

Chemical Recycle of Plastics

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ABSTRACT: Various chemical processes currently prevalent in the chemical industry for plastics recycling have been discussed. Possible future scenarios in chemical recycling have also been discussed. Also analyzed are the effects on the environment, the risks, costs and benefits of PVC recycling. Also listed are the various types of plastics and which plastics are safe to use and which not after recycle.

Keywords - Plastic Recycle, Mixed Plastic Waste (MPW), Polyvinyl chloride (PVC)

I. INTRODUCTION

About 50% of the plastic waste collected as general waste is recycled today. The remaining half is disposed of at landfill sites or simply burned in incinerators. In countries like Japan, the capacity of landfill sites is continually decreasing. However, this plastic waste can be recycled and used as raw material, solid fuel and waste power generation and as heat source.

Furthermore, flame-retardant materials such as polyvinyl chloride (PVC) are known to cause corrosion in incinerators during combustion due to their constituent halogen substances; these materials also produce halogen compounds such as dioxins. Moreover, CO₂ discharged from the combustion of polymers causes environmental problems such as global warming and acid rain. In addition, suspected endocrine disrupting chemicals, typically Bisphenol A, can dissolve out of polycarbonate (PC).

Common recycled plastics include:

1. Polyethylene Terephthalate (PETE): Excellent clarity, strength, toughness, and barrier to gas and moisture. These are commonly used in soft drinks, water, salad dressing bottles, and peanut butter jars.
2. High Density Polyethylene (HDPE): Excellent stiffness, strength, toughness, resistance to moisture and permeability to gas. These are commonly used in milk, juice, and water bottles; trash and retail bags.
3. Polyvinyl Chloride (PVC): Excellent versatility, clarity, ease of bending, strength, and toughness. These are commonly used in juice bottles, cling films, and PVC piping.
4. Low Density Polyethylene (LDPE): Excellent ease of processing, strength, toughness, flexibility, ease of sealing, and barrier to moisture. These are commonly used in frozen food II

II. CHEMICAL PROCESSES FOR PLASTIC WASTE RECYCLE

Processes in recycling of plastics can be divided into three categories:

1. Chemical recycling of mixed plastic waste (MPW).
2. Chemical recycling of PVC-rich waste.
3. Alternatives for chemical recycling (incineration, mechanical recycling).

Processes used under each of these categories are discussed below:

1. Chemical recycling of mixed plastic waste

Listed are the processes that were operational in practice, temporarily shut down since the necessary waste supply was not ensured, or which had a fair chance of becoming operational in the short term as of year 2000:

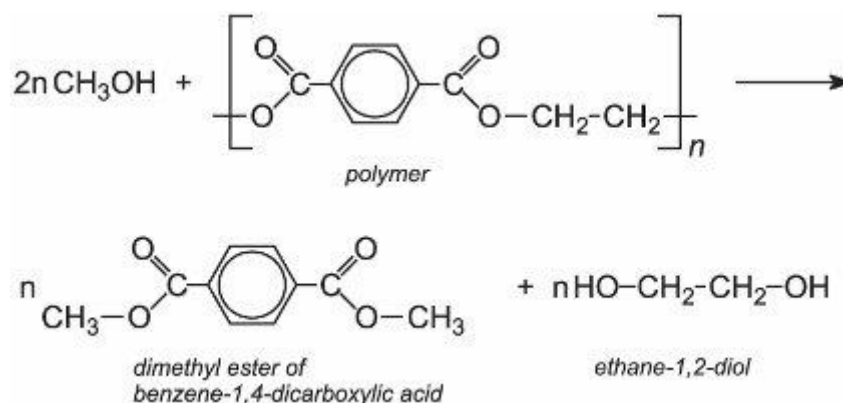
- Texaco gasification process
- Polymer cracking process
- BASF conversion process
- Use as reduction agent in blast furnaces
- VEBA Combo Cracking process
- Pressurized fixed bed gasification of SVZ

These processes are discussed below one by one:

1.1 Texaco gasification process

Texaco has had commercial experience with its gasification process for over 50 years. During this period, it has proven its high reliability and feedstock flexibility in 100 installations worldwide. Experiments with mixed plastics waste were carried out at the pilot plant site (10 t/day) in Montebello, California, USA. The Texaco process (Figure 1) consists of a **liquefaction step** and an **entrained bed gasification step**. In liquefaction, the plastic waste is mildly thermally cracked (de-polymerization) into synthetic heavy oil and some condensable and non-condensable gas fractions. The non-condensable gases are reused in the liquefaction as fuel (together with natural gas). The heavy oil is filtered to remove large inorganic particles. The oil and condensed gas are then injected to the entrained gasifier. Also, Cl-containing gases from the plastic waste are fed to the gasifier. The gasification is carried out with O₂ and steam at a temperature of 1200 – 1500 °C. The gasification pressure is normally adjusted to the pressure of the process which will consume the resulting synthesis gas. After a number of cleaning processes (amongst others, HCl and HF removal), a clean and dry synthesis gas is produced, consisting predominantly of CO and H₂, with smaller amounts of CH₄, CO₂, H₂O and some inert gases. Virtually all Cl present in MPW is captured by washing the raw syn-gas under addition of NH₃ and converted into saleable NH₄Cl. S from MPW is won back in a pure, saleable form. Ash from the process is converted into slag and fines. Filtrated waste water from the scrubber and quench is distilled, yielding reusable water, crystallized NH₄Cl and a brine purge that is re-circulated to the gasifier.

De-polymerization step involves following chemical reactions in general. PET waste is dissolved in the dimethyl ester of benzene-1, 4-dicarboxylic acid (dimethyl terephthalic acid) and then heated with methanol under pressure at 600 K. This produces the two monomers of PET, ethane-1, 2-diol and the dimethyl ester which are subsequently purified by distillation.



Input specifications are:

- Material texture Dry to the touch, not sticky, free flowing
- Physical description Shredded or chipped
- Size Less than 10 cm
- Physical fines content Less than 1% under 250 μm
- Bulk density > 100 g/liter
- Form at delivery baled or agglomerated
- Plastics content > 90 wt%
- Free metals < 1 wt%
- PVC content < 10 wt%
- Ash content < 6 wt%
- Residual moisture < 5 wt%
- Paper content < 10 wt%

Products are:

- Synthesis gas: 150 tons of mixed plastics per day produce roughly 350,000 Nm^3 per day of clean synthesis gas. This gas (predominantly H_2/CO) can be used as feedstock in petrochemical processes.
- Pure S.
- Saleable NH_4Cl .
- Vitrified slag.
- Fines.

1.2 The Polymer Cracking Process

BP Chemicals has led promotion of Polymer Cracking technology for feedstock recycling since its beginnings in the early 1990's. Support has been provided by a Consortium of European companies to develop the technology for recycling of plastics. The consortium members at the time of the successful pilot plant trials in 1997 were BP Chemicals, Elf Atochem, EniChem, DSM, and CREED. The "Polymer Cracking Process", a fluid bed cracking process, was first tested on small lab-scale equipment in the early 1990's. The pure research phase has now ended with successful demonstration of the process at continuous pilot plant scale at BP's Grangemouth site using mixed waste packaging plastics. This pilot plant, which started up in 1994, has a nominal 400 ton per year feed capacity, but runs continuously on a campaign basis at 50 kg/hr scale as it has limited product storage. The technology is now in the development phase with modifications in progress to the BP pilot plant to allow optimization and scale-up. Some elementary preparation of the waste plastics feed is required, including size reduction and removal of most non-plastics. This prepared feed is fed directly into the heated fluidized bed reactor (Figure 2). The reactor operates at approximately 500°C in the absence of air. The plastics crack thermally under these conditions to hydrocarbons which vaporize and leave the bed with the fluidizing gas. Solid impurities, including metals from e.g. PVC stabilizers and some coke, are either accumulated in the bed or carried out in the hot gas as fine particles for capture by cyclone. The decomposition of PVC leads to the formation of HCl, which is neutralized by bringing the hot gas into contact with a solid lime absorbent. This results in a CaCl_2 - fraction that has to be land filled. The purified gas is cooled, to condense most of the hydrocarbon as valuable distillate feedstock. This is then stored and tested against agreed specifications before transfer to the downstream user plant. The remaining light hydrocarbon gas is compressed, reheated and returned to the reactor as fluidizing gas. Part of the stream could be used as fuel gas for heating the cracking reactor, but as it is olefin-rich, recovery options are being considered. Hydrocarbon is recovered in two stages since the heavy fraction becomes a wax at about 60°C. Once recovered, the light and heavy fractions could be combined together in a commercial plant ready for shipment to downstream refinery processing. The process shows very good results concerning the removal of elements like Cl. With an input of 10,000 pap (or 1%) Cl, the products will contain around 10 ppm Cl. This is somewhat higher than the specifications of 5 ppm

typical for refinery use. However, in view of the high dilution likely in any refinery or petrochemical application, BP assumes that this is acceptable. Also, metals like Pb, Cd and Sb can be removed to very low levels in the products. Further, all the hydrocarbon products can be used for further treatment in refineries.

Utilities include:

- electric power 60 kW/ton feed plastic (approx)
- cooling water 40 m³/ton feed plastic
- steam 1.2 ton/ton feed

1.3 BASF Conversion Process

Before the waste plastics can be fed to the process (Figure 3), a pretreatment is necessary. In this pretreatment the plastics are ground, separated from other materials like metals and agglomerated. The conversion of the pretreated mixed plastic into petrochemical raw materials takes place in a multi-stage melting and reduction process. In the first stage the plastic is melted and de-halogenated to preserve the subsequent plant segments from corrosion. The hydrogen chloride separated out in this process is absorbed and processed in the hydrochloric acid production plant. Hence, the major part of the Cl present in the input (e.g. from PVC) is converted into saleable HCl. Minor amounts come available as NaCl or CaCl₂ effluent. Gaseous organic products are compressed and can be used as feedstock in a cracker. In the subsequent stages the liquefied plastic waste is heated to over 400 °C and cracked into components of different chain lengths. About 20-30% of gases and 60-70% of oils are produced and subsequently separated in a distillation column. Naphtha produced by the feedstock process is treated in a steam cracker, and the monomers (e.g. ethylene, propylene) are recovered. These raw materials are used for the production of virgin plastic materials. High boiling oils can be processed into synthesis gas or conversion coke and then be transferred for further use. The residues consist of 5% minerals at most, e.g. pigments or Al lids. It seems likely that metals present in PVC-formulations mainly end up in this outlet. The process is carried out under atmospheric pressure in a closed system and, therefore, no other residues or emissions are formed.

Products are:

- HCl, which is neutralized or processed in a hydrochloric acid production plant
- naphtha to be treated in a steam cracker
- monomers, e.g. ethylene, propylene, which can be used for the production of virgin plastic materials
- high boiling oils, which can be processed into synthesis gas or conversion coke and then transferred for further use

1.4 Use of Mixed Plastic Waste in Blast Furnaces

For the production of pig iron for steel production, iron ore (Fe₂O₃) has to be reduced to Fe. This process takes place in a blast furnace. Coke, coal and heavy oil are normally used as reducing agents in this process. Iron and steel companies try to lower the consumption of coke, by partly replacing it with coal, gas or fuel oil (30% in weight seems to be the maximum), via coal injection technology. Recently, new developments have started to replace the conventional reducing agents by plastics waste. Though others like British Steel (UK) have done trials as well, the best-known pioneer in this field is Stahlwerke Bremen (SB), Germany. It is a large German steel manufacturer which operates two blast furnaces to produce over 7000 t/day, or some 3 Million ton per annum pig iron. Currently, German blast furnaces are the only plants in Europe using plastics waste in this way. However, other blast furnace companies have also used waste as a reducing agent, like waste oil. SB uses plastic waste as a substitute for fuel oil. In the blast furnace plastics are injected to the tuyeres in a similar way as coal or fuel oil. From a silo or big bags the plastics are filled on a screen where the fraction > 18 mm is separated. Also, no fibers or metal particles like wires or nails are allowed in the plastic waste. The smaller plastic waste particles (< 18 mm) go to the injection vessel where the injection pressure of about 5 bars is built up. The discharge and dosing work pneumatically without mechanical support. For continuous operation, it was found that a minimum value for the bulk density of 0.3 t/m³ should be set. One advantage of plastic waste is its low S content compared with coal. However, plastic waste has a relatively high Cl content due to the presence of PVC. The main part of the Cl forms HCl going into solution in the washer. Various groups have expressed concern about the possible formation of dioxins and furans. However, measurements during experiments have

indicated that the emissions of dioxins and furans were not significantly elevated, in relation to the strongly reducing atmosphere at 2100 °C.

1.5 VEBA COMBI Cracking (VCC) Process

The plant configuration includes a de-polymerization section and the VCC section (Figure 4). De-polymerization is required to allow further processing in the VCC section. In the de-polymerization section the agglomerated plastic waste is kept between 350-400°C to effect de-polymerization and de-chlorination. The overhead product of the de-polymerization is partially condensed. The main part (80 %) of the Cl introduced with PVC is present as HCl in the light gases. It is washed out in the following gas purification process, yielding technical HCl. The condensate, containing 18 % of the Cl input, is fed into a hydro-treater. The HCl is eliminated with the formation water. The resulting Cl-free condensate and gas are mixed with the de-polymerisate for treatment in the VCC section. The de-polymerizate is hydrogenated in the VCC section at 400-450°C under high pressure (about 100 bars) in a liquid phase reactor with no internals. Separation yields a product which after treatment in a fixed-bed hydro-treater is a synthetic crude oil, a valuable product which may be processed in any refinery. From the separation a hydrogenated residue stream also results, which comprises heavy hydrocarbons contaminated with ashes, metals and inert salts. This hydrogenation bitumen is a byproduct which is blended with the coal for coke production (2 wt %). It is most likely that the major part of any metals present in a PVC formulation end up in this residue flow. Light cracking products end up in off-gas, which is sent to a treatment section for H₂S and ammonia removal. As indicated above, the main part of the Cl present in the input (i.e. from PVC) is converted into usable HCl.

Products are:

- HCl
- Syn-crude from the VCC section (This liquid product is free of Cl and low in O and N)
- hydrogenated solid residue (blended with the coal for coke production)
- off-gas

The input specifications for the plastic waste input in the de-polymerization section are:

- particle size < 1.0 cm
- bulk density $\geq 300 \text{ kg/m}^3$
- water content < 1.0 wt%
- PVC < 4% ($\leq 2 \text{ wt\% Cl}$)⁷
- inerts < 4.5 wt% at 650 °C
- metal content < 1.0 wt%
- content of plastic $\geq 90.0 \text{ wt\%}$

1.6 SVZ gasification process

The Sekundärrohstoff Verwertungs Zentrum (SVZ) operates a plant that converts several waste materials, included plastics, into synthesis gas, methanol and electricity. It originated from a coal gasification plant, but after several major investments it is currently mainly operating on waste material. It is currently fully operational. Waste and material that are accepted include contaminated wood, waste water purification sludge (including industrial sludges), waste derived fuel from MSW, paper fractions, plastic fractions, the light fraction of shredder waste, and liquid organic waste that arises from SVZ-related plants. The total capacity is about 410,000 tons per annum for solid material and 50,000 tons per annum for liquid material. The capacity for plastic waste is estimated at some 140,000 tons per annum in the near future. The MPW is fed into a reactor, together with lignite (in the form of briquettes) and waste oil. This reactor is a solid bed gasification kiln. O and steam are used as gasification media, and are supplied in counter flow with the input materials. This processes synthesis gas (a mixture of hydrogen and CO), liquid hydrocarbons, and effluent. The liquid hydrocarbons are further processed by oil pressure gasification. The raw gases from this process, as well as from the solid bed reactor, are purified by the rectisol process. There components like H₂S and organic S compounds are removed. The clean synthesis gas is used for various purposes. The main part, around 70 %, is used for the production of methanol. About 20 % is used for electricity production. The remainder is used in other processes. Waste gas

products are incinerated; in the flue gas cleaning an amount of gypsum is produced which is proportional to the amount of S in the input. The gasification process has a high tolerance for various input parameters. The plant has proven to be capable of dealing with mixed plastics waste, waste derived fuel (a mixture of plastics, wood and paper), the shredder light fraction of car wrecks, and the plastic fraction from shredded white goods and electronics. Acceptance criteria for input is indicated below:

- Particle size: > 20 to 80 mm
- Cl content: 2% as default, though higher concentrations are tolerable
- Ash content: up to 10% or more
- Caloric value: not critical

2. Chemical recycling of PVC-rich waste

The processes in this category are:

- BSL incineration process
- AKZO Nobel steam gasification process
- Linde gasification process
- NKT pyrolysis process

2.1 BSL Incineration process

The plant (Figure 5) consists of a pretreatment of the waste, the thermal treatment and energy recovery, the flue gas purification, the purification of the HCl and a waste water treatment installation. 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. In the next step, the flue gas purification, the HCl is absorbed from the flue gas by water. Also, other impurities are removed from the gas. The raw HCl is then purified to a useful feedstock. The inert products from the incineration are dependent on the chemical composition of the waste. It is likely that the main part of any metals present in a PVC-formulation will end up in this slag.

Products are:

- HCl of high quality, which can be used in several production processes;
- Steam;
- Inert slag.

The process has been designed for a mix of high-chlorinated wastes (solvents, chlorinated tars, plastics). Hence, such kilns are usually fed with a mix of different wastes (e.g. PVC waste and other waste streams with a lower caloric value) in order to obtain a waste stream with an optimum composition. If the kiln were fed 100% PVC waste, this would on average produce an input with too high caloric values, leading to problems with temperature control. The Cl content, on the other hand, is not critical. As long as the caloric value is within the acceptable range, the accepted Cl content can be higher than 50%. The accepted particle size for the incineration process is 10x10x10 cm.

2.2 Steam Gasification Process

Akzo Nobel, as a producer of Cl and vinyl-chloride, started to study a process for feedstock recycling of mixed plastic waste containing PVC in 1992. Based on an investigation, Akzo Nobel chose in 1994 to use fast pyrolysis technology in a circulating fluid bed reactor system. This technique has been developed by Battelle, Columbia, USA, for biomass gasification. The process (Figure 6) consists of two separate circulating fluid bed (CFB) reactors at atmospheric pressure:

- A gasification (or fast pyrolysis) reactor in which PVC-rich waste is converted at 700-900 °C with steam into product gas (fuel gas and HCl) and residual tar.
- A combustion reactor that burns the residual tar to provide the heat for gasification.

Circulating sand between the gasifier and combustor transfers heat between the two reactors. Both reactors are of the riser type with a very short residence time. This type of reactor allows a high PVC waste throughput. The atmosphere in the gasifier is reducing, avoiding the formation of dioxins. Depending on the formation of tars (as happened in the trial with mixed PVC waste), a partial oxidation (a gasifier) may be required to convert these tars into gaseous products. The product stream consisting of fuel gas and HCl is quenched to recover HCl. HCl is purified up to specification for oxy-chlorination. Additives in the waste stream, mainly consisting of chalk and metal stabilizers present in a PVC-formulation, are separated from the flue gas or as a bleed from the circulating sand. The output of the reactor is a synthesis gas with variable composition, which is dependent on the input. If the input contains a lot of PP and PE, relatively a lot of ethylene and propylene will be formed. With proportionally more PVC, HCl and CH₄ will be more evident in the product gas. In any case CO and H₂ will be the main components. Also the feed/steam ratio will influence the composition of the gas. A broad spectrum of materials like wood, biomass, mixed plastic and pure PVC waste is acceptable as input.

2.3 Linde Gasification Process

Linde KCA in Germany is offering a process to gasify waste materials in a slag bath. The basic technology was developed in the 1950s for gasification of lignite and coal. The process was made suitable to treat PVC waste with the following objectives:

- Maximum possible conversion of the Cl contained in the PVC into an HCl gas suitable for use in oxichlorination
- Maximum possible conversion of the chemically bound energy of the waste PVC into other forms of energy;
- Disposal of the unavoidable waste products of the process in a way complying with environmental regulations.

The European Council of Vinyl Manufacturers (ECVM) has pronounced a preference for this process for the treatment of PVC-rich waste. They regard the process as robust and economical. A pilot plant based on the Linde process was planned, supported by a financial commitment of 3 Million Euro from ECVM and constructed in year 2000. The plastic waste as delivered passes a conditioning process (Figure 7) in which it is pre-crushed and separated from steel and non-ferrous metals before entering the reactor. A pressurized reactor filled with slag is heated up to 1400-1600 °C. The slag mainly consists of silicates. PVC, sand, O 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 / H₂) containing HCl and a slag. It is likely that this slag contains most of any 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 heavy metals chlorides and other halogens. 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 to produce power. With these process waste streams containing up to 100% PVC waste can be recycled. This can be all kinds of PVC, hard and softened types. Conditioning of waste to meet the requirements for handling by the slag bath gasifier includes crushing and screening of the waste to the required particle size and then separation of iron and heavy non-ferrous metals from the waste by magnet or gravity sifter, respectively. Washing steps are not necessary. Also, drying of the waste is not necessary, because moisture is not a problem for the process.

2.4 NKT Pyrolysis process

The investigation into the treatment of PVC cable waste started in 1993 on a laboratory scale and was continued in 1995 on a semi-technical scale. This project was financed by the Danish Environmental Protection Agency (EPA) and NKT Research Centre. During the period February 1998 - June 1999, a PVC building waste project was carried out. In this project, the process was optimized for the treatment of mixed PVC building waste on a semi-technical scale. This project is financially sponsored by the Danish EPA, the NKT holding, ECVM and the Norwegian company Norsk Hydro. The process transforms PVC waste into chemical products/raw materials (Figure 8). In the pretreatment section light plastics such as PE, PP, wood and the like are sorted out. Also, sand, iron, steel, brass, copper and other metallic pollutants are separated from the PVC. The chemical and thermal degradation of the PVC waste takes place in a reactor at low pressures (2-3 bar) and moderate temperatures (maximum 375°C). In the process Cl from the PVC reacts with fillers, forming calcium chloride. Simultaneously, the metal stabilizers that may be present in PVC-waste (lead, cadmium, zinc and/or barium) are converted to metal chloride. This consists of over 60 % lead and may be purified and re-used. After completion of the reactions, three main intermediate products are formed: a solid phase product, a liquid product and a gas phase product. From the gas phase produced in the reactor (see figure 2.8), HCl is collected by absorption in water, and the light gases (mainly carbon dioxide, propane and ethane) are released after incineration. The liquid phase is separated into an organic condensate and an aqueous condensate. Hydrogen chloride solutions are reused in the downstream separation process. The solid phase is treated in a multistage extraction-filtration process. By controlling pH, temperature and the amount of water added, heavy metals are separated from the coke in the filtration and/or evaporation step. Part of the chloride that is not internally re-used finally comes available as calcium chloride from the evaporation step.

Products are:

- Calcium chloride product (< 1 ppm lead), which may be used as thaw salt or for other purposes
- Coke product (< 0.1 wt% lead and Cl, respectively), which may be used as fuel in a cement kiln
- Metal concentrate (up to 60 wt% lead), which may be further purified and re-used
- Organic condensate, which may be used as fuel for the process

3. Alternatives to chemical recycle

These processes for chemical recycle of plastics include:

- Vinyloop® process
- Cement Kilns
- Municipal solid waste incinerators
- Landfill and mechanical recycling

Each of these processes is discussed below.

3.1 The Vinyloop® PVC-recovery process

Solvay has developed Vinyloop® as a response to a challenge from one of its customers, Ferrari Textiles Techniques (France). This company is specialized in the production of architectural tarpaulin and canvas in PVC/polyester compound. They consider it important that their products be recyclable. The process is quite simple in principle. First, the products to be recycled are cut and reduced in size. After that, PVC and its additives are selectively dissolved in a specific solvent such that they become separated from other elements. Finally, PVC is recovered by means of precipitation and dried and is ready for a new life. As indicated, this has to be labeled as mechanical recycling, since the PVC polymer is not broken down into its feedstock. Yet, unlike classical mechanical recycling processes, where the full PVC formulation is kept intact, here the components that make up the full formulation are separated. The Vinyloop® process is therefore capable of dealing with rather complicated formulations. Solvay claims that the regenerated PVC is comparable in quality to the primary product. The process deals with selectively collected PVC products. The quality has to be about the same as for mechanical recycling. Pilot plant results show that the Vinyloop® process is suitable for recycling all PVC-

compound materials tested so far: cables, pharmaceutical blister packs, floor coating, car dashboards, etc. The process is a closed loop system; i.e. there are no emissions to water.

3.2 Cement kilns

Cement kilns produce a clinker by sintering alkali raw materials such as lime (CaCO_3), clay (SiO_2 and Al_2O_3) and gypsum (CaSO_4) in a kiln at a very high temperature (1450°C in the solid fraction). The kiln can, in fact, be seen as a rotary kiln with a much longer length (200 meters). Furthermore, the solid materials flow in the opposite direction to the incineration gases. The length of the kiln results in a long residence time of incineration gases at high temperatures: 4 to 6 seconds at $1,800^\circ\text{C}$ and 15 to 20 seconds at $1,200^\circ\text{C}$. Compared to regular waste incineration the O content, however, is much lower. Two processes are used to produce a clinker: a so-called wet process and a dry process. In the dry process the alkali raw materials are introduced in dry form into the kiln. In the wet process, these materials are introduced in the form of slurry. A clear disadvantage of the wet process is that it needs much more energy than the dry process (5,000 MJ/ton and 3,600 MJ/ton clinker), as in the dry process no water has to be evaporated. Because of the high temperatures, organic substances like MPW are effectively destroyed. Acidic substances such as HCl and SO_x are neutralized by the alkali raw materials, which act in fact as a caustic scrubber. Metals are bound in the clinker or in the fly ash. Fly ash is captured with an electro filter and subsequently added to the clinker. In general, no other flue gas cleaning is applied. Cement kilns have proved to be relatively robust with regard to their input material. In most cases the input material should be chipped or shredded. The PVC content is generally limited by license obligations, 1-2% Cl often being the maximum for individual waste streams.

3.3 Municipal solid waste incinerators

Municipal Solid Waste Incinerators (MSWIs) are in principle built for the treatment of municipal or similar industrial wastes. In such a kiln the waste, after it is tipped into storage and has been made more homogeneous, is transferred to a grid-type kiln. This rolling grid is placed under a certain slope, so that the waste is slowly transported with such a speed, that full incineration takes place. At the end of the grid slag remain. The slag is treated in order to recover the ferrous and non-ferrous fraction. In some countries these slag are re-used, mainly in road construction. Just like in the case of a rotary kiln, the flue gases pass through cleaning equipment such as an electro filter, an acid scrubber, a caustic scrubber, an active carbon scrubber and a DeNO_x installation in order to comply with the demands of the EU incineration directive. In modern MSWIs, the energy is also recovered as much as possible. The flue gas cleaning process leads to fly ash and flue gas cleaning residue, which has to be land filled. The main part of any metals present in a PVC formulation ends up in these residues. A large fraction of the Cl input into the MSWI ends up in the flue gas cleaning residue. Normal municipal solid waste and similar material, including the regular plastics and PVC content, can easily be accepted by MSWIs. For dedicated waste streams, some elements have to be taken into account. First, if one wants to produce re-usable slag, the heavy metal input into the incinerator should be limited.

3.4 Landfill and Mechanical Recycling

Finally, other relevant treatment options for PVC or plastics waste include landfill and mechanical recycling. Mechanical recycling of plastics (be it PVC or other plastics), needs dedicated collection of the plastic waste in question. This seems only feasible for selected PVC flows. Landfill can accept PVC in any waste context (pure PVC, MPW, mixed materials).

III. ENVIRONMENTAL COMPARISON

Human and ecotoxicity

In this qualitative analysis, since it concerns MPW with a Cl-containing material like PVC, dioxin formation is a point of attention. As a general rule, reducing environments and high temperatures promote the breakdown and prevent the formation of dioxins. This would suggest that blast furnaces and gasification processes like VEBA and Texaco have advantages in this respect. However, drawing conclusions is rather difficult. In principle, one should take into account aspects such as the Cl content in the feedstock produced, their future fate, etc. This is well beyond the scope of this study.

Ozone depletion

The most important ozone-depleting substances have been phased out. There is no reason to assume why one of the technologies at stake would score worse or better than others concerning this aspect.

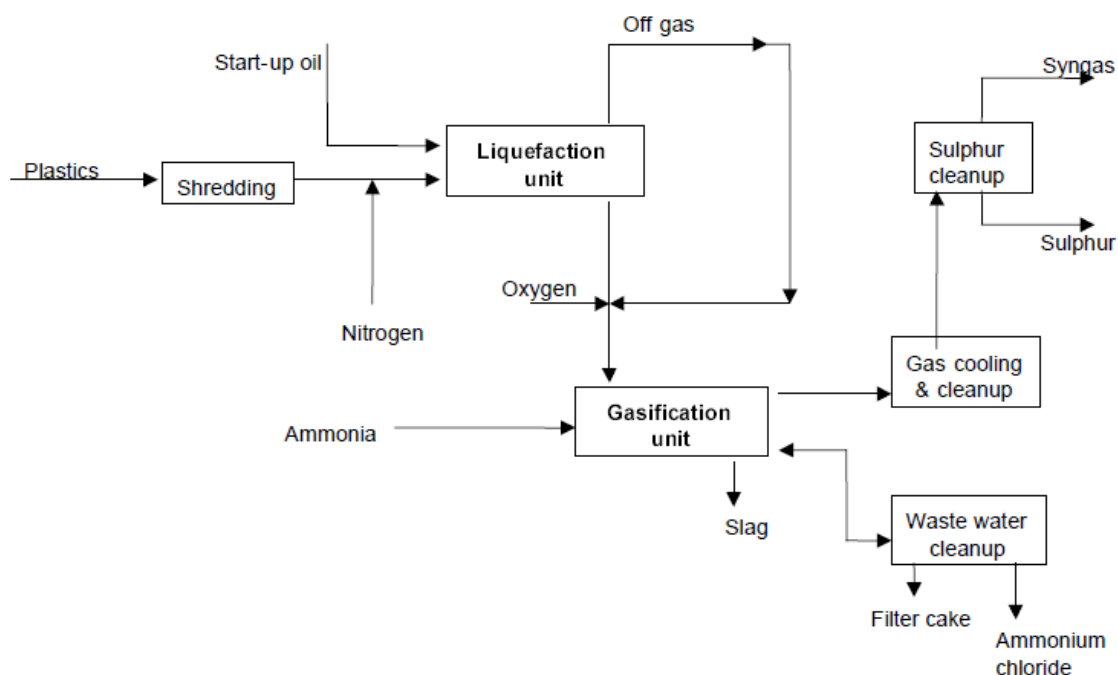
Photochemical Ozone Creation (POCP), eutrophication (NP) and acidification (AP)

The themes of photochemical ozone creation, eutrophication and acidification often tend to be correlated with energy use. Additionally, however, the processes avoided related to the useful by-products are relevant, as well as the quality of the flue gas cleaning. Here, one often sees the following difference between coal and oil as replaced products. Usually, oil refining results in relatively important emissions of NO_x, SO_x and VOC. If the recycling process produces a product that avoids this process step, it will score relatively well on POCP, NP and AP. Here this effect may be relatively less important since many processes produce feedstock that still have to be processed further in refineries. Mechanical recycling, however, can score somewhat better under favorable conditions (minor effort for collection, etc.).

Waste and other resource use

One aspect that needs to be addressed here is the fate of Cl in the process. In some processes (VEBA, BASF and Texaco) the Cl becomes generally available as a product (HCl or NH₄Cl). The advantage is that this prevents the production of primary materials and that a waste salt is produced in the process that has to be land filled. In its current form, the Polymer cracking and probably also the SVZ process has the disadvantage that the Cl comes available as a residue that has to be land filled. In blast furnaces Cl has no added value and will leave the furnace in the slag or as HCl emission. Classical MSWIs may let the Cl end up in part in the flue gas cleaning residues. In virtually all cases, any metals present in a PVC-formulation probably end up slag, fly-ash, or another residual flow.

IV. FIGURES AND TABLES



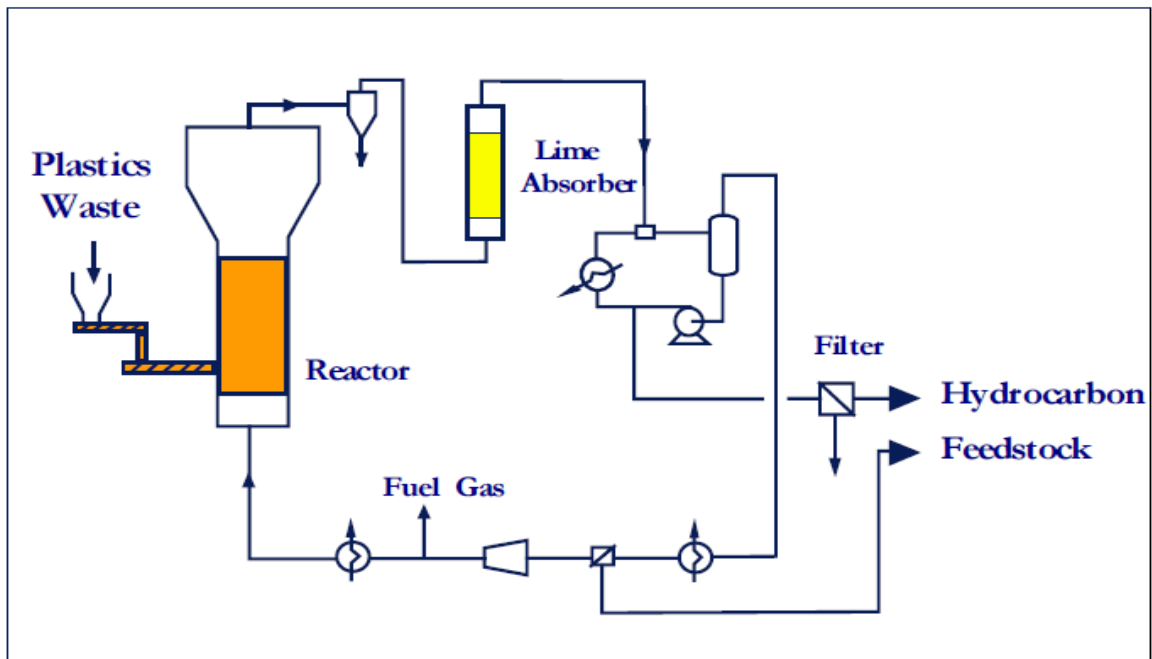


Figure 2: BP Process for Plastic recycles

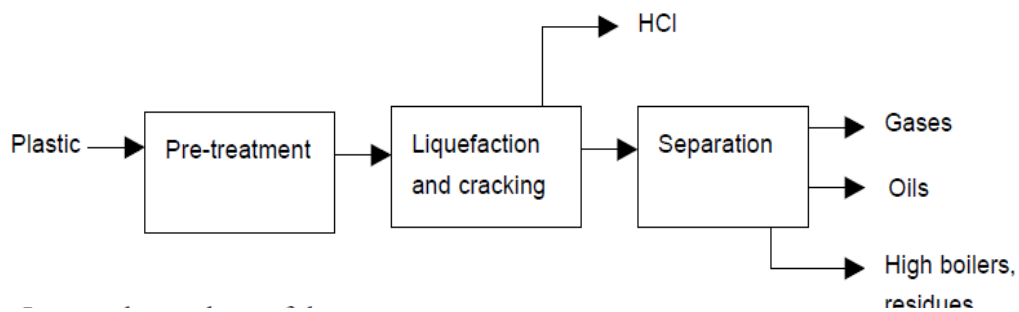


Figure 3: The BASF Pyrolysis process for plastic recycles

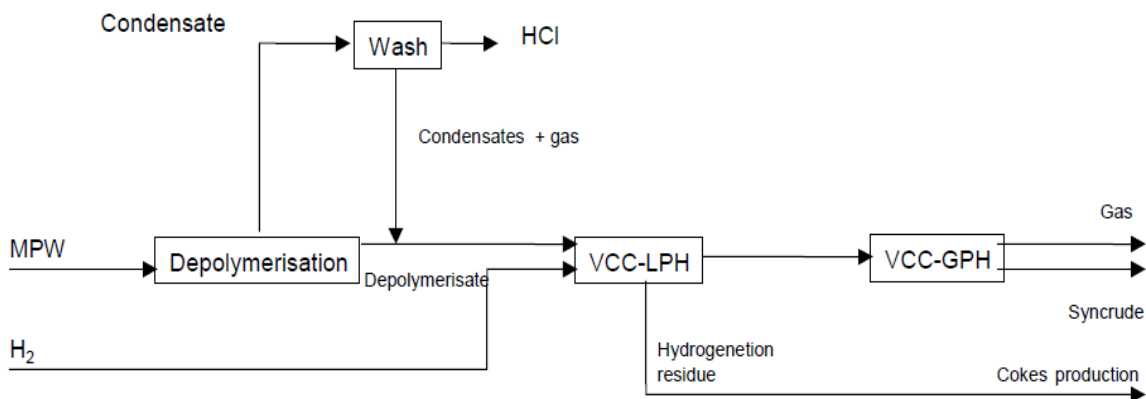


Figure 4: Veba Combi process for Plastic Recycle

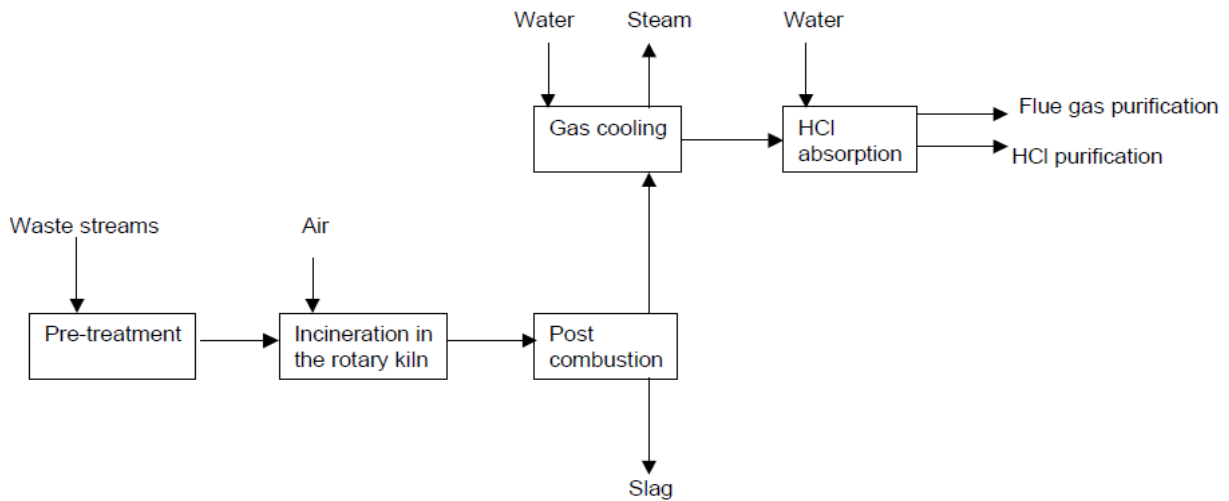


Figure 5: BSL incineration process for Plastic recycles

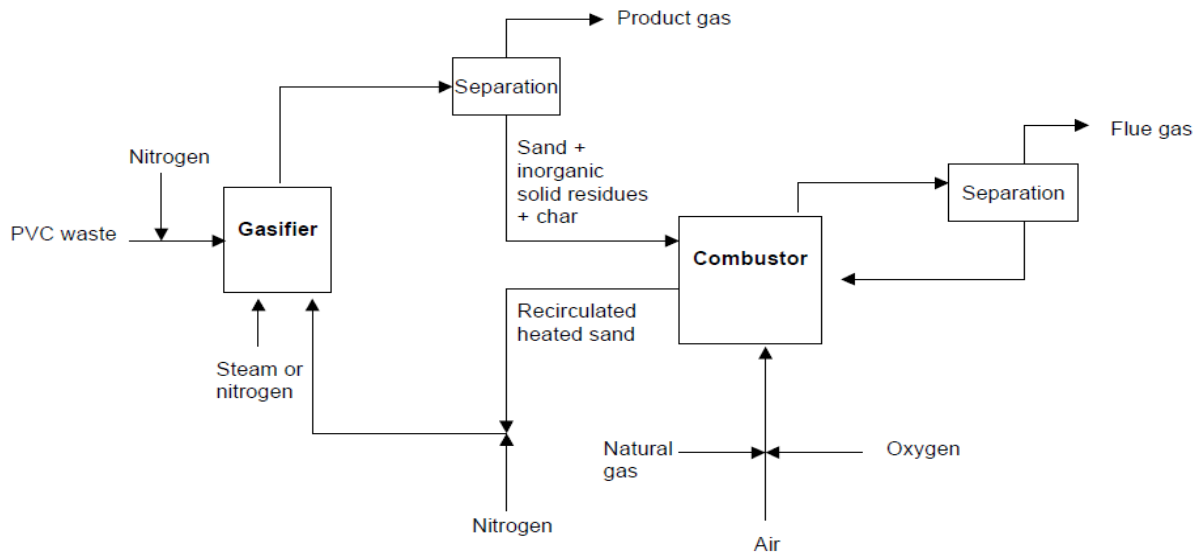


Figure 6: AKZO Steam gasification process for plastic recycles

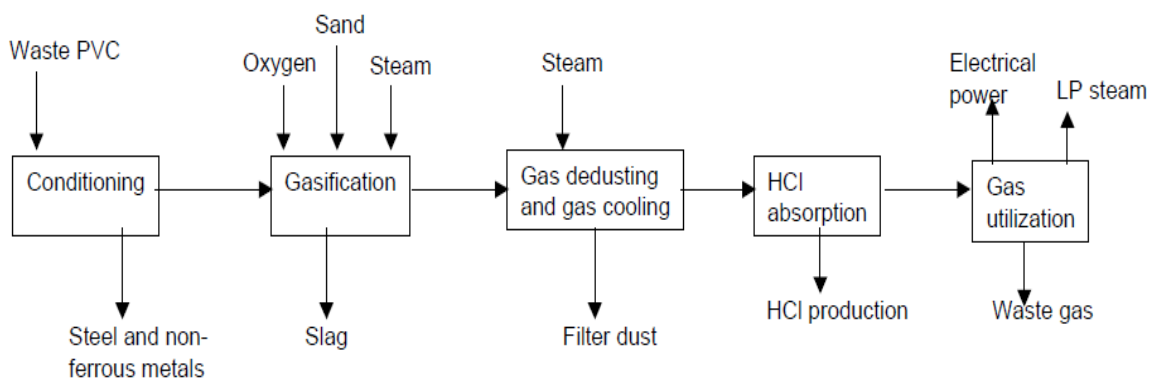


Figure 7: Linde Gasification process for Plastic recycles

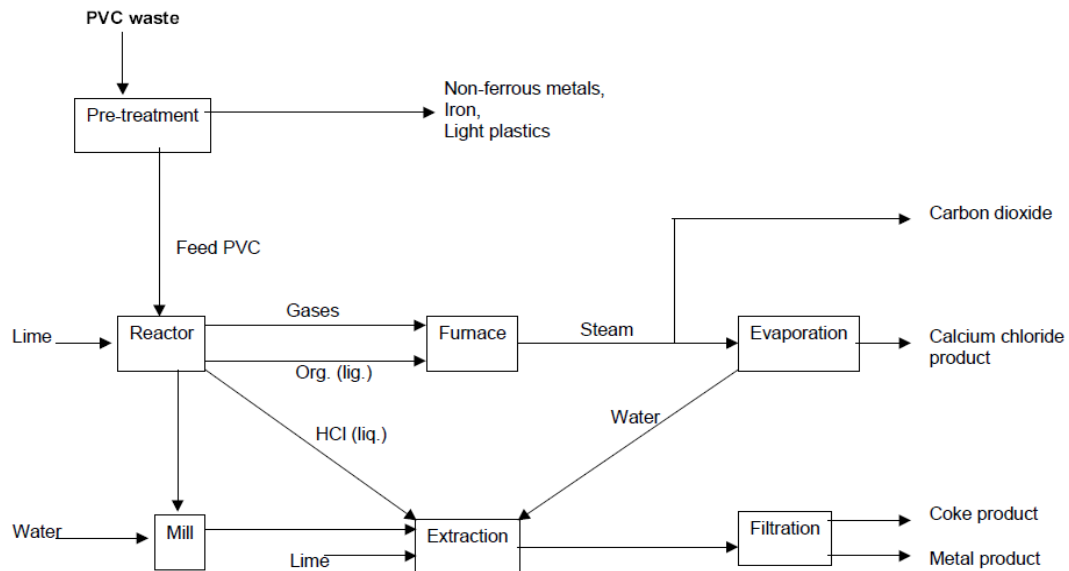


Figure 8: NKT Pyrolysis process for Plastic recycles

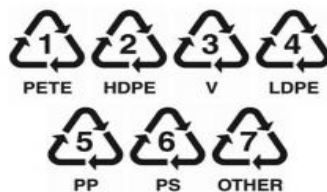


Figure 9: Numbers denotation of plastics, internationally

Table 1: Input specifications for the Polymer Cracking Process

Material	Unit	Normal	Limits
Polyolefin	wt. %	80	min. 70
Polystyrene	wt. %	15	Max. 30
PET	wt. %	3	Max. 5
PVC	wt. %	2	Max. 4
Total Plastic Content	wt. %	95	min. 90
Ash	wt. %	2	Max. 5
Moisture	wt. %	0.5	Max. 1
Metal pieces	wt. %		Max. 1
Size	mm	1-20	
Fines sub-250 micron	wt. %		Max. 1
Bulk Density	Kg/m^3	400	300

Table 2: Cost specification of the Polymer Cracking process (in £ per ton in 1999)

Costs		Income	
Capital charges	152	Products	100
Fixed costs	90	Gate fee	172
Variable costs	30		
Total	272	Total	272

Table 3: Inputs and outputs of the SVZ process

Inputs		Outputs	
MPW-agglomerate	763 g	Methanol	712 g
Waste oil	256 g	Synthesis gas	204 g
Lignite	1.25 kg	Electricity	2,28 MJ
Water	7.9 l	CO ₂	6,32 kg
O	1,47 kg	Water vapor	9,9 kg
Fuel oil	40 g	Effluent	9,9 kg
Natural gas	0,1 m ²	Gypsum	0,1 kg
		Slag	0,9 g

Table 4: A review of technical aspects and gate fees (as of December, 1999)

Process	Input	Max. input Cl	Gate fee (Euro). Excl. collection /pretreatment	Status	Products/fate - Organic fraction - Cl - Metals	Capacity	Future potential
Texaco	MPW	5 %	100 (50)	Pilot	Syngas NH ₄ Cl-product In vitrified slag	-	Uncertain*
Polymer Cracking	MPW	2 %	200 (100-175)	Pilot	Liquid/gas CaCl ₂ (landfill) In various residues	-	Uncertain*
BASF	MPW	2.5 %	250 (160)	Demo (closed)	Liquid/gas HCl (product) In residues	15 ktpa before 1996	-
Blast Furnace	MPW	1.5 %	Few-100?	Operational	Coal replacement Cl (to water) In iron or slag	162,5 ktpa in 1998	5 Mio tpa in the EU**
Veba	MPW	2 %	250	Operational (to be closed)	Gas/syncrude HCl (product) Hydrogenated resid.	87 ktpa before 2000	-
SVZ	MPW	2-5%	150	Operational	Singes/Methanol Cl to waste In landfill class 1 slag	110 ktpa in 1998	
BSL	PVC-rich, Various mixes	> 50 %	250	Operational	Energy HCl (product) Various solid residues	15 ktpa in 2000	
Kazoo Nobel	PVC-rich, Various mixes	High	Not known yet	Lab/pilot	Syngas HCl (>90 %) Various solid residues	-	
Linde	PCV-rich, Various mixes	> 50 %	200	Pilot operational from 2001	Syngas HCl (product) Various solid residues	2 ktpa in 2000	25 ktpa . 2005
NKT	PVC-rich, Various mixes	High	125-250	Pilot	Coke CaCl ₂ -product Metalchloride	< 1 ktpa in 1999	25 ktpa in future
Vinyloop ®	PVC-rich waste	High	350	Pilot, operational from 2001	PVC resin Other by-products	< 1 ktpa	17 ktpa in 2002
MSWI	MSW ca	n.r.	100-150	Operational	Energy (20-40 %); Cl and metals to waste	N/A	N/A
Cement kilns	MPW	1-2 %	Few-100?	Operational	Energy (100 %), metals and Cl in cement	Some 100+ ktpa	3 Mio tpa in the

Mechanical recycling	PVC mono waste flow	High	Some 200+, much lower for cables	Operational	Recovered PVC	N/A	N/A
Landfill	MSW ca	n.r.	1-280	Operational	-	N/A	N/A

Table 5: A review of options for chemical recycling of MPW and PVC-rich waste, including cement kilns

Technology	Status	Capacity	Future potential
<i>MPW</i>			
Texaco (NL)	Pilot/on hold	-	Uncertain*
Polymer cracking (UK)	Pilot/on hold	-	Uncertain*
BASF (D)	Closed in 1996	15 ktpa before 1996	-
VEBA (D)	Closed by 1-1-2000	87 ktpa before 2000	-
Blast furnaces	Operational (D)	162,5 ktpa in 1998	5 Mio tpa in the
SVZ (D)	Operational	110 ktpa in 1998	
Cement kilns	Operational		3 Mio tpa in the
<i>PVC-rich waste</i>			
BSL (D)	Operational	15 ktpa in 1999	
Linde (D/F)	Pilot under constr.	2 ktpa in 2001	15 ktpa > 2005
NKT (Dk)	Pilot under constr.	< 1 ktpa in 1999	15 ktpa in future

* Typical capacities considered are 50 ktpa up to 200 ktpa

** Theoretical potential *** No decision on realization yet

Table 6: Tentative cost comparison of treatment of MPW or PVC-rich waste, including collection and pre-treatment

Technology	Typical waste input	Max. PVC content	Tentative costs over the full chain (Euro per ton)
<i>Mixed plastic waste</i>			
Landfill	MSW	n.r.	250
MSWIs	MSW	n.r.	325
Cement kilns	MPW	2-3%	275-335
Blast furnaces	MPW	2-3%	400
Chemical recycling of MPW	MPW	10% or less	500
<i>PVC-rich waste</i>			
Chemical recycling of PVC	PVC-rich mixture	n.r.	390
Mech. recycling cables	Cable sheeting	n.r.	50
Mech. recycling flooring	Flooring waste	n.r.	350
Mech. recycling other	Profiles etc.	n.r.	250

V. CONCLUSION

Figure 9 shows the different numbers given by plastic industry to different plastic products. Following plastics are a big no-no to be used after recycle from health point-of-view:

1) Plastic No. 3

Found in condiment bottles, teething rings, toys, shower curtains, window cleaner and detergent bottles, shampoo bottles, cooking oil bottles, clear food packaging, wire jacketing, medical equipment, siding, windows and piping, No. 3 plastics are at risk of releasing toxic breakdown products like phthalates into food and drinks. Also, the manufacturing of PVC is known to release highly toxic dioxins into the environment.

2) Plastic No. 6

Better known as polystyrene or Styrofoam, No. 6 plastics are found in disposable plates and cups, meat trays, egg cartons, carry-out containers, aspirin bottles and compact disc cases. You should particularly watch out for insulated Styrofoam cups which, when heated, can release potentially toxic breakdown products like styrene into your coffee or tea. Number 6 plastics have also become notorious for being one of the most difficult plastics to recycle.

3) Plastic No. 7

The so-called "miscellaneous" plastic, No. 7 is a catch-all for various types of plastics, including those found in baby bottles, three- and five-gallon water bottles, 'bullet-proof' materials, sunglasses, DVDs, iPod and computer cases, signs and displays, certain food containers and nylon. Number 7 plastics are made up of various resins, which fit into no other categories; while some are safe, some are suspect. Some contain Bisphenol A (BPA), a synthetic estrogen that could disrupt the human hormone system, causing various health effects.

Concerning the environmental performance of the different chemical recycling processes, we made a comparative analysis based on existing practices for treatment of MPW. MSWIs have a number of disadvantages, like a relatively low energy recovery compared with chemical recycling. Chemical recycling plants for MPW do not differ substantially in a mutual comparison. As for cement kiln incineration, it is unlikely that it will score substantially different to blast furnaces since in both cases coal (or oil) is replaced as a primary resource. It may be that chemical recycling plants which also recycle the Cl (e.g. as HCl) have some advantages. As for PVC-rich waste, it is likely that mechanical recycling scores better than chemical recycling provided it concerns high-quality recycling and the need for pretreatment is limited. Hence, clear environment winners between the four technologies discussed could not be identified.

REFERENCES

- [1]. Tukker, A, Simons, L and Wiegiersma, S. (1999), "Chemical Recycling of Plastics Waste (PVC and Other resins)", A report, Netherlands.