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RECYCLING OF PLASTICS WASTE

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RECYCLING OF PLASTICS WASTE

Present situation - the attempt of a state of the art document

About 4 % of the total crude oil production are used for the manufacture of plastics materials. The resins again are processed into products suitable for the use by means of optimum technical properties being adventageous with respect to ecological and economic requirements. But even the optimum product has a lifetime and the question of disposal arises. In Austria there are more than 250000 tons of plastics waste generated anually of which an amount of 60000 tons has been collected in 1993. More than 80 % of plastics refuse in households is generated by packaging material making up to 50 % of total volume of waste.

For reuse of recycled plastics contaminants and specifically so-called commingled plastics and their influence of the properties of developed new products play an important role.

Contaminations caused by the practical utilisation of virgin products mostly consist of etiquettes, metal caps and residues of the contents. Caused by the relatively low weight of the plastics packages in comparison to the contents the residue in the range of about 1 % of the original charge makes up a partial amount of between 10 % and 35 % of the total and in the worst case the contaminations can reach up to the 10 - 30-fold of the total weight of the waste packaging. Mixtures of different types of plastics commonly impair the quality of the products to a great extent. It is well-known that the big four commodity plastics which are used for products of daily life are more or less incompatible with each other.

Requirements for reclamation and reuse of plastic materials

The basic question is the degree of purity of the waste plastics intended for reclamation. When plastics are recycled immediately in the same premisses the so-called "internal recycling", they appear in most cases as pure materials of the same type and also their thermal prehistory is well-known. The reclamation process becomes more complicated when the plastic materials have been used also not commingled i.e. not mixed with other types of plastics there may still arise problems through differing tension upon the particular plastic during use. Additional problems may be caused by reuse of plastics through waste collection. It cannot entirely be excluded that under the separation technique practiced that material of a completely different chemical structure or physical behaviour may appear in the mixture of the plastics fraction. The resulting regranulate mostly consists of different types with differing properties.

"Sortenreine" plastics (a particular type of pure plastic)

Non-damaged plastics: recovered by "internal recycling". Sufficiently stabilised material will not be degraded or at least only to a very slight extent even by manifold processing by adding of recycled material to the virgin material in an amount of about 20 % no deterioriation of the properties will occur.

Damaged plastics:

material which has been damaged by thermal processing procedures.

Attempts are being made, by addition of virgin material, to improve the properties of the plastic, thus enabling a reutilisation. Through such measures it is inevitable that some mechanical properties are extensively deteriorated. Such a regranulate can be reprocessed into products which command strongly reduced requirements.

Waste plastics

Contaminated plastics: Very often the recycled plastics are no longer of one type. Reasons for this amongst others are contaminations which cannot completely be removed by reprocessing procedures or caused by materials which have contaminated the plastics by migration. The mechanical properties decrease almost linearly with increasing degree of contamination. For this reason it is necessary to carefully clean and purify the plastics during the recycling processes.

Commingled plastics: During the recycling processes it is very often difficult to avoid a joint, blending, remelting and coextrusion of different types of plastics which cannot be separated by the separation process.

Compatibility of plastics

Specifically polyolefines which are widely used in the field of packaging are known to be slightly compatible. For example PE and PP which practically cannot be seperated by the common swim and sink processes which by means of differences of specific gravity shall be separated.

Another important parameter is the processing temperature - if this falls below the processing level the plastification cannot be sufficient but if it exceeds the range of processibility the material might be decomposed. From which arises that in the case of mixtures the ranges of processibility may strongly be limited.

By the addition of compatibilizers, however, mixtures can be provided which - although not compatible with each other - can be melted into a practicable system of useful combinations of properties. Such compatibilizers, however, are not yet available for all combinations of waste plastics. Recycled plastics materials can be reprocessed more or less without great problems if they are clean (sortenrein) and free from contamination. The mechanical properties can be made impure significantly by already small amounts of impurities. Compatibilizers significantly can improve the properties of the recycled plastics. From the economical point of view the recycling of plastics has not come to a break-through yet.

Characterisation of plastics fractions by analytical methods

Requirements for identification:

There are mainly two different systems that exist. The first one is used for separation of plastic packaging materials. In this case only the limited number of 6 packaging plastics has to be identified. But in this case the velocity plays an important role.

The second system is suitable for the separation of products made of engineering plastics. An example would be the demontage of used vehicles. Such a system is required to be able to distinguish between approximately 30 different plastics, resins and blends. The velocity is of minor importance.

Suitable spectroscopic processes:

Two different types of spectroscopies are distinguished. The first one analyses the polymer without change of its structure or appearance or avoiding any kind of damaging or change of its appearance. The second type is a process which by rapid pyrolysis destroys the polymer into those fragments. Figure 1 shows a collection of suitable processes.

Technical methods suitable for separation and recycling of bottles and containers from municipal solid waste.

In the following chapter some technically available and suitable processes for the identification and separation of plastics bottles and containers will be described.

Important factors that influence the method of choice

- complexity of the mixture (number and concentration of the different components)
- shape (size and figure)
- quality and possible markets (properties of the recycled material)
- contaminations of non-plastics materials
- costs and expenditure

Process for identification and separation of containers

Manual sorting: This is currently the most practiced method. The efficiency of such systems lies between 50 and 200 kg/h. The sorting accuracy lies between 80 and 95 % mainly influenced by errors of the person. Additional problems may arise by the application of different types of plastics for the same shape and type of bottle. Some problems caused by manual sorting concerning the velocity and accuracy have lead to the development of automatic sorting systems.

Semi-automatic bottle sorting

These are auxiliary techniques for the manual sorting where the worker starts with a visual sorting and subsequently the bottles are sorted out by means of an automatic mechanism. See figure 2.

fig. 2

Automatic bottle sorting:

The first automatic systems for this type of bottle sorting which are based on detection of chlorine in PVC and subsequently by a series of mechanical mechanisms sort cut the PVC bottles work on the basis of X-ray-small angle scattering (XRA).

The bottles pass side by side lying on a conveyor belt, a detector. The detector recognizes the PVC bottle and determines its size. Subsequently a certain number of air nozzles are opened separating the PVC bottles from the others. The systematic sequence is given in figure 3.

fig. 3

Bottle recycling system of technical scale

The typical large scale system is described by the "BottleSort System" of Siemens Company. Plastic bottles from separate waste collection are being pressed into big bales and delivered to the plastics processing industry for recycling. The system is designed for a differentiation of plastic bottles according to type, colour and shape.

Fig. 4

Sensory: The identification unit is built of a number of different sensors which are able to carry out up to 6000 tests per bottle. Fast electronics with suitable software evaluate the data and check within approximately 5 ms which types of plastics are involved. At this point also disturbances such as stickers, residues of contents etc. are recognized by the electronic system and taken into consideration for the identification of the resin.

Way of function

Mixed plastic bottles which are pressed into bales are automatically opened and divided into single bottles. The bottles are moved to the sensor individually and one after the other. After identification of the resin type, its colour and shape the bottles are to be moved on the conveyor belt. The separating stations are placed at right angles to the transport direction. By means of a dosing mechanism the identified plastic bottles are pushed by a compressed air push into the collecting pins.

Processing

The processing of plastic residues and wastes is only possible if there is a suitable preparation technology. Through this the waste is altered in respect to its structure and composition in such a way that it may be processed by suitable processing techniques.

Also a number of chemical and energetical recovery processes have certain requirements which the waste must fulfill.

The most important steps are:

- disintegration
- classification
- sorting
- washing and drying
- agglomeration and regranulation

Size reduction

For the reuse of the plastics it is advantageous to have a particle size which is similar to the one of the primary virgin material. So in most cases every recycling process will start with a size reduction. After having brought the waste plastics into the desired particle size and shape the recycling process can go on. For dry grinding of plastics cutting mills (Schneidmühlen) are the most suitable technique.

The cutting mills have to meet the following requirements:

- stable mechanics
- rapid change of knives
- easy cleaning
- high output and performance

Modern cutting mills have the following characteristics:

- welded steel construction
- outlying bearing separated from the mill's housing
- openable casing with lines of separation in the area of the shaft
- screen casily exchangeable
- a sloping double cut
- pre-adjustable knife

The wet-cutting is adventageous because the energy which is to more than 99 % converted into friction heat can be utilised for the intensive cleaning of the waste material. And additionally the wear on the knives is reduced.

Classification

Classifying or sizing means the separation of a mixtures of particles by means of differences of size and shape - the so-called "bed properties". The classification influences the particle size distribution and perhaps also the shape of the particles of the material. This separation into different beds which also may be turned as fractions or classes may be carried out according to different principles of function namel; screen classifying and stream classifying

Screen classifying

Sizing separation takes place by means of a semi-permeable sorting plate i.e. a perforated bottom provided with almost identical geometrical holes. This method can be applied with devices disposing of fixed or movable perforated bottoms, as well.

Stream classifying

Thus the velocity resp. the way of flowing covered by particles in a fluid (under influence of flowing and inertia forces) depending on size and shape of grains, can be utilised.

Cleaning and drving

By cleaning we mean the removal and separation of solid as well as liquid contaminants of the cut plastics.

Cleaning can be carried out in three steps:

- Soaking and dissolving (short time of detaching requires a thorough circulation)
- Detaching of contaminants: By intensive stirring and shearing of the fluid high relative velocities between grain and washing solvent are produced resulting into a separation of plastics particles and the contaminants.
- Separating of contamination: by sedimention of the washing solution

By drying the moisture content of the plastics material is reduced. We distinguish between mechanical and thermal drying.

Through mechanical drying the moisture of the dressing material is separated by field or inertia forces. At the same time some fine particles of dirt, dispersed in the fluid, are eliminated, as well.

For thermal drying of granulated plastics mainly the convectional heat transfer is used. By convectional heat transfer from the hot-air stream on the one hand the plastics particles are warmed up considerably on all sides and without overheating, on the other hand the steaming moisture can be removed directly.

Production of high quality recycled materials by elimination of printing inks and disturbing ingredients (NOREC-method)

The recyclability of the polyolefines PE-LD, PE-LLD, PE-HD and PP is deteriorated by the applied blends and additives, connected with the technique of application.

The most important difficulties and interferences as to the preparation of plastics film are:

- Accidental discoloration of regranulated material by pigments of printing inks
- Greying of transparent recycled material by degraded sheeting components of the plastics films.
- Intensive odor (smell) of film caused by oxidizing decomposition products of polymers, components and residues of additives and extender.
 - Additives of unknown quantity and type with non-recognizable effects on processing and durability of packaging.
- Indefinable film components, liable to migration, with hazard of contamination for goods to be packed.
- Film specks and pimples with negative effects on optics, quality of compression strength and application.

Cleaning

The procedure of cleaning starts from plastics film reduced into small pieces i.e. chips of the size of a penny. According to the pollution of the primary (virgin) material these chips are precleaned pneumatically, mechanically or wet (through water) and conveyed to the NOREC-process. Then follows a thorough cleaning by means of a single organic solvent.

Different select criteria for the adequate solvent are named below which were at the same time a basis of the processing development:

- free of FCKW
- non toxic
- not dissolving the polymer
- likewise well detaching printing inks and removing sheeting components
- density lower than that of polyolefines
- chemically stable and of manifold ability to be regenerated
- at convenient prices

The NOREC-method is carried out continously (steadily) in several partial steps of procedure, as described below and shown in fig. 5.

fig. 5

- Feeding of film chips (E)
 - compression of chips
 - displacement and compensation of air by inert gas
 - volume-dosed (batched) channelling of the airless stream of chips
- cleaning phase R 1
 - suspending of the chips in a solvent warmed up to 60 65 °C
 - rapid detaching of printing inks by friction
 - total removal of the remaining (left-over) mineral and greasy contaminations
 - starting extraction of sub-surface, slightly migrating film additives.

• cleaning phase R 2

- separating of the polluted solvent at the transition point to R 2
- by cleaning of the surface the residues of printing inks are removed i.e. rinsing by means of the already used extraction solvent
- extraction of the sub-surface ingredients is continued
- separating of the solvent

• cleaning phase R 3

- supply of clean and warm solvent of 60 65 °C in a "counterflow"
- extraction of waxy depolymerized polymers, low-molecular weight particles and additives, liable to migration, as well as their oxidizing products from within the chips
- separating of the solvent

• cleaning phase R 4

- rinsing of the wet chip surface with hot water of approx. 60 70 °C and ejection of the solvent from the inner chip
- discharging of the chips moist with water from the capsulated NOREC plant and transition from the "ex-sphere" to the normal atmoshere
- drying of film chips (T)
 - mechanical drying
 - thermal drying
- output of the chips
 - transport of dry chips to a buffer silo for further preparation

The film chips cleaned according to the NOREC-method can be easily regranulated and may be extruded, bonded and welded to new film. In order to avoid yellowing and pimples it is useful to add a processing stabilizer with the regranulation for freshing up the used polymers. Strength measurements of such film showed no significant differences in comparison to new film made from raw materials.

Sorting technique for plastics

Sorting means separating of commingled plastics due to their differing properties such as density, surface structure, ferro-magnetism, conductivity, colour and so on. In this way sorting accuracy influences the purity of the finished product.

Distinction is made betw een:

- sorting due to density
- sorting due to flotation
- electrostatic sorting
- thermal separating procedures
- · sorting of plastics by hand-picking method

Sorting according to density

Referring to the important sorting properties plastics are very similar to each other. Density of the most comodity polymers is to be found between 0,9 and about 1,4 g/cm³ (see the following table).

Polymer	Density (g/cm²)
LDPE	0,92
HPPE	0,96
PP	0,91
PS	1,13
PA	1,05
PMMA	1,18
PVC	1,39
PTFE	2,20

The fundamental idea of this procedure is to separate the various plastics of about the specific gravity of the separating liquid which can be varied. This happens by dissolving material with a density, lower or higher than water, e.g. alcohols or salts, or by suspension of fine solid particles of a density higher than water, such as "caolin" or ferromagnetic minerals.

Swim-sink-separating under the influence of gravity:

In this field steady continuous separators have been successful by consisting of one or several simple, open troughs equipped with feed and output devices.

In the course of residence in troughs the particles can rise or dip in the separating agent due to their density.

fig. 6

Swim-sink-separating in the centrifugal field e.g. "hydrocyclone":

The separating agent loaded with plastics particles streams - under pressure - into the tangential inlet of the apparatus and is diverted into a rotary motion by the geometry of the unit, circulating like a whirl. By rotary motion centrifugal accelerations are generated exceeding acceleration due to earth gravity, by a lot. This acceleration whirls those particles which are heavier than the fluid outwards, whereas the lighter ones are pressed to the centre of the whirl. In this centre an air surface exists. On principle the detaching process takes place in the same way as in the static swim-sink-separator. In the whirl, however, it is subjected to a multiple earth's attraction, practiced not in vertical but in radial direction.

fig. 7

Sorting according to density in streaming fluids:

In a fluid-grain-suspension, sorting according to density is carried out if the flow velocities are chosen adequately and a suitable preclassification of the waste materials in question has been applied. The sorting takes place either within a flow through a channel or in a film flow across an inclined plane.

Centrifugal technique:

This method deals with a three-phase separation (solid - liquid - solid). That is a horizontal located so-called "double cone - fully coated - screw centrifuge. The centrifuge is partly filled with the separating agent which forms a fluid ring because of the rapid rotation. The mixed plastics are put in as suspension by means of a vertical tube axially into the centrifuge and meet with the surface of the rapidly rotating fluid ring. Here the particles entering the surface are exposed to very strong shear forces. A strong turbulence takes place which results in an isolating of the plastics particles and at the same time liberating from sticking dirt.

Particles which density is higher than that of the fluid are hurled radially to the centrifuge "mantel" whereas the higher components can rise towards the interior. The separated partial fractions in this way are conveyed to each of two conical ends by the screws. They are lifted out of the fluid ring and leave the centrifuge in a dewatered stage.

Sorting according to flotation

Flotation is a wet seperating method which utilises the different surface behaviour of the various plastics caused by different molecular structure. In this way advantage is taken of the flotation with water so that a certain part of the material is equipped with air bubbles because of its hydrophobia which let it rise. The other part of material, however, absorbs water completely because of its hydrophilia and sinks to the bottom.

fig. 8

Electrostatic sorting

By means of electrostatic sorting of solid materials a separation into different components may be achieved. For this purpose the components in question have to meet two requirements:

- 1. They may not be incorporated e.g. must appear as free particles side by side.
- 2. They may be distinguished with regard to electric conductivity or tribological charging properties.

Utilising the different electric conductivity as sorting or separating parameter a so-called "rotor (magnetic) separator" is applied as separating device. With respect to the different tribological charging properties i.e. charging by friction sorting happens by means of a "falling separator".

Physical recycling methods

Filtering systems for reprocessing procedure

Recycling means physical separation of contaminants from the melt through suitable filter materials. Polymer contaminants are either solid foreign particles or hard meltable polymer particles. They can, therefore, be separated physically. In order to detect all contaminants, as far as possible, the separation takes place in the melt between the extruder and extrusion mould.

Many kinds of melting contaminants are due to the waste processing.

Table I shows the usual polymer enclosures being arranged according to the filtering purpose, suitable filtering system, necessary mesh size, recommended filter area, ensuing filter leading and the most relevant final product.

polymer enclosures	filtering purpose	filtering system	inesh size μm	filter area	filter loading	application products
bar fraction screws a. o.	machine protection, extruder pump, roll	perforated plate	very coarse > 500	0,004-0,04	> 100 000	granular material all half stuffs
sand, dust	machine protection, avoidance of holes without break	alternating plate, gate, cont. filter belt, drum	rough 500-200	0,004-0.04	> 50 000	granular material all half stuffs
fibres papers	avoidance of break or defects	tube filter LLF	medium 200-100	0,1-0,5	700-1000	granular material all half stuffs
additive agglomerates	colour homogeneity safety of products	tube filter LLF	fine 80-60	0,1-3	500-750	monofils films
crystalline polymer particles	avoidance of break or defects	large-face- filter NSF, LLF	very fine 40-50	2-46	150-400	continous fibres stretch films for video and X-ray-films
gel-like polymer particles agglomerates	quality of products avoidance of break	large-face filter in two chamber designs NSF, LSF	extremely fine 15,10,5	1-6	50-150	micro fibres sound carrier film condenser film

The mentioned enclosures result into different effects as to the extrusion process. Coarse contaminants must be filtered out in order to protect the extruder screw, gear pump, extrusion mould and roll surface. Mesh size, filtering area as well as the arrangement (grouping) of the filter material (media) are adjusted to the purpose of application.

Filtering systems are machine aggreg this which are able to take up the various kinds of filters in simple or multiple arrangement between plates resp. in pressure-proof, heatable casings and enable their exchanging as required. Additive agglomerates and gel particles can be separated from the meit by means of fine-pored filter media in large-face filters and retained, as well.

Table 2 gives a survey of the filter systems in (on) the market.

filtration systems	arrangement of filter media	alternating device	examples/articles
leaf (disc) filter	perforated plate	gate (disc) cont. gate (disc) ram (plunger)	Bematec, Beringer, FBM, Gneuß, CHIVA, JPL, Kreyenberg
tube filter	cylindrical support	ram, gate with tubes, pre-assembled insert	Barmag, Werner u. Pfleiderer
band filter	perferated plate with filter band (belt)	continuous shift	Auto Screen, HITECH, Lenzing
selfpurifying plate filter	a double- disc system rotating disc	back-washing	Erema, Gneuß, Kleen Screen, Siemens, Reifenhäußer
autopurifying drum filter	drum rhythmically rotating	back-washing in segments	Berstorff
drum filter with filtrate outlet	drum with separate system	discont. outlet of filtrate	Extrudex
large-face filter	2 chambers as above with change- over valves	change of plate when machine is running	ASKA, Barmag, Fluid Dynamics, Fuji Filters, LCJ

Improvement of quality by means of additives (stabilizers)

All organic materials are exposed to natural ageing, the polymer materials included.

To avoid or at least decelerate degradative reaction, plastics are supplied with additives, the so-called processing-, thermal- and light stabilizers.

The antiageing agents, as stabilizers are called, serve to (contribute to) protection of the sources, twofold:

- By prolongation of life they reduce the application needed of non renewable raw materials (oil for example).
- By means of stabilizing improvement in most cases the amount of plastic materials can be used more efficiently and economically which leads to thin-walled articles.

Restabilizing of recycling material

The damage grade of plastic waste depends on the type of polymer, the way of stress (thermal) and the primary stabilizing. To preserve material at as high a quality as possible some measurements are to be observed (desirable ideal case):

- Clean, if possible, "sortenreine" (particular type of pure plastic) used plastics.
- Determination of kind and quantity of additives originating from the first (primary) application.
- Careful definition for the new use (restabilizing).
- Testing of processing and long-term stability of the new definition.

The testing of stabilizers of the new plastics material as well as the recycled one mostly refers to three fields: processing-, long-term- and light stability.

Compatibilizers of plastics material

Certain kinds of polymers can be commingled with each other - in this way the so-called blends arise which show certain defined properties. Not all plastic material is inter-mixable - which applies to the recycled material, as well.

Polymers are provided with compatibilizers for improvement. Compatibilizers are substances for making compatible those polymer components which are partially mixable or non-mixable. Adding pre-prepared compatibilizers is one of the most frequent and successfully applied techniques.

A relatively new technique is the use of compatibilizers in recyclable plastic material mixtures. In this way, plastic blends whose properties have thus been modified, can be used for the various applications.

Compatibilizers diminish the surface tension, reduce size of particles, improve connection between matrix and dispersed phase and finally work against coagulation (flocculation) of the dispersed phase.

Worth mentioning is the fact that homogeneous blends have one glass transition temperature, whereas heterogeneous have two.

Table 3 shows the miscibility of different plastics materials:

	PS	SAN	ABS	PA	PC	PMMA	PVC	PP	PE-LD	PE-HD	PET
PS	1										
SAN	6	1									
ABS	6	1	1								
PA	5	6	6	1							
PC	6	2	2	6	1						
PMMA	4	1	1	6	1	1					
PVC	6	2	3	6	5	1	1				
PP	6	6	6	6	6	6	6	1			
PE-LD	6	6	6	6	6	6	6	6	1		
PE-HD	6	6	6	6	6	6	6	6	ı	1	
PET	5	6	5	5	16	6	6	6	6	6	I

1 = mixes well, 6 = mixes badly

Chemical recycling methods

Under this topic processes are described which use plastic waste as cracking feed. These processes are hydrogenation, gasification, cracking, carbonization (coking) but in most cases the feed material has to meet certain qualitative requirements such as trace metals, halogen content, concentration of heavy metals and fillers which may vary from waste to waste. So that in most cases pre-treatment is necessary, to convert the waste material into a suitable feed material for petro-chemical industry. The next table shows the composition of plastics packagings in household products.

Articles		Resins	
film	32 %	PE	54,2 %
beakers	12 %	PVC	8,4 %
bottles	14 %	PP	18,7 %
foames	1 %	PS	13,4 %
others	41 %	others	5,3 %

Petro-chemical processes for the recycling of plastic waste

pvrolvsis

Used plastics can be transfered into raw materials by pyrolysis. That means the production of liquid and gaseous pyrolysis products such as oils and technical gases by thermal degradation under exclusion of air or at least deficiency of oxygen which then are further conditioned with common technical separation technique. Pyrolysis in comparison to combustion yields a volume of crack gases (methane, ethane, ethylene, propylene, butylene and so on) which is by 5 - 20 lower than the amount of flue-gases from incineration plants.

Another advantage is that commingled plastics can be used without any need for sorting or classification. Pyrolysis of plastics is specifically advantageous if it is carried out in a fluidized bade reactor. By means of strong heat and material transfer an adequate constant of temperature can be produced. Consequently it is possible to keep a constantly good quality of the products. Up to 50 % of the feed material can be obtained as liquids.

Fluidized bed:

If fine grain material placed on horizontal, perforated bottoms is percolated a state is reached under certain conditions which is similar to a boiling fluid. The boiling zone produces bubbles and the particles within this zone are in a permanent fluidizing up and down movement thus remaining in a floating position.

Fig. 9

The butt of the plant is a fluidized bed reactor. The plastic waste is fed in by a screw or a sluice and pyrolysed in a fluidized bed of quartz sand at temperatures between 600 and 900 °C. As fluid agent pyrolysis gas pre-heated up to 400 °C can be used. The heat is applied indirectly by radiate heat tubes by combustion of the pyrolysis gas and the flue gas is transported from the reactor to a heat exchanger into the stack. The crack gas which has been formed by pyrolysis leaves the reactor and is purified in a cyclone and small particles are removed. In a quench cooler it is cooled down to room temperature by circulating of the product oil. Consequently the gas passes through two quenching columns filled with glass beds. During this process oils are formed which are separated in two destillation columns whereby the fraction with the boiling range from 150 and 170 °C is used as quenching liquid. Furthermore high boiling tar is obtained which contains tuloulene and benzene. The produced gas is purified by means of an electric precipitator or filtration system and compressed (2 - 3 bar) and stored.

Hvdrogenation

Hydrogenation is a suitable process for the re-using of mixed and/or contaminated plastics waste products. By hydrocracking the macromolecules are thermally decomposed into very reactive fragments which during their generation are saturated with molecular hydrogen. A suitable high pressure of about 200 bar will make sure that enough hydrogen is present for keeping the hydrogenation process working.

The process is carried out in a bottom phase reactor and based on living organisms (bacteria, fungi, yeasts, algae). In this special case it is a double column reactor. The temperatures in the reactor vary from 440 - 480 °C, the pressure lies between 150 and 250 bars.

Furthermore there is a process based on the old "leuna-technique" which depolymerizes the plastic waste. The mixed plastic waste is heated up to 260 and 420 °C together with heavy oils. The plastics are degraded into small molecular fragments showing a significantly lower viscosity. Simultaneously hydrochloric acid is formed from the PVC present in the mixture as well as low boiling hydrocarbons which can be condensed and recovered separately.

• classification of used plastics

At temperatures of 1600 °C and pressures up to 150 bar the product is a gas which due to its composition, colorific value and range of application may be defined as:

poor gas and water-gas
 4600-12500 kJ/Nm³

• synthesis gas and reducing gas 12500 kJ/Nm³

• town gas and rich gas 16700-20000 kJ/Nm³

rich gas and synthetic natural gas
 25000-3700 kJ/Nm³

The classification process with the equation:

$$C_nH_m + {}^n/_2 O_2 \rightarrow nCO + {}^m/_2H_2$$

 $C_nH_m + nH_2O \rightarrow nCO + ({}^m/_2 + n)H$

can be divided into three parts:

- 1. Heating and cracking: Hydrocarbons are cracked down to carbon, methane and hydrocarbon radicals.
- Oxidation and classification: The hydrocarbons partly react with oxygen forming CO₂ and H₂O. Oxygen is consumed during this process. Simultaneously some of the oxidized hydrocarbons react with the generated CO₂.

3. Consecutive reactions: The formation of methane and soot in the lot departments of the reactor is influenced by pressure, temperature and the amount of steam.

fig. 11

Reduction in a blast-furnace

The blast furnace is a reactor for the transformation of ore into iron. For this transformation reaction high temperatures are necessary which are generated by the burning of fuel like heavy oils or coke. Plastics mainly the so-called commodities (PE, PP, PS, PVC) consist of carbon and hydrocarbons resp. like coal and heavy oils and are therefore suitable for the reduction process in a blast furnace if the concentration of chlorine is not higher than 2 %.

Of course one has to consider that the process may be influenced by certain components of the plastic waste originating from the collection such as metallic packages e.g. caps of aluminium and so on.

Interferences on the blast furnace process may come from:

 Titanium oxide (TiO₂) 	(from the white pigment) none, if the concentrations
	are too high, will be removed with the slag.
• Sodium, potassium	none, if in the common order of magnitude,
	removed with the slag.
• Copper	none, the small amounts will be accepted from the
	pig iron.
Cadmium, lead	(from pigments and stabilizers) will be at present in
	the blast-furnace dust.
• Chalk, talcum, glass fibres	(from filler and reinforcing additives) are removed
	together with blast-furnace dust and slag.
• Sulphur	none, plastics contain very low quantities of sulphur

content of up to 2,5 %.

in comparison to heavy oils which have a sulphur

The advantage of plastics as energy producers in the blast-furnace process lies mainly in the replacement of coke, coal and heavy oil saving the natural resources. Plastic waste contains in contrary to the heavy oil almost no sulphur.

Depolymerization of PMMA

Polymethyl methacrylate (acrylic glass) is a high quality material which is almost entirely processed into long life goods (for optical purposes, motor vehicle industry, building industry, light advertizing leaflets). One way articles of PMMA only arise from medical applications. A regular and continously packaged component of the household refuse may be excluded. Total PMMA consumption in Western Europe in 1993 was about 200 000 t.

Recycling processes are almost exclusively concentrated on production- and processing wastes. It is a requirement of quality controlled recycling that a mixing up with other types of piastics is definitely avoided.

PMMA belongs to that low number of plastics which under the influence of heat can be transformed into the original monomer. Temperatures must significantly be higher than 300 °C to ensure that PMMA is quantitatively depolymerized.

Processing of PMMA-wastes: The wastes can be seen as pure by type and kind of resin. Smaller quantities of foreign matter practical do not play any role because they will not be depolymerized nor decomposed under the conditions in practice.

Depolymerization starts continously at a certain temperature, the purification lasts only a few minutes. Temperature and purification have a great influence on the quality of the produced monomer.

The monomer formed by the depolymerization of PMMA-waste is regularly contaminated with small amounts low and high boiling substances as well as with water and for this reason it successively needs further processing. From practical experience it has been proved that almost all products made of virgin MMA-monomer can also be manufactured from recycled MMA-monomer. The products have shown nearly the same practical properties as products made of virgin material, so in the case of PMMA a closed material-circle could be realized.

In processes it is very often difficult to avoid a joint grinding, remelting and coextrusion of different types of plastics which cannot be separated by the separation process.

plastic	non-plastic products			plastic products		total consumption
	applicability	(in %)	(in 1000 t)	(in %)	(in 1000 t)	(in 1000 t/a)
PE-LD				100	5548	5548
PE-HD	fibres	2	64	98	3285	3349
PP	fibres	26	1120	74	3183	4303
PVC				100	5095	5095
PS/EPS				100	2235	2235
PET	fibres	59	995	41	696	1691
ABS/SAN				100	487	487
PMMA				100	234	234
Azetal				100	97	97
PC				100	184	184
PA	fibres	61	560	39	353	913
polyacrylonitrile		98	399	2	10	409
others				100	272	272
total		13	3138	87	21679	24817
alkyd resin	coating	100	340			340
amino resin	wood binding agent	57	980	43	725	1705
phenolic resin	coating	57	278	43	209	487
	adhesive					
epoxy resin	coating	76	185	24	60	245
polyester resin	coating	17	83	83	412	495
polyurethane		24	400	76	1275	1675
total		46	2266	54	2681	4947
total		18	5404	82	24360	29764

Consumption according to field of application

packaging	41%
electrical engineering / electronics	12%
agriculture	4%
motor vehicle industry	7%
construction industry	20%
others	16%

Consumption of plastic packaging according to products resp. processing technology

injection-moulded packaging	11,3%
blow moulded packages	21,2%
thermoformed packages	11,2%
films	49,0%
extruded coatings	3,9%
others	1,8%
foamed packages	1,6%

Plastic component in total flow of waste

	origin of waste						
	agriculture	construction industry	origin of domestic waste	trade, industry	motor vehicle industry	electronic s	others
total amount of waste (1000 t)	560 000	230 00	138 556	290 00	12 030	4 090	1 565 324
percentage share - total waste	20	8,2	4,9	10,4	0,4	0,2	55,9
total amount of plastic waste (in							
i 060 t)	636	753	10 928	2636	842	518	0

Reuse of plastic waste according to recycling processes

		1989	1990	1991	1992	1993
amount of waste	(in 1000 t)	11433	13594	14637	15230	16211
material recycling	(in 1000 t)	846	958	1080	1043	915
	(in%)	7,4	7,0	7,4	6,8	5,6
energy recycling	(in 1000 t)	1675	2108	2138	2422	2425
	(in%)	14,7	15,5	14,6	15,9	15,0
total recycled amount of	(in 1000 t)	2521	3066	3218	3465	3340
waste	(in%)	21,1	22,5	22,0	22,7	20,6

Table I: Plastic consumption for the EC in 1992, by polymer

Polymer	Consumption ('000 tonnes)	%
LDPE/LLDPE	5,063	22
HDPE	2,812	12
PP	3,012	13
PVC	4,763	21
PS/EPS	2,160	10
PET	536	2
Other thermoplastics	1,603	7
PU	1,265	6
Other thermosets	1,397	6
Total	22,612	100

<u>Table II</u> Age analysis of post-user plastic wastes generated in Western Europe in 1992 (percentage of all plastic waste arising)

Polymer	Less than 2 years	2-10 years	10-20 years
LDPE/LLDPE	25,9	5,7	1,3
HDPE	9,1	3,8	1,3
PP	6,9	3,9	0,8
PVC	5,8	2,7	2,5
PS/EPS	5,8	3,5	1,0
PET	3,3	0,3	0,0
PU	1,0	3,9	0,8
Other	2,2	6,0	2,4
Total	60,2	29,7	10,1

Table III Packaging and non-packaging consumption and waste arising in the EU in 1992

	Consumption ('000 tonnes)	Waste arising ('000 tonnes)	Waste arising as a percentage of consumption (%)
Packaging	9,010	8,156	91
Non-packaging	13,602	5,610	41
Total	22,612	13,766	61

Table IV: External EC trade in plastics waste, 1992

Category	Imports		Exports	
	tonnes	7000s ECU	tonnes	'000s ECU
Polymers of vinyl chloride	10,422	2,101	56,031	8,782
Polymers of ethylene	18,487	6,141	54,870	8,685
Polymers of propylene	6,090	1,762	5,038	1,963
Polymers of styrene	4,015	1,301	1,808	581
Acrylic polymers	618	410	9,336	3,015
Additional polymerisation products	5,831	3,290	18,934	11,035
Epoxide resins	211	148	409	1,187
Other plastics	27,791	13,547	39,255	20,168
Total	73,465	28,700	185,681	55,416

Table V: Estimate of mecanical recycling of post-user plastic waste by polymer for Western Europe (1992)

Polymer	Percentage of total tonnage recycled	Range of estimates of percentage of tonnage recycled
LDPE/LLDPE	59,0	30-75
HDPE	8,4	2-3
PP	13,6	3-25
PVC	5,0	6-14
PS	4,2	5-7
PET	1,0	1-25
PA	1,3	
Others	7,5	3-11
Total	100,0	

Factors affecting the economic viability of recycling

Recycled plastics must compete on price and quality with virgin polymers if these are to be used to manufacture the same products. The costs of reprocessing plastic wastes are essentially fixed, so that any change in the price of virgin polymers directly affects the price of recycled plastics which is in turn reflected in the price paid for recyclable plastics.

Recycled plastics may have to be sold at a lower price than virgin equivalents, in order to compensate for any increase in production costs arising from the use of recycled plastic, for example as a result of slower machine running speeds or thicker product wall sections.

The low bulk density of plastic wastes causes the collection and transport costs for plastic wastes to be high relative to other recyclable materials. This fact, together with the high costs of processing and reprocessing, can make plastic waste recycling unviable unless the costs of disposing of the plastic wastes by landfill or incineration, are equally high.

The economic viability of mixed plastic recycling to produce wood-substitute materials is marginal, since the manufactured products compete with relatively low cost alternatives (wood). The main advantage that such material offers in comparison with wood is its claimed long-term durability. However, it has yet to be proven that the anticipated longer life, justifies the higher initial cost.

The markets for recyclable plastics are limited by the available reprocessing capacity and by the required quality of the recycled polymer. Recycled plastics cannot compete in all virgin polymer applications, for example for hygiene reasons, recycled plastics are not used in food-contact applications (unless they are enclosed within a virgin polymer coating), except in a few specific cases such as the recent introduction by a soft drinks manufacturer of recycled PET bottles in Belgium. The re-use of plastics food packaging and the use of recycled plastics for food contact applications is a subject of debate and is currently being studied.

New production techniques have been developed to make use of recycled plastic, for example multi-layer bottle blowing, which encloses the recycled plastic within an inner and outer layer of virgin polymer. Existing production equipment may also need to be adjusted or even modified in order to use recycled plastic.

Unless recyclable plastic material is colour sorted prior to reprocessing, the resulting recycled plastic can have an unattractive colour, such as grey or green. Some reprocessors do colour sort bottles prior to reprocessing and can then produce a range of colours of recycled material. The colour of the recycled plastic can limit the markets for its use, for example, much recycled plastic is used in grey or black coloured applications, such as street furniture or piping. This colour limitation can result in recycled plastics being used primarily in lower grade and hence, lower value applications.

The only legislation which has affected the recycling of post-use plastics is that of national legislation relating to packaging recovery. Such legislation, which has been independently introduced by a number of States, notably Austria, Germany, France, Denmark and Belgium (with similar voluntary agreements in the Netherlands and Italy), has set targets for the levels of plastic recycling, which in all cases has led to an increase in plastic recycling. The draft EC Directive on Packaging and Packaging Waste will have a similar effect.

Possible environmental problems caused by recycling

The two primary environmental impacts of plastics recycling are those resulting from an increased use to transport compared with localised disposal, and waterborne effluent from the washing stages of the reprocessing operations.

Plastics have a low bulk density, so that the transportation of a given weight of plastics will have a greater environmental impact than for other recyclable materials. Given the automated nature of plastics reprocessing plants, there is a minimum economic capacity to such plants which is estimated to be in the range 10,000 - 15,000 tonnes per annum. The collection of such a tonnage of plastic recyclable material will have to take place over a considerable catchment area, with resultant transport implications.

The impact of the effluent arising from the washing of recyclable plastic material during reprocessing, is dependant first on the original contents of the plastic containers and secondly on the quality of the effluent treatment plant. With regard to the first issue, some reprocessing plants do not add detergents during the washing process, since there are sufficient detergent recidues in the material being reprocessed (this is primarily the case with plastic bottles). The collection of plastic containers which have been used for product categories such as pesticides or other hazardous household products are discouraged in some collection schemes, to minimise the contamination of the washing effluent and since there is concern that the recycled plastic could contain traces of the original product.

The development of appropriate standards and specifications and the need for harmonisation

The standards and specifications for recycled plastics are set by the reprocessors in order to compete with the virgin alternatives. The reprocessors therefore also set the standards for recyclable material in order that they can achieve the required recycled plastic standards.

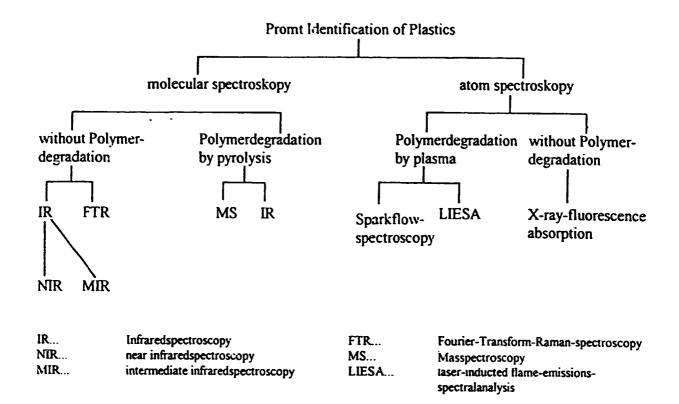
Since the collection and reprocessing of post-use plastics is a relatively local activity (the long distance transport of recyclable plastics is unusual due to the costs involved), there seems to be no need for harmonised standards yet.

The one international standard which has already been referred to is the standard on plastics identification.

References:

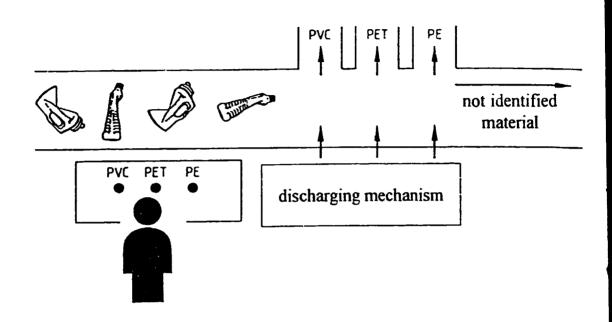
- [1.] Die Wiederverwertung von Kunststoffen; Brandrup/Bittner/Michaelis/Menges Hanser-Verlag 1995
- [2.] Siemens AG Anlagentechnik, BottleSort technische Dienstleistung, Langen
- [3] Recyclingpraxis Kunststoffe, Tiltmann Verlag TÜV Reinland
- [4.] Kunststoffrecycling in Westeuropa, Chapelle, Brüssel/Belgien; Kunststoffe 85 (1995)10, Carl Hanser Verlag, München
- [5.] An Analysis of the Current Situation and Prospects for the Development of Recycling Nov. 1994, Anfor/Paris

Figure 1:



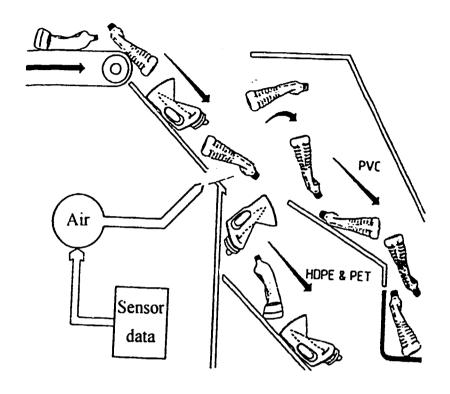
taken from Keith Engstrom "Die Wiederverwertung von Kunststoffen" [1]

Figure 2: semiautomatic bottle sorting



taken from Keith Engstrom "Die Wiederverwertung von Kunststoffen" [1]

Figure 3: automatic bottle sorting



taken from Keith Engstrom "Die Wiederverwertung von Kunststoffen" [1]

Figure 4:
Schematic presentation of the **BottleSort** sequence of operation

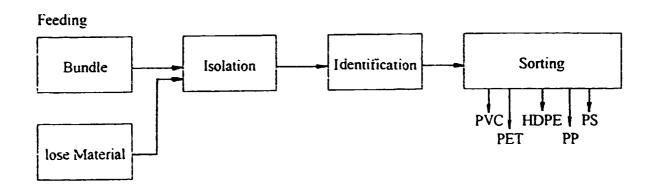
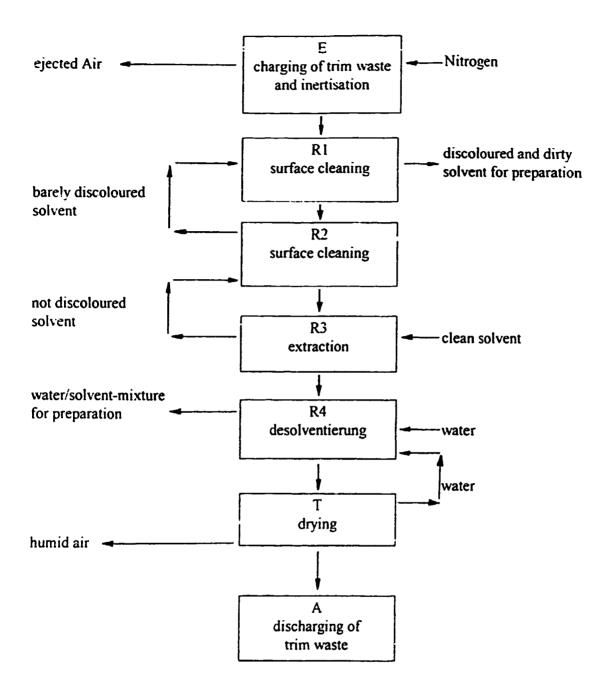


Figure 5



taken from H. P. Walter "Die Wiederverwertung von Kunststoffen" [1]

Figure 6

heavy-liquid separation [3]

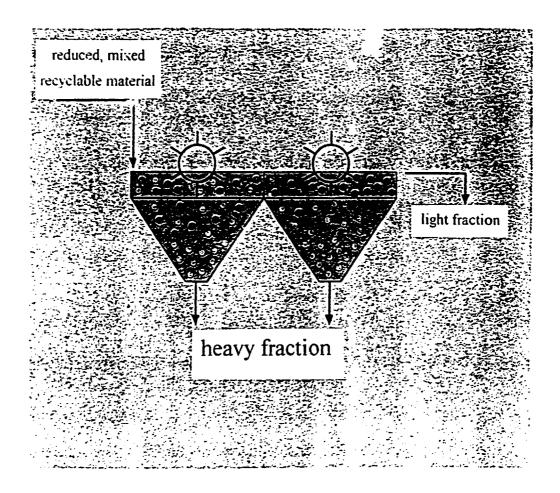


Figure 7
Hydrocyclone [3]

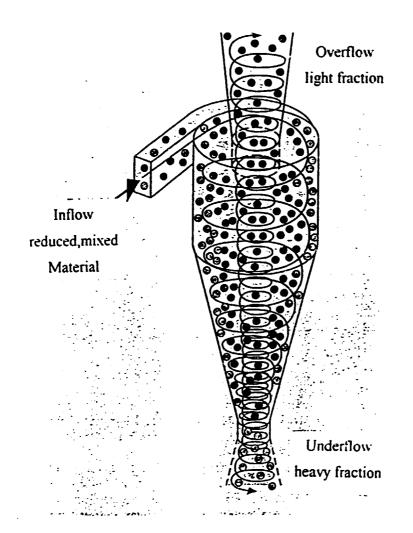
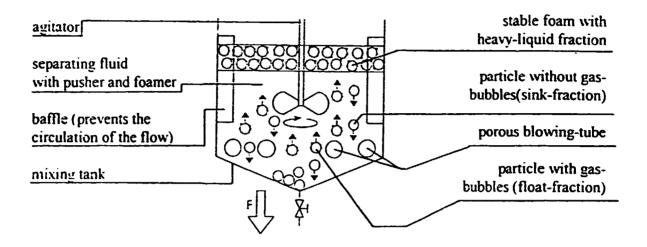


Figure 8 schematic diagram of a flotation plant



taken from W. Michaeli, M. Bittner "Die Wiederverwertung von Kunststoffen" [1]

Figure 9
fluid bed pyrolysis[3]

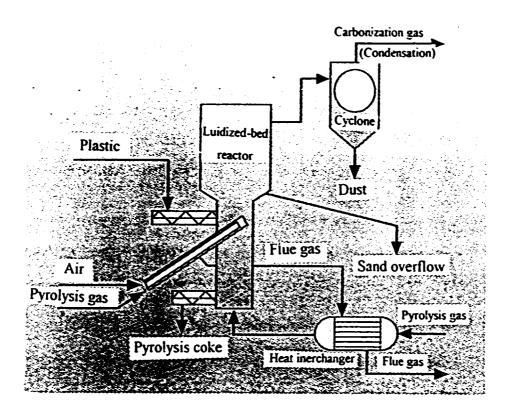


Figure 10
Polymer hydrogenation [3]

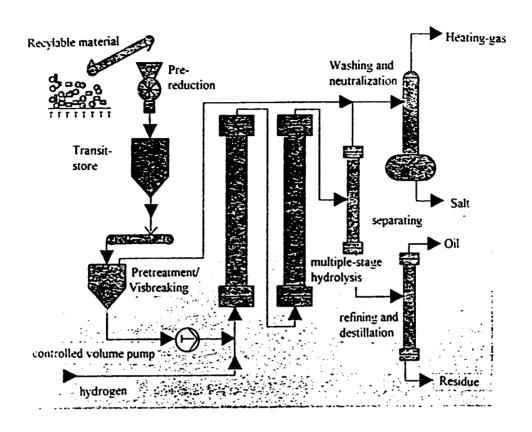


Figure 11
Shell-process for gasification of heavy oil [3]

