
MINI BREF 4

INSTALLATIONS FOR MATERIAL RECOVERY

[extract from *BREF for the Waste Treatments Industries* from August 2006]

Note: Text in blue corresponds to references also mentioned in MINI-BREF 1-Common techniques

Mini-Bref 4 : Installations for material recovery	1
1. General information	3
Installations for treatment of waste oil	3
Installations for treatment of waste solvent	6
Installations for the treatment of waste catalysts, waste from pollution abatement and other inorganic waste	7
Installations for treatment of activated carbon and resins	8
Installations for the treatment of waste acids and bases	9
2. Applied processes and techniques	11
2.1. The re-refining of waste oils	11
2.1.1. Pretreatment of waste oil	14
2.1.2. Cleaning of waste oil	14
2.1.3. Fractionation of waste oil	15
2.1.4. Finishing of waste oil	15
2.1.5. Technologies used for the re-refining of waste oils	16
2.2. Regeneration of waste solvents	21
2.3. Regeneration of waste catalysts and recovery of components from abatement techniques	24
2.4. Regeneration of activated carbon	25
2.5. Regeneration of resins	26
2.6. Regeneration of waste acids and bases	26
2.6.1. Regeneration of spent sulphuric acid	27
2.6.2. Regeneration of spent hydrochloric acid	27
2.7. Treatment of solid photographic waste	28
2.8. Treatment of liquid photographic waste	28
3. Current consumption and emission levels	30
3.1. Waste IN treated to obtain a recycled material	30
3.2. Consumptions of waste treatments to obtain a recycled material	38
3.3. Emissions from waste treatments to obtain a recycled material	44
3.3.1. Emissions from the re-refining of waste oils	44
3.3.2. Emissions from the regeneration of waste solvents	60
3.3.3. Emissions from the regeneration of waste catalysts	63
3.3.4. Emissions from the cleaning and regeneration of carbon	63
3.3.5. Emissions from the regeneration of ion exchange resins	67
3.3.6. Emissions from waste acids and bases treatments	67
3.3.7. Emissions from the treatment of photographic waste	67
3.4. Waste OUT from re-recycling/regeneration treatments	68
4. Techniques to consider in the determination of BAT	73
4.1. Waste oil	73
4.1.1. Generic techniques to increase the yield of re-refining	73
4.1.2. Selection of waste oils to be re-refined	74
4.1.3. Distillation/clay process	74
4.1.4. Distillation and chemical treatment or solvent extraction	75
4.1.5. Solvent extraction process and distillation	75
4.1.6. Thin film evaporator and different finishing processes	76
4.1.7. Thermal de-asphalting process	77
4.1.8. Recycling in a lubricating oil refinery	78
4.1.9. Hydrotreatment	78
4.1.10. Direct contact hydrogenation process	79
4.1.11. Solvent extraction	80
4.1.12. Caustic soda and bleaching earth treatment	80
4.1.13. Treatment in a refinery	81
4.1.14. Water management in waste oils re-refining installations	83
4.1.15. Waste management in waste oils treatment installations	86

4.2.	Waste solvents	86
4.2.1.	Selection of waste solvents to be recycled	86
4.2.2.	Improvement of regeneration treatment of waste solvents	87
4.2.3.	Waste water treatment in waste solvent facility	88
4.2.4.	Evaporation of distillation residues	89
4.2.5.	Full automatisisation of residue incineration	90
4.3.	Waste catalysts	90
4.3.1.	Generic techniques used in the treatment of waste catalyst.....	90
4.3.2.	To improve control of the process	91
4.3.3.	Abatement techniques used in the waste catalyst regeneration sector.....	92
4.4.	Activated carbon	92
4.4.1.	Choice of furnace used to regenerate the waste activated carbon	92
4.4.2.	Flue-gas treatment	93
4.4.3.	Waste water treatment plants	95
4.4.4.	Pollution control techniques applicable to activated carbon regeneration.....	96
4.5.	Resin regeneration	96
4.5.1.	Techniques for the regeneration of resins	96
4.5.2.	Pollution control techniques applicable to activated carbon and for resin regeneration	97
4.6.	Waste gas treatments	97
4.6.1.	Fabric filters.....	97
4.6.2.	Condensation	98
4.6.3.	Biofilters	101
4.6.4.	Scrubbing.....	106
4.6.5.	Chemical scrubbing	108
4.6.6.	Incineration	109
4.6.7.	Combined combustion	111
4.6.8.	Catalytic combustion.....	112
4.6.9.	Regenerative catalytic oxidiser.....	114
4.6.10.	Regenerative thermal oxidiser	115
5.	Best available techniques	118
6.	Emerging techniques	120

1. General information

Installations for treatment of waste oil

Used lubricating oils can be recovered to a quality essentially equal to some groups of base oils used to produce lubricating oils (some base oil groups III and IV rarely, if ever, contain re-refined oils). This process is typically referred to as 'oil re-refining'.

The recovery of oil from waste is typically a part of the waste industry. There are licensed sites that specialise in the recovery of oil from different waste streams. In addition, a number of chemical treatment plants and transfer stations have oil separation units that undertake a first separation of oil from water before sending the oil layer through to a specialist plant for further processing. Some factors that define this sector are:

- companies that serve particular industrial sectors tend to offer a general waste service to that sector, and this may include waste oils
- companies that collect used lubricating oils from garages are also likely to collect oil filters, steering, brake and transmission oils, antifreeze and batteries
- companies handling transformer oils are likely to collect oils with some small amounts of PCBs
- some chemical and biological treatment plants undertake small scale oil recovery operations as part of their pretreatment processes. These are generally simple gravity separation systems.

There are large numbers of dedicated oil treatment and processing plants in the EU. Some companies carry out simple purification, removing the sediment and water from waste oil. Two type of treatments are applied to waste oils. One refers to its use as fuel and the other one corresponds to the re-refining of it so that part of it (typically 50 – 60 %) can be re-used as a base oil for lubricants. Oil processors show a wide range of intrinsic knowledge about their operations.

There are a wide variety of processes and licensors currently offering ways to deal with waste oils. There are four main processes used for the treatment of waste oils: blending, separation-chemical treatment, distillation and cracking.

In all waste oil treatment processes, the economic and calorific values of the waste oils are recovered to varying degrees. The two main techniques used are re-refining and direct burning (mainly in cement factories), each accounting for about 30 % of the total quantity recovered. The two other methods which, together, account for the remaining third are reprocessing and reclaiming, the latter principally being used for hydraulic oils.

The level of knowledge about oils is markedly different between sites. Partly due to the fact that waste oil is an extremely complex and changing material with a huge potential range of individual components that are not all categorised at present.

Data currently available regarding waste oil (WO) management in Europe are of very poor quality, particularly concerning regeneration. Figure 1.1 shows a summary of the percentages of the types of treatments used for the WO in each EU country. According to data from the sector in 1993, the used oils collected were disposed of by direct burning (32 %), by re-refining to base oils (32 %), by reprocessing to industrial fuel (25 %) and by reclaiming specific industrial oils 11 %. These percentages however have since changed considerably, as shown in the following figure.

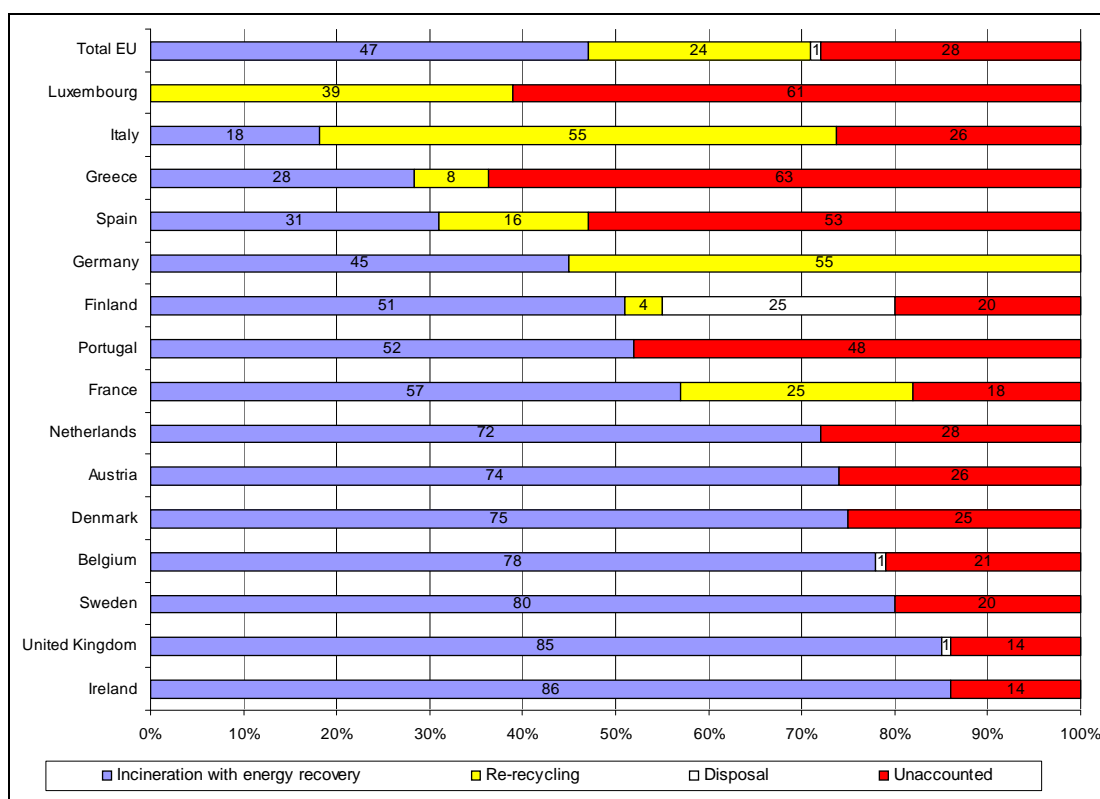


Figure 1.1: Management of waste oils in the EU in 1999
 [7, Monier and Labouze, 2001], [86, TWG, 2003], [150, TWG, 2004]

Re-refining

About 220 kt of re-refined base oil was produced in 2000 according to [7, Monier and Labouze, 2001], which accounts for less than 5 % of the overall base oil demand in Europe.

In recent years, the level of regeneration carried out has noticeable decreased in some EU countries which were pioneers in its use such as France, Germany, Italy and others such as the UK. This is tempered by the fact that there are some new projects emerging in several countries: France, Germany, Italy, Spain.

The known installed feed capacity for re-refining base oil throughout Europe is just over 500 kt/yr, with installation capacities ranging from 35 to 160 kt/yr. Currently, there are around 400 re-refining facilities worldwide, with an overall capacity of 1800 kt/yr. Although most of these plants are located in East Asia (India, China and Pakistan), their individual capacity is mainly low, c.a. 2 kt/yr each, on average. Most of these plants use acid/clay and there are few which produce good quality re-refined base oils or which take into account environmental issues.

Country	Number of known installations	Known capacity (kt/yr)
Belgium	2	45
Denmark	1	40

Germany	8	770
Greece	1	40
Spain	2	69
France	2	200
Ireland	0	0
Italy	7 ¹	273 ¹
Luxembourg	0	0
Malta	2	2.4
Netherlands	0	0
Austria	0	0
Poland	1	80
Portugal	0	0
Finland	5	88
Sweden	0	0
United Kingdom	3 ²	5 ²
Yugoslavia	1	
TOTAL	35	1612.4
¹ two installations are currently not working. Capacity of the two installations not working is 25 kt/yr. ² A TWG member questioned such figures to not be correct Note: Numbers within this table may not reflect the real number of installations or capacity. The main reasons are that the market is so dynamic that numbers change rapidly and/or because no data have been provided by the TWG at all on certain topics. Cells without numbers mean that no information has been provided.		

Table 1.1: Installations for re-refining waste oil in European countries
[5, Concawe, 1996], [7, Monier and Labouze, 2001], [13, Marshall, et al., 1999], [36, Viscolube, 2002], [86, TWG, 2003], [128, Ribí, 2003], [150, TWG, 2004]

Re-refining plants can adjust the quantity of re-refined base oil and fuels produced according to the international and local situation (crude oil prices, market demand, subsidies, etc.).

Preparation of waste oil to be used mainly as fuel

About 50 % of WOs (i.e. waste oil from ship and tank cleaning, waste oil from oil/water separator, waste oil from emulsions, etc.) is not waste lubricant oil or cannot be regenerated into base oil. These WOs can be converted into other oil products (e.g. fuel).

About 50 % of WOs were used as fuel in the EU in 1999. About 400 kt of WO are burned in cement kilns at the European level, which represents about 17 % of the total WO and 35 % of the WO burned, with the rate varying greatly between different countries. It represents the major exploitation route in France, Greece and Sweden, but only one of several alternative routes in Austria, Belgium, Italy and the United Kingdom. Some other sectors in the EU using WO as fuel are:

- blast furnaces, as a substitute for coke (e.g. Belgium)
- brick kilns (e.g. Spain)
- ceramic kilns (e.g. Spain)
- large combustion plants (e.g. Spain)
- lime kilns (e.g. Spain, Belgium)
- cracking plants, to produce new fuels (e.g. in Belgium in accordance with legal standards)
- port receiving facilities which convert waste oil into ship's fuel (e.g. Malta)
- waste incinerators (e.g. 2 kt in 2002 in hazardous waste incinerators in Belgium)
- space heaters (e.g. service stations, greenhouses, etc.)
- asphalt plants.

The two latter applications are no longer used in Flanders (Belgium) because of more stringent environmental regulations brought into force in January 1999. Table 1.2 indicates the amount of used oil burned in some EU countries

Burning options	Amount of waste oil (kt)	%
Cement kilns	307	42
Mixed with fuel oil	213	29
Other	120	16
Waste incinerators	52	7
Garage heaters	40	6
Total burned	732	100
Data only correspond to Denmark, Finland, France, Germany, Italy, the Netherlands, Norway, Spain and the United Kingdom. Note: Obtaining a complete set of data on volumes of used oil burned in all EU countries in this study is difficult as details of the burning options are not consistently recorded.		

Table 1.2: Volumes of used oil burned in EU per year
[5, Concawe, 1996]

There is also a significant volume of oil contaminated waters collected for recovery. These wastes have a net negative value but are processed so as to maximise the recovery of the hydrocarbon for use as a fuel. Table 1.3 shows some installations carrying out this activity.

Country	Number of known installations			Known capacity (kt/yr)		
	Using waste oil in direct burning	Using reprocessed waste oil as fuel	Non-hazardous oil	Using waste oil in direct burning	Using reprocessed waste oil as fuel	Non-hazardous oil
Belgium	1	10				
Denmark	4	Y				
Germany	12	1		310	100	
Greece	0					
Spain	4	Y	1			
France	60			725		
Ireland		Y				
Italy	2					
Luxembourg	0	0		0	0	
Malta	0	1		0	4.7	
Netherlands		Y				
Austria	4	0	0		0	0
Portugal	Y	Y	1			
Finland	3	4	1	155	54.5	0.2
Sweden	2	3				
United Kingdom	160	Y				
TOTAL	252	19	3	1190	159.2	0.2
Y: exists but no data is available Note: Columns related to non-hazardous oil correspond to the production of biodiesel from used vegetable oil. Note: Numbers within this table may not reflect the real number of installations or capacity. The main reasons are that the market is so dynamic that numbers change rapidly and/or because no data have been provided by the TWG at all on certain topics. Cells without numbers mean that no information has been provided.						

Table 1.3: Installations where waste oils are used as fuel or where waste oil is reprocessed to produce a fuel
[7, Monier and Labouze, 2001], [13, Marshall, et al., 1999], [56, Babbie Group Ltd, 2002], [86, TWG, 2003], [128, Ribí, 2003], [150, TWG, 2004]

Under EU legislation, it is illegal to dispose of WO in landfills, storm-water or waste water drains. In some cases, used oil is applied to unsealed roads as a dust suppressant in some rural areas. About 25 % of the WO in the EU was unaccounted eliminated for in 1999.

Installations for treatment of waste solvent

Solvents are extensively used in chemical and biological processes. During these processes, waste solvent is produced and it is recycled in-house. These treatments are an integral part of the chemical/biological processes and they are covered in the different BREF documents. However for economic or technical reasons, sometimes the waste solvents are delivered to a third party (e.g. waste manager) for treatment. In some cases, the product of the treatment is returned to the waste producer and in other cases this does not happen.

Waste solvents are also produced in the area of solvent-based surface treatment (such as cleaning or degreasing in many different industrial sectors and in dry cleaning installations). In most cases, the contaminated solvents or the bottoms of the distillation columns (solvent content 1–10 % in the case of closed cleaning installations/devices with internal distillation devices) are delivered to solvent distillation installations and regenerated. The quality of the distillation products is as good as that of new solvents.

In accordance with the Waste Framework Directive, the first option for waste solvents, as well as for the rest of waste, is that it should be recycled. This has helped to generate an active solvent recycling market. Similarly to waste oils, waste solvents which are not suitable for regeneration because of certain compositions or because of very low purity can also be recovered as a secondary liquid fuel (SLF), for example, in the cement industry and hazardous waste incinerators. A fundamental difference with waste oils is that waste solvent qualities fluctuate much more than the quality of waste oil.

Solvent regeneration facilities separate contaminants from waste solvents and thus restore the solvent to its original quality or may be to a lower grade product (e.g. in the case of lacquer thinner). Distillation (batch, continuous, or steam) is used by most commercial solvent processors, and typically recovers about 75 % of the waste solvent. The residue, known as 'distillation bottoms', can be a liquid or a sludge, depending upon a number of conditions, and typically requires management as a hazardous waste. Other separation technologies used by solvent processors include: filtration, simple evaporation, centrifugation, and stripping.

Country	Number of known installations	Known capacity (kt/yr)
Belgium	5	>8
Denmark	0	
Germany	21	
Greece	3	
Spain	14	64
France	27	90.7
Ireland	2	
Italy	2	
Luxembourg	0	
Netherlands	8	
Austria	2	
Portugal	1	10000 m ³
Finland	4	11
United Kingdom	8	>12
Iceland	0	
Norway	11	
TOTAL	108	185.7
Note: Numbers within this table may not reflect the real number of installations or capacity. The main reasons are that the market is so dynamic that numbers change rapidly and/or because no data have been provided by the TWG at all on certain topics. Cells without numbers mean that no information has been provided.		

Table 1.4: Waste solvent installations in European countries

[40, Militon and Becaud, 1998], [60, Azkona and Tsotsos, 2000], [61, Weibenbach, 2001], [86, TWG, 2003], [129, Cruz-Gomez, 2002]

Installations for the treatment of waste catalysts, waste from pollution abatement and other inorganic waste

The treatment of waste catalysts depends on the type of catalyst (catalytic active substance and supporting structure or carrier) as well as the included by-products from the catalytic process. These treatments include:

regeneration of catalysts to be re-used as catalysts again, recycling of components from catalysts and disposal in landfills. An example installation is an Austrian facility for the recovery of Ni from food industry catalysts (Fe/Ni alloy).

Hydrometallurgical technology can be used to extract and concentrate metals from liquid waste. Non-liquid wastes first require dissolution.

In Malta, there are two underground asbestos storage sites and one overground pending treatment. The asbestos originated from ships being repaired in dock yards and from unused asbestos pipes.

Country	Treatment of waste catalysts		Treatment of other inorganic waste (excluding metals and metal compounds)		Recovery of waste from pollution abatement	
	Number of known installations	Known capacity (kt/yr)	Number of known installations	Known capacity (kt/yr)	Number of known installations	Known capacity (kt/yr)
Belgium	0	0	13		1	
Denmark	0	0	3		1	
Germany	1		63		2	
Greece	5		0	0	0	0
Spain	0	0	6	195	15	3
France	3	4.9	0	0	0	0
Ireland	4		0	0	0	0
Luxembourg	0	0	0	0	0	0
Malta			3			
Netherlands	2		17		1	
Austria	3		14		0	0
Portugal	0	0	0	0	0	0
Finland ¹	0	0	9	3	0	0
Iceland	0	0	0	0	0	0
Norway	2		1		0	0
TOTAL	20	4.9	129	198	20	3

¹ The treatment of 1 million lamps containing mercury is not included.
Note: Numbers within this table may not reflect the real number of installations or capacity. The main reasons are that the market is so dynamic that numbers change rapidly and/or because no data have been provided by the TWG at all on certain topics. Cells without numbers mean that no information has been provided.

Table 1.5: Installations for the treatment of waste catalysts, waste from pollution abatement and other inorganic waste in European countries
[40, Militon and Becaud, 1998], [60, Azkona and Tsotsos, 2000], [61, Weibenbach, 2001], [150, TWG, 2004]

Installations for treatment of activated carbon and resins

Most waste activated carbon and resin is a result of water purification processes. It is very difficult to estimate the regeneration throughput in Europe, mostly due to the fact that many operators regenerate their adsorbent on site (often sporadically) rather than sending it to large centralised reactivation plants.

Activated carbon is used in three principal applications: the treatment of drinking water; in the food and drink industry, for example for removing colour in the refining of sugar; and in general industrial applications, e.g. removal of VOCs from process vent streams. These applications affect the type of contamination on the carbon and the regeneration process that is then required. For example, carbon which has been used in industrial applications ('industrial carbons'), such as in effluent treatment, requires a more stringent pollution abatement system than that used for the treatment of potable water or for that from the food industry.

At some point in the lifetime of the process, the carbon will become exhausted with the material that it is adsorbing. The carbon should then be regenerated or, if this is not possible, disposed of. The choice of route is naturally determined by economics and scale. In the treatment of potable water, the carbon is used in large quantities and is contained in large open topped concrete-lined carbon beds. These have a life expectancy before

exhaustion of a few years. When they are regenerated, they result in large quantities to be treated. It is this application that represents the most common in the UK in terms of volume and it is regenerated either on site by a purpose built plant or transported off site for regeneration by a merchant operator. Because of the nature of the market there is a tendency that more regeneration facilities, once designed purely for 'in-house' materials, now offer a merchant regeneration service.

There are at least 19 sites in Europe regenerating activated carbons from off site. The estimated numbers are mentioned in the next Table 1.4.

Country	Number of known installations	Known capacity (kt/yr)
Belgium	2	
Germany	3	
France	1	
Italy	5	
Netherlands	1	
Austria	1	
Finland	1	
Sweden	1	
United Kingdom	4	
TOTAL	19	>50
Note: Numbers within this table may not reflect the real number of installations or capacity. The main reasons are that the market is so dynamic that numbers change rapidly and/or because no data have been provided by the TWG at all on certain topics. Cells without numbers mean that no information has been provided.		

Table 1.6: Activated carbon installations in European countries
[150, TWG, 2004]

The most common reactivation furnaces are direct fired rotary kilns and multiple hearth furnaces. Indirect fired rotary kilns, fluidised bed, vertical tube type and infrared are sometimes used. The type of granular activated carbon (GAC) reactivation furnaces in use worldwide in early 1990 are shown in Table 1.7.

Type of GAC reactivation furnace	Number of units
Multiple hearth	>100
Fluidised bed	<20
Indirect fired rotary kiln	>50
Direct fired rotary kiln	<30
Vertical tube-type	<30
Infrared furnaces (horizontal and vertical)	<9

Table 1.7: Type of GAC reactivation furnaces in use worldwide
[42, UK, 1995]

Quantitative figures for ion exchange resin regeneration facilities are not available.

Installations for the treatment of waste acids and bases

There are several installations in the EU which regenerate HCl. No installations have been identified to recover HBr. Waste sulphuric acid can be regenerated in the following ways:

- thermal decomposition of waste/spent/recovered sulphuric acid, the result then being used as a primary or supplementary source of SO₂ feed to a sulphuric acid contact process. This is covered in the LVIC(AAF) BREF [62, EIPPCB, 2003], as is any process that produces SO₂ as a feedstock by decomposition/calcinations
- a process based on the reconcentration of weak/spent/waste sulphuric acid, with or without separation of potential impurities (e.g. salts). This will be included in this document

- industrial processes that use sulphuric acid and include a recycling of the spent sulphuric acid as an integral part of the process. This will be covered in the BREF where the industrial process is covered (e.g. BREF LVIC-solids and others for titanium dioxide production).

Country	Number of known installations	Known capacity (kt/yr)
Belgium	1	
Denmark	1	
Germany	2	
Greece	0	
Spain	1	42
France	3	2
Ireland	1	
Luxembourg	0	
Netherlands	0	
Austria	4	
Portugal	0	
Finland	0	
Iceland	0	
Norway	0	
TOTAL	13	44
Values correspond to regeneration installations covered by this document and the LVIC-AAF BREF Note: Numbers within this table may not reflect the real number of installations or capacity. The main reasons are that the market is so dynamic that numbers change rapidly and/or because no data have been provided by the TWG at all on certain topics. Cells without numbers mean that no information has been provided.		

Table 1.8: Installations for the regeneration of waste acids or bases
 [40, Milton and Becaud, 1998], [60, Azkona and Tsotsos, 2000], [61, Weibenbach, 2001], [86, TWG, 2003]

Acid recovery usually involves the separation of unreacted acid from an acid waste such as spent pickle liquor generated by the steel industry. One method used in the steel industry, involves cooling the sulphuric acid to precipitate ferrous compounds. In another method, acid can be regenerated by injecting it into a spray roaster.

Chapter 3 : economic and institutionnel aspects of waste treatment sector

Waste oils

Environmental consciousness in the 1980s has had a number of consequences on the waste oils treatment sector, in particular:

- the shutting down of many acid/clay re-refining plants, mainly in the US, for both economic and environmental reasons
- the use of improved equipment and devices to reduce the potential pollution from burning used oil
- the development of improved re-refining technologies for both environmental and product quality reasons.

2. Applied processes and techniques

Treatments applied mainly to recover the materials from waste

This section includes those treatments and processes mainly designed to recover the materials or portions of materials contained in waste. Typically these processes are very dependent on the type of waste treated and the materials that are wanted or that need to be produced. The materials produced from these treatments are materials that can be re-used for the same purpose (e.g. lubricant oils) or recovery for other non-energy purposes (e.g. recovery of metals from catalysts). When the material is treated to be used subsequently as fuel, this is included in the Section 2.5.

'Regeneration' is the term used in this document to describe these treatments except in the case of regeneration of waste oils where the term 're-refining' is used. This is not an attempt to make any kind of definition. This should be taken only as a convention to aid reading this document.

2.1. The re-refining of waste oils

[5, Concawe, 1996], [7, Monier and Labouze, 2001], [11, Jacobs and Dijkmans, 2001], [13, Marshall, et al., 1999], [56, Babbie Group Ltd, 2002], [86, TWG, 2003], [96, Straetmans, 2003], [150, TWG, 2004], [152, TWG, 2004]

There are two main options for the treatment of waste oils. One is the treatment of the waste oil to produce a material that will be used mainly as fuel or for other uses (e.g. absorbant, mould release oil, flotation oil). These include treatments as cleaning of waste oil, thermal cracking and gasification for example and are covered in Section **Error! Reference source not found.** The other way, is to treat the waste oil to reconvert it to a material that can be used as a base oil to produce lubricants. This latter way is referred to as 're-refining' in this document. This section details the different treatments that are actually applied to waste oils for clean-up and re-refining. As it is the case in the whole document, this classification has been adopted for this document and it is not intended to provide any attempt to define any of the 'R' codes from EC waste legislation.

A lot of treatment processes exist (or are currently under development) today in Europe. The most significant ones are listed below in Figure 2.1. This figure also gives an overview on how these treatments have been included in this document.

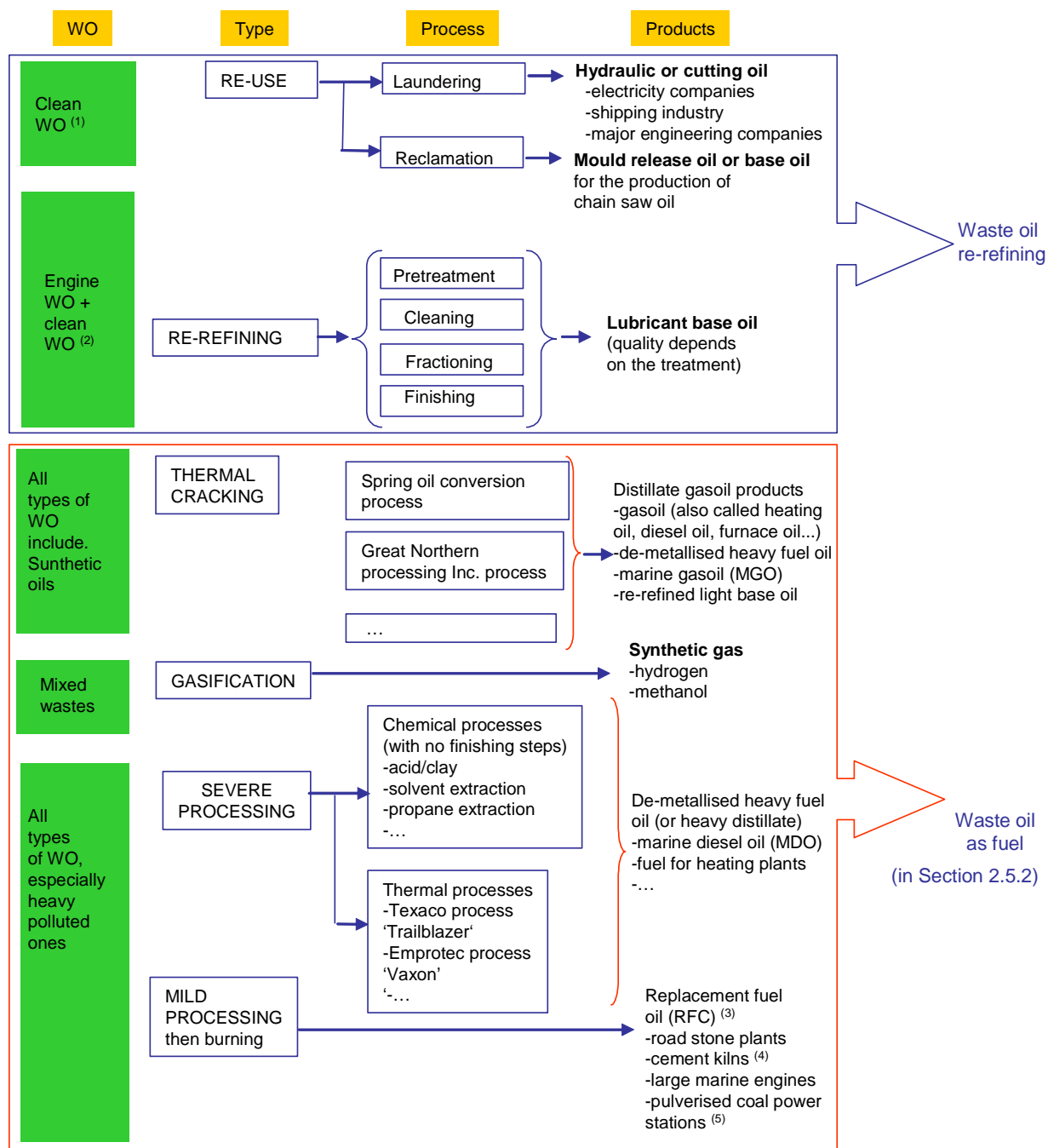


Figure 2.1: Waste oil treatments and division approach used in this document
 [7, Monier and Labouze, 2001], [86, TWG, 2003], [150, TWG, 2004]

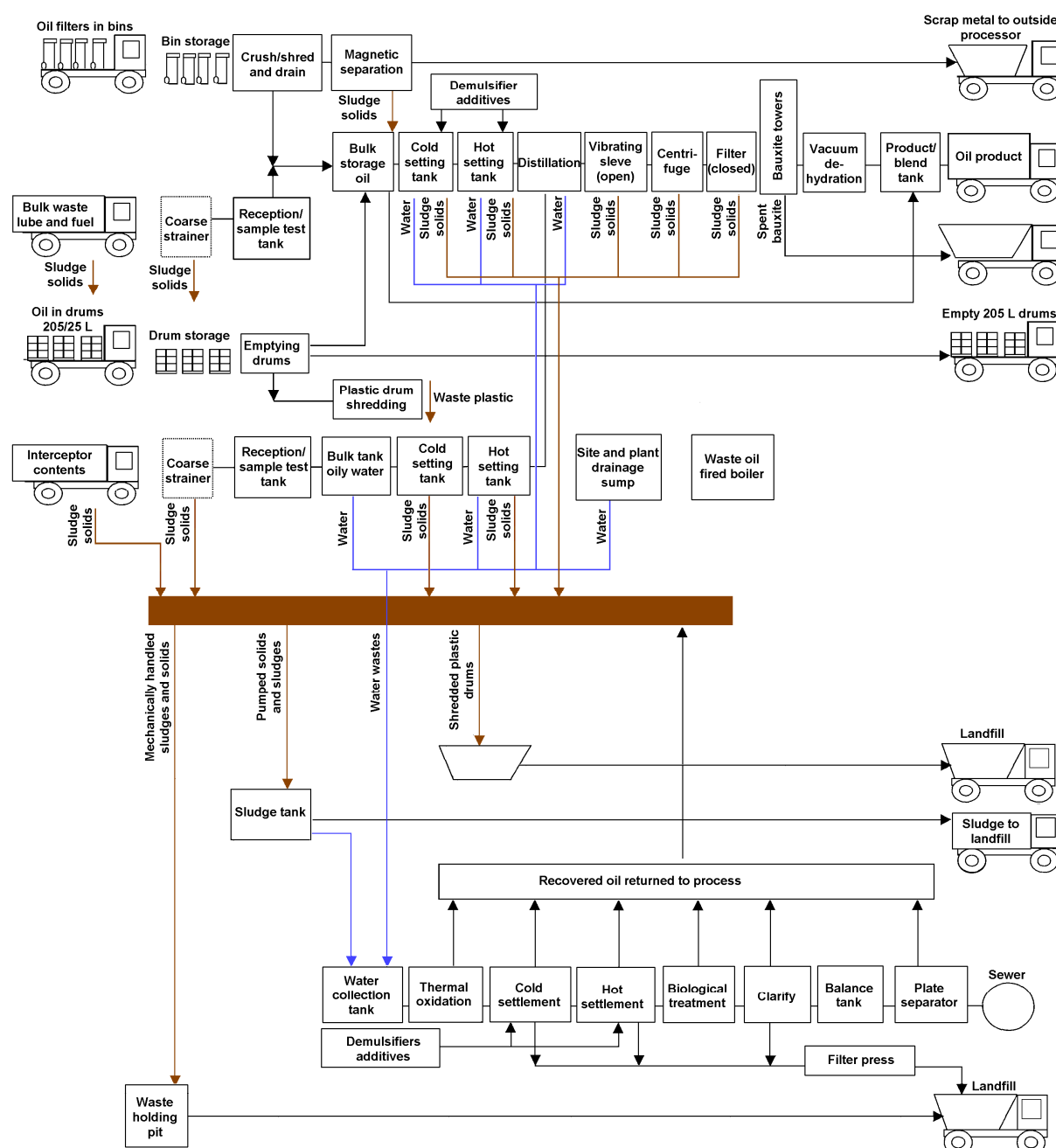
Note: (1) Especially hydraulic or cutting oil

(2) Engine oils without chlorine + hydraulic oils without chlorine +
 hydraulic mineral oils + mineral diathermic oils (according to the API classification)

(3) Treated oil still containing the heavy metals, halogen and sulphur contained in the original waste oil (WO)

(4) Substitutes other secondary liquid fuel (SLF) or heavy fuel or coal or petroleum coke

The main processes used in oil recovery plants are shown in Figure 2.2. This is an amalgamation of unit operations. Not all operations are applied in every plant. In practice, most plants only use a few of the processes shown, and usually there are two or more parallel streams from each process.



Based on [56, Babbie Group Ltd, 2002]

Re-refining treatments may differ depending on the technology used for one or several of the following operations: pretreatment, cleaning, fractionation and finishing. Each of these processes are briefly described in the following sections.

2.1.1. Pretreatment of waste oil

Purpose

To dewater (removal of water), de-fuel (removal of light ends and fuel traces such as naphtha, etc.) and remove sediments. This pretreatment process is not compared with the other oil treatment systems because it does not yield an end-product, nor does it achieve the final aim of treatment.

Principle of operation

Water and sediments are removed from the waste oil by a simple physical/mechanical treatment. Settling is used in some cases to remove water and sludge from waste oil and in the effluent treatment systems for removing oil and solids from the effluent. Generally, settling takes place using the gravity effect in settling tanks, clarifiers or plate separators, but centrifuges or distillation can also be used.

Feed and output streams

The typical feed is collected waste oil. The product is cleaned waste oil. After this treatment the cleaned oil can be used in one of the options described below (Sections 2.1.2 to 2.1.4).

Process description

The main techniques used are settling, sedimentation, filtering and centrifuging.

Settling

A tank is filled and left until it settles, the upper oil strata is skimmed off and similarly the water layer is drawn off. Depending on how dirty the feedstock is, the sludge might be left at the bottom of the tank to accumulate over several settlement cycles before it is removed. The settling process is often aided by heating, to reduce the viscosity. In many cases, an interface layer of an oil/water emulsion remains. This can be encouraged to separate by the addition of heat and chemicals. Further settling processes applied to the 'water' layer can separate the oil/water phase even better.

Sedimentation

Filtering/straining

Particulates are removed by strainers, filters or sieves.

Centrifuging

Distillation

Water may be removed by this technique.

Users

Used in many of the waste oil re-refining technologies (see Table 2.2)

2.1.2. Cleaning of waste oil

Purpose

Cleaning includes deasphalting and the removal of asphaltic residues: heavy metals, polymers, additives, other degradation compounds.

Principle of operation

Distillation and the addition of acids are the most typical ways to achieve the above results.

Feed and output streams

Process description

Acid cleaning: additives, polymers, oxidation and degradation products are removed by contact with sulphuric acid or precipitated as sulphates (e.g. metals). Clay cleaning is also considered, where the clarified oil is mixed with clay by absorption to remove any polar and undesirable compounds still present.

Users

Used in many of the waste oil re-refining technologies (see Table 2.2).

2.1.3. Fractionation of waste oil

Purpose

This involves a separation of the base oils using their different boiling temperatures, to produce two or three cuts (distillation fractions).

Principle of operation

This physical separation process utilises the boiling point differences of components.

Feed and output streams

Typically pretreated waste oil.

Process description

Vacuum distillation units can range in complexity from a simple splitting column to a full fractional distillation column, as used in mineral oil refineries.

Users

Used in many waste oil re-refining technologies (see Table 2.2).

2.1.4. Finishing of waste oil

Purpose

Final cleaning of the different cuts (distillation fractions) is carried out to achieve specific product specifications (e.g. improve colour, smell, thermal and oxidation stability, viscosity, etc.). Finishing may also include the removal of PAHs in the case of a severe (high temperature and high pressure) hydrofinishing or solvent extraction (low temperature and low pressure).

Principle of operation and feed and output streams

Technique	Principle of operation	Feed and output streams
Alkali treatment	KOH or NaOH is used	Colour properties are enhanced.
Bleaching earth	This is a tertiary treatment, to remove the black colour from the oil (caused by the carbon breakdown from the additives), so it can visually be compared with virgin base oil.	The new goals, set up by the implementation of upcoming specifications for passenger car motor oils, cannot be achieved. In particular, the colour of the produced oils is darker than required.
Clay polishing	This is a process similar to the acid/clay process but acid is not used. Bentonite is the clay typically used. The clay is then separated from the oil using a filter press.	Generally, clay polishing does not produce the high quality base oils of solvent extraction or hydrotreatment.
Hydrotreatment	Chlorine and sulphur are removed from the waste oil fraction at a high temperature under a hydrogen atmosphere and in contact with a catalyst, being converted into HCl and H ₂ S. Phosphorus, lead and zinc are also removed in this process. PAHs can be removed by severe hydrofinishing (high temperature and with hydrogen under high pressure)	The quality of the distillates is very high and the petroleum fractions are immediately marketable. Hydrogen is needed for the process. Hydrogen sulphide is formed, which can later be reduced to sulphur.
Solvent cleaning	PAHs are removed from the base oils by	The feed into the extraction must be a good

	extracting them into the solvent (into ppb range). The solvent extraction also improves the colour and viscosity index.	quality base oil with all heavy metals etc. removed and already fractioned into wanted cuts. The products are a high quality base oil, the used solvent which is regenerated, and a small stream of base oil (c. 3 % of the total base oil stream) with a high PAH concentration, which is used as a fuel product.
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Table 2.1: Finishing techniques used for the treatment of waste oils

[7, Monier and Labouze, 2001], [86, TWG, 2003], [139, UBA, 2003]

Process description

The hydrotreatment process can be found in the Refinery BREF.

Users

Used in many waste oil re-refining technologies (see Table 2.2)

2.1.5. Technologies used for the re-refining of waste oils

Table 2.2 summarises the different technologies used for the regeneration of waste oil.

Technology	Feed and output streams	Process description			
		Pretreatment	Cleaning	Fractionation	Finishing
Laundering	Transformer oils, industrial lubricants (e.g. hydraulic and cutting). Product: clean industrial lubricant returned to users	Adsorption Heating Filtration Vacuum dewatering			
Reclamation	Industrial oils (especially hydraulic oils). Product: clean industrial lubricant returned to users	Centrifugation and/or filtering			
Clay processing	Product presents poor characteristics in terms of viscosity and volatility. It can only be employed in the formulation of a limited type of industrial lubricant	<i>Pre-flash unit</i> Atmospheric vacuum stripping	<i>Clay treatment</i> By contact with a large quantity of adsorption clay		
Acid/clay + distillation		<i>Atmospheric or vacuum flash stripping</i>	<i>Acid or clay treatment</i> Removal of waste oil contaminants by acid treatment (typically sulphuric acid) or clay treatment	<i>Distillation</i> The cleaned oil is then distilled to recover two or three cuts, plus an overhead gasoil	<i>Neutralisation and filtration</i> The lubricating oil cuts, along with the gasoil, are neutralised with calcium hydroxide and filtered
Acid surfactant flocculation					
Distillation/ chemical treatment or solvent extraction		<i>Vacuum distillation</i> The 1 st stage removes the water, naphtha and light end. The 2 nd stage removes the gasoil, spindle oil or light fuel oil	<i>Vacuum distillation</i> The 3 rd /4 th stages separate the different lubricating oil cuts from the residue (in which all the metals, additives and degradation products are concentrated)		<i>Chemical treatment is carried out in a blocked operation, followed by a distillation/stripper to correct volatility and the flashpoint. Alternatively, a solvent extraction stage can be supplied to remove the PAHs</i>
Distillation and solvent extraction (Vaxon process)			<i>Vacuum distillation</i>		<i>Solvent extraction</i>

Technology	Feed and output streams	Process description			
		Pretreatment	Cleaning	Fractionation	Finishing
Solvent extraction and distillation (Sener-Interline process)	The recovered base oils have a good quality.	<i>Chemical pretreatment</i>	<i>Extraction with propane.</i> Liquid propane extracts the base oils and rejects water, asphalt, additives, and other non soluble contaminants.	<i>Atmospheric and vacuum distillation</i> The extracted oil is firstly distilled in an atmospheric distillation column to separate light hydrocarbons and some propane. The remaining oil is fractioned in a vacuum distillation column to recover lubricant base oils.	
Propane deasphalting and hydrofinishing	The technology produces good quality base oils and an alphaltic residue (suitable as bitumen)	<i>Pre-flash</i> In a distillation column	<i>Extraction with propane</i> Propane deasphalting	<i>Atmospheric vacuum distillation</i>	<i>Hydrofinishing with a NiMo catalyst</i>
Distillation and alkali treatment (Vaxon - C.F.T. – Cator)	Motor and industrial waste oils, all types of synthetic lubricants except PAG water-soluble, silicon oils and some type of esters. Base oils and asphatic residue are the main products Impurities and sediments remain in the final solid waste, which has an asphaltic nature.	<i>Distillation</i> Throughout the process, pretreatment forms part of the same process, since the first phase produces a dewatering through whole distillation with all used oil types.			<i>Alkali treatment</i>
Thin film evaporators (TFE) and different finishing processes *	Heavy metals, polymers, additives and other degradation products are removed as an asphaltic residue.	<i>Pre-flash and chemical treatment (1st)</i> Water, light ends and fuel traces contained in the used oil are removed. Atmospheric vacuum stripping + chemical treatment (optional) to minimise the corrosion and fouling of downstream equipment.	<i>TFE(2nd)</i> Performed at very high temperatures and vacuums.	<i>Distillation (4th)</i> The lubricating oil fraction is separated into different oil cuts in a vacuum column.	<i>One of the following (3rd)</i> a) <i>Hydrotreatment</i> b) <i>Clay treatments</i> c) <i>Solvent extraction</i> d) <i>Solvent extraction + hydrotreatment</i>

Technology	Feed and output streams	Process description			
		Pretreatment	Cleaning	Fractionation	Finishing
Thermal de-asphalting process (TDA)		<i>Pre-flash</i> Atmospheric vacuum stripping + chemical treatment. The last treatment is used to minimise the corrosion and fouling of downstream equipment and to facilitate the subsequent deasphalting step.	<i>Settling + TDA</i> Deasphalted by settling. Residue removal is achieved by flashing at the bottom of the distillation column, which performs the fractionation of the different lubricating oil cuts.		a) <i>Clay</i> b) <i>Hydrotreatment</i>
Direct contact hydrogenation process (DCH)	Waste oil and hot hydrogen gas pass the process as a mixture It produces good quality base oils (group II)	<i>Pretreatment</i> Not necessary	<i>Guard hydrogenation reactor (1st)</i> Hydrogen and oil vapour is routed to a two stage fixed bed catalytic reactor. The guard reactor removes any trace metal contaminants, following by a cracking of any sulphur, nitrogen, halogen compounds in the conversion reactor.	<i>Fractionation (3rd)</i> The lubricating oil fraction is separated into different oil cuts in a vacuum column	<i>Hydrotreatment (2nd)</i> High pressure flash separator. Fixed bed catalytic reactor
Caustic soda and bleaching earth treatment (ENTRA)	Waste oil and caustic soda. The base oil produced is of good quality (group II) with good yields	<i>Pre-flash</i> Dewatering. Feed with the addition of caustic soda (3 % referred to dry used oils) and bleaching earth (2 % referred to dry used oil)	<i>Tubular reactor</i> Break-down of the undesired metallorganic, sulphur, nitrogen and halogen compounds takes place. An advanced control of temperature and retention time in a linear tubular reactor minimises the break-down of those organic molecules which are still viable as lubricating oil components	<i>Fractionation</i> The lubricating oil fraction is separated into different oil cuts in the linear tubular reactor	<i>Neutralisation</i> Neutralisation with acid, clay treatment
Integration in a base oil production of a refinery	Oil produced represents a good quality of re-refined base oil.	a) Pre-flash in a distillation column b) Atmospheric vacuum stripping.	<i>TFE</i>	<i>Aromatic extraction unit</i> of the refinery to remove PAHs and other undesirable compounds.	<i>Hydrofinishing</i>

Technology	Feed and output streams	Process description			
		Pretreatment	Cleaning	Fractionation	Finishing
Integration in a refinery after pretreatment	Waste oil is reprocessed in a refinery to allow blending into fuel products. Contaminants within waste oils normally preclude their use as catalytic cracker feedstock or in lubricant oil production.	Water and sediments are removed from the waste oil by a pre-flash step	The pre-flashed waste oil is directly blended with the regular atmospheric residue of a refinery.		
* 1st, 2nd, 3rd, 4th stands for the sequence of when the operations are carried out within the process. When no such numbers are present, the sequence is the most common one, i.e. pretreatment, cleaning, fractionation and finishing.					

Table 2.2: Waste oil re-refining technologies

[5, Concawe, 1996], [7, Monier and Labouze, 2001], [86, TWG, 2003], [139, UBA, 2003], [150, TWG, 2004]

2.2. Regeneration of waste solvents

[53, LaGrega, et al., 1994], [83, Indaver, 2002], [129, Cruz-Gomez, 2002], [130, UBA, 2003], [150, TWG, 2004], [152, TWG, 2004], [156, VROM, 2004], [157, UBA, 2004]

Purpose

Once the waste solvent is passed to a waste manager, there are two main options for its treatment:

- utilisation of the calorific value by using them directly as a fuel or blended with other fuels. The use of the waste solvents as fuels is covered in Section **Error! Reference source not found.**
- treatment of the waste solvent to reconvert it to a material that can be re-used as solvent. This treatment is referred to in this document as 'regeneration'. This section details different treatments that are actually applied to waste solvents for their clean-up and to regenerate them to produce solvents.

The solvents and organic acids can be treated to a degree such that they can be returned into the production cycle as secondary raw material.

Principle of operation

Clean-up is achieved by different types of distillations which are the main types of separation process used.

Feed and output streams

Solvent regeneration is common practice in many industries, with a wide range of solvents currently being regenerated, the more common of which are shown in Table 2.3.

Hydrocarbon family	Chemicals
Alcohols	Ethyl, isopropyl
Aliphatics	Hexane, heptane
Aromatics	Benzene, aromatic naphtha, toluene, xylene, turpentine
Chlorinated	Trichloroethylene, perchloroethylene, methylene chloride
Esters	Ethyl acetate, butyl acetate
Ketones	Methyl ethyl ketone, methyl iso-buthyl ketone
Mixtures of solvents	Toluene/xylene, ketones, alcohols, phenols, toluene/heptane

Table 2.3: Commonly regenerated waste solvents
[53, LaGrega, et al., 1994], [150, TWG, 2004], [152, TWG, 2004]

Process description

Figure 2.3 and Figure 2.4 give examples of flow diagrams of waste solvent regeneration plants.

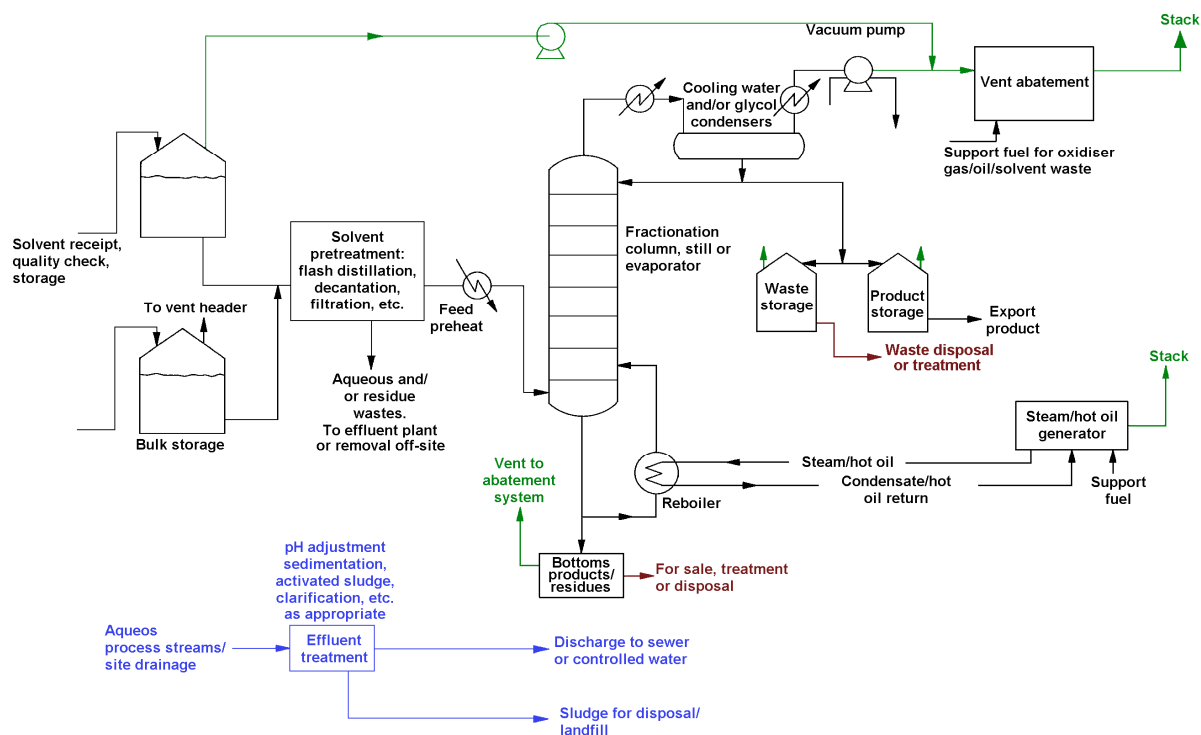


Figure 2.3: Example of waste solvent regeneration installation
[129, Cruz-Gomez, 2002]

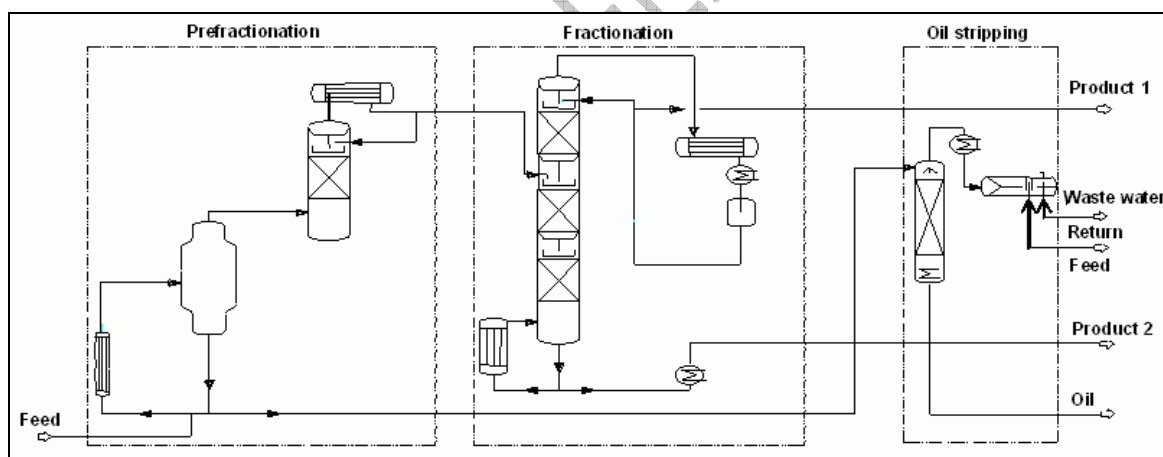


Figure 2.4: Example of chlorinated solvent regeneration flow diagram
[150, TWG, 2004]

Table 2.4 shows the techniques typically used for the regeneration of waste solvents.

Technique	Purpose and principle of operation	Users
Absorption	Transfer solvent from a gas to a liquid	
Adsorption	Recover solvent from solvent laden air	
Centrifugation	Removes suspended solid or separates two distinct (or insoluble) liquid phases, one phase is, for instance, the solvent being recovered	
Condensation	Eliminates solvent vapours from gas streams	
Decantation	Phase separation due to different densities. Separation of liquid solvent and water	
Distillation	Separation of liquid mixtures. Thin film evaporators. Rectification. Fractionation	The distillation of contaminated solvents for partial subsequent use as a fuel in boilers is one technique used (for reducing metal levels in the solvent), (some plants exist in Belgium, Italy, Spain)
Evaporation	Removal of solvent as a vapour form from a solution or slurry	
Filtration	Separation of solid particles from liquid solvent	
Liquid-liquid Extraction	Applied to liquid solvents	
Membrane separation	Recovery of solvents from liquid or gas streams	
Neutralisation	Applied to liquid solvents	
Salting out	Applied to liquid solvents	
Sedimentation	Applied to liquid solvents with a high level of solids	
Storage	See Section Error! Reference source not found.	
Stripping	Transfer of solvent from a liquid stream to a gas stream	

Table 2.4: Unit operations used for the regeneration of waste solvents
[129, Cruz-Gomez, 2002], [130, UBA, 2003], [150, TWG, 2004]

Users

This activity is carried out in the chemical, pharmaceutic and painting industries. Five plants are currently in the Netherlands. An example is described below:

The evaporation capacity depends on the specific evaporation heat of the distilled solvents and amounts to up to 1.3 t/h. The use of a reflux separator can further improve the separation; however, the flowrate is then reduced. Multiphase distillates are cooled and then separated in heavier and lighter phases which are then collected in different containers. Distillation can be performed both under ambient pressure and under vacuum. Furthermore, the facility can carry out other processes such as azeotrope solvent drying or azeotropic esterification. Additionally, organic acids may be treated in a specific ceramics bubble.

The input material containing solvents is pumped into the distillation containers. These containers are heated indirectly by fresh vapour of maximum 6 bar at approximately 158 °C. For heavily contaminated solvents, distillation bubbles of steel are available which are equipped with stirrers for homogenising the contents. Waste solvent mixtures containing only small quantities of residues, or highly corrosive substances such as organic acids, can be distilled using enamelled bubbles. The resulting plumes are transported through a packed column and condensed at the pipes of the overhead cooler.

2.3. Regeneration of waste catalysts and recovery of components from abatement techniques

[86, TWG, 2003], [125, Ruiz, 2002], [150, TWG, 2004]

As mentioned in the Scope, this section covers the regeneration of waste catalysts and the recovery of components from abatement techniques. Alternative ways to regenerate spent catalysts exist, such as the recovery of the metals from catalysts (some precious metals recovery treatments are already covered with in the Non-Ferrous-Metals BREF), regeneration of catalysts (covered in this document) and the treatment of spent catalysts as raw materials for other processes, which are not covered in this document (e.g. the treatment of spent alumina-supported catalysts in the cement industry which is covered in the Cement and Lime BREF). This document only includes ex-situ regeneration installations. In-situ regeneration is typically part of a production process where a catalyst is used, thus is not covered in the scope of this document.

This section is intended as well to include information on the recovery of components from waste generated from abatement techniques (see also Section 0)

Purpose

Waste catalysts and waste from abatement techniques are typically disposed of. However, most catalysts used in abatement techniques (e.g. NO_x abatement) are regenerated.

Principle of operation

Regeneration of precious, platinum and noble metal catalysts to remove coke deposits can successfully restore the activity, selectivity, and stability performance of the original fresh catalyst. Coke deposits are removed by controlled combustion.

Feed and output streams

Catalysts from the refinery industry such as used in hydrotreating, hydrocracking, reforming and isomerisation are typically regenerated. Noble metal catalysts are also regenerated. The metals that are typically economically interesting to be recovered are Rh, Cd, Pt, Ir, the Nickel Raney and some petroleum catalysts with Ni-Co, Co-Mo, Co.

Process description

Ex-situ thermal regeneration is performed in specially designed equipment as well as in standard equipment, e.g. moving-bed belt calciners or rotary calciners.

The regeneration of precious, platinum and noble metal catalysts to remove coke deposits can successfully restore the activity, selectivity, and stability performance of the original fresh catalyst. Coke deposits are removed by controlled combustion.

As an example, after the coke is burned off, a catalyst containing platinum can be regenerated by chlorine treatment at an elevated temperature. The chlorine treatment causes redispersion of the platinum by converting it to a volatile platinum chloride, which is then transported through the gas phase and deposited on the pore walls, where it is treated in H₂ and reduced. The result is an increased dispersion of the platinum and a reactivated catalyst.

The common unit operations used in this sector are dryers, furnaces, leaching equipment and solvent extraction. Some end-of-pipe processes used to control air emissions are dust removal techniques (e.g. electrostatic precipitators, cyclones, fabric filters, ceramic filters, scrubbers, flares), gas scrubbing systems (e.g. scrubbers, dioxins capture systems, VOC abatement systems), and waste water treatments.

Users

There is a very precise process in France (Eurocat) which is applied to the recycling of one specific catalyst family (hydrotreatment) coming mainly from refineries. There is only one moving belt calciner process plant in the EU, which has been located in Luxembourg since 1979.

2.4. Regeneration of activated carbon

[29, UK Environment Agency, 1996], [41, UK, 1991], [42, UK, 1995], [150, TWG, 2004]

Purpose

To treat the spent activated carbon to produce a material with properties and qualities very similar to the original activated carbon.

Principle of operation

Thermal treatments are the main processes used for regeneration. During the process, drying, thermal desorption and heat treatment are carried out.

Feed and output streams

Activated carbon is commercially available in three forms: extruded, granular and powder. Since powdered carbon is extremely difficult to regenerate, this activity is not carried out on powdered carbon. Only the first two forms are therefore considered in this section.

Process description

Regeneration is normally carried out thermally and is typically composed of the following operations:

Receipt, handling and dewatering

Spent activated carbon is normally received on site as a drained solid in tankers. Water is added at the regeneration site in order to turn the carbon into slurry, which is fed to a tank where it is dewatered and charged into a kiln to be regenerated.

Thermal regeneration

After separation from the water, the moist carbon is fed into the furnace for regeneration. During thermal regeneration, drying, thermal desorption (i.e. removal of the organic chemicals) and high temperature (650 to 1000 °C) heat treatment in a slightly oxidising controlled atmosphere are carried out.

The types of equipment generally used are multiple hearth furnaces, directly fired rotary kiln furnaces and indirectly fired rotary kiln furnaces. Fluid bed furnaces and infrared furnaces may also be used.

Flue-gas treatment

Users

The most common use of these techniques is in the thermal regeneration of activated carbon, especially in facilities regenerating industrial or potable water/food grade carbons. This is because of the potential for carbons from a variety of sources to be contaminated with a range of organics. The other methods, such as steam regeneration, tend to be applied in specific areas and typically undertaken on-site.

Multiple hearth furnaces are used extensively worldwide. In conjunction with multiple hearth furnaces, rotary kilns (directly and indirectly fired) are one of the most common types of furnaces employed. Fluid bed furnaces are mainly used in Europe on potable water applications and also in North America for waste water and decolourising.

Other treatments are available as steam, chemical and biological regeneration. However they are only used for in-situ regeneration on-site and not at separate facilities. Steam regeneration is a non-destructive technique and is primarily used where the spent carbon contains highly volatile compounds. The resulting steam/VOC vapours are condensed. Chemical regeneration is a non-destructive technique that uses a variety of gaseous or liquid desorbants. There are numerous regenerant materials available, many of them highly specific to the individual application.

2.5. Regeneration of resins

[41, UK, 1991], [42, UK, 1995], [150, TWG, 2004]

Purpose

To regenerate ion exchange resins for their re-use.

Principle of operation

Thermal regeneration may be accomplished by using hot water or steam.

Feed and output streams

The feed corresponds to spent resin with the output of the process being regenerated resin. The attractive forces encountered in resin adsorption are usually weaker than those of granulated activated carbon adsorption. Due to this, regeneration of resins can be achieved by simple, nondestructive methods such as solvent washing, and the solute can be recovered. Thermal regeneration of resin adsorbents is generally not possible due to their temperature sensitivity, although in recent years some new products are becoming available that can be regenerated by hot water.

Process description

Steam regeneration

Steam regeneration is only possible if the temperature limits of the resins are within those of the available steam pressure. For example, styrene based polymeric adsorbents are usually stable to 200 °C, whilst acrylic based resins are only stable up to 150 °C. The adsorbed solvent and other organic constituents can cause the resin matrix to swell and weaken. It is important therefore, that removal of these constituents by steaming does not result in disruption and breakup of the resin matrix.

Hot water regeneration

Users

This technique is not widely used, but it may be applied to the desalination of brackish water for a cleaner process water usage. It would not be used for deionised water applications.

2.6. Regeneration of waste acids and bases

[40, Militon and Becaud, 1998], [86, TWG, 2003], [144, TWG, 2002], [150, TWG, 2004]

As described in Section 0, only waste sulphuric and hydrochloric acids are regenerated.

2.6.1. Regeneration of spent sulphuric acid

As mentioned in Section 0, two alternative methods for regenerating spent sulphuric acid exist. One is the thermal decomposition of spent sulphuric acids to give SO_2 , achieved in a furnace at temperatures of around 1000 °C. The SO_2 produced is then used as a feedstock in the production of H_2SO_4 . Both processes (thermal decomposition and SO_2 conversion to H_2SO_4) are covered in the LVIC-AAF BREF [62, EIPPCB, 2003]. There are some industrial processes where sulphuric acid is used (e.g. production of titanium dioxide). In such cases, the recycling of the spent sulphuric acid is an integral part of the process and will be covered in the BREF where that industrial process is covered. The second alternative process to regenerate spent sulphuric acid is based on the reconcentration of weak/spent/waste sulphuric acid, with or without a separation of the potential impurities (e.g. salts). This is also included in this BREF document.

Purpose

To re-use the spent sulphuric acid for the same purpose as it was originally used for or for a new use.

Principle of operation

Reconcentration of the weak sulphuric acid by evaporation.

Feed and output streams

Spent/weak sulphuric acid is concentrated to a stronger acid solution.

Process description

Concentrations close to 70 % H_2SO_4 have been achieved and the process consists of water evaporation, without too much H_2SO_4 in the vapour phase. The range of temperatures vary with the processes. There are many processes but the most common are based on the forced circulation evaporators, which allow a very stable operation; due to the big circulation, any solid in the acid will remain in the suspension and can be separated out in the concentrated acid, if necessary.

Because of the cost of the process is very dependent on energy, (medium pressure steam), a multiple effect evaporator can reduce the operating costs very much; vacuum operation allows lower operation temperatures and the use of more standard materials for equipment construction.

Another process for weak acid concentration uses hot gases (from sulphuric acid or any other process), by contacting hot gases and weak acid, the water will be evaporated towards the water saturation; the process takes place at atmospheric pressure but, due to the relatively high gas volume, some acid carry over must be prevented, by demisters or other similar devices.

Submerged combustion processes consist in the production of flue-gases at very high temperatures, (in excess of 1500 °C), directly over the spent acid level; the flue-gas passes through the spent acid allowing water evaporation from it, suffering an adiabatic cooling down to 150 – 250 °C; before being discharged into the air, the gases need to be cooled and scrubbed out; in general, no especially high SO_2 emissions will be expected but NO_x levels should be important.

Other processes, such as Chemico, have been used for 70 years for sulphuric acid concentration; the principle is quite the same, except that the combustion does not take place within the vessel and the temperature is considerably lower (in the range of 600 °C).

Users

The metal industry.

2.6.2. Regeneration of spent hydrochloric acid

Most often, HCl is produced as a by-product from chlorination processes. HCl is generally produced in the gaseous phase and directly re-used in a chemical process. It can also be dissolved in water and used as a raw material for the production of other chemicals, such as water treatment product (e.g. FeCl_3) in electrolysis or as a neutralisation agent. HCl can be used in applications such as metal pickling or ion exchange regeneration.

Afterwards, spent hydrochloric acid is neutralised rather than regenerated. Then, reference to Sections **Error! Reference source not found.** and **Error! Reference source not found.** needs to be made. Some other regeneration treatments exist, for example, re-use as a picking acid. However, in this use, no treatment is carried out to these streams, so these are not covered in this BREF document.

2.7. Treatment of solid photographic waste

Purpose

Separate the waste in two main streams: one containing some valuable components (e.g. Ag) and the other to be used as fuel.

Principle of operation

The silver containing fixer is desilvered by means of electrolysis (see Section 2.8 on treatment of liquid photographic waste). The chemical reaction for dissolving silver from film is: $\text{Ag} + \text{Fe}^{3+} \leftrightarrow \text{Ag}^+ + \text{Fe}^{2+}$.

Feed and output streams

Silver and energy.

Process description

The film waste is cut into little pieces by a shredder. The shreds are washed with a desilvering liquid and rinsed with water. Possible desilvering agents are desilvered bleach-fix (contains iron) or iron chloride. When desilvered bleach-fix is used, the consumption of raw materials is reduced. When iron chloride is used, silver chloride is separated and then dissolved again by means of a fixer. The plastic shreds are dried, after which they can be incinerated with energy recovery or used as a secondary fuel in a cement kiln.

Users

Photographic industries.

2.8. Treatment of liquid photographic waste

Purpose

Separate the waste stream into valuable components (e.g. Ag).

Principle of operation

Desilvered liquids and photo processing waste with a low silver content, such as developers, are treated by means of sulphide precipitation and membrane filtration. By adding a sodium sulphide solution, silver ions and other metals are precipitated. By pressing the solution through membranes the solid particles are filtered out. The permeate from membrane filtration undergoes further treatment. The silver contained in the sludge is recovered by means of pyrometallurgic treatment and refinement. These treatments are described in the Non Ferrous Metals Industries BREF. Photo processing liquid wastes with a low silver content are treated by chemical removal. By adding sodium borohydride, metallic silver is precipitated. The silver is recovered from the containing sediment. The desilvered liquid undergoes further treatment.

Feed and output streams

Silver.

Process description

The treatment of the desilvered liquid photo processing waste with a high silver content consists of the following steps:

- silver is removed from photo processing waste with a high silver content (>100 mg/l) by means of electrolysis. After refining, the silver is re-used
- for a concentration of concentration of silver of 5 to 100 mg/l, desilvering by electroflocculation or sulphide precipitation and membrane filtration is applied. The created sludge is sent for incineration
- colour processing waste water is, prior to further treatment, evaporated in a vacuum evaporator because of the presence of toxic and not easily degradable organic compounds
- treatment in an activated carbon filter, where large organic and metal containing complex agents are absorbed by the carbon. When the carbon is saturated, it is regenerated and re-used
- purification by means of flocculation and flotation
- biological treatment
- evaporation in a vacuum evaporator. The condensate can be used as processing water or discharged
- the sludge from the flocculation/flotation and biological treatment and the residue from the evaporator are incinerated or landfilled.

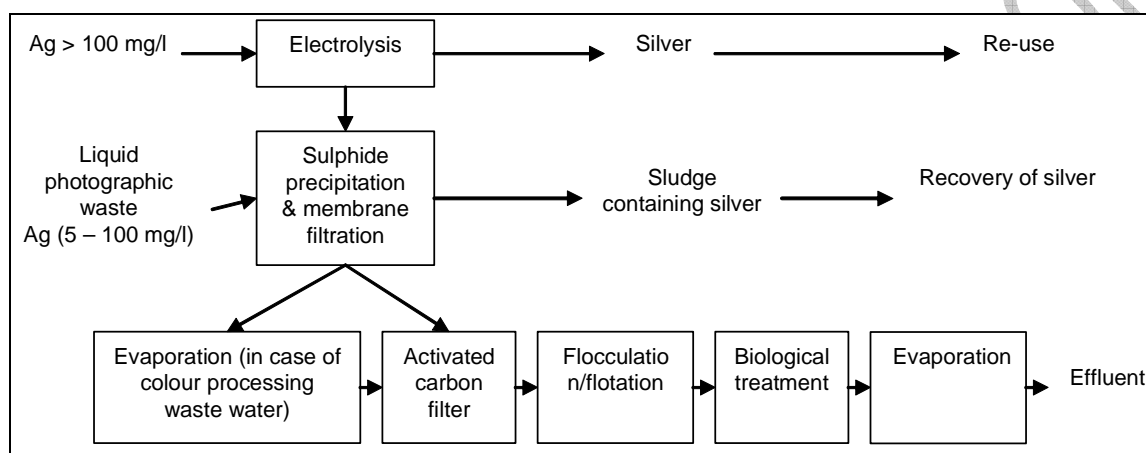


Figure 2.5: Treatment of liquid photographic waste
[156, VROM, 2004]

Users

Photographic industries.

3. Current consumption and emission levels

Emissions and consumptions from waste treatments applied mainly to recover the materials from waste

[6, Silver Springs Oil Recovery Inc., 2000], [13, Marshall, et al., 1999], [14, Ministry for the Environment, 2000], [29, UK Environment Agency, 1996], [41, UK, 1991], [42, UK, 1995], [56, Babbie Group Ltd, 2002], [66, TWG, 2003], [86, TWG, 2003], [96, Straetmans, 2003], [125, Ruiz, 2002], [129, Cruz-Gomez, 2002], [147, UBA, 2003], [150, TWG, 2004], [156, VROM, 2004], [157, UBA, 2004]

This section contains the emissions and consumptions of treatments mentioned in Section 2.4. The following sections (Sections 3.4.X) details information available to site WT operators from their current recording systems and highlights areas where emissions are likely to occur. The structure of each of the following sections in this section is the same as the one followed in Section 2.4. Emissions associated with ancillary treatments, e.g. transfer station operations, are covered in Section 3.1.

3.1. Waste IN treated to obtain a recycled material

When the aim is to obtain useable materials and not just material to be disposed of, the treatment given to each type of waste will typically be very specific, and will target the conversion of the waste into the useable end-product required.

Waste oils

Oils have many uses, e.g. they are used as a fuel, as lubricants, as a heat transfer medium, as cutting fluids, and as hydraulic fluids. Each has its own specification, usually based upon the hydrocarbons occurring within a specific boiling point range from the distillation of crude oil. Oils that need to be stable at high temperatures will not include large quantities of low boiling point hydrocarbons, whereas, oils used as fuel are more likely to include these lower boiling point hydrocarbon mixtures.

Before marketing, most base oils produced in mineral oil refineries are blended with a variety of additives to give them the required properties. Typical additive packages comprise between 5 and 25 % of the base oil. However, probably at least half of the additive package is base oil used as solvent. Lubricating oils contain large numbers of additives, but the actual formulae are in most cases trade secrets. Data on the components and additives in new oils are given in the Safety Data Sheet which accompanies fresh products as supplied, however precise details of the formulations are company proprietary. Hydraulic oils contain very few additives.

Some general classes of additives have been identified and are shown in Table 3.1 below. The information is not specific, but suggests that a number of metal additives, some chlorinated organic compounds, aromatic hydrocarbons, phenolic compounds and different kinds of polymers are used.

Additive	Compounds used
Anti-corrosion	Zinc dithiophosphates, metal phenolates, fatty acids and amines
Anti-foam	Silicone polymers, organic copolymers
Anti-oxidant	Zinc dithiophosphates, hindered phenols, aromatic amines, sulphurised phenols
Anti-wear	Zinc dithiophosphates, acid phosphates, organic sulphur and chlorine compounds, sulphurised fats, sulphides and disulphides
Detergent	Metallo-organic compounds of sodium, calcium and magnesium phenolates, phosphonates and sulphonates
Dispersant	Alkylsuccinimides, alkylsuccinic esters
Friction modifier	Organic fatty acids, lard oil, phosphorus
Metal deactivator	Organic complexes containing nitrogen and sulphur amines, sulphides and phosphites
Pour-point depressant	Alkylated naphthalene and phenolic polymers, polymethacrylates
Seal swell agent	Organic phosphates, aromatic hydrocarbons
Viscosity modifier	Polymers of olefins, methacrylates, di-enes or alkylated styrenes

Table 3.1: Types of additives used in lubricants
[67, DETR, 2001]

Additives need to be retained in the oil over its whole useful life. This means that even if the individual substance would be expected to be driven off at normal engine operating temperatures, there must be another additive incorporated that binds it within the oil formulation.

This requirement to keep additives in circulation, and to keep breakdown products in circulation to increase the longevity of the oil, creates one of the discussion points for emissions of waste oil. Although a number of components are solid at ambient temperatures and could be expected to settle out of the oil and into the sludge layer, dispersants in the oil will tend to keep them within the oil layer. Larger solids are taken out of the engines by the oil filters.

During use, the composition of the oil will change markedly, due to the breakdown of the additives, the formation of additional products of combustion and unburned fuels, the addition of metals from wear and tear on the engine and from the breakdown of the base oil itself.

Large treatment sites recognise that there will be a range of species in waste oil and thus screen the incoming waste for flashpoint, metal and chlorine levels; whereas smaller sites will typically just accept the oil waste. There is a distinct shortage of analysis data for incoming wastes, although the screening activities of a few sites show that industry anticipates high metal levels and contamination by flammable solvents, giving a measurable flashpoint.

Used oils collected by high volume users can be more tightly controlled and may hence be more consistent in composition.

Type of waste containing waste oils	Comment
Oil filters	No specific analysis has been found but these are known to contain waste engine oils plus the residues of larger sized solids formed in the engine and that have been trapped in the filter. In addition, there is the plastic and metals of the filter. Metals tend to go for recycling
205 litre steel drums	Waste oil and steel
25 litre drums	Waste oil and plastics
Bulk used engine oil	Used engine oil is the main wastestream processed at waste management licensed sites. Most of the emissions will be due to this material

Table 3.2: Type of waste containing waste oils
[56, Babbie Group Ltd, 2002]

There are no comprehensive analyses available of the waste oils entering oil treatment plants. Instead the next couple of tables (Table 3.3 and Table 3.4) show the data gathered on the chemical components that typically exist in the different types of waste oils. It is not expected that in reality all waste oils will be covered by the lower or top ends of the ranges mentioned in these two tables.

Waste oil components	Concentration range (ppm)	Origin/comments
Al	4 – 1112	Bearing wear or engine
Alkyl benzenes	900	Petroleum base oils
Aromatic compounds	14 – 30 w/w-%	For used motor oil, these arise from the lubricant base oil
Aliphatic compounds	65.4 w/w-%	N-alkanes are about 0.4 % waste oil, but the distribution is slanted towards the longer molecules that are less likely to evaporate: <ul style="list-style-type: none"> tetralin 0.0012 % dodecane 0.014 % tridecane 0.014 % octadecane 0.07 % nonadecane 0.2 %
Antifreeze		
As	<0.5 – 67	
Ash content	0.4 – 0.64 ¹	
Ba	50 – 690	Detergent additives, additive package
BTEX	300 – 700	A composite analysis shows a high level of short chain hydrocarbons (benzene (0.096 – 0.1 %), xylenes (0.3 – 0.34 %), toluene (0.22 – 0.25 %)), with boiling points below 150 °C.
Ca	900 – 3000	Detergent additives
Cd	0.4 – 22	
Cl	184 – 1500 ²	Chlorine in used oils arises from: <ul style="list-style-type: none"> contamination (either accidental or deliberate) with chlorinated solvents and transformer oils, both of which are now more closely controlled lubricating oil additives the lead scavengers added to leaded gasoline it is used as a cold-flow additive
Chlorinated hydrocarbons	37 6300 18 – 2800 18 – 2600 3 – 1300	dichlorodifluoromethane trichlorotrifluoroethane trichloroethanes trichloroethylene perchloroethylene used oils can have a significant, but variable, chlorine content, including organochlorines as PCB, dichlorodifluoromethane, trichlorotrifluoroethane, 1,1,1-trichloroethane, trichloroethylene, tetrachloroethylene. They may be formed chemically during the use of contaminated oil
Cr	2 – 89	Engine wear
Cu	<11 – 250	Bearing wear
Engine blowback	8 – 10 w/w-%	Absorbed gas, gasoline and diesel fuel. A variety of ‘thermal breakdown products’ are also included in the composition of waste oil
Fe	100 – 500	Engine wear
Halides	Up to 500	
Heavy hydrocarbons		Arise from polymerisation and from the incomplete combustion of the fuel
Hg	0.05 – <11	
Light hydrocarbons	5 – 10 w/w-%	A certain amount of unburned fuel (gasoline or diesel) dissolves in the oil and also arise from breakdown of the oil

Waste oil components	Concentration range (ppm)	Origin/comments
Lubricant base oil	Up to 95 w/w-%	Major components are aliphatic and napthenic hydrocarbons and/or olefin polymers (e.g. polybutenes and poly-alpha-olefins in some lube base oils). Smaller amounts of aromatic and polyaromatic hydrocarbons are also present. The heavy metal content is less than 500 ppm. Phenols may be present at a few ppm
Metals such as Al, As, Ba, B, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Mg, Mn, Na, Ni, P, Pb, Sb, Si, Sr, Ti, V, Zn	Up to 10000 combined	These originate from the lube oil additives, engine wear and foreign sources. They appear in waste oils as additives within lubricating oil, from wear and tear on engines and with machining oils. Additives (particularly the metals) typically remain in the oil after use
Mg	100 – 500	Detergent additives
Ni	10	Engine wear
Naphthalenes	9.7 – 470 – 2300 ⁴	From base oils
Nitrogen compounds		From the addition of nitrogen compounds
Non – lubricant related compounds		Used oil often becomes contaminated by all kinds of materials, usually because of bad collection/segregation. Materials that may appear are brake fluid and antifreeze, vegetable oils, cigarette packets, solvents, etc.
P	6 – 1000	Anti-oxidant/anti-wear additives
PAH	30.3 – 204 – <1000 ⁴ Sum of 26 individual PAHs represented 0.17 % of the oil or 1.2 % of the aromatic fraction	The aromatics also include a huge range of PAHs in concentrations of up to 700ppm for an individual species. They appear from base oils and from incomplete combustion. Examples are benz(a)anthracene (0.87 – 30 ppm), benzo(a)pyrene (0.36 – 62 ppm), pyrene (1.67 - 33 ppm), naphthalene (47 ppm), biphenyl (6.4 ppm) and also chlorinated polyaromatics
PCB	<0.5 – 11 – <50	Under the Waste Oil Directive, the maximum content of PCB allowed in used oils to be treated for disposal is 50 ppm. It occurs due to contamination with transformer oils
Pb	8 – 1200 Up to 14000 when leaded gasoline is used	Leaded gasoline/bearing wear
S	0.1 – 2.8 w/w-%	From base oil and combustion products.
Sediments	0.5 – 2 w/w-%	Soot and sediment from the combustion chamber, free metals and dirt. Sediment formation is aggravated by the mixing of used oils from several manufacturers' additive packages, and collection sources
Si	50 – 100	Additives/water
Sn	Trace amounts	Bearing wear
Tl	0.1	
V	300	From base oil
Water	5 – 10 w/w-% ³	Combustion
Zn	6 – 4080	Anti-oxidant/anti-wear additives
Note: Additions of figures cannot be made to fit perfectly because they correspond to different sets of data. ¹ Both parameter limits are average values ² Up to 8452 ppm in collected used oil due to contamination with chlorinated solvents and sea salt from ship slops ³ Up to 30 % ⁴ When three numbers appear in a range, the middle number corresponds to the average		

Table 3.3: Indicative list of components present in used oils

[4, Langenkamp, 1997], [5, Concawe, 1996], [6, Silver Springs Oil Recovery Inc., 2000], [14, Ministry for the Environment, 2000], [37, Woodward-Clyde, 2000], [56, Babbie Group Ltd, 2002], [42, UK, 1995], [150, TWG, 2004]

Used industrial oils

A variety of oils are used in industry including soluble oils and some halogenated oils, although these are becoming less common. Oil is used as hydraulic oil, as lubrication, as a heat transfer medium, as an electrical medium and as a cutting fluid.

Soluble oils/machining oils are very common, but there is no information so far about their composition. Many of these industrial oils undergo intensive in-house recycling to extend their useful life, and the majority of any metal contaminants associated with grinding operations are removed by in-house systems and recovered. In the absence of other data, the following assumptions have been made:

- these oils are used in open systems. Their formulations do not include very low boiling point/volatile hydrocarbons because of the fire risk and health risks during use and the need to retain the product characteristics during use. They are agitated during use, and take away excess heat from machining surfaces, thus in operation they are heated above the ambient temperature. Therefore, VOC emissions during waste treatment are typically very small
- the metal content will vary considerably from source to source. The main metals worked with will be copper, zinc, nickel and chromium.

	Concentration	Reason
Cadmium	50 % of concentration in lubricating oil or 0.000155 %	Cadmium is currently being phased out from the manufacture
Chromium	100 % of concentration in lubricating oil or 0.0028 %	Common: typically used at the same level as in engine oil
Copper	100 % of concentration in lubricating oil or 0.025 %	Common: typically used at the same level as in engine oil
Lead	0	No particular reason to machine this
Naphthalene	0.0042 %	No data at all, naphthalene is in all oils, but would expect the formulation to have the lowest amount possible (taken from fuel oil n ^o 6 content) because it would be a solid at room temperature and does not seem to add anything chemically useful to the formulation
Nickel	0.0028 %	No data for lubricating oils
PCB		Found in transformer coolant oils
Xylenes	0.22 %	
Zinc	50 % of concentration in lubricating oil or 0.029 %	Common machining component, but zinc appears to be a major additive in lubricating oils

Table 3.4: Estimated metal concentrations in industrial waste oils
[56, Babbie Group Ltd, 2002], [86, TWG, 2003]

Electrical oils are specialist oils which undergo a laundering process, so very little waste arises from them. The main concern with these oils is the risk of PCB contamination. Typically waste treatment facilities do analyse for PCBs.

Oily water from interceptors

Most waste from interceptors comes from car parks and vehicle service areas. It is, therefore, reasonable to assume that it is similar in content to used engine oil but will contain additional silt, possibly vehicle tyre wear particles, fuel combustion products and road making tars. Spilt fuel will also be collected at the interceptor, but any materials that are capable of evaporating to the air at ambient temperatures will have done so before the interceptor waste is collected.

A proportion of oil interceptors arises from manufacturing sites and collected waste industrial oils. These will have far lower concentrations of combustion products, but might have higher metal concentrations, depending on the industrial application.

Waste solvents

Waste solvents may be generated in the following industrial sectors:

- paints, coatings and paint removers
- inks
- chemical and pharmaceutical industry
- film production
- production of synthetic fibres
- rubber, plastic and resin solutions
- solvents for degreasing
- solvents for dry cleaning
- for agriculture products
- aerosol cans and dispensers.

The wastes that are considered as solvents correspond mainly to EWL codes 07, 08, 09 and 14. The final code corresponds to a category especially devoted to organic solvents. There are four main classes of solvent mixtures which make the solvent unusable in its present state and this promotes its recovery. These are:

- mixture with air. This usually occurs when the solvent has been used to dissolve a resin or polymer which is laid down by evaporating the solvent. Recovery from air can pose problems because the solvent may react on a carbon bed adsorber or be hard to recover from the steam used to desorb it
- mixture with water. Whether this arises in the solvent-based process or in some part of the recapture of the solvent, it is very common to find that the solvent may be contaminated with water. Removal of water is a simple matter in many cases but in others it is so difficult that restoration to a usable purity may prove to be uneconomic. It should always be borne in mind that the water removed in the course of solvent recovery is likely to have to be discharged as an effluent and its quality is therefore important
- mixture with a solute. A desired product is often removed by filtration from a reaction mixture. The function of the solvent in this case is to selectively dissolve the impurities (unreacted raw materials and the products of unwanted side reactions) in a low viscosity liquid phase, with a very low solvent power for the product. The choice of solvent is often limited in such cases, but significant improvements in the solvent's chemical stability can sometimes be found by moving up or down a homologous series without sacrificing the selectivity of the solvent system. A less sophisticated source of contamination by a solute occurs in plant cleaning, where the solvent power for any contaminant is of primary importance but where water miscibility, to allow cleaning and drying to take place in a single operation, is also an important property
- mixtures with other solvents. A multi stage process such as that found typically in the fine chemical and pharmaceutical industries can involve the addition of reagent dissolved in solvents and solvents that are essential to the yields or even to the very existence of the desired reaction.

Vegetable waste oils

Cooking oils from restaurants and hotels.

Waste catalysts

The spent catalysts that may be regenerated ex-situ are:

Metal catalysts

For example, platinum-alumina reforming catalysts which can be regenerated by the removal of carbonaceous deposits from the catalyst surface using a carefully controlled combustion procedure, followed by platinum redispersion and rechloriding of the catalyst support).

Noble metal catalysts

These can be regenerated by removing the coke deposits to successfully restore the activity, selectivity, and stability performance of the original fresh catalyst. Coke deposits are removed by controlled combustion.

Base metal catalysts

Hydroprocessing catalysts can be regenerated using different methods such as regenerative oxidation treatment to remove coke (ex-situ regeneration) or redispersion of the metals in the case of poisoning by the sintering of metals.

Zeolites

These can be regenerated relatively easily by using methods such as heating to remove adsorbed materials, ion exchanging with sodium to remove cations, or a pressure swing to remove adsorbed gases. However, they are not regenerated ex-situ because the structure is, in most cases, damaged and depending on the application the pores can be contaminated with heavy metals or other catalyst poisons.

Waste activated carbon

Most industrial plants tend to send their spent carbon off-site for regeneration by a large centralised carbon manufacturer. Quantities of spent carbon from industrial sources (textiles, refinery products, carpet mills, plastic industry, phenolic resins, herbicides, explosives, detergents, solvents, dyes), whilst reasonably substantial, do not approach those obtained from potable water purification. From discussions with various carbon regenerators, it appears that water treatment provides the single largest source of spent carbon. Activated carbon adsorption systems can be used for a wide variety of applications, and can potentially contain a cocktail of adsorbed pollutants. The contaminants found in spent activated carbons are typically:

- chlorine
- COD/BOD
- pesticides
- bulk organics imparting colour, taste and/or odour (i.e. humic acids)
- general organics such as phenol
- metals such as iron, aluminium, cadmium and mercury
- inorganic elements such as calcium and phosphorus
- dyes (cause of colour)
- detergents
- phenols
- explosives (only in material that comes from the manufacture of explosives).

Activated carbon products are basically available in three forms: extruded activated carbon, granular activated carbon, and powder activated carbon. The last form is not regenerated.

Waste ionic resins

A large proportion of resins sold worldwide are used in water treatment (i.e. water softening). The remaining balance is divided between chemical processing, extractive metallurgy, and food and pharmaceutical processing.

Operating ion exchange resins may concentrate toxic ions such as chromate and cyanide, or heavy metals. Due to the predominance of water applications, they may also contain pesticides, chlorine, phenol and inorganic elements such as calcium, sodium, manganese and phosphorus.

Conventional ion exchange resins are bead-shaped, and behave as plastic ball bearings when handled. They contain ion-active sites throughout their structure, have uniform distribution of activity, and can usually resist breakages resulting from handling, or from osmotic shock (i.e. a rapid change in solution environment). Most beads are sold in the 40 µm to 1.2 mm size range.

Treatment of liquid photographic waste

Parameter	Concentration (mg/l)	
Hydrocarbons	6000	emission in evaporation step (colour photo processing waste)
EOX	10	
Respiration inhibition	5 %	
Metals (Zn, Ni, Pb, Cr, Mo)	50	
Ag	50/100	black and white/colour photo processing waste
Cd	1.0	
Cu	25	
Hg	1.0	

Table 3.5: Acceptance criteria for desilvered photographic liquid waste and similar waste waters (with the same processing path)
[156, VROM, 2004]

3.2. Consumptions of waste treatments to obtain a recycled material

Consumptions in the re-refining of waste oils

Other than transportation, the main operating overhead relates to the generation of steam for heating waste oil.

Process	Compounds used within the process	Consumptions (values in kg/tonne of waste oil if not otherwise specified)
Acid/clay process	Sulphuric acid as a precipitate agent of heavy metals. Clay as a filtration/neutralisation agent	36
Pretreatment of waste oil	Demulsifiers to help in the settling process	
Distillation/clay process	Clay	40
Propane de-asphalting (PDA)	Consumption of energy is higher than in the regeneration by chemical treatment or by hydrogenation	
Thin film evaporator (TFE) + clay process	Clay	60
TFE + hydrofinishing	Hydrogen and catalysts	
TFE + solvent extraction	Solvent	
TFE + chemical treatment + solvent extraction	Energy Caustic Solvent	3.2 MJ/kg of used oil 10 0.3
TFE + solvent extraction + hydro-finishing	Hydrogen catalyst Mohawk chemical Hydrogen gas	0.25 12 2
TDA (thermal de-asphalting) + clay treatment	Clay	100
TDA + hydrofinishing (high pressure)	Catalyst	0.5
PDA (propane de-asphalting) + hydro finishing (medium pressure)	Propane	8.25
With thermal clay treatment	Fossil energy resources	4.26 MJ/kg of used oil
With hydro-finishing	Energy	9.93 MJ/kg of used oil
Vacuum distillation + chemical treatment	Fossil fuel consumption Primary energy Water consumption	47 kg eq crude oil 2681 MJ 3300
Regeneration process	Fossil energy resources	42.46 MJ/kg of oil
Caustic soda and bleaching earth treatment (ENTRA)	Caustic soda Bleaching earth	30 20
Direct contact hydrogenation (DCH)	Hydrogen Catalyst	70 Nm ³ /t 0.5

Table 3.6: Consumptions of different waste oil re-refining techniques
[6, Silver Springs Oil Recovery Inc., 2000], [7, Monier and Labouze, 2001], [11, Jacobs and Dijkmans, 2001], [13, Marshall, et al., 1999], [56, Babbie Group Ltd, 2002], [86, TWG, 2003], [150, TWG, 2004]

Table 3.7 gives the consumptions for the re-refining of part of the waste oil to base oil which can then be re-used as lubricating oil, together with the regeneration of the remaining waste oil to fuel oil.

	Consumptions	Units
Economics		
Capital investment expenses for treatment plant	4.85 (36)	EUR (DKK) millions
Maintenance	0.094 (0.7)	EUR (DKK) millions per year
Operation period	20	years
Labour input	10	number of persons
Resources used		
Chemicals	291.5	tonnes
Water	8000	m ³
Electricity	1150	MWh
Fuel oil	1200	m ³
Base: 26000 tonnes yearly collected waste oil to base oil (8000 tonnes), fuel oil (12000 tonnes) and asphalt (4000 tonnes)		

Table 3.7: Consumptions of waste oil re-refining activities
[12, Birr-Pedersen, 2001]

Figure 3.1 depicts a block diagram showing a comparison between the inputs and outputs of different re-refining processes.

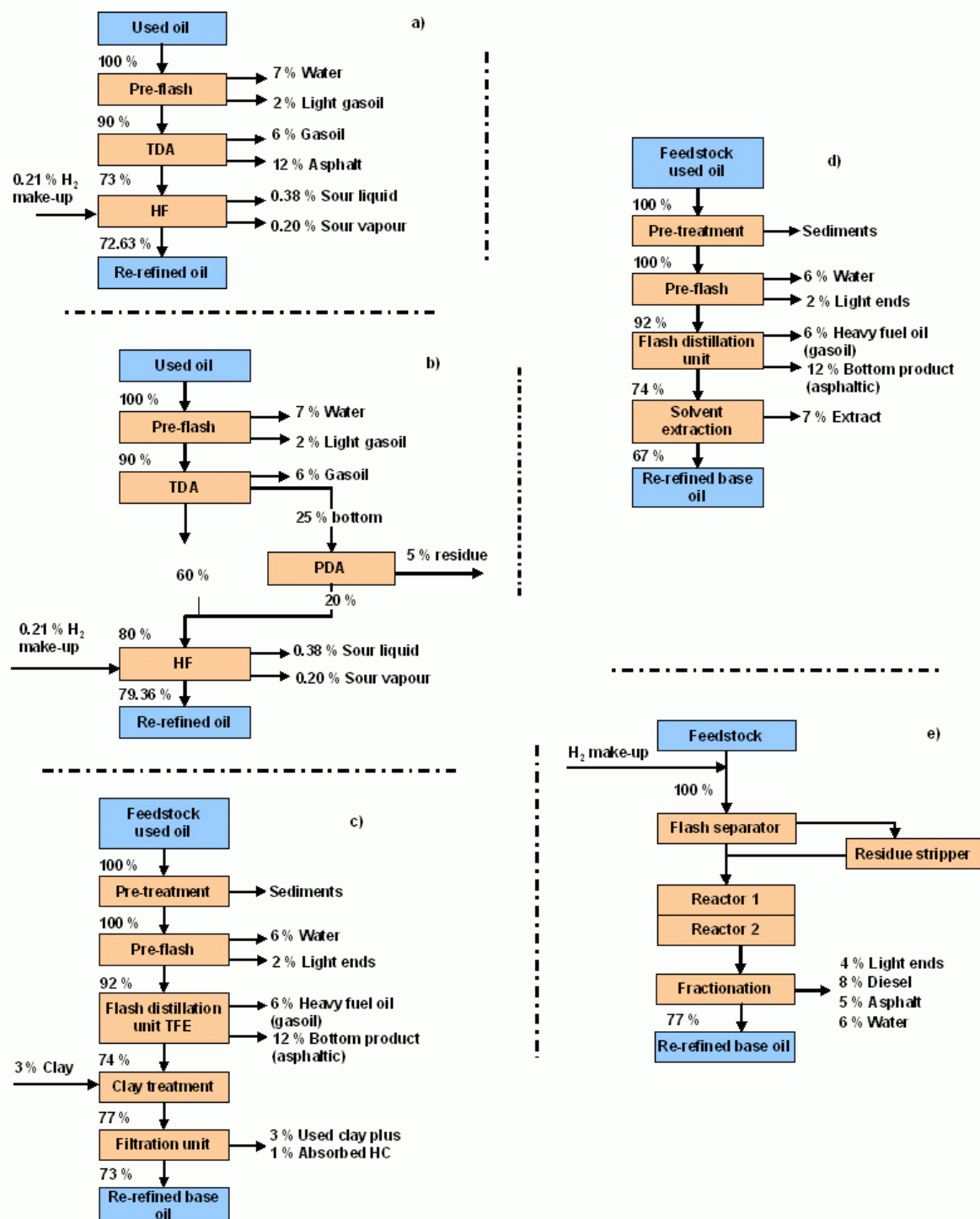


Figure 3.1: Inputs and outputs of the re-refining treatment

Note: a) TDA/HF, b) TDA/PDA/HF, c) TFE/clay treatment, d) TFE/solvent, e) DCH

HF = Hydrofinishing. % represents the amount that goes in that stream based on 100 % used oil entering the system

[36, Viscolube, 2002], [86, TWG, 2003], [150, TWG, 2004]

Table 3.8 shows the consumptions of the TDA system and the TDA combined with a PDA.

Traditional TDA/HF system						
Consumption and utilities	PF	TDA	HF		Total	Unit
Electrical consumption	1.5	12	20		33.5	kWh
MP steam	285	322	70		677	kg
Cooling water (make-up) ⁽¹⁾	1.1	5	0.3		6.4	tonne
Fuel (absorbed heat)	/	670	711		1380	MJ
Hydrogen	/		2.1		2.1	kg
Catalysts	/		0.2+0.05 ⁽²⁾		0.2+0.05 ⁽²⁾	tonne
Propane make-up						kg
High recovery system						
Consumption and utilities	PF	TDA	HF	PDA	Total	Unit
Electrical consumption	1.5	12	20	13	46.5	kWh
MP steam	285	322	70	135	812	kg
Cooling water (make-up) ⁽¹⁾	1.1	5	0.3	4	10.4	tonne
Fuel (absorbed heat)		670	711	920	2300	MJ
Hydrogen			2.1			kg
Catalysts			0.2 + 0.05 ⁽²⁾		0.2 + 0.05 ⁽²⁾	tonne
Propane make-up				0.8	0.8	kg
⁽¹⁾ Based on 10 % evaporation losses ⁽²⁾ Demetalisation catalyst + Refining catalyst Note: Consumption based upon 100 kt/yr waste oil capacity, considering 10 % water contents. All the parameters are expressed in unit/tonne of waste oil. HF: hydrofinishing, PDA: Propane de-asphalting, TDA: Thermal de-asphalting, PF: Pre-flash, MP: medium pressure						

Table 3.8: Consumption values of the TDA system and the TDA combined with a PDA processes [66, TWG, 2003], [150, TWG, 2004]

1. Capacity	2. t/yr	3. 2001	4. 4600	5. 6824	6. 15000	7. 17171	8. 19960	9. 46208	10. 90500
11. Fuel consumption	12. GJ/yr	13.	14. 19146	15. 33486	16. 40671	17. 54751	18. 16705	19. 405883	20.
21. Electricity consumption	22. MW h/yr	23. 345	24. 225	25. 1200	26. 1380	27. 2024	28. 655	29. 9215	30.
31. Heat consumption	32. MW h/yr	33. 157	34.	35.	36. 0	37. 15208	38.	39.	40.
41. Water	42. m ³ /yr	43. 617	44.	45. 80000	46. 9848	47. 9929	48. 1557	49. 407000	50. 2213000
51. Cooling	52. MJ/yr	53.	54.	55.	56. 44000	57.	58.	59.	60.
61. Electricity /Plant capacity	62. kWh /t	63. 172.4	64. 48.9	65. 175.8	66. 92	67. 117.9	68. 32.8	69. 199.4	70.
71. Heat/Plant capacity	72. kWh /t	73. 78.5	74.	75.	76.	77. 885.7	78.	79.	80.

Table 3.9: Consumptions from different waste oil re-refining plants in the EU [66, TWG, 2003]

Consumptions of the regeneration of waste solvents

Table 3.10 shows consumption data for two facilities operating in the EU. Other data reported energy consumptions lower than 1 GJ/tonne.

Consumption parameter	Units		
Capacity	kt	12	27.5
Gas fuel	GJ/yr	19651	
Fuel consumption	GJ/yr		31628
Electricity	MWh/yr	1571	2984
Water	m ³ /yr	19000	40776

Table 3.10: Consumptions of two regeneration treatment of waste solvents
[66, TWG, 2003], [130, UBA, 2003]

Consumptions of regeneration of spent catalysts

Table 3.11 shows an overall material balance for an example regeneration. Almost 375 t of catalyst was recovered for re-use.

Overall material balance	Values in kg	
As received material		620982
Inert support	27099	
Unregenerated dust and fines	9569	
Total unregenerated feed to regenerator		584314
Shorts from length grading and regenerated dust and fines	37191	
Loss on ignition	172143	
Net regenerated catalyst		374980

Table 3.11: Mass balance in a commercial regeneration of CoMo catalyst
[125, Ruiz, 2002]

Consumptions in treatment of solid photographic waste

The electricity consumption for shredding, washing/rinsing and electrolysis amounts to 100 to 300 kWh/t film waste. Depending on the process of desilvering, auxiliary materials are used. These are shown in Table 3.12.

Desilvering with bleach-fix	Desilvering with iron chloride
Sodium hydroxide (20 %): 6 l/t film	Iron chloride (40 %): 11 l/t film
Sulphuric acid: 6 l/t film	Hydrochloric acid (36 %): 8 l/t film
Sodium bisulphite: 12 l/t film	Sodium sulphite: 12 l/t film
	Hydrogen peroxide (35 %): 4 l/t film

Table 3.12: Used amounts of auxiliary materials for desilvering film waste
[156, VROM, 2004]

Consumptions in the treatment of liquid photographic waste

Consumption of energy

The required electricity for electrolysis ranges from 12 to 46 kWh/t photographic liquid waste. The electricity consumption is dependent on the iron content. For bleach-fix, the consumption is higher due to the higher iron content. The ultrafiltration requires approximately 27 kWh_e and 13 MJ/t liquid waste for the heating of the rinse-water. The electricity consumption of chemical removal of silver is estimated on 3.5 kWh/t liquid photographic waste.

The energy consumption for evaporation is approximately 220 MJ/t waste water. If evaporation is also applied as a pretreatment, in the case of colour photo processing waste water, the energy consumption is approximately 350 MJ/t waste water. The required electricity for electroflocculation, in the case of extra

desilvering, is approximately 80 kWh/t waste water. Further physico-chemical and biological treatment requires approximately 5 kWh_e/t waste water.

Consumption of chemicals

Table 3.13 shows the consumption of chemicals for sulphide precipitation/ultrafiltration of photographic liquid waste.

Chemical	Consumption (kg/t photo processing waste)	Function
Sodium sulphide (40 %)	0.1	Precipitation of silver (and other metals)
Citric acid	0.7	Cleaning of the membranes
Sodium hydroxide	0.01	Cleaning of the membranes
Detergents	0.01	Cleaning of the membranes
Water	75	Cleaning of the membranes

Table 3.13: Consumption of chemicals for sulphide precipitation/ultrafiltration [156, VROM, 2004]

For chemical removal of silver, the consumption of chemicals is estimated at 1.5 sodium borohydride and 2.5 sulphuric litres per tonne of photographic liquid waste.

In the physico-chemical treatment of desilvered photographic liquid waste, several chemicals are used. The consumptions are shown in Table 3.14. If evaporation is applied as a pretreatment, practically no chemicals are consumed in the following treatment steps. Most contaminants have already been removed in the evaporation step.

Chemical	Consumption (kg/t waste water)	Comments
Sodium hydroxide (33 %)	0.007	
FeCl ₃	0.003	
Powder carbon	0.5	
Flocculant	5	In the case of desilvering
Na ₂ S (40 %)	15	In the case of desilvering

Table 3.14: Consumption of chemicals in the treatment of desilvered photographic liquid waste [156, VROM, 2004]

3.3. Emissions from waste treatments to obtain a recycled material

3.3.1. Emissions from the re-refining of waste oils

In order to evaluate emissions from the re-refining of waste oils several issues need to be considered:

- waste lubricating oils contain shorter chain organics than new lubricating oils and therefore VOCs are likely to be relevant
- sulphur and chlorine are known 'problem' compounds found in waste oils
- aromatic compounds are more polar in general than aliphatic molecules and are therefore more likely to be present in the aqueous phase.

The oil processing sector has a narrow range of operations and is the most likely to respond to a generic method of calculating emissions if the oil constituents can be identified. The following detail the different pollutants and media where they can be found. Some tables have been constructed to focus on the pollutants (Table 3.15 and Table 3.16) whereas others focus on the activities that may lead to pollution (Table 3.17).

Species	Air	Water	Waste and soil
<i>Organic compounds</i>			
Benzene	yes - some data, but difficult to apportion between air/water/land	yes - some data, but difficult to apportion between air/water/land. Polar compound	yes - some data, but difficult to apportion between air/water/land
Ethyl benzene (VOC)	No data available	yes (as BTEX)	yes (as BTEX)
Toluene		yes - some data, but difficult to apportion between air/water/land	yes - some data, but difficult to apportion between air/water/land
Xylenes	yes - some data, but difficult to apportion between air/water/land	yes - some data, but difficult to apportion between air/water/land	yes - some data, but difficult to apportion between air/water/land
VOCs	yes - some incomplete data, but difficult to apportion between air/water/land. Lower chain alkanes likely to go to air. Since used oil usually contains light ends such as gasoline, VOCs may be emitted from storage (from the tank and their associated pipework) for every process considered. The behaviour of oils undergoing heating and agitation generates VOCs emissions	BTEX in particular are polar molecules, but also volatile, and are present in the aqueous phase and/or evaporated to the air	
Naphthalene		Some data available	Some data available
Biphenyl		Limited data, may not be relevant	Limited data
Phenol	Not air emissions expected because too soluble in oil and water	Relevant but no data	Relevant but no data
Sulphur and nitrogen compounds	The gradual increase in sulphur and nitrogen additives in lubricating oils may require sites to monitor for these		Found in used oil sludge
PCBs and chlorinated solvents: Identified as present in some analyses		Solvents and lighter compounds are removed in the dewatering. Naphtha and light distillate cuts are typically distilled off upstream of the main processing facilities. If the hydrocarbon streams are fed to a hydrotreater, the chlorides may be removed	Used oil sludge

Species	Air	Water	Waste and soil
PAHs. These used to be a problem in re-refined base oils. However, recent tests indicate that it is possible to remove PAHs in the regeneration process of modern plants, thus avoiding the accumulation of PAHs. PAHs are destroyed by severe hydrogenation which also removes nitrogen, sulphur, metals and chlorides	PAHs are unlikely to be discharged to the air during the oil treatment processes. They are not volatile compounds, and their position as an air carcinogen is due to them being released as a combustion product from fossil fuels. Potential for PAH emission may be during the processing of oil filters. Most filters are crushed at some point, producing a fine oil mist. There may be a hood and an exhaust vent, but this is a potential mechanism to deliver PAHs to the air and the oil in oil filters have a larger concentration of particulate matter and hence PAHs. This may not be of significant importance, as it is the smaller particles that are more likely to form an air discharge. The behaviour of oils undergoing heating and agitation may generate PAHs emissions.	Relevant but no data	The heavy PAHs in the regeneration plants end up in either the residue stream and/or the asphalt blends. The lighter ones remain in the lube oil cuts. Also possibly found in a used oil sludge. Relevant but no data
<i>Other air pollutants</i>			
CO ₂ from many combustion processes			
Odour	Odour has been identified as an important problem in re-refining installations		
<i>Typically water and waste parameters</i>			
Total nitrogen		Nitrogen and phosphorus additives	Nitrogen and phosphorus additives
Total phosphorus		Nitrogen and phosphorus additives	Nitrogen and phosphorus additives
TOC		Calculated from COD as 1/3 of COD	Not available except as calculated from oil content, but this will be too low (or COD)
Chloride		Additives in oil and salt on roads	Additives in oil and salt on roads

Species	Air	Water	Waste and soil
Oil		The oil itself is a visual pollutant when it floats on water, and drinking water is rapidly tainted by the taste of oil	Used oil sludge
Metals			
Metals			The metals from regeneration processes are mostly in the residue cut. The volatile metals are removed by the hydrotreatment guard reactor if they are hydrotreated. Also possibly found in used oil sludge
Arsenic	Not expected	Some data available	Some data available
Cadmium	Not expected	Some data available, but being questioned	Some data available, but being questioned
Chromium	Not expected	Some data available	Some data available
Copper	Not expected	Limited data	Limited data
Lead	Not expected	Some data available, but being questioned	Some data available, but being questioned. In the re-refining options, lead ends up in the heavy residues which results in it being 'locked up' in a bitumen product
Manganese	Not expected		
Nickel	Not expected	yes, but no data	yes, but no data
Zinc	Not expected	Some data available	Some data available

Table 3.15: Common emissions from waste oil treatment plants

[5, Concawe, 1996], [6, Silver Springs Oil Recovery Inc., 2000], [14, Ministry for the Environment, 2000], [56, Babbie Group Ltd, 2002], [86, TWG, 2003]

The following Table 3.16 reflects how the components of the waste oil distribute emissions to air, sewer and products. As can be seen, most of the contaminants remain in the recovered oil. The main exception to this is VOCs, where there is a possibility of their transfer to the air, with the amount depending on the type of oil and whether the oil is heated during treatment.

Input substances	Hot processing			Cold processing		
	Air	Products	Water	Air	Products	Water
Benzene	0.6	0.3	0.1	0.2	0.7	0.1
Toluene	0.3	0.7	0	0.1	0.9	0
Xylenes	0.1	0.8	0.1		0.9	0.1
Naphthalene		1			1	
Biphenyl		1			1	
Benz(a)anthracene		1			1	
Benzo(a)pyrene		1			1	
Heptane	0.2	0.8			1	
Octane	0.1	0.9			1	
Nonane		1			1	
Decane		1			1	
Undecane		1			1	
Arsenic		1			1	
Cadmium		1			1	
Chromium		1			1	
Copper		1			1	
Lead		1			1	
Nickel		1			1	
Zinc		1			1	
Note: Figures correspond to the share distribution of substances in output streams. E.g. for each kg of benzene entering into the hot processing, 0.6 kg ends up as an emission to the air, 0.3 kg goes into the oil and 0.1 kg into the waste water. 1 means that all the input goes to that output						

Table 3.16: Matrix for allocating input species to air, oil and water streams for hot and cold processes [56, Babbie Group Ltd, 2002]

Activity/Plant	Point source emissions		
	To air	To water	To disposal
Filter shredding	Oil mist		
Magnetic separation	Oil mist		
drum emptying/shredding	Oil mist		
Tanker unloading	Tank venting		
Coarse straining	Oil mist		
Bulk storage	Tank venting. Very few tank vents are linked together. Tank vents will discharge the 'air' that the tank contains when it is displaced during tank filling. This emission is unlikely to carry significant pollution unless the tank contents have been heated or agitated	Settled water (via treatment)	Settled sludge
Cold oil settling	Tank venting	Settled water (via treatment)	Settled sludge
Hot oil settling	Tank venting	Settled water (via treatment)	Settled sludge
Vibrating sieve	Mist and vapour		Sludge
Enclosed filters			Used elements and sludge
Bauxite towers			Spent bauxite
Vacuum dehydration	Vapour (via scrubbers)		
Product blending	Tank venting		
Pumped sludge storage/decanting	Tank venting		
Cold effluent settling	Tank venting		
Hot effluent settling	Tank venting		
Biological effluent treatment	Aeration air		
Filter press			Filter cake
Plate separator		Effluent	Settled sludges
Mechanically handled sludge/solids storage and loading			Mixed solid wastes
Waste oil fired boiler	Stack emissions		
Old interceptor waste	Since it usually comes from paved surfaces where it has already been exposed to air, it will probably have already emitted all that it is capable of emitting to the air at this stage unless it is heated during treatment		

Many sites have an accidental spillage of oils to the site base during unloading, or during the storage or

transfer of materials on the site. The site base is usually designed to retain liquid spills and to return these to the plant, but there will be some evaporation in the air

Table 3.17: Principal emission sources at oil recycling premises
[56, Babbie Group Ltd, 2002], [150, TWG, 2004]

The following table identify emissions to air, water and solid waste generated for each type of waste oil treatment. In some cases, the emissions are quantified with data in the table.

Process	Emissions (values in kg/tonne of WO if not otherwise specified)		
	Air	Water	Soil and residues
Oil separation from water stream	Could produce a range of other emissions such as metals, naphthalene, additional nitrogen, toluene, xylenes and PAHs	Could produce a range of other emissions such as metals, naphthalene, toluene, xylenes and PAHs	Could produce a range of other emissions such as metals, naphthalene, toluene, xylenes and PAHs
Laundering. Closed loop recycling of industrial oil	From the oil recovery process the emission is 20 – 40 mg/m ³ VOCs whilst heating. 262 kg VOC was released against 100 mg/Nm ³ and 10 t/yr limits	Waste water	Laundering can be considered as a closed loop system because it generates very little (if any) waste oil. The contaminated filter sludge contains 20 – 30 % oil. This waste stream is reprocessed with quicklime and made suitable for co-combustion in a cement kiln. The acceptability of one technique, which used a clay known as 'fuller's earth' to remove contaminants, is waning as conditions for disposal to landfill become more stringent. The technique is still used in New Zealand, but disposal of the contaminated clay is likely to become an issue. Releases to land are: filter cake which includes solids and metal fines (<100 t/yr against a consent limit of 600 t/yr) and in some cases chlorinated solvent sludges. 80 – 85 % of drums are recycled while the others are scrapped
Reclaiming industrial lubricants		Waste water from dewatering processes	
Vacuum distillation	Vacuum distillation of waste oils produces sulphur compounds, mercaptans (odorous) and PAHs (some may be carcinogenic)		All the metals contained in the used oil end up in the vacuum residue. This residue may be blended with a crude vacuum residue in such a proportion so as to enable its use as a component in bitumen

Process	Emissions (values in kg/tonne of WO if not otherwise specified)		
	Air	Water	Soil and residues
Distillation/clay process			Produces large quantities of the oil-absorbed clay which need to be disposed of. High temperature activated clay allows a lower clay/oil ratio, thus increasing the overall yield and reducing the quantity of oily clay needing to be disposed of
Thin film evaporator (TFE) + clay treatment		Water: 90	Clay: 50 – 60 Bitumen (metals and additives): 130 Sludge and light ends: 35 The process produces residues (requiring disposal)
Acid/clay process			This process produces large quantities of sludges and solids requiring disposal. These sludges (acid tars) are highly acid and contain high concentrations of PAHs, sulphuric acid and sulphur compounds, as well as most of the metals from the used oils. These tars are unsuitable for landfill because of their physical and chemical properties. This latter constraint can sometimes be overcome by: <ul style="list-style-type: none"> • dispatching the acid sludge jointly with the oily clay, in granulated form, to cement factories or to contractors • incinerating, but the gases need to be treated with caustic soda and the resulting waste water needs to be dealt with. This neutralisation treatment generates in quantity as much inactive waste as the amount of acid tar treated • treating to produce sulphuric acid or SO₂. The used clay (4 % by weight of feedstock + absorbed oil content) also needs to be incinerated by the same method as described above
Vacuum distillation + chemical treatment or clay treatment.			Used clay and used chemicals need to be safely disposed of. The route currently in use is to burn them in cement kilns or in a chemical waste incinerator
Vacuum distillation and hydrotreatment	Emissions common to any process handling oil products		The disposal of spent hydrotreating catalysts needs to be handled by a specialised company familiar with this problem. The residue produced from the vacuum distillation stage is similar to asphalt and may be sold. Fuels that are taken out in the de-fuelling stage can also be used on site or sold. The catalyst used is nickel-molybdenum and is either recycled by a nickel smelter or landfilled
TFE + hydrofinishing		Water: 90	Sludge and light end: 30 Sulphur: 35 Bitumen: 130

Process	Emissions (values in kg/tonne of WO if not otherwise specified)		
	Air	Water	Soil and residues
TFE + solvent extraction		Water: 90	Sludge and light end: 30 Extract: 60 Bitumen: 130
TFE + solvent extraction + hydro-finishing		Water: 65	Sludge and light end: 20 Sulphur: 4 Bitumen: 160
TDA (thermal de-asphalting) + clay treatment		Waste water: 770	Light ends/solvents: 35 Clay: 130 Bitumen (metals and additives): 120
TDA + hydrofinishing (high pressure)		Waste waters: 770	Light ends/solvents: 35 Spent catalyst: 0.5 Bitumens: 120
PDA (propane de-asphalting) + hydro finishing (medium pressure)		Waste waters: 770	Light ends/solvents: 30 Bitumens: 130
Vacuum distillation + chemical treatment	1116 kg eq CO ₂ 2.8 kg eq SO ₂ VOC: 0.04 kg eq. C ₂ H ₄ 3.6 g particulates	0.0011 kg eq phosphates in water	Waste to eliminate: 24 Waste to recover: 33
Distillation and alkali treatment (Vaxon-Cator)		None. Recycled to a product	Small
Solvent extraction and distillation (Sener-Interline)		Discharges to water are from the residuum/water separator	None
Direct contact hydrogenation (DCH)		Waste water: 60	Bitumens: 50 Spent catalyst: 0.75
Thin film evaporator (TFE)		Process water, water decanted from storage tanks and contaminated surface water is treated in the effluent plant. This presents a problem to the site; in that the water has a very high COD which can vary between 40000 to 100000 mg/l against a discharge consent limit of 80000 mg/l. It contains materials such as glycols, polyglycols, esters and glycerols	The residue from the TFE is extracted whilst still mobile and blended with other secondary fuel oils which are also produced on site. Most of the organometallic constituents of the additives end up in the residue, so their ultimate destination is in a secondary fuel oil released to air as combustion products. There is a high dilution of the residue into the secondary fuel oil formed and the blend meets fuel oil specifications. Other residues, which include storage tank and effluent plant sludges, are removed from the site and centrifuged for reclamation of the oil. The solid residue from that process then is being landfilled
Caustic soda and bleaching earth treatment (ENTRA)		Waste water: 60	Bleaching earth, caustic soda and residue: 150

Process	Emissions (values in kg/tonne of WO if not otherwise specified)		
	Air	Water	Soil and residues
Waste oil transfer station		Waste water: 102	Sludge and solids: 2.13 Shredded steel: 85
Treatment of transformer oils			Spent bauxite catalyst Non-returned drums and pallets
Treatment of oil interceptor waste, soluble cutting oils, Spray booth waste from water based paint, gully waste, leachates		Waste water: 1613	Pumpable sludge: 47 Tank and tanker 'dig out' and screened waste: 43
Re-refining of lubricant oil ¹	CO ₂ : 123 SO ₂ : 1.04 NO _x : 0.35	Waste water: 84	Oil/chemical waste – sludge: 0.088
Used solvent oils and oily waters		Waste water: 444	Solids and sludge: 171
Treatment of oil water mixtures and leachates		Effluent: 1042	Filter cake and sludge: 55
Integration in a mineral oil refinery	Provided that adequate pretreatment of used oils is performed to remove water and light ends and to reduce the organic chloride content the emissions are related to those occurring in a refinery (see Refinery BREF)		Metals are encapsulated in asphalt, so the leaching of metals will be extremely low. However some problems of corrosion damage to the plant and loss of cracking catalyst activity need to be solved before this can be considered a viable option
Integration to a lubricant part of a refinery	It could release particulates, sulphur, halides, heavy metals and their oxides to the air		Most of the lube oil additives are bottomed out in this cut. The metals in the residue after the solvent extraction process are still leachable. There could be problems in its disposal to asphalt, especially in winter, when the market may slow. This cut would not be fit for blending in heavy fuels, not only for failing the filtration tests, but also for environmental reasons. The aromatic extracts which are contaminated with chlorine are believed to be disposed of outside the refinery

Process	Emissions (values in kg/tonne of WO if not otherwise specified)		
	Air	Water	Soil and residues
Regeneration	CO ₂ equivalent (kg eq. CO ₂ /kg of oil) 3.19 Acidification potential (g eq. H ⁺ /kg of oil) 0.06 VOC emissions (g/kg of oil): 9.05 CO emissions (g CO/kg of oil) 9.74	COD (g COD/kg of oil): 35.02	Waste (g/kg of oil): 411
Chemical treatment + distillation + HF			
¹ Calculations were made based on the yearly treatment/usage of 26000 tonnes dehydrated waste oil and producing 8000 tonnes of base oil, 12000 tonnes of fuel oil and 4000 tonnes of asphalt			

Table 3.18: Environmental issues generated by different waste oil re-refining techniques [6, Silver Springs Oil Recovery Inc., 2000], [7, Monier and Labouze, 2001], [11, Jacobs and Dijkmans, 2001], [12, Birr-Pedersen, 2001], [13, Marshall, et al., 1999], [14, Ministry for the Environment, 2000], [42, UK, 1995], [56, Babbie Group Ltd, 2002], [86, TWG, 2003], [139, UBA, 2003], [150, TWG, 2004], [152, TWG, 2004]

Emissions to air

The emissions to the air are partially controlled at some sites, but uncontrolled at others. VOCs are known to occur. Although the lubricating system is a semi-closed system, it is not gas tight, therefore it would be expected that the volatile gases would have boiled off and left the system during normal operating temperatures.

Abatement systems for reducing oil emissions to the air are in place in some plants. At other sites, the excess oil concentration in buildings is simply vented to the air through exhaust fans; with all the tanks having vents to the air.

Most plants will accept that there is an odour problem from the oil. The control of odour from such plants requires a high level of management control and attention. Odours are typically generated during the storage, e.g. odours problems can arise by leaving hatches open at the top of each settlement tank and oil storage tank, or in open vibrating sieves.

No generally recognised reliable figures have been found for the concentration of contaminants in the air emitted from waste oil re-refining processes. However, some matrix distributions are shown in Table 3.19.

Activity	Oil filters	25 litre oil drums	205 litre oil drums	Bulk used engine oil	Used industrial oils	Oil y waters (interceptors)	Fuel oils	Electrical oils
Filter bin unloading								
Filter bin storage								
Filter crushing								
Filter shredding	*							
Magnetic separation	*							
205 litre drum unloading								
205 litre drum storage								

Activity	Oil filters	25 litre oil drums	205 litre oil drums	Bulk used engine oil	Used industrial oils	Oil y waters (interceptors)	Fuel oils	Electrical oils
205 litre drum emptying								
25 litre drum unloading								
25 litre drum storage								
25 litre drum emptying/shredding		*						
Tanker unloading								
Coarse straining								
Bulk storage								
Cold oil settling								
Hot oil settling				*	*			
Distillation				*	*			
Vibrating sieve								
Centrifuge								
Bauxite towers								*
Vacuum dehydration								*
Product blending								
Pumped sludge storage/decanting								
Effluent incineration				*	*	*	*	
Cold effluent settling								
Hot effluent settling				*	*	*	*	
Biological effluent treatment				*	*	*	*	
Effluent clarification								
Effluent balance tank								
Plate separator								
Mechanically handled sludge/solids storage and handling								
Waste oil fired boiler				*	*	*	*	
Note: The grey blocks indicate emissions are likely and the asterisks indicate the locations that are thought to be the larger sources								

Table 3.19: Air emissions matrix for all common process in oil and solvent regeneration plants
[56, Babbie Group Ltd, 2002]

Capacity	t/yr		6824	15000		17171	46208		90500	
Fumes generated		Million Nm ³ /yr			14.89			175.4		210.5
Oxygen	%			4		7.4	3		10	
CO ₂	t/yr						24000			
PM	mg/Nm ³	kg/yr	4	0		4.23	11.17	1960	28.4	
SO _x	mg/Nm ³	kg/yr	14	4000	60000		529.7	92910	4.2	884
NO _x	mg/Nm ³	kg/yr	63.7			90	225.8	39610	802.5	168891
TOC	mg/Nm ³			0					3	
CO	mg/Nm ³	kg/yr	501.6	0		193	7.4	1300	18.9	3978
HCl	mg/Nm ³	kg/yr		0		2.8	1.5	263	0.8	
HF	mg/Nm ³			0					0.08	
Total metals	mg/Nm ³			0					0.423	
Hg	mg/Nm ³			0					0.026	
Cd + Tl	mg/Nm ³	kg/yr		0			0.0008	0	0.0008	
PAH	mg/Nm ³	kg/yr	0.0008	0			8E-07	0.000175	0.0008	
PCB	mg/Nm ³	kg/yr		0			8E-07	0		
Chlorobenzenes	mg/Nm ³	kg/yr		0			0.08	0		
PCDD/PCDF	ngTEQ/Nm ³	g/yr		0			0.008	0.00175	8	
CFC	mg/Nm ³	kg/yr		0			0	0		
Odour	EU O.U./Nm ³			0						
Noise	dB(A)			75			55			

Note: For the installations having only one column, the figures correspond to the concentration column

Table 3.20 Air emissions from several re-refining waste oil installations operating in the EU [66, TWG, 2003]

Emissions to water

The emissions to water are generally well documented. This is due to regulations and enforced limitations regarding discharges to foul sewers or disposal by alternative routes. The quantities of effluent discharged are thus usually well known.

Discharges are typically sampled regularly, providing monitoring data to allow a calculation of emissions for the radicals on the analysis programme. Sites handling large volumes of water and that have a constant discharge to sewerage system are usually sampled daily; those where the water volume is small tend to be tested on a batch basis prior to each discharge. Table 3.21 and Table 3.22 show the concentrations of water parameters and the emission matrix of the emissions to water, generated by the re-refining of waste oil.

Water parameters	Oily water ² (mg/l)	Process water ² (mg/l)	Effluent concentration (mg/l)
Temperature			25 °C
pH			7.8
Colour			clear
COD ¹ (TOC)	120	17000	20 – 20000
Oil/grease			<10
Hydrocarbons			5 – 15
Anionic tensioactives			0.2 – 0.5
Non-anionic tensioactives			1.0 – 2.0
Total tensioactives			1.2 – 2.5
Benzene			364
Toluene			1306
Phenols	1.5	180	0.2 – 0.4
Naphthalene			283
Chlorinated solvents (various)			309 – 666
1, 2 Dichloroethane			<1.0
Hexachlorobutadiene			<0.001
Hexachlorobenzene			<0.001
1, 2, 4 Trichlorobenzene			<0.001
Various PCBs			<0.001
Benz(a)anthracene and benzo(a)pyrene			each below 0.02
Ammonia			4.0 – 6.0
Suspended solids			<400
Chloride			
Total nitrogen			
Total phosphorus			0.05 – 0.2
Total metals:			<10
• aluminium			<0.5
• arsenic			3.4
• barium			80
• cadmium			<0.01 – 0.34
• chromium			10
• copper			
• iron			<0.6
• lead			271
• zinc			250

¹ Partially are demulsifiers and detergents

² Water parameters of the waste water sent to biological treatment after stripping treatment

Table 3.21: Waste water parameters from different re-refining processes of waste oil
[42, UK, 1995], [56, Babbie Group Ltd, 2002], [66, TWG, 2003]

Activity	Bulk used engine oil	Used industrial oils	Oil waters (interceptors)	Fuel oils	Electrical oils
Cold effluent settling	*	*	*	*	*
Hot effluent settling	*	*	*	*	*
Biological effluent treatment	*	*	*	*	*
Effluent clarification	*	*	*	*	*
Effluent sludge filter press	*	*	*	*	*

Activity	Bulk used engine oil	Used industrial oils	Oil waters (interceptors)	Fuel oils	Electrical oils
Effluent balance tank	*	*	*	*	*
Plate Separator	*	*	*	*	*

Table 3.22: Water emissions matrix for all common process in oil and solvent recycling plants [56, Babbie Group Ltd, 2002]

Capacity	t/yr		6824	15000	17171	19960	46208	90500
Waste water generated		m ³ /yr		1800		6180	298287	375000
Waste water generated/plant capacity		m ³ /t		0.12		0.3096	6.4553	4.1436
Suspended solids	mg/l	kg/yr				931	6860	22.99
TOC	mg/l	kg/yr					1490	4.99
BOD ₅	mg/l	kg/yr		4000	7200			13300
COD	mg/l	kg/yr		8000	14400	300	27703	25650
Hydrocarbons	mg/l	kg/yr	0.18				430	1.44
Phenols	mg/l	kg/yr	0.4	0	0.8	42.58	14	0.04
AOX	mg/l	kg/yr					0	0
BTX	mg/l	kg/yr	0.4				0	0
Total Nitrogen (as N)	mg/l	kg/yr					10000	0.033
Nitrit N (NO ₂ - N)	mg/l	kg/yr					180	0.6
CN, free	mg/l	kg/yr					0	0
Sulfid (free)	mg/l				1			
F, total	mg/l							
P, total	mg/l	kg/yr					2980	9.99
Total metals	mg/l		0.56					
Al	mg/l	kg/yr	0.08				476	1.6
Fe	mg/l	kg/yr	0.08				952	3.2
As	mg/l	kg/yr	0.08				116	0.4
Cr, total	mg/l	kg/yr	0.08				952	3.2
Cr(VI)	mg/l	kg/yr	0.08				44	0.16
Cu	mg/l	kg/yr	0.08				92	0.32
Hg	mg/l	kg/yr	0.08				1.12	0.004
Ni	mg/l	kg/yr	0.08				476	1.6
Pb	mg/l	kg/yr	0.08			0.291	68	0.24
Zn	mg/l	kg/yr	0.08			1.276	236	0.8

Note: when only one column exists for a certain capacity, it refers to concentration values

Table 3.23: Water emissions from different re-refining installations operating in the EU [66, TWG, 2003]

Solid waste and discharges to land

Sludges are typically tested for metals content, oil content and moisture content. This is carried out less frequently than the testing of the aqueous waste to sewerage systems. Table 3.24 and Table 3.25 show the concentrations of water parameters and the emission matrix of the emissions to water, generated by waste oil re-refining.

Type of waste	Waste parameters				
	Metals	Moisture	HC and TOC	S compounds	Other
Sludges	Some toxic metals may be contained	X	X	X	
Tank bottom sludges			X		
Solid particulates from filters	X		X		PAH and PCBs
Interceptor waste	X	Low	X		Phosphates, PAH, non-lubricant related solids
Cleaned oil filters	X				

Table 3.24: Types of waste generated in re-refining processes of waste oil
[42, UK, 1995], [56, Babbie Group Ltd, 2002], [66, TWG, 2003]

Activity	25 litres Oil drums	205 litres Oil drums	Bulk used engine oils	Used industrial oils	Oily waters (interceptors)	Fuel oils	Electrical oils
Bulk storage			*	*	*	*	*
Cold oil settling			*	*	*	*	*
Hot oil settling			*	*	*	*	*
Distillation			*	*	*	*	*
Vibrating sieve			*	*	*	*	*
Centrifuge			*	*	*	*	*
Enclosed filters			*	*	*	*	*
Effluent sludge filter press			*	*	*	*	*
Mechanically handled sludge/solids storage and handling	*	*	*	*	*	*	*

Table 3.25: Emissions to land matrix for all common process in oil and solvent recycling plants
[56, Babbie Group Ltd, 2002]

Table 3.26 gives the environmental performance criteria of different treatment systems arising from an industry survey. In the survey, a profound discussion for each figure in the table is given. Each figure represents the absolute value that is assigned to that treatment system, concerning a specific criterion and estimating the performance of the system relative to the other systems for this said criterion.

Process	Environmental criteria				
	S-compounds	Metals	Products of incomplete combustion + VOCs	Re-use of materials	Re-use of energy
Laundering. Closed-loop recycling (re-use)	1	1	3	1	5
Chemical re-refining without distillation	2	2	3	1	5

Re-refining with distillation	1	1	1	1	5
Blending into vacuum residue of a refinery	5	3	4	5	1
Note: S-compounds: the ultimate destination of the sulphur content originating from the waste oil Metals: the ultimate destination of the metals originating from the waste oil Products of incomplete combustion + VOCs: the emission of VOCs or products of incomplete combustion (CO, PAHs, soot, dioxins, furans, etc.) originating from the waste oil Values: 1 best performance, 5 worst – on a relative scale					

Table 3.26: Evaluation of the environmental performance of several re-use and re-refining activities [11, Jacobs and Dijkmans, 2001]

3.3.2. Emissions from the regeneration of waste solvents

The most important concern in the solvent recovery sector is the volatile organic emissions, which result from waste solvent reclamation. Acidic gaseous and particulate emissions can also result from solvent recovery operations.

Acidic gaseous emissions mainly consist of gaseous chloride, hydrogen fluoride, and sulphur oxides. Since the unit operation presenting the major source of acidic gases and particulate from the solvent recovery industry is that of incineration, this issue will be part of the waste incineration BREF. Incinerator stack emissions consist of solid contaminants that are oxidised and released as particulates, unburned organics, and combustion stack gases.

In solvent recovery operations, bottom streams consist of organics such as oily wastes and sludges or an aqueous residue. If water is treated on-site, sludges or other wastes may be created. Other emissions may come from discarded containers or samples, vessel washing residues, or from volatilisation to the air. Some residues and sludges are removed hot from stills into drums and allowed to cool and solidify. They may then be removed for further treatment or disposal. In industrial systems there can be traces of impurities, which can arise from inhibitors, denaturants or plant rinsing; these impurities can cause problems, particularly when using azeotropic distillation techniques.

Emission points include storage tank vents, condenser vents, incinerator stacks and fugitive losses. VOC emissions from equipment leaks, open solvent sources (e.g. sludge draw-off and the storage to material from distillation and initial treatment operations), solvent loading, and solvent spills are classified as fugitive.

Solvents may be accidentally spilled during handling, distillation, or purification activities. Materials that are spilled onto the ground may spread over an area, vaporise, and then result in air, water, or land emissions. Emissions resulting from significant accidental situations such as spills also need to be estimated.

Releases to the air may arise from a number of sources including non-condensable vapours from distillation/fractionation operations, and breathing losses from storage tanks and local extraction vents (LEV) located at material handling or drumming off points. Emission concentrations would be expected to be high except from sources such as LEVs. Concentrations and types of emitted compounds may vary significantly. The flowrates from continuous fractionation columns operating under vacuum at steady conditions are generally very low (1 – 10 m³/hr). However, when manifolded together, emission flows could be up to 500 m³/hr. Where LEV systems are tied into abatement equipment this can significantly increase flowrates and the dilution of vent gases. To minimise the size of abatement equipment there is a benefit in keeping process and LEV vents separate.

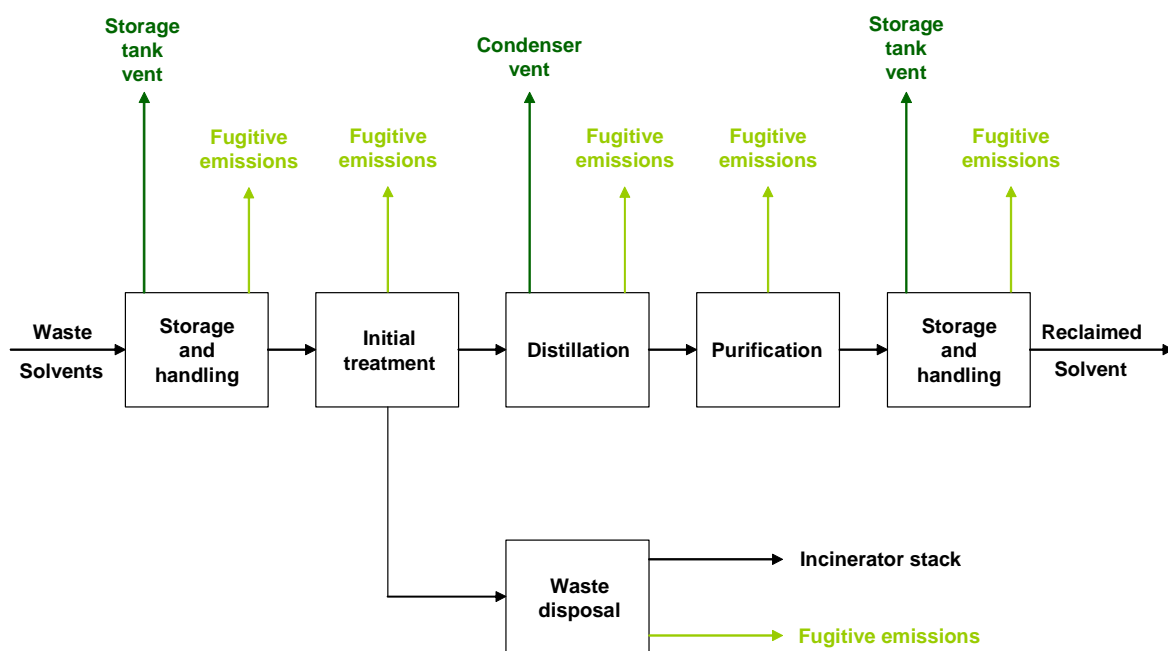


Figure 3.2: Example of a waste solvent regeneration scheme and emission points
 [129, Cruz-Gomez, 2002]

Activity/Plant	Emissions			Accidental Emissions
	To air	To water	To landfill	
Filter bin unloading				Drainage, spillage and bursts discharging contents to ground
Filter bin storage				Spillage to ground
Filter crushing				Spillage to ground
Filter shredding	Oil mist			Spillage to ground
Magnetic separation	Oil mist			Spillage to ground
205 litre drum unloading				Spillage to ground
205 litre drum storage				Spillage to ground
205 litre drum emptying				Spillage to ground
25 litre drum unloading				Spillage to ground
25 litre drum storage				Spillage to ground
25 litre drum emptying/shredding	Oil mist			Spillage to ground
Tanker unloading	Tank venting			Spillage to ground
Coarse straining	Oil mist			Spillage to ground
Bulk storage	Tank venting	Settled water (via treatment)	Settled sludge	Spillage to ground
Cold oil settling	Tank venting	Settled water (via treatment)	Settled sludge	Spillage to ground
Hot oil settling	Tank venting	Settled water (via treatment)	Settled sludge	Spillage to ground

Activity/Plant	Emissions			Accidental Emissions
	To air	To water	To landfill	
Distillation	Venting and fugitive			Spillage to ground
Vibrating sieve	Mist and vapour		Sludge	Spillage to ground
Centrifuge				
Enclosed filters			Used elements and sludge	Spillage to ground
Bauxite towers			Spent bauxite	Spillage to ground
Vacuum dehydration	Vapour (via scrubbers)		Spillage to ground	
Product blending	Tank venting			Spillage to ground
Pumped sludge storage/decanting	Tank venting			Spillage to ground
Incineration	Stack emissions (NO _x , CO, VOC, HCl, SO ₂ , etc.)			
Cold effluent settling	Tank venting			Spillage to ground
Hot effluent settling	Tank venting			Spillage to ground
Biological effluent treatment	Aeration air			
Effluent clarification				
Filter press			Filter cake	
Effluent balance tank				Spillage to ground
Plate separator		Effluent		
Mechanically handled sludge/solids storage and loading			Mixed solid wastes	Spillage to ground
Waste oil fired boiler	Stack emissions			

Table 3.27: Principal emission sources and emissions matrices of oil and solvent recycling plants
[56, Babbie Group Ltd, 2002], [150, TWG, 2004]

81. Parameter	82. Concentration value	83. Concentration units	84. Load value	85. Load units
<i>86. Air emissions</i>				
87. Fumes generated	88.	89.	90. 14400000	91. Nm ³ /yr
92. Oxygen	93. 6	94. %	95.	96.
97. CO ₂	98.	99.	100.1268018	101.kg/yr
102.CO	103.49	104.mg/Nm ³	105.700	106.kg/yr
107.SO ₂	108.86.9	109.mg/Nm ³	110.850	111.kg/yr
112.NO _x	113.44.1	114.mg/Nm ³	115.635	116.kg/yr
117.TOC	118.540	119.mg/Nm ³	120.237	121.kg/yr
<i>122. Water emissions</i>				
123.Waste water	124.	125.	126.2969	127.m ³ /yr
128.Suspended solids	129.16	130.mg/l	131.47.5	132.kg/yr
133.COD	134.534	135.mg/l	136.1585	137.kg/yr
138.Phenols	139.0.08	140.mg/l	141.	142.kg/yr
143.AOX	144.0.25	145.mg/l	146.0.742	147.kg/yr

148.Total N (as N)	149.16	150.mg/l	151.47.5	152.kg/yr
153.Total P	154.0.43	155.mg/l	156.1.27	157.kg/yr
158.Sulphide (free)	159.0.08	160.mg/l	161.	162.kg/yr
163.Note: Capacity of the installation 27.5 kt/yr				

Table 3.28: Air and water emission from an EU solvent regeneration installation [66, TWG, 2003]

During storage and handling, and in the distillation process, hydrocarbons are emitted to the air. The emission of hydrocarbons (C_xH_y) through the distillation process is estimated to be 0.5 kg/t waste solvent.

Some contaminated solvents contain water. After dewatering, the water fraction contains traces of solvent. This water fraction ranges from a negligible amount to a maximum of 5 to 10 %. It is purified in a waste water treatment plant and discharged.

The amount of distillation bottom depends on the composition of the waste solvent. On average, the amount is estimated to be 25 % of the processed amount.

3.3.3. Emissions from the regeneration of waste catalysts

Knowing the source of the spent catalyst can often provide information on potential emissions due to the presence of acids, oils, organic contaminants (they may produce PCDD during melting processes), etc. This directly influences the potential emissions to air, water and land.

The physical state of the waste catalyst can also influence the emissions (e.g. the particulate emissions depend on the particulate size of the waste catalyst, oil content, etc.). Some potential emissions from different catalyst regeneration plants are shown in Table 3.31.

Air pollutant	From
Particulates	Fugitive emissions
SO ₂	
NO _x	
VOC	
Dioxins	
Metals	
Water pollutants	
Suspended solids	
Oil	
TOC	
Metals	
Solid waste	
Oil	
Metals	
Dust	e.g. from abatement systems
Reference conditions of flue-gas: dry gas, 6 % O ₂	

Table 3.29: Potential emissions found in different catalyst regenerators [125, Ruiz, 2002]

3.3.4. Emissions from the cleaning and regeneration of carbon

The main environmental issues related to the thermal regeneration of activated carbon is primarily gaseous effluents such as carbon dioxide. Acidic gases and pesticides may prove a problem if there are no control measures such as afterburners and/or scrubbers.

Figure 3.3 shows a schematic of a generic activated carbon regeneration process, including the release routes that are listed in Table 3.30.

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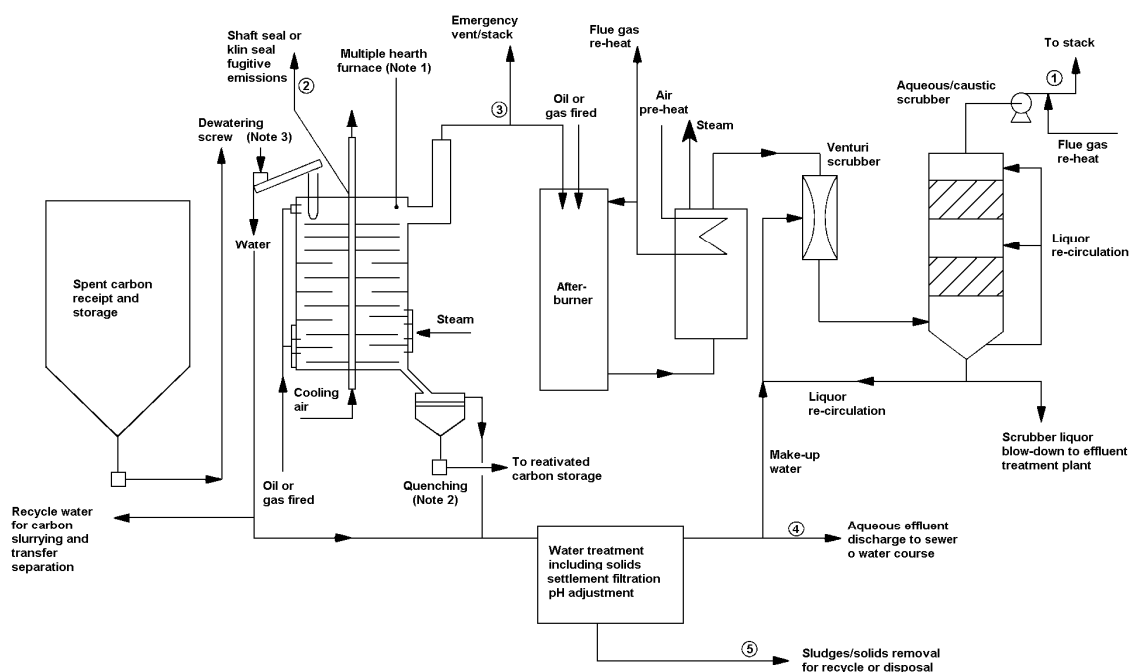


Figure 3.3: Schematic flow diagram of a generic carbon regeneration plant
[29, UK Environment Agency, 1996]

Notes: Numbers in the diagram refers to the numbers of the first column of the following Table 3.30.

Note 1 Multiple hearth furnace illustrated but thermal reactivation may also be carried out in a rotary kiln

Note 2 Carbon exiting the kiln may also be cooled by other means

Note 3 Other techniques for dewatering may be used.

Releases to the environment commonly associated with the regeneration of activated carbon processes are listed in Table 3.30.

	Source releases to:	Dust/ solids	CO + CO ₂	NO _x	SO _x	Halogens	Organic compounds or partial oxidation products	Metals, metalloids or compounds
1	Flue-gases from flue-gas treatment	A	A	A	A	A	A	A
2	Fugitive emissions from seal leakages	A	A	A	A	A	A	A
3	Emergency vent stack (if applicable)	A	A	A	A	A	A	A
4	Aqueous effluent discharge	W					W	W
5	Effluent treatment plant sludge						L	L

Note: The releases to each medium will be determined to a significant degree by the application for which, the carbon has been used, and hence release of some substances to water and land are possible
Legend: A: Air, W: water and L: residues (land)

Table 3.30: Potential release routes for prescribed substances and other substances which may cause harm
[29, UK Environment Agency, 1996]

Emission results from different regeneration plants are shown in Table 3.31.

Air pollutant	Concentration (mg/Nm ³)
Particulates	1 – 34
CO	<3 – 160
NO _x (as NO ₂)	126 – 354
SO ₂	<2 – 60
HCl	<1 – 22
HF	<1
VOC (TOC)	5 – 15
Dioxins and furans PCDDs and PCDFs (TEQ)	<0.01 – 0.18 ng/Nm ³
Cd	<0.05
Hg	<0.05
Other heavy metals	0.1 – 0.5
Water pollutants	Concentration (mg/l)
Suspended solids	50 – 300
COD	400
Simazine	0.001
Atrazine	0.001
TEQ (TCDDs and TCDFs)	0.28 – 0.4 ng/l
Al	30
Cd	0.0005
Hg	0.0001
Mn	30
Solid waste	Composition
Refractory linings	
General industrial waste	
Sludge from settlement ponds	Mainly carbonaceous fines
Reference conditions of flue-gas: dry gas 6 % O ₂	

Table 3.31: Range of emissions found in different carbon regenerators
[42, UK, 1995]

Liquid effluent from regeneration plant

Water is used for the transport of activated carbon as slurry to and from the regenerator. This gives rise to a black water effluent which should be clarified and recycled. Water separated from the slurry will contain suspended solids and possibly prescribed substances (e.g. pesticides) and are routed to the effluent treatment plant.

The clean hot activated carbon is either dry cooled or quenched in cold water. For the wet cooling system, the water becomes alkaline and is therefore dosed with acid. This water should be purged from the system to prevent accumulation of mineral salts, with fresh/recycled water make-up as necessary.

Water is also used intermittently in large amounts to backwash activated carbon storage hoppers both to remove fines and to level the top surface of the activated carbon. Sufficient water storage needs to be provided so that this water can be clarified and recycled.

Techniques for controlling releases to land

In the regeneration of activated carbon most deliveries of carbon are made in bulk tankers. In certain circumstances drums may be used. Where this is the case, drums should be reconditioned and re-used so that disposal is minimised. Other process waste includes sludge or filter cake from filter presses or settlement tanks in an effluent treatment plant. In the case where disposal is to land the method of disposal should ensure that

if the cake or sludge were to dry out, windblown dust of fine carbon particulates cannot occur. Other wastes will include refractory bricks and linings where repairs to kilns and furnaces have taken place periodically.

3.3.5. Emissions from the regeneration of ion exchange resins

The releases from a process of this nature are small and confined mainly to those to water. Some emissions resulting from different regeneration plants are shown in Table 3.31.

Air pollutant	From	Concentration (mg/Nm ³)
HCl	from filling of a bulk storage	<5
Water pollutants		Concentration (µg/l)
Effluent flowrate ²		5 – 10 m ³ /h
Cd		<0.5 – 3 ¹
Hg		0.86 ¹
Organic Sn		<0.3 – 2.0 ¹
Solid waste		
Waste resins		
Fines		
Backwash filter	When resin is combined with activated carbon as a guard or a backwash filter	
Reference conditions of flue-gas: dry gas, 6 % O ₂		
¹ Values that correspond to peak values		
² Steam regeneration can produce large quantities of contaminated aqueous effluent		

Table 3.32: Range of emissions found in different ion exchange regenerators
[41, UK, 1991], [42, UK, 1995]

3.3.6. Emissions from waste acids and bases treatments

Activity	Air	Water	Soil and wastes
Treatment of waste acids	Halogens: HCl and HF NO _x	Halogens: HCl and HF	
Treatment of sulphuric acid	Sulphur oxides		

Table 3.33: Emissions from the treatments of waste acids and bases
[55, UK EA, 2001]

3.3.7. Emissions from the treatment of photographic waste

Treatment of solid photographic waste

In shredding, emissions of dust occur. These are treated with a dust filter. The emission of dust to the air ranges from 2 to 5 mg/Nm³. The amount is estimated to be 29 g/t film waste.

Treatment of liquid photographic waste

Emissions to air

Treatment of photographic waste, especially fixers, can generate emissions to the air of ammonia, acetic acid and VOCs.

The emissions from physico-chemical treatments are reduced by treating the exhausted air in a wet oxidising scrubber. The concentrations in the exit gases of C_xH_y are approximately 600 mg/Nm³ and of NH₃ <2 mg/Nm³. The emissions from the biological treatment are reduced by means of a continuous automatic monitoring and

regulation of the air or oxygen supply. The total C_xH_y emission is estimated to have a maximum of 20 g/t waste water.

In evaporation, some compounds will evaporate together with the water. Most of them will condense. Not condensed compounds are passed through the biological treatment that functions as a scrubber. The emissions from the evaporation step are negligible.

Emissions to water

In Table 3.34, emissions to water from physico-chemical and biological treatments are presented. Desilvered photographic liquid waste is just one of the processed waste waters. Therefore, the presented emissions give a rough indication of possible emissions from the treatment of this waste stream.

Component	Emission (g/t waste water)
Suspended solids	9
Chloride	29
Sulphur	0.3
COD	172
BOD	4
N-total (Kjeldahl)	351
Phosphorus	2

Table 3.34: Emissions to water from the treatment of photographic liquid waste and other waste waters [156, VROM, 2004]

3.4. Waste OUT from re-recycling/regeneration treatments

In some cases the materials obtained by these treatments are commercial products with only minor differences compared to virgin products.

Re-refined waste oil

The quality of the base oil obtained is dependent upon the level of treatment applied, for example, severe processing involving hydrotreatment will be required in order to significantly remove PAHs.

Used oils vary according to the origin and type of oil collected. These variations are reflected in the base oil products from acid/clay treatment plants, in terms of their density, viscosity, viscosity index, sulphur level, etc. Less variation occurs in these parameters in the base oil products from vacuum distillation/hydrotreating units, with the exception of the sulphur content. Re-refined base oils from different processes and production plants vary greatly in their characteristics.

Some re-refining technologies allow the production of premium quality base oils: i.e. at least Group I according to the API base oils classification; and, when resorting to a severe hydro or solvent finishing, Group II base oils (e.g. topping purpose). The base stocks produced by the European re-refining industry today belong to Group I. Group I base stocks are solvent refined mineral oils. They contain the most saturates and sulphur and have the lowest viscosity indexes. They define the bottom tier of lubricant performance. Group I stocks are the least expensive to produce. They currently account for about 75 % of all base stocks comprising the bulk of the 'conventional' base stocks.

Almost all waste oil re-refining installations test for chlorine content and water content, and usually for PCBs. The final recovered oil is analysed because it has to satisfy specifications from the end user, but not all oil treatment plants blend a final product for sale or carry out such analyses. Table 3.35 shows an example of an

analysis of the product made in an oil recovery installation, where several degrees of hydrotreatment are carried out to three different types of base oil (spindle, light and heavy lube oil).

Type of feed	Spindle lube oil	Low severity ^{*1}	High severity ^{#2}	Light lube oil	Low severity ^{*3}	High severity ^{#4}	Heavy lube oil	Low severity ^{*5}	High severity ^{#6}
Density 15/4	0.8678	0.8606	0.8526	0.8767	0.8699	0.8604	0.8868	0.8786	0.8676
Viscosity @ 40 °C (cSt)	26.91	23.8	21.19	56.52	49.85	38.18	117.2	97.86	70.08
Viscosity @ 100 °C (cSt)	4.76	4.5	4.2	7.78	7.32	6.37	12.24	11	9.1
Viscosity index	93	103	100	102	107	117	94	97	105
Colour	6.5	L 0.5	L 0.5	7.5	L 1	L 0.5	>8	L 2	L 0.5
Asphaltenes (w/w-%)	0.0105	-	-	0.0092	-	-	<0.01	-	-
Carbon Conradson (w/w-%)	0.63	<0.1	<0.1	0.12	<0.1	<0.1	0.33	<0.1	<0.1
Nitrogen (ppm)	280	49	<1	312	57	<1	307	137	<1
Sulphur (ppm)	0.412	0.1025	0.0005	0.526	0.163	0.0008	0.7285	0.2735	0.0021
ndM method (w/w-%)									
Aromatic carbon	12.11	10.72	8.72	11.63	10.25	8.48	11.94	10.22	8.18
Parafinic carbon	71.20	72.06	72.76	72.66	73.42	75.09	72.68	73.75	75.57
Naphthelic carbon	16.70	17.22	18.52	15.70	16.32	16.43	15.38	16.03	16.25
Gas Chromatography analysis in ppm									
Anthracene	<1	<1	<0.5	<1	<1	<0.5	<1	<1	<0.5
Benzo(a)anthracene	37	<1	<0.5	4	<1	<0.5	3	<1	<0.5
Benzo(k)fluoranthene	5	<1	<0.5	2	<1	<0.5	<1	<1	<0.5
Benzo(b)fluoranthene	25	<1	<0.5	11	<1	<0.5	4	<1	<0.5
Benzo(ghi)perilene	16	<1	<0.5	40	4.7	<0.5	12	2.30	<0.5
Benzo(a)pyrene	16	<1	<0.5	11	<1	<0.5	4	<1	<0.5
Chrisene	3	<1	<0.5	2	<1	<0.5	-	<1	<0.5
Dibenzo-ah-anthracene	<1	<1	<0.5	2	<1	<0.5	<1	<1	<0.5
Fluoanthene	24	<1	<0.5	2	<1	<0.5	<1	<1	<0.5
Indeno(123-cd)pyrene	10	<1	<0.5	27	<1	<0.5	6	<1	<0.5
Phenanthrene	2	8.7	<0.5	<1	1	<0.5	<1	1.30	<0.5
Pyrene	34	5.8	<0.5	<1	<1	<0.5	2	<1	<0.5
PNA IP 346 (w/w-%)	2.8	1	0.2	1.3	0.6	-	1	0.6	0.2
* Low severity in the hydrotreatment of light fraction: Temperature of first catalyst: 300 °C. Temperature 2 nd catalyst: 280 °C. H ₂ partial pressure: 105 bar # High severity in the hydrotreatment of light fraction: Temperature of first catalyst: 340 °C. Temperature 2 nd catalyst: 340 °C. H ₂ partial pressure: 105 bar Total LHSV (h ⁻¹): ¹ :0.507; ² :0.5; ³ :0.507; ⁴ :0.292; ⁵ :0.481; ⁶ :0.295									

Table 3.35: Effect of hydrofinishing on the pollutants of the feed after de-asphalting [36, Viscolube, 2002]

Base oil produced is more dependent on the technology used to treat the waste oil than to the differences of the waste oil collected. Some examples of this are shown in Table 3.36.

Process (de-asphalting, demetalisation + finishing)	Main products (Values correspond to kg/tonne of WO unless otherwise stated)
Sulphuric acid + clay treatment	Low quality re-refined base oil: 621 PAH content of the base oils produced can be comparatively high (4 to 17 times higher than virgin base oils) Gasoil: 70
Caustic soda and bleaching earth treatment (ENTRA)	High quality re-refined base oil (Group II): 520 Light ends: 170 Diesel: 170
Vacuum distillation	In modern vacuum distillation equipment designed for processing used oils, the distillate produced has a metals content of less than 1 ppm (according to licensors)
Vacuum distillation + chemical treatment or clay treatment.	The base oils produced by clay treating or by chemical treatment have a metal content of <1 ppm. This process may not reduce the PAH content of the oil by as much as hydrotreatment
Thin film evaporator (TFE) + clay treatment	Medium quality re-refined base oil: 530 – 650 Gasoil: 150
TFE + hydrofinishing	High quality re-refined base oil: 630 Gasoil: 100
TFE + solvent extraction	High quality re-refined base oil: 600 Gasoil: 120 – 150
TFE + solvent extraction + Hydro-finishing	High quality re-refined base oil <ul style="list-style-type: none"> • Lubricant Group II: 370 • Lubricant Group I: 300 Gasoil: 85
TDA (thermal de-asphalting) + clay treatment	Medium quality re-refined base oil: 500 - 600 Gasoil: 60 – 80
TDA + Hydrofinishing (high pressure)	High quality re-refined base oil: 670 Gasoil: 70
PDA (propane de-asphalting) + hydro finishing (medium pressure)	High re-refined base oil: 660 – 700 Gasoil: 43 – 55 This process yields more marketable products than regeneration by a chemical treatment
Distillation and alkali treatment (Vaxon – Cator)	
Vacuum distillation + chemical treatment or clay treatment	As much as by hydrotreatment or solvent extraction
Direct contact hydrogenation (DCH)	Base oil (group II): 770 – 820 Light ends: 20 – 40 Heavy fuel or diesel: 70 – 80
Thermal clay treatment	
Hydro-finishing	

Vacuum distillation + chemical treatment	Base oil: 540 kg Fuel oil: 6105 MJ Bitumen fluxant: 48 kg Other fuels: 3720 MJ Fuel saving
--	--

Table 3.36: Product issues related with different waste oil regeneration techniques
[6, Silver Springs Oil Recovery Inc., 2000], [7, Monier and Labouze, 2001], [11, Jacobs and Dijkmans, 2001], [13, Marshall, et al., 1999], [56, Babbie Group Ltd, 2002], [86, TWG, 2003], [139, UBA, 2003], [150, TWG, 2004]

Regenerated solvents

Probably the most desirable product of solvent recovery is one that can be used instead of a purchased new solvent in the place where it was used initially. This does not necessarily mean that the recovered solvent meets the same specifications as the virgin material. The specifications of new solvent will usually have been drawn up by a committee formed of representatives of both users and producers, who know what the potential impurities are in a product made by an established process route. The specifications have to satisfy all potential uses but for any given user, some specifications may be immaterial.

Product property	Unit	DIN 53978	PERC
Colour	HAZEN	<15	<5
Water	ppm	<50	<25
PERC	Area-%	≥99.9	>99.98
Sum of 1,1,1-trichloroethane and trichloroethylene	Area-%	0.025 ± 0.003	<0.02
Relative density	g/ml	1.620 - 1.625	1.624
Alkalinity	ppm NaOH	≤30	25
<i>Evaporation</i>			
Residue	ppm	≤50	25
Free chlorine		0	0
Information on a chlorinated hydrocarbon distillation installation			

Table 3.37: Specification of products for treatment of chloro-organic compounds versus DIN-Standard
[147, UBA, 2003]

Regenerated catalysts

Table 3.38 shows carbon and sulphur levels, the surface area, and the average length of the spent catalyst feed and the regenerated product from the belt-only and fine regenerations. The spent catalyst was analysed for its surface area after laboratory regeneration.

Product quality	Spent catalyst from top bed of second reactor	Belt only regeneration	Fine regeneration
Carbon, w/w-%	22	0.7	0.9
Sulphur, w/w-%	7.5	0.9	0.8
Surface area, m ² /g	185	190	197
Average length, mm	2.56	2.72	2.68
The values above correspond to the regeneration of more than 580 tonnes of spent CoMo hydrotreating catalyst from a customer's distillate hydrotreater in 1997. The unit had two reactors with two catalyst beds per reactor. The pre-job analyses showed that the catalyst could be recovered from all four beds, but, as expected, the highest quality catalyst was toward the back end of the unit			

Table 3.38: Commercial regeneration of CoMo catalyst
[125, Ruiz, 2002]

Overall, the spent catalyst was heavily loaded with hydrocarbon (15 w/w-%) and coke (total loss on ignition 30 %). The company started regenerating the highest quality catalyst from the bottom bed of the second reactor and worked back toward the catalyst at the front of the unit. The job began prior to the fine regeneration installation, so initially the catalyst was being stripped with inert gas in the belt-stripping unit.

The properties of both regenerated products compare favourably with that of the spent catalyst. The surface areas of the regenerated samples are slightly higher than those from the laboratory regeneration.

NON OFFICIAL FEAD VERSION

4. Techniques to consider in the determination of BAT

Techniques to consider for treatments applied mainly to recover the materials from waste

This section contains techniques considered to have a good environmental operating performance (e.g. use of a good energy system) or that can help lead to a good environmental performance (e.g. environmental management systems). They relate to treatments to recover mainly materials from waste.

4.1. Waste oil

This section covers the techniques to be considered in the determination of BAT for the re-refining of waste oil.

4.1.1. Generic techniques to increase the yield of re-refining

Description

The yield of a re-refining plant varies between 55 to 75 %, depending on the process and to a minor degree on the composition of waste oil. Some techniques to increase efficiency include:

- sending the residue from the vacuum distillation column to a selectopropane unit, where 80 % of the brightstock can be recovered, reducing the residue content at the same time
- sending the bottom residue from the vacuum distillation column to a thermal cracking unit to produce gasoil
- selecting the appropriate vacuum in the vacuum distillation units (e.g. a three-stage group with steam ejectors at 17 mm Hg). Vacuum can be generated by dry vacuum pumps or high efficient multistage steam injectors.
- using a scrubbing unit to reduce VOC emissions and to recuperate raw material
- using sieves to remove matter such as polymer fibre
- having in place an intermediate tank between the dehydrotreatment and the distillations, in order to separate the materials that can provoke fouling of the following plant section (i.e. the furnace and distillation column) and also utilising a sufficient residence time for the additive reaction with the used oil to occur. The precipitate from this reaction is extracted from the bottom of the tank and pumped to storage, where the dehydrated oil content can be separated to allow its re-use.

Achieved environmental benefits

Increases the efficiency of the waste oil re-refining treatments. Related with technique b in the description section above, the use of dry vacuum pumps does not generate contaminated water.

Cross-media effects

Increases the use of energy or other utilities. The use of steam injectors as the vacuum system generates contaminated water.

Operational data

The operation of dry pumps may be affected by (solid) impurities.

Driving force for implementation

In the EU there already exists a legally binding precept to promote the re-refining of waste oil into base oil.

Example plants

Emissions to the air are partially controlled on some sites and uncontrolled on others.

Reference literature

[5, Concauwe, 1996], [7, Monier and Labouze, 2001], [14, Ministry for the Environment, 2000], [36, Viscolube, 2002], [55, UK EA, 2001], [56, Babbie Group Ltd, 2002], [86, TWG, 2003], [150, TWG, 2004]

4.1.2. Selection of waste oils to be re-refined

Description

Waste oils suitable to be recycled are:

- (black) engine oils, which have homogeneous characteristics and are sought by re-refining plants
- black industrial oils are potentially suitable for regeneration but due to the content of additives and other substances are not typically preferred by re-refining plants
- light industrial oils, which are relatively clean. They can either be re-refined on-site or can be re-used for other purposes. Their market is very specific and independent from the classical supply routes of recycling.

Achieved environmental benefits

Improvement of the feedstock quality can enhance the environmental performance of an installation as well as the quality of the product. Segregated used lubricants can have a higher recovery value as fuel and as a new material for re-refining. If chlorinated compounds (e.g. solvents or PCBs) are prevented to enter in the re-refining process, then operational and environmental problems can be avoided.

Applicability

One report states that 60 to 65 % of waste oils are eligible for regeneration, although other experts suggest a figure of around 50 % of waste oils. The waste oils most suitable for regeneration are those that are not too heavily polluted, and that have a high viscosity index and an absence of esters and biolubricants. (Black) engine oils represent more than 70 % of the waste oil stream. Black industrial oils represent about 5 % of all waste oil, with light industrial oils representing about 25 %. Experts consider the following waste oils to be re-recyclable:

- engine oils without chlorine (EWL code: 130205)
- hydraulic oils without chlorine (EWL code: 130110)
- non-chlorinated mineral diathermic oils (EWL code: 130306)
- engine oils with chlorine (EWL code: 130204) – although only under certain conditions (i.e. limitation of chlorine or PCB content)
- hydraulic oils with PCB (EWL code: 130101) – although only under certain conditions (i.e. limitation of chlorine or PCB content)
- hydraulic oils with chlorine (EWL code: 130109) – although only under certain conditions (i.e. limitation of chlorine or PCB content).

Driving force for implementation

Economic reasons to produce a good product.

Reference literature

[7, Monier and Labouze, 2001], [55, UK EA, 2001], [86, TWG, 2003], [150, TWG, 2004], [153, TWG, 2005]

4.1.3. Distillation/clay process

Description

See Section 2.1.5.

Achieved environmental benefits

This process potentially has a high adverse environmental impact, due to the large quantity of the oily clay to be disposed of. High temperature activated clay allows a lower clay/oil ratio, thus increasing the overall yield and reducing the quantity of oily clay to be disposed of. Compared to the acid/clay process, there is less oily clay to be disposed of.

Cross-media effects

Poor product quality and low yield.

Operational data

The lubricating oil yield expected with this process is in the region of 50 % on a dry basis.

Example plants

No plants have been identified.

Reference literature

[56, Babbie Group Ltd, 2002]

4.1.4. Distillation and chemical treatment or solvent extraction

Description

This consists of a series of vacuum cyclone evaporators followed by a chemical treatment of the lubricating oil cuts obtained.

Achieved environmental benefits

The lubricating oil yield expected with this process is in the range of 65 – 70 % on a dry basis. Adequate process selection can lead to the removal of virtually all PAHs, for instance by utilising solvent extraction. Some processes of this type do not generate residues because they transform the residues into products (e.g. production of a fertiliser by re-utilisation of the reaction waters).

Applicability

Medium sized refining plants (~25 kt/yr).

Economics

Financially attractive. The investment cost of a 108 kt/yr installation is USD 29 million (1994). Assumptions: applies vacuum distillation plus clay or chemical treatment, storage: 15 days and working capital: 15 days.

Example plants

A plant designed using this process is in operation in Spain.

Reference literature

[5, Concawe, 1996], [86, TWG, 2003]

4.1.5. Solvent extraction process and distillation

Description

See Section 2.1.5. The Interline propane extraction process, improved by Sener, comprises three stages and no finishing step is required:

- a. chemical pretreatment, with reagents and catalysts
- b. liquid propane extraction of the lubricant bases, separating water and asphalt

c. atmospheric and vacuum distillation, to separate the light fractions and the base oils for lubricants.

Achieved environmental benefits

The process does not produce solid waste. The chemical treatment of the resulting oil fraction with a mixture of chemicals converts the organically bound chlorine into NaCl. After further distillation, all end-products have a reduced chlorine content (less than 10 ppm). The chemical reactor removes contaminants and virtually all chlorine down to less than 5 ppm.

Operational data

The lubricating oil yield declared for this process is 79 % on a dry basis. Another source shows that the yields that are foreseen by the technology providers are 72 – 74 % of base oils and 21 – 22 % asphalts on a dry basis.

Applicability

There is a possibility of re-refining in areas with low productions of waste oil, because the plant is well adapted to relatively small capacities (25 – 30 kt/yr).

Economics

Reduced capital and operating costs. Technology providers claim that this technique reduces investment and operational costs, when compared with other re-refining technologies. The economy of the process is well balanced for relatively low capacity plants (25 – 30 kt/yr).

Example plants

A plant in Spain, working since 2000, shows that air emissions can be reduced by directing the vent streams and gas phase of the the distillation units to a thermal oxidiser where pollutants are oxidated at 850 °C for a residence time of two seconds.

Reference literature

[5, Concawe, 1996], [11, Jacobs and Dijkmans, 2001], [86, TWG, 2003], [150, TWG, 2004]

4.1.6. Thin film evaporator and different finishing processes

Description

The vacuum distillation (thin film evaporator - TFE) is a common component in many re-refining plants. A technique to consider is to apply mechanical seals on rotating shafts in wiped thin film evaporators.

Achieved environmental benefits

TFE technology together with	Yields (%) (related to the input for each activity)
Clay treatment	Total yield: 54 – 73 % Dewatering: 88 – 92 %; TFE distillation 80 – 81 %; Vacuum distillation 76 %, clay treatment 95 %
Hydrotreatment	High product quality The lubricating oil yield declared by the licensors is in the region of 72 % on a dry basis Two existing plants reported yields of up to 94 – 98 %

	Other sources give the following yields: 88 % dehydradistillation; 84 % TFE distillation; 86 % hydrofinishing giving a total yield of 64 %
Solvent extraction	Total yield ranges from 50 – 67 % 88 – 92 % dehydration distillation; 80 – 91 % vacuum distillation; 83 – 91 % finishing extration
Solvent extraction and hydrofinishing	Total yield 91 % dehydration distillation 81 % vacuum distillation; 97 % finishing extraction

Table 4.1: Achieved environmental benefits of TFE technology
[13, Marshall, et al., 1999], [139, UBA, 2003], [150, TWG, 2004]

Cross-media effects

TFE installations without further treatment produce a dark coloured oil, which is suitable for a diesel extender but not as a base oil suitable for blending into lubricants. Experience reported so far suggests odour problems may occur.

Applicability

The size of these installations ranges from 25 – 160 kt/yr.

Economics

The investment necessary for a vacuum distillation and hydrotreatment installation of 108 kt/yr capacity is USD 43 million (1994). Some other more recent data showed that the cost of TFE clay installation with a capacity of 100 kt/yr is EUR 221/t oil; the cost of a TFE hydro installation with a capacity of 50 kt/yr is EUR 333/t oil; and the cost of an TFE solvent installation with a capacity of 50 kt/yr is EUR 308/t oil.

Example plants

A plant in Newcastle (Australia) and two in Germany (85 and 160 kt/yr respectively) use this technology. At least six different commercial processes are available.

Reference literature

[5, Concauwe, 1996], [13, Marshall, et al., 1999], [150, TWG, 2004]

4.1.7. Thermal de-asphalting process

Description

For more information on thermal de-asphalting (TDA) see Section 2.1.5.

Achieved environmental benefits

The lubricating oil yield claimed by the licensor on a dehydrated waste oil basis is 74 % with clay finishing (97 % dewatering defuelling, 80 % de-asphalting, 95 % finishing) and 77 % with hydrotreatment (97 % dewatering defuelling, 80 % de-asphalting, 96 % finishing) on a dry basis.

Applicability

This process is applied in large installations of 100 – 180 kt/yr and in installations of 40 - 100 kt/yr for hydrotreatment.

Economics

The cost of a TDA clay installation with a capacity of 100 kt/yr is EUR 280/t oil and for a TDA hydro installation of EUR 304/t oil.

Example plants

One plant in Italy and two more outside the EU.

Reference literature

[13, Marshall, et al., 1999], [36, Viscolube, 2002], [86, TWG, 2003], [150, TWG, 2004]

4.1.8. Recycling in a lubricating oil refinery

Description

See Section 2.1.5.

Achieved environmental benefits

The lubricating oil yield expected with this process is in the range of 65 – 70 % on a dry basis. This technology improves the quality of the re-refined oil, when compared with existing re-refining plants using pre-flash, de-asphalting and clay finishing. Moreover, the oil quality is claimed to be even higher in some respects compared to the conventional mineral oil produced on the same production run.

Economics

With regard to the location of the plant, the pre-existence of some infrastructure and other equipment will of course reduce the capital cost. It is difficult to quantify any saving because of the maintenance and upgrading costs which would be necessary in any case.

Capital cost (1995): USD 45 million. Assumptions: treatment of 108 kt/year, storage of 15 days and working capital of 15 days.

Example plants

This route has recently been commercialised in Germany.

Reference literature

[5, Concawe, 1996], [13, Marshall, et al., 1999]

4.1.9. Hydrotreatment

Description

See Section 2.1.4. A technique to consider is to scrub (see Section **Error! Reference source not found.**) or incinerate (see Section 4.6.6) the acid off-gases from hydrotreatments.

Achieved environmental benefits

Hydrotreatment is a very efficient finishing process because, it:

- reduces or removes the remaining metals and metalloids of the waste oil
- reduces the Conradson carbon (measurement of the tendency of a hydrocarbon to form coke)
- reduces the organic acids and compounds containing chloride, sulphur and nitrogen
- restores the colour, UV and thermal properties
- reduces PAHs when operating under high pressure and at high temperatures
- allows a viscosity index equal to or better than the original feed.

Cross-media effects

Hydrogen needs to be generated or purchased. It seems that hydrotreatment does not alter the synthetic oil content already present in the waste oil.

Operational data

Hydrotreatment typically increases the safety risks (due to the need for the handling of hydrogen being under pressure and at an elevated temperature). Pressure: 100 barg partial pressure; Temperature: 340 °C; Catalyst: NiMo.

Economics

The capital cost of the hydrotreatment plant is very high. Table 4.2 gives some examples

Plant	Cost
Modern re-refining with hydrotreatment without collection	EUR 4 – 47/tonne ¹
Average collection cost within Europe	EUR 110/tonne
Modern re-refining with hydrotreatment when collection cost is included	EUR -106 to -63/tonne
Severe hydrofinishing standalone plant	EUR 10 million
Severe hydrofinishing standalone plant if Claus unit fitted, H ₂ production, sour water stripper and amine units are also necessary	EUR 20 million
Hydrotreatment for a 108 kt/yr installation	USD 65 million (1994) ²
¹ value at plant gate (1994) assuming an IRR of 15 % after tax and working capital of 15 days. A new report from Europa (2003) reports values of EUR 300 – 333/tonne	
² solvent extraction and hydrotreatment, storage: 15 days and working capital: 15 days	

Table 4.2: Economics of hydrotreatment plants

[5, Concawe, 1996], [36, Viscolube, 2002], [86, TWG, 2003], [150, TWG, 2004]

Driving force for implementation

To increase the quality of the products.

Example plants

Hydrotreatment is the only re-refining process endorsed by the American Petroleum Institute (API). Two hydrofinishing plants exist in Italy (one severe hydrofinishing and another mild hydrofinishing).

Reference literature

[5, Concawe, 1996], [7, Monier and Labouze, 2001], [13, Marshall, et al., 1999], [36, Viscolube, 2002], [66, TWG, 2003], [86, TWG, 2003], [150, TWG, 2004]

4.1.10. Direct contact hydrogenation process

Description

See the description of direct contact hydrogenation (DCH) in Section 2.1.5.

Achieved environmental benefits

Some benefits of the technique include the following:

- the process is very efficient at separating contaminants from waste oil
- halogenated and oxygenated compounds are destroyed
- generate cleaner products (e.g. lower sulphur (<0.03 w/w-%) fuels)
- the entire waste oil is treated in a reducing environment that exhibits the formation of polymeric and carbonaceous by-products
- the treatment is further catalytically treated to convert the toxic sulphide compounds present to non-toxic sulphates
- hydrogen rich gas is recycled

-
- the acid gases generated in the conversion reactor are neutralised with caustic solution.

Cross-media effects

Hydrogen needs to be generated or purchased. Solid materials requiring disposal will include the spent catalyst, sodium chloride and sodium sulphate. It produces a low COD, sulphide free and organochloride-free aqueous effluent and a stable heavy residue which is claimed to be suitable for asphalt blending.

Economics

Economically attractive high quality products and a higher yield per tonne of input.

Driving force for implementation

Increase the base oil quality produced by:

- better quality and characteristics than those of virgin oils
- group II base oil with low sulphur and phosphorus, low aromatic content
- increase viscosity index and oxidation stability.

Example plants

The direct contact hydrogenation process has been used industrially since the first plant was completed in Germany in November 2003.

Reference literature

[5, Concawe, 1996], [139, UBA, 2003], [150, TWG, 2004]

4.1.11. Solvent extraction

Description

See Section 2.1.4.

Achieved environmental benefits

Does not result in polluted clay as a waste product.

Cross-media effects

Only 98 % of the solvent is regenerated after extraction of the base oil.

Applicability

Fully applicable in the sector.

Economics

Cheaper than the hydrofinishing option.

Example plants

At least one plant is operational in Germany

Reference literature

[86, TWG, 2003]

4.1.12. Caustic soda and bleaching earth treatment

Description

See Section 2.1.5.

Achieved environmental benefits

A high lubricating oil yield is obtained as a result. The base oil produced is of high quality (group II) with greater yields of base oils than other available technologies. Neutralisation is carried out with acid and clay treatment. Only 25 % of clay and acid is used compared to the usual clay / acid amount.

Operational data

Use of caustic soda.

Applicability

Applied to waste oils.

Economics

It is reported to be economically attractive because there are high quality products and a higher yield per tonne of input.

Driving force for implementation

This technique increases the base oil quality:

- same quality and characteristics as virgin oils
- group I base oil with low sulphur and phosphorus, low aromatic content
- high viscosity index and oxidation stability.

Example plants

An installation has been operating in Germany since 2000.

Reference literature

[5, Concawe, 1996], [150, TWG, 2004]

4.1.13. Treatment in a refinery

Description

There are two possible mixing options in a refinery:

Mixing with the feedstock (typically crude oil)

The pretreated oil is mixed with the crude oil and the blend passes the desalter before it is fed to the crude oil distillation unit of an existing refinery. In this option, the waste oil passes through all the refinery processes, and the main part of the waste oil ends up in the bottom product of the vacuum column. This vacuum residue contains most of the metals and sulphur components from the waste oil. Its final use depends on the refinery.

Blending into the vacuum residue

Pretreated waste oil is used as a supplementary component to be mixed with the bottom product of the vacuum column. In this option, the waste oil hardly enters some of the refinery units of the plant. The blend contains all the metals, chlorides and sulphur components originating from the waste oil.

Tests have shown that most of the metals from the used oil go to the asphalt bottoms. The vacuum gasoil quality is not altered apart from only slightly elevated chlorine contents and might be considered suitable for use in the catalytic cracking operation. However, tests have also indicated that additional pretreatment of the pre-flashed used oil will be necessary to reduce polyorganic chlorides which are not removed by the pre-flash operation. Otherwise, these chlorides would distil with the light ends of the vacuum column, causing corrosion of the overheads of that column and to any downstream hydrotreatment.

Achieved environmental benefits

Along with its use to provide a secondary feedstock to the fuels unit, it reduces the crude oil requirements to the complex. It typically reduces the utility consumption of the lubricant plant because the regeneration of waste oils requires less utilities than virgin basestock production, mainly due to the minor content of wax (therefore less dewaxing is required). The reduction of emissions of sulphur oxides are minor.

Cross-media effects

The (potential) presence of organic chlorides can produce a weak acid during hydrotreating, resulting in severe corrosion problems and potential incidents. The normal refining process sequence does not remove all the metals from waste oil, with the result that the metals left can poison the catalytic cracker catalyst.

Moreover, refineries may blend the waste oil, without further processing, with heavy oil and use it as a secondary feedstock for the fuel unit. Burning this fuel may yield higher SO_x and metal emissions. In some countries, these heavy fuel burners are not equipped with an off-gas treatment system, because the permits of these industries adapt a bubble principle (see the Refinery BREF).

Operational data

This technique can be integrated in the refinery works. Mixing waste oil with a crude oil alternative is not applied because of the severe technical problems the waste oil may cause in the plant, e.g. catalyst fouling and severe corrosion.

Recycling of waste oil within a mineral oil refinery is generally not applied because of the severe technical problems the waste oil may cause in the plant. Some examples are the presence of metals in the waste oil, which can poison the catalytic cracker catalyst bed, and the presence of organic chlorides in the waste oil, which can cause corrosion problems as they are converted to weak hydrochloric acid in the hydrotreating stages.

Applicability

This technique creates a distortion in the product slate of the mineral oil refinery. For example, to meet the needs of their heavy lubricant customers, the mineral oil refinery will have to produce that fraction also required (by increasing the crude consumption to the fuels unit).

The technical feasibility of the technique is not guaranteed because it may cause severe technical and operational problems.

Economics

The approximate value of used oil without collection EUR 27/t (the value at the plant gate (1994) assuming an IRR of 15 % after tax and a working capital of 15 days) and of -83 including the collection cost (at an average collection cost of USD 110/t within Europe). With regard to the location of the plant, the pre-existence of some infrastructure and other equipment can reduce the capital cost. It is difficult to quantify the saving for this because of the maintenance and upgrading costs which may be necessary to utilise this resource.

The investment cost is USD 11 million (1994) with the following assumptions: 120 kt/year, storage: 15 days and working capital: 15 days.

Economic advantages are linked to the process synergies as well as to the reduction in the crude oil and energy consumption. According to [7, Monier and Labouze, 2001], integration of a thermal cracking unit would be economically more preferable for refineries than integration of a re-refining unit.

Driving force for implementation

The potentially severe operating problems make this method of treatment unattractive for refinery operators.

Example plants

The process does not yet have any industrial application. The method has been the subject of a pilot study in France and a study in Canada.

Reference literature

[5, Concawe, 1996], [6, Silver Springs Oil Recovery Inc., 2000], [7, Monier and Labouze, 2001], [11, Jacobs and Dijkmans, 2001], [86, TWG, 2003], [150, TWG, 2004]

4.1.14. Water management in waste oils re-refining installations

Description

Some techniques include:

- ensuring that any effluent water (e.g. water distilled from the used oil, process water including the caustic scrubber blowdown) are treated before discharge
- using a waste water treatment unit (e.g demulsifier and flocculant, flocculation and biological treatment, ultrafiltration and microfiltration). More information can be found in Section **Error! Reference source not found.**
- re-using the cleaned waste water as cooling water by applying a suitable WWTP and by generating water products that may be re-used outside the installation
- feeding the effluent water to the heater along with the oils in order to incinerate the harmful constituents.

Achieved environmental benefits

Three examples on the achieved values treatments are shown in Figure 4.1, Figure 4.2, Figure 4.3 and Table 4.3 and Table 4.4.

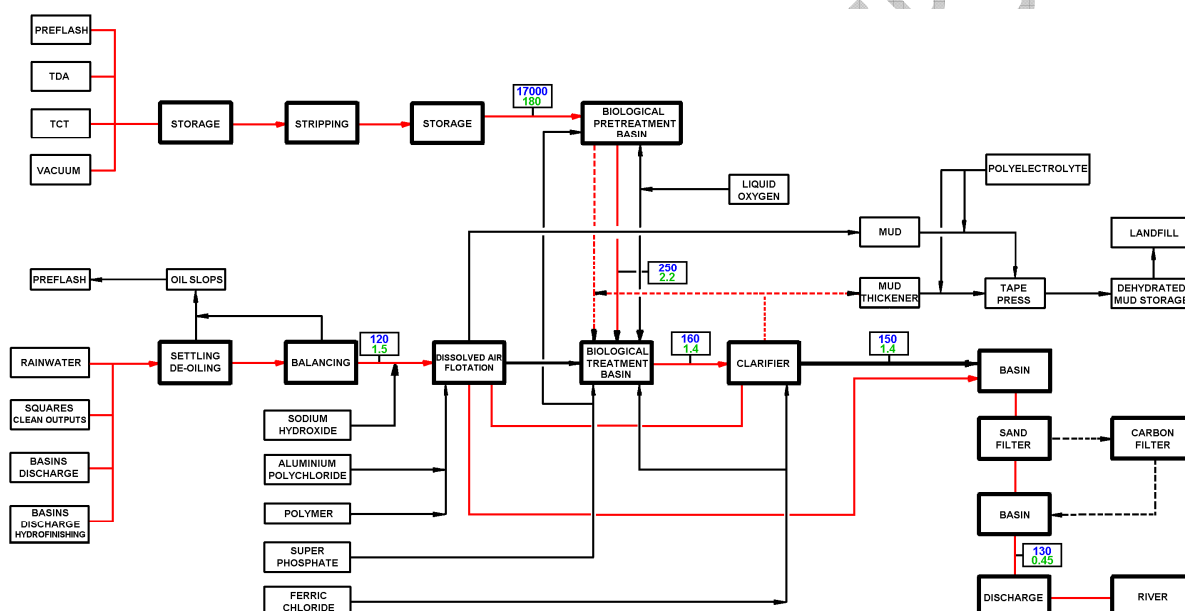


Figure 4.1: Achievable levels in a waste water treatment used in a re-refining process [36, Viscolube, 2002]

Note: Figures in boxes are all given in ppm. The upper figures correspond to COD and the lower figures correspond to phenol content

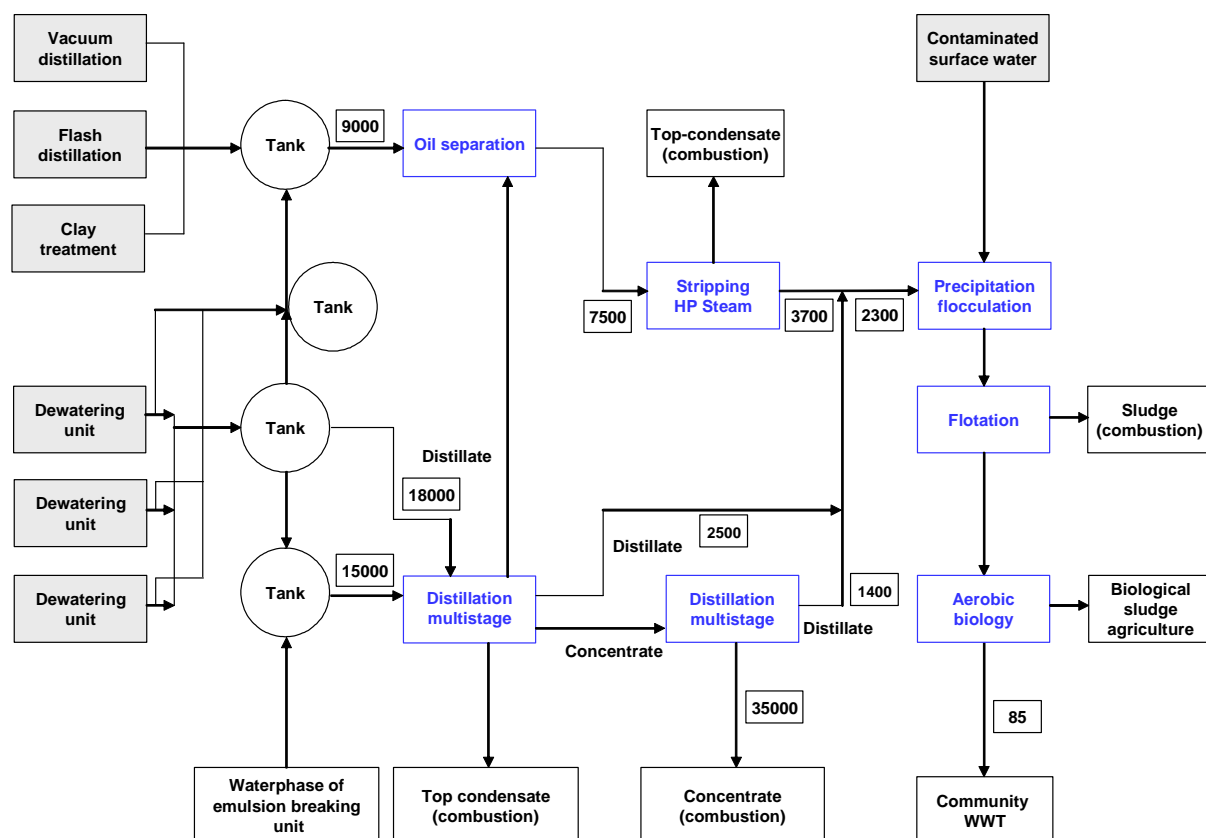


Figure 4.2: Waste water treatment used in a re-refining process (TFE/clay treatment) [139, UBA, 2003]

Note: Values in the figure correspond to TOC contents in ppm

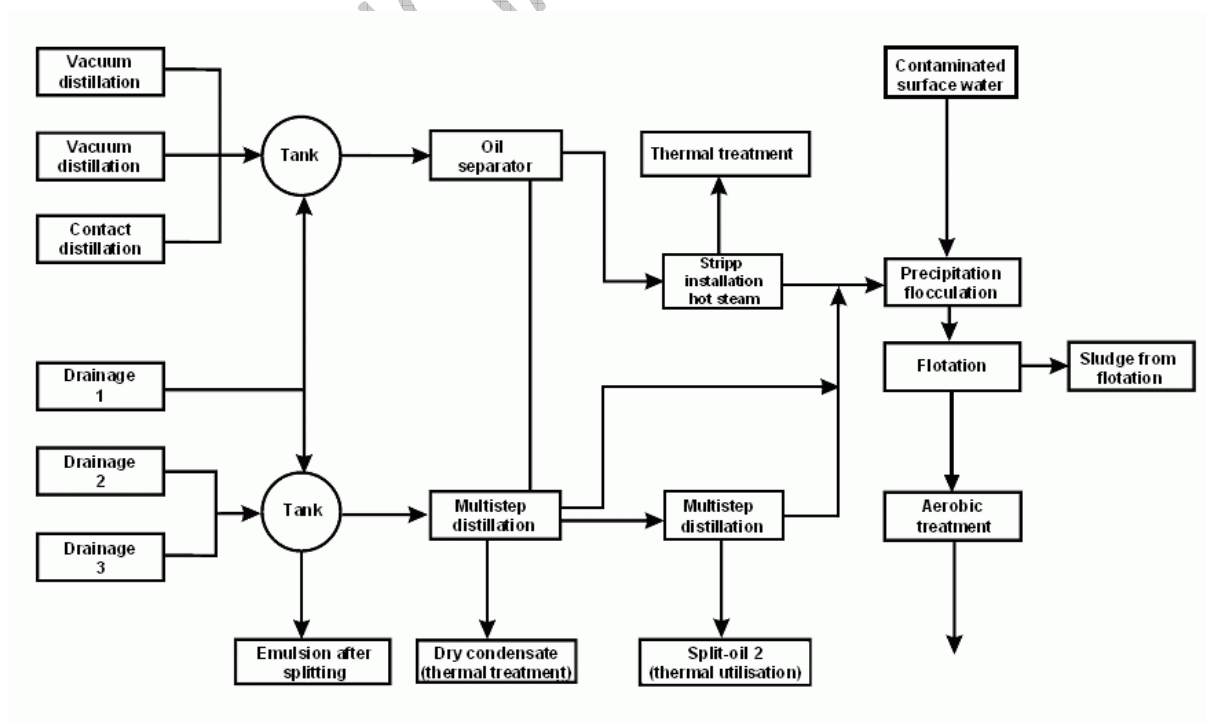


Figure 4.3: Waste water treatment used in a waste oil treatment plant

[150, TWG, 2004]

The parameters in the Table 4.2 below can be achieved with a waste water treatment plant the same as above.

164.Parameter	165.branch precipitation/flocculation (mg/l)	166.branch biology 167. 168.(mg/l)	169.downpipe in- house biology 170.(mg/l)
171.COD	172.	173.	174.200 – 500
175.TOC	176.1800 – 3500	177.1300 – 2200	178.60 – 150
179.Nitrite- N	180.	181.1 – 20	182.<0.1 – 1.0
183.Total nitrogen	184.	185.80 – 280	186.10 – 60
187.Total phosphorous	188.	189.1 – 15	190.2.0 – 5.0
191.AOX	192.	193.0.1 – 0.4	194.<0.10 – 0.25
195.Hydrocarbons	196.50 – 300	197.<1.0 – 10	198.<0.1 – 2.0
199.Benzene and derivatives	200.	201.0.01 - 0.03	202.<0.01
203.Phenol index	204.	205.1 – 50	206.<0.2
207.Pb	208.<0.05 – 0.06	209.<0.05	210.<0.05
211.Cd	212.<0.02	213.<0.02	214.<0.02
215.Cr	216.<0.02 – 1.0	217.<0.02	218.<0.02
219.Fe	220.1 – 10	221.1 – 20	222.1 – 10
223.Cu	224.<0.02 – 0.2	225.<0.02 – 0.1	226.<0.02 – 0.1
227.Ni	228.<0.02 – 0.5	229.<0.02 – 0.3	230.<0.02 – 0.1
231.Zn	232.<0.1 – 1.0	233.<0.1 – 0.1	234.<0.1

Table 4.3: Composition of different inputs and outputs from different streams of the WWTP in a waste oil refinery
[150, TWG, 2004]

Waste water parameter	Value (ppm)
Hydrocarbons	<0.01 – 5
COD	20 – 400*
Phenols	0.15 – 0.45
* Values of 400 can be achieved without dilution of the treated waste water with other water streams	

Table 4.4: Achievable levels in the effluent after biological WWTP in waste oil treatment units
[42, UK, 1995], [150, TWG, 2004], [152, TWG, 2004], [153, TWG, 2005]

Cross-media effects

WWTPs typically generate ammonia and VOC emissions to the air.

Operational data

Biological treatment is an option to consider, however it has not been found to be reliable. Daily monitoring of the sewer discharge includes the monitoring of ammonia levels, but not total nitrogen. There is no monitoring of phosphorus levels.

Example plants

The biological section of a UK oil recovery plant consisted of four aeration units which were used tanks to treat the aqueous layer from oil treatment as well as landfill leachates. There are some re-refining processes that do not generate waste water for external treatment. These systems make a total utilisation of the water contained in used oil (e.g. utilisation of treated water as refrigeration fluid or in the production of a fertilising compound).

Reference literature

[36, Viscolube, 2002], [42, UK, 1995], [56, Babbie Group Ltd, 2002], [86, TWG, 2003], [139, UBA, 2003], [150, TWG, 2004], [152, TWG, 2004]

4.1.15. Waste management in waste oils treatment installations

Description

Some techniques include:

- a. burning the non-lubricant recovered oils in a heater equipped with a gas scrubber to raise energy for the plant
- b. treating and disposing of all used filters
- c. applying a thermal treatment for all residues
- d. using the residues from the vacuum distillations and evaporators as asphalt products.

Achieved environmental benefits

Reduces the amount of residues generated by the treatment.

Driving force for implementation

To reduce waste generation.

Example plants

Typically used in waste oil regeneration facilities.

Reference literature

[56, Babbie Group Ltd, 2002], [150, TWG, 2004]

4.2. Waste solvents

4.2.1. Selection of waste solvents to be recycled

Description

Waste solvents composed by monostreams are typically regenerated. A waste solvent can be considered regenerative if, e.g.:

- it is a monostream (one batch from one waste generator)
- it yields a minimum of 60 % distillate
- it has a certain minimum amount per load
- the costs of distillation are the same as or lower than for incineration.

Achieved environmental benefits

Avoid environmental problems in the installation. By means of distillation, waste solvents are separated into a reusable solvent and a non-reusable distillation bottom.

Applicability

Non-chlorinated solvents, CFCs and halons.

Reference literature

[150, TWG, 2004], [156, VROM, 2004], [157, UBA, 2004]

4.2.2. Improvement of regeneration treatment of waste solvents

Description

Some techniques include:

- a. applying azeotropic distillation
- b. applying vacuum distillation
- c. using thin-film evaporators
- d. heating the feed stream with the distillate by means of a heat-exchanger and insulation measures
- e. applying a cascade re-use of solvent (i.e. where the solvent is used once for high quality cleaning and then used again for other cleaning or for operations that do not require a pure solvent)
- f. using vapour balancing systems and directing the waste gas to abatement techniques (e.g. activated carbon filtration, enclosed systems and using vapour balance lines during loading). The removal efficiency of an activated carbon filter is at least 90 %.
- g. using distillation for the separation of organic solvents from solids
- h. using rectification for the removal of contaminating substances and achieving a certain quality of the wastes OUT
- i. dewatering by means of a decanter if the solvents contain water.

Achieved environmental benefits

Improves the separation of waste solvents and the efficient use of solvents. The energy consumption of distillation can be reduced (e.g. techniques b-d in the description section above).

Emission values of 50 mg C/Nm³ in the waste gas after the treatment mentioned in technique f in the description section above are achievable.

Cross-media effects

The application of cascade re-use of solvents could develop using solvents in open devices and for instance, to clean machines or coating devices. In such cases a defined composition of the solvent mixture needs to be known and the solvents should not contain volatile organic compounds which are assigned as risk materials for human health.

Distillation of waste solvents produce emissions of hydrocarbons to the air and waste water that need to be treated.

Operational data

The use of vapour balancing systems during solvent charge is typically used to reduce fugitive VOC-emissions (e.g. Germany). The waste gas is usually treated by adsorption on activated carbon.

Applicability

The distillation technique is applicable to all regenerative solvents and refrigerants. The capacities of the example installations range from approximately 2 – 60 kt/yr.

Azeotropic distillation is commonly used to enhance solvent recovery. An azeotrope or azeotropic mixture is a mixture of liquids that behave as a single substance when boiled (i.e. both the vapour and the liquid have the same composition). Azeotropic distillation consists of adding a substance (typically steam) to form an azeotropic mixture with the solvent to be recycled. The azeotropic mixture will have a lower boiling point than the original mixture and recovery of the solvent will thus be facilitated.

Vacuum distillation is designed to handle solvents with higher boiling points (above 200 °C).

Driving force for implementation

Some organic solvents are especially dangerous compounds for human health. Some restrictions (e.g. closed installations) are mentioned in Directive 1999/13/EC.

Preference order for waste management in accordance with the Waste Framework Directive and the Sixth Environmental Action Programme of the European Community.

Example plants

Re-refining of N-methyl-2-pyrrolidone (NMP) used in electronic manufacturing.

Reference literature

[53, LaGrega, et al., 1994], [130, UBA, 2003], [150, TWG, 2004]

4.2.3. Waste water treatment in waste solvent facility

Description

See Section **Error! Reference source not found..** Some techniques that have been used in waste solvent facilities are waste water stripping plants, bio-reactors, waste water storage tanks, waste water intermediate storage tanks and ultrafiltration facilities.

Achieved environmental benefits

The characteristics of the effluent after treatment is shown in the Table 4.5:

Compounds	Average value	Units
Colour	-	
Odour	-	
pH	8.7	
Electric conductivity	989	µS/cm
P total	0.46	mg/l
N total	32.9	mg/l
COD	18	mg/l
BOD ₇	<3	mg/l
Sb	<0.01	mg/l
Pb	<0.010	mg/l
Cd	<0.002	mg/l
Cr total	<0.002	mg/l
Co	0.006	mg/l
Ni	<0.002	mg/l
Zn	0.02	mg/l
Lightly volatile halogenated hydrocarbons	4	µg/l
AOX	320	µg/l
Note: Data from 2002		

Table 4.5: Characteristics of the effluent of a WWTP in a waste solvent regeneration facility [130, UBA, 2003]

Cross-media effects

See Section **Error! Reference source not found..**

Operational data

See Section **Error! Reference source not found..**

Applicability

See Section **Error! Reference source not found..**

Economics

See Section **Error! Reference source not found..**

Driving force for implementation

See Section **Error! Reference source not found..**

Example plants

Waste solvent treatment plants typically have waste water treatment facilities.

Reference literature

[130, UBA, 2003]

4.2.4. Evaporation of distillation residues

Description

Vacuum dryer and other drying techniques are in use for distillation bottoms.

Achieved environmental benefits

Increase the percentage of solvent recovered. Valorisation of 99 % of the container solvents. This can reduce the total solvent concentration by approximately a factor of ten. Also resins and pigments may be valorised. At the same time they may reduce odour and VOC emissions that may be generated by the bottoms.

Cross-media effects

The solid residue that is generated should be treated. VOC are emitted to the air and they are treated before being emitted.

Operational data

Energy (heat and power) is necessary to run such systems. There are systems for the treatment of up to 4000 tonnes of distillation residues per year. From that, it is possible to obtain between 1500 to 2000 tonnes of solvents per year. The specific kneading energy is up to 0.1 kWh/kg. The separation of heating and cooling zones facilitate efficient product temperature control.

Applicability

It does not need so much surface and it is easily applicable to existing installations. It is applicable to distillation residues of painting solvents, polymers, elastomers, pharmaceutical products and food products. VOCs arise from a wide range of waste types. Obvious examples are waste oil and solvents. For example, a distillation bottom sludge may have a significant concentration of solvent, which, if the material was in liquid form, may render it suitable for recovery.

Economics

Investment cost of EUR 1.2 million. Operating costs vary between EUR 100 to 150 per tonne of residue treated.

Driving force for implementation

To improve the recovery of solvents and waste minimisation

Example plants

At least six installations use this system around the world. At least four are in the EU. Drying techniques are in use in the UK for the distillation of bottom sludges.

Reference literature

[50, Scori, 2002], [55, UK EA, 2001], [66, TWG, 2003], [150, TWG, 2004]

4.2.5. Full automatisisation of residue incineration

Description

In a solvent distillation plant the discharge of the distillation sludge is optimised. For working and environmental protection reasons the process of discharge is now fully automatised. Because of the high heating value the transfer of the sludge to the in-house incineration plant is fully automatised.

Achieved environmental benefits

Treatment of the residues from waste solvent treatment.

Applicability

This technique of quasi-dry discharge does not necessarily have to be the adequate solution when process is optimised as a whole.

Example plants

A solvent distillation plant located in Münster (Germany).

Reference literature

[150, TWG, 2004]

4.3. Waste catalysts

4.3.1. Generic techniques used in the treatment of waste catalyst

Description

Some techniques include:

- applying heat recovery in the form of energy production or recuperation. For this aim, recuperative burners, heat-exchangers and boilers can be used to recover heat. Steam or electricity can be generated for use on or off site, e.g. to preheat process or fuel gases
- using oxygen or oxygen enriched air or oxygen in the burners
- preheating the combustion air used in burners
- preheating the material charged to the furnace
- automatically controlling the point of extraction using dampers and fan controls so that the systems are deployed when and where they are needed, for example, during charging or during 'roll out' of a converter.

Achieved environmental benefits

Heat and energy recovery, which is an important factor in this industry due to the high proportion of costs that energy represents.

The use of oxygen enriched air or oxygen in the burners reduces the overall energy consumption by allowing the complete combustion of carbonaceous material. At the same time, waste gas volumes are significantly reduced allowing smaller fans, etc. to be used.

The advantage of preheating the combustion air used in burners is well documented. If an air preheat of 400 °C is used, there is an increase in flame temperature of 200 °C, while if the preheat is 500 °C the flame temperature increases by 300 °C. This increase in flame temperature results in a higher efficiency and a reduction in overall energy consumption. The alternative to preheating combustion air is to preheat the material charged to the furnace. Theory shows that 8 % energy savings can be obtained for every 100 °C

preheat and in practice it is claimed that preheating to 400 °C leads to a 25 % energy saving, while a preheat of 500 °C leads to a 30 % energy saving.

Applicability

The technique used to recover heat varies from site to site, depending on a number of factors such as the potential uses for heat and energy on or near the site, the scale of operation and the potential for gases or their constituents to foul or coat heat-exchangers

Many techniques aimed at energy recovery are relatively easy to retrofit but occasionally there may be some problems with deposition of metal compounds in heat-exchangers. A good design is based on a sound knowledge of the compounds released and their behaviour at various temperatures. Heat-exchanger cleaning mechanisms are also used to maintain their thermal efficiency.

Reference literature

[125, Ruiz, 2002]

4.3.2. To improve control of the process

Description

Some techniques include:

- a. adjusting the temperature levels and residence time of the catalyst in the unit, in order to achieve desired levels of carbon and sulphur
- b. applying cooling prior to a bag filter installation
- c. using sealed furnaces, which can allow a very high capture efficiency of the fumes
- d. using ducts and fans to convey the collected gases to abatement or treatment processes. Variable speed fans are used to provide extraction rates that are suitable for changing conditions such as the gas volume, with a minimum energy consumption
- e. having a good temperature control during the regeneration process
- f. designing the residence time in the pretreater to be very short (in the order of a few minutes), to minimise attrition normally associated with fluidised bed processes
- g. applying sizing (i.e. length graded) technology after regeneration. The length grading technology removes short catalyst particles (typically those with lengths 1 – 2 times the diameter) that cannot be removed with conventional screening. In an example, length grading was set up to accept only a relatively small cut, to increase the average length by 0.1 – 0.2 mm without discarding too much material.

Achieved environmental benefits

Improves the control of the process and the efficiencies of abatement techniques. The effectiveness of collection depends on the efficiency of the hoods, the integrity of the ducts and on the use of a good pressure/flow control system.

Operational data

Applying cooling prior to a bag filter installation is an important technique as it provides temperature protection for the filter and allows a wider choice of fabric. It is sometimes possible to recover heat at this stage. The temperature of the gases after this heat-exchanger can be between 200 and 450 °C. The second heat-exchanger reduces the gas temperature to 130 °C before the bag filter. The heat-exchangers are normally followed by a cyclone, which removes larger particles and acts as a spark arrester.

Driving force for implementation

Product requirements.

Reference literature

[125, Ruiz, 2002]

4.3.3. Abatement techniques used in the waste catalyst regeneration sector

Abatement technique	Location where it is applied	Section in this document where the abatement technique is analysed
Fabric filter	Exit of the furnaces	4.6.1
Wet scrubbers	Exit of the furnaces	4.6.4

Table 4.6: Abatement techniques applied to waste catalyst regeneration plants
[125, Ruiz, 2002]

4.4. Activated carbon

4.4.1. Choice of furnace used to regenerate the waste activated carbon

Description

The options are 'multiple hearth furnaces', 'direct fired rotary kilns' and 'indirect heated kilns' (where there is no contact between the kiln content with flue-gases generated from a burner).

Achieved environmental benefits

The multiple hearth furnace has significant advantages over other types of furnace from the standpoint of regeneration efficiency because the temperature of each hearth may be independently controlled. The direction of the exit gases may be either co-current or countercurrent to the flow of carbon. In some designs, the afterburner may be incorporated within the furnace at the 'zero' hearth level. The multiple hearth furnace shows better mass transfer and temperature control characteristics than the rotary kiln and has a carbon residence time of typically one to two hours. Carbon losses may be up to 10 % by weight.

Direct fired rotary kilns may be operated with the carbon flowing either co-currently or countercurrently to the flow of combustion air. In the countercurrent mode of operation, the exit gases leaving the kiln are at a higher temperature than in the co-current mode, which allows the potential for designing the afterburner to less stringent criteria while still destroying gaseous contaminants.

Indirectly heated kilns offer the advantages of eliminating the need for the mixing of burner flue-gases with process gases. The lower volume of gas requiring heating saves on energy and the size of abatement equipment. Burner flue-gases that have indirectly heated the kiln are then directed to the base of the stack where they may be combined with the kiln off-gases to reduce the visibility of the emitted plume. This method may offer the advantage of affording higher partial pressures of steam in the kiln, which is likely to reduce formation of oxides of nitrogen. Also the formation of halides is likely to be promoted rather than elemental halogens, with the halides being more easily removed in downstream scrubber systems.

Operational data

Owing to the absence of exposed metal surfaces, rotary kilns are normally able to operate at higher temperatures than multiple hearth furnaces. Carbon losses on rotary kilns may be in the range 5 – 15 % by weight. Careful attention needs to be paid to the seals between the rotating kiln and the end plates to prevent any leakage of gases and particulate matter. Fugitive emissions from this area are normally controlled by operating the kiln at a slightly negative pressure.

Indirect furnaces are normally constructed with a metal tube and are not likely to be suitable for industrial applications due to corrosion problems that may appear during treatment of some industrial carbons.

Applicability

The applications of the indirect fired kiln are generally for the treatment of industrial carbons where more onerous temperature criteria apply to the afterburner.

Example plants

The indirect fired kiln concept is becoming more widespread. Infrared furnaces are relatively new in application and are predominantly found in the United States. Their mode of firing is by infrared elements and indirect heating of the carbon. As a result, they avoid the production of a combustible gas, production which can result in lower volumes of air requiring treatment in the abatement chain. They are, however, limited to maximum capacities of around 1000 t/yr.

The only known indirect fired rotary kiln example in Europe was in the UK and this is believed to be no longer functional.

An activated carbon regeneration plant located on a drinking water site using a multiple hearth furnace: the plant consists of silos for containing spent and reactivated carbon, separate spent and reactivate transfer water system to transport carbon from silos and to and from the furnace. The unit also has a direct transfer system to the water works for treating the carbon from that particular site. Spent and reactivated carbon is transported from other sites using bulk road tankers.

Reference literature

[29, UK Environment Agency, 1996], [41, UK, 1991], [42, UK, 1995], [150, TWG, 2004]

4.4.2. Flue-gas treatment

Description

Some techniques include:

- using an afterburner for the gases exiting the furnace or kiln. The afterburner needs to be in operation at all times when carbon is present in the kiln
- designing the regenerator and associated ducting and equipment to operate under a reduced pressure, in order to prevent the escape of regenerator gases into the air
- applying heat recovery. Typically this involves gas/gas heat-exchangers to allow the preheat of combustion air and flue-gas reheating. There may also be a waste heat boiler used for the generation of steam, which is also used in the reactivation of the carbon
- cooling the flue-gases with a quench section or venturi scrubber
- using an aqueous or caustic scrubber. Spray absorption techniques may also be used. It will be necessary to provide a pH control on the scrubber liquor
- routing the flue-gases to the stack via an induced draft fan with partial reheating of the flue-gases
- using either wet or dry electrostatic precipitators, venturi scrubbers or fabric filters. Inertial separators, e.g. cyclones when used alone, are unlikely to meet low emission values.

Achieved environmental benefits

Reduces the emissions of the flue-gas generated. A spray dryer followed by fabric or ceramic filters has the additional advantage of allowing further neutralisation reactions to occur between the trapped solid residues and the exhaust gas stream. This can lead to a reduction in alkali requirements for a spray dryer of 10 – 15 % against a wet scrubber.

Table 4.7 shows the achievable levels for key substances in the context of the processes concerned.

Substance	Achievable levels (mg/Nm ³)
Total particulate matter	20

Hydrogen chloride	30
Sulphur dioxide (as SO ₂)	50
Oxides of nitrogen (as NO ₂)	350
Carbon monoxide (measured after last injection of air)	50
VOC (as C) (excluding particulate matter)	20
Dioxins and furans (International Toxicity Equivalent – ITEQ)	1 ng/m ³
Notes: The above concentrations are for non continuous monitoring.	

Table 4.7: Air emissions benchmark release to air
[29, UK Environment Agency, 1996]

Cross-media effects

Technique f in the Description section, requires reheating of the flue-gas.

Operational data

The regenerator includes an afterburner chamber, which is equipped and operated in such a way so that the flue-gas resulting from the regeneration of the carbon is raised, after the last injection of air, in a controlled and homogeneous fashion and taking account of the most unfavourable conditions, to a temperature of at least 850 °C as measured at the inner wall of the combustion chamber. This needs to be held for at least two seconds in the presence of at least 6 vol-% oxygen dry gas, as measured at the exit of the afterburner. For carbon which has been used in industrial applications where halogenated or other thermally resistant substances are likely to be present (e.g. containing more than a certain small percentage), the temperature is typically raised to at least 1100 °C. The residence time, minimum temperature and the oxygen content of the exhaust gases needs to be verified. However, in some circumstances not specified by the TWG, it may be possible to achieve an equivalent effect with less stringent conditions (some generic information on this issue can be found in the WI BREF).

Applicability

Flue-gases from either multiple hearth furnaces or rotary kilns generally follow a similar path of treatment. In the case of co-currently fired rotary kilns, it may be possible to achieve these same conditions without an afterburner.

The flue-gas treatment depends on the application to which the carbon has been put and the nature of the fuel used to fire the kiln and afterburner. The equipment described above may typically be used for carbons that have been used for potable water treatment and for food grade applications. For carbon used in industrial applications, more extensive abatement measures may be required.

Waste gas treatment facilities may vary depending on the application for which the carbon has been used. More stringent requirements may be needed for carbon that has been used for industrial applications. In these cases, further chemical scrubbing may be needed to attain the desired achievable release levels. It may also be necessary for the post-regeneration stage to be maintained at temperatures of at least 1100 °C for a two second residence time in the presence of at least 6 vol-% oxygen and dry gas, to ensure complete oxidation of certain refractory compounds.

Driving force for implementation

In certain local circumstances and because of visual issues (e.g. visible plume suppression), sometimes technique c and f in the description section above are required by certain authorities.

Reference literature

[29, UK Environment Agency, 1996], [41, UK, 1991], [42, UK, 1995], [150, TWG, 2004], [152, TWG, 2004], [153, TWG, 2005]

4.4.3. Waste water treatment plants

Description

These processes need a system for the treatment of the liquid effluent generated in the flue-gas treatment plant. Some techniques include:

- applying two-stage hydroxide precipitation at different pH values
- utilising sulphide precipitation to remove metals
- utilising flocculation, settlement, filtration or centrifuges to separate the suspended materials. A preliminary chemical or physical pretreatment stage may also be necessary to condition the suspended solids and improve the separation
- adjusting the pH to promote the precipitation of specific chemicals and to achieve an acceptable effluent
- using natural zeolites, ion exchange resins, activated carbon and reverse osmosis techniques to remove noxious impurities (e.g. pesticides). Concentration by evaporation is also a possibility
- applying a biological treatment to remove BOD, phenols, cyanides and ammonia.

Achieved environmental benefits

Table 4.8 indicates the achievable release levels for key substances in the context of the processes concerned.

Substance	Achievable ¹	Units
COD		
Suspended solids	50 ²	mg/l
Cadmium	5 ³	µg/l
Mercury	1 – 10	µg/l
Other heavy metals	<0.5	mg/l
Dioxins and furans, PAHs and other organics		
Simazine	1 ⁴	µg/l
Atrazine	1 ⁴	µg/l
Notes:		
¹ The levels quoted represent a flow weighted monthly average concentration		
² By sedimentation or settlement. Lower releases may be achieved by filtration, if necessary, depending on the receiving water and the level of contamination with other pollutants		
³ By precipitation and filtration which can be expected to achieve 70 % reduction. Subsequent treatment in the biological treatment plant of a sewage treatment works will reduce this to below the limit of detection		
⁴ For waste water carbons, trace quantities of pesticides may be leached from granulated activated carbon (GAC) into waste water prior to discharge to sewer. Many GAC regeneration plants install small GAC filters on the outlet to the sewer as a precaution		

Table 4.8: Achievable water emission values
[29, UK Environment Agency, 1996], [150, TWG, 2004]

Applicability

Applied to the effluent from quenching or scrubbing flue-gas treatment.

Example plants

Many examples exist in the sector.

Reference literature

[29, UK Environment Agency, 1996], [150, TWG, 2004]

4.4.4. Pollution control techniques applicable to activated carbon regeneration

Pollution control techniques for the abatement of particles and acid gases	Applicability to activated carbon regeneration
Primary measures for particulate control	Furnace temperature Turning rate of the rotary furnace Fuel type
Secondary measures for particulate and acid gases control	Mechanical collectors Wet scrubbers Dry scrubber Electrostatic precipitators (ESP) Fabric filters
Primary measures for NO _x control	Reduce furnace and combustion temperatures Reduce excess air and thus lower the concentration of atomic oxygen in higher temperature zones Reduce residence time in all higher temperature areas Control the furnace heat release rate, and eliminate high temperature peaks Flue-gas recirculation (FGR) Air staging Fuel staging Furnace insulation Low entrance of secondary (cold) air Reduced air/fuel ratio
Secondary measures for NO _x control	Selective catalytic reduction (SCR) Selective non-catalytic reduction (SNCR) The DESONOX process The SNOX process The EDTA-Chelate process The SO _x NO _x RO _x BOX

Table 4.9: Applicability of techniques in the activated carbon regeneration for the treatment of flue-gases [41, UK, 1991], [150, TWG, 2004]

4.5. Resin regeneration

4.5.1. Techniques for the regeneration of resins

Description

Some techniques include:

- applying a pH balancing system
- applying hot water regeneration.

Achieved environmental benefits

Increases the rate of resins regeneration. The alternative use of heat (i.e. hot water) to regenerate resins, potentially provides reductions in effluent volume and requires lower energy requirements, particularly where heat recovery is employed on the regenerated fluid.

Applicability

Hot water regeneration is only possible for thermally stable resins.

Economics

The principal technique employed to control releases to water is a pH balancing system. Such a system can cost in the region of GBP 30000 to 40000. This compares with a total plant cost in the order of GBP 250000, excluding civil works. Hot water regeneration lowers the operating costs.

Reference literature

4.5.2. Pollution control techniques applicable to activated carbon and for resin regeneration

The same type of techniques can be used as are used for activated carbon regeneration. Thus refer to Section 4.4.4.

4.6. Waste gas treatments

4.6.1. Fabric filters

Description

The creation of a barrier separates the dust from the flue-gases. Solid particles are trapped by a woven fabric while the gas flow can pass through it. Filter efficiency may be enhanced by pre-coating the filter cloth prior to being brought online.

Achieved environmental benefits

- high collection efficiency for both coarse and small particles
- efficient with a large concentration range
- collected dust may be re-used in the process
- high collection efficiency at high temperatures, if special materials, e.g. teflon, are used.

Characteristics	Fabric filter
Input flow range (m ³ /hour)	1000 to 50000
Input concentration (mg/Nm ³)	100 to 5000
Output concentration (mg/Nm ³)	<10
Risks	Explosion
Consumption (per tonne waste fuel produced)	
Electricity (kWh)	2.5 to 3.5
Fuel/gas (litre)	-
Reactant (nature and kg)	-
Residues	-
Costs (EUR/t waste fuel produced per year)	
Investment cost	Up to 4
Operation cost	0.15
Maintenance cost	0.1

Table 4.10: Dust filtration by a fabric filter
[122, Eucopro, 2003]

Cross-media effects

Cyclones and fabric filters create a pressure drop in the gasflow requiring a higher energy consumption to overcome this drop and therefore this leads to higher overall emissions. A major source of hazardous waste at a number of industries is the dust emanating from air pollution control equipment (e.g. from a baghouse). As with sewerage systems, common dust collectors are utilised in different production areas resulting in a mixing of different types of dust and, thereby, precluding recycling. In some cases, modifications can be made to dust collectors so that each different source of waste goes to a different compartment, thereby, preventing the mixing of different waste types and increasing the recycling potential.

Operational data

Insitu cleaning can be achieved by air pulse, counter flow air or mechanical tapping. The reliability highly depends on the filter material. Fabric filters may create a risk of explosion. Fabric filters are equipped with

pressure drop monitoring, including alarms and often, with measurement of inlet and exit concentrations. Pressure is often used as an instantaneous surrogate for concentration analysis. From time to time, however, a laboratory control is carried out on the exit concentration in order to quantify the emissions. An opacity meter or particle impingement detector can be used to monitor performance. There need to be a programme in place for the regular cleaning of physical filters.

Applicability

Applied for both fugitive emissions and point source emissions to air. Fabric filters are typically used as secondary or tertiary gas cleaning devices in combination with a cyclone or a dry scrubber located upstream. Fabric filters are not generally suitable for use in moisture laden streams or those with acidic, tarry or sticky characteristics. This is due to the adverse effects of fabric 'blinding' and adherence problems.

Example plants

Bag filters are used in the preparation of waste fuel. They are also used in the mixing vessel in the stabilisation process in the production of aerosol cans (e.g. for the removal of dust) and for the treatment of the exhaust gases of Ph-c plants.

Reference literature

[53, LaGrega, et al., 1994], [55, UK EA, 2001], [122, Eucopro, 2003], [126, Pretz, et al., 2003], [150, TWG, 2004]

4.6.2. Condensation

Description

VOCs can be removed by condensation with liquid nitrogen or other cooling agents (e.g. cooling water). The condenser is a vessel incorporating a heat-exchanger where a gas is cooled to change to the liquid phase (i.e. condensation). VOC recovery by nitrogen cryogenic condensation in solvent (-130 °C). More information on this issue can be found in the BREFs on Large Volume Organic Chemicals (LVOC) and on Common Waste Water and Waste Gas Treatment (CWW).

Achieved environmental benefits

The condensed VOCs can be recovered. VOC emissions achievable can be as little as 10 to 50 g/h. Efficiencies of 99.3 % can be achieved. Chloroform emissions can be as little as 20 mg/Nm³. Nitrogen is re-usable for other means in the plant.

Characteristics	Value
Input flow range (Nm ³ /h)	<100
Input VOC concentration (g/Nm ³)	2 – 500
Efficiency (%)	>95
Need for preliminary de-dusting	no
Residues	no
Consumption (per tonne waste fuel produced)	
Electricity (kWh)	25
Fuel/gas (kWh)	-
Other fuels or biogas	
Reactant (kg)	Nitrogen
Costs	
Investment cost (EUR/t capacity)	20 to 60
Operational costs (EUR/t waste fuel produced)	2 to 6
Maintenance costs (EUR/t waste fuel produced)	<0.5

Table 4.11: Data on liquid nitrogen condensation
[122, Eucopro, 2003]

Cross-media effects

Consumption of nitrogen and electricity. Direct discharge of nitrogen contaminated with other compounds may occur.

Operational data

Sensitivity to water presence. The presence of water vapour in the air can block the system and the water condenses to ice, which could then frost or ice up the flow systems. A defrosting period is then necessary. Consumption of nitrogen of 18 kg/t solvent recovered. Elimination of the security risks. Temperature and pressure controls are simple.

Applicability

Used in cases where only relatively small volumes or low flows need to be treated, and when liquid nitrogen is available and the concentration of VOC is quite high. This technology is available for stable volumes and compositions. Applications typically include treating the emissions from oil reprocessing heating vessels, which also incorporates a recovery of the oil components. Condensation can be used as a pretreatment for thermal oxidation, reducing the fuel requirement and the overall size of the oxidiser required. Applicable to flows of between 50 - 100 Nm³/h and loads from 1 to 10 kg/h. It is easily applicable to existing plants and it is very flexible to adapt to changes in flow and concentration.

In Ph-c plants, the volatile components are cooled and condensed for their treatment.

Economics

Typically high operating cost. Operational cost of EUR 2/t solvent treated for a liquid nitrogen condensor.

Technical specification		
Capacity	10000 t/yr	
Oil types	Used lubricating oils	
Process operation	Batch	
Waste gas flow	0 – 50 Nm ³ /hr	
Age of plant	10 years old	
Age of pollution control equipment	2 years old	
Possible Control Techniques	Capital Cost (GBP)	Operating Cost (GBP)
Glycol chiller	30000	8000

Table 4.12: Cost of controlling releases to air from a typical oil recycling plant
[42, UK, 1995]

Driving force for implementation

Safety regulations.

Example plants

Preparation of waste fuel from hazardous waste and solvent recovery. At an example waste oil re-refining plant, the dehydration and defuelling units use air-cooled, condensing heat-exchangers for vapour recovery. The vacuum-distillation vapour recovery uses oil and cooling-water condensers. Vapour and non-condensable streams are then routed to the process heater for destruction of the organics and any odorous substances that may be present. There are at least eight plants in the EU.

Reference literature

[42, UK, 1995], [55, UK EA, 2001], [56, Babbie Group Ltd, 2002], [66, TWG, 2003], [122, Eucopro, 2003], [150, TWG, 2004], [152, TWG, 2004]

4.6.3. Biofilters

Description

'Biofilter' is the generic term covering all biological oxidation processes taking place in a packed system. This includes conventional trickling filters, bioscrubbers (microbial population supported in scrubber liquor) or biobeds (packed system using soil, peat and bark).

The biofilter consists of an apparatus filled with decomposable material such as compost, bark or a mixture of turf and heather, etc. Micro-organisms (fungi, bacteria, viruses and algae) are resident on the material. The exhaust airflows through the material while the micro-organisms decompose the harmful substances. Water and airflow normally run countercurrently. A biofilter is not a filter in the mechanical sense (i.e. it does not lead to a separation of particles), but it is a reactor where a certain range of harmful substances are metabolised to harmless substances. The desired qualities of a biofilter are outlined in Table 4.13.

Characteristic	Description
Filter media	Biologically active, but reasonably stable
	Organic matter content >60 %
	Porous and friable with 75 – 90 % void volume
	Resistant to water logging and compaction
	Relatively low fines content to reduce gas headloss
	Relatively free of residual odour
Moisture content	Specifically designed mixtures of materials may be desirable to achieve the above characteristics
	50 – 80 % by weight
Nutrients	Provisions must be made to add water and remove bed drainage
	Must be adequate to avoid limitations
pH	Usually not a problem with aerobic digestion gases because of the high NH_3 content
	7 to 8.5
Temperature	Near ambient, 15 – 35 or 40 °C
Gas pretreatment	Humidification could prove to be useful in order to achieve near 100 % inlet gas humidity
	Dust and aerosols may be removed to avoid media plugging, but for most biofilters this is not a problem (unless they have a tissue layer in the bottom)
Gas loading rate	<100 $\text{m}^3/\text{h}\cdot\text{m}^3$, unless testing supports higher loadings
Gas residence time	30 - 60 seconds, unless testing supports shorter residence time
Media depth	>1m, <2 m
Elimination capacity	Depends on media and compound (typically in the range 10 – 160 $\text{g}\cdot\text{m}^{-3}\cdot\text{h}^{-1}$)
Gas distribution	The manifold must be properly designed to present a uniform gas flow to the media

Table 4.13: Qualities of biofilter media
[59, Hogg, et al., 2002]

In contrast to the biofilter, in bioscrubbers the micro-organisms are not fixed in the bioscrubber on organic materials. The biomass swims quasi free in the suspension, which is sprayed on the exhaust gas in a countercurrent flow. The principal difference this brings about is that the absorption of the harmful substances is local and is separated from the metabolism.

In an aerosol can treatment facility, the exhaust air from the different operational parts is led through an air-permeable filter layer by means of ventilators. While the airflows through the filter layer, the degradable contents are decomposed by micro-organisms that populate the filter. In order to ensure that the filter layer remains air-permeable, which is essential for the supply of air oxygen to the micro-organisms, the exhaust air is

cleaned beforehand so that solids (dusts) are removed. Simultaneously, cleaning moisturises the exhaust air, which is necessary to prevent drying of the filter layer. The biofilter, thus, represents an aerobic fixed bed reactor for the biochemical decomposition of organic substances. The biofilter, e.g. with an area of 1800 m², can treat an exhaust air stream of approximately 200000 m³/h, which results in a specific filter load area of 111 m³/m²/h. Below the biofilter, there are supply areas that are utilised by the different treatment facilities (provision for treatment and dispatch). This area is designed as a collection tray. Moreover, a stationary foam extinguishing installation is present.

Achieved environmental benefits

Reduces odour and VOC emissions from natural compounds and from the synthesis of inorganic compounds (e.g. H₂S and NH₃), aromatic and aliphatic compounds (e.g. acids, alcohols, hydrocarbons). Other compounds that may be degraded are non-chlorinated solvents, mercaptans, amines, amides, aldehydes and ketones. The treatment capacity ranges from 50 - 150 Nm³/h/m² depending on the type of pollutant.

Substance (group)	Input concentration (mg/Nm ³)	Output concentration (mg/Nm ³)	Biofilter efficiency (%)
Aldehydes, alkanes			75
Alcohols			90
AOX, aromatic hydrocarbons (benzene)			40
Aromatic hydrocarbons (toluene, xylene)			80
NM VOC			83
PCDD/F			40
Odour			95 – 99
NM VOC (Values in total carbon)	30 – 70	10 – 40	80

Table 4.14: Biofilter efficiency in MBT waste gas treatment [81, VDI and Dechema, 2002]

The removal efficiency of a biofilter is determined by the gas residence time in the media bed. Effective residence times typically range from 30 to 60 seconds for most aerobic digestion applications. Studies have reported high removal efficiencies for specific compounds such as H₂S (>99 %), methyl mercaptan, dimethyl disulphide, dimethyl sulphide (>90 %) and various terpenes (>98 %).

Environmental benefits include low energy requirements and the avoidance of potential cross-media transfer of pollutants. Measurements in the practical application of biofilters in physico-chemical treatment plants have shown results of approx. 95 to 98 % degradation for organic solvents, with concentrations in exhaust air to be purified from 400 to 1600 mg/Nm³.

In biological treatment plants, malodorous gases will be fed through a scrubber (e.g. acidic wet scrubber), which reduces the ammonia content to an acceptable level for the biofilter. The biofilter removes odours and any remaining ammonia. The filtering process does not create any compounds that are harmful to the environment and after use, the filter can be treated by composting and additional waste will not be generated. The levels of ammonia and odour after treatment are <1 mg/m³ and 1000 – 6000 ouE/m³ (90 % reduction), respectively.

Table 4.15 and Table 4.16 show the effectiveness of biofilters applied to MBTs.

Parameter	Concentration (µg/m ³) min – max	Effectiveness (%) min – max	Concentration (µg/m ³) min – max	Effectiveness (%) min – max	Concentration (µg/m ³) min – max	Effectiveness (%) min – max
Acetaldehyde	2100 – 2500	78 – 89	46 – 740	89 – 96	4900 – 6100	99

n-Butylacetate	150 – 425	97 – 99	30 – 120	83 – 96	170 – 980	73 – 99
Ethylbenzene	250 – 310	12 – 42	60 – 190	27 – 61	250 – 740	16 – 43
2-Ethyltoluene	180 – 220	33 – 41	25 – 105	14 – 89	80 – 270	25 – 55
3,4-Ethyltoluene	480 – 640	23 – 45	70 – 260	38 – 96	230 – 1000	48 – 77
Limonane	1700 – 4300	29 – 40	810 – 2200	94 – 98	1300 – 3700	30 – 63
Toluene	490 – 550	16 – 39	130 – 280		460 – 1000	7 – 36
m/p-Xylene	850 – 1400	9 – 42	280 – 620	30 – 71	720 – 2000	19 – 45
o-Xylene	260 – 290	23 – 41	60 – 150	7 – 63	160 – 650	20 – 45
Acetone	2450 – 2900	99 – 100	1200 – 2800	99 – 100	4700 – 8200	93 – 97
2-Butanone	960 – 2800	99 – 100	80 – 770	94 – 99	370 – 11000	95 – 100
Ethanol	5200 – 5300	100	88 – 750	94 – 99	14000 – 18000	100
α-Pinene	370 – 700	8 – 44	280 – 790	53 – 83	560 – 930	5 – 39
β-Pinene	330 – 800	12 – 44	120 – 300	53 – 81	230 – 490	38 – 49

Table 4.15: Concentration ranges for some parameters of the exhaust air from MBTs, showing the retention efficiency of the biofilter for these compounds [132, UBA, 2003], [150, TWG, 2004]

Biological exhaust gas purification processes are able to reduce the exhaust air/exhaust gas contents from municipal waste treatment plants only to a limited extent (typically NMVOC of more than 300 g/t waste). Table 4.16 shows some measurement results from well maintained biofilters with upstream air humidifiers.

Compounds of the exhaust air	Separation efficiency (%)		
	Facility A	Facility B	Facility C
Acetaldehyde	-18 to -99	99	99
n-Butylacetate	83 – 96	73 – 99	97 – 99
Camphor	60 – 88	60 – 90	88 – 91
Dichloromethane	-53 to -80	-300 to -33	43 – 62
Dimethyldisulphide	44 – 78	-55 to -89	10 – 31
2-Hexanone	75 – 80	-	80 – 82
Naphthalene	50 – 75	38 – 93	58 – 82
Phenol	-25 to -79	75 – 88	47 – 94
1,4-Dichlorbenzene	0 – 73	-1900 to -89	-130 to -13
Ethyl benzene	27 – 61	16 – 43	12 – 42
2-Ethyl toluene	14 – 89	25 – 55	33 – 41
3/4-Ethyl toluene	38 – 96	45 – 77	23 – 45
Limonene	94 – 98	30 – 63	29 – 40
Styrene	64 – 89	44 – 66	21 – 50
Toluene	29 – 50	7 – 36	16 – 39
m/p-Xylene	30 – 71	19 – 45	9 – 42
o-Xylene	7 – 63	20 – 45	23 – 41
Acetone	99 – 100	93 – 97	94 – 97
2-Butanone	94 – 99	95 – 100	99 – 100
Ethanol	94 – 99	100	100
Ethylacetate	74 – 93	82	97 – 99
α-Pinene	59 – 83	5 – 39	8 – 44
β- Pinene	53 – 81	38 – 49	12 – 44
Benzene	0 – 17	-	0 – 20
Trichlorethene	-108 to -3	67 – 90	20 – 46
Combinations of air humidifiers and biofilters may provide varying purification power for organic substances of the first and second group			

Table 4.16: Separation efficiency of organic compounds in the biofilter [132, UBA, 2003]

Table 4.17 gives a summary of current measurement results from the biofilter of an aerosol can treatment facility. Note that other parts of the exhaust air of the treatment process are treated by the in-house high temperature incineration facility.

Component	Average concentration of raw gas	Average concentration of cleaned gas
Total carbon (FID)	206	49
CHC/CFC	9.69	8.17
Benzene	1.07	0.35
Aromatic compounds	35.4	8.07
Ester, alcohols	80.8	0.57
Results from 2003 and data in mg/m ³		

Table 4.17: Raw gas and treated gas by a biofilter in an aerosol can treatment facility [157, UBA, 2004]

Cross-media effects

N₂O and NO emissions are typically increased. However, it has been demonstrated that the use of an acid scrubber for ammonia (NH₃) removal prior to biofiltration can reduce potential N₂O and NO emissions. Methane is neither biodegraded nor produced by the biofilter. Terpenes are produced by the biofilter itself and arise from the degradation of any wooden materials in the biofiltering media. Some references question whether biofilters really decrease VOCs since, they claim, VOCs are actually produced by the biofilter itself.

The degrees of decomposition of the studied biofilters in MBT plants for single compounds are not as high as for several special applications in industry (80 % or >90 %). For non-methane TOC (NMTOC) they achieve on average an efficiency rate of only 40 – 70 %. For methane, the efficiency is close to 0 %. The decomposition efficiency for single compounds in the exhaust gas of MBT plants exhibit good values for NMTOC (e.g. acetone, acetaldehyde, limonene and ethanol), moderate values for BTEX and no reduction for CFCs.

The partly low degradation efficiencies for NH₃ also with a potential inhibition of carbon decomposition, may be improved by the use of acid scrubbers (e.g. sulphuric acid for the absorption of ammonia) instead of neutral scrubbers. The NH₃ emissions will be minimised not only because they are odorous but also because, in the biofilter, close C/N relations of the MBT exhaust air may lead to the formation of NO and N₂O.

Operational data

Biofilters are typically one metre thick of porous material. The material used in the biofilter is usually a mix of green compost typically mounted over a certain structure. These systems are very easy to be built and maintained. High porosity (80 – 90 %), the humidity (60 – 70 %), pH, temperature, and the contact time between the nutrients need to be controlled for good biofilter performance. The humidity in the biofilter can be maintained with a special water system or by humidifying the gas to be purified before it is passed pass through the biofilter.

The NMVOC removal in biofilters strongly depends on the temperature (e.g. weather conditions), which can reduce the efficiency of the biofilter.

In some cases, the materials used for the biofilter media may not be able to fully satisfy the demands for all the essential nutrients of the micro organisms in the biofilter for a longer time. In these cases supplying additional nutrients can significantly increase the efficiency of the biofilter.

The pressure drop is less than 50 mm H₂O. The surface load per unit area of the biofilters should not exceed approx. 80 Nm³/m² x h.

Some issues to consider include:

- incoming air must have a relative humidity of >90 % (this may require the use of a humidifier)
- particulates must be removed
- hot gases may need to be cooled closer to the optimal activity temperature for aerobic micro-organisms, generally 25 to 35 °C and the potential temperature rise across the bed of up to 20 °C needs to be taken into account
- the major operating parameters, such as the off-gas temperature and the back-pressure, need to be checked daily
- the moisture content in the filters needs to be monitored regularly
- a low temperature alarm needs to be fitted to warn of freezing, which can damage the filter and could affect the growth of the microbes
- the packing media must be supported to allow a fast, even airflow without any pressure drop
- the media needs to be removed when it starts to disintegrate, thus affecting the airflow (bark is less resistant than, for example, heather)
- the choice of media and supporting system affects the power requirement for maintaining the airflow, with the power needed to overcome the bed resistance being the largest operational cost
- consideration needs to be given to the effect of a loss of biomass due to the introduction of toxic compounds and a stand-by procedure needs to be developed for such an event.

Even in the case of optimisations (combinations with bio-scrubbers instead of water scrubbers) a low and reliable emission cannot be permanently achieved. For the odorous emissions, a strong reduction can be achieved (with only the filter's innate smell remaining) if an appropriate conditioning of the exhaust air is carried out.

In the case of flue-gas treatment from aerobic digestion of the digestate generated in anaerobic treatments, the concentration of ammonia is rather high (>30 mg/Nm³) being in this case necessary to chemically pretreat the flue-gas before it is guided to the biofilter.

Applicability

Biofilters are applied for great volumes of exhaust gas streams which carry low organic loads in the particular exhaust gases but which have intensive odours. Concentrations of components to be treated need to be relatively stable for a good performance. Biobeds have been installed on waste treatment sites for the abatement of odorous emissions. Applicable to all types of WWTP.

Biofilters are used for the treatment of exhaust gases in aerosol can treatment facilities, thermal distillative drying of sludge, biological treatment (MBT) plants and Ph-c plants. In Ph-c plants, biofilters are used for the adsorption of the volatile components to compost material and for the biological decomposition of the adsorbed components by micro-organisms in the compost material. If the biofilter is in danger of desiccating, the exhaust air that is to be cleaned has to be moisturised.

Biofilters are suitable only for low polluted exhaust gas streams and are thus only used for the purification of the hall exhaust air streams. Flue-gas cleaning by biofilters or biological cleaning generated in anaerobic digestion plants has been proven to be of value.

Economics

Biofiltration and bioscrubbing have lower operating costs than many other air pollution control technologies for treating low concentrations of biodegradable organic pollutants. Bioscrubbers have the higher maintenance cost of the two. Treatment gas flows of more than 1500 Nm³/h are considered cost-effective. Investment cost of EUR 550000 for a biofilter applied to treatment of WWTP odours with a flow of 1800 Nm³/h.

Characteristics	Value
Input flow range (Nm ³ /h)	<100000
Input VOC concentration (g/Nm ³)	<1
Efficiency (%)	<90 %

Need for preliminary de-dusting	No
Risks	Destruction of micro-organism
Residues	Yes
Consumption (per tonne waste fuel produced)	
Electricity (kWh)	15
Fuel/gas (kWh)	-
Alternative fuel or biogas	
Reactant (kg)	Barks
Costs	
Investment costs (EUR/t capacity)	10 to 20
Operational costs (EUR/t waste fuel produced)	<1
Maintenance costs (EUR/t waste fuel produced)	<0.25

Table 4.18: Consumptions and costs of biofilters
[122, Eucopro, 2003]

Driving force for implementation

Reduction of odour emissions. The German and Austrian Governments have set limit values for MBT facilities for odour emissions with 500 GE/Nm³ and for VOCs (Austria: 100 g/t treated waste, Germany: 55 g/t treated waste). Furthermore, such systems cannot achieve the TOC emission limit values demanded by some German standards (e.g. less than 55g TOC per tonne of MBT input and a TOC concentration of less than 20 mg/Nm³).

Example plants

Widely used in the sector. Applied in the treatment of flue-gases from biological treatment plants and from physico-chemical treatment of waste waters and immobilisation. It is also commonly used in other industrial sectors, such as in the chemical, iron and steel, and food industries and in waste water treatment plants. Many examples of the use of biofilters exist in the EU.

Reference literature

[52, Ecodeco, 2002], [55, UK EA, 2001], [56, Babbie Group Ltd, 2002], [59, Hogg, et al., 2002], [66, TWG, 2003], [81, VDI and Dechema, 2002], [121, Schmidt and Institute for environmental and waste management, 2002], [122, Eucopro, 2003], [126, Pretz, et al., 2003], [132, UBA, 2003], [135, UBA, 2003], [150, TWG, 2004], [157, UBA, 2004]

4.6.4. Scrubbing

Description

Absorption techniques are typically called scrubbers. Some techniques include:

- having in place a scrubber system for the major inorganic gaseous releases (e.g. Cl₂, ClCN, HCl, H₂S, NH₃, NO_x), organic compounds (e.g. VOC) and odour from some unit operations treating certain types of waste (containing these volatile compounds), which have a point discharge for process emissions. In circumstances of highly variable emissions, the installation of a secondary scrubber unit to certain pretreatment systems may be a solution if the discharge is incompatible, or too concentrated for the main scrubbers
- correctly operating and maintaining the abatement equipment, including the handling and disposal of spent scrubber medium.

Water sprays are a commonly used control method for particulate matter emissions. The addition of dust control chemicals such as polymers or acrylics to the water increases the effectiveness of the spraying.

Achieved environmental benefits

Reduces emissions to air of VOC, acids, ammonia, particulates, etc. Increases the efficiency of pollutant adsorption, due to the particle-gas contact (particularly relevant for the removal of acid gases by basic particles injected at the scrubber, if applicable).

Cross-media effects

This technique generates liquid effluents and sludge that require further treatment.

Wet scrubbers generate steam plumes. Releases from wet scrubber vents need to be hot enough to avoid visible plume formation in the vicinity of the vent. This is to prevent the condensation or adsorption of environmentally harmful substances by the condensing water vapour. Exhaust gases from a wet scrubber can be heated by the use of waste heat to raise the temperature of the exhaust gases and to prevent immediate condensation on the exit from the vent. This procedure also aids the thermal buoyancy of the plume.

Operational data

Usually some level of air monitoring will be carried out, either at the scrubber discharge or at the site boundary. Typically the monitoring of the exit gases from the scrubber systems/filter systems is spasmodic. The assumption is that the abatement systems are fit for this purpose and will reduce the emission to an acceptable background release. Discharge points may be monitored on a quarterly or monthly basis for those acid gases that are expected to be collected.

Water supply and effluent disposal facilities must be available. Monitoring provisions include:

- pH, flowrate and level of scrubber liquors and scrubber pressure drop
- pressure drop monitoring with alarms
- periodically monitoring the exit concentrations under different operating conditions.

There also needs to be a programme in place for the regular changing of absorbent in the absorption units.

Applicability

Suitable for high flow, low concentrations (e.g. 1 – 200 mg/Nm³ VOC), low temperature gas streams and when the pollutant is chemically reactive (or soluble in the case of VOC contaminants).

These techniques are typically applied to point source emissions related to those compounds which result from the collection of gas from a vessel or area and which are passed on either via abatement or direct to a stack or vent. This technique can be used for the treatments of off-gases generated during the loading of storage tanks.

Acid scrubbers are applied to capture the ammonia emissions liberated during the acidic treatment in the re-refining of waste oils. Mineral oil scrubbers are also used to trap VOCs and odours in waste oil treatment facilities.

Hypochlorite or hydrogen peroxide may be used for cyanide scrubbing and odour control. A two-stage system could be utilised, e.g. alkali and oxidiser scrubbers in series. Water supply and effluent disposal facilities need to be available to run these systems. There needs to be a programme for the regular changing of absorbent in the absorption units.

Alkaline potassium permanganate or hypochlorite can be used as oxidisers for the treatment of cyanide compounds.

Economics

Table 4.19 below shows a summary of scrubbing costs for emission controls for area sources applied to excavation and removal.

Emission control technique	Material cost (USD/m ²)	Comments
Water spray	0.001 (varies)	Assuming municipal water cost of 1 USD/1000 litres. Water requires constant re-application. Water

		truck rental: 500 USD/week.
Additives:		Costs vary with chemical use
Surfactant	0.65	
Hygro salt	2.58	
Bitumen/adhesives	0.02	

Table 4.19: Summary of costs for emission controls for area sources applied to excavation and removal [30, Eklund, et al., 1997]

Example plants

A common use is the treatment of extracted air from the reactor vessel with a scrubber liquor, typically a caustic solution. The process is extensively applied in Ph-c plants (e.g. wet scrubbing). Used as a pretreatment, e.g. before biofilters, for the treatment of the exhaust gases of biological treatment plants.

Pretreatment processes capable of liberating toxic gases tend to have their own scrubbing systems, with the scrubber vent leading into the main site exhaust system, and with the aqueous liquors being treated in the plant.

All of the oxidation systems seen in the UK have their own local scrubber systems, and the residues from both the oxidation and the scrubber solutions are treated in the main plant. Where the plant has a total exhaust system for the site, the exhaust from the oxidation scrubbers typically goes through the main plant exhaust scrubbing system prior to discharge to the air.

Caustic scrubbing is employed to strip hydrogen sulphide in plants treating waste oil.

Reference literature

[30, Eklund, et al., 1997], [42, UK, 1995], [55, UK EA, 2001], [56, Babbie Group Ltd, 2002], [86, TWG, 2003], [126, Pretz, et al., 2003], [150, TWG, 2004]

4.6.5. Chemical scrubbing

Description

Chemical exhaust gas treatment can be one-step or multi-step scrubbing with chemical scrubbers. Up to now, plants of this type have been produced, e.g. as one-step or multi-step carrier material cleaners with controlled pH values in each step or with an addition of oxidants.

Achieved environmental benefits

Scrubbers of this type are well suitable for removing single components (e.g. ammonia).

Cross-media effects

This scrubber is required for the reduction of N-compounds prior to the subsequent treatment. Multistage exhaust air scrubbers (acid-alkaline), or scrubbing with H₂O₂, can only reduce the concentration of certain components (e.g. VOCs) due to the high crude gas concentrations generated especially by recirculating treatments.

Applicability

A state-of-the-art technique in biological treatment (MBT) plants is a combination of acid scrubbers and thermal regenerative exhaust gas treatment. The release of the treated exhaust air is carried out via a stack.

Driving force for implementation

It is reported that scrubbed gas concentrations required by a German regulation cannot be reached by these systems alone.

Example plants

Currently no information is available on its use as an independent treatment step in biological treatment (MBT) plants. All information in this section corresponds to experiences in other types of plants.

Reference literature

[132, UBA, 2003], [150, TWG, 2004]

4.6.6. Incineration

Description

In the decontamination of thermal exhaust air, the exhaust air is treated in a combustion chamber at temperatures of up to 850 °C and for a minimum residence time of at least 2 seconds. Within this space of time, the harmful substances will be totally oxidised and the cleaned gas can then be released to the air.

In biological treatment plants, incineration can be differentiated into post-combustion, with or without heat recovery. As in thermal post-combustion, the carbohydrates are oxidised to carbon dioxide and water in a combustion chamber.

Achieved environmental benefits

Used for VOC control and will usually require the addition of supplementary fuel to support the combustion process. The operator can offset the cost of the supplementary fuel when there is a requirement elsewhere on site for the waste heat that is generated. Values of less than 50 g of VOC per tonne of waste can be achieved with this technique.

In biological treatment plants, by using special heat-exchangers, high quality heat recovery of up to 98 % may be achieved. These high rates of heat recovery are based on the use of special ceramic heat-exchangers, which combine a high mass and a large surface area in an ideal way.

Operational data

Usually requires the addition of supplementary fuel to support the combustion process. The flowrate is 1500 Nm³/h and the operating temperature is 1050 – 1200 °C. The specification of 850 °C with 2 seconds residence time may be justified in waste incineration when a complete flue-gas treatment installation achieves the full removal of residual contaminants. The burning conditions are more extreme (e.g. 1100 °C with 2 seconds residence time) to completely destroy some odorous and VOC components as well as destroy dioxins and dioxin pre-cursors.

Table 4.20 shows the energy requirements of incineration for different hydrocarbon concentrations in the gas.

Parameter				
Hydrocarbon concentration in the gas (g/Nm ³)	0.5	1.5	3	6
Incineration	9	8	6.2	3.2
Heating energy in kWh required for the treatment of 100 Nm ³ /h of gas contaminated with VOCs				
The flows that have been treated range from 500 Nm ³ /h up to 11000 Nm ³ /h				

Table 4.20: Energy requirements of incineration for different hydrocarbon concentrations in the gas
[30, Eklund, et al., 1997]

Applicability

There are no limits for its application.

Economics

The following two tables (Table 4.21 and Table 4.22) show cost data for incineration.

Treatment	Maximum flow (Nm ³ /h)	Capital cost (USD)
Incineration	110	13000 ¹
	160	25000 ¹
	915	44000 ¹
Internal combustion engine	96	62000
	160	50000

¹The cost includes blower, sampling valves, and controls. Heat recovery systems are not included

Table 4.21: Capital costs for controlling VOC emissions from soil venting extraction systems [30, Eklund, et al., 1997]

Capital cost (GBP)	Operating cost (GBP)
30000	3000
Incineration of 2.5 kg fuel oil/hour @ GBP 0.13p/litre Capacity: 10000 t/yr Oil types: used lubricating oils Process operation: batch Waste gas flow: 0 – 50 Nm ³ /hr Age of plant: 10 years old Age of pollution control equipment: 2 years old	

Table 4.22: Cost of controlling releases for air from a typical oil recycling plant using incineration [42, UK, 1995]

In biological treatment plants, cost-efficiency of the operation is determined by the size of the volume flow to be treated and by the pollutant concentrations. The ideal conditions are autothermal operation, where the amount of energy released by the combustion of the pollutants exactly corresponds to the energy demand for maintaining the combustion temperature. The necessary heating energy can, in this case, be gained completely from the combustion of the carbohydrates. This energy demand is directly dependent on the degree of heat recovery. Pollutant concentrations are low making heat supply necessary and, consequently, generating high operation costs.

Driving force for implementation

Waste Incineration Directive (2000/76/EC).

Example plants

At least two waste oil treatment plants use such a system. Used in biological treatment plants.

Reference literature

[30, Eklund, et al., 1997], [42, UK, 1995], [66, TWG, 2003], [86, TWG, 2003], [122, Eucopro, 2003], [126, Pretz, et al., 2003], [132, UBA, 2003], [150, TWG, 2004]

4.6.7. Combined combustion

Description

In some plants where combustion takes place, it is possible to inject polluted air collected in the workshop directly into the secondary air circuit of the burner or into the primary air that goes into the burner. This might require a specific adaptation of the combustion process (modification of gas cleaning and stability of combustion).

Achieved environmental benefits

- synergy with existing combustion facilities
- allows an energy recovery from burning the VOCs in the combustion.

Table 4.23 shows VOC removal data using combined combustion.

Characteristics	Value
Input flow range (Nm ³ /h)	<50000
Input VOC concentration (g/Nm ³)	~ 3 <explosion limit of the compounds
Output VOC concentration (mg/Nm ³)	10 – 50
Need for preliminary de-dusting	no
Residues	no
Consumption (per tonne waste fuel produced)	
Electricity (kWh)	*
Fuel/gas (kWh)	*
Costs	
Investment cost (EUR/t capacity)	*
Operational costs (EUR/t waste fuel produced)	*
Maintenance costs (EUR/t waste fuel produced)	*
*depends on each case	

Table 4.23: VOC removal using combined combustion
[122, Eucopro, 2003]

Cross-media effects

- not available during maintenance of the burner
- specific instrumentation and valves must be installed to prevent a 'domino effect' between each process
- fluctuations in quality or quantity of the VOC could cause some trouble in the combustion system.

Applicability

Needs prior dilution with air when an explosive concentration may be reached.

Economics

Adaptation costs can be high. The operator can offset the cost of the supplementary fuel when there is a requirement elsewhere on site for the waste heat that is generated.

Driving force for implementation

Waste Incineration Directive (2000/76/EC).

Example plants

Used for the preparation of waste fuel from hazardous waste and laundering of waste oils.

Reference literature

[30, Eklund, et al., 1997], [42, UK, 1995], [66, TWG, 2003], [86, TWG, 2003], [122, Eucopro, 2003], [126, Pretz, et al., 2003], [150, TWG, 2004]

4.6.8. Catalytic combustion

Description

The polluted air is burned but, in this technique, the combustion temperature is reduced by the use of a catalyst. The catalyst allows the same destruction efficiency of the VOC at a lower temperature.

In biological treatment plants, catalytic combustion may be used to remove TOC from the exhaust gas. The pollutants are oxidised at temperatures between 200 and 500 °C using noble-metal or metal oxide catalysts.

Achieved environmental benefits

- low fuel consumption
- complete destruction of VOC
- efficiencies range from 95 to 99.9 %
- output concentrations of 5 – 50 mg C/Nm³ are achievable. The actual range depends on the type of compound and the input concentration.

Table 4.24 shows VOC removal data using catalytic combustion.

Characteristics	Value
Input flow range (Nm ³ /h)	20000 – 50000
Input VOC concentration (g/Nm ³)	1 – 3
Output VOC concentration (mg/Nm ³)	10 – 50
Need for preliminary de-dusting	Yes
Risks	Catalyst poisoning
Residues	no
Consumption (per tonne waste fuel produced)	
Electricity (kWh)	25 – 75
Fuel/gas (kWh)	70 – 140
Reactant (kg)	Catalyst
Costs	
Investment costs (EUR/t capacity)	20 – 30
Operational costs (EUR/tonne waste fuel produced)	1 – 3
Electricity	1 – 2
Fuel/gas	
Maintenance costs (EUR/t waste fuel produced)	<1

Table 4.24: VOC removal using catalytic combustion
[122, Eucopro, 2003]

In biological treatment plants, purification efficiencies of more than 99 % can be achieved.

Cross-media effects

The catalyst is sensitive to some compounds (e.g. metal and organic), and their build up may progressively decrease their efficiency.

In biological treatment plants, among the disrupting substances are catalyst toxins, such as organometallic compounds, organic silicon compounds and arsenic compounds. The treatment of halogenated compounds, organic sulphur compounds and organic nitrogen compounds is possible only to a limited degree. Methane can be catalytically reduced to CO₂ only under certain conditions. High temperatures of over 600 °C are necessary for the catalytic oxidation of methane. The energy use of a thermal treatment without heat recovery is very high. The catalytic-thermal oxidation in biological treatment (MBT) is, therefore, questioned under both an economical and environmental point of view.

Operational data

- needs a gas pretreatment in some cases (e.g. ESP, bagfilters and gas scrubber)
- needs prior dilution with air when explosive concentrations are reached
- the energy consumption is lower than for incineration.

Table 4.25 shows the energy requirements of catalytic combustion for different hydrocarbon concentrations in the gas.

Parameter				
Hydrocarbon concentration in the gas (g/Nm ³)	0.5	1.5	3	6
Catalytic combustion	2	1.2	0	0
Heating energy in kWh required for the treatment of 100 Nm ³ /h of gas contaminated with VOCs. The flows that have been treated range from 500 Nm ³ /h up to 11000 Nm ³ /h				

Table 4.25: Energy requirements with catalytic combustion for different hydrocarbon concentrations in the gas
[122, Eucopro, 2003]

In biological treatment plants, the operating life of such catalysts may be more than 30000 operating hours, depending on the operating temperature and on the disrupting substances in the process gas.

Applicability

Given the numerous interfering factors, the practical applicability of catalytic oxidation in biological treatment plants seems problematic. Furthermore, operational experience from biological treatment (MBT) plants is not available.

Economics

The cost of investment is relatively high. Table 4.26 shows the capital costs for controlling VOC emissions from soil venting extraction systems.

Treatment	Maximum flow (Nm ³ /h)	Capital cost (USD)
Internal combustion engine	96	62000
	160	50000
Catalytic oxidation	160	25000 ^a
	320	31000 – 69000 ^a
	800	44000 – 86000 ^a
	1600	77000 ^b
	8000	140000
^a Includes burner, blower, flame arrestor, gauges, filters, knockout pot, sampling port, controls, and skid mounting		
^b Dilution system available for an additional 22000 USD.		

Table 4.26: Capital costs for controlling VOC emissions from soil venting extraction systems
[30, Eklund, et al., 1997]

Driving force for implementation

Waste Incineration Directive (2000/76/EC).

Reference literature

[30, Eklund, et al., 1997], [42, UK, 1995], [66, TWG, 2003], [86, TWG, 2003], [122, Eucopro, 2003], [126, Pretz, et al., 2003], [132, UBA, 2003], [150, TWG, 2004]

4.6.9. Regenerative catalytic oxidiser

Description

VOCs are burned in combustion chambers at a temperature ranging from 750 to 950 °C. The energy produced by the combustion of the VOCs is used to preheat the polluted air on the ceramic bed before combustion. The combustion temperature can be adapted according to the VOC concentration. The polluted process air is heated to the necessary reaction temperature by a heating system and then guided over a combined catalyst and heat accumulating bed reactor. In this reactor, the process air is decomposed to CO₂ and water. The heat from this reactor is then guided over a second combined bed reactor and accumulated there. After this reactor's accumulator bed has been heated, the process air stream is switched so that it enters the second reactor. The heat from the second reactor is then used to preheat the process air, whilst the pollutant oxidation takes place in the first reactor. During further operation, the unit is switched cyclically between the two stages described above.

Achieved environmental benefits

- high VOC destruction rate (>99 %)
- reduced use of fossil fuel or waste fuel (high energy efficiency)
- at high VOC concentrations (>3 g TOC/Nm³), it is possible to operate in an autothermal zone. This means that minimum external energy is needed to be added to sustain the reaction.

Table 4.27 shows VOC removal data using regenerative catalytic oxidation.

Characteristic	Value
Input flow range (Nm ³ /h)	20000 – 80000
Input VOC concentration (g/Nm ³)	2 – 4 with peaks of up to 10
Output VOC concentration (mg/Nm ³)	15 – 50
Efficiency (%)	>99 %
Need for preliminary de-dusting	Yes
Risks	
Residues	No
Consumption (per tonne waste fuel produced)	
Electricity (kWh)	10 – 50
Fuel/gas (kWh)	50 – 200*
Alternative fuel or biogas	Yes
Reactant (kg)	-
Costs	
Investment costs (EUR/t capacity)	10 – 25
Operational costs (EUR/t waste fuel produced)	
Electricity	1 – 3
Fuel/gas	2 – 6
Maintenance costs (EUR/t waste fuel produced)	<1
*according to the VOC concentration	

Table 4.27: VOC removal using regenerative catalytic oxidation
[122, Eucopro, 2003]

Cross-media effects

High energy consumption if there is only a low VOC concentration.

Operational data

- accepts fluctuations of VOC concentrations
- needs prior dilution with air when an explosive concentration may be reached
- needs a de-dusting when dust concentration inlet is higher than 20 mg/Nm³.

Table 4.28 shows the energy requirements of regenerative catalytic oxidation for different hydrocarbon concentrations in the gas.

Parameter				
Hydrocarbon concentration in the gas (g/Nm ³)	0.5	1.5	3	6
Regenerative catalytic oxidation	0	0	0	0
Heating energy in kWh required for the treatment of 100 Nm ³ /h of gas contaminated with VOCs. The flows that have been treated range from 500 Nm ³ /h up to 11000 Nm ³ /h				

Table 4.28: Energy requirements with regenerative catalytic oxidation for different hydrocarbon concentrations in the gas
[122, Eucopro, 2003]

Applicability

It is designed for low to medium VOC concentrations because of its low energy costs.

Economics

Low operation costs and high investment cost.

Driving force for implementation

Waste Incineration Directive (2000/76/EC).

Reference literature

[30, Eklund, et al., 1997], [42, UK, 1995], [66, TWG, 2003], [86, TWG, 2003], [122, Eucopro, 2003], [126, Pretz, et al., 2003], [150, TWG, 2004]

4.6.10. Regenerative thermal oxidiser

Description

The aim of a regenerative thermal oxidiser is the permanent and high quality recovery of a large part of the heat energy that is necessary for heating the waste gas stream to the required oxidation temperatures for treatment.

This heat energy is stored in flow-through heat-exchangers. Such heat-exchangers consist either of a ceramics fill material or are fin heat exchangers. The performance of this recuperative process is expressed by the degree of heat recovery achieved, which is defined as follows:

$$\text{Performance} = 1 - \frac{T_{\text{scrubbed gas}} - T_{\text{crude gas}}}{T_{\text{combustion chamber}}} \quad T = \text{temperature}$$

The incoming exhaust air is heated up in the 'hot' heat-exchanger bed. The air is heated up to a temperature a few degrees below that of the combustion chamber, depending on the heat storage capacity. In the combustion chamber, oxidation takes place. In the case of low pollutant concentrations in the process air, the missing energy has to be brought in by primary energy sources. After passage through the combustion

chamber the exhaust gas, which is now at the reaction temperature, gives off its heat to a 'cold' heat-exchanger bed.

Due to the high energy demand for heating up the exhaust gas and due to the optimal heat exchange the greatest part of the heat stored in the 'hot' heat-exchanger bed is given off to the exhaust gas after approx. 120 seconds. Conversely the hot exhaust gas heats up the 'cold' heat-exchanger bed.

Achieved environmental benefits

The realised heat recovery rates vary between 90 and 98 % depending on the pollutant content of the exhaust gas. An additional supply of energy in this case is not necessary. With regards to the required values for the scrubbed gas, the systems currently available on the market differ in the technical method utilised for ensuring the lowest scrubber gas values. This is necessary because at the stream reversal point, remnants of the crude gas may pollute the scrubbed gas. Systems optimised with respect to this problem can achieve scrubbed gas concentrations of less than 10 mg/Nm³.

Operational data

In order to maintain permanent operation, the stream direction has to be controlled in such a way that the heat-exchanger bed when heated up at a given time can be used for heating up the waste gas. This results in an alternating heating and cooling of the respective heat-exchanger beds.

Also crucial for the design of the plant is the amount of the enthalpy chemically bound in the pollutants that are to be oxidised. The operation is autothermic if the sum of the heat stored in the heat-exchanger beds and the reaction enthalpy released is sufficient to maintain the necessary temperature in the combustion chamber.

If the enthalpy bound in the pollutants is not sufficient to reach oxidation temperature, this has to be achieved and ensured by the use of an external energy supply. Some individual providers realise this by the installation of controlled burners in the combustion chamber, others enrich the exhaust gas with the additional combustibles so that the system can be kept in autothermic conditions. In this case, the plant can be operated flamelessly. In energy-optimised plants, an energy consumption of 8 kWh heat output per 1000 Nm³ of waste gas can be expected.

For the starting period until reaching operational temperature and during operation with low organic substance concentrations (<2 g C/Nm³), an external energy supply is necessary due to the as yet insufficient energy storage in the heat-exchanger beds. In the starting phase of flameless systems electrical heating is usually used, otherwise the heat energy can be brought in by natural gas or propane gas burners.

For operation with gaseous waste fuels such as landfill gas or biogas, it needs to be taken into account that these gases may be contaminated by pollutants. For starting an operation that has not yet reached the required combustion chamber temperatures, these gases should not be used. This can only be done with conventional fuels such as natural gas or propane gas. Additionally it has to be ensured in the safety chain that in the event of any service interruption and the resulting decrease of the temperature in the combustion chamber, the supply of the waste fuels is regulated and thus always available.

Applicability

In the context of research projects and for plant operation, combinations of acid scrubbers and regenerative thermal oxidisers have proven valuable. This process combination has advantages in terms of cleaning capacity as well as in terms of operational costs.

Example plants

In practice, there are several different designs of regenerative thermal oxidisers, which differ primarily in the design of the individual heat-exchanger beds and in the selection of the heat-exchanger material. For low concentrations, these processes have become widely used in post-combustion with heat recovery.

Regenerative thermal oxidisers have been used in Germany for several years for the purification of biological treatment (MBT) plants' exhaust gas. In Austria, an MBT plant has also recently installed and started operation of these types of systems.

Reference literature

[132, UBA, 2003], [150, TWG, 2004], [152, TWG, 2004]

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5. Best available techniques

Recovery of materials from waste

For the re-refining of waste oils, BAT is to:

235. operate a careful control of the incoming materials supported by analytical equipment (viscometry, infrared, chromatography and mass spectrometry as appropriate), laboratories and resources (see Section **Error! Reference source not found.**)
236. check at least for chlorinated solvents and PCBs (see Sections **Error! Reference source not found.** and 4.1.2)
237. use condensation as a treatment for the gas phase of the flash distillation unit (see Section 0)
238. have vapour return lines for loading and unloading vehicles, routing all vents to a thermal oxidiser/incinerator or an activated carbon adsorption installation (see Sections **Error! Reference source not found.**, **Error! Reference source not found.** and 4.6.6)
239. direct vent streams to a thermal oxidiser with waste gas treatment if chlorinated species are present in the vent stream. If high levels of chlorinated species are present then condensation followed by caustic scrubbing and an activated carbon guard bed is the preferred treatment path (see Section **Error! Reference source not found.**)
240. utilise a thermal oxidation at 850 °C with a two seconds residence time for the vacuum distillation vent of vacuum generators or for the air from process heaters (see Section **Error! Reference source not found.**)
241. use a highly efficient vacuum system (see Section 4.1.1)
242. use the residues from vacuum distillation or thin film evaporators as asphalt products (see Section 4.1.15)
243. use a re-refining process of waste oil which can achieve a yield higher than 65 % on a dry basis (see Sections from 4.1.1 to 4.1.12)
244. achieve the following values in the discharged waste water from the re-refining unit (see Section 4.1.14):

Waste water parameter	Concentration (ppm)
Hydrocarbons	<0.01 – 5
Phenols	0.15 – 0.45
For other water parameters, refer to BAT number Error! Reference source not found. in the Generic BAT section	

by using a suitable combination of process-integrated techniques and/or primary, secondary, biological and finishing treatments (see Sections 4.1.14 and **Error! Reference source not found.**).

For the treatment of waste solvent, BAT is to:

245. operate a careful control of the incoming materials as supported by analytical equipment, laboratories and resources (see Section **Error! Reference source not found.**)
246. evaporate the residue from the distillation columns and to recuperate the solvents (see Section 4.2.4)

For the regeneration of waste catalyst, BAT is to:

247. use bag filters to abate particulates from the fumes generated during the regeneration process (see Sections 4.3 and 4.6.1)
248. use a SO_x abatement system (see Section 4.3.3).

For the regeneration of waste activated carbon, BAT is to:

249. have an effective quality control procedure in place to ensure that the operator can differentiate between the carbon used for potable water or food grade carbon and the rest of spent carbons (the so-called 'industrial carbons') (see Section 4.4.2)
 250. require a written undertaking from customers indicating what the activated carbon has been used for (see Section **Error! Reference source not found.** and this is also related to BAT number **Error! Reference source not found.****Error! Reference source not found.**)
 251. utilise an indirect fired kiln for industrial carbons –it may be argued that this could equally be applied to potable water carbons. However, limits on capacity and corrosion may deem that only multiple hearth or direct fired rotary kilns may be used (see Section 4.4.1)
 252. utilise an afterburner with a minimum of 1100 °C, two seconds residence time and 6 % excess oxygen for the regeneration of industrial carbons where refractory halogenated or other thermally resistant substances are likely to be present. In other cases, less stringent thermal conditions are sufficient (see Section 4.4.2)
 253. utilise an afterburner with a minimum heating temperature of 850 °C, two seconds residence time and 6 % excess oxygen for potable water and food grade active carbons (see Section 4.4.2)
 254. apply a flue-gas treatment train consisting of quench and/or venturi and aqueous scrubbing sections, followed by an induced draft fan (see Section 4.4.2)
 255. utilise a caustic or soda ash scrubbing solutions to neutralise acid gases for industrial carbon plants (see Section 4.4.2)
- have a WWTP containing an appropriate combination of flocculation, settlement, filtration and pH adjustment for the treatment of potable water carbons. For effluents of industrial carbons, applying additional treatments (e.g. metal hydroxide precipitation, sulphide precipitation) are also considered BAT (see Section 4.4.3)

6. Emerging techniques

Emerging techniques for treatment of waste oil

Presently, around the world, there are many activities to improve the existing used oil recycling technologies and to develop new ones. Next table summarises those techniques under development:

Technique	Comment
FILEA Process by C.E.A.	Supercritical CO ₂ filtration
MRD solvent extraction	<p>Solvent extraction of used oil vacuum distillates produced by TFE with a high efficient and selective solvent (e.g. NMP). Complete waste free technology with high efficiency and flexibility and production of high quality base oils. Their major advances are:</p> <ul style="list-style-type: none"> quantitative reduction of PNAs to a level not achievable by any other re-refining technology (ppb level) complete retention of the high valued synthetic base oil components more and more present in used oils resulting in very high qualities of the produced base oils. <p>It is expected that a unit will be in operation in Germany by March 2005</p>
New Meiken technology	<p>It has been developed a new process applying a novel absorbent to vacuum distillates. The catalyst absorbent seems to be an activated clay. No industrial application is currently known</p>
Probex Process)	
ROBYS TM Process	Catalytic cracking and stabilisation for diesel production
Supercritical treatments	<p>This technology applies to the deasphalting and also the fractionation. Pre-flash and hydrotreating do not change with respect to the standard assembly of a PDA unit.</p> <ul style="list-style-type: none"> <i>Supercritical Deasphalting</i>: the asphaltic fraction is separated by extraction with light hydrocarbons (C₂/C₃) under supercritical conditions. The clarified oil is separated from the extraction medium and fractionated in a standard column under vacuum conditions. <i>Supercritical Fractionation</i>: the clarified oil from the supercritical deasphalting unit, still mixed with the extraction medium, is directly separated into two or more cuts by varying the physical conditions of the mixture. <p>Both technologies reduce the investment and operating costs when compared with the standard PDA technologies (1 and 2 stages). Two independent pilot plant projects have been developed</p>

Table 6.1: Waste oil treatment technologies under development
[5, Concawe, 1996], [36, Viscolube, 2002], [150, TWG, 2004]

Regeneration of activated carbon

	Stage of development
<i>Activated carbon regeneration technologies</i>	
Biological regeneration of spent activated carbon	Currently at the research and development stage
Oxidative regeneration	Currently at the research and development stage
<i>Novel pollution control techniques for the abatement of emissions</i>	
Circulating fluidised bed absorber	
Electrocatalytic oxidation of sulphur dioxide (the ELCOX process)	
Electrochemical processes	

Flue-gas irradiation	
Methanol injection	

Table 6.2: Emerging techniques that may be applied to activated carbon regeneration
[41, UK, 1991], [150, TWG, 2004]

Cracking of polymer materials

Liquid or gaseous fuels like gasoils or heavy fuel oils can be also substituted with a prior step to crack the waste polymer into a liquid or a gas. Efforts in this field have mostly not progressed further than pilot scale tests.

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