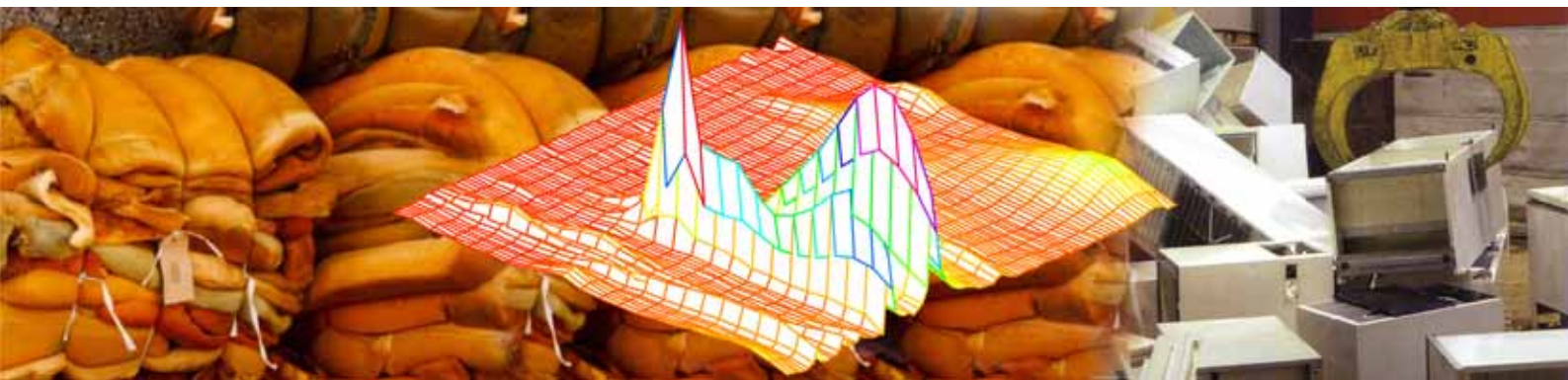


TREATMENT AND DISPOSAL OF POLYURETHANE WASTES: OPTIONS FOR RECOVERY AND RECYCLING

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[52] (left), [23] (center), [49] (right)

Preface

Polyurethane (PU) wastes from end-of-life vehicles, scrapped refrigerators, district heating tubes and many other sources are receiving increased attention worldwide as a result of rapidly rising amounts and increasingly tight legislation on its treatment and disposal. Also in Finland recycling and recovery methods for these materials, which can be mainly either in flexible foam, rigid foam or elastomer form, must be further developed and taken into use. Special features for Finland are, for example, an extended district heating system, a powerful system for the collection of scrapped refrigerators and, in comparison with the numbers of end-of-life vehicles that are being disposed of, a small car industry. Other specific problems or issues are:

- for PU foams, the presence of CFC (chlorofluorocarbon)- type gases in the material makes processing more complicated,
- thermal processing, including combustion, of PU poses the risk of formation of nitrogen oxides (NO_x, N₂O), ammonia, pyridines and other hazardous or toxic nitrogen compounds as a result of the high nitrogen content of the material,
- there is little information as to the behaviour of PU on landfills,
- market potential for recovered and recycled PU must be identified and developed,
- the latest EU legislation, for example on end-of-life vehicle treatment, or landfill disposal of wastes, has to be taken into consideration.

This aim of this work is to make an overview of the volumes of different PU waste streams in Finland, the methods currently in use for the treatment and disposal of these wastes and the options Finland has to control and process these waste streams in the future, in compliance with local and global legislation.

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Finnish summary

Polyuretaani (PU)-jätteen käsittely ja loppusijoitus: kierrätys ja talteenottomahdollisuudet

Romutetuista autoista, vanhoista jääkaapeista, kaukolämpöputkista ja muista vastaavista lähteistä tulevan polyuretaanijätteen kohtalo on alkanut kiinnostaa maailmanlaajuisesti, koska sen käsittelyyn ja hävitykseen liittyvät säädökset tiukentuvat jatkuvasti. Tämän takia myös Suomen täytyy kehittää ja ottaa käyttöön kierrätys- ja talteenottomenetelmiä näille materiaaleille, eli PU-vaahdoille ja koville polyuretaaneille.

Suomelle ominaisia piirteitä ovat mm. laaja kaukolämmitysverkosto, tehokas vanhojen kylmälaitteiden talteenottojärjestelmä ja romuautojen suuri määrä verrattuna pieneen autoteollisuuteen. Erityisen ongelmallisia ovat esim. PU-vaahtojen korkeat CFC-pitoisuudet (ponneaineena), NO_x:in ja N₂O:n muodostumisriski termisissä käsittelyprosesseissa PU:n korkean typpipitoisuuden takia ja tiedon puute jätteen käsittelypaikoilla. Tämän lisäksi talteenotetun ja kierrätettävän PU:n kaupalliset mahdollisuudet tulee selvittää huomioiden uusimmat asiaa käsittelevät EU-säädökset.

Tämän työn tavoite on selvittää Suomen polyuretaanijätevirtojen suuruudet, tämän hetkiset käsittely- ja hävitysmenetelmät sekä Suomen mahdollisuudet näiden jätevirtojen hallintaan tulevaisuudessa, kansallisten ja kansainvälisten lakien ja määräysten mukaisesti.

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1. Introduction

1.1 What is polyurethane ?

Polyurethanes (PUs) are polymers invented in Germany during the 1930s, as a result of research efforts to develop polymeric fibre material similar to but different from polyamid (nylon) fibres, discovered earlier but protected by US patents [1]. PUs are produced by reacting di-isocyanates with di-ols via the reaction $R-NCO + OH-R' \rightarrow R-NH-CO-O-R'$. They cannot be melted or converted into a single monomer by, for example heat-up, instead their thermal degradation will give a mixture of products. **Figure 1.1** gives the typical PU structure; the urethane bond from which the material derives its name is shown in **Figure 1.2**.

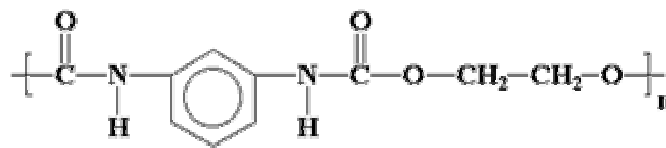


Figure 1.1 Chemical structure of a typical polyurethane [2]

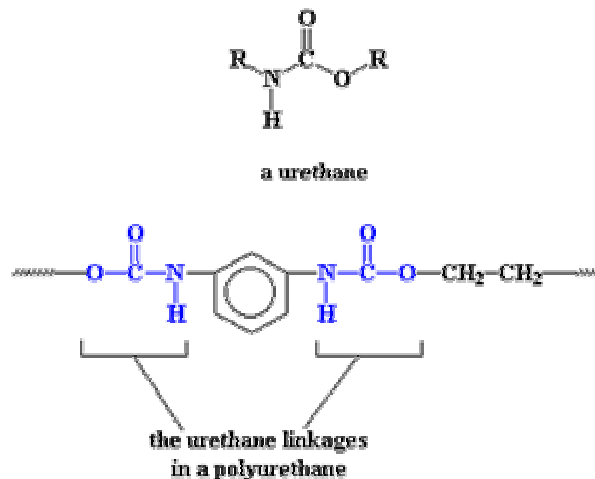


Figure 1.2 Urethane bonds in polyurethane [2]

Commercial polyurethanes are composed of segments with the structure $-(O-R'-O)-(CO-NH-R-NH-CO)-(O-R''-O)-(CO-NH-R-NH-CO)-$, with organic groups R, R', R''. They can be composed from 1) a di-isocyanate $OCN-R-NCO$ like MDI (diphenylmethane diisocyanate) or TDI (toluene diisocyanate), 2) a polyol (or polyether) or polyester $HO-R'-OH$ such as polypropylene glycol (PPG) or polytetramethylene glycol (PTMG), or polycaprolactone (PCL) or polybutylene adipate (PBA), and 3) small-molecule chain extenders $(OH-R''-OH)$ like 1,4-butanediol (BDO) or 1,6-hexanediol (HDO), linking diisocyanates in "hard segments" [3]. Szycher's Handbook gives extensive discussions on isocyanates, polyols and chain extenders [1, chapters 4, 5 and 6].

It is obvious that since the organic chemistry of isocyanates, polyols and polyesters allows for almost endless chemical processing routes, numerous different materials may be synthesised that will fall under the definition “polyurethane”, *i.e.* containing repeated carbamate linkages as shown in **Figure 1.2**. Besides these urethane linkages, PU structure may for an important be defined by for example ether-, urea- or amide- linkages. As a result, “polyurethane” stands for a product range or plastics industry segment rather than for a single, well-defined polymer resin such as for example polyvinyl chloride, and the range of application of the different PU materials is extensive. A classification can be made based on density and hardness, as shown in **Figure 1.3**.

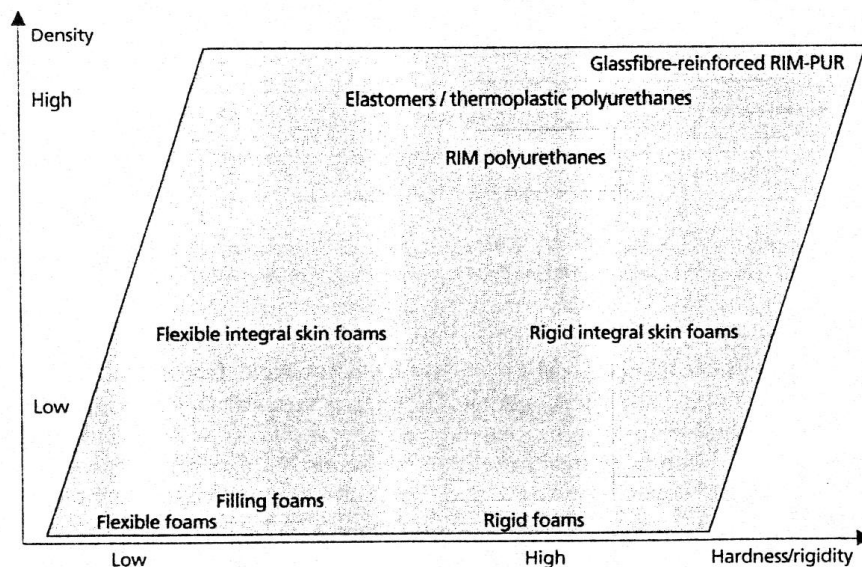


Figure 1.3 Properties of various polyurethanes (density 20-1300 kg/m³) [4]

Rigid and flexible foams represent, besides the rubber-like elastomers and RIM (reaction injection moulding) products, by far the largest market (more than 75 % in mid-1990s USA, [1].) Producing PU foam is relatively straightforward and can be accomplished by adding water. This will result a larger amount of urea -(NH-CO-NH)- linkages in the polymer chain plus the release of CO₂ gas, which is trapped as bubbles [2]. Using water alone, however, won't result in satisfactory product quality or durability for most applications. Low-boiling organic liquids were found to produce better results, with the additional benefit (found when developing rigid PU foam boards) of improving the insulating properties of the foam. Soon chlorofluorocarbons (CFCs) such as CFC-11 (CCl₃F) were widely used since these are non-toxic, non-flammable, stable, cheap, effective, well soluble in isocyanate and polyols but not in the PU, and give excellent thermal insulation performance (see also section 1.4) [1]. For a typical refrigerator or freezer the energy saved by using PU as insulator is a fraction of the energy needed to produce that PU.

Rigid and flexible PU foams, in short PUR and PUF foams can be distinguished, which depends on whether the cell structure is “open” or “closed”. In PUR foams only a few % of

the cells is open and bulk densities are typically 30-35 kg/m³. The blowing agent gas contained in the cells results in a very low thermal conductivity, and the main use of PUR foams is in insulating boards, refrigerators and freezers. A cross-section of a commercial PUR foam is given in **Figure 1.4**. Flexible PU foams have a virtually completely open cell structure with typical densities 20-45 kg/m³ and are thus not good good insulators; these materials are mainly found in mattresses, furniture and seats in automobiles. Around year 1990, the ratio of usage of PUR and PUF foam was of the order 1:3 [5].

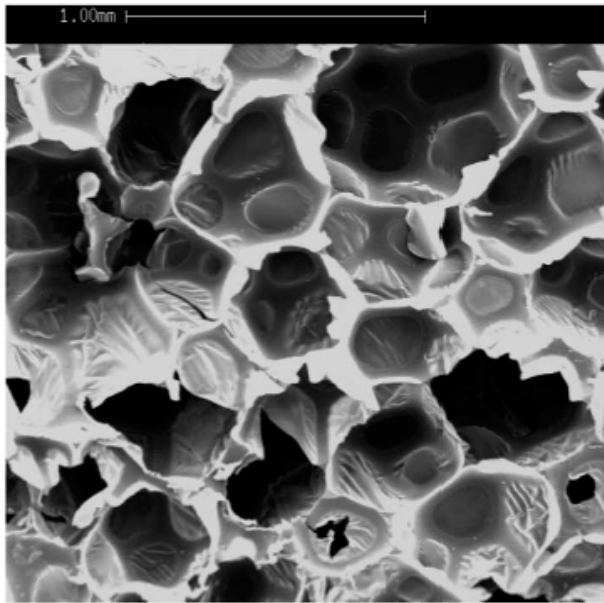


Figure 1.4 Scanning electron microscope (SEM) photo of commercial rigid PU foam with density 38 kg/m³ used in refrigerators *etc.* [6]

1.2 Polyurethane foams and the ozone layer

The use of CFC's was recognised during the 1970s to be a major cause for the depletion of tropospheric ozone by interfering with ozone formation/destruction mechanisms, and CFC-11 became the reference ozone depleting substance (ODS), with ozone depleting potential (ODP) = 1 (by definition). A range of ODS compounds were recognised besides the CFCs, such as CCl₄, CO, CH₄, NO and halons (for example halon-1211 = CF₂ClBr, halon-1301 = CF₃Br) used in fire extinguishers. ODSs are nowadays classified in two classes (class I and less harmful class II). The production and use of most CFCs were to being phased out by year 1996 under the 1987 Montreal protocol, resulting in a shift to less harmful fluorocarbons such as hydrofluorocarbons (HFCs) and perfluorocarbons (PFCs). Unfortunately, these appear to be rather potent greenhouse gases [7].

Due to all this there is a lot of activity in the area of PU foam blowing agents, but more importantly for this work the processing PU waste streams, especially those containing PU foams involves not only the "standard" features of recovery and recycling but deals also with handling ozone depleting species. An urgent example is a 30-year old refrigerator that contains 5-10 kg rigid PU foam, including around 500 g CFC-11 [8]. The handling of PU

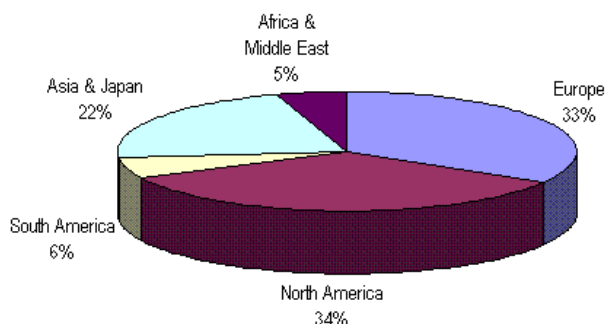


Figure 1.5 Worldwide PU consumption by region in year 2000 [13].

Important are also the world-wide distribution of isocyanate and polyether/ polyol production capacity. The four major PU types are made from either polyester polyol or polyether polyol, reacted with either MDI (diphenylmethanediisocyanate) or TDI (toluenediisocyanate). Consumption data and forecasts for these are given in **Table 1.2** [13].

Table 1.2 Worldwide PU consumption quantities (thousand tonnes) [13]

	Polyether polyol	Polyester polyol	MDI	TDI	Total
2000	3465	1180	2370	1441	8460
2002	3880	1330	2650	1610	9470
2004	4350	1490	2970	1800	10610

For Europe, PU consumption values of around 3 Mt/yr are reported for the early 21st century, composed of ~1.8 Mt PUF foam, ~0.7 Mt PUR foam and ~0.5 Mt of this as elastomer, RIM and other PU products [15,16,17].

Data for Finland are scarce in the public information domain, but with 1/3 of the world's PU production to Europe and Finland's economy representing 3-4 % of the EU-25 economy a PU consumption of 100 kt (1 kt = 1000 tonnes) PU can be estimated. This can be further subdivided into 60 kt PU foam, 24 kt PUR foam and 16 kt other PU products based on average values for worldwide PU consumption. Since Finland has some polymer industry (Borealis polymers Oy, Urepol Oy, and many others) the numbers will probably somewhat higher, although on the other hand Finland does not have a large automobile industry nor oil/gas reserves. These estimates can be compared with an annual sale of 200000 refrigerators/freezers in Finland, with each ~10 kg PUR foam [8], which gives 20 kt PUR foam, and the renewal of 30 km of district heating tubes annually which gives 0.2 kt PUR foam waste. Also, an annual 25000 – 30000 tonnes of automotive shredder residue (ASR) from end-of-life vehicle processing in Finland [18], with a PU content of ~15 %, , mainly PUF foam, gives a 4 - 5 kt of PUF foam that almost completely ends up on landfills.

1.4 Properties of polyurethane

Several physical and chemical properties of PU materials are listed in **Tables 1.3 and 1.4**.

Table 1.3 Physical properties of PU materials

Property	Value	Type of PU	Reference
Density	20 kg/m ³	PUR foam	19
	24.6 kg/m ³	PUR foam CFC-11 13.9 %	20
	39.0 kg/m ³	PUR foam HFC-134a 7.1 %	20
	32.2 kg/m ³	PUR foam HCFC-141b 11.7 %	20
	30.7 kg/m ³	PUR foam HFC-245fa 11.9 %	20
	1120–1240 kg/m ³	PUR elastomer	1
Specific heat	1400 J/kg K	PUR foam	19
Heat conductivity	0.034 W/mK	PUR foam	19
	0.25-0.33 W/mK	PU elastomer	1
Flash ignition temperature	310 °C	Rigid foam	19, 5
Auto ignition temperature	415 °C	Rigid foam	19, 5
Lower heating value	27.0 MJ/kg	PU – based adhesive	21
	27.0 MJ/kg	PUF foam	22,23,24
Melting point	204 – 232°C	PU elastomer	1

Table 1.4 Chemical properties of PU materials

Property	Value	Type of PU	Reference
C, H, N S, O + ash (diff.)	63.9, 8.3, 1.6 %-wt 0, 26.2 %-wt	PU – based adhesive	21
C, H, N (dry) S, O, Cl (dry)	63.2, 6.7, 6.6 %-wt 0.01, 13.5, 9.6 %-wt	PUF foam	22,23,24
Moisture (as received) Volatiles (dry) Ash (dry) Fixed carbon (diff.) (dry)	1.8 %-wt 88.2 %-wt 11.5 %-wt 0.3 %-wt	PUF foam	22,23,24
S, Cl, F	< 0.1, < 0.3, 0 %-wt	PUF foam	25
	< 0.1, 1.5-13, 0.3-1.5 %-wt	PUR foam	
	0, < 0.1, 0 %-wt	RIM PU	
Hg, Cd + Tl, SbSn*	0, 0, 0 mg/kg	PUF foam	25
	0, 0, 10-250 mg/kg	PUR foam	
	0, 0, 250 mg/kg	RIM PU	

* Sb+As+Pb+Cr+Co+Cu+Mn+Ni+V+Sn

One major feature of PU (especially PUR) foams is the low heat conductivity: for the blowing agent CFC-11 that is around 1/3 of that of air. About 50 % of the heat is transferred through PU foam via the gas that is trapped in the closed-cell structure, at a total thermal conductivity of around 0.035 W/m.K at ambient conditions [26]. An analysis of a 374 kg/m³ PU foam over the range 30–200°C resulted in polynomes *versus* temperature T (°C): effective conductivity $\lambda_{\text{eff}} = 0.0444 + 0.000288 \times T$ (W/m.K) and specific heat $c_p = 308 + 4.41 \times T$ (kJ/kg.K) [27].

In a study for European industry, Brunner *et al.* [28] made a characterisation of end-of-life automobile seat foams, analysing around 8000 kg of old PU foam from France, Italy and the Netherlands. The information on composition and quality of the material would be used to find the “most eco-efficient treatment method”, *i.e.* strategies for recovery and recycling. The results are summarised in **Table 1.5**. Relatively high are the levels of tin, zinc and antimony (Sn, Zn, Sb); the chlorine (and then also the antimony) may be related to a flame retardant, for example an haloalkyl phosphate. Low moisture content prevents bacterial growth; the presence of metals will result in higher processing costs and risk of equipment damage. For a low PCB content it is crucial to avoid contact with automotive shredder residue (ASR).

Table 1.5 Properties of old car seat foam polyurethane in year 2000 [28]

Average seat foam mass per car	~7.7 kg
Contamination	1/3 slightly contaminated, 3 % heavily soiled
Decoloration	85 % only slightly decolorated
Non- PU plastics used	in 1 -2 %
Rebonded PU foam used	in 4 - 5 %
Moisture content	1 – 2 %-wt
Calorific value (LHV)	25600 kJ/kg
Ash content (dry)	0.92 %-wt
Metal content (dry)	~1.4 % wt
Halogen content Cl ; F ; Br (dry)	1142 ; < 30 ; < 29 mg/kg
Fe ; Al ; Zn (dry)	323 ; 897 ; 50 mg/kg
Hg ; Cd, Tl (dry)	< 0.1 * ; < 1.1 * ; < 0.4 * mg/kg
Sn ; Sb ; As (dry)	168 ; < 14.4 ; < 2 * mg/kg
Pb ; Cr ; Co ; Cu ; Mn ; Ni ; V (dry)	< 9.4 ; 13.5 ; < 1* ; < 8.2 ; 5.3 ; 7.4 ; < 1* mg/kg
Dioxins/furans PCDD/Fs (dry)	0.002 – 0.005 ppb
PCB (dry)	< 0.01 * mg/kg

* = detection limit

1.5. Thermal degradation of polyurethane

The thermal degradation of PU foams and elastomers has been studied extensively since the 1950's, with inevitable scatter and inconsistencies in the reported results due to a wide range of PU types and products. Factors of importance are the isocyanate, polyol and chain extender used to produce the PU, since the different linkages in the polymer chain have different thermal dissociation temperatures, as illustrated in **Table 1.6**. Depending on the PU considered and the analysis method used (typically at atmospheric pressure), thermal degradation of PU has been reported to start in the temperature range 110-270°C.

Table 1.6 Thermal dissociation temperature ranges for linkages in PU [1]

Linkage		Onset of dissociation, °C
Allophanate	aliphatic/aromatic	85-105 / 100-120
Biuret	aliphatic/aromatic	100-110 / 115-125
Urea	aliphatic/aromatic	140-180 / 160-200
Urethane	aliphatic/aromatic	160-180 / 180-200
Disubstituted urea		235-250

Cullis and Hirschler [29] give the mechanism thermal degradation shown in **Figure 1.6a**, which involves three routes for the cleavage of PU linkages at 200-300°C. The first route is basically the return reaction from the PU to the original isocyanate and polyol. Depending on processing conditions, the polyol as well as the isocyanate can be recovered, but under certain conditions the isocyanate can be converted to diamines. Ravey and Pearce [30] for example, pyrolysed a PU foam based on toluene di-isocyanate (TDI) which can be recovered, unless it is rapidly removed from the reaction zone. When confined in the reaction zone for a longer

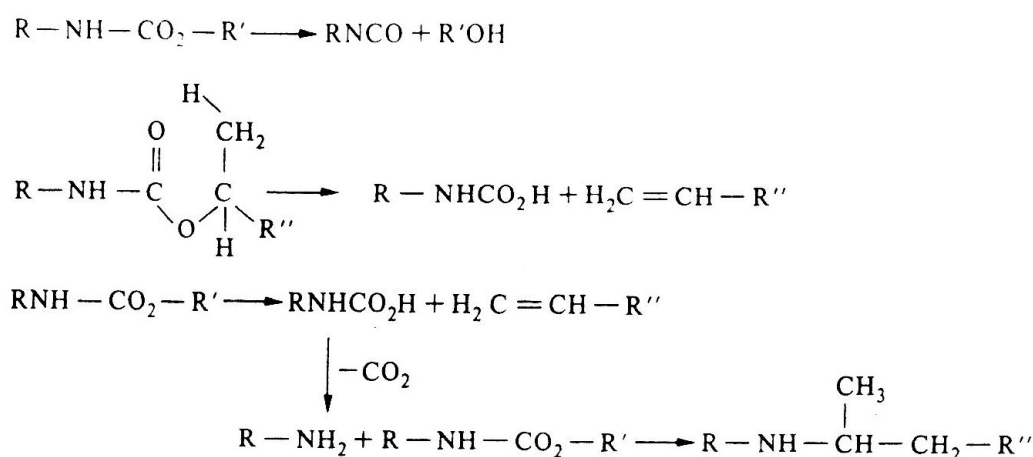
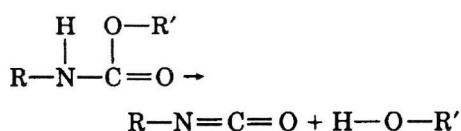


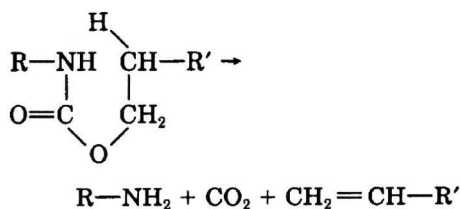
Figure 1.6a PU thermal degradation scheme according to three reactions [29]:
 - dissociation into isocyanate and alcohol
 - dissociation into carbamic acid and olefin
 - dissociation of carbamic acid into CO₂ and secondary amine

time the formation of diamino toluene (DAT) sets in, via the second and third route in **Figure 1.6a**. This would explain why many other studies report high polyol recovery while recovering only a fraction of the isocyanate. Furthermore, it was reported that the TDI and DAT recombine in the gas phase to form a polyurea aerosol, visible as “yellow smoke” also observed during other studies. Heat-up to 360°C yielded (when formation of DAT and CO₂ was avoided) vapours of TDI corresponding to ~33 %-wt of the initial PU mass and about 96 % of initial PU nitrogen. The condensed residue was a dark yellow/light brown viscous liquid that contained around 0.35 %-wt nitrogen, which is mainly recoverable polyol, and a small amount of dark brown/black solid with a nitrogen content of 11-15 %-wt. In this important study a somewhat different three-reaction pathway is given as in **Figure 1.6b**, very similar to the one given above, with the remark that no indications of the third pathway were found in the experimental work [30]:

- 1) Depolymerization; that is, dissociation to the precursors, the isocyanate and the alcohol, the reverse of the following formation reaction:



- 2) Dissociation to a primary amine, an olefin, and CO₂ via a putative six-membered ring transition state, as follows:



- 3) Extrusion of CO₂ leading to the replacement of the urethane link by a secondary amine group. A four-membered ring transition state was postulated.

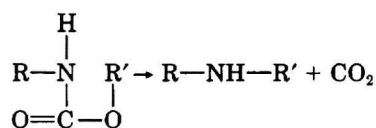


Figure 1.6b PU thermal degradation scheme according to three reactions [30]

Similarly, low temperature (250-350°C) PU “glass tube pyrolysis” studies by Lattimer *et al.* [3,31], using matrix-assisted laser desorption/ionisation mass spectroscopy (MALDI-MS) for pyrolysis residue analysis, confirm that at temperatures >300 °C nitrogen is no longer present in the pyrolyzate oligomers. It was concluded that at temperatures < 300°C depolymerisation (mechanism 1 above) and cyclic pyrolyzate oligomer formation occurs, both of pure polyester and urethane polyester. At higher temperatures (> 300°C) the linear and cyclic polyester pyrolyzates are dehydrated, giving unsaturated olefinic end groups, without, however, any formation of the primary or secondary amine products (as in mechanisms 2 and 3 above). In the second study [31] some evidence of primary amine formation was however found (mechanism 2).

Thermogravimetric (TGA) studies on PUF foam were conducted by Bilbao *et al.* [32], aiming at determining degradation kinetics parameters. The results are shown in **Figures 1.7a** and **1.7b** for nitrogen or air as gas atmosphere at 200-500°C, 1 bar, heat-up 5 K/min). Clearly a two-step degradation to a mass loss of 90 % below ~400°C is seen. Kinetics parameters are reported, which are strongly dependent on temperature and gas atmosphere (the assumption of first-order kinetics seems invalid): in nitrogen 28800 J/mol for 200-240°C, 63300 J/mol for 240-282 °C, and 180900 J/mol for 315-393°C; in air 97700 J/mol for 230-300°C. In air the decomposition is significantly faster than in nitrogen [32, 29].

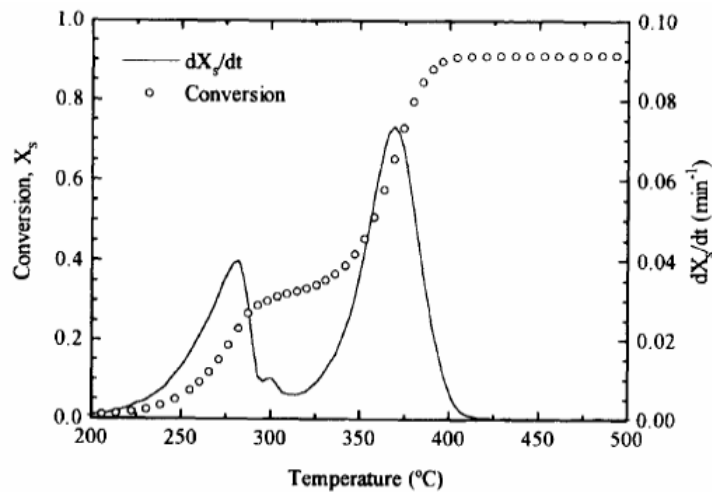


Figure 1.7a Mass loss of a PU foam during heat-up (5 K/min) in N₂ [32]

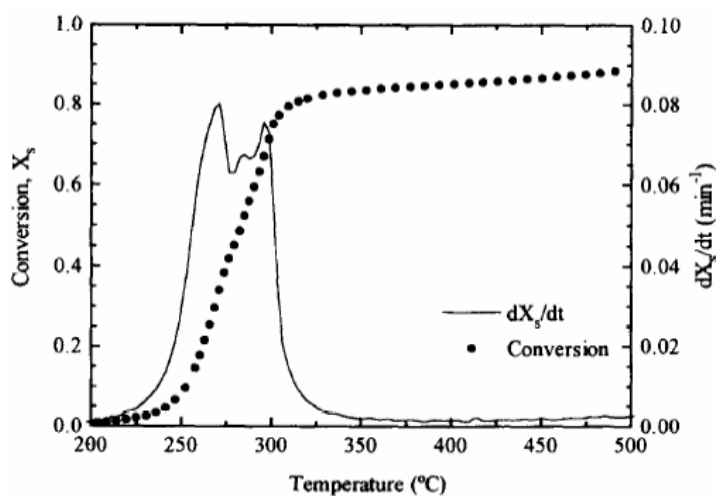


Figure 1.7b Mass loss of a PU foam during heat-up (5 K/min) in air [32]

More recently PUR foam degradation in air was analysed by TGA by Branca *et al.* [6]. Results from that study showed that depending on heating rate (5-20 K/min) degradation started at 165-205°C and gave three peaks, at 205-230°C, 320-360°C and 540-590°C, respectively, corresponding to releasing around 8 %, 38% and 50% of the sample mass, with estimated activation energies 134 kJ/mol, 81 kJ/mol and 180 kJ/mol for the three peaks. A transition from flaming combustion (peak 2) to smouldering combustion (peak 3) was seen.

Due to their high surface-to-mass ratio PU foams often pyrolyse instantaneously, especially when in contact with air or oxygen. The low thermal conductivity of rigid PU foams results in accumulation of heat on the particle surface [5].

A Finnish study on the behaviour of nitrogen from polymers and plastics in waste-derived fuels during combustion included a PUF foam as well [22,23,24]. A thermo-chromatographic (ThGC) analysis of the PU (which is a temperature resolved, multi-injection gas chromatography technique, heat-up rate 10 K/min, at 200-550°C) showed that the material decomposed via a two-step mechanism as illustrated by **Figure 1.8**, in agreement with **Figures 1.7**.

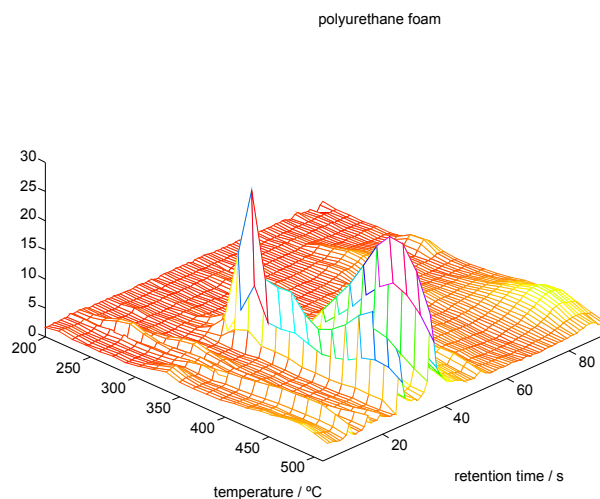


Figure 1.8

Thermo-chromatography mesh plot for a PUF foam [23,24]

Also, flash pyrolysis (heat-up to 700°C in a few microseconds over a platinum filament) combined with GC/mass spectroscopy (Py/GCMS) was made which gave the decomposition products CH₃, CN, HCNO and CO₂/N₂O [23]. Pyrolysis of the PUF in nitrogen in an entrained gas quartz tube reactor at 750-950°C, heating rate ~1000 K/s, resulted in 10-15 %-wt of the PUF as char, for which the fractions of PU fuel remaining in the char were (at 850°C) 15 % for C, 2% for H, 6 % for O and 16 % for N [23]. The amount of char and its nitrogen content are of great importance to emissions of NO and other nitrogen oxides during combustion (see section 3.5).

As to be behaviour at somewhat higher temperatures, say, above 500°C, it was found that weight loss from PU is complete in air at ~725 °C (1000 K), compared to slow decomposition up to almost 1000°C (1250 K) in nitrogen. The main products under those conditions are CO, HCN and nitrogen oxides (NO, NO₂, ...), with HCN release showing a maximum at ~525°C (800 K), depending on the PU type [29].

Toxic products from combustion and pyrolysis of PU materials are, besides HCN and CO, nitrogen oxides, benzonitril and other nitrils and (from aromatic foams) TDI. Besides this the flame retardants (see next section) may produce acidic gaseous, dioxins/furans, highly toxic bicyclic phosphate esters or toxic zinc ferrocyanide (used as smoke suppressant in PU and other polymers) [29,33,34].

1.6. Flame retarded polyurethane

The resistance of polymeric materials such as polyurethane against thermal degradation can be improved by adding flame retardants. These interfere with the thermal decomposition of the material (resulting in enhanced charring or carbonisation), and/or interfere with the flame chemistry (*i.e.* the gas phase radical pool). Although this eventually won't prevent full combustion it will provide valuable delay time during which the fire may be extinguished.

Flame retardants are often based on chlorine or bromine compounds, which upon sufficient heat-up produce Cl and Br radicals in the gas phase that interfere with the combustion chemistry in the gas phase. Better performance is found when also antimony oxide Sb_2O_3 , is added. For PU foam, Elomaa [19] gives typical values of 18-20 %-wt Cl or 12-20 %-wt Br, which change to 4 % + 4 % Cl + Sb_2O_3 , or 1.5 % + 2.5 % Br + Sb_2O_3 . The use of the very powerful and successful brominated flame retardants (BFRs) [34] is being reduced for environmental and health reasons, and flame retardants based on (organo-) phosphorus or nitrogen are alternatives. Cullis and Hirschler [29] mention that the thermal stability of polyurethanes is “considerably increased” when phosphorus is part of the structure of the polyol used.

PU foams are often flame-retarded using phosphate polyols, which contain ~10 %-wt phosphorus. The open cell structure of PUF foams makes flame retardation difficult, and increasing the tendency of the foam to char is an important effect. For PUR foams additive flame retardants are used. An overview is given in [5, Chapter 5]. Work on the synthesis and characterisation of a phosphorus-containing PU (PU-P) showed that the starting temperature for thermal degradation shifts to a somewhat higher temperature (270 → 288°C) and char yields at 700 °C increase as well (35 → 48 %), for 2 %-wt phosphorus PU, based on a thermogravimetric analysis in air. LOI increased from 23.0 to 24.3 [35]. Detailed studies by Ravey *et al.* [36,37,38] on haloalkyl phosphates and phosphoric acid as flame retardant for flexible PU foam suggests that the decomposition products from the haloalkyl phosphate dilute the “fuel” vapors rather than interfere with the radical pool. During the first stages of PU thermal degradation, flame temperature is apparently too low for the latter.

The emission of smoke from PUs can be reduced by increasing the crosslinking of the material, using cyanurate structures (increasing its charring tendency instead), or introduce smoke suppressants into the polymer structure, for example alcohols such as furfuryl alcohol [5, Chapter 6].

2. Polyurethane (in) waste streams

2.1 Polyurethane waste stream amounts

Of a current world production of 9 Mt/yr PU materials, around 1/3 is consumed in Europe, roughly distributed over PU foams and other products as in **Figure 2.1**.

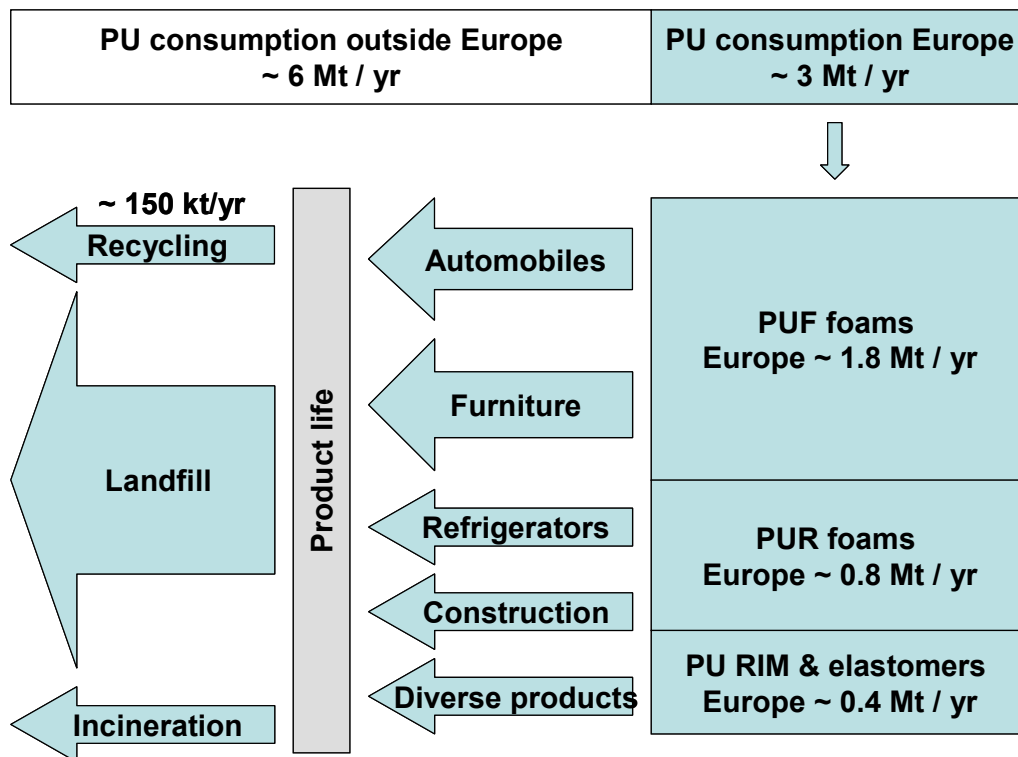


Figure 2.1 PU products consumption in Europe and post-consumer disposal

During the mid-1990s European PU recycling involved a mass flow of ~100000 t/yr in Western Europe, including an export of ~60000 t/yr to North America (see section 3.1). Around 25000 t PUF foam was recycled by regrinding, 4000 t PU by adhesive pressing, 2000 t PU by glycolysis and 1000 t PU by regrind/powdering in 1995, besides 9000 t PU disposal by energy recovery. (Chapter 3 gives more detail on these methods). Most of the PUF foam scrap that is processed is from end-of-life vehicle seats. Compared with a PU consumption of ~2 Mt in Europe at that time, this shows a degree of recycling/recovery (including energy recovery) of 2 % in Western Europe plus an export to North America of 3 % [39]. Despite much R&D efforts and initiatives from PU producers, PU users and the waste processing sector the recycling and recovery of plastics materials, especially plastics commingled with other wastes and contaminants is still very marginal. The fraction of PU that is landfilled is nowadays still around 90 % of all PU materials found in waste streams, with incineration and recovery/recycling together making up the other 10 %. Therefore the estimated number of 150000 t/yr (including export) for current European recycling/recovery in **Figure 2.1**.

For example, worldwide, utilisation in automobiles, mainly as flexible PU foams is around 1 Mt /yr, which in Europe currently results in an estimated 2 Mt/yr stream of automotive shredder residue (ASR) that ends up on landfills. Of this around 16 %-wt, (thus 320.000 tonnes) is PU foam [40]. With the data given section 1.3 this amount corresponds to 10-15 % of the annual European PU consumption following this trajectory, for Finland the annual ASR stream of around 25000 t gives a PU waste stream of 4000 – 5000 t/yr into landfills.

2.2 Polyurethane in landfill

In the developed countries most PU scrap ends up on landfills, for foams often after a compacting step that gives bricks of a density of around 500 kg/m³. It must be noted that besides end-of-life PU also significant amounts of production waste must be disposed of, which during the late 1990s could be up to 15-20 %-wt of the total PU foam production [41].

The fate of PU wastes in a landfill was investigated in a US study, focussing on the formation of aromatic amines (for example diamino toluene) and its release into soil or groundwater [42]. In this lab-scale study several PU foam types were put into canisters and were kept under anaerobic landfill conditions while being percolated with water. Leachates were monitored during a period of 700 days. No aromatic amines were detected - which came somewhat as a surprise to the researchers -, neither was any visible degradation of the PU foam evident after the test.

A study on the biodegradability of PU [43] concludes that especially esterase enzymes are capable of breaking bonds in the chain (*i.e.* ester bonds). Also the enzymes urease and papain have this capacity. Bacterial degradation of PU was reported by species of *Bacillus* and *Pseudomonas*: also values for Michaelis-Menten growth parameters are given. Two types of PU-ase enzymes have been isolated and characterised: cell associated PU esterase and water-soluble extra-cellular PU esterase, the latter having a greater mobility. Biodegradation of PU varies strongly with PU crystallinity, molecular structure, cross-linking and the length of repeating units. Unfortunately no products of the biological breakdown are specifically mentioned or listed.

2.3 Polyurethane and district heating systems

In Finland, a district heating network of around 9000 km (situation year 2001) exists of which around 30 km must be replaced each year. The waste stream this generates is made of concrete, steel, PUR foam and other plastics, mainly high density polyethylene (HDPE). By far the largest amount of tubing (6900 km, 76 %) is made of plastic protection covered tubes (in Finnish: *muovisuojakuoriset johdot*). Distinguished are free-lying and fixed plastic

protection covered types, these types are illustrated in **Figure 2.2** as (2)Mpul and (2)Mpuk, respectively, with 5600 and 1300 km; all other types involve a concrete housing. [44].

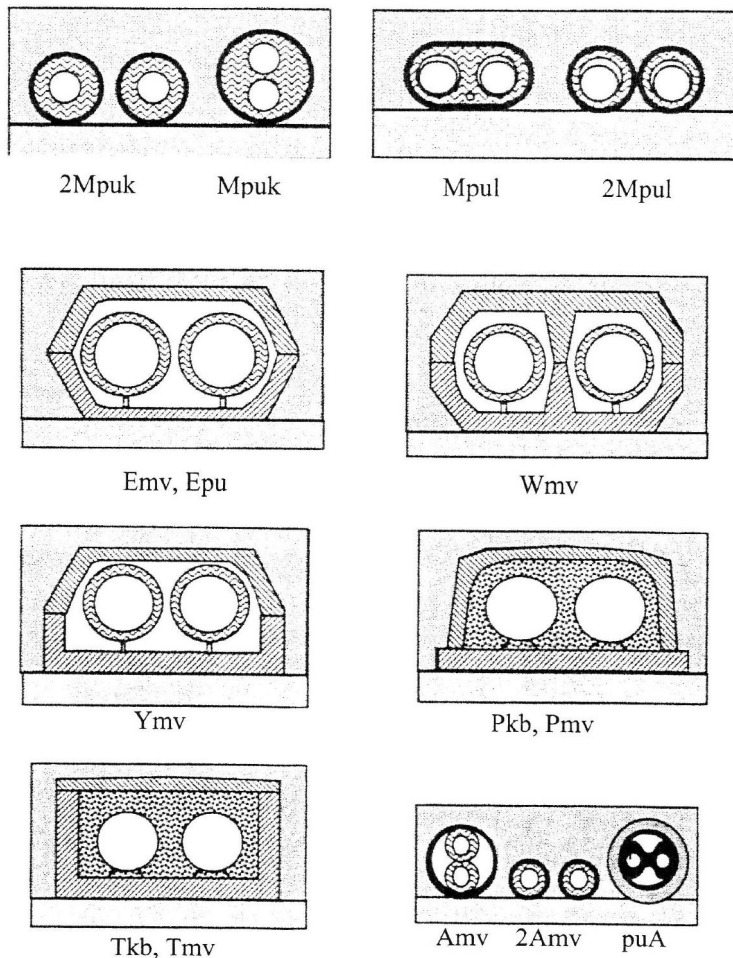


Figure 2.2 [44]

District heat tubings used in Finland

pu = polyurethane

M = plastics protection cover

l = free-lying

k = fixed

E = element channel

mv = mineral wool

Y = upper element channel

P = half element channel

A = asbestcement protection tube

kb = light concrete

T = on-site casted concrete

Typically district heating tubes are supposed to last more than 60 years, even up to 150 years for concrete covered tubes. Renewal of district heating tubes in year 2001 involved around 20 km Mpul/2Mpul-type tubing, 6 km concrete covered, 3 km Mpuk/2Mpuk-type tubing plus 1 km others. During the renewal process around 90-95% of the material is removed, the rest stays at the location. Important is the diameter of the tubes: three diameter classes DN20-DN80, DN100-DN200 and DN250 – are distinguished, with the DN giving diameter in mm. **Table 2.1** gives the various amounts of waste material obtained during year 2001. A relatively large amount of the Mpuk/2Mpuk tubes is re-used, of the largest DN250- type tubes around 70% is reused, against estimated 10 % and 30% values for DN20-DN80 and DN100-DN200, respectively. Altogether this gives a reuse of 36000 kg. For the Mpuk/2Mpuk-type tubes around 5% of the material can be re-used, mainly in repair work. The processing of scrapped tubes of the (2)Mpuk/(2)Mpul type implies that the steel is recovered for new steel production whilst the PU and HDPE material is landfilled; **Table 2.1** suggests a total amount of around 145 tonnes of landfilled PU foam in Finland year 2001, *i.e.* ~5000 kg per km renewed district heating tubing. One example is the processing of scrapped tubing from Helsingin Energia Oy by (metal) recycling company Kuusakoski Oy. There is no information as to the fate of CFCs

and other blowing agents during the processing of the scrapped PU material; none of it was (at least until summer 2002) sent to hazardous waste processing company Ekokem Oy, Riihimäki [45]. Replacing concrete covered tubes yield steel for recycling plus a large amount of concrete waste that can be used, for example, in road construction work [44].

Table 2.1 Estimated material amounts recovered during district heating tube renewal and the fate of the PU and HDPE fractions (Finland, year 2001) assuming that 10 % of the PU, HDPE and concrete and 5 % of the steel is not removed from the site [44]

	PU (tonnes)	Steel (tonnes)	HDPE (tonnes)	Concrete (tonnes)	Re-used PU (tonnes)	landfilled PU (tonnes)
Mpuk/2Mpuk	59.1	84.8	24	-	~36	~23
Mpul/2Mpul	129	269	77	-	~7	~122
Concrete cover	-	478	-	6172	-	-
TOTAL	188.1	831.8	101	6172		~145

2.4 Rigid PU foam from scrapped refrigerators/freezers (Finland)

In Finland, CFC-containing PU foams are considered hazardous waste, and must therefore be processed at Ekokem Oy, Riihimäki. This especially concerns scrapped refrigerators and freezers, classified as problematic waste in the EU as of year 2002, due to the CFC, HCFC- or HFC-containing rigid PU insulation foams and compressor oils. A processing unit for scrapped refrigerators and freezers was taken into use at Ekokem at the end of year 2001, in cooperation with metal recycling company Kuusakoski Oy. After draining of the liquids the scrapped refrigerators/freezers are disassembled and shredded – see **Figure 2.3** - during which the CFC gases are collected. The shredded material is separated into PUR foam, other plastics such as polystyrene, and metals such as iron and steel, aluminum and copper [46,47]. Altogether more than 90% of the material is currently recovered for material recycling or energy recovery. The collected CFCs are directly sent for thermal treatment, *i.e.* incineration (giving mainly CO₂, H₂O, HCl and HF) in one of the three thermal processing units [48].

Table 2.2 gives some data related to refrigerator/freezer processing at Ekokem during years 2002 and 2003 [49,47]. Whilst initially the shredded PU foam was stored in big-bags for further processing, the combustion of the material for energy recovery in one of the thermal processing units started in 2002/2003 and was common practice during year 2003 [47,48,50]. Comparing the emissions from years 2002 and 2003 shows a higher NO₂ emissions per tonne of hazardous waste (in Finnish: *ongelmajäte*) processed (1.75 kg in 2003 versus 1.63 kg in 2002), identical HCl emissions (0.01 kg) but lower HF emissions (1.5 g in 2002 versus 0.6 g in 2003) per tonne of waste.

Table 2.2 Scrapped refrigerator / freezer processing at Ekokem Oy [47,49].

	Year 2002	Year 2003
Scrapped refrigerator/freezer processed	1500 tonnes	2100 tonnes
Materials recovered from scrapped refrigerator/freezers	~83 % = ~1250 tonnes	1900 tonnes = 95 % (60 % metals + 35 % plastics)

However, the combustion of PU foams during 2003 is shown from the emissions of the ten trace elements Sb+As+Pb+Cr+Cr+Co+Cu+Mn+Ni+V+Sn, which increased from 0.15 g in 2002 to 0.23 g in 2003, per tonne of waste. Earlier also Weigand *et al.* reported increased emissions of especially Sn (tin) from PU foam waste incineration [25] – see section 3.5. (Further study of the data in Ekokem’s annual reports for 2002 and 2003 shows that especially incineration line 2 shows an increase in the average emissions of the above mentioned ten trace elements: 9 µg/m³ in 2002 increased to 30 µg/m³ in 2003, (both very far below the emission standard of 1000 µg/m³) suggesting that the shredded PU foam is incinerated in that unit.)



Figure 2.3 Post-consumer refrigerator/freezer processing at Ekokem Oy [49]

2.5 Flexible PU foam from end-of-life vehicles (Sweden)

Plastics represent roughly 10% of the weight of an automobile, and around 10% of these plastics are PU materials. Plastics consumption in Western Europe was of the order of 25 – 30 Mt (million tonnes) during the late 1990s, and with around 7 % of this used in car manufacturing gives an amount of 15000 – 20000 tonnes of PU being used in new automobiles annually in that region [51]. The recycling of flexible PU foam from ELVs would require a well-functioning product chain with cooperating PU foam producers, PU foam product manufacturers, automobiles industry and ELV dismantlers. Closed loop recycling of ELV seat PU foam (producing car seats from scrapped car seats) is, however, not seriously considered by the actors in the product chain, worrying about “how to get rid of the waste” instead [51]. ELV dismantlers have limited ability and lack motivation to express their

influence up the product chain, and car manufacturers appear to focus on chemical recovery (*i.e.* open loop recycling, or downcycling), for example glycolysis. The plastics manufacturers advocate energy recovery, claiming that the environmental benefits of plastics lie in the product phase, and neither technology nor markets for plastics recycling have properly developed. The driving force towards recycling and recovery has to come from legislation, but at the same time, the European Directive on ELVs [12] does not exclude downcycling as a recycling option, with the result that short term solutions are chosen based on what is technically and economically optimal today. As a result, at a dismantler in Jönköping, Sweden car seats were not removed during ELV dismantling (in year 1999) since there was no market for the PU foam, and the material ended up in incinerators or on landfills [51].



Figure 2.4

Recovered seats from end-of-life vehicles at ARN, the Netherlands [52]

What is needed for functioning product chain management is a design-for-recycling approach that involves standardisation of PU materials used in car manufacturing and two-way interaction up and down the product chain, including exchange of information amongst the different actors. A first step to such multi-organisation is Auto Recycling Nederland bv (ARN) in the Netherlands, set up during the 1990s to unite car manufacturers, importers, garages, ELV dismantlers, shredders and repair companies – see **Figure 2.4**. Similarly, the European Car Manufacturers Association (ACEA) aims at coordinating life cycle analysis (LCA) activities undertaken by car manufacturers via European Car Recycling (EUCAR). According to ACEA, the option of energy recovery for ELV waste materials should not be restricted, supported by the 1994-1998 project ECRIS (Environmental Car Recycling in Scandinavia). Nonetheless, PU recycling is taking place in the automotive industry in some cases, for example PU from bumpers is used in other car parts by Toyota, while some of BMW's dashboard modules can be reused in other car parts as well [51].

3. Processing of polyurethane waste

3.1 Overview of options

The methods of recovery and recycling of PU waste can be separated into the three categories as in **Figure 3.1** [4,25]:

- mechanical recycling (*i.e.* material recycling) which involves physical treatment,
- feedstock recycling (*i.e.* chemical recycling) which involves chemical treatment that produces feedstock chemicals for chemical process industry; and
- energy recovery (including waste-to-energy) which involves complete or partial oxidation of the material, producing heat and power and/or gaseous fuels, oils and chars besides by-products that must be disposed of, such as ashes.

Due to the typically long lifetime of PU-containing products the fourth option of product recycling (or “closed loop” recycling) is limited, because markets change rapidly and the concept of “downcycling” (or “open loop” recycling) strongly applies to products based on bulk chemicals such as PU.

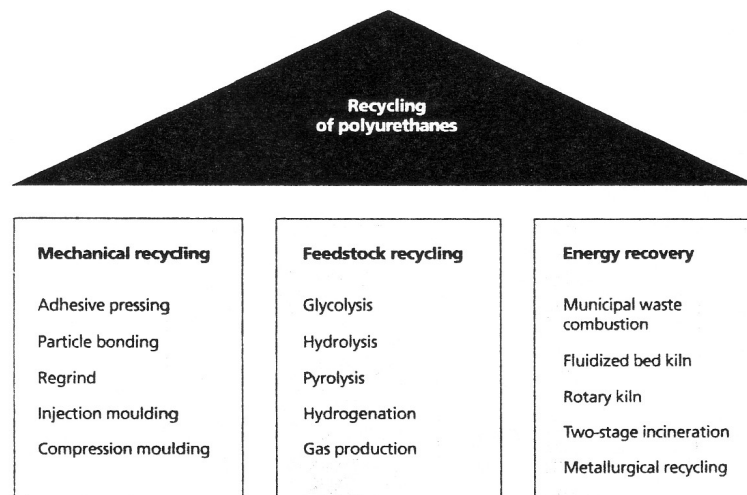


Figure 3.1 Overview of options for polyurethane recycling [4]

Besides recovery and recycling two other options exist, being those of landfilling or exporting the PU waste. Landfilling of PU is still common practice around the world and is addressed elsewhere in this report (section 2.2). Exporting of PU foam is actually taking place: around year 2000 about 60000 tonnes of of PU foam production waste was exported from Europe to the US where it was recycled into carpet underlay by rebonding. These shipments may soon suffer from competition from Latin America and Asia and it is questionable whether an additional 70000 tonnes of scrapped PU foam from ELVs can be disposed of by exporting them to outside the US as well [51]. It need not be mentioned that dumping PU foams in developing countries cannot ever be an acceptable approach for the future.

3.2 Mechanical recycling

Four major processing routes determine this field [4,51,41,39,53]:

3.2.1 Regrinding

Regrind or powder incorporation implies the use of finely grinded PU in the production of new PU products, usually by adding it to the liquid (polyol/polyether) reactant. The necessary particle fineness is obtained by granulation followed by fine grinding. During the early 1990s two-roll milling – see **Figure 3.2** – was found to give the best result for flexible PU foam grinding, whilst for rigid PU foams ball mills may yield particle sizes as small as 85 μm . One factor that limits the amount of scrapped PU foam that can be recycled by regrinding is the viscosity of the polyol/fine particle mixture that can be handled by the processing equipment. In practice this typically allows for up to 15 %-wt regrind when MDI polyol is used, up to 25 % with TDI [41].

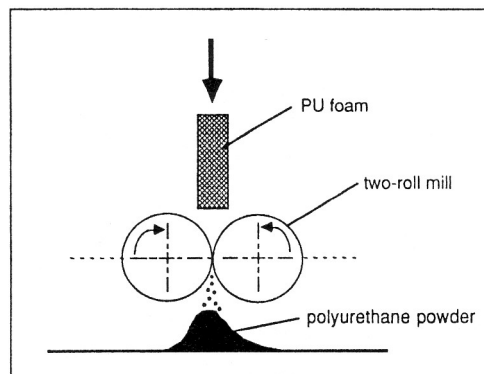


Figure 3.2 Schematic of a two-roll milling process [41]

The major problem of grinding processes for waste processing is that of economy: grinding scrap PU foam to size below 100-125 μm is no exception to that. Development work during the late 1990s reported by Stone *et al.* [54] has shown that two-roll milling can be economically viable alternative to cryogenic processes. This is demonstrated in a large commercial plant that produces around 450 kg/h fine powdered PU foam with an average particle size 50 μm . This powder can be used as filler in new PU foam, introduced by mixing it into the polyol at a concentration of around 20 pphp (parts per hundred parts polyol). This keeps the viscosity of the powder/polyol slurry in the range 2-5 Pa.s (2000 – 5000 cP), below the practical limit of 20 Pa.s where a transition from viscous fluid to paste was theoretically shown to occur, near a PU foam powder loading of 40-45 pphp. A drawback of using fine scrapped PU foam powder is that this will affect the new PU foam (as would also another type of filler!) since the powder does not contribute (energetically) to the chemical reaction yet adds heat capacity, and provides no CO_2 for foam blowing. The loss of hardness and firmness can be corrected for by reduction of other blowing agent, in this process here total elimination of dichloromethane (CH_2Cl_2) against an increase in water and (costly) isocyanate.

One benefit compared to other (mineral) filler materials is that the PU powder has a density similar to the new foam that is produced. Overall, the new process showed cost savings of around 2.7-2.8 % with a recycle content of 7-10 %-wt in the new foam, while hardly changing mechanical properties [54].

Recycled powder from rigid PU is an excellent material for absorbing oil spills, and as officially approved oil binder is commercially available for that purpose, and recycled RIM PU powder has used, up to 10 %-wt, in new and approved RIM PU vehicle parts in Europe and USA [4].

3.2.2 Adhesive pressing

Adhesive pressing is a method where scrap PU particles are surface coated with a binder and bonded in a heated press. Applicable to many types of plastics wastes and mixtures of these this is a short route to a (semi-)finished product. Probably being the oldest method for flexible PU foam recycling this allows for the production of mats, carpet underlay, sports hall floor parts and automotive sound insulation. In the mid 1990s manufacturers saw here a market potential of 10000-20000 t/yr for Western Europe, and the North American market was so large that ~50000 t/yr post-consumer PUF foam is imported from Europe since the 1990s [4].

PUR foam scrap (from end-of-life refrigerators and freezers, for example) can be rebonded by mixing scrap particles (size ~1 cm) with di-isocyanate MDI followed by form-shaping at 100-200°C, 30-200 bar. PU construction boards with excellent water and moisture resistance are obtained, or insulation panels for use in new refrigerators or freezers. PUF foam can likewise be rebonded to blocks that find use in carpets, sports hall mats or furniture. The enormous amount of PUF foam recovered from scrapped vehicles may satisfy a large part (in the US almost 50%) of the market of carpet underlay [41]. For PUR foam from scrapped buildings this recycling option is very important as well but is more complicated and often impossible due to the use of flame retardants in these materials [4].

In Europe, RIM PU particles are being recycled in under-floor heating pipes in buildings, which has a very large recycling capacity especially in Germany [4].

3.2.3 Compression moulding

Compression moulding involves moulding PU particles at temperatures and pressures high (180°C, 350 bar) enough to generate the shear forces needed to flow the particles together, without the need for additional binders. This method is successfully applied to reaction injection moulding (RIM) PU recycling into automotive parts (so-called fascias) although the recycling of painted parts is problematic. For example mud-flaps and athletic fields can be

produced, often co-processed with rubber chips. Door panels and dashboard panels for cars can be produced using around 6 % regrinded RIM plus 15 % glass fibres. Especially important is SRIM (structural reaction injection moulding) recycling for coarsely grinded PU scrap, where the recycled PU material (which may be up to 30 %-wt) is “sandwiched” between fibreglass reinforcements covered by a two-component PU resin, as illustrated by **Figure 3.3**. This procedure gives products with increased stiffness for use in automotive parts [41]. A recent study from the UK [55] showed that polyester resins compounded with RIM PU granulates gives increased flexibility and toughness to mouldings when compared to compounds with mineral (*e.g.* talc) fillers.

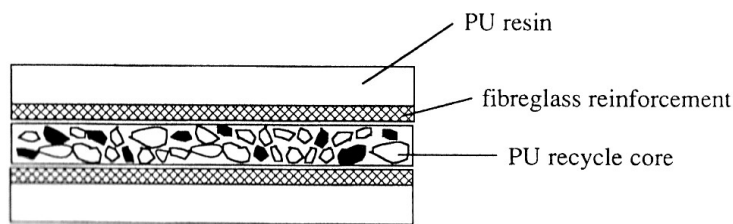


Figure 3.3

SRIM recycling of PU scrap [41]

3.2.4 Injection moulding

Injection moulding also allows for (moderately) crosslinked PU recycling. Also this method allows for processing of mixes of PU and other plastics, addition of some thermoplast is actually preferable. In one application, (Bayer’s hot compression moulding, or HCM process) granulated PU (250-1000 μm) is processed at $\sim 180^\circ\text{C}$ and high shear compression (> 350 bar) to produce thermoshaped products such as automotive parts [41].

3.2.5 Release of fluorocarbon compounds from PU foam

A Danish study [20,56] addresses the release of CFC-11 and also other fluorinated hydrocarbon blowing agents from PU foams during and after shredding. Between the mid-1960s and 1996 mainly CFC-11 was used. Nowadays the less harmful (from an ozone layer depletion perspective) fluorocarbons HCFC-141b and HFC-134a are being used, besides non-halogenated compounds such as pentane, cyclopentane or CO_2 , with new HFCs such as HFC-245fa on the horizon in the US. The typical lifetime of PU foam can be 30-80 years when used in construction materials, around 15 years when used as in a refrigerator or freezer. While very little of the blowing agent is lost during product life, although dissolution from the gas bubbles into the organic PU matrix can be extensive: numbers up to 60% have been reported [56]. During shredding, the CFCs must be trapped, after which they can be destroyed. Danish regulations require 80% destruction of CFC from PU foam waste [56].

In the US, around 8 million refrigerators and freezers are scrapped annually which

corresponds to a disposal problem for around 4000 tonnes CFC-11. As a result, PU foam disposal on landfills results in CFC-11 concentrations of 20 – 220 mg/m³ in landfill gas which, due to the chlorine and fluorine content is very problematic when firing this gas in a gas engine. The Danish research involved shredding PU foam from three refrigerators (density 30-40 kg/m³, porosity 0.97-0.98, CFC-11 content ~13 %-wt = 4-5 kg/m³) to 2 cm cubes and found that ~10 % of the CFC-11 was released within a few weeks. Around 40 % of the CFC-11 had dissolved in the PU matrix. For particles ranging from 0.5 to 5 cm the estimated time for release of 50% of the CFC ranges from 1.35 to 135 years [56].

The second part of the study [20] addressed the release of fluorocarbons from PU foam during and after shredding and considered, besides CFC-11 also the newer blowing agents HCFC-141b, HCF-134b and HCF-245fa. One feature of the newer, partly hydrogenated blowing agents is their higher diffusivity in the PU foam: reported values are $1-15 \times 10^{-14}$ m²/s against $0.05-12 \times 10^{-14}$ m²/s for CFC-11 at 25 °C. **Figure 3.4** gives an image of one of the foams.

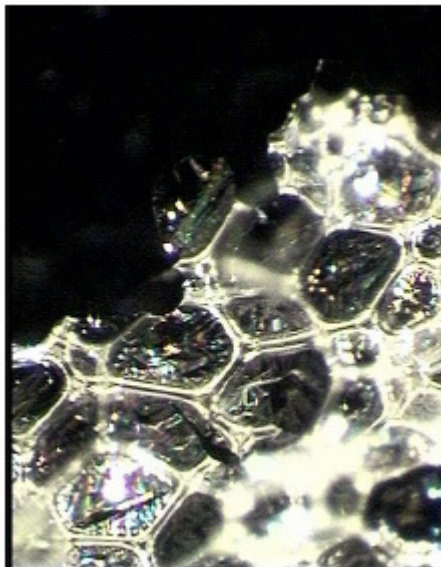


Figure 3.4 Microscope picture of a PU foam blown with CFC-11, showing open cells and closed cells with cracks [20, supporting info]

One finding was that of little difference between the four blowing agents. Instantaneous, short term and long term release of the blowing agent could be distinguished, corresponding to time scales of minutes, weeks or years, respectively. The instantaneous releases measured ranged from 35-40% for shredded particle size 2-4 mm to ~10% for 16-32 mm particles. The results lead to an estimated 18-24 % release for particles from the full-scale shredder at the Danish Recycling Center that produces particles mainly in the size range 4 – 32 mm.

For CFC-11, the results can be translated into a release versus time and shredded foam particle size diagram as given in **Figure 3.5**. For shredded particles < 4 mm this implies instantaneous (minutes) release of 40 % and short term (weeks) release of 60 % of the blowing agent, and for particles > 32 mm releases of 5 %, 2 % and 93 % over instantaneous, short term and long term (years) time scales, with some small dependence on the type of blowing agent. For the shredded foam produced at the Danish Recycling Centre the predicted CFC-11 release profile is shown in **Figure 3.6**.

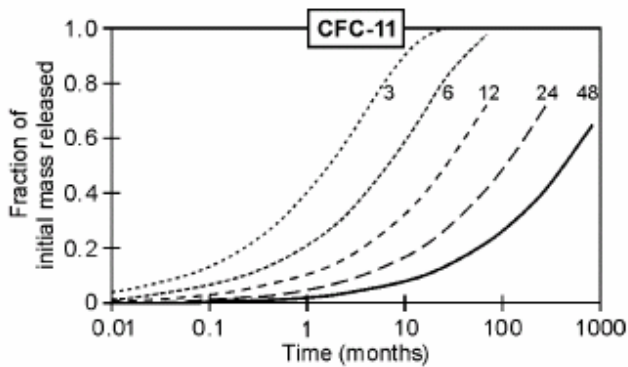


Figure 3.5 (left)

CFC-11 mass release from shredded PU foam waste as function of time and shredded particle size in mm [20]

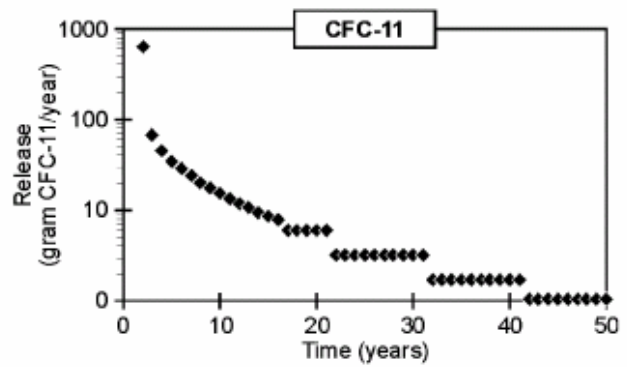


Figure 3.6 (right)

Estimated release of CFC-11 from the PU foam waste from one refrigerator/freezer unit shredded as currently done at the Danish Recycling Centre [20]

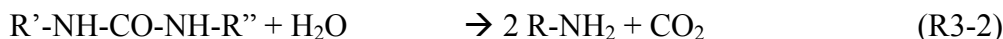
These results suggest that if storage of PU foams is needed after shredding (before further processing) collection of the released gases during storage is necessary as to avoid release into the atmosphere, if particle size is such that significant short-term release is expected. If removal of the fluorocarbon blowing agent from the PU foam is the primary objective, shredded scrap sizes much smaller than a few mm will be needed, since instantaneous release should approach 100%.

The extraction of blowing agents CFC-11 and HCFC-141b from rigid PU foams using supercritical CO₂ (sc-CO₂) was discussed by Filardo *et al.* [57]. After crushing and grinding to ~100 μm (breaking almost all cells) still a significant amount of the CFCs is still present in the material, dissolved in the polymer. Extraction efficiencies higher than 99% were reported with su-CO₂ and (slightly less efficient) su-CO₂/C₃H₈ mixtures, compared 14% removal with N₂ and 40% with liquid CO₂, and at much shorter times for the su-CO₂ as well. The very high diffusivity of the su-CO₂ through the polymer is an important factor.

3.3 Chemical processing

3.3.1 Hydrolysis

Material recovery by hydrolysis was applied to PU foam waste from junk cars already during the 1970s in the USA. Superheated steam of 200°C was found to convert PU foam from scrapped car seats into a two-phase liquid within around 15 minutes, at a volume reduction by a factor of 30. The chemistry can be summarised as



It was at that time suggested that the liquids can be landfilled or distilled, separating the polyols and diamino toluenes (DATs) for reuse [58]. Focussing later on the recovery and recycling of the polyol showed that superheated steam temperature should be around 288°C, producing a polyol that gave excellent new PU foam for seat cushions when mixed at 5% to virgin material. Too high temperature gives a decrease in useful polyol recovery, while polyol recovered at too low steam temperature produces unstable new PU foam [59]. PU hydrolysis suffers from unfavourable economics and lack of markets for the recycle products. [41,4]. Recent studies nonetheless address the recovery of other products besides polyols, and the alkaline compounds that may accelerate the hydrolysis, *e.g.* [60].

3.3.2 Glycolysis / alcoholysis

Glycolysis is by far the most widely used chemical recycling method for PU, mainly PUR and PUF foam. Developed during the early 1980s (mainly in Italy, Germany, France and the USA) the aim is the recovery of polyols for the production of new PU material. The chemistry is summarised in **Figure 3.7**.

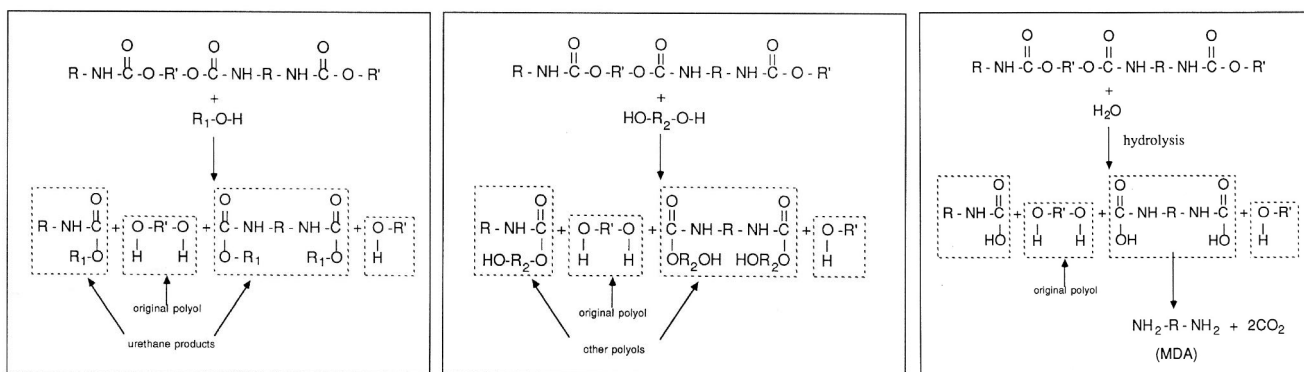


Figure 3.7 Chemistry of alcoholysis / glycolysis of PU. The presence of water (right side box) results in the formation of diamines like diphenyl methane diamine (MDA) [41].

Basically, glycolysis/alcoholysis implies the heat-up of pre-grinded PU scrap, preferably rigid PU foam to 180-220°C in high-boiling point glycols with a catalyst. The glycol is usually diethylene glycol (DEG) with co-reagent diethanol amine (DEA). A temperature below 180°C gives too low catalyst activity; a temperature above 220°C gives undesired side reactions towards amines. For the catalyst it is important that the formation of aromatic amines is avoided. Since the glycol is both a reactant and a solvent, glycol/PU scrap ratios 60/40 are necessary. Scheirs [41] distinguishes two approaches, wherein 1) a single polyol is recovered

or 2) flexible and rigid polyols components are recovered. An example of a process where a single polyol is recovered is the alcoholysis process developed by Getzner Werkstoffe Austria. A process for double recovery of polyols was developed by ICI, referred to as the Split-Phase Glycolysis (SPG) process, as shown in **Figure 3.8**. In the SPG process scrap PU foam, preferably based on MDI, is reacted with DEG producing a two product phases in the reactor. The lighter layer contains the flexible polyol, the heavier layer contains the MDI-derived compounds which are converted into a rigid polyol using propene oxide. The recovered polyols can be used to produce new PUR and PUF foams. Reaction times, at 200°C, are several hours. PU foam waste densified to around 1100 kg/m³ is used. The SPG process is sensitive to contamination by styrene-acrylonitrile (SAN). [41,61]

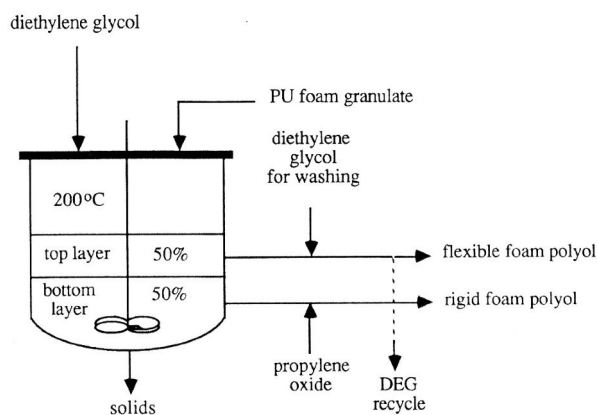


Figure 3.8 Schematic of the Split-Phase Glycolysis (SPG) process for PU foam recycling [41]

In the presence of hexamethylenetetramine (HMTA) the glycolysis of water-blown PUF foams in ethylene glycol (EG) yields the polyol and a solution of ureas, carbamates and amines in the EG. The HTMA suppresses the formation of solid phases in the products, and a diaminotoluene (DAT) content below 100 ppm [62].

Recent work from Taiwan optimised the process conditions for glycolysis of PUR from waste refrigerators/freezers, as to produce high quality polyol recyclate [63]. In a stirred tank reactor at ~220°C (1 bar) a residence of 2 h was sufficient for 87-95% recovery yield with DEG reactant + KAc (potassium acetate) as catalyst (2 g/100 g PU). A second study on PUF foams from ELVs gave an optimal residence time of 1½ h at the same temperature, pressure and KAc catalyst (1 g/100 g PU). The recovered product polyols had then boiling points in the range 245-260°C [64]. For both studies initial PU scrap size was 0.15 – 0.85 mm.

Also recycled polyol from RIM PU scrap glycolysis has been used to replace up to 60% of original for new PU RIM parts in Germany [4].

3.3.3 Other chemical processes

Hydroglycolysis basically implies adding water to a glycolysis process (see previous section) for PUF foam and the use of the catalyst LiOH, at around 200°C. Developed by Ford Motor Company it is claimed that this produces a simpler and more valuable product mixture. Although it is more expensive than conventional glycolysis, (purification of the polyol-rich product is more complicated) it has the advantage that complex mixtures of dirty and contaminated PU wastes can be processed as well, which otherwise would have to be landfilled [65]. The recovered polyol may replace up to 50% of virgin polyol material for PUF foams. The extraction of pure polyether triols from the products is accomplished using hexadecanes or similar boiling point hydrocarbons [66]. The Ford process is shown schematically in **Figure 3.9**.

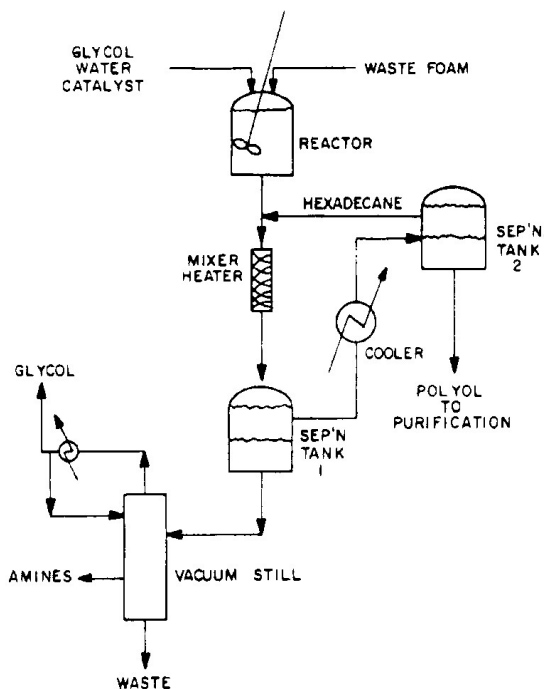


Figure 3.9 The Ford hydroglycolysis process [66]

A process similar to the above given SPG process yet somewhat different, where PU foams are converted into the original flexible polyol plus a rigid polyol is Dow's aminolysis process [41]. Here, the PU waste is dissolved (at up to 1 m³ foam in 1 liter solution!) in a KOH/alkanolamine solution at 120°C. The three main products from the first step are polyols, aromatic amines and carbamates. In a second step ethene oxide or propene oxide is used to convert the amines, after which the polyols are separated. The can be used without further purification to produce new PU foams that can completely replace PU foams produced from virgin polyol.

3.4 Thermochemical processing

An overview of thermochemical processes for recovery of chemicals, fuels and recovery from PU (- containing) waste streams is given in **Figure 3.10** [41]. Some more detail is given below.

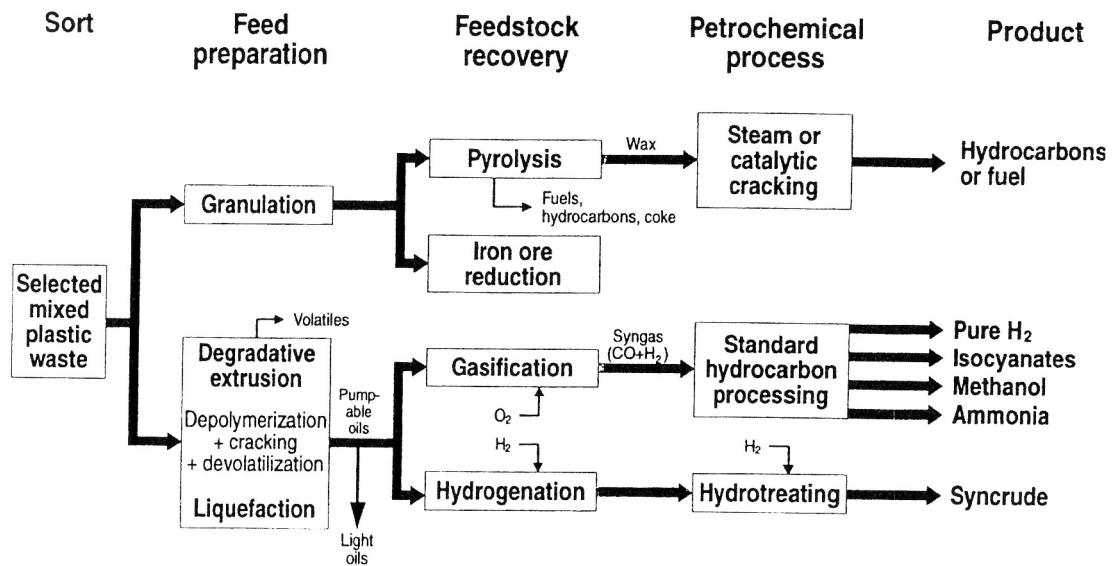


Figure 3.10 Thermochemical recycling options for PU waste [41]

3.4.1 Pyrolysis

A study by Rogaume *et al.* [67] addressed the pyrolysis of PUF foam from automobile seats. (The authors considered combustion as well – see section 3.5). First, thermogravimetric, calorimetric (TGA/DTA + DSC) tests were made under an air flow. Mass loss starts at $\sim 250^{\circ}\text{C}$ and levels off at a mass loss of $\sim 80\%$ at 300°C , while the remaining 20% is decomposed until temperature reaches 500°C . The DSC shows several exothermic peaks, the most important being at $250\text{--}300^{\circ}\text{C}$ and others at the start (340°C) and end (490°C) of the second decomposition stage. An additional test in a small furnace also showed two-stage decomposition, with the production of yellow smoke and viscous liquid during the first stage, followed by slow decomposition of the liquid into gaseous products. The second set of tests involved experimenting in a cylindrical quartz tube reactor inside a tubular furnace. Samples (50 mg) were heated at 300 K/s under a flow of nitrogen or air, and product gases were analysed for CO , CO_2 , CH_4 , NO , N_2O , NO_2 , HCN and NH_3 . Maximum temperatures were 850°C or 1000°C , holding times were $0.5\text{--}2$ seconds. The results (roughly the same for all residence times) showed the release of significant amounts of CO , CH_4 , HCN , NH_3 and NO , plus probably some small amounts of C_2H_4 and C_2H_2 . The measured amounts as fraction of PU foam carbon (for the CO and CH_4) and nitrogen (for HCN , NH_3 , NO) were 26% , 18% , 34% , 8% , 21% at 850°C and 24% , 17% , 64% , 14% , 9% at 1000°C . The formation of CO and NO was explained through intermediates such as HNCOO . It is argued that first some PU

nitrogen is released directly as NO, followed by a large release of HCN, which may be oxidised in the gas phase to NO as well.

Pyrolysis of a PU adhesive as widely used in the furniture industry (for example in Spain) was analysed using TGA up to 450°C (in nitrogen, 5-20 K/min heat-up) and a “pyroprobe” pyrolysis reactor composed of a platinum coil around a 2 mm quartz tube at 500 - 800°C (in nitrogen, heat-up ~300 K/s) plus a secondary reactor [21]. The results from the TGA tests allowed for determining chemical rate parameters: for the two-parallel-reactions model used activation energies 134 kJ/mol and 190 kJ/mol were found (see also section 1.5 of this report for similar values reported by other researchers). Decomposition of the PU to a mass loss of ~95% occurred between 230 and 380°C. The tests in the “pyroprobe” set-up yielded gas mixtures containing at 500°C large fractions of toluene, benzene, methyl 1,4-pentadiene, ethane + ethylene, propylene and butadiene, at 900°C mainly benzene, ethane + ethylene, and methane. Also, ammonia (NH₃), pentene and the semi-volatiles 5-hexen-1-ol and 1,6-hexane diol were found in significant amounts in the products, as also some hydrogen cyanide (HCN), aniline (aminobenzene), benzonitrile and naphthalene, at levels depending on temperature.

RIM PU pyrolysis typically gives (at >450°C) 5-25%-wt char, 10-45 %-wt liquids and >40%-wt gases. The liquid is a red-coloured viscous single-phase oil with a viscosity that increases with time. In order to increase the amount, quality and marketability of especially the liquid product, the use of activated carbon and PU chars in a secondary pyrolysis reaction step was tested [68]. First goals were to achieve a maximum char yield and minimum liquid product viscosity. Using activated carbon gave a less viscous oil that eventually separated into an organic fraction plus water; char amounts remained the same. Using PU char gave a much higher char yield (up to 40 %-wt), slightly less liquid, which again separates in oil + water, and much less gases. A two-zone pyrolysis reactor as shown in **Figure 3.11** was suggested, with PU char as promotor for the secondary reactions.

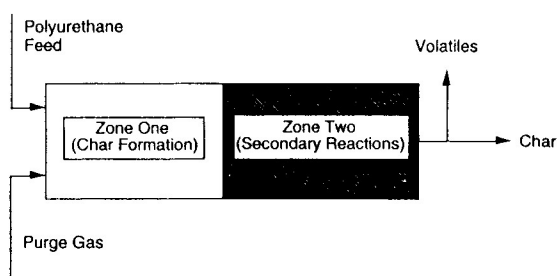


Figure 3.11 Pyrolysis reactor using PU char as promotor of secondary pyrolysis reactions [68].

3.4.2 Gasification

Gasification of (waste derived) fuels is an exothermic process that produces heat, ashes plus a product gas (or synthesis gas, “syngas”) that contains large fractions of combustible gases H_2 and CO . An example for plastics waste processing by this route is given in **Figure 3.12**. A study by ICI, Texaco and University of Ghent (Belgium) from 1996 [41] showed that PU waste from refrigerators can be gasified, with the benefit that chlorine (from CFCs) is bound by the ammonia formed (from PU nitrogen) to form ammonium chloride (NH_4Cl).

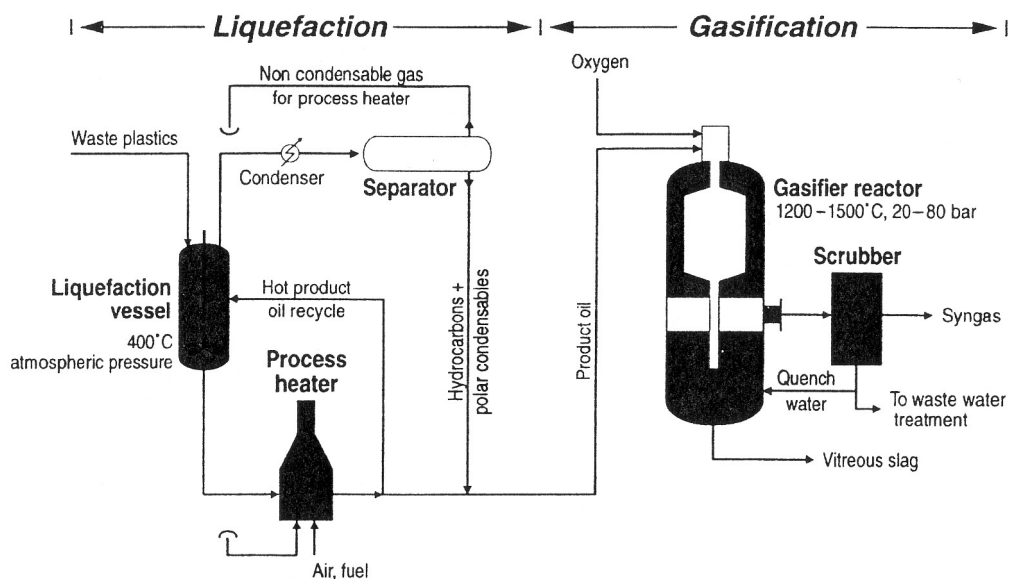


Figure 3.12 Plastics waste liquefaction / gasification [41]

The process given above needs a pumpable liquid feedstock which is obtained by liquefaction; the gasification takes place in oxygen at 1200-1500°C, 20-80 bar, where a residence time of a few seconds gives a 98-99 % conversion into gases plus a slag. The CO produced can be used to produce isocyanates for new PU material, the hydrogen can be used to produce other PU feedstocks such as formaldehyde and polyether.

In the UK, a gasifier plant for nitrogen-containing organic residues from BASF plc's Seal Sand plant was recently taken into use [69,70]. Around 110.000 t/yr residues from acrylonitrile synthesis are gasified, a liquid, ash-free mixture containing nitriles, amines and ammonia sulphates with nitrogen contents up to 24 %-wt. These are gasified at 1400°C, 30 bar in steam + oxygen to a gas with the following specification: $< 10 \text{ mg/m}^3_{\text{STP}}$ dust, $< 25 \text{ mg/m}^3_{\text{STP}}$ sulphur (H_2S , COS), $< 20 \text{ mg/m}^3_{\text{STP}}$ bound nitrogen (NH_3 , HCN), pressure > 25 bar. The gasifier is an entrained flow gasifier of the Noell type shown in **Figure 3.13**. These reactors are suitable for homogeneous solid (coal, petcoke) and liquid fuels (sludges and tars).

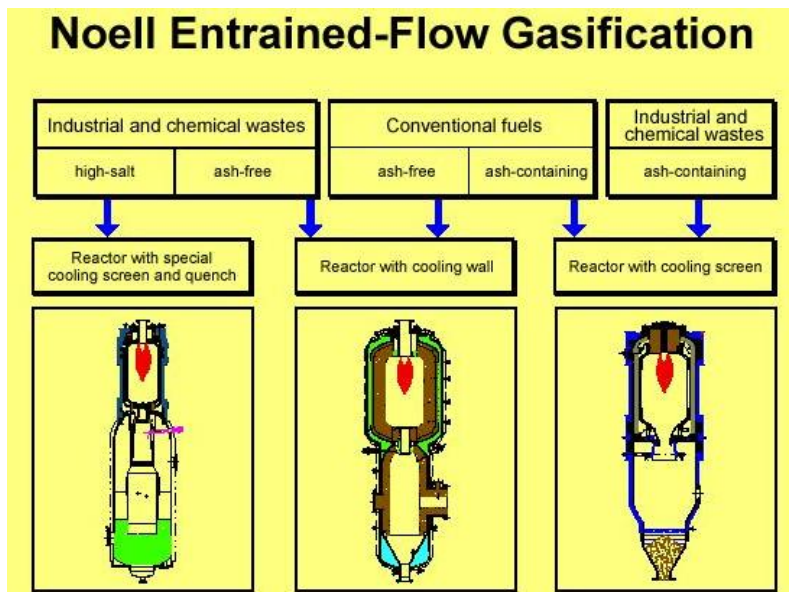


Figure 3.13 Noell Entrained-Flow Gasification reactors [69,70]

3.4.3 Other thermochemical processes

Hydrogenation can be seen as a compromise between pyrolysis and gasification; the effect of heat and high pressure hydrogen (H_2) results in gaseous and liquid products. These can be used as fuel (partly used as energy source for the process) and chemical feedstock [53]

3.5 Energy recovery (combustion / incineration)

Energy recovery is often considered the only suitable disposal method for recovered material for which no markets exist or can be created. This strongly applies to scrap with PU laminates to wood, leather or fabrics, or commingled materials. Also, flame retarded materials make recovery and recycling very difficult. Incineration of a PU foam results in a volume reduction of around 99% which has large implication to reducing the landfilling of this material, at the same time destroying CFCs and other harmful foam blowing agents [41]. Yet again the presence of flame retardants complicates things, and the effect of these compounds on combustion processes receives much attention nowadays [34].

The European PU industry, specifically for rigid PU foam, consider the recovery of energy from scrap material PUR foam from construction and demolition waste to be the best disposal option as laid down in various position papers [71,72]. Reference is usually made to a detailed study by Rittmeyer *et al.* [73,74] on the co-firing of CFC-containing PU foams in municipal solid waste incineration plants (MSWIPs). Two facilities were used, being the TAMARA test incinerator at the Karlsruhe Research Centre and a full-scale MSWIP plant, in Germany. In the TAMARA facility, a counter-current grate furnace with gas clean-up

equipment, ~250 kg/h of a mix household waste with ~25 % refuse-derived fuel (RDF) was fired and effect of the addition of 1-3 %-wt fuel input of 50 mm relatively old (~6.5 %-wt CFC-11) PU foam cubes was investigated. Combustion temperature was 850-1000°C. In the MSWIP, based on a roller-grate counter-current furnace with gas clean-up, 1.3 %-wt of the feed, *i.e.* 120 kg/h of a total of 9000 kg/h, was replaced by ~20 cm pieces of relatively old (~11.3 %-wt CFC-11) PU foam particles. Samples of CFCs, HF, HCl, dioxins/furans (PCDD/Fs) and other emissions were measured at both facilities [74].

The tests with the TAMARA facility showed that CFC-11 emissions stay in the range 0 – 10 µg/m³, against an air background of ~4 µg/m³. With a CFC-11 loading of 180-700 ng/m³ this implies a destruction of ~99.999 %. No effect of furnace temperature was seen. **Table 3.1** shows some of the other emissions measured. No effects of the increased amounts of nitrogen in the feed were seen, nor was there an increased carbon-in-ash. (At ~5 %-wt the concentration of nitrogen in PU foam is around seventimes higher than in “normal” MSW). SO₂ concentrations fluctuated somewhat with the temperature, presumably due to sulphates in layers deposited on the furnace walls. CFC’s are effectively destroyed immediately after their escape from the PU foam matrix. Emissions of CH₂Cl₂, CH₃Cl and CCl₄ were measured to be ~100 µg/m³, ~60 µg/m³ and ~6 µg/m³, respectively. No chlorofluoro-methanes were detected at above 1 – 10 µg/m³.

Table 3.1 Emissions from the TAMARA facility at Karlsruhe during MSW / PU foam co-firing [74]

component	mean values of on-line monitoring			
	0	1	2	3
PUF feed [wt. %]				
HCl [mg/m ³]	524 ± 5	571 ± 58	589 ± 84	761 ± 45
CO [mg/m ³]	< 5	< 5	< 5	< 5
NO [mg/m ³]	209 ± 5	209 ± 9	202 ± 21	209 ± 8
O ₂ [%]	11,0 ± 0,5	11,2 ± 1,3	11,4 ± 1,7	11,1 ± 0,6
SO ₂ [mg/m ³]	274 ± 39	306 ± 92	248 ± 84	278 ± 60
temperature [°C]	943 ± 6	961 ± 21	957 ± 21	985 ± 7
waste [kg/h]	298 ± 1	280 ± 45	253 ± 54	240 ± 27

The MSWIP showed CFC-11 emissions of ~18 µg/m³ against a background of ~13 µg/m³, which implied a destruction efficiency of ~99.998 %. Around 20-50 % of the increased chlorine feed was found as HCl, which presents no problem to the gas clean-up equipment. For fluorine ~40 % was found as increased HF concentrations, which implied an increase by a factor of 10: 4 → 40 mg/m³. This will give increased concentrations in wet scrubber solutions that may in the long run cause corrosion problems. The EU waste incineration emission limit for HF is 1 mg/m³_{STP} @ 10 %-vol O₂ (dry gas) [9]. A second problematic feature is the feeding of the foam into the MSWIP which gives a risk of fires starting in the feeding hopper and waste bunker. It was concluded that PU foam waste can be co-fired at ~1 %-wt of the

input of an MSWIP without any changes necessary: burning all PU foam wastes from household refrigerators in Germany in MSWIP facilities would mean a loading of 0.3 %-wt of the feed to these facilities [74].

A parallel study in the same two facilities addressed the incineration of CFC compounds CFC-11 and CFC-113 [73]. These were injected directly into the furnaces during MSW incineration and emissions of CFCs, HCl, HF and PCDD/Fs were measured and ashes were analysed. Similar to CFC-11 -containing PU foam combustion, > 99.9 % of the CFCs were destroyed, and also CH₂Cl₂, CH₃Cl and CCl₄ were measured to be very much the same as with CFC-11 -containing PU foam incineration. HF concentrations in the raw flue gas increased by a factor of ten, HCl concentrations doubled. For the dioxins/furans PCDD/Fs it was found that dioxin emissions decreased somewhat (13 → 11 ng/m³) whilst furans increased (18 → 23 ng/m³), as illustrated by **Figure 3.14a**. The corresponding data for dioxin/furan precursors chlorobenzene and chlorophenol are given in **Figure 3.14b**. Based on the findings the researchers state that the destruction of CFCs in PU foams can be successfully accomplished in MSWIP facilities, but for destroying CFC gases other, specially dedicated equipment should be used [73].

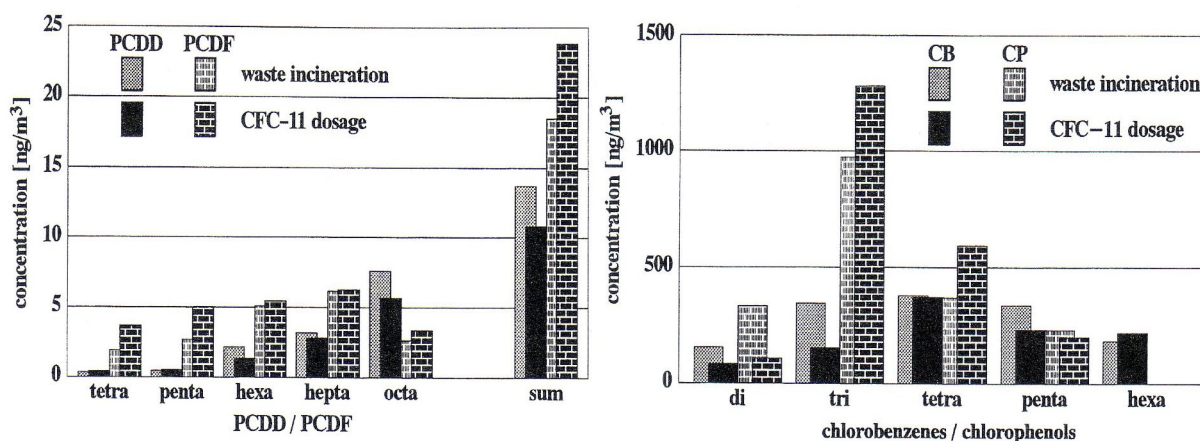


Figure 3.14a (left) Dioxin / furan emissions from CFC-11 incineration in the TAMARA facility at Karlsruhe Research Centre [73].

Figure 3.14b (right) Chlorobenzenes/chlorophenols emissions from CFC-11 incineration in the TAMARA facility at Karlsruhe Research Centre [73].

Another German study addressed the co-firing of PU wastes in a 39 MW_{thermal} coal-fired bubbling fluidised bed combustion (FBC) plant (steam parameters 475°C, 64 bar) [25]. The coal/brown coal mix had a heating value of 17.6 MJ/kg; to this a pulverised (70-700 µm) PUF foam waste from mattresses, car seats and furniture compressed to a bulk density of 300 kg/m³, with heating value 24-30 MJ/kg was fed at 13-20 % energy input. No operational problems were found during 35 hours of testing, in fact a burner for burnout of flue gas CO could be turned off. Emissions of pollutants or carbon-in-ash did not increase, except for the

concentration of the ten trace elements grouped as Sn+As+Pb+Cr+Co+Cu+Mn+Ni+V+Sn which increased by a factor of three to four (0.06-0.09 → 0.22 – 0.32 mg/m³) which is mainly due to the presence of Sn (tin) in the PU foam (used as catalyst in PU production) [25]. Costs for co-firing PU foam wastes at the facility were at that time estimated at ~50 €/tonne. Rigid and flexible PU foams from furniture without flame retardants were considered suitable for co-firing with coal in an FBC. It was expected that the combustion of RIM PU waste in an FBC will lead to problems due to the large amount of glass fibres in that material. Also rigid PU foams from construction waste were claimed to be problematic for FBC due to the high chlorine/fluorine content [25].

In another study, the combustion of PUF foams from automobile seats under grate incineration exhaust gas recirculation conditions was studied by Rogauze *et al.* [67], aiming at optimising combustion conditions that result in minimal NO and CO emissions. (The authors considered pyrolysis as well – see section 3.4.1). Besides NO, also NO₂ and N₂O are measured in the exhaust gases from the reactor, which was a 15 cm inner diameter, 130 cm length cylinder, with a 55 cm solid bed (of 4×4×4 mm³ PU foam particles) resting on a plate fixed 10 cm from the bottom. Primary air was fed from below the grid and secondary air was added above the bed. Tests were made at 850°C and 1000°C, respectively, at atmospheric pressure. Combustion efficiency was followed by comparing CO and CO₂ emissions; O₂ is measured as well. The percentage of PU foam nitrogen (implicitly neglecting air nitrogen) found as NO, NO₂ or N₂O were 51 %, 0 % and 9 %, respectively at 850°C and were 62 %, 0 % and 5 %, respectively at 1000°C. At the same time, CO+CO₂ emissions corresponded to 4+88 % and 3+96 % of the PU foam carbon, respectively, at these two temperatures.

Aiming at reducing CO and NO emissions, first the effect of excess air was studied aiming at a combustion temperature between 900 and 1000 °C (850°C was considered to be too low looking at the low carbon burnout at that temperature). This showed a minimum CO emission at excess air factor 1.6 without air staging, and a slightly better result with air staging at primary excess air factor 0.8, total excess air factor 1.35 – 1.6 (reactor temperatures not given). NO emissions were found to increase with increasing primary air as well as with secondary air flow, and optimal conditions were thus found at primary air factor 0.8, total excess air factor 1.35. The conversion of PU nitrogen to NO was then 5.7 %, the conversion of PU carbon to CO was 0.55 %. Further reduction of NO emissions was obtained using recirculation of flue gases to the primary air, which would also complete the burnout of traces of hydrocarbons, HCN and NH₃. Two tests, involving 50% and 100 % of the primary air by recirculated flue gas at the same secondary air flow, showed a further reduction of the CO and NO emissions by 15 % and 45 %, respectively [67].

The behaviour of nitrogen from polymers and plastics in waste-derived fuels during combustion including a PUF foam was considered in a Finnish study (see also section 1.5) [22,23,24]. It was found that the emissions of NO+NO₂ during combustion in an entrained gas quartz tube reactor (at 750 - 950°C, in 7% O₂/93% N₂) depended strongly on the amount of

char produced from high-nitrogen fuels (PU foam, nylon, RDF, MSW, urea/formaldehyde glue, sewage sludge) and the nitrogen content of the fuels. At a nitrogen content of 6.6 %-wt, less than 10 % of the PUF nitrogen was emitted as NO+NO₂.

4. Legislative aspects

Polyurethane recovery and recycling is hardly driven by other motivations than local and international legislation. As a polymer used in long life-time applications, product recycling is hardly feasible, and with the complicated mixed wastes produced nowadays neither material recycling nor chemical recycling can compete with virgin material. Incineration and energy recovery do not present large problems except some flue-gas clean-up issues, but by far the most widely and extensively used route for scrapped PU is the landfill.

Within the EU, PU-containing waste disposal is limited and prescribed by recent Directives:

- Waste incineration directive 2000/76/EC [9], which enforces control of emissions such as NO_x, HCl, HF and dioxins/furans that may arise from (CFC-containing) PU incineration
- Landfilling of waste directive 1999/31/EC [10] which restricts the landfilling of untreated waste, biodegradable wastes
- End-of-life vehicle directive 2000/53/EC [12] which will become increasingly restrictive as to how much of an ELV must be recovered/recycled, eventually making the processing of automotive shredder residue (ASR), for about 15% composed of PU, a necessity. In fact, recovering ELV car seat PUF foams is seen as essential for meeting longer term future requirements.
- Ozone layer directive 2000/2037/EC [11] which applies to the production, use and post-consumer processing of products containing CFCs, HCFCs, halons and several other ozone depleting species. This directly applies to most PUR foams currently in use as insulation materials, to be scrapped for a long period to come.

For PU, the largest impact so far has come from the ozone layer directive, resulting in the use of new blowing agents such as pentane in PUR foams, for example by Finnish company Urepol. The processing of PUR scrap from post-consumer refrigerators/freezers at Ekokem Oy (see section 2.4) is a direct result of that, with further support from Finnish legislation Nr. 1187/2001 [75].

Besides legislation dealing with disposal of waste, also some other legislative issues hold for PU recycling: for example vehicle parts from recycled materials need approval, to guarantee that consumer safety is not in danger when using a product (partly) made from recycled material. For automobiles this can apply for example to bumpers but many other parts as well.

Finally, international law and regulations will certainly leave open options for disposal of scrap PU outside the EU, for example by exporting to Northern America as already during the 1990s.

5. Concluding remarks

Recovery and recycling of materials is motivated by the wishes to minimise wastes, conserve resources and reduce environmental pollution. An “ecologically sound” [41] recycling rate will not be 100% for reasons of energy and other resources consumed during collection and transport of waste streams. Nonetheless recycling and recovery of PU containing wastes is almost completely driven and dictated by local and international legislation.

Polyurethane is found in several products that make special post-consumer treatment necessary. Currently this applies to PUR foams with CFC-type blowing agents, in the future the recovery and recycling PUF foams from ELVs will become urgent as well. In the meantime, as this study shows it is essential to remove CFC-type gases from PU foams at close to 100%, especially if the “CFC-free” PU material is landfilled or stored in the open air after shredding.

Increasing waste-to-energy and other thermal processing activities involving gasification, pyrolysis and two-stage combustion (removing problematic components in a first stage) will also allow for the disposal of significant amounts of scrap PU without many difficulties. This may however be slowed down by lack of support for technology development: current trends focus very much on renewable energy (biomass, wind power), a revival of nuclear power and more efficient fossil fuel-derived heat and power instead.

Several methods for material and chemical recycling of PU materials have been developed, by far the most important being glycolysis and regrinding. But until reasonable size markets for PU materials can be created the final destination for most PU wastes will be the landfill, for years to come, until this is halted by legislation.

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List of abbreviations

ABS	Acrolonitrile-butadiene-styrene
ASR	Automotive shredder residue
BFR	Brominated flame retardant
CFC	Chlorofluorocarbon
DAT	Diaminotoluene
DEA	Diethylamine
DEG	Diethylglycol
DSC	Differential scanning calorimetry
DTA	Differential thermal analysis
EG	Ethylene glycol
ELV	End-of-life vehicle
FBC	Fluidised bed combustion
HCFC	Hydrochlorofluorocarbon
HFC	Hydrofluorocarbon
HMTA	hexamethylene amine
ISOPA	European Isocyanate Producers Association
LHV	Lower heating value
LOI	Lower oxygen index
MDI	Diphenylmethanediisocyanate
MSW	Municipal solid waste
MSWI	Municipal solid waste incineration
MSWIP	Municipal solid waste incineration plant
ODP	Ozone depleting potential
ODS	Ozone depleting substance
PA	Polyamide ("nylon")
PFC	Perfluorocarbon
pphp	parts per hundred parts
PU	Polyurethane
PUF	PU flexible
PUR	polyurethane (<i>often used in literature, avoided in this report</i>)
PUR	PU rigid
RDF	Refuse-derived fuel
RIM	Reaction injection moulding
SAN	Styrene Acrylonitrile
SPG	Split phase glycolysis
SRIM	Structural reaction injection moulding
su	super-critical
TDI	Toluenediisocyanate
TGA	Thermogravimetric analysis
yr	year

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