

ROLF BÜHL

EVC Belgium SA/NV
Excelsiorlaan 3, 1930 Zaventem, Belgium

Progress in PVC feedstock recycling^{*)}

Summary — The PVC industry is actively involved in the development of recycling solutions for contaminated mixed plastics waste streams with a high PVC content. Potential technologies for achieving this goal are tested at present at pilot scale. This paper provides an overview of the projects under investigation and the results obtained so far, whilst development work continues.

Key words: poly(vinyl chloride), feedstock recycling, gasification, combustion, hydrolysis, pyrolysis, dechlorination.

The PVC industry supports an integrated waste recovery strategy for plastics, in which each of the recovery options, *i.e.* mechanical recycling, feedstock recycling and incineration with energy recovery, is to be used when and where it can make the greatest contribution to saving resources.

Feedstock (or chemical) recycling should be seen as complementary to mechanical recycling. This option is gaining in importance for the treatment of mixed and contaminated plastics waste streams, which are often impossible to economically separate into single, homogeneous polymer streams, for which mechanical recycling is the preferred option.

There are a number of processes that can be considered for feedstock recycling. The Netherlands Organization for applied scientific research (TNO) report "Chemical Recycling of Plastics Waste (PVC and other Resins)", contracted by the European Commission and published in December 1999, provides a comprehensive overview on developments taking place worldwide [1].

TNO describes the activity in this area as young and evolving, with technologies ranging from laboratory to industrial scale.

The TNO study differentiates rightly between technologies for mixed plastics with a low PVC content and dedicates processes capable of treating "PVC rich" waste streams. It also makes an attempt to quantify the potential for treating larger waste volumes *via* this route in Europe, but confesses that the database is still insufficient to identify the real "technology winners".

Today, some 520 ktms of PVC waste products from processing, installation and post use are already recycled [2]. These include roughly 12 ktms of post-use PVC

packaging waste treated in feedstock recycling processes for mixed plastics waste under the regime of the "Duale System" in Germany, *i.e.* in plants with a distinct chlorine input limitation.

In 1995, ECVM (European Council of Vinyl Manufacturers) started an R&D programme to investigate potential feedstock recycling technologies for treating "PVC rich" waste streams. Such processes should be capable to recover both the chlorine and the hydrocarbon contents of the waste products: chlorine in the form of purified hydrochloric acid or salt and hydrocarbons in the form of energy and/or as feedstocks for the petrochemical industry.

Results from this start-up programme were presented at [3], but were also fed into the above-mentioned TNO report.

This paper summarises the progress being made with a selection of PVC feedstock recycling projects whilst development work still continues.

PVC INDUSTRY VOLUNTARY COMMITMENT

What started as an ECVM sponsored R&D programme, became more recently an integrated element of the PVC industry's "Voluntary Commitment" as originally signed in March 2000. The "Voluntary Commitment", which was further developed and approved in October 2001 into its present form [4], is a 10-year programme addressing all stages of the PVC life cycle, from manufacture to end-of-life. All sectors working with PVC are involved, from PVC manufacturers to additive producers and converters. It is the industry's response to the EU's "Horizontal Initiative on PVC" manifested in the publication of the "PVC Green Paper" in July 2000 with its focus on waste management and additive issues [5].

The chapter on waste management of the "Voluntary Commitment" includes, amongst others, the objective to

^{*)} Lecture presented during International Conference "PVC 2002 — Towards a Sustainable Future", 23—25 April 2002, Brighton, Great Britain.

increase post consumer recycling in 2010 by 200 ktons and this in addition to present levels and to any recycling from legislated waste streams, *i.e.* packaging, end-of-life vehicles and E+E equipment. It is also stated that potential PVC feedstock recycling technologies will receive financial support to demonstrate their technical and economical feasibility so that decisions for the building of commercial scale plants can be made.

A first Report [6] was published in 2001, giving insight into an initial selection of recycling projects.

PROGRESS WITH SELECTED PVC FEEDSTOCK RECYCLING PROJECTS

The objective of the PVC industry's feedstock recycling programme is to investigate potential technologies in order to select the most promising ones and to help commercial scale plants becoming available. Focus is on technologies capable of treating "PVC rich" waste streams but this is not exclusive as the involvement with the Reduction of Iron Ore by Plastics (REDOP) project shows.

There is no simple definition for a "PVC rich" waste stream other than its composition consists of different materials, with PVC polymer presenting a prominent share. Subsequently, potential technologies should be capable to treat waste products with a high chlorine content.

However, the high CaCO_3 filler levels present in many PVC products, such as cable and flooring, can be detrimental to the complete liberation of HCl during the decomposition step. Such liberation ("yielding") is critical for assessing the recovery performance of PVC feedstock recycling processes under real life conditions, when purified HCl is one of the target products.

To investigate such real life effects, the trial programmes for the different processes try to cover an as wide as possible range of "as available PVC post consumer waste products", with a focus on cables, flooring and coated fabrics. A simplified characterization of these waste products is shown in Table 1.

Table 1. Typical weight fractions and heating values for "PVC rich" waste streams (approximate values)

Waste stream	Chlorine wt. %	Hydrocarbons wt. %	Inorganics wt. %	Heating value, MJ/kg
Flooring	18	33	49	13
Cables	21	53	26	17
Coated fabrics	27	62	11	23

Gasification in slag bath

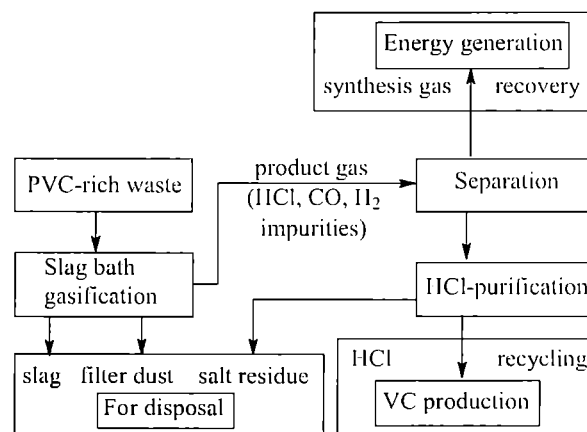
Based on positive results from the laboratory work with the slag bath gasification technology from Linde-

-KCA, Germany [3], an industry consortium under the leadership of ECVM has built a pilot plant in Tavaux, France, with a capacity of 100 kg/h.

Core part of the construction is the gasification reactor where decomposition of the PVC waste products takes place in a molten slag bath at 1400 to 1600°C, with HCl, CO and H_2 as the target recovery products.

A comprehensive commissioning period started end 2000 and was completed in June 2001. Technical problems, not related to the technology itself, required corrective actions including some modifications in the auxiliary parts of the plant.

A trial programme is currently under way to check the design configuration of the reactor, optimise the operating conditions and select the preferred waste feeding system. The complete destruction of the PVC molecular structure that had been observed in the laboratory has not yet been confirmed in the plant. The effects of residence time and waste feeding are currently being investigated. However, slag formation and overflow as well as gasification effects have been observed (Scheme A).



Scheme A. Gasification of PVC in a slag bath

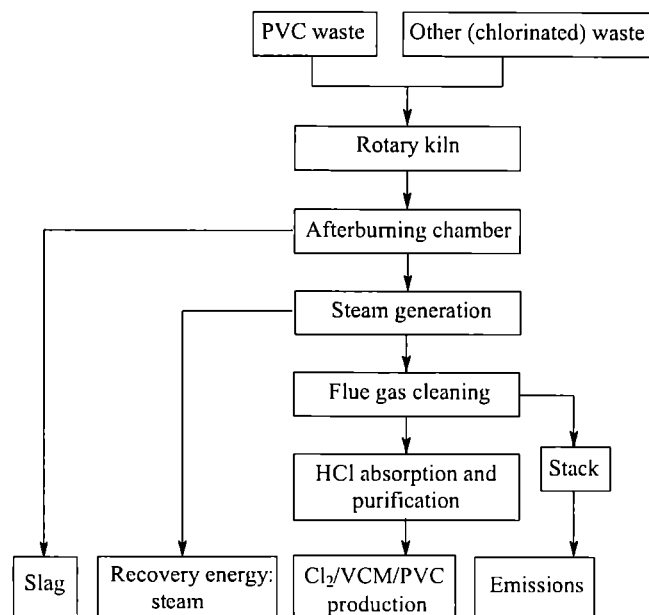
At this stage of the trial programme, it is too early to draw any conclusions. Completion of the programme is scheduled before the end of 2002, with preliminary conclusions expected by mid 2002.

Combustion in rotary kiln

In 1999, DOW/BSL started operating a new recycling plant at their Schkopau site in Germany for the treatment of chlorinated waste products (Scheme B, Table 2).

Main sections of the plant are:

- rotary kiln with after-chamber for efficient conversion,
- energy recovery to medium pressure steam,
- HCl absorption and purification,
- flue gas cleaning,
- effluent treatment.



Scheme B. DOW/BSL rotary kiln process

Table 2. Results of large scale trial with PVC waste products in DOW/BSL recycling plant

Chlorine recovery	≥ 90%
HCl (20%) quality for on-site use	within specification
Energy surplus from total operation	approx. 50%
Slag quality	class Z2 = suitable for re-use (according to German LAGA regulation)
Dioxin emissions	<0.1 ng TEQ/m ³
All other emissions	below regulated limits

Annual capacity is 45 kt. Temperatures are 950°C in the rotary kiln and 1100°C in the after-chamber. The 55 kt. treatment capacity for the 20% HCl solution includes all required purification steps for it to meet the specifications for on-site use in electrolysis and/or oxy-chlorination to make respectively chlorine or VCM.

The plant is designed to handle vents, liquid and solid waste products. Waste products are to be delivered according to a delivery specification and subject to payment of a gate-fee.

The plant usually operates under co-feeding conditions, e.g. liquid and solid waste products are co-injected via their specific feeding systems to obtain optimum combustion and melt flow of the slag. Concerning PVC waste products, the co-feed processing window is estimated at max. 15 kt. capacity.

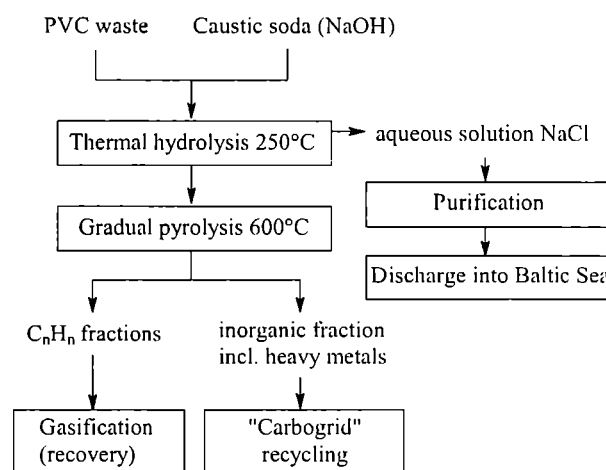
In 2000, trials involving large quantities of PVC waste products from a variety of waste sources were run in this plant, including cables, flooring, garden hoses, roofing membranes and automotive dashboard skins. They concluded with positive results and confirmed that the installed technology is robust and suitable to treat large

quantities of PVC waste products with only minor post-investment required (e.g. installation of a local shredder) [7].

The current trial programme is set up to generate experience on logistics for moving PVC waste quantities in the 1000 ton range and above, i.e. the development of an efficient (centralized?) management link between the individual waste suppliers and the operator of the recycling plant.

Hydrolysis with subsequent pyrolysis

Stignaes Industrimiljø A.S. in Denmark has developed at laboratory scale a 2-step process (Scheme C).



Scheme C. Stignaes process

Step 1 — PVC waste products in a slurry with caustic soda are hydrolysed under pressure at 250°C for dechlorination.

Step 2 — The dechlorinated fraction is pyrolysed at 600°C to separate into organic (hydrocarbon) fractions and an inorganic fraction, consisting of fillers' and heavy metals.

The aqueous and purified NaCl solution from Step 1 is discharged into the Baltic Sea. For a commercial scale operation it is considered to recover the NaCl after evaporation.

Products from Step 2 are recovered, with the C_nH_n fractions for use as a feedstock in industrial gasification processes and the inorganic fraction to be used in the onsite "Carbogrid" sandblasting plant.

Behind this development is an existing hydrolysis plant for achieving Step 1: a tubular reactor, pumps and mixing tanks for continuous operation and annual capacity of 50 kt.

No such commercial scale equipment for Step 2 is available yet, except for the "Carbogrid" plant (under construction) and the infrastructure for effluent treatment.

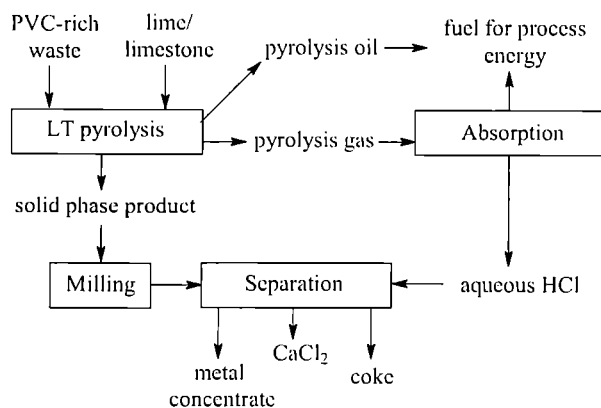
Laboratory scale trials with various PVC waste products, including cables and flooring, confirmed the dechlorination effect in a batch operated hydrolysis reactor. Residual chlorine level was below the applied detection level (≤ 0.1 wt. %).

The PVC industry, together with the Danish EPA and Stigsnaes have agreed to financially support a programme to test performance of the large tubular reactor (Step 1) and, for trial purposes, to add a pyrolysis oven at pilot scale (Step 2). First results when feeding cables and flooring into the tubular reactor confirm the good dechlorination performance as seen at laboratory scale, but also the need for further plant modifications within Step 1 to fulfil its function [8].

At present, work is in progress to simulate Step 2 at pilot scale. A final assessment of the total process is expected by mid year 2002 and should form the decision basis for further possible investments.

Pyrolysis with subsequent metal extraction

Another novel recycling process has been developed in Denmark by Watech, a subsidiary of cable producer NKT ([3, 9], Scheme D, Table 3).



Scheme D. NKT-Watech process

Table 3. NKT-Watech Process — estimated output from 15 kttons plant (approximate values)

End product	kttons
Other plastics from pre-sortation	2
Thaw-salt	7.7
Coke	3.15
Oil/Condensate	2.1
Metals	0.15 (Pb) 0.03 (others)

Chemical and thermal degradation of the PVC waste takes place in a pyrolysis reactor at low pressures (2–3 bar) and at moderate temperatures (max. 375°C). In the

process, chlorine from PVC reacts with fillers and lime, forming CaCl_2 . Simultaneously, the metal stabilizers are converted to metal chlorides. After completion of the reactions, three main intermediate products are formed: a solid phase product (mixture of coke, CaCl_2 and metal chlorides), pyrolysis oil (condensate) and gas. The solid phase is treated in a multistage extraction — filtration process under controlled pH to separate coke, CaCl_2 and metals into single fractions.

PVC waste products are hereby transformed into new, high purity products, such as:

- CaCl_2 , which satisfies the specification for thaw-salt and industrial uses,
- coke with chlorine level below 0.1 wt. %, for use as a fuel in power plants,
- pyrolysis oil and gas for internal use as process fuel,
- metal concentrate for re-use in metal refineries.

Positive results from laboratory trials led NKT-Watech to build a pilot plant in 2000, with a capacity of 800 tons/y. Various PVC waste products, mainly building and cable products, have been trial run by now in this plant confirming efficiency of the process and quality of the end-products.

Today, NKT-Watech is looking for investment partners for building a first commercial plant with a capacity of 15 kttons. Capital expenditure and running costs for the first four years are estimated with approx. 25 mill euro and include the costs for logistics and pre-treatment.

Dechlorination of mixed plastic waste — the “REDOP[®]” process

Different from the processes to treat “PVC rich” waste streams as described in the previous chapters, the REDOP process targets the mixed plastics fraction from household waste collections, for which the chlorine content is usually in the range of 0.5 to 5.0 wt. % (PVC content approx. 1 to 10 wt. %).

The REDOP process stands for Reduction of Iron Ore by Plastics in blast furnace plants and comprises the following main steps:

Step 1 — post separation of plastic and paper from municipal solid waste,

Step 2 — separation of the mixed plastics (MP) fraction from the paper fraction,

Step 3 — dechlorination of the MP-fraction,

Step 4 — co-injection of the dechlorinated MP (together with coal) into a blast furnace for the production of pig iron.

The project is run in The Netherlands, initiated by the Dutch plastics packaging industry (VMK), and managed by DSM Research. Further participation comes from waste management companies, steel manufacturer CORUS, the Association of Plastic Manufacturers in Europe (APME) and ECVM.

The project has reached the stage of bench and pilot plant scale (a few kg up to a few tons). Objective is to provide data for the design of a commercial plant that could treat around 400 ktons/y of waste.

Of special interest for PVC is the dechlorination Step 3 with a chlorine limit of max. 0.15 wt. % for making the MP-fraction suitable as a reduction agent in blast furnaces. It is applied a batch process, patented by DSM Research, where a MP water slurry is heated in a stirred reactor under conditions suitable for dechlorinating the PVC. Some cellulose is still present in the MP after Step 2, but this is not hindering; it appears that degradation products from the cellulose act as emulgators, thereby contributing to stabilise the slurry. The reaction takes place under autogenous pressure, the released HCl is neutralised by addition of a diluted water-soluble base.

Under these conditions the dechlorinated MP melt into droplets, yielding MP granules with a chlorine content comparable to coal and a calorific value which is at least equivalent.

Intention is now to produce a larger quantity of dechlorinated MP granules for feeding a blast furnace under practical conditions.

Later in 2002 a decision will be taken for possible scaling up the process into a commercial plant.

ECONOMICS

For energy recovery and feedstock recycling processes, it is common practice for the operator to charge the waste supplier with a gatefee for covering his costs. Usually, these are made up from the sum of fixed and variable costs, minus the revenues from the sales of recovered products, and by excluding the costs for collection and transport. A significant cost factor in feedstock recycling is, however, the level of pre-treatment (*i.e.* costs for sortation and grinding), which varies from process to process. For some operations, pre-treatment costs are included in the gatefee, simply because such processing steps exist onsite. Where such facilities do not exist, these significant costs occur somewhere else in the chain.

For allowing meaningful comparisons between different feedstock recycling processes, it is therefore important that gatefee quotations cover a well defined, consistent processing framework, adjusted by the costs for pre-treatment, wherever these occur.

For the processes described it is too early to provide valid information on their economics whilst development work continues. The establishment of delivery specifications for the waste supplies is an important element of this development programme, because of their heavy influence on the gatefee. Early gatefee estimates for the processes described indicate that they may fall into a range from 100 to 400 euro/ton waste supplied, with the REDOP process more at the lower, and the DOW/BSL process more at the upper end.

CONCLUSIONS AND FUTURE

Feedstock recycling technologies, capable of treating "PVC rich" waste streams, have left the laboratory and are currently tested in pilot or even exploited in industrial plants. They have the potential of making a significant contribution to the PVC industry's "Voluntary Commitment" for more recycling. However, development work still has to be completed to fully demonstrate commercial and technical viability for the various processes. It is assumed that, by the end of 2002, most of this information will be made available to form a basis from which industry can select and take investment decisions.

Other promising developments in PVC recycling and recovery are taking place at present too, offering the possibility to combine conventional recycling and feedstock recycling with novel technologies like selective dissolution (*e.g.* Solvay's "Vinyloop" recycling process) and modern municipal solid waste incineration (MSWI) with energy and HCl recovery (*e.g.* MVR Hamburg-Rugenberger Damm).

Considering all the potential options and by applying a flexible approach, the PVC industry should be confident in meeting the challenges of sustainable developments.

ACKNOWLEDGMENTS

ECVM and/or Vinyl 2010 provide financial support into the projects as described. Within ECVM, a taskforce consisting of P. Gabriels (LVM), P. Gloriod (Atofina), H. Leitner (Solvay), U. Musdaslien (Norsk Hydro), W. Schmitt (Vestolit), A. Sevenster (ECVM) and R. Bühl (EVC) is providing technical expertise and supervising progress.

REFERENCES

1. Tukker A.: "TNO Report on Chemical Recycling of Plastics Waste (PVC and Other Resins)", December 1999.
2. Prognos Report: "Mechanical Recycling of PVC Wastes", January 2000.
3. Bühl R.: "Options for PVC Feedstock Recycling — Results of the ECVM R&D Project on Feedstock Recycling Processes", PVC '99 Brighton Conference, April 1999.
4. Vinyl 2010: "The Voluntary Commitment of the PVC Industry", October 2001.
5. EU Commission: "Green Paper on Environmental Issues of PVC", July 2000.
6. ECVM *et al.*: "Voluntary Commitment of the PVC Industry, Progress Report 2001", March 2001.
7. ECVM Internal Report: "Large Scale PVC Trials in DOW/BSL Rotary Kiln Recovery Plant", June 2000.
8. Stigsnaes Internal Report: "Development of a Process for PVC Recycling, Phase 1", October 2001.
9. NKT Research Centre: "A New Process for Treatment of PVC Waste", Leaflet, November 1998.