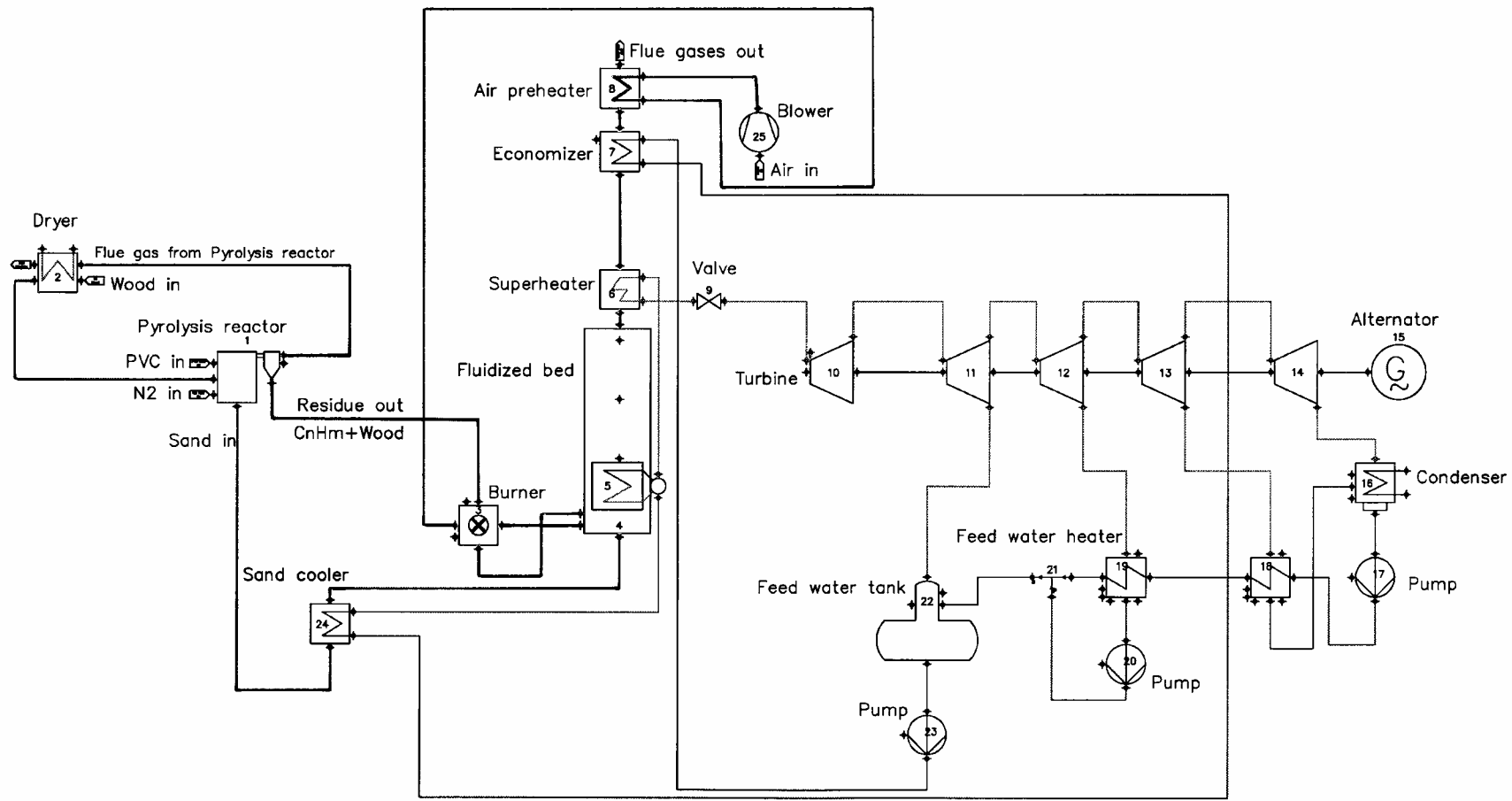


Fig. 3.1 Flowsheet of two-stage combustion of high PVC solid waste

Feedwater from the feedwater tank with a 12.60 kg/s mass flow rate at 134.7°C and 78 bar is preheated to 186°C in the economizer (7) and further to 293°C in the sand return cooler (24). The feedwater reaches the fluidized boiler (5) in the liquid phase and is then superheated in the superheater (6) to 510°C/78 bar. The steam parameters 510°C/ 78 bar are optimal for the heat available in the superheater. Pressure was increased from an initial value of 60 bar to 78 bar in order to increase the saturation temperature from 276°C to 293°C so as to utilize the heat in the return sand cooler (24). At a pressure lower than 78 bar, the feed water will be partly evaporated inside the sand cooler before it goes to the evaporator (5). This would result in a two-phase mixture in the sand cooler, which would increase the size of the sand cooler and the piping. The approach temperature is 0°C, i.e., the water leaving the cooler (24) is at the saturation temperature for 78 bar but is still in the liquid phase. This is the optimum case to utilize the heat in the sand that is returned to the pyrolysis reactor. The minimum stack temperature of 150°C was selected to insure that there would be no condensation of aggressive compounds from the flue gases that cause corrosion. It would be possible to go below 110°C for the design case to reduce the exergy losses and increase the thermal efficiency.

For the design case, with 38 MW fuel thermal input, the thermal efficiency is 36.8% (14.173 MW electricity output), which has been calculated accounting for the power needed to drive the pumps (0.139 MW) and the blower (0.014 MW). The chlorine content in the fuel for the FBC is then 0.029%-wt. The temperature of the FBC is chosen at 800°C to reduce the operational problems, which are known to be related to ash behavior, when firing biomass or waste-derived fuels. On the other hand, regulations requiring at least 2 seconds resident time at a minimum of 850°C may enforce a higher temperature in reactor 2. The FBC is fired with air at 2 % oxygen in the dry flue gases (stoichiometric ratio,  $\lambda = 1.1$ ).

### ***3.3.2 Analysis result for changing pyrolysis reactor temperature***

Similar to the later experimental work, the pyrolysis reactor temperature range 250-400°C has been selected here. The PVC tested for this work starts to decompose by 250°C with a conversion of 21% (conversion of PVC to HCl and residue) (Zevenhoven et al., 2002).

The temperature in the pyrolysis reactor has an effect on thermal efficiency, on the chlorine content in the fuel that is burnt in the FBC and on the HCl emissions from the FBC. Results of simulations with pyrolysis temperatures from 250 to 400°C are given in publication II (Table 3). The thermal efficiency of the process appears to vary from 36.6% to a maximum of 37% for pyrolysis at 310°C. The emissions of HCl are high at temperatures below 340°C, while above 350°C the emission of HCl will be even below the allowable emission for Finland/EU (10 mg/m<sup>3</sup> at 11% O<sub>2</sub>) for waste combustion.

### **3.4 Design of conventional solid waste incineration plant**

#### ***3.4.1 Process description***

The process flow sheet of a more or less conventional solid waste incineration plant is shown for comparison in Fig. 3.2. The air is preheated in an air preheater (5) from 20°C to 35°C before it goes to the burner. The input fuel (80% wet wood + 20% wet PVC) is fed directly to a furnace (2) where it is burnt with air. The furnace is modeled as a burner (1) plus a radiant furnace (2). The radiant furnace is followed by the heat recovery system including a superheater (3), economizer (4) and air preheater (5). Electric power is generated using the same steam turbine set-up as described for the two-stage process. Table 3.2 gives the specifications for this case also. Feedwater from the feedwater tank at 133°C, 78 bar and 12.30 kg/s mass flow rate is reheated in the economizer (4), the radiant furnace (2) and superheater (3). The steam parameters used in this design are 510°C/78 bar, the same as used in the two-stage combustion design. This allows for making a comparison between the two processes. The minimum stack temperature of 230°C was selected to insure that there would be no condensation of aggressive compounds from the flue gases that cause corrosion problems (Korobitsyn et al., 1999). The emission of HCl without gas cleaning would be 20718 mg/m<sup>3</sup><sub>STP</sub> dry at 2% O<sub>2</sub>, which is very high and needs an effective cleaning system to fulfill the local emission limits.

For the design case, with 38.7 MW fuel thermal input, the thermal efficiency is 33.4 %, (13.43 MW), which has been calculated accounting for the power needed to drive the pumps (0.136 MW) and the blower (0.116 MW) from the net steam turbine power. The combustion in the furnace is fired with air at 2 % oxygen in the dry flue gases ( $\lambda = 1.1$ ).

### **3.5 Comparison between two-stage combustion plant with HCl recovery and conventional solid waste incineration plant**

#### ***3.5.1 Technical comparison***

Conventional incineration uses air for the combustion and oxidation reactions, while the two-stage combustion operates with an absence of air (pyrolysis) or in a partial oxidation mode (gasification) in the first stage. The second stage uses air for the combustion reactions. Table 3.2 shows the technical output data for both plants.

The reference case for the two-stage combustion plant (outlet steam with a temperature of 510°C, pressure 7.8 MPa, feedwater heaters working at pressure 117 kPa and 24 kPa, respectively) gives 36.8% thermal efficiency. The reference case for the conventional incineration plant (outlet steam temperature 510°C, pressure 7.8 MPa, feedwater heaters also working on pressure 117 kPa and 24 kPa, respectively) gives 33.4% thermal efficiency. Besides the design case simulations for both plants, two parameters were varied during the calculation in order to see their effects on plant performance: the amount of PVC in the fuel, and the amount of moisture in the fuel.

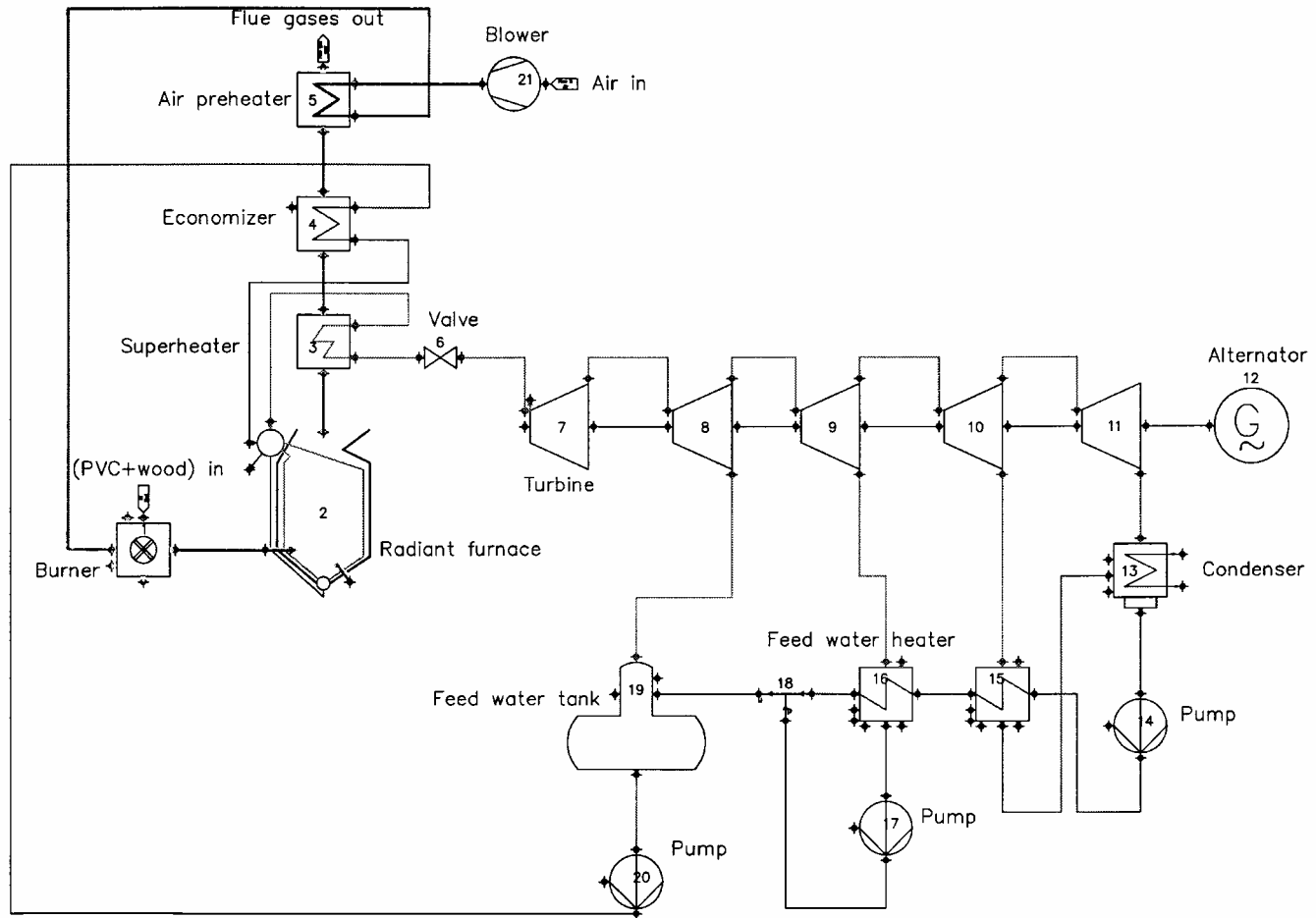


Fig. 3.2 Flowsheet of conventional solid waste incineration plant

The content of PVC in the fuel is a very important parameter and affects the thermal efficiency of the plant. For the two-stage combustion, the PVC content in the fuel is varied from 0% to 35%; and the same amount is used in the conventional incineration plant. When feeding only wood (0% PVC) to the pyrolysis reactor, the thermal efficiency is 36.1%, while using 35% PVC will increase the thermal efficiency to 37.4%. For the conventional incineration, using only wood (0% PVC) gives 33.1% thermal efficiency. Increasing the PVC content in the fuel to 35% increases the efficiency to 33.7%. Figure 3.3 shows the effect of PVC content in the fuel on the thermal efficiency of the plant. In both plants, the efficiency has increased with increasing PVC content in the fuel. The reason for that is the higher net heating value of PVC (20.1 MJ/kg) as compared to the heating value for the wood (17.8 MJ/kg). Also, as shown in Fig. 3.3, there is a difference between the two plants that is related to the high exergy losses in the radiant furnace for the conventional incineration, which is caused by the high temperature difference between the flue gases and feedwater.

Also, the mass flow rate of the sand from the sand cooler (return sand) to the pyrolysis reactor is decreasing with an increase of PVC content in the fuel, which means that the energy needed in the pyrolysis reactor to decompose the fuel is decreasing. This is related to the fact that, for this PVC, decomposition is exothermic. With no PVC pyrolysed, the mass flow rate of the sand is 19.75 kg/s, while it is only 7.62 kg/s for 35% PVC in the fuel.

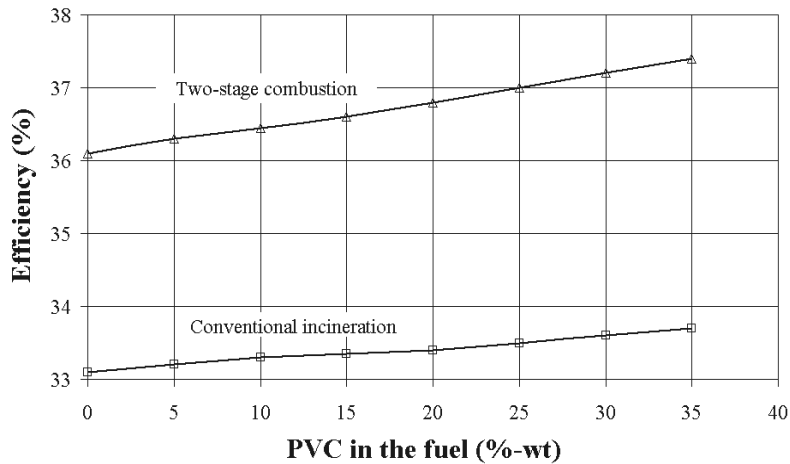


Fig. 3.3 Effect of PVC content in the fuel on the plant thermal efficiency

The moisture content of the fuel also has an important effect on the plant efficiency. When it increases, it causes a decrease in the heat from the fuel when it is burnt and, consequently, it will decrease the electrical output and plant efficiency. For the design case, the moisture content was 15% in the wood and 5% in the PVC for fuel composition 80% wood + 20% PVC. Three more cases are calculated for both plants with respectively 7.5%, 30% and 45% moisture content in the wood, with, at the same time, respectively 2.5%, 10% and 15% in the PVC. Thus, the total water content in the incoming fuel mix will be 7%, 13%, 26% and 39%, respectively. Figure 3.4 shows that the changes in the plant efficiency of the two-stage combustion for the first case is (36.9%) and for the

design case (36.8%) are small, but for the third (35.8%) and fourth case (34.2%) they are significant.

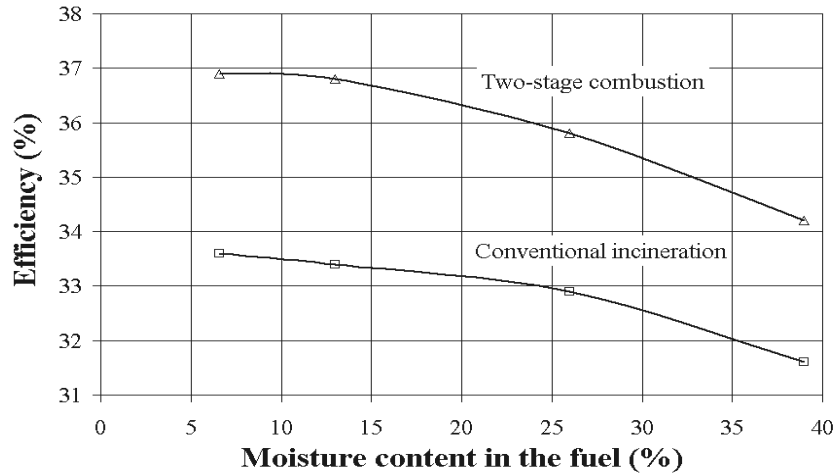


Fig. 3.4 Effect of moisture content in the fuel on the plant thermal efficiency for 20% PVC + 80% wood (pine).

For the conventional incineration plant, the thermal efficiency for the first case is (33.6%) and for the design case (33.4%). The third and fourth cases are (32.9%) and (31.6%), respectively. Drying the fuel (wood) in the dryer before going to the first reactor (pyrolysis reactor) by using the flue gases from the first reactor will decrease exergy losses and increase efficiency. This is also why there is a significant difference between the thermal efficiencies of the two plants. The moisture content in the wood after the dryer (for these four cases) is 0%, 0%, 9% and 27%, respectively.

The temperature of the inlet steam for the conventional incineration plant should be limited to below 500°C to avoid high temperature fireside corrosion in the superheater area, which is related to the aggressive nature of the flue gases (Salmenoja et al., 1999). Thus, the low inlet steam condition for the steam turbine will decrease electricity production and plant thermal efficiency. With the two-stage combustion process, it will be possible to go above these limits without problems related to HCl. For the same reason, the capital and maintenance costs would be higher for the conventional incineration plant because it would need special materials to resist corrosion. In our design case, we used inlet steam conditions above 500°C for the conventional incineration plant in order to compare it with the two-stage combustion process. Decreasing the inlet steam condition below 500°C will reduce the efficiency even further.

Waste plastics can be a valuable source of energy. Although the standard incinerators are capable of handling municipal refuse containing plastics, they cannot usually handle a large plastic fraction or pure plastics waste (Leidner, 1981). With two-stage combustion, it will be possible to increase the fraction of plastic waste.

In order to avoid the problems explained above, in a conventional incinerator, the amount of plastic waste incinerated is typically less than 5% of the total; this is related to the high heating value of the plastic. In general, plastics have much higher heating values than municipal refuse as such (2 to 4 times), require more air for complete combustion, and have higher flame temperatures. Most conventional incinerators are not capable of

supplying an adequate amount of air for the complete combustion of plastics. Air-supplying equipment has to be able to provide 2.5 to 3 times the amount of air theoretically required for combustion of the plastics. During incomplete combustion, soot that will stick to the tube walls of the heat exchanger unit, affecting the performance, is produced (Leidner, 1981). Flue gas flow rates for conventional incinerators are higher than with two-stage combustion; this will require, for example, a larger diameter for the stack.

### ***3.5.2 Environmental comparison***

The difference in uncontrolled HCl emissions from each design is obvious and can be seen in Table 3.2. The conventional incineration plant needs an effective cleaning system in order to comply with HCl emission standards, while for the two-stage combustion design uncontrolled HCl emissions will be close to, or below, this limit. In addition to that, there is the risk of polychlorinated dibenzo-p-dioxins (PCDD) and dibenzofurans (PCDF) formation. The formation of PCDD/PCDFs requires the presence of their constituent elements, namely carbon, oxygen and chlorine, as well as a certain temperature range and the presence of specific catalysts (e.g., copper) (Olie et al., 1998; Frankenhaeuser et al., 1992). Although PCDD/PCDFs are destroyed at temperatures exceeding 600°C, they are known to form in the cooler zones in furnaces where temperatures in the range 250-350°C exist (Manninen et al., 1994). However, the levels of dioxins from properly designed and maintained incinerators operating at high temperatures do not pose a measurable health risk. At temperatures of 1300°C or above, practically all dioxins are destroyed in less than one second (Scheirs, 1998).

Incomplete burning of plastics will produce soot. Generally, plastics require 3 to 10 times more combustion air than typical municipal refuse. If they are burned in conventional incinerators, there will be a shortage of oxygen. With the pyrolysis process for PVC, HCl recovery can be above 90 % at temperatures above 310°C and reaches 100% above the 350°C. After recovery, HCl can be re-utilized as a raw material (see Table 3, publication I).

### ***3.5.3 Summary of the main finding from the theoretical design work***

A waste-to-energy process is described here for high-PVC solid wastes that combines combustion with HCl recovery. It differs from processes based on (staged) gasification of these types of wastes (e.g. Jaspers, 1999) by the low temperature of the pyrolysis reactor. An advantage is that no hot HCl containing gases have to be handled. The process has a thermal efficiency of approx. 36%, depending on pyrolysis temperature and the PVC content in the solid waste. This efficiency is higher than for a conventional incineration plant (which has been modified with air preheating system and two feedwater heaters).

For the two-stage combustion process, HCl recovery can be above 90 % at pyrolysis temperatures above 310°C, combined with low uncontrolled HCl emissions which can be even below the current legislative emission limits. For the conventional incineration plant the uncontrolled HCl emission is very high, and requires an effective cleaning system.

Because of the low HCl concentration in the hot gases during two-stage combustion it is possible to go above 500°C as steam outlet condition from the superheater, which consequently will increase the electricity production from the steam turbine. The very small HCl concentration will eliminate the risks of fireside corrosion in the superheater area and the formation of dioxins (PCDD) and furans (PCDF).

Finally, it is noted that very many different types of PVC exist, which may have implications for the process discussed here. Also, the exergy analysis for the suggested process could not be done yet because the product after the pyrolysis process (the residue) is not well-defined from a thermodynamic point of view.



## 4. Test facility design description and experimental procedure

(See also publication III and IV)

The design of the test facility built at Helsinki University of Technology (see Fig. 4.1) is based on:

- Kinetic data on de-hydrochlorination for a typical PVC (Bockhorn et al., 1996; Bockhorn et al., 1999; Zevenhoven et al., 2002) and on combustion of chars from PVC and wood (Zevenhoven et al., 1997), and
- Process optimization calculations for a 40 MW<sub>thermal</sub> plant design case (Saeed, 2000; Zevenhoven and Saeed, 2000; Zevenhoven et al., 2000b), scaled down from 40 MW to 40 kW thermal fuel input (see Chapter 3).

In addition, information from the literature for the both fluidized bed designs were used (Kunii and Levenspiel, 1991; Basu, 1991, Fan and Zhu, 1998).

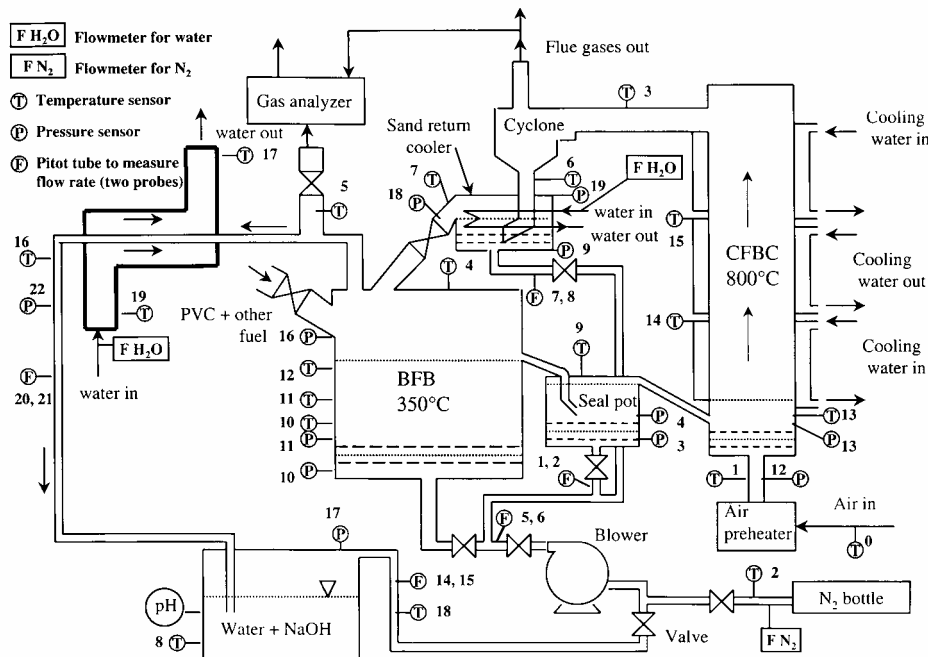


Fig. 4.1 Test facility scheme

### 4.1 Kinetic calculation

Many researchers have investigated PVC thermal decomposition (e.g., Bockhorn et al., 1999). PVC decomposes in two steps. The first decomposition step is the de-hydrochlorination between 220 and 350°C, the second step, between 400 and 550°C, is the formation of a mixture of hydrocarbons containing mostly aromatic compounds.

The kinetics of the decomposition of PVC is important for the determining size of the fluidized bed pyrolysis reactor. From kinetic calculations, the residence time can be estimated and the feeding rate into the reactor will then determine its size. Bockhorn et al.

(1999) presented kinetic data for several pure plastics (without fillers, stabilizers and colors) including PVC. These data include the apparent Arrhenius kinetics activation energy,  $E_a$  (J/mol), pre-exponential factor,  $k_0$  (1/s), and apparent order of reaction  $n$  (-). By using these data, the effect of residence time distribution in an FB reactor is accounted for according to (Levenspiel, 1972), assuming perfect mixing for the bed material. See publication II.

The apparent order of reaction for the PVC de-hydrochlorination was reported to be  $n = 1.54$  (Bockhorn et al., 1999). Therefore, the solution for our process design calculation is calculated by taking the logarithmic mean of the kinetics in a FB reactor for  $n = 1$  and  $n = 2$  with perfect solids mixings. Based on this, a residence time of 30 minutes was chosen for the BFB reactor design.

## 4.2 Test facility description

### 4.2.1 Reactors

The facility contains two fluidized bed reactors: a bubbling fluidized bed (BFB) pyrolysis reactor operating with nitrogen at  $\sim 350^\circ\text{C}$  and a circulating fluidized bed combustor (CFBC) operating at  $800\sim 850^\circ\text{C}$ . The gases from the first reactor will contain mainly  $\text{N}_2$ ,  $\text{HCl}$ ,  $\text{H}_2\text{O}$  and small amounts of other gases. The solid residue, which is the hydrocarbon residue from the PVC plus the rest of the incoming fuel, can be combusted as any other low-chlorine or chlorine-free solid fuel. This is accomplished in the second reactor without environmental hazard or corrosion problems. Table 4.1 gives the design parameters for the facility. The entire facility is built using ASTM 316 type steel. For process control and data logging, probes are connected to a PC-computer, i.e., nineteen signals for temperature, eleven for pressure, five for flow rate and one from the pH meter.

Table 4.1 Design parameters for the two fluidized bed reactors in the test facility

Parameter	BFB reactor	CFB combustor
Temperature, ( $^\circ\text{C}$ )	200-400	< 900
Circular diameter, $d_i$ (m)	0.4	0.11
Height, $H_r$ (m)	0.8	2.3
Residence time of fuel, $t$ (s)	1800	1-2
Fluidizing gas	Nitrogen	Air
Superficial gas velocity, $U_o$ (m/s)	0.36 (at $350^\circ\text{C}$ )	5 – 7 (at $800^\circ\text{C}$ )
Minimum fluidization velocity, $U_{mf}$ (m/s)	0.04 (at $350^\circ\text{C}$ )	0.03 (at $800^\circ\text{C}$ )
Particles terminal settling velocity of, $U_t$ (m/s)	2.6 (at $350^\circ\text{C}$ )	1.8 (at $800^\circ\text{C}$ )
Gas flow, (liter/s STP)	$\sim 20$	12 ~ 17
Expected product gas composition, (%-vol)	95 $\text{N}_2$ , 1 $\text{H}_2\text{O}$ 4 $\text{HCl}$	71 $\text{N}_2$ , 12 $\text{H}_2\text{O}$ , 15 $\text{CO}_2$ , 1 $\text{O}_2$ , $\sim 20$ ppm $\text{HCl}$

Figure 4.2 gives an impression of the test facility. Visible at the front of the picture is the gas blower for the fluidisation gas for the BFB reactor and the exhaust gas pipe from the top of the cyclone leading out of the building. The pressure (drop) measurement lines are seen as thin wiring.

Reactor 1 is a bubbling FB reactor (inner diameter 0.4 m, height 0.8 m); the fluidizing medium is nitrogen. This BFB is operated in the temperature range 200 - 400°C: 350°C may be the optimum temperature for producing low-chlorine or chlorine-free fuel in this de-hydrochlorination reactor (with a solids residence time of approx. 30 minutes) without significantly pyrolysing any of the other combustible fractions (Zevenhoven et al., 2002). Heating coils are mounted around this reactor for heat-up during a cold start and for temperature regulation during the test.

Reactor 2 is a circulating FB combustor (inner diameter 0.11 m, height 2.3 m). The fluidizing gas is air and the reactor typically operates at a temperature of 800-850°C. The air is preheated to approx. 600°C with heating coils until char from the first reactor can provide sufficient combustion heat for temperature regulation during the test. The cooling system of this CFBC is divided into three parts in order to cool separate parts of the reactor when necessary (as indicated in Fig. 4.1). The total footprint of the facility is less than 10 m<sup>2</sup>.



Fig.4.2 Front view of the two-stage combustion test facility (May 2002)

The sand in the CFBC exit gas is collected by a high efficiency cyclone operated at ~15 m/s inlet velocity. The collected sand is cooled with water to below 400°C before returning to the BFB in an FB heat exchanger. The fluidizing medium is nitrogen gas.

#### ***4.2.2 Non-mechanical valves (seal pot)***

In the test facility, there are two non-mechanical valves of a seal pot type, one after the BFB and the second, which works also as a heat exchanger, for cooling the return sand from the CFBC after the cyclone. The higher pressure in the seal pot prevents the CFBC air from entering the first reactor where the fluidizing gas is nitrogen. Also, the seal pot after the cyclone prevents the nitrogen from escaping via the cyclone and prevents the flue gas from the CFBC from entering the BFB. For more details see publication IV.

#### ***4.2.3 Gaseous products and gas analysis***

The pyrolysis gases from the BFB are cooled to below 80°C by a heat exchanger that is mounted directly after the BFB. The cold gases are then fed to an NaOH/water solution to separate the HCl from the pyrolysed gas, which mainly contains N<sub>2</sub>. The HCl will be neutralized to produce NaCl and water. (For a larger scale process, HCl is to be recovered as hydrochloric acid!) By on-line measuring the pH of the solution, the HCl concentration can be followed. A 99.9 % pure NaOH was purchased for neutralising the HCl released from the low-temperature reactor. For gas analysis, a Fourier transform infrared (FT-IR) spectrometer is used for measuring the pyrolysis gases from the BFB pyrolyser and the flue gases from the CFBC. More details about the FT-IR can be found in Section 4.4.

#### **4.3 Pressure drop around the test facility**

The test facility includes many parts with different height levels and two different gas phases. Nitrogen gas is used in the first reactor (BFB) and in both non-mechanical valves as fluidizing gas. Air is used in the second reactor (CFBC) as fluidizing and combustion gas. Figure 4.3 shows the pressure distribution across the test facility. Table 4.2 gives the specification of all distributors used in the test facility. Details about calculation pressure in the fluidized bed are given in publication IV.

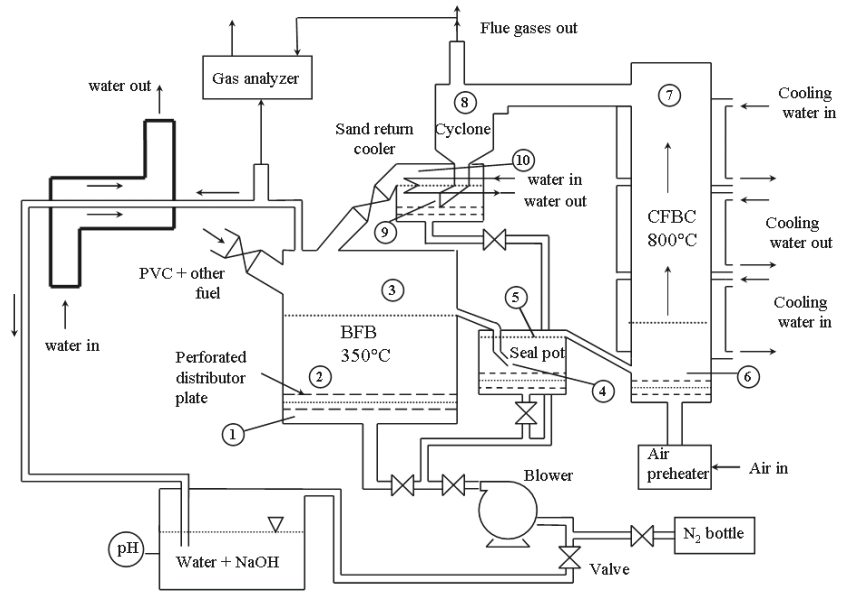
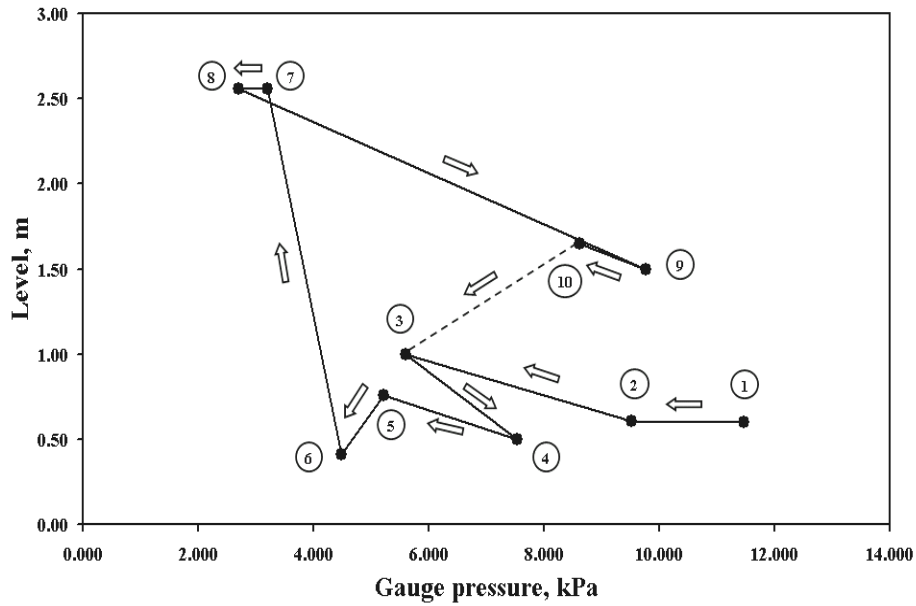


Fig. 4.3 Pressure distribution of two-stage combustion test facility

Table 4.2 Data of the distributors for both reactors and both non-mechanical valves

	Bubbling fluidized bed	Circulating fluidized bed	Seal pot after BFB	Seal pot after CFB
Distributor type	perforated	perforated	perforated	perforated
Number of orifices	190	141	54	500
Plate thickness, mm	3	3	3	3
Plate diameter, m	0.4	0.11	0.11	0.4
Open area, %	1.06	10.5	4	2.8
Orifice diameter, mm	3	3	3	3
Bed material density, kg/m <sup>3</sup>	1570	1570	1570	1570
Bed material (sand) size, mm	0.3	0.3	0.3	0.3

Silica sand with a mean particle size of 0.3 mm is used as bed material. The particle size distribution is given in publication IV.

#### 4.4 Measurement equipments and accuracy

In the test facility, various types of measurement devices were used to measure the temperature, pressure (also used for flow rate), pH and to carry out the spectral analysis of the gases. The specification of temperature, pressure and pH measurement devices are shown in Table 4.3.

Table 4.3 Measurement equipments used in the test facility

Measurements	Units	Type	Number	Scale	Accuracy
Temperature	°C	Type K (NiCr-Ni)	19	-200 to 1300	±0.75%
Pressure	kPa	48J4-2065 (scanivalve) Druck 10/35L (press. probe)	21 port	0-3450	0.05%-1.21%
pH	-	HANNA Ins. HI 1333B	1	0-14	±0.2
Rotameter	l/min	Kytölä KLA-HK35	1	0-25	± 2 % F.S.*
Rotameter	l/min	Platon R6AHS	1	0-1800	± 5 % F.S.
Weight meter	g	Mettler Toledo PB8000-P	1	20-8100	2%

\* F.S. = full scale

#### 4.4.1 Temperature measurements

For temperature measurements, 19 probes were used, distributed around the test facility at the most important locations. The most important probes are the ones connected to both reactors walls. These were mounted on the walls of the reactors very carefully, especially for the first reactor (BFB) because the heating for the BFB was obtained through an electrical heater mounted on/around the BFB walls. One could expect that, during the test, the wall temperature would be higher than the temperature inside the reactor (sand temperature), despite the fact that the fluidized bed material intensely mixed all the time, which would normally have been expected to reduce this effect. Therefore, the probes in the BFB (No. 10, 11, 12) and the probes for the CFBC (No. 13, 14, 15) were each insulated carefully from the walls by a 7 cm (length) and 7 mm (diameter) ceramic tube, as shown in Fig. 4.4.

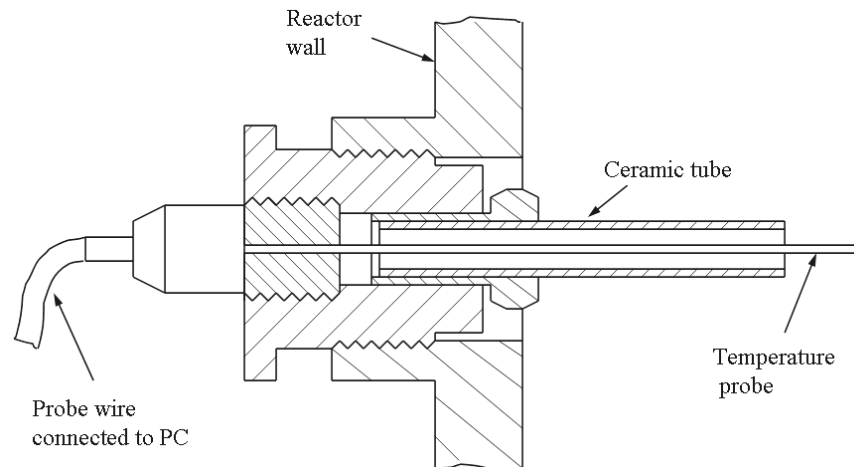


Fig. 4.4 Scheme of the temperature probes surrounded by ceramic tubes before being mounted on the BFB and CFBC walls

With the configuration shown in Fig.4.4, heat from the wall should not affect the temperature probe readings. In addition, the probe was inserted a bit deeper inside the bed, i.e., at a distance of about 7 cm from the wall for the BFB and about 4 cm for the CFBC. Beside that, the heater surrounding the BFB was kept at set-point 400°C. Therefore, the only parameters that affected the temperature-probe readings were the flow rate of the fluidizing gas. The flow rate was kept at 18 l/s for temperatures above 300°C. The profile of the temperature in some tests (see Chapter 5) is fluctuating because of the endothermic effects of the fuel added in the test.

All temperature probes used in the facility test were type K (NiCr-Ni thermocouples), where the typical accuracy error is between 2-3°C (for maximum reading below 375°C) for the first reactor readings. This error might be considered very small to have such a great affect on the tests results; for the second reactor also, the maximum temperature was (below 600°C) with an error about 4.5°C.

#### 4.4.2 Pressure and flow rate measurements

For the pressure and mass flow rate measurements, there were twenty-one points. Eleven of these were reserved for pressure measurements and the rest for mass flow rate measurement. Five pitot-static tubes were used to measure the flow rate; for each one, two pressure points were reserved (for static and total pressure, respectively). All these points were connected to a so-called scanivalve device, which sequentially gives the pressure at each point. Figure 4.5 shows a picture of the device.

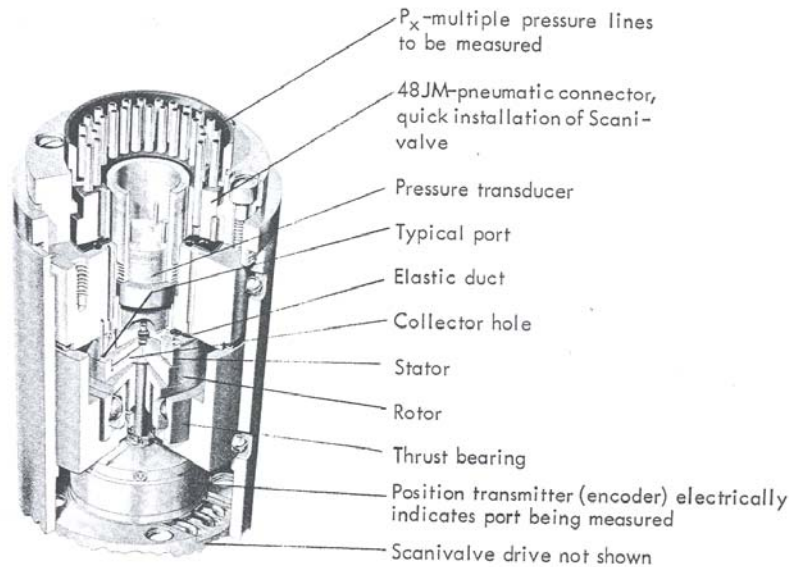


Fig. 4.5 Section view show the parts inside the scanivalve

In the scanivalve, the transducer is sequentially connected to the various  $P_x$  ports via a radial hole in the rotor that terminates at the collector hole. As the rotor rotates, this collector hole passes under the  $P_x$  port in the stator. Referring to the cut-away drawing, the rotor is rigidly supported by a ball thrust bearing. The stator is elastically connected to the block in a manner that allows the stator to follow the surface of the rotor. The pneumatic forces (pressure times area) at each  $P_x$  port, which tend to blow the rotor away from the stator, are thereby withstood by the ball thrust bearing. Each  $P_x$  pressure is elastically ducted from the block to its port in the stator. The stator is prevented from rotating by dowel pins anchored into the block.

For FB pressure points 4, 11, 13, 19, a purge gas was pumped into each one at 5 liter/min to reduce the sand effects from blocking the small tubes that go to the scanivalve, which would affect the readings from these probes. All these points are located above the distributor plate as shown in Fig 4.1. The flow rate of the purge gas was controlled using a small rotameter. During the last two tests for the two-stage combustion, point 4 and point 13 were connected directly to two additional separate probes that gave the pressure directly at these points. The type of the pressure probe (1 bar) used with the scanivalve was (Druck 10/35L), where the accuracy is between (0.05%-1.21%).



Pressure measurements are important both for the operation of both reactors (BFB and CFBC) and to ensure the circulation of the sand between them. The influence of the pressure measurements on the results was very small, especially for the BFB, where the degradation of PVC occurs because the fluidization flow rate does not change much.

#### 4.4.3 pH measurements

The digital probe for measuring pH was immersed in the HCl removing tank with a scale of (0-14) and an accuracy of about ( $\pm 0.2$ ). Unfortunately, during most of the pyrolysis tests, when only the BFB was used, there was a stray current and zero looping; a small electric current in the NaOH solution tank made it impossible to obtain a useful on-line signal. Therefore, a repeated sample had to be taken for each test. Later, with both tests for the two-stage combustion, the problem had been solved and pH-readings were taken on line throughout these tests. For the pyrolysis test where just the BFB was used, the pH measurement was used to check the release of HCl that had been measured using the FT-IR. For the two-stage combustion, the pH measurement was very important for measuring the HCl release from the BFB because the FT-IR was used for measuring the HCl release from the CFBC. The error in the reading was very small and did not affect the calculation of chlorine release as HCl from the BFB.

#### 4.4.4 Gas analyzer

Concentrations of HCl and several other species in the pyrolysis gas from the BFB pyrolyser and the flue gases from the CFBC were measured with a Fourier transform infrared (FT-IR) spectrometer (Temet Instruments DX-4000), which is a multicomponent gas analyzer (see Fig. 4.6 and Table 4.4).

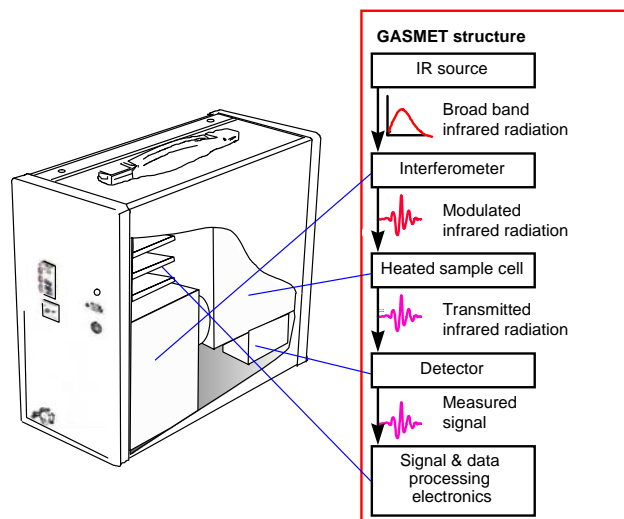


Fig. 4.6 Basic structure and an outline of the GASMET DX 4000 sample cell system (GASMET instruction manual, 2001)

Table 4.4 Specification of Temet Instruments DX-4000 type FT-IR used in all tests

<b>GASMET Dx-4000</b>	<b>Specification</b>
<b>General parameters:</b> Measuring principle Performance Response time, T90 Operating temperature Storage temperature Power supply	Fourier Transform Infrared, FT-IR. Simultaneous analysis of up to 30 gas compounds. < 120 s, depending on the gas flow and measurement time. 20 ± 20°C, non condensing. 0 - 60°C, non condensing. 110 - 250 V / 50 -60 Hz or 12 V DC.
<b>Sample cell:</b> Structure Mirrors Volume Connectors Gaskets Temperature	Multi-pass, fixed path length 5 m gold coating 1.0 l Swagelok 6 mm Viton® O-rings 120°C
<b>Measuring parameters:</b> Zero point calibration Zero point drift Sensitivity drift Linearity deviation Temperature drifts Pressure influence	24 hours, calibration with nitrogen (4.0 or higher N <sub>2</sub> recommended). 2 % of smallest measuring range per zero point calibration interval. none 2 % of smallest measuring range 2 % of smallest measuring range per 10 K temperature change 1 % change of measuring value for 1 % sample pressure change
<b>Spectrometer:</b> Interferometer Resolution Scan frequency Detector Source: Beam splitter Window material Wave number range	Temet Carousel Interferometer 8 cm <sup>-1</sup> 10 scans / s Thermo-electrically cooled MCT SiC, 1550 K BaF <sub>2</sub> BaF <sub>2</sub> 900 - 4200 cm <sup>-1</sup>

The resolution used was 8 cm<sup>-1</sup>, absorption path length 500 cm (multipass gold coated gas cell) and sample cell temperature 120 °C. The whole sampling system (pump, filter unit, sampling lines) was heated. The analysis calculation was based on a modified classical least square method (CLS). Further details are reported in (Saarinen, 1991). Figure 4.6 shows the basic structure and the outline of the GASMET DX4000 analysis system. For calibration, single component calibration gases and multipoint calibration for each compound was used. Specification details for the FT-IR DX-4000 type can be found

in Table 4.4. Figure 4.7 shows a picture of the FT-IR with the sampling system used in the tests.

During some of the tests (see Chapter 5), there was a problem with the FT-IR at the beginning of the test for a period of 8-10 minutes, during which no spectrum was measured. This problem was related to human error (the command for *continuous* measurements was not chosen during this period).



Fig. 4.7 Front view of the DX 4000 FT-IR spectrometer with the sampling system

#### ***4.4.5 Calibration gases***

The FT-IR analyzer was calibrated for H<sub>2</sub>O, CO<sub>2</sub>, CO, HCl, CH<sub>4</sub>, NO, NO<sub>2</sub> and N<sub>2</sub>O. Later, several other compounds were added, most importantly benzene C<sub>6</sub>H<sub>6</sub>, ethene C<sub>2</sub>H<sub>4</sub>, styrene C<sub>8</sub>H<sub>8</sub>, ethane C<sub>2</sub>H<sub>6</sub>, toluene C<sub>7</sub>H<sub>8</sub>, butadiene C<sub>4</sub>H<sub>6</sub>, propene C<sub>3</sub>H<sub>6</sub>, methanol CH<sub>4</sub>O, formaldehyde CH<sub>2</sub>O, acetaldehyde C<sub>2</sub>H<sub>4</sub>O, a-pinene C<sub>10</sub>H<sub>16</sub>, propane C<sub>3</sub>H<sub>8</sub>, propanol C<sub>3</sub>H<sub>8</sub>O and acetone C<sub>3</sub>H<sub>6</sub>O, for which the FT-IR device had been calibrated several months earlier.

### **4.5 Fuel types used and test procedure**

#### ***4.5.1 Fuel types used for the tests***

For the tests, a bottle-grade PVC (Dynea type 8021 BE) that contained, besides PVC, small amounts (0.17%-wt) of Sn-based stabilizer and a few %-wt MBS (methylmetacrylate-butadiene-styrene) as an impact modifier was used. The PVC particles are colorless transparent particles, half-spherical in shape, and about 5 mm in diameter (see Fig. 4.8a).

Two types of sewage pipe PVC waste were also tested. Unfortunately, dealing with waste PVC, there was no detailed information about which stabilizers and additives had been used when these materials were produced. The first waste PVC type was an old, light grey sewage pipe with 4% lead compounds and a small amount of Ca/Zn as stabilizer; the second was a newer, orange colored sewage pipe with Ca/Zn compounds and 0.6% lead-based stabilizer (see Fig.4.8d & Fig.4.8e). Both types were ground to small particles of 2-5 mm. The compositions of the bottle-grade PVC and the PVC waste pipes (sewage pipes) are given in Table 1. All PVC fuel samples and the char samples after the tests were analyzed at an external, commercial laboratory. The multi-functional CHN-O-RAPID elemental analyzer was used for the determination of C, H and O. For C and H, analysis determination is based on fast combustion in oxygen at 950°C-1050°C, followed by separation of the products and amounts determination using a thermal conductivity detector (TCD). For oxygen analysis determination, the sample oxygen is converted to CO using carbon black at around 1120°C, followed by non-dispersive IR-photometer (NDIR) for CO determination. Chlorine analysis is made by reacting the sample chlorine with sodium peroxide followed by electrometric titration with silver nitrate (EN ISO 1158). The metals (Pb, Cd, Sn, Ca, Zn) were analyzed by dissolving them from the organic matrix using mineral acids, followed by determination using atomic absorption spectroscopy (AAS). In addition, wood (pine) and Polish coal with a particle size of around 1-5 mm (kindly provided by VTT Processes, Espoo) were pyrolysed and co-pyrolysed with the bottle-grade PVC in the BFB (see Fig.4.8b & Fig.4.8c). Table 4.5 presents the properties of all fuel types used in this work.

Table 4.5 Properties of the bottle-grade PVC, wood (pine) and Polish coal

Substance	Bottle-grade PVC	PVC waste 1 (sewage pipe)	PVC waste 2 (sewage pipe)	Wood (pine)	Polish coal
Ultimate analysis (%-wt, dry)					
C %-wt	42.51	37.89	36.86	50.2	82.32
H%-wt,	5.35	4.82	4.54	6.00	5.12
N%-wt,	NA*	NA	NA	0.30	1.42
S%-wt,	NA	NA	NA	NA	0.77
O%-wt,	1.08	NA	2.67	43.2 (diff) <sup>†</sup>	10.4 (diff)
Cl%-wt, l	50.93	52.28	53.54	NA	NA
Sn%-wt,	0.17	< 0.002	NA	NA	NA
Pb%-wt,	NA	4.00	0.63	NA	NA
Cd (mg/kg),	NA	< 1	< 5	NA	NA
Ca%-wt,	NA	0.04	1.62	NA	NA
Zn (mg/kg)	NA	36	13	NA	NA
Sum	100.04	99.03	99.88	100	100
Proximate analysis (%-wt)					
Fixed carbon	~92 <sup>+</sup>			7.50	NA
Volatile	~8 <sup>+</sup>			84.2	NA
Moisture	0			8.00	6
Ash	0			0.30	8.3
Higher heating value MJ/kg	NA			20.7	NA
Lower heating value MJ/kg	NA			19.4	NA

\* Not analyzed, + Assumed, from (Zevenhoven et al., 2002), <sup>†</sup> Oxygen is calculated by difference not measured

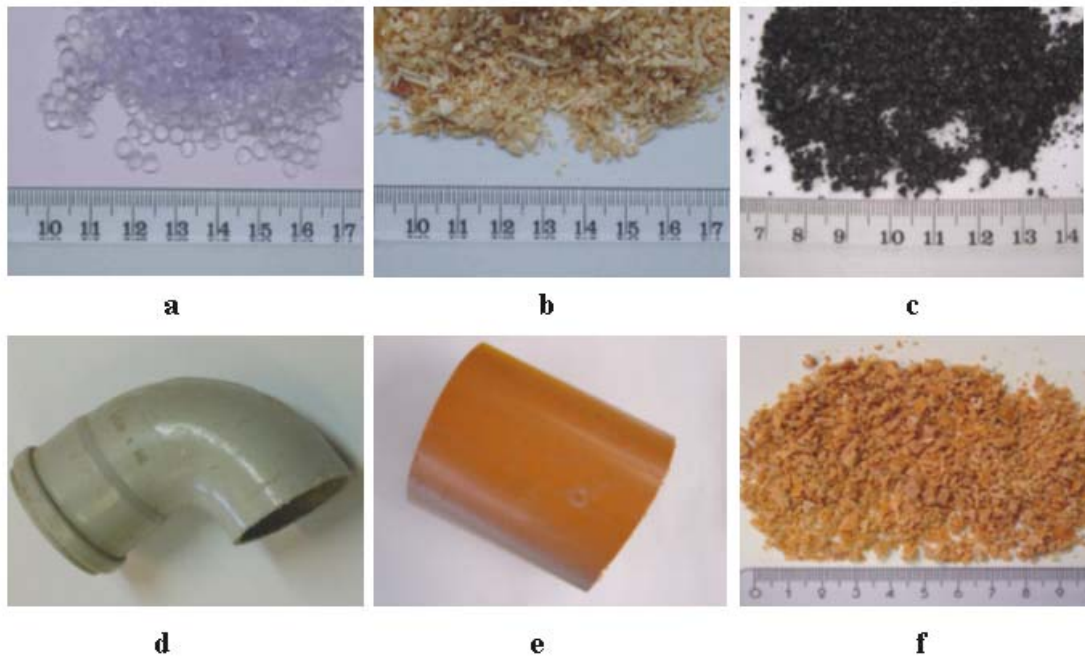


Fig.4.8 Fuel types used in the facility tests, a: bottle grade PVC, b: wood Finnish pine, c: Polish coal, d: light grey sewage PVC pipe (old), e: orange sewage PVC pipe (new), (f) orange sewage PVC pipe after grinding.

#### 4.5.2 Pyrolysis tests

Several tests were performed using the BFB reactor. A bed of 72 kg sand was heated up during fluidization with nitrogen. Only the wood (pine) was pyrolyzed during fluidization with air. The tests involved either 100% PVC (728 g bottle-grade PVC), 100% sewage pipe PVC waste No. 1 (117 g), 100% sewage pipe PVC waste No. 2 (727g), 100% wood (1.61 kg), 100% Polish coal (100 g), or 20% PVC (145 g) + 80% wood (583 g), 20% PVC (145 g) + 80 % Polish coal (583 g). For all tests, the concentrations of H<sub>2</sub>O and CO<sub>2</sub> at the beginning of each test were approx. 3-4 %-vol and 100 ppm, respectively. The gas flow through the BFB was ~ 18 liter/s (at 30°C inlet temperature).

Off-line analysis for pH measurements were carried out in most of the tests; because of a stray current and zero looping giving small electric currents in the NaOH solution, it was impossible to obtain a useful on-line pH signal during the first experiments. In these cases, repeated samples had to be taken. On-line pH measurements were accomplished during the test for the sewage pipe PVC waste No.2. The temperature in the tank of the NaOH/water solution was kept below 50°C during the whole test.

The heating rate in the BFB for all PVC tests was around 30-40 °C/hr (0.5-0.67 °C/min) and the heating rate for other tests was around 20-60°C/hr (0.33-1°C/min). The heat flux from the heater around the BFB walls to the sand in the bed was the same, where the temperature of the heater was kept at set-point 400°C.

### ***4.5.3 Two-stage combustion tests***

Two tests involving both reactors of the test facility were performed. The first test was performed with 100% bottle-grade PVC and the second with 100% sewage pipe PVC waste No. 2. In both tests, the bed of the BFB (80 kg of sand) was heated up during fluidization with nitrogen. The initial concentration of H<sub>2</sub>O and CO<sub>2</sub> were 0.71 %-1.35 vol and 0%- vol, respectively. Gas flow through the BFB was approx. 20 liter/s (at 30°C).

For the first test, the temperature in the BFB was increased to 44°C/hr until it was around 365°C. When the temperature had reached 231°C, a total of 900 g of bottle-grade PVC was fed at five stages for different temperatures. During the first stage, 300 g was fed. After one hour and eight minutes, an amount of 600 g of bottle-grade PVC was fed in four stages: 150 g was fed at 1:08, 1:25, 1:36 and 2:05 hrs, respectively. The temperatures of the bed at these feeding times were 260°C, 276°C, 322°C and 349°C, respectively. The purpose of such feeding was to see the effect of bed temperature on PVC de-hydrochlorination, i.e., HCl release from both reactors. The following chapter gives a detailed description of the test results.

For the second test, the temperature in the BFB was increased at about 26°C/h until it was around 365°C. A total of 900 g of waste PVC was fed to the BFB when the temperature had reached over 300°C, at a rate of 100 g every ten minutes. The temperature of air from the pre-heater for the CFBC appeared not high enough to completely burn the char (coke) provided by the BFB: char was found in the FB cooler after the cyclone.

## 5. Test results and discussion

(See also publication IV, V and VI)

### 5.1 Bottle-grade PVC pyrolysis

The result from the FT-IR data analysis shows that hydrogen chloride (HCl) is the main gas released. Methane ( $\text{CH}_4$ ), benzene ( $\text{C}_6\text{H}_6$ ), CO,  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ , ethane ( $\text{C}_2\text{H}_6$ ), ethene ( $\text{C}_2\text{H}_4$ ), styrene ( $\text{C}_8\text{H}_8$ ), toluene ( $\text{C}_7\text{H}_8$ ) and propene ( $\text{C}_3\text{H}_6$ ) were present in significant amounts (see Figs. 5.1, 5.2 and 5.3). There are small amounts (below 20 ppm) of butadiene present in the product gases as well. The MBS does not have any effect on the thermal stability of PVC unless the blend ratio (PVC/MBS) is above (90/10) (Andričić and Kovačić, 1999). In our case, there was a very small amount in the bottle grade PVC. This type of PVC contains only 0.17% Sn as a stabilizer; it can be seen in Fig. 5.1 that at temperatures below  $200^\circ\text{C}$  and within a period of 20 minutes the chlorine started to be released as HCl.

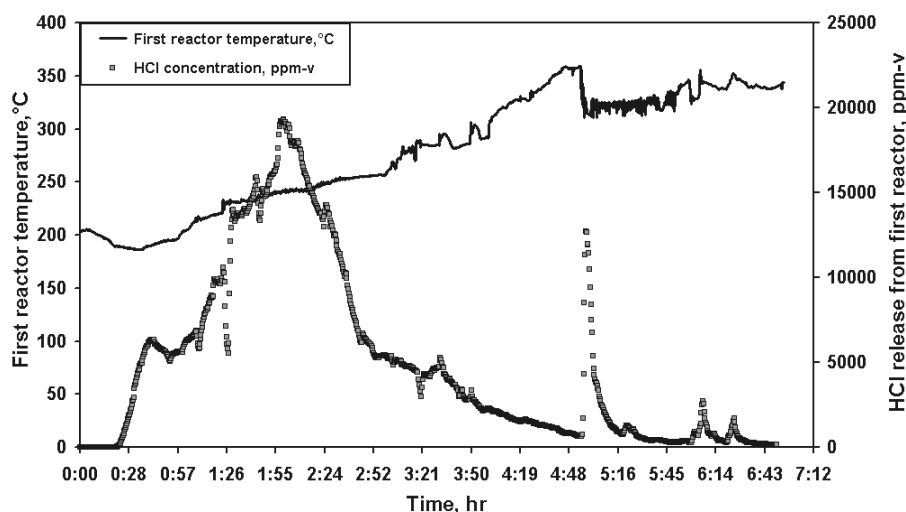


Fig. 5.1 Release of HCl and BFB reactor temperature versus time for bottle-grade PVC with  $0.5^\circ\text{C/hr}$  heat-up

Figure 5.1 also shows that the PVC decomposes in the temperature range  $200^\circ\text{C}$ - $350^\circ\text{C}$ . In addition, it can be seen that after 5 hours and 13 minutes of testing, some HCl is suddenly released (apparently from some PVC that was not properly mixed with the rest of the bed) and a sudden decrease in temperature is seen. This may be related to some changes in the fluidizing pattern of the bed near the temperature probe or to the endothermic de-hydrochlorination of this type of PVC.

The release of other vapors is plotted together with the temperature of the BFB as shown in Figure 5.2. Benzene starts to appear at low temperatures (below  $200^\circ\text{C}$ ) together with CO. Benzene is released immediately after the dehydrochlorination step; this is consistent with the theory and studies that state that under the dehydrochlorination step, a portion of hydrocarbons in the form of benzene is released together with HCl (Bockhorn et al., 1996; Sørnum et al., 2001). At  $240^\circ\text{C}$ , benzene and CO release reached

over 1180 ppm and 250 ppm, respectively. At temperatures between 310 and 350°C, methane release starts to increase and reaches more than 2000 ppm at 340°C. At temperatures above 250°C, other gases like ethene, styrene, toluene and propene are released in significant amounts (above 50-100 ppm).

The oxygen needed for CO and CO<sub>2</sub> (see publication V, Fig. 5) formation apparently comes from the PVC or from moisture; no other oxygen-containing compounds were detected. It is possible that CO, CO<sub>2</sub> and benzene circulate in the loop BFB → NaOH/water tank → recirculation blower → BFB, being much less water-soluble than HCl. This implies that measured concentrations may overestimate the release of CO, CO<sub>2</sub> and benzene. The large amount of water in the gas must be related to entrainment from the NaOH solution in the HCl removal tank (see publication V, Fig. 5).

The release of HCl from the PVC was also followed by neutralization with NaOH, i.e., the pH in the aqueous solution, as shown in Fig. 5.3.

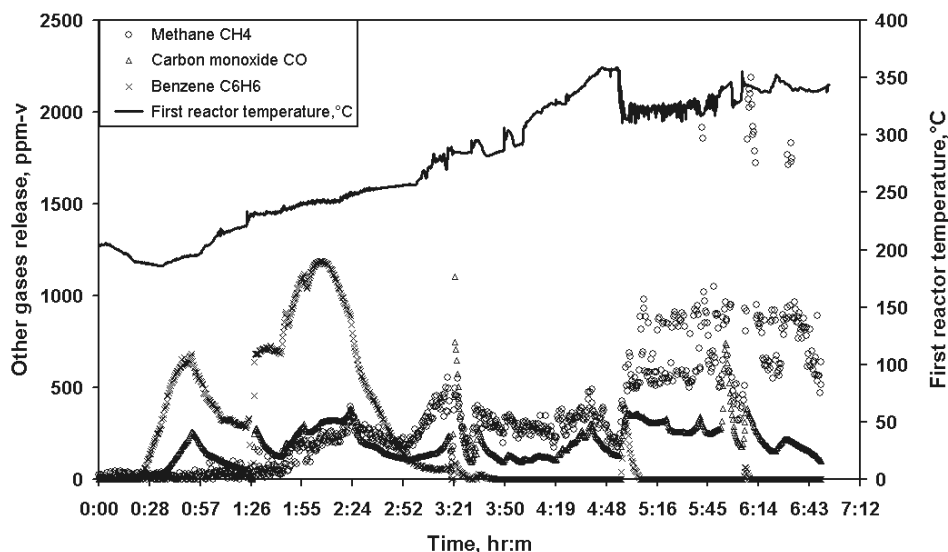


Fig. 5.2 Other vapors evolution and BFB reactor temperature versus time for bottle-grade PVC

Samples of char particles taken from the middle and the top of the BFB bed after the test were sent for chemical analysis (C, H, Cl). This showed a chlorine content in the residue for a sample from the middle of the bed below 0.05 %-wt, at chlorine-to-carbon mass ratio < 0.001 kg Cl / kg C. For the sample from the top of the bed, the chlorine content was below 0.08 %-wt, at chlorine-to-carbon mass ratio < 0.001 kg Cl / kg C. Table 5.1 gives the chemical analysis of the char samples.

The difference in chlorine content between the sample that was from the top and the one taken from the middle may be related to the mixing quality of the bed, which will be affected by the type of distributor plate used in the BFB – in our BFB, perforated distributed plates were used. This type of distributor is the cheapest (Kunii and Levenspiel, 1991) and may be regarded as the lowest performance type. As a result, there may be some high temperature spots in some areas, which cause this difference in char quality. Despite that however, the chlorine content difference between the top and the



middle of the bed is not that big, and the chlorine-to-carbon ratio is almost the same. The chlorine content in the char might be affected significantly by many parameters, such as the PVC type, the types of additives (e.g., stabilizers and plasticizer) used in the PVC, the temperature of the BFB bed (the middle may be hotter than the top of the bed), the heating rate and the mixing quality of the bed materials. A bed temperature in the range 340-350°C appears to be the optimum temperature for this PVC de-hydrochlorination.

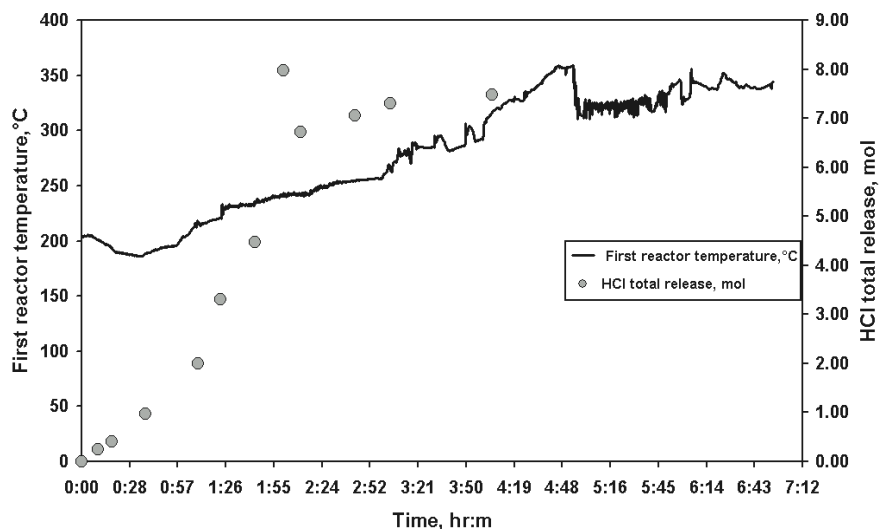


Fig. 5.3 Release of HCl from pH measurement and neutralization (NaOH) with BFB temperature versus time for bottle-grade PVC (input chlorine with PVC: 10.44 mole)

## 5.2 PVC waste No.1 (sewage pipe) pyrolysis

The result from the FT-IR data analysis shows again that hydrogen chloride (HCl) is the main gas released besides some methane (CH<sub>4</sub>), benzene (C<sub>6</sub>H<sub>6</sub>), CO, ethene (C<sub>2</sub>H<sub>4</sub>), styrene (C<sub>8</sub>H<sub>8</sub>), toluene (C<sub>7</sub>H<sub>8</sub>) and propene (C<sub>3</sub>H<sub>6</sub>) (see Figs. 5.4, 5.5 and 5.6).

The PVC waste No.1 (sewage pipe) first starts to decompose after almost one hour and 22 minutes, at a temperature above 250°C. Despite the fact that the amount of bottle-grade PVC used in the first test was more than six times the amount of PVC waste No.1 (i.e., the heat available per kg PVC waste is much higher), it was still stable at 250°C. The reason for this must be related to the presence of the stabilizers in this PVC waste; the analyses in Table 4.5 show around 4% lead based and other stabilizer compounds that give the PVC the ability to resist heat. From Fig. 5.4, the effect of the temperature on the necessary residence time in the BFB for this type of PVC can be seen; this can be shorter for bed temperature above 300°C than for a bed temperature below 250°C.

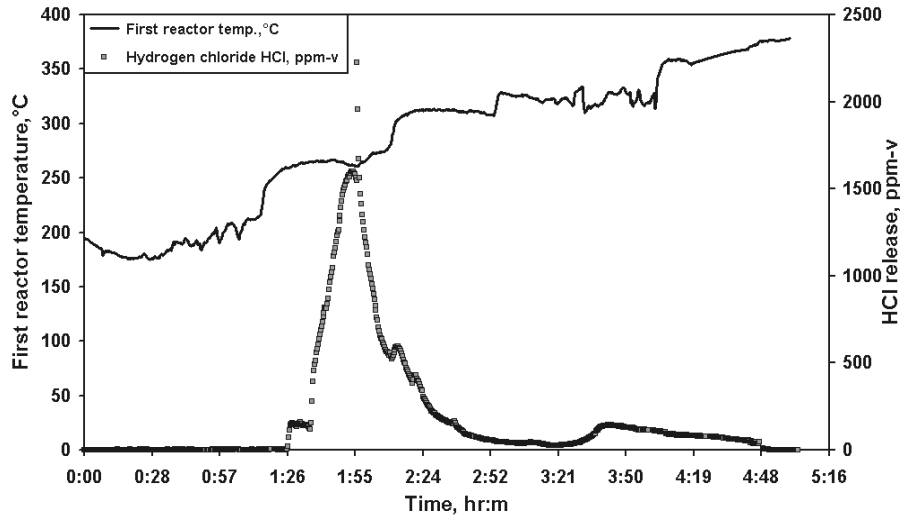


Fig. 5.4 Release of HCl and BFB reactor temperature versus time for PVC waste No.1 with 0.62 °C/hr heat-up

Figure 5.5 shows the release of other vapor compounds and the BFB temperature by time. Benzene and carbon monoxide start to appear at temperatures below 200°C and even before HCl release. At 263°C, the C<sub>6</sub>H<sub>6</sub> release reached 1860 ppm, CO 780 ppm and CH<sub>4</sub> 320 ppm besides small amounts (below 100 ppm) of C<sub>2</sub>H<sub>4</sub>, C<sub>7</sub>H<sub>8</sub> and C<sub>3</sub>H<sub>6</sub>. When the temperature starts to rise above 270°C, the C<sub>6</sub>H<sub>6</sub> release starts to decline and, at the same time, other gaseous emissions increase. CH<sub>4</sub> releases its peak at 2510 ppm at 325°C and 1580 ppm for CO at 318°C.

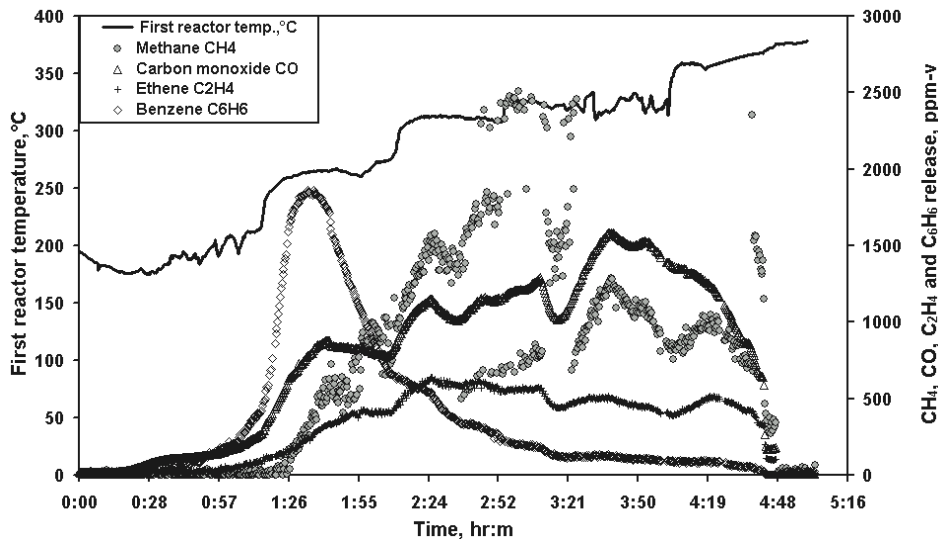


Fig. 5.5 Other vapors evolution release and BFB reactor temperature versus time for PVC waste No.1

There were several other vapor compounds released in significant amounts (between 50-200 ppm) like styrene, toluene and propene, which starts at a temperature above 250°C, and the propane reached more than 200 ppm at temperature above 310°C, as shown in Fig 5.6. Figure 5.7 shows the relationship between the chlorine releases as HCl from the BFB with the temperature increase. Most of the chlorine was released as HCl when the temperature reached above 300°C.

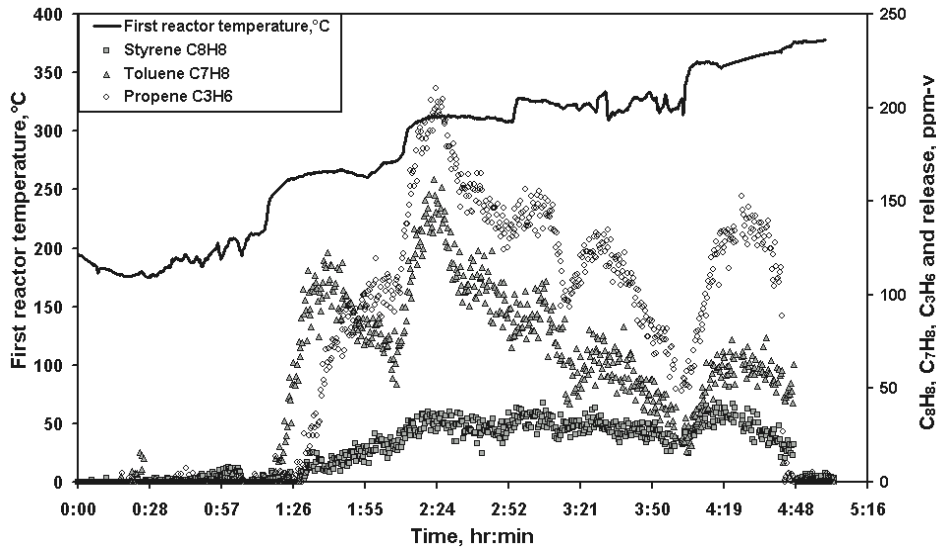


Fig. 5.6 Other vapor compounds release and BFB reactor temperature versus time for PVC waste No.1

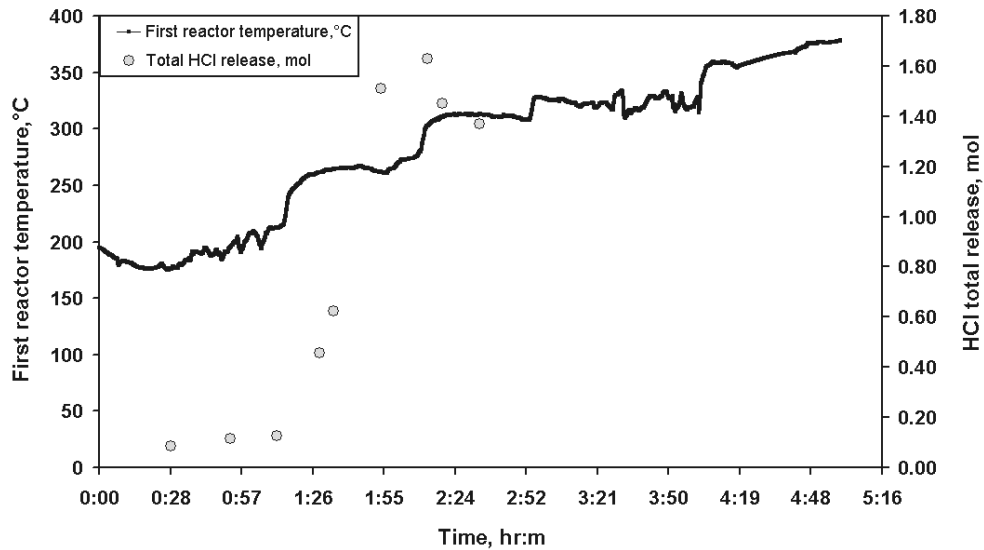


Fig.5.7 Release of HCl from pH measurement and neutralization (NaOH) with BFB temperature versus time for PVC waste No.1 (input chlorine with PVC: 1.73 mole)

### 5.3 PVC waste No.2 (sewage pipe) pyrolysis

Compared to the previous types, there was a slight drop in the bed temperature after feeding this type of PVC. The release of HCl is shown in Fig.5.8.

The result from the FT-IR data analysis shows again that hydrogen chloride (HCl) is the main gas released; some methane ( $\text{CH}_4$ ), benzene ( $\text{C}_6\text{H}_6$ ), CO, ethene ( $\text{C}_2\text{H}_4$ ), toluene ( $\text{C}_7\text{H}_8$ ) and propene ( $\text{C}_3\text{H}_6$ ) was also released. The release of HCl is plotted together with BFB temperature in Fig. 5.8. This type of PVC starts to decompose at a temperature of  $200^\circ\text{C}$  and the highest chlorine release as HCl occurs in the temperature range  $200^\circ\text{C}$ - $310^\circ\text{C}$ . Figure 5.8 also showed that, when the bed temperature reached  $330$ - $350^\circ\text{C}$ , most of the chlorine had already been released from the char. Apparently at temperatures between  $310$  and  $350^\circ\text{C}$ , most of the chlorine can be quickly removed from the char for this PVC. With very good mixing in the bed, the residence time for the PVC in the BFB can be reduced. In addition, it can be seen from Fig. 5.8 that this type of PVC starts to decompose within 15 minutes, which is shorter than the time needed for bottle-grade PVC (20 minutes) and, despite the fact that this type of PVC contains 1.62 % calcium compound, 0.63 % lead based compound and small amounts of zinc-based and cadmium compound, as shown in Table 4.5. This may, to some extent, be related to the higher heating rate used in this test, which is  $10^\circ\text{C/hr}$  higher than the heating rate used in the bottle-grade PVC test.

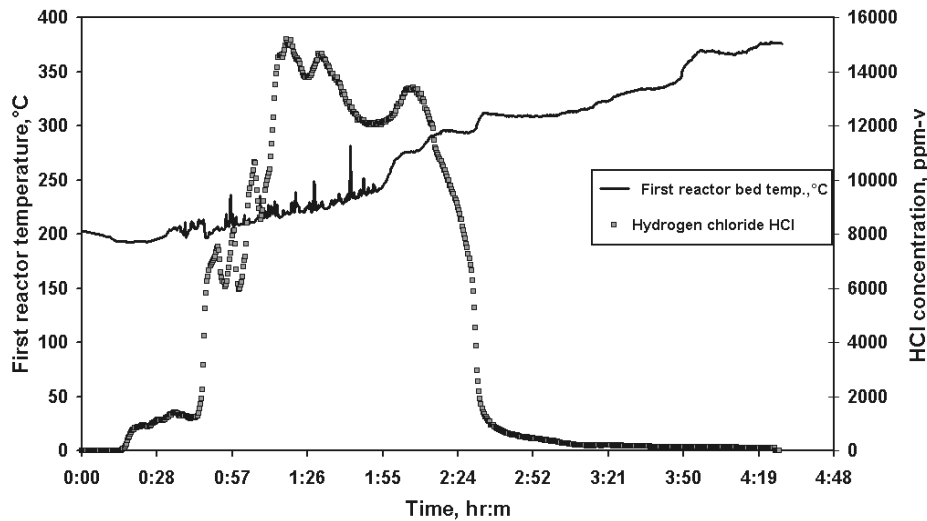


Fig. 5.8 Release of HCl and BFB reactor temperature versus time for PVC waste No.2 with  $40^\circ\text{C/hr}$  heat-up

The release of other vapors like methane, benzene, CO, ethene, toluene, and propene is shown in Figs. 5.9 and 5.10. Table 4.5 shows that this type of PVC contains 2.67% oxygen; this might explain the formation of CO. At about  $250^\circ\text{C}$ , the benzene, methane and ethene release started; the release of methane reached more than 9000 ppm above  $300^\circ\text{C}$ .

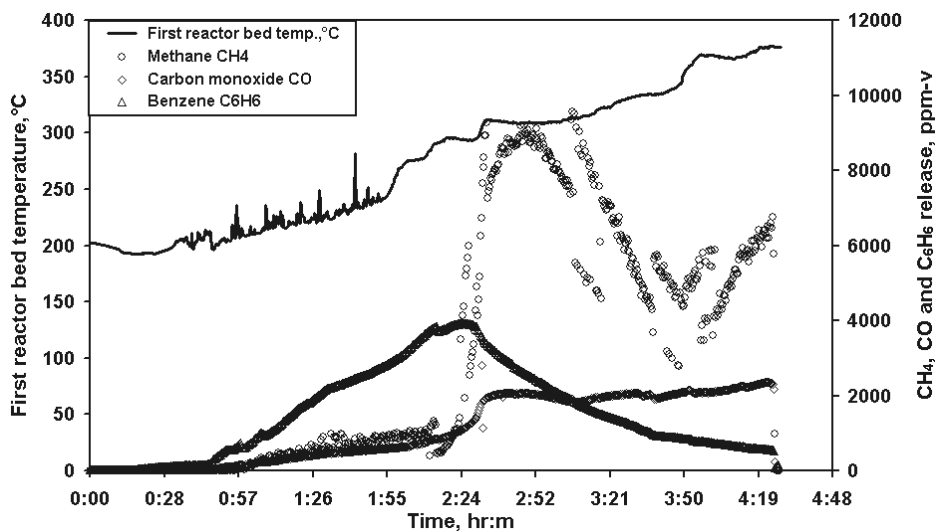


Fig. 5.9 CH<sub>4</sub>, CO and C<sub>6</sub>H<sub>6</sub> release and BFB reactor temperature versus time for PVC waste No.2

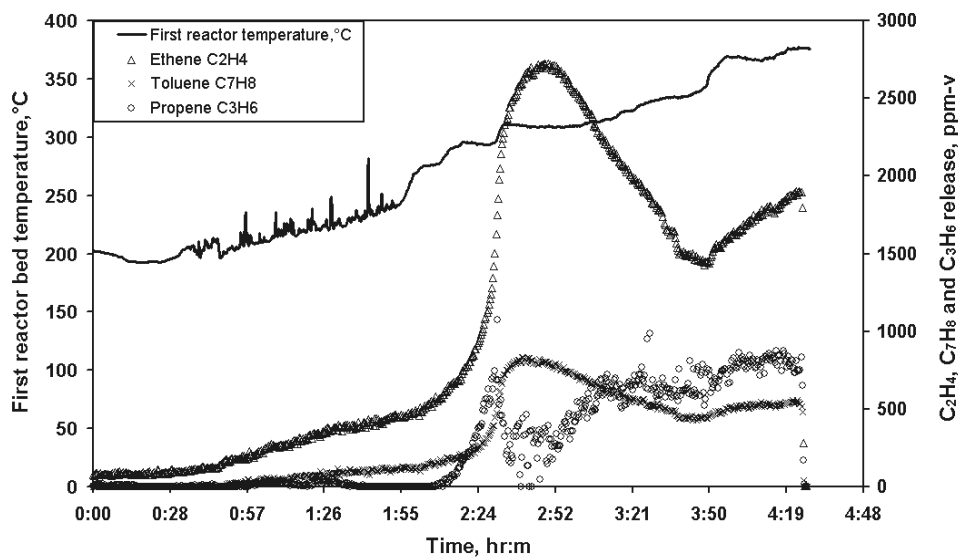


Fig. 5.10 C<sub>2</sub>H<sub>4</sub>, C<sub>7</sub>H<sub>8</sub> and C<sub>3</sub>H<sub>6</sub> release and BFB reactor temperature versus time for PVC waste No.2

The release of HCl from the PVC was followed by neutralization with NaOH and, following the pH, in the aqueous solution, as shown in Fig. 5.11. From this figure, it can be seen that most of the chlorine was released as HCl when the bed temperature was above 300 °C.

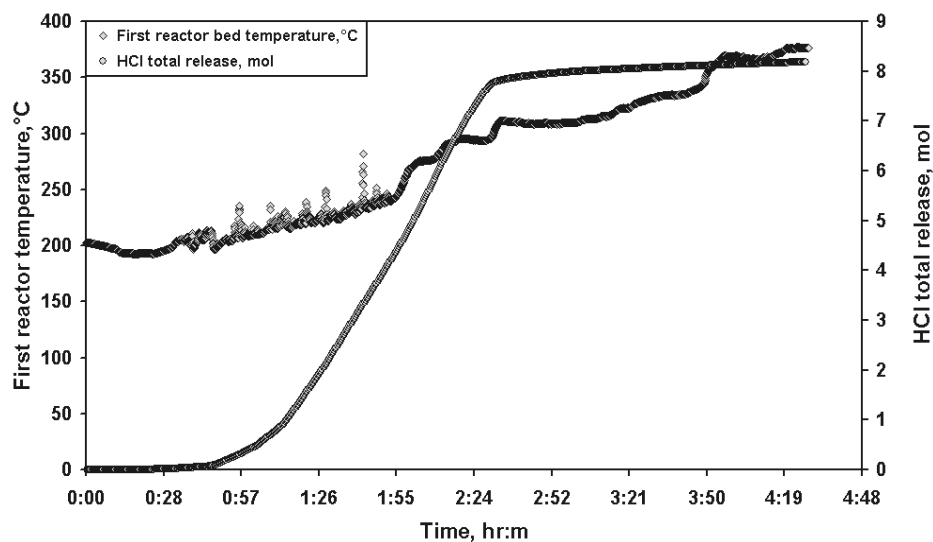


Fig. 5.11 Release of HCl from pH measurement and neutralization (NaOH) with BFB temperature versus time for PVC waste No. 2 (input chlorine with PVC: 10.96 mole)

#### 5.4 Comparison of PVC types

A comparison of the results of the three tests shows that the decomposition performance of PVC differs from type to type, depending mainly on the mass fraction and type of the stabilizer in the PVC, and on the heating rate for heating the bed of the BFB. For all three PVC types tested, the HCl release is plotted against the temperature of the BFB reactor bed in Fig. 5.12<sup>2</sup>.

From Fig. 5.12, it can be seen that the test for bottle-grade (experiment time: 7 h at 30 °C/h heat-up) starts to decompose below 200°C; the PVC waste No.1 (experiment time: 5 h at 37 °C/h heat-up) starts to decompose at temperatures above 250°C, mainly due to the presence of an effective lead-based heat stabilizer; PVC waste No.2 (experiment time: 4 h 30 min. at 40 °C/h heat-up) starts to decompose at around 200°C. The PVC dehydrochlorination appears to be complete at 300-320 °C in all cases.

A factor of importance is the mixing quality of bed material during each test and the distributor plate (perforated plate) type used in the BFB reactor. A good distributor type should provide uniform and stable fluidization over the entire range of operation, a minimum of dead zones on the distributor and minimum plugging over extended periods of operation (Basu, 1991). These properties of the distributor may not be achieved by the perforated type that has been used in the BFB; this type has the lowest performance of all distributor types.

<sup>2</sup> To be able to draw this figure, the reactor temperature had to be fitted to a polynome as a function of time, since FT-IR readings were taken every 20 s and temperature readings every 0.2 s. This may give a temperature error of a few degrees C in Fig. 5.12.

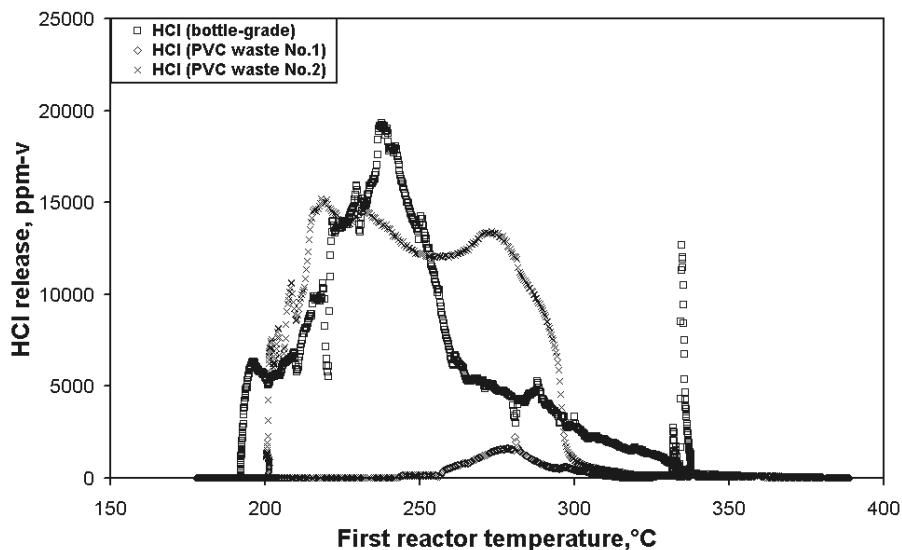


Fig. 5.12 Comparison of the HCl release in three types of PVC

#### 5.4.1 FT-IR spectrometer gas analysis results

The bottle-grade PVC, PVC waste No. 1 and PVC waste No. 2 gave different FT-IR spectra at different temperatures, 250°C, 300°C and 350°C. A discussion about FTIR spectrum analysis and peak identification is available in (Publication VI, Fig. 15).

#### 5.4.2 Char samples analysis

After each test, samples of char particles (black color) were sent from the bed for chemical analysis as shown in Table 5.1. The results show that the chlorine content in the residue and the chlorine-to-carbon ratio are different from one type to another. The chlorine content of chars from bottle-grade PVC, PVC waste No.1 and PVC waste No.2 are 0.021 %-wt, 0.43 %-wt and 0.8 %-wt, respectively.

The char chlorine-to-carbon ratio is  $< 0.001$  kg Cl / kg C for bottle-grade PVC, 0.03 kg Cl / kg C for PVC waste No.1 and 0.12 kg Cl/ kg C for PVC waste No.2. The difference between the three PVC types must be related mainly to the presence of different stabilizers and their ability to resist heat, which affects the decomposition of the PVC. Another factor may be the heating rate, although this was in the range 30-40 °C/h for all tests. At a lower heating rate, there will be higher conversion (more chlorine freed as HCl) and more char produced (Wu, 1994).

Table 5.1 also shows the difference in chlorine content between samples of bottle-grade PVC taken from the top and the middle of the bed. The difference may be related to the mixing quality of the bed, which was affected by the type of distributor plate used in the BFB. There might be some high temperature spots in some areas inside the reactor, which cause this difference in char quality. Despite that, the chlorine content difference between the top and the middle of the bed is not that big, and the chlorine-to-carbon ratio

is almost the same (see publication IV). All tests were made using the same BFB reactor and using the same gas distributor.

Table 5.1 Chemical analysis of char sample taken from the pyrolysis reactor for bottle-grade PVC, PVC waste No.1 and PVC waste No.2.

Substance	Bottle-grade PVC		PVC waste 1 (sewage pipe)	PVC waste 2 (sewage pipe)
	Top of the bed	Middle of the bed		
C (%-wt)	31.4	15	14.2	6.6
H (%-wt)	2.29	0.93	0.97	0.44
O (%-wt)	NA	NA	NA*	1.6
Cl (%-wt)	0.03	0.01	0.4	0.8
Sn (%-wt)	NA	NA	NA	NA
Pb (%-wt)	NA	NA	1.62	0.21
Cd (mg/kg)	NA	NA	NA	NA
Ca (%-wt)	NA	NA	NA	0.78
Zn (mg/kg)	NA	NA	NA	28
Bed material (%-wt)**	66.3	84.1	82.8	89.6
Sum %-wt	100.00	100.00	100.00	100.00

\*NA = not analysed

\*\* By difference

### 5.5 Pyrolysis test with 100% wood (Finnish pine)

In this test, there was a sudden jump in the measured temperature after 40 minutes from feeding the wood to the BFB, which increased from 80°C to over 450°C for about six minutes, but after that, dropped to 145°C, to increase gradually from then on until the end of the test. The reason for that was presumably related to the burning of some small particles of the wood, which ignited near the hot wall of the reactor. This could be seen through the window in the reactor side. The temperature in the BFB for the whole test was increased by about 0.87°C/min (52°C/hr) until around 350°C.

Figures 5.13 and 5.14 show the amounts of H<sub>2</sub>O, CO<sub>2</sub> and CO are increased significantly during this period. The analysis of the FT-IR spectrum shows there were many other gases released besides H<sub>2</sub>O, CO<sub>2</sub> and CO. These gases were methane, methanol CH<sub>4</sub>O, formaldehyde CH<sub>2</sub>O, acetaldehyde C<sub>2</sub>H<sub>4</sub>O, a-pinene C<sub>10</sub>H<sub>16</sub>, propane C<sub>3</sub>H<sub>8</sub>, acetone C<sub>3</sub>H<sub>6</sub>O, nitrogen oxide NO and a small amount of nitrogen dioxide NO<sub>2</sub> (see Figs. 5.14 and 5.15). There was a problem with the FT-IR at the beginning of the test for a period of less than 15 minutes; there was no spectrum taken during that period. It can be stated that the volatile release for the wood was completed at 320-350°C.



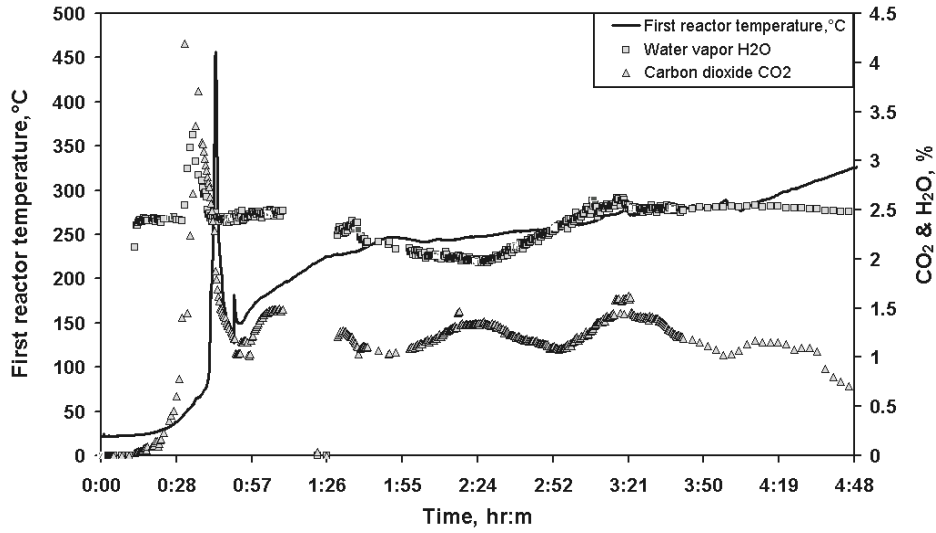


Fig. 5.13 H<sub>2</sub>O and CO<sub>2</sub> release and BFB reactor temperature versus time for wood (pine) with 0.87°C/min (52°C/hr) heat-up

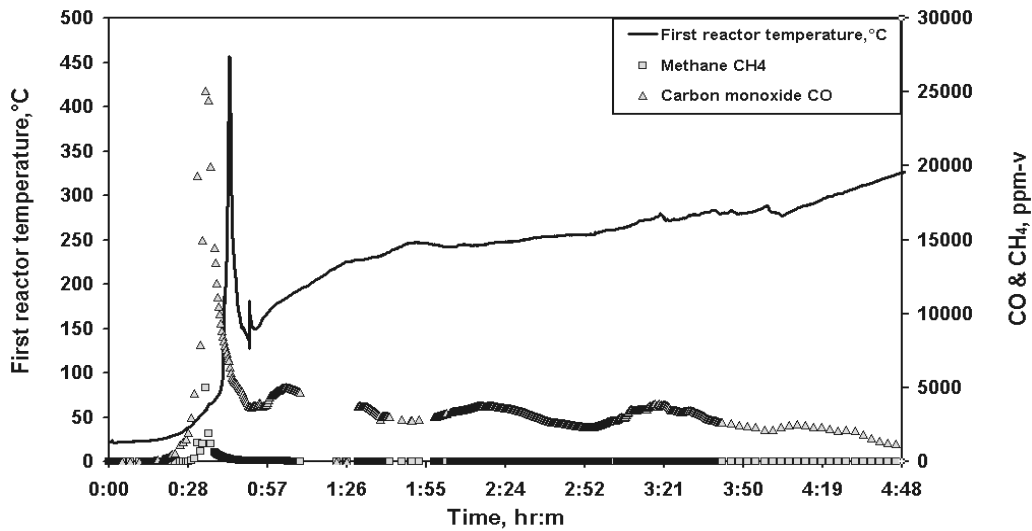


Fig. 5.14 CH<sub>4</sub> and CO release and BFB reactor temperature versus time for wood (pine)

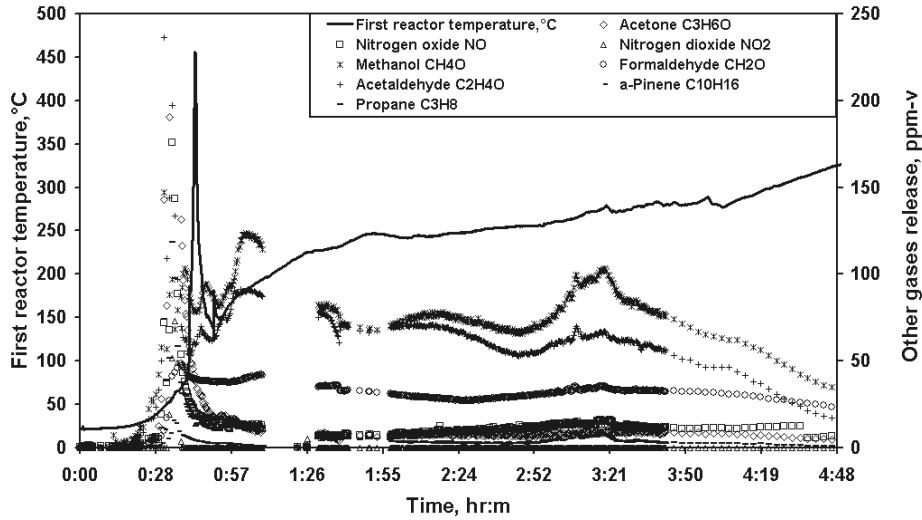


Fig. 5.15 Other gases release and BFB reactor temperature versus time for wood (pine)

### 5.6 Pyrolysis test with 100% Polish coal

At the beginning of the test, the concentration of H<sub>2</sub>O and CO<sub>2</sub> were approx. 4 %-vol and 500 ppm, respectively, and, at the end of the test, the water concentration had increased to 11.5% (mainly from the NaOH solution tank) with just 0.8 % for CO<sub>2</sub>, as shown in Fig. 5.16. The heating rate for this test was 0.58°C/min (35°C/hr).

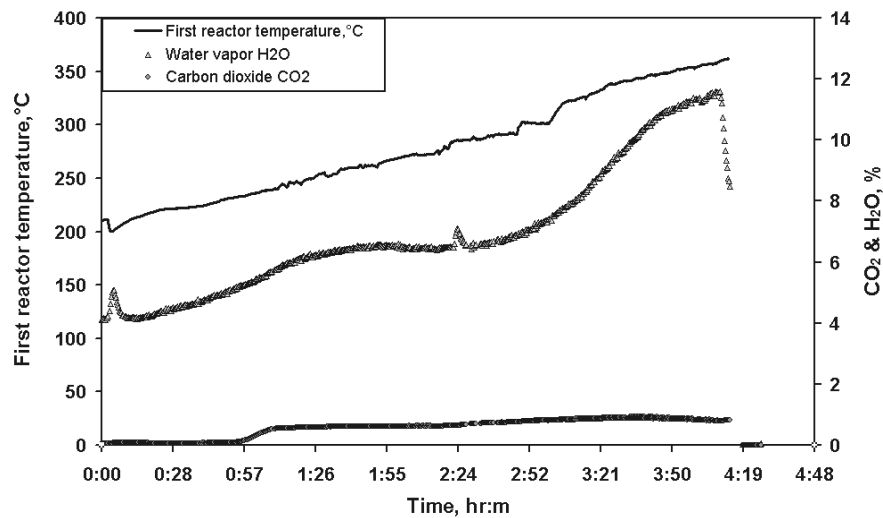


Fig. 5.16 H<sub>2</sub>O and CO<sub>2</sub> release and BFB reactor temperature versus time for Polish coal with 0.58°C/min (35°C/hr) heat-up.

The sample spectrum from the FT-IR shows that there are different hydrocarbons released from the coal, which starts to degrade at 240°C. There was a significant amount of CH<sub>4</sub> (~3000 ppm) and CO (~1360 ppm), as shown in Fig. 5.15. Other gases evolution

release like ethane  $C_2H_6$ , ethene  $C_2H_4$ , propane  $C_3H_8$ , propene  $C_3H_6$  and benzene  $C_6H_6$  can be seen in Figs. 5.17 and 5.18.

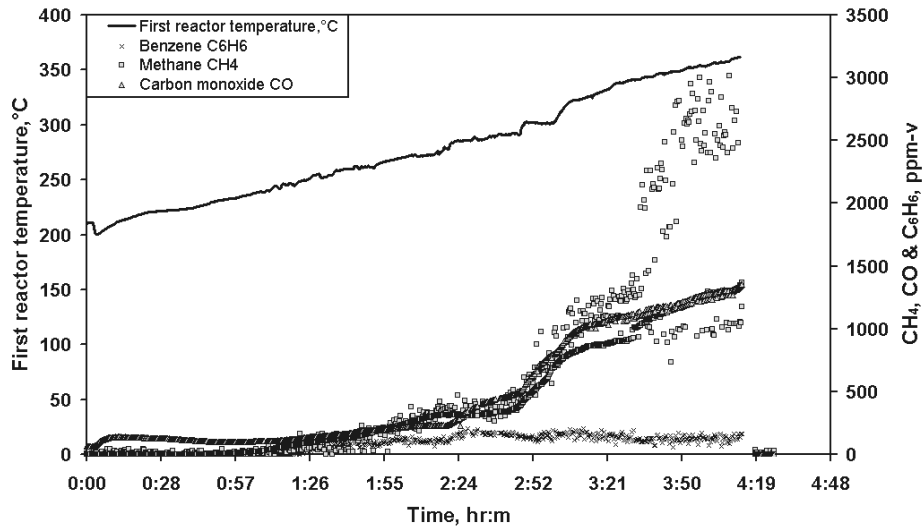


Fig. 5.17  $C_6H_6$ ,  $CH_4$  and CO release and BFB reactor temperature versus time for Polish coal

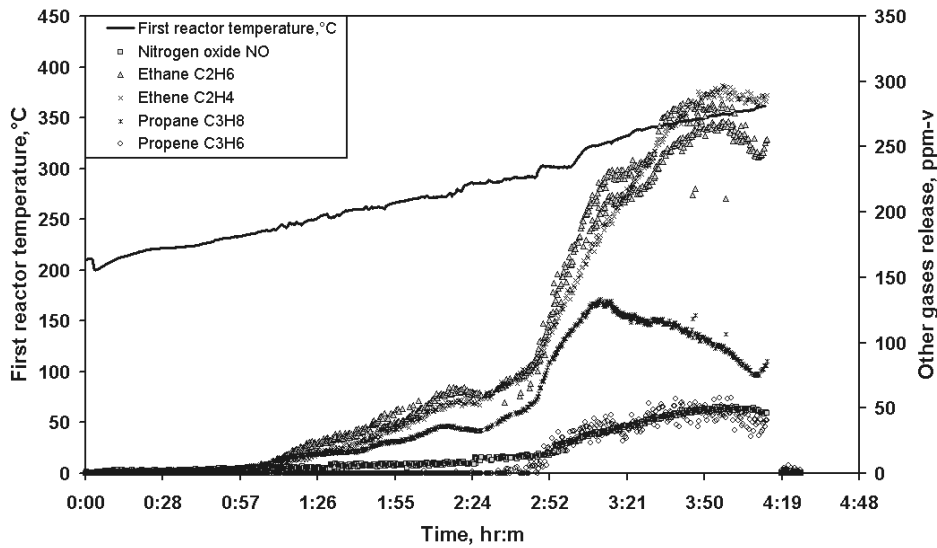


Fig. 5.18 Other gases evolution and BFB reactor temperature versus time for Polish coal

### 5.7 Pyrolysis test with 20% bottle-grade PVC + 80% wood (Finnish pine)

Comparing the results with the single fuel tests, it was apparent that interactions were taking place. Bottle-grade PVC in the mixture (20% PVC + 80% wood) degrades at a higher temperature than 100% PVC. Similar results for PVC mixed with wood pyrolysis were obtained by McGhee et al. (1995) and by Matsuzawa et al. (2001). Figure 5.19

shows that the peak release of chlorine as HCl from PVC/wood pine mixture occurs at a temperature of 248°C, compared to the peak for pure PVC, which occurred at 240°C (see Fig. 5.1). Similarly, for PVC/wood mixture, the peak for benzene release occurs at 258°C (Fig. 5.19) compared to 242°C for 100% PVC, as shown in Fig. 5.2. The heating rate in this test was 0.58°C/min (35°C/hr), which is almost the same as the 100% bottle-grade PVC test.

The analysis of the FT-IR spectrum shows there were many additional gases released beside HCl, CH<sub>4</sub>, C<sub>6</sub>H<sub>6</sub>, H<sub>2</sub>O, CO<sub>2</sub> and CO. These gases were formaldehyde CH<sub>2</sub>O (100 ppm), acetaldehyde C<sub>2</sub>H<sub>4</sub>O (above 750 ppm),  $\alpha$ -pinene C<sub>10</sub>H<sub>16</sub> (250 ppm), ethane C<sub>2</sub>H<sub>6</sub> (650 ppm), ethene C<sub>2</sub>H<sub>4</sub> (880 ppm), styrene C<sub>8</sub>H<sub>8</sub> (790 ppm) and toluene C<sub>7</sub>H<sub>8</sub> (600 ppm).

There is additional evidence for this interaction in PVC/wood pine mixtures, which appears to increase the char yield. The char chemical analysis (C, H, Cl) for samples taken from the middle of BFB bed for the PVC/wood test shows that the char content in the bed for the PVC/wood mixture test is higher than the char content in the bed for the 100% PVC test, as seen from the chemical analysis results in Tables 5.1 and 5.2. The char content for the 100% PVC test are 14.94% C, 0.0075% Cl and 0.93 % H, while the char content for the PVC/wood mixture test are 30.55% C, 0.022% Cl and 2.37% H. The chlorine-to-carbon ratio was almost the same for the PVC/wood pine and for the 100% PVC test, which is <0.001 kgCl/ kg C. For both tests, when the temperature reached above 330-350°C, most of the chlorine was released from the char. There is a high CO release, as shown in Fig. 5.19. The same figure shows a high release of benzene and methane. The oxygen needed for CO formation apparently comes mainly from the wood that contains 43.2% oxygen (see Table 4.5). Oxygen might also come from moisture or the PVC (additives).

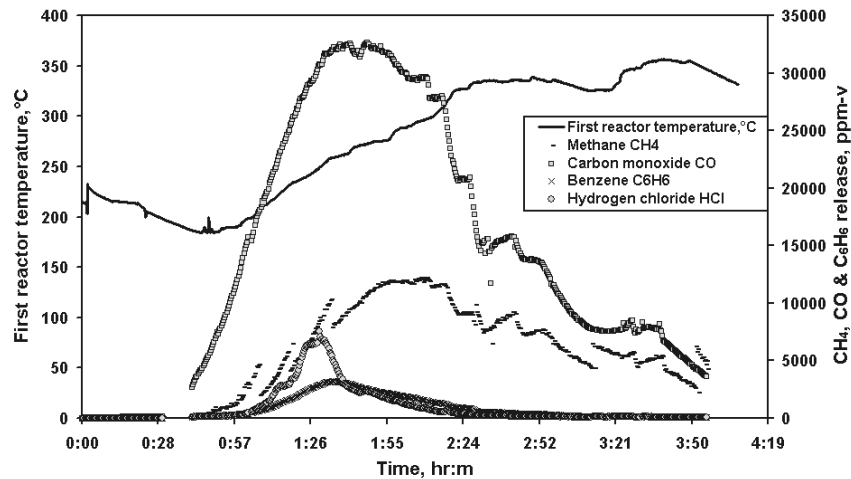


Fig. 5.19 Release of HCl and other gases with the BFB reactor temperature versus time for 20% bottle-grade PVC + 80% wood (pine) as fuel with 0.58°C/min (35°C/hr) heat-up

A high amount of water vapor in the BFB (the maximum reached over 10%) probably comes from the NaOH solution tank. There is also an increase in CO<sub>2</sub> (up to 3.3%) (publication V, Fig. 8).

For measuring the pH in the HCl removal tank, a sample was taken every 20 minutes. Figure 5.20 shows the relationship between the release of HCl from pH measurement and neutralization (NaOH) and BFB temperature versus time. The figure also shows that, at temperatures between 250-350°C, all the chlorine was released as HCl and captured in the NaOH/water solution tank.

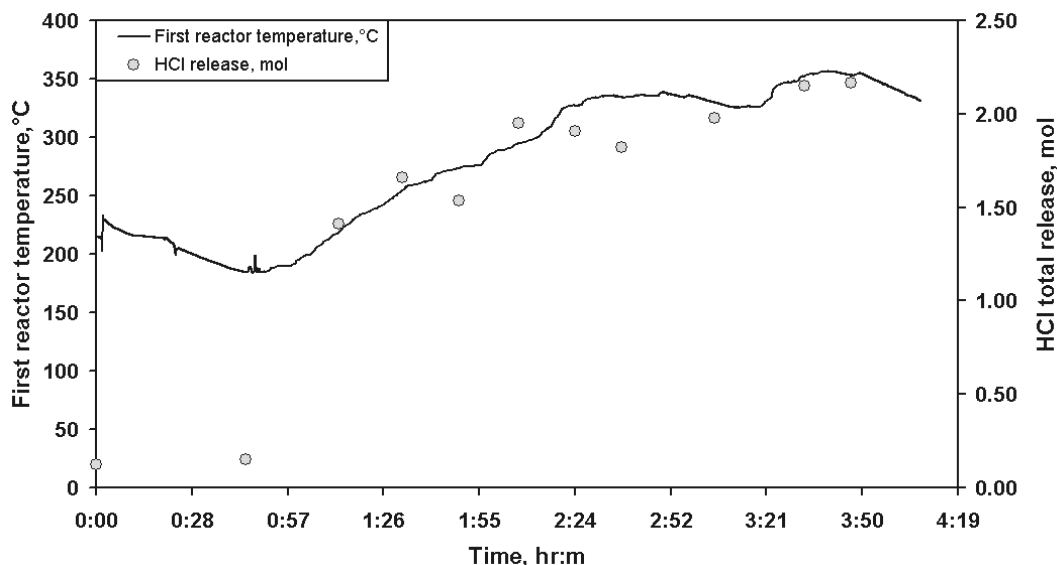


Fig. 5.20 Release of HCl calculated from pH measurement and neutralization (NaOH) with BFB temperature versus time for 20% bottle-grade PVC + 80% wood (pine) (input chlorine with PVC: 2.1 mole)

Table 5.2 Chemical analysis of char sample taken from the pyrolysis reactor after the test for 20% bottle-grade PVC+ 80% wood (pine)

Substance	Char sample bed material free	Char sample with bed material
Sample from middle of the bed		
C %-wt	92.74	30.55
H %-wt	7.19	2.37
Cl %-wt	0.067	0.022
Bed material %-wt*	-	67.06
Sum %-wt	99.997	100.00
Sample from top of the bed		
C %-wt	92.07	21.82
H %-wt	7.13	1.69
Cl %-wt	0.8	0.19
Bed material %-wt*	-	76.30
Sum %-wt	100.00	100.00

\* By difference

## 5.8 Pyrolysis test with 20% bottle-grade PVC + 80% Polish coal

In this test, PVC starts to degrade after 30 minutes and its temperature drops to below 200°C, as shown in Fig. 5.21. The reason for this is related to the endothermic dehydrochlorination of this type of PVC. Despite the low heating rate (0.33°C/min compared to 0.5°C/min for the 100% bottle-grade PVC test) in this test, the peak release of HCl was at a temperature of 260°C compared to 241°C for 100% bottle-grade PVC test (see Fig. 5.1). This implies an interaction between coal and PVC degradation. When the temperature of the bed increased above 300°C, the HCl release started to drop; most of the chlorine had been released when the temperature reached 340-350°C.

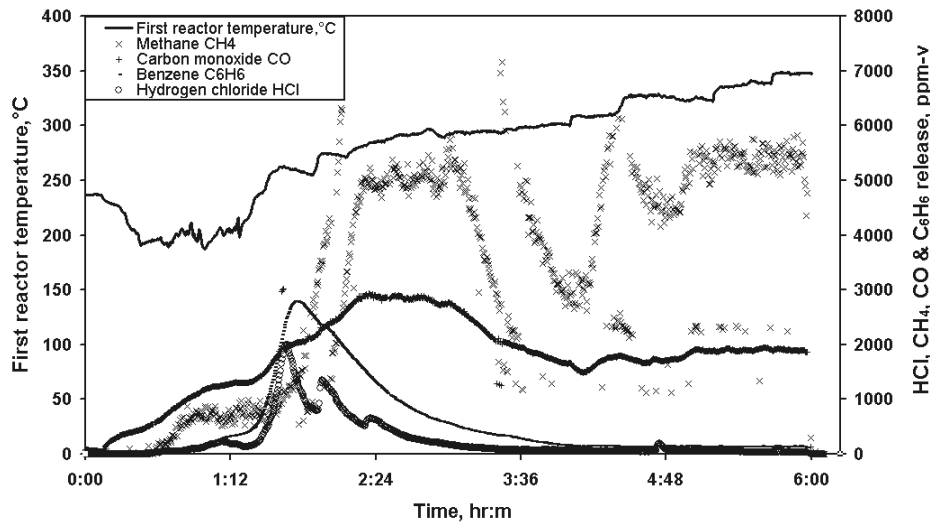


Fig. 5.21 Release of HCl and BFB reactor temperature versus time for 20% bottle-grade PVC + 80% Polish coal as fuel with 0.33°C/min (20°C/hr) heat-up

CO starts to be released at temperatures above 225°C; this comes mainly from the coal, as shown in Fig. 5.21, since it does not correlate with benzene and HCl as was the case for pure PVC. The maximum CO release (above 2900 ppm) takes place at above 280°C. Benzene release showed the same trend as HCl, while methane release started a bit earlier, showing a strongly fluctuating release during the test. The reason for that may be a hot-spot area in the bed. There was a high concentration of water vapor during the test (over 20% at the end of the test) (publication V, Fig. 11). This large amount of water vapor must have come mainly from the NaOH solution tank.

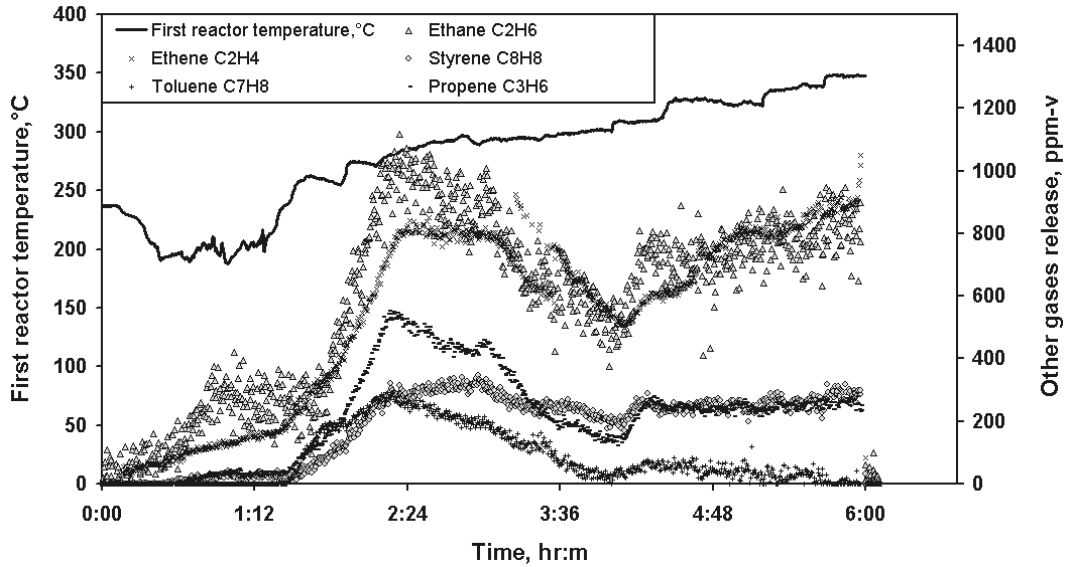


Fig. 5.22 Other vapor evolution and BFB reactor temperature versus time for 20% bottle-grade PVC + 80% polish coal

Other vapor evolution can be seen in Fig. 5.22. There are large amounts (above 1000 ppm) of ethane and ethene released, typically for coal pyrolysis. There are also significant amounts of propene (600 ppm), styrene and toluene. Figure 5.23 shows the relationship between the release of HCl calculated from pH measurement and neutralization (NaOH) with BFB temperature versus time in this test. Most (more than 80%) of the chlorine had been released when the bed temperature was above 280°C.

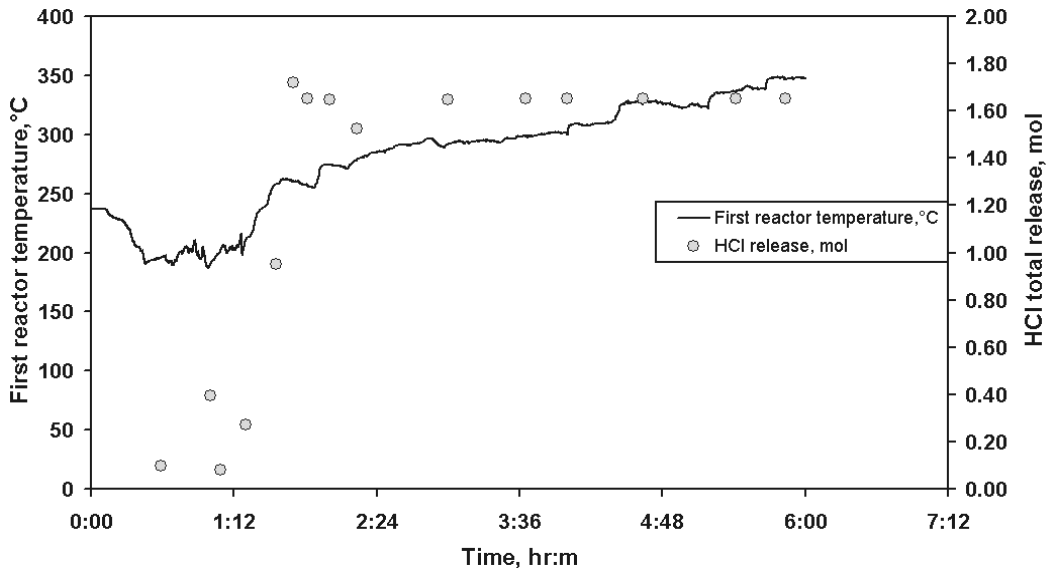


Fig. 5.23 Release of HCl from pH measurement and neutralization (NaOH) with BFB temperature versus time for 20% bottle-grade PVC + 80% polish coal (input chlorine with PVC: 2.1 mole)

## 5.9 Two-stage combustion test with 100% bottle-grade PVC

Despite preheating the air to 700°C (before the CFBC distributor plate), the temperature of the air in the CFBC was, unfortunately, not high enough to completely burn the char (coke) circulating from the BFB; char particles were found in the FB after the cyclone. It is noted that chlorine acts as a flame retardant, slowing down CO burnout and interfering with char ignition. The results from the FT-IR data analysis, taken from a sampling point mounted above flue gases exit pipe after the cyclone, are shown in Figs. 5.24 through 5.27.

HCl emission from the CFBC is shown in Fig. 5.24, which shows that the HCl release is variable, following (with some delay) the fuel feeding in the first reactor. Some PVC particles might spend a very short residence time in the BFB and jump straight to the seal pot and to the CFBC. This can be seen from the difference in times between the feeding of PVC in the BFB and the peak of HCl release from the CFBC (Fig. 5.24). The residence time of the PVC particles for the four feeding stages is then 17, 9, 12, 15 minutes, respectively. The chlorine content in such a particle can be high; this can be seen from the high emission of HCl from the CFBC. Another reason is the mixing quality of the bed: a very cheap perforated distributor plate is used in the BFB. Despite this unwanted emission of HCl, the total amount of chlorine released with the flue gases as HCl is less than 6.5% of the Cl input with the PVC, as shown in Fig. 5.25. In this figure, the release of HCl from the PVC in the BFB was followed via the neutralization with NaOH, this time successfully following the pH of the aqueous solution on-line. This shows that less than 50% of the incoming chlorine was captured as HCl in the aqueous solution tank. The temperature effect on PVC dehydrochlorination can also be seen. Most of the chlorine was released when the BFB bed temperature was 300-350°C.

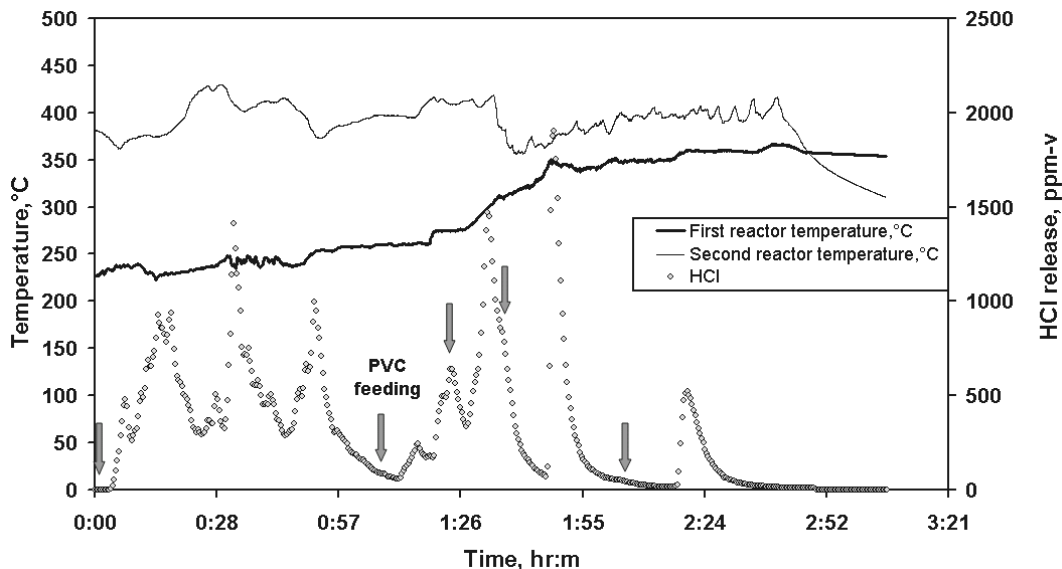


Fig. 5.24 HCl, emission from the CFBC and BFB and CFBC temperatures for 100% bottle-grade PVC as a fuel (300 g PVC was fed at the beginning of the test and 150 g for the followed four stages at the times 1:08, 1:25, 1:36 and 2:05 hr, respectively)



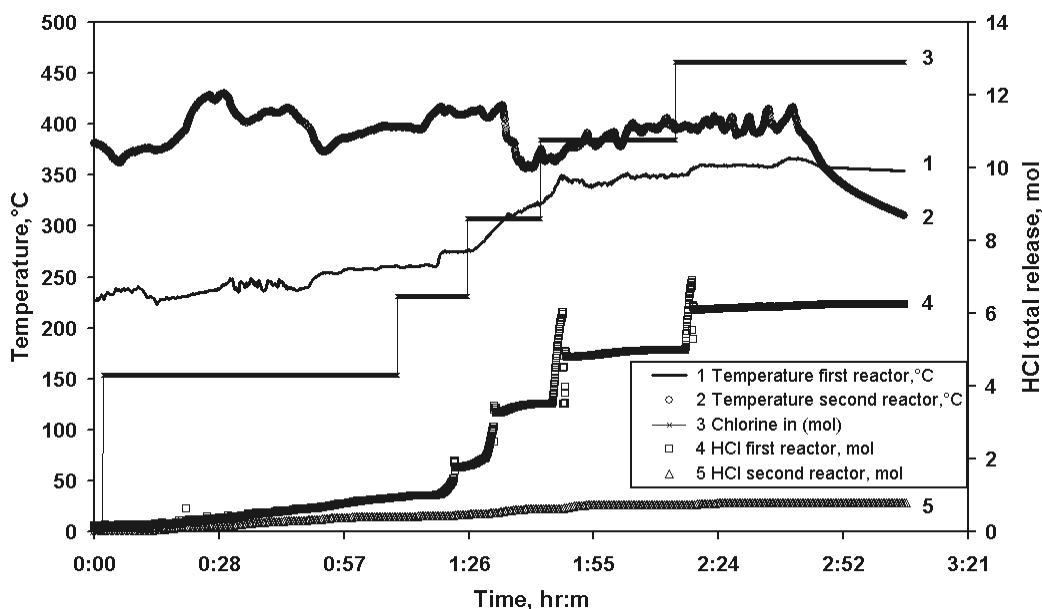


Fig. 5.25 Release of HCl from BFB and HCl from CFBC fractional release of chlorine from pH measurement, neutralization (NaOH consumption) and FT-IR spectrometer for two-stage combustion test with 100% bottle-grade PVC (input chlorine with PVC:12.9 mole)

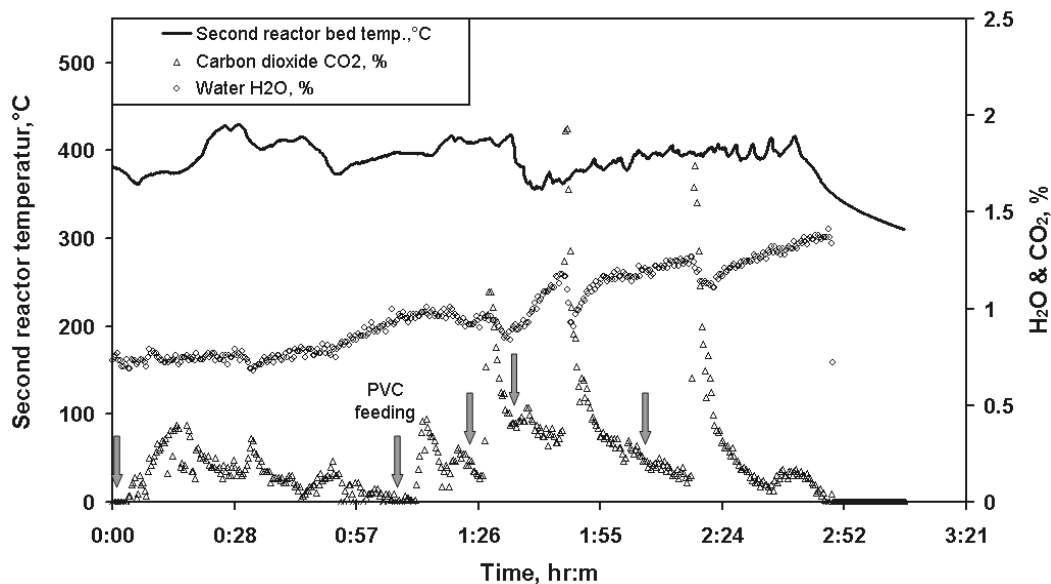


Fig. 5.26 CO<sub>2</sub> and H<sub>2</sub>O from the CFBC with the CFBC temperature for 100% bottle-grade PVC as a fuel

The emissions of H<sub>2</sub>O and CO<sub>2</sub> were increasing during one period and dropping in another, despite the fact that the temperature in the CFBC was not high enough to completely burn the char coming from the BFB, as shown in Fig. 5.26. There is a

significant amount (almost 450 ppm) of CO released from the CFBC, as shown in Fig. 5.27. The reason for this is related to the sometimes-high HCl concentration, which reduces the combustion efficiency of CO to CO<sub>2</sub>. A more continuous fuel feeding may show better performance. Figure 5.27 shows some release of benzene and very small amounts (below 50 ppm) of ethene and methane.

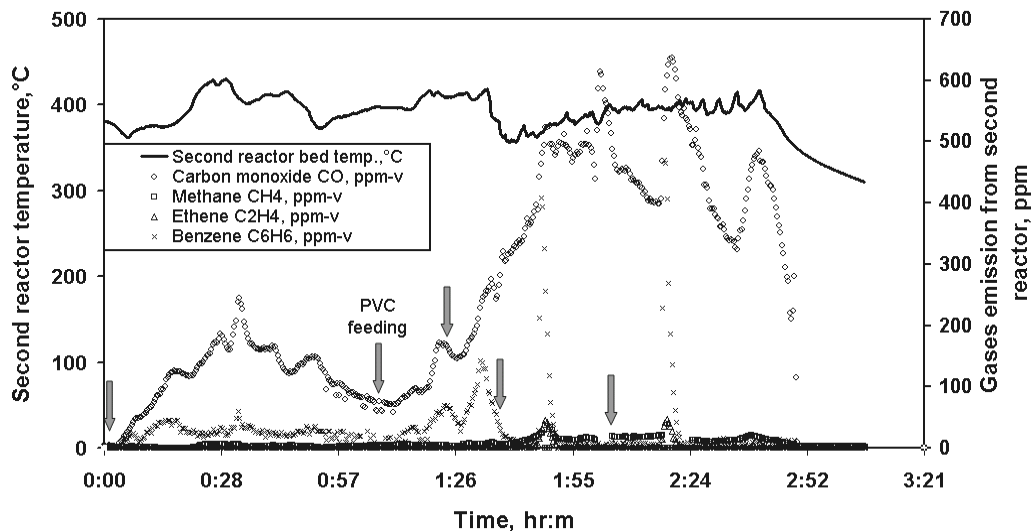


Fig. 5.27 Other gases release from the CFBC with the CFBC temperature for 100% bottle-grade PVC as a fuel.

It would be very interesting to make an accurate chlorine mass balance for the whole test facility (reactors, sand cooler, seal pot and the NaOH-water tank), but there are several factors that prevent this being done. For example, collecting and separating char from the sand after the test was difficult because a large fraction of char particles was very small (less than 1 mm) and difficult to be sieved and separated from a total of 120 kg of sand from the test facility. Also, there was some tar condensate in the heat exchanger after BFB before the NaOH solution tank, which would have made it difficult to estimate the exact amount of HCl captured in the tank. In addition to that, the capturing efficiency of the tank might not have been perfect so there was a good possibility that some HCl would pass the tank with the circulated gas flow and condensate in the tubes before the blower. Besides all the previous points, there was also the possibility of emission of other chlorine chemical species that the FT-IR was not able to recognize (such as chlorobenzene). Nevertheless, around 70% of incoming Cl could be accounted for, and was roughly distributed as follow: ~ 50% BFB product gas, ~ 7 % CFB product gas, ~ 6% BFB bed char, ~ 1% CFB bed char, ~ 6% others (seal pot non-mechanical valves, sand cooler and heat exchanger after the BFB).

The char-particle size, as collected after the test from the BFB bed, was 2-6 mm (Fig. 5.28). The bigger particles were related to some agglomeration between the partly degraded PVC particles and bed material (sand). Uniform and stable fluidization of the bed during the entire test would affect the quality of the char (e.g., chlorine content and low level of particle agglomeration) that goes to the CFBC to ensure a uniform temperature distribution around the whole bed.

The chemical analysis (C, H, Cl) of a sample of char particles taken randomly from the bed of the BFB after the test showed a chlorine content in the residue of below 0.05 %-wt, at a chlorine-to-carbon mass ratio  $< 0.001$  kg Cl / kg C. Table 5.3 gives the chemical analysis of the char sample. The chlorine content in the char ( $< 0.08\%$ -wt) is almost the same as for the 100% PVC pyrolysis test (0.05%-0.08%-wt) with the same chlorine-to-carbon ratio ( $< 0.001$  kg Cl / kg C). It is noted that the test time for two-stage test was less than half the time for the pyrolysis test. The main reason for that was temperature: the temperature of the BFB bed for this two-stage test was higher than the temperature of the BFB bed for the pyrolysis test with this PVC. The bed temperature range 340-350°C might be an optimum choice to ensure the fast release of chlorine from the PVC and reduce the PVC particle residence time in the BFB.



Fig. 5.28 Image of char particles taken from BFB for 100% PVC in two-stage combustion test (scale in centimeters)

Table 5.3 Chemical analysis of char sample taken from the pyrolysis reactor after the test for 100% bottle-grade PVC

Substance	Char sample Bed material free	Char sample with bed material
C %-wt	93.8	57.42
H %-wt	6.12	3.75
Cl %-wt	0.08	$<0.05$
Bed material %-wt*	-	38.78
Sum %-wt	100.00	100.00

\* By difference

## 5.10 Two-stage combustion test with 100% PVC waste as a fuel

The second test involved both reactors of the test facility using 100% of the same waste PVC (sewage pipe 2). The bed of the reactor (80 kg of sand) was heated up during fluidization with nitrogen. When the temperature had reached over 300°C, a total of 900 g of waste PVC was fed at a rate of 100 g every ten minutes. The initial concentration of H<sub>2</sub>O and CO<sub>2</sub> were ~ 1.35 %-vol and 0%-vol, respectively. The gas flow through the BFB was ~ 20 liter/s (at 30°C). Again, the temperature in the BFB was increased at about 26°C/h until it was around 365°C. The temperature of the air pre-heater for the CFBC appeared not high enough to completely burn the char (cokes) provided by the BFB; also, this time, char was found in the FB cooler after the cyclone. The results from the FT-IR data analysis, taken from a sampling point mounted above the flue gas exit pipe after the cyclone are shown in Figs. 5.29 and 5.30. The result shows that the total amount of chlorine released with the flue gases as HCl was less than 5% of the whole Cl input.

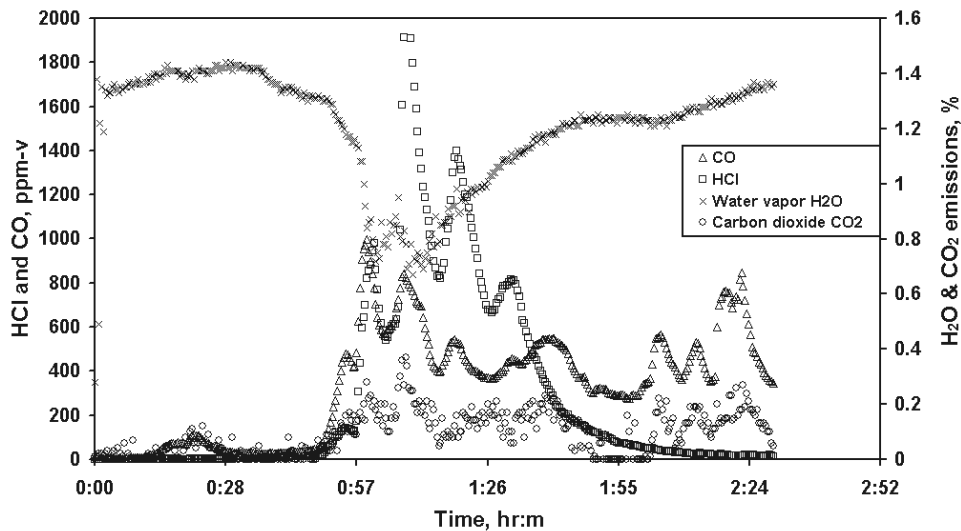


Fig. 5.29 HCl, H<sub>2</sub>O, CO<sub>2</sub> and CO emission from the CFBC

Figure 5.29 shows that, after two hours of testing, the water concentration in the CFBC gases starts to drop and the CO emission starts to increase. The reason for this is related to the presence of a high HCl concentration, which reduces the combustion efficiency of CO to CO<sub>2</sub>. Instead, some CO is now oxidized to CO<sub>2</sub> via the water/shift reaction, which explains the lowered H<sub>2</sub>O concentration. Figure 5.30 shows other vapour evolution from the char in the CFBC, like benzene, CO, methane, ethene, ethane, propene and toluene. The release of HCl from the PVC in the BFB was again followed via the neutralization with NaOH, i.e., following the pH of the aqueous solution on-line. This shows that ~ 50% of the incoming chlorine was captured as HCl in the aqueous solution (see Fig. 5.31).

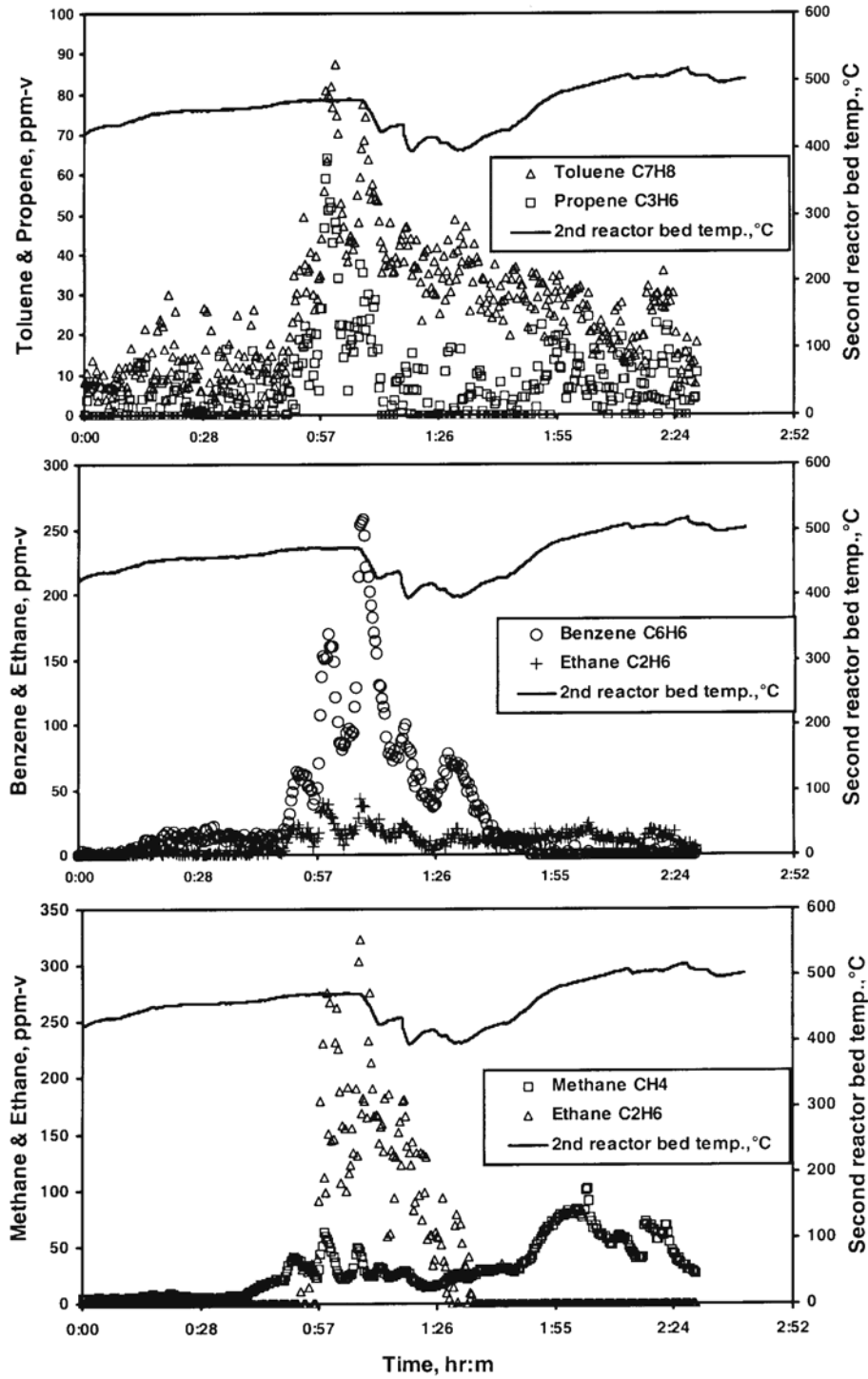


Fig. 5.30 Other vapor evolution from the CFBC with the bed temperature versus time

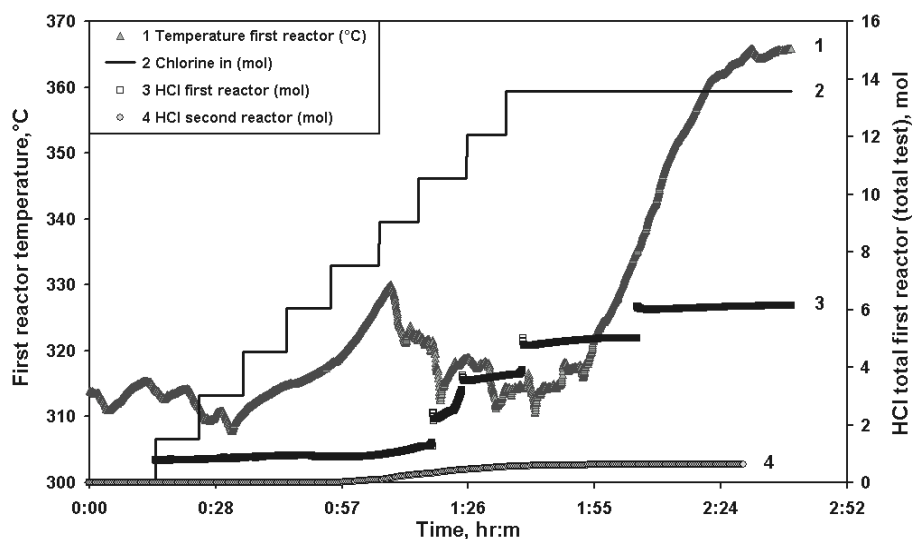


Fig. 5.31 Release of HCl from BFB and HCl from CFBC fractional release of chlorine from pH measurement (NaOH consumption) and FT-IR spectrometer. (chlorine input with PVC 13.56 mole)

Table 5.4 Chemical analysis of char sample taken from the pyrolysis reactor

Substance	Char sample bed-material free	Char sample with bed material
C %-wt	88.3	45.30
H %-wt	6.6	3.4
Cl %-wt	5.1	2.6
Pb %-wt	NA*	NA
Ca %-wt	NA	NA
O %-wt	NA	NA
Zn %-wt	NA	NA
Bed material %-wt*	-	48.7
Sum %-wt	100.00	100.00

\* Not analyzed

\*\* By difference

A sample of char particles from the bed of the BFB after the test was sent for chemical analysis. This showed a chlorine content in the residue of 2.6 %-wt, at a chlorine-to-carbon mass ratio  $< 0.058$  kg Cl / kg C. Table 5.4 gives the chemical analysis of the char sample. The chlorine content in the char from the first test is higher than for the second test due to lower BFB reactor temperatures in the first test, despite a longer residence time. This must be an effect of the presence of stabilizer in this PVC waste.

### 5.11 Dioxins/Furans (PCDD/Fs)

Samples of the solid char from the two-stage combustion test using the real PVC waste 2 were taken from the BFB bed after the test and sent to an external laboratory for analysis of the polycyclic aromatic hydrocarbon and chlorinated organic compounds.

As part of the analysis, internal standards were added to the sample before extraction:

- 4 deuteriated polycyclic aromatic hydrocarbons
- 2,4,6-trichlorobiphenyl
- 2,4,6-tribromophenol
- 16 <sup>13</sup>C-labelled polychlorinated dibenzo-p-dioxins and furans.

The samples were then extracted over a period of 20 hours in Soxhlet-equipment using toluene as a solvent. Chlorinated phenols were extracted in K<sub>2</sub>CO<sub>3</sub>, acetylated and extracted in hexane. The other compounds were concentrated and purified with H<sub>2</sub>SO<sub>4</sub> and aluminum oxide. Polycyclic aromatic hydrocarbon (PAH), chlorinated phenols, chlorinated biphenyls (PCBs) and chlorinated benzene were analyzed with a GC/MSD (gas chromatograph Hewlett Packard 5890 with mass selective detector HP 5970; column HP-5Ms, 30 m 0.25 mm I.D., film thickness 0.25 μm). Polychlorinated dioxins and furans were analyzed with High Resolution Mass Spectrometer VG 70-250 SE (column; DB-dioxin 60m, 0.25 mm I.D., film thickness 0.15) at the resolution of 10000 at a recognized Laboratory of Chemistry in the National Public Health Institute. Table 5.5 shows the analysis results for the dioxins, furans and other chlorinated compound.

Table 5.5 shows that PCDD (0.78 ng/g) and PCDF (2.51 ng/g) formation is very low in the char (solid) from the pyrolysis stage in the BFB. Also, the corresponding I-TEQ concentrations are very low (0.155 ng TEQ/g for dioxins and 0.35 ng TEQ/g for furans). It was not possible to measure Cl<sub>2</sub> emissions, which might have provided indications as to the possibility of the formation of PCDD/Fs, but again Cl<sub>2</sub> is an extremely reactive species that is very difficult to measure reliably in the flue gases (LIEKKI, 1993). PCDD/Fs are mainly formed in the temperature window of 250-450°C by reactions of unburned or incompletely oxidized hydrocarbons escaping the high-temperature region of the combustion chamber and Cl containing species such as Cl<sub>2</sub> (Anthony et al., 2001). In addition, the presence of catalysts (especially Cu) and oxygen is essential for the formation of PCDD/Fs. In all tests that we performed, pure nitrogen was used as fluidizing gas in the BFB. Attempts to identify combustion parameters that might be indicators of the formation of PCDD/F, such as CO or HCl, have not proved very successful (LIEKKI, 1993); emissions of CO and HCl do not automatically mean that there will be formation of PCDD/Fs. Many researchers have investigated the ratio between the content of PCDD/Fs in the flue gases (gas phase) and the residue (solid phase). Hutzinger and Fieldler, (1993) estimated the ratio of PCDD/Fs remaining on fly ash transferred by the flue gas to the electrostatic precipitator (ESP) unit at 300°C in the range of 10:1, while, on the other hand, Carroll Jr. (2001) speculates that 90% of PCDD/Fs resides in the gas phase. Mohr et al. (1997) also give very interesting results that show the PCDD levels in the pyrolysis gas are almost ten times those in the solid residue and that show the contrary for PCDF, which resides in the solid residue by more than six times than in the pyrolysis gas. However, many parameters such as the

temperature of the reactor, the fuel type and the type of the process itself (gasification, pyrolysis and combustion etc.) affect the ratio of the PCDD/Fs in the gas and solid phase.

Table 5.5 Analysis result for the dioxins, furans and other chlorinated compound (char from PVC waste 2)

Compounds	TEF	Char (ng/g)	I-TEQ (ng/g)
<b>Dioxins (PCDD):</b>			
2,3,7,8-TCDD	1.00	0.035	0.035
1,2,3,7,8-PeCDD	0.50	0.173	0.086
1,2,3,4,7,8-HxCDD	0.10	0.052	0.005
1,2,3,6,7,8-HxCDD	0.10	0.153	0.015
1,2,3,7,8,9-HxCDD	0.10	0.119	0.012
1,2,3,4,6,7,8-HpCDD	0.01	0.172	0.002
1,2,3,4,6,7,8,9-OCDD	0.001	0.77	0
<b>Total PCDD</b>		<b>0.780</b>	<b>0.155</b>
<b>Furans (PCDF):</b>			
2,3,7,8-TCDF	0.10	0.367	0.037
1,2,3,7,8-PeCDF	0.05	0.357	0.018
2,3,4,7,8-PeCDF	0.50	0.44	0.22
1,2,3,4,7,8-HxCDF	0.10	0.298	0.03
1,2,3,6,7,8-HxCDF	0.10	0.262	0.026
2,3,4,6,7,8-HxCDF	0.10	0.127	0.013
1,2,3,7,8,9-HxCDF	0.10	0.035	0.004
1,2,3,4,6,7,8-HpCDF	0.01	0.333	0.003
1,2,3,4,7,8,9-HpCDF	0.01	0.085	0.001
1,2,3,4,6,7,8,9-OCDF	0.001	0.207	0
<b>Total PCDF</b>		<b>2.51</b>	<b>0.35</b>
Polycyclic aromatic hydrocarbon (PAH)		23180	
Polychlorinated phenols		352	
Polychlorinated biphenyls (PCB)		all < 10	
Polychlorinated benzenes		149	



## 6. Conclusion

This work contains two parts that described a waste-to-energy process for high-PVC solid waste, including HCl recovery. The first part contains the theoretical design calculations using a Process Simulation Program (PROSIM) and data from the literature. The second part of the work contains the building of a test facility and the testing of the process in the Laboratory of Energy Engineering and Environmental Protection at Otaniemi. The process described in this work is different from other processes based on (staged) gasification of these types of wastes (e.g., Jaspers, 1999) by the low temperature of the pyrolysis reactor. An advantage is that no hot HCl-containing gases have to be handled, allowing for the use of cheap steel; moreover, temperatures are probably too low for dioxin/furan formation.

### 6.1. Theoretical work

A new pyrolysis module had to be developed for the PROSIM software to allow for the special feature of the PVC in the solid waste and to support the research idea, i.e., to recover the HCl and then burn the residue. The simulation calculations show:

- The process has a thermal efficiency of  $\sim 37\%$ , depending on pyrolysis temperature, the PVC content in the solid waste and the moisture content in the solid waste. This efficiency is higher than for a conventional incineration plant (CIP) that has 33.4% thermal efficiency. These calculations were based on 80% wood (pine) + 20% PVC fuel mixtures and a temperature of the superheated of  $510^\circ\text{C}$ . The efficiency for CIP might be much lower than 33.4% because the aggressive nature of the flue gases in CIP does not allow the temperature of steam in the boiler to rise above  $400^\circ\text{C}$ .
- For the two-stage combustion process, HCl recovery can be above 90 % at pyrolysis temperatures above  $310^\circ\text{C}$ , combined with low uncontrolled HCl emissions, which can be even below the current legislative emission limits. For the conventional incineration plant, the uncontrolled HCl emission will be much higher, and requires an effective cleaning system. Also, because of the low HCl concentration in the hot gases during two-stage combustion, it is possible to go above  $500^\circ\text{C}$  as the steam outlet condition from the superheater, which consequently will increase the electricity production from the steam turbine. In addition to that, the low HCl concentration will eliminate the risks of fireside corrosion in the superheater area and the formation of dioxins (PCDD) and furans (PCDF).

### 6.2. Experimental work

A test facility for the two-stage combustion of high-PVC solid waste was built and put into operation. The design of the test facility was based on the kinetic data of dehydrochlorination for a typical PVC, combustion of chars from PVC and wood, process optimization calculations for a  $40 \text{ MW}_{\text{thermal}}$  plant design case, which were scaled down

from 40 MW to 40 kW thermal fuel input, and on information from the literature. Several tests were performed; the most important points about these can be summarized as follows:

- Bottle-grade PVC was used as fuel in a two-stage combustion process. Other fuels like wood (pine) and Polish coal were pyrolyzed or co-pyrolyzed with this PVC. The tests show that there is an interaction when PVC is mixed with wood or coal. This mixing will affect the degradation of PVC, wood and coal. PVC degrades at a higher temperature when mixed with wood pine compared to the degradation of 100% PVC, and, at the same time, the wood degrades at a lower temperature than 100% wood. The same holds for the coal.
- The chlorine content in the char for the pyrolysis and the two-stage combustion test using 100% bottle-grade PVC is almost the same for both tests. Pyrolysis tests of the bottle-grade PVC shows that, at a temperature between 250 and 350°C, hydrogen chloride HCl was the main product gas, besides CO, benzene and some other hydrocarbon gases. The chlorine content in the chars was below 0.1%-wt (from 51%-wt in the PVC), at chlorine-to-carbon mass ratio  $< 0.001 \text{ kg Cl} / \text{kg C}$ ; this means that a char is in Class I (less than 0.15%-wt Cl) for Finnish classification of solid recovered fuel (SRF) that can be produced using this process.
- The two-stage combustion test with 100% waste PVC (sewage pipe) shows that the char chlorine content 5%-wt (from 54%-wt in the PVC) at chlorine-to-carbon mass ratio  $< 0.06 \text{ kg Cl} / \text{kg C}$  can be produced. It is obvious that the chlorine content in char from this PVC type is higher than the one from bottle-grade PVC. The reason for this is related to the stabilizer type and the fractional weight of the stabilizer, which have a large effect on the behavior of PVC waste dehydrochlorination at 200-400°C. The presence of lead based stabilizers applied at high mass fractions in PVC, as found in older PVC wastes (sewage pipe), seems to give more resistance to heat when compared to other, more modern, stabilizers such as calcium, zinc and tin compounds.
- The char sample analysis of sewage pipe PVC for the determination of polychlorinated compounds showed a very small amount (0.78 ng/g) of polychlorinated dibenzo-p-dioxins (PCDD) and (2.51 ng/g) of polychlorinated dibenzofurans (PCDF). The I-TEQ values are also low (0.155 ng TEQ/g for dioxins and 0.35 ng TEQ/g for furans). The formation of PCDD and PCDF in the gas phase was not measured, but it is expected that it would have been of the same order of magnitude.
- Uniform and stable fluidization of the BFB bed over the entire range of the test will affect the quality of the char (e.g., chlorine content) produced, which will be forwarded to the CFBC. Also, residence time of the PVC waste in the BFB can be reduced if the bed temperature is in the range of 340°C-350°C, ensuring the fast release of most of the chlorine as HCl.
- The result shows that the process has the potential to remove most of the chlorine from a fuel input that contains large amounts of PVC chlorine, i.e., amounts that are problematic for other thermal processes. This is despite the fact that a cheap perforated distributor plate was used that may have affected the bed material mixing (especially in the BFB) and the quality of the char obtained. For both two-

stage combustion tests (using the bottle-grade PVC and sewage pipe PVC), the total amount of chlorine released with the flue gases as HCl is less than 6.5% of the Cl input with the PVC.

- A mass balance calculation for chlorine in the test facility was difficult to perform because of the large amount of small char particles (less than 1 mm), which makes them difficult to separate from the sand. Also, there was some tar condensate in the heat exchanger before the NaOH solution tank, which makes it difficult to estimate the exact amount of HCl captured in the tank. In addition to that, the capturing efficiency of the NaOH scrubber may not be perfect and there is a good possibility that some HCl will pass the tank with the circulated gas flow and condensate in the tubes before the blower. Besides these, there is also the possibility that there may be other chlorine chemical species emissions that the FT-IR is not able to recognize (such as chlorobenzene).

### 6.3 Contribution of the work

A test facility for two-stage combustion of high-PVC solid waste was built and put into operation at Helsinki University of Technology. This facility contains two reactors. The first reactor is a BFB and the second a CFBC. This work presents the performance of the two-stage combustion process using 100% PVC waste, together with the design procedures relating to all parts of the test facility. The most important features of this work can be summarized as follows:

- A new PROSIM module for the pyrolysis reactor was built for use in the simulation of the two-stage combustion process. The result from the simulation shows that the process has an approx. 37% efficiency using 20% PVC and 80% wood pine compared to 33% efficiency for a conventional incineration plant.
- Most of the chlorine can be removed (recovered) as HCl from the BFB, which leaves a small percentage to be removed from the flue gases after the CFBC; at the same time, it reduces the HCl corrosion problems with little risk of the formation of toxic chlorinated species such as dioxin and furans. For a conventional incineration plant, an effective cleaning system should be installed.
- One hundred percent of two types of PVC (bottle-grade PVC and sewage pipe PVC) was used as a fuel in a two-stage combustion test facility. The results from both tests were very promising. The chlorine content in the chars for the bottle-grade PVC was below 0.1 %-wt (from 51%-wt in the PVC) at chlorine-to-carbon mass ratio  $< 0.001$  kg Cl / kg C. This means that the char (which is forwarded to the CFBC) lies in Class I (less than 0.15%-wt Cl) of the Finnish classification of solid recovered fuel (SRF) that can be produced using this process. The char chlorine content for the sewage pipe PVC was about 5%-wt (from 54%-wt in the PVC) at chlorine-to-carbon mass ratio  $< 0.06$  kg Cl / kg C.
- Very small amounts of PCDD (0.78 ng/g, 0.155 ng TEQ/g) and PCDF (2.51 ng/g, 0.35 ng TEQ/g) were found in the char from the sewage pipe PVC 2 test; this supports the theory on which the process is based.
- In this work, the tests bring to light new information about different types of PVC behavior in a two-stage combustion process. The results show that the optimal

temperature range for operating the BFB during pyrolysis to release most of the chlorine from the PVC is 340-350°C.

- The tests results also show the effect of stabilizers on the degradation of different PVC types during pyrolysis in the BFB reactor and that this will affect the quality of the char forwarded to the CFBC. In addition, the result shows that the process has the potential to remove most of the chlorine from a fuel input that contains large amounts of PVC chlorine, i.e., amounts that are problematic for other thermal processes. This, despite the fact that a cheap perforated distributor plate has been used that may affect the bed material mixing (especially in the BFB) and the quality of the char that is forwarded to the CFBC. The results also shows that the total amount of chlorine released with the flue gases as HCl is less than 6.5% of the Cl input with the PVC.
- Many tests were performed in this work to examine PVC behavior when it is mixed and pyrolyzed or co-pyrolyzed with other fuels like wood (pine) and Polish coal. The tests show that there is an interaction when PVC is mixed with wood or coal. This mixing will affect the degradation of PVC, wood and coal. PVC degrades at a higher temperature when mixed with wood pine compared to the degradation of 100% PVC; at the same time, the wood degrades at a lower temperature than 100% wood. The same holds for the coal. The result for PVC and wood mixture agrees with previous studies. This work presents new information about the behavior of the PVC + coal mixture during pyrolysis in a BFB. There was very little information (Fig. 2.4) in the literature about the behavior of PVC when mixed with coal and pyrolysed in a BFB.

#### **6.4 Recommendations and future work**

When building the process of two-stage combustion for high chlorine solid waste on a large scale, it is likely to be more profitable if built near a plant producing vinyl chlorine monomer (VCM). The process can then be integrated with the plant and the operational cost be reduced. Figure 6.1 shows a simple scheme of the process integrated with the VCM production plant.

The VCM plant usually needs an air separation unit to produce the oxygen that is used in the oxyhydrochlorination process; the nitrogen left from the air separation can then be used in the two-stage combustion process. Electricity and the heat needed for the VCM plant can be provided by the two-stage combustion plant. Also, the HCl recovered from the two-stage plant can be used in the VCM plant.

For future work, it would be interesting to investigate the process performance when air is used instead of nitrogen in the first reactor (BFB) and see the effect of that on PVC decomposition. When using air in the first reactor and within the low temperature range of 300-350°C, there may be some dioxin and furan formation. This problem can be solved if some changes are made to the process in the first reactor. The pyrolysed gases, which contain mainly hydrogen chloride, dioxin/furan and other hydrocarbons gases, can be passed into a scrubber to remove the HCl; the other gases included with the dioxins/furans can be passed to be burned in the second reactor, where the temperature reaches above 800°C. Figure 6.2 shows the simple diagram of the process using air as a fluidizing gas in both reactors.

To improve the process in the future, further testing is needed to address char burnout, for example. Besides that, an exergy analysis for the suggested process could be made if the product after the pyrolysis process (the residue) is well defined from a thermodynamic point of view.

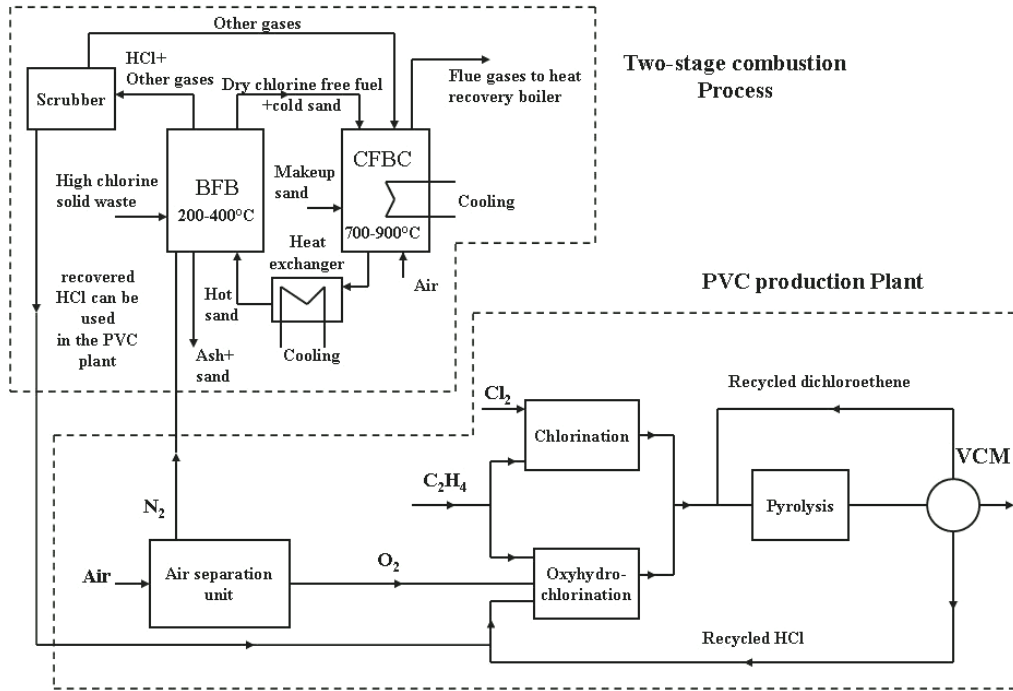


Fig. 6.1 Scheme of PVC production plant integrated with two-stage combustion of high PVC solid waste process

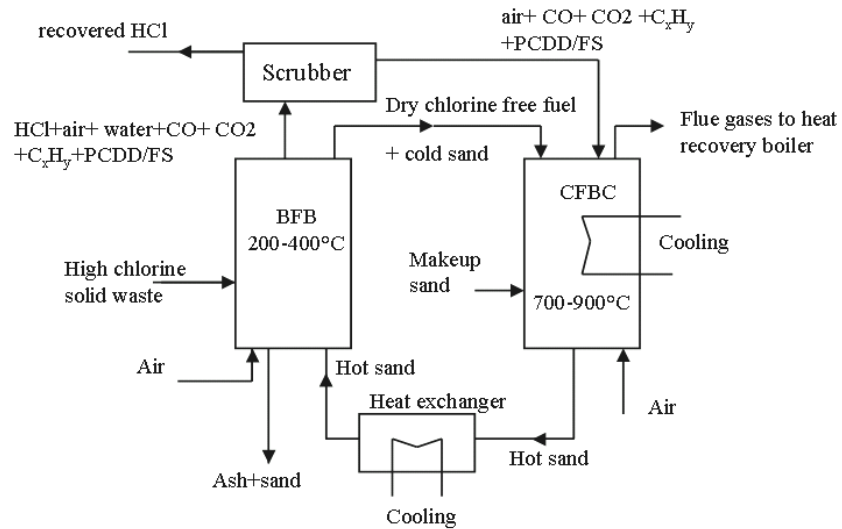


Fig. 6.2 Two-stage combustion process with high PVC solid waste using air as fluidizing gas in both reactors.

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