#### Section VI.M.

Guidance by source category: Annex C, Part III Source Categories

Waste oil refineries

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	04 May 2004
Note to reviewers:	
recommendations for best available tech The reason is that I have not found PCD processes. In addition, I do not feel to b	and no conclusions are drawn, neither are hniques/best environmental practices given. DD/PCDF information for the different be in a position to make a general judgment on ment options: reuse/regeneration, cracking, and
Bottom line: I look for outside input to	shape the document.
Thanks.	
	Heidi Fiedle

## Information Document on Waste Oil Refineries

# **1** INTRODUCTION

Used oil is exactly what its name implies: any petroleum-based or synthetic oil that has been used. During normal use, impurities such as dirt, metal scrapings, water or chemicals, can get mixed in with the oil, so that in time, the oil no longer performs well. Eventually, this used oil must be replaced with virgin or re-refined oil to do the job correctly.

Waste oils may originate from two large sources: industrial waste oils and vegetable waste oils. Among the industrial waste oils, three main oil streams can be identified:

- 1. industrial oil (hydraulic oil, engine lubricant, cutting oil, etc.);
- 2. garage/workshop oil, and
- 3. transformer oil.

The second big waste oil stream, the vegetable oils, mainly are from outlets such as restaurants, canteens, *etc.*; it is a relatively small source. This should be dealt with through specialist contractors, who will normally pay for sufficiently large collections, of the order of 80 liters or more. However, improper management of vegetable oil, which has been contaminated with industrial waste oil caused the Belgium chicken crisis in 1998. Since that, more attention has been paid to separate industrial and vegetable oil streams and some countries have established legislation in order to properly manage the collection and recycling of these types of waste oils.

Although life-cycle analyses have been performed for several regeneration options and for the incineration in cement kilns, asphalt plants, *etc.*, these reports did not evaluate the emissions of PCDD/PCDF (or other toxic emissions) (EC 2001).

The following chapters address industrial oils only. There was not much information found as to waste oil recycling plants and processes. The information available is summarized in the following chapters.

## **2** WASTE OIL MANAGEMENT OPTIONS

Although dumping and illegal burning are practiced in most countries (including developed countries), they are not listed here since they are forbidden in most cases.

The most common causes of oil pollution are inadequate storage and deliberate disposal down drains. This applies both to waste oil and to virgin oil.

The disposal options for waste oils are the following:

- 1. Reuse, including regeneration;
- 2. Thermal cracking; and
- 3. Incineration/Use as fuel.

The following segmentation of WO is based on market considerations:

- (black) engine oils: they represent more than 70 % of the WO stream. With homogeneous characteristics, they are sought by regeneration plants.
- black industrial oils: they represent about 5 % of WO. They are potentially suitable for regeneration but due to the content of additives and other substances, automotive oils are preferred by regeneration plants.
- light industrial oils: they represent about 25 % of WO. Relatively clean, their selling price is high. They can either be regenerated on site or be re-used for other purposes. Their market is very specific and independent from the classical supply routes of regeneration.

Even if most of the existing capacities are still operating the old acid/clay process, numerous major processes exist in Europe and world-wide.

They may differ by the technology used for one or several of the following operations:

- de-watering and de-fuelling (removal of water, light ends, and fuel traces (naphtha10...)),
- de-asphalting (removal of asphaltic residues: heavy metals, polymers, additives, other degradation compounds),
- fractionation (in two or three cuts),
- finishing.

#### 2.1 Re-use and Regeneration

Re-use falls into two categories: regeneration and laundering. These basically differ only in the degree, and possibly the type, of processing or cleaning required to recover reusable material from the waste product. Usually laundering applies to less heavily contaminated materials, which can be returned to original use with production of relatively little by-product. Regeneration applies to more heavily contaminated, or complex, lubricating products which, when processed, produce a base stock and, usually, a greater proportion of by-products.

A variety of proprietary technologies has been tried for regeneration with mixed success and various yields of base oil and by-products. They all seek to recover the base blending fluid, predominantly mineral hydrocarbon with growing amounts of synthetic petrochemical material, by separating it from additive chemicals and any breakdown products that arise during use. Invariably, there is a trade off between the quality of the recovered base oil and the sophistication of the technology. Lubricant requirements are becoming more severe, particularly in automotive applications as vehicles are subject to longer service intervals, smaller sumps and higher operating temperatures. The proportion of additives and synthetic components in lubricating oil is increasing, thus setting higher standards for recycled base oil.

Regeneration creates by-product streams that, in the case of the lighter components, may be used as fuel. The heavier residual stream, containing additives and carbonaceous species,

may be used as a blending component in the bitumen industry, for incorporation into construction products such as road surfaces.

In Europe, three technologies can be considered being representative of a diversity of existing regeneration technologies, including modern processes:

- Vacuum distillation + clay treatment,
- Vacuum distillation + chemical treatment,
- Hydrogen pre-treatment + vacuum distillation.

When considering used oil recycling or reuse, attention has to be given to contaminants other than PCDD/PCDF and PCB. Especially in countries where leaded gasoline is still in use, data from Germany obtained in the early 1980s when leaded gasoline was used in vehicle transportation, the lead contents ranged from 17 to 3,000 ppm in used oils. Chlorine contents were from <100 ppm to 2,200 ppm (Bröker 1980). At this time, the most common technologies for used oil recycling were the sulfuric acid/bleaching earth and the IFP (Institut Français du Pétrole) processes. Both processes generate significant amounts of residues, such as sludges from sedimentation, acid tars, filter cake from bleaching earth, and waste waters, which contained high concentrations of heavy metals, *e.g.*, Pb up to 6,000 ppm (data from USA) and sulfuric acid in the range of 17 % (w/w). The acid tars were burned in rotary kilns or other furnaces.

The mass balance for used oil recycling in 1980 was as follows:

From 1 ton of used oil, 0.8 t of recycled oil could be regenerated by using 120-150 kg of sulfuric acid and 50-70 kg of bleaching earth (= clay). The process generated 300-400 kg of residues and 200-350 kg of waste water (Bröker 1980).

Re-refined base oil is the end product of a long process involving used oils. The oils are first cleaned of their contaminants - such as dirt, water, fuel, and additives - through vacuum distillation and then hydrotreated to remove any remaining chemicals. Finally, the re-refined base oil is combined with a fresh additive by the blender to make the finished lubricant. In Europe, fourteen percent of used oil collected is turned over to re-refiners who return used oil to its original virgin oil state.

Principally, used oil can be re-refined over and over again, and is subject to the same stringent refining, compounding, and performance standards as virgin oil. In the United States, the American Petroleum Institute (API) has established criteria for motor oil products to guarantee the performance level, viscosity, and energy-conserving properties as well as a certification mark to tell the customer that the product one is buying has met all the current performance specifications established by the oil industry, and the vehicle and engine manufactures.

#### 2.1.1 Type of Waste Oil Eligible for Regeneration

In general, WO (waste oils) not too heavily polluted and with a high viscosity index (HVI) are the most suitable to regeneration. The GEIR (Groupement Européen de l'Industrie de la Régénération GEIR, Belgium) and re-refiners consider the following WO suitable for regeneration:

- engine oils without chlorine (European Waste Category<sup>1</sup> EWC code: 130205),
- hydraulic oils without chlorine (EWC code: 130110),
- non-chlorinated mineral diathermic oils (EWC code: 130306).

Under certain conditions (limitation of chlorine or PCB content), this list could be extended to the following categories:

- engine oils with chlorine (EWC code: 130204),
- hydraulic oils with PCB (EWC code: 130101),
- hydraulic oils with chlorine (EWC code: 130109).

Several experts insist on the fact that the WO composition is becoming more and more complex, due to different factors:

- The increasing use of dispersants as well as esters and poly-alpha-olefins, *e.g.*, to increase the life of the oil. As a result, the WO become more complex and dirty over time.
- The progressive displacement of conventional mineral based auto lubricants by "synthetic" products which have enhanced performance characteristics. Whereas some of these synthetic products can be regenerated along with mineral oils, others (based upon esters for instance) are less suitable to regeneration because they tend to be less stable in the presence of caustic (often used by regeneration processes) and less stable to the hydrofinishing step.

## 2.1.2 Quality of the Base Stock Produced Outlets

Re-refined base oils are speciality products used in automotive lubricants and industrial lubricants (hydraulic oils). The quality of the base oils produced by regeneration is still a matter for discussion between industrial actors, even though that quality has largely improved with processes such as hydro-treatment and solvent extraction.

Modern regeneration technologies (*i.e.* not for instance the acid/clay process) allow to produce premium quality base oils: 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.

There is a perfect comparability between severely hydro-treated re-refined base oils and virgin base oils (viscosity index, volatility, chlorine content, *etc.*).

As for the base oils quality:

- it is not very dependent on the variation of the origin and type of WO collected (the variations of base oils quality are actually not different from the variations of virgin base oils quality); it is thus possible to obtain reasonably consistent base oil products from a specific regeneration plant,
- it is very dependent on the different processes and production plants.

<sup>&</sup>lt;sup>1.</sup> European codes used by the EC to classify WO according to Commission Decision 2000/532/EC as amended

#### 2.1.3 <u>Regeneration Options (WO back to Base Oil)</u>

## 2.1.3.1 Acid/Clay Process

The polycyclic aromatic hydrocarbon (PAH) content of the base oils produced can be comparatively high (4 to 17 times higher than virgin oils, according to the authors), and the health implications need to be assessed.

### 2.1.4 Other Processes

#### 2.1.4.1 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. Used clay and used chemicals must be safely disposed of; the best route is to burn them in cement kilns or in a chemical waste incinerator.

#### 2.1.4.2 Vacuum Distillation + Hydro Treatment

This process reduces the PAH content of oil much more (no figure) than the clay treatment or chemical treatment. The disposal of spent hydro-treating catalyst should be handled by a specialised company familiar to this problem.

#### 2.1.5 <u>New Regeneration Options under Development</u>

#### 2.1.5.1 UOP-DCH-Process

By treating the whole used oil with hydrogen, the DCH process generates effluents with low environmental loads. By-products requiring disposal will include spent catalyst, sodium chloride and sodium sulphate.

## 2.1.5.2 *Refinery Recycling*

This disposal option has been studied on a small scale in France. All the metal contaminants will be encapsulated in asphalt and leaching of metals will be extremely low (no figure in the report). However, problems of corrosion damage to the plant need to be solved before this can be considered viable option.

PCB content is not considered to be a significant problem for WO disposal in Europe (as under the WO directive, the maximum content of PCB allowed in WO to be treated for disposal is 50 ppm).

WO can have a significant, but variable, chlorine content, including organochlorines. This has implications for all the disposal options considered, whether regeneration or combustion. The fate of these chlorine compounds will vary, not only with the disposal route, but also with the form in which the chlorine is present. It is therefore difficult to make any general comment on the effects of chlorine other than that in the combustion routes there is a risk of dioxin formation and that in the reprocessing options there are risks of corrosion problems, acid gas emissions and contamination of products and by-products. These can only be assessed and compared with emissions from other sources on a case-by-case basis.

## 2.2 Thermal Cracking

Various technologies exist for cracking waste oils for use as automotive or gaseous fuels. A typical process starts with filtering the oil to remove any particulates that might damage the equipment, after which any water is flashed off. The remaining oil is cracked in a vessel such as a kettle or a kiln (depending on the duty required), before fractionation into various cuts. The main drawback is that it is an energy intensive process requiring sophisticated, and thus costly, equipment. The process can not compete directly with the direct use of waste oil as a fuel.

Thermal cracking can accept various types of hydrocarbon feedstock: WO, waste marine fuels, deep frying oils and, possibly with design considerations, waste plastics. The strategy of thermal cracking is to produce high quality products ranging from de-metallized heavy fuel oil to re-refined light industrial lube oil, including gasoil products. Thermal cracking is a common refinery process that is well known and proven; the first plant in Europe was scheduled to be operational by the end of 2001 in Belgium<sup>2</sup>.

## 2.2.1 <u>Type of WO Eligible for Thermal Cracking</u>

Thermal cracking can accept various types of hydrocarbon feedstock: WO, waste marine fuels, deep frying oils and, possibly with design considerations, waste plastics.

#### 2.2.2 <u>Type of Outputs Produced and Markets</u>

The strategy of thermal cracking is to produce high quality products ranging from demetallised heavy fuel oil to re-refined light industrial lube oil, including gasoil products. As described below, thermal cracking offers a big adaptability to the changing market values of products.

According to the promoters of thermal cracking, the gasoil products for instance presents the following advantages:

- a relative high value compared to other fuels (heavy distillate fuel oils, residual replacement fuels) derived from WO by other re-processing technologies,
- a cleaner burning,

<sup>&</sup>lt;sup>2</sup> No information available

- as a commodity product, large markets and marketable anywhere in the world.

#### 2.2.3 Available Processes

Thermal cracking is a common refinery process that is well known and proven. No plant already exists in Europe for WO: the first plant will be operational by the end of 2001 in Belgium.

Thermal cracking, visbreaking, catalytic cracking, fluid catalytic cracking, hydrocracking and coking are all variations on the basis of the basis principle of breaking or cracking the large hydrocarbon molecules ( $C_xH_y$  with 30 carbons) into smaller ones ( $C_xH_y$  with 10 to 18 carbons) by the application of sufficient heat in a pressurised vessel. In this fashion, larger molecules of more viscous and less valuable hydrocarbons are converted to less viscous and more valuable liquid fuels. The yield can reach 70 %.

A 20 kt facility (Guascor group) operates in Spain a simple thermal cracking process and mixes all the light and heavy fractions obtained to feed a thermal engine producing electricity. But this process is very specific and differs from those described in this chapter.

Several processes exist today, such as:

- the Springs Oil Conversion,
- the Great Northern Processing Inc. (GNP) used oil thermal cracking process.

The Springs Oil Conversion is developed by Silver Springs Oil Recovery Inc, Canada. Two processes are available:

 SOC1: the de-watering is followed by the thermal cracking performed in fired heater coils with soaking drums or heated kettles.

This process is suitable to small plants, in the 6 kt to 15 kt/a range. But it is limited in the feed.

- SOC2: the de-watering is followed by the thermal cracking performed in an indirectly fired rotary kiln.

It is suitable to large capacities and can process also oils more refractory to thermal cracking (such as synthetic oils) and higher carbon residues (bunker fuels, *etc.*).

The GNP technology is developed in the United States, offered under license by Propak Systems Ltd., Canada, and marketed by Par Excellence Developments, Canada.

This thermal cracking of WO, utilizing 'refinery calibre' systems and equipment, is a relatively recent development: in 1995-96, this process was successfully re-applied in a 30 kt commercial operating plant by a US company to produce high quality gasoil distillate from a feedstock of WO.

It is this technology which will be installed in Belgium by the end of 2001. The 40 kt/a plant will be operated by WATCO. The process consists in a screening and de-watering section, followed by a thermal cracking section, then a separation or distillation depending on the product slate desired and finally a purification and stabilisation stage.

This technology is characterised by a large operational and product flexibility and adaptability to the changing market values of products. It can also be manipulated to maintain product quality with feed variability.

As a matter of fact, the process operational conditions (temperature, pressure, residence time, *etc.*) can be varied to produce a primary product (be it heavy fuel oil, gasoil or base oil) to be maximized and secondary product streams (consumed in the process for calorific value or sold) to be minimized.

## 2.3 Burning Options

Waste oil used as a direct source of energy must undergo basic treatment to remove water and particulates before it is fit for use as fuel. In the UK, the majority of the waste oil is currently used as fuel by industries such as power generation, road-stone coating and cement manufacturing. Higher levels of pre-treatment can remove water, sediments, heavy hydrocarbons, metals and additives. The oil products from these processes have similar properties and emissions levels to virgin oils, but cost and volume constraints mean that these do not tend to compete directly.

## 2.3.1 Cement Kiln Disposal

High operating temperatures are required in a cement kiln to convert the raw materials into cement and the raw materials used are highly alkaline. PCDD/PCDF measurements from co-incineration of waste oils are available and presented in detail in the Guidance Document on "Cement Kilns Firing Hazardous Waste" (Draft 2004).

#### 2.3.2 Burning in Space Heaters

Used oil is burned in space heaters specially designed for burning WO and are typically used in some countries to heat automotive repair garages. Volatile metals and chlorine compounds are emitted with the stack gas from the burner. The metal of most concern is lead (from leaded gasoline). Although the lead problem must soon disappear, as leaded fuel is banned from 2000, combustion in such equipment cannot be tightly monitored.

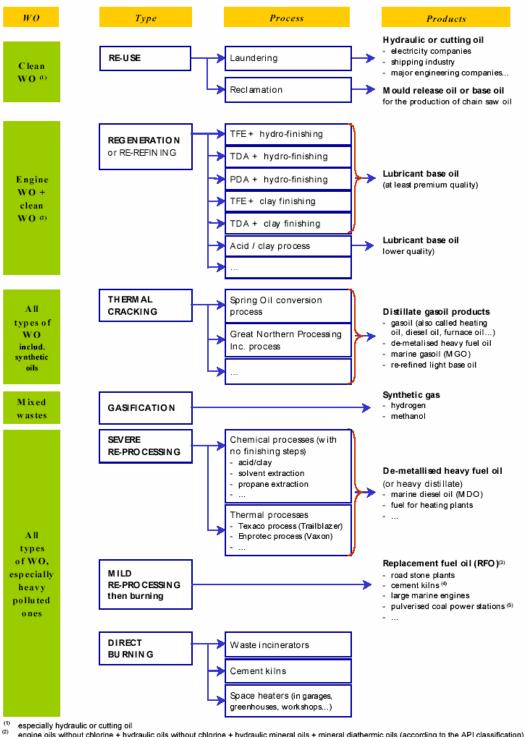
#### 2.3.3 Burning after "Mild" Reprocessing in Road Limestone Coating Plants

According to a report on the range of emissions observed at 26 sites in UK, the emissions of metals from stone coating plants was, in 1996, above those of cement kilns, but below the European emission limit values. In these plants, the pollutants, particularly metals, are captured by the stones, which are then encapsulated by bitumen for roads thus preventing leaching. The combustion temperature is not high enough to destroy PCBs and the report did not include information on emissions of chlorinated compounds such as PCDD/PCDF, PCB, and HCB.

# **3** EXISTING TECHNOLOGIES FOR WASTE OIL REGENERATION

## 3.1 European Situation

The different waste oil (WO) disposal routes as they exist in the European Union are shown in Figure 1.



engine oils without chlorine + hydraulic oils without chlorine + hydraulic mineral oils + mineral diathermic oils (according to the API classification) still containing the heavy metals, halogen and sulphur contained in the WO substitutes other secondary liquid fuel (SLF) or heavy fuel or coal or petroleum coke (3)

(4) (5)

as a furnace start up fuel

Figure 1: The different waste oil disposal routes (from EC 2001)

# 4 WASTE OIL RECYCLING: MARKETS, CAPACITIES, AND CONSTRAINTS

Five aspects of the regeneration need to be addressed:

- the type of WO which are regenerable (input),
- the quality of the base stock produced (out put) and the outlets,
- the existing technologies,
- the success criteria for a regeneration plant,
- the economics of regeneration.

Oil filter recycling also needs to be included into the management options for waste oils: most garages and workshops send oil filters for recovery at specialist plants. The standard process is to compress the filters, squeezing out the oil, which can then be treated using one of the above processes. The solid remainder, compressed into a block, is passed to metal reprocessing plants, although the contaminated nature of the filters means that the consignment has to be treated as special waste.

## **5** EXISTING REGENERATION TECHNOLOGIES

Even if most of the existing capacities are still operating the old acid / clay process, numerous major processes exist in Europe and world-wide.

They may differ by the technology used for one or several of the following operations:

- de-watering and de-fuelling (removal of water, light ends and fuel traces (naphtha10...)),
- de-asphalting (removal of asphaltic residues: heavy metals, polymers, additives, other degradation compounds),
- fractionation (in two or three cuts),
- finishing.

The following table describes most of them.

As for the finishing, the hydro-treatment is today the most efficient one. It aims at reducing or removing remaining metals and metalloids, organic acids, compounds containing chlorine, sulphur and nitrogen. Operating under a high pressure and at high temperatures, it also reduces the PAH (polycyclic aromatic hydrocarbon) content to an acceptable level (health implications said to be comparable to those of virgin base oil). Considering the quality demand by users and the increasing complexity of engine oils composition, a severe hydro-treatment may be less and less an optional extra in the future.

		Proc	ess <sup>12</sup>	_	Com-	Expecte			
Technology	De- watering <sup>14</sup>	De- asphalting <sup>15</sup>	Fractiona- tion <sup>16</sup>	Finishing <sup>17</sup>	mon plant size	d yield (dry basis) <sup>13</sup>	Advantages	Drawbacks	Comment
EXISTING TECHN	OLOGIES								
Acid/clay	(1) Atmospheric vacuum stripping <sup>18</sup>	sulphuric acid	(3) Distillation unit then neutralisa- tion and filtration	-	Small (2 to 10 kt/yr)	63%	<ul> <li>Relative low capital cost</li> <li>Relative simplicity of operations</li> </ul>	<ul> <li>Low product quality<sup>19 20</sup></li> <li>Localised adverse environmental impact of by- products (acid sludge &amp; clay)</li> </ul>	<ul> <li>The 1<sup>st</sup> regeneration process</li> <li>The most widely use (~90% of total capacity)</li> </ul>
Distillation / clay	(1) Atmospheric vacuum stripping	(2) Content with absorption clay	-	-		50%	<ul> <li>Less oily clay (than the acid/clay process) to be disposed of</li> </ul>	<ul> <li>Poor product quality</li> <li>Low yield</li> </ul>	<ul> <li>Projects do not come out</li> </ul>
Distillation / chemical treatment or solvent extraction	(1) Vacuum distillation (2 stages)	Vacuum	2) distillation tage)	(3) Chemical treatment or solvent extraction	Medium size (~25 kt/yr)	65 – 70%			<ul> <li>Vaxon process</li> <li>1 plant in Spain</li> </ul>

#### Description of the Main Regeneration Technologies

The chronological order of the operations are indicated with (1) or (2)...

<sup>13</sup> WO contains an average of 20% additives, 10% water, 8% engine blowback (gasoline and diesel fuel) and other contaminants

<sup>14</sup> De-watering + de-fuelling = removal of water, light ends and fuel traces (naphtha ...) <sup>15</sup> De-schelling = comparison of the schelling (between schelling) additions (between schelling)

<sup>16</sup> 2 or 3 cuts recovery

<sup>17</sup> Including the polycyclic aromatic hydrocarbons (PAH) removal in the case of a severe hydro-finishing (high temperature & high pressure)

The vacuum distillation indicated for the different processes takes place in a pre-flash unit The vacuum distillation indicated for the different processes takes place in a pre-flash unit

According to the Concave report [43], 4 to 17 times higher PAH content than virgin base oils (the health implications still need to be assessed)

<sup>20</sup> They are usually darker in colour and tend to have a noticeable odour

Figure 2: Description of main regeneration technologies

<sup>&</sup>lt;sup>15</sup> De-asphalting = removal of asphaltic residues (heavy metals, polymers, additives, other degradation compounds)

		Pro	cess	_	Commo	Expecte			
Technology	De- watering	De- asphalting	Fractiona- tion	Finishing	n plant size	d yield (dry basis)	Advantages	Drawbacks	Comment
EXISTING TECHNO	XISTING TECHNOLOGIES (CONTINUED)								
Propane	(1) Administration	(2)	(3)	(4)		74%	<ul> <li>High yield</li> <li>Coord module</li> </ul>	- More or less	- Viscolube
de-asphalting (PDA)	Atmospheric vacuum stripping	Liquid propane	Vacuum distillation	Clay or hydro- treatment			<ul> <li>Good product quality (if hydro- treated)</li> </ul>	expensive according to the number of stages for the PDA - Significant amount of by- products to be disposed of	
Interline	(2) Atmospheric vacuum stripping	(1) Liquid propane	(3) Vacuum distillation			79%	<ul> <li>Reduced capital &amp; operating costs</li> <li>High yield</li> </ul>		<ul> <li>Was existing in the UK</li> </ul>
Thin film evaporator (TFE)	(1) Atmospheric vacuum	(2) TFE (very high	(4) Vacuum distillation	(3) Hydro- treatment		72%	<ul> <li>High product quality</li> </ul>		<ul> <li>KTI process</li> <li>Revivol process</li> </ul>
& hydro-treatment	stripping (+ chemical treatment in some cases)	temperature and pressure)							

Figure 2 (cont'd): Description of main regeneration technologies

		Proc	ess		Com-	Expecte			
Technology	De- watering	De- asphalting	Fractiona- tion	Finishing	mon plant size	d yield (dry basis)	Advantages	Drawbacks	Comment
EXISTING TECHNO	DLOGIES (CON	TINUED)							
Thermal de-asphalting	(1) Atmospheric	(2) Settling + TD/		(3) Clay or	Large size (100	74 – 77%			<ul> <li>Agip Petroli / Viscolube in</li> </ul>
(TDA)	vacuum	Setting + 10/	•	hydro-	-180				Spain
	stripping + chemical treatment			treatment	kt/yr)				
TFE + lubricant refinery recycling		(2) TFE (very high temperature and pressure) ment in a tion plant		(3) Aromatic extraction + hydro- treatment Recycling in a refinery		65 – 70%			- DEA in Germany

Figure 2 (cont'd): Description of main regeneration technologies

		Pro	cess		Com-	Expecte			
Technology	De- watering	De- asphalting	Fractiona- tion	Finishing	mon plant size	d yield (dry basis)	Advantages	Drawbacks	Comment
NEW OPTIONS UN	DER DEVELOP	MENT							
UOP hydrogen	(3)	(1)	(4)	(2)					- At the
de-asphalting / treating	Atmospheric vacuum	Hydrogen flashing at	Vacuum distillation	Hydro- treatment					laboratory stage in 1996
	stripping	high temperature							_
ENTRA	(3) Atmospheric vacuum stripping	(1) Tubular reactor				High			
Supercritical extraction	(1) Atmospheric vacuum stripping	t2) Supercritical de- asphalting	<sup>(3)</sup> Supercritical fractionation				<ul> <li>Reduced capital &amp; operating costs when compared to the standard PDA technologies</li> </ul>		<ul> <li>Pilot plant stage in 1996 (Snamprogetti and Krupp)</li> </ul>

Source: mainly Concawe [19]

Remark 1: other combinations, not described in this table, could exist (e.g. TFE + clay contact, TFE + solvent extraction...).

Remark 2: as for the new options under development, the information available in the existing literature date from 1996 (the Concawe report [19]). Some of these projects may have been finished or given up in the meantime.

Figure 2 (cont'd): Description of main regeneration technologies

## 6 OCCURRENCE OF PCDD/PCDF IN USED OILS AND EMISSIONS

Hagenmaier and Brunner (1986) analyzed new motor oils, used motor oils (after 10,000 km in cars fueled with leaded gasoline), and recycled oil products for PCDD/PCDF. At a limit of quantification of 0.05  $\mu$ g/kg per congener, no PCDD/PCDF could be quantified in the fresh and used motor oils. However, higher chlorinated PCDD/PCDF were identified in recycled oils (sum of PCDD(Cl<sub>6</sub>-Cl<sub>8</sub>) = 24.8-69.1 ng/g and sum of PCDF(Cl<sub>7</sub>-Cl<sub>8</sub>) = 1.9-4.8 ng/g). Pentachlorophenol and its sodium salt, which in Europe were used in the mineral oil industry<sup>3</sup>, were identified as the source of the contamination.

The first limit value for PCDD/PCDF in Germany was established in September 1985 when a survey on various emitters in the State of Northrhine-Westphalia gave high concentrations in the stack gases from waste oil refineries. The regulation stipulated that only used oils with a PCB content of <1,000 mg PCB could be incinerated; the emission limit value was set at 0.1 ng/Nm<sup>3</sup> for 2,3,7,8-Cl<sub>4</sub>DD (TCDD) and 1 ng/Nm<sup>3</sup> for 2,3,7,8-Cl<sub>4</sub>DF (TCDF) (Bröker and Gliwa 1986). Concentrations of PCB in waste oils and PCDD/PCDF emissions from three plants that burned used oils (plants 1 and 2) and waste oil sludges (plant 3) are shown in Table 1 and Table 2. As can be seen the emissions from plant 3 clearly exceeded the limit of 0.1 ng 2,4,7,8-Cl<sub>4</sub>DD and all emissions were above the 1 ng/Nm<sup>3</sup> limit for 2,3,7,8-Cl<sub>4</sub>DF.

Table 1:	Concentrations of PCB in used oils (Bröker and Gliwa 1986)

Type of oil	PCB (6 congeners)	Total PCB (6 congeners x5)
	mg/kg	mg/kg
Used oil from plant	6.1	30.5
Used oil from motor vehicles	0.8	4.0
Scrap oil	13.3	66.5
Pooled sample from 5 garages	0.6	3.0

Table 2:Concentrations of PCB in used oils being burned and PCDD/PCDF emissions<br/>in the stack gases from three waste oil recycling plants incinerating these oils<br/>(Bröker and Gliwa 1986)

Plant	PCB input	2,3,7,8-Cl <sub>4</sub> DD	PCDD	2,3,7,8-Cl <sub>4</sub> DF	PCDF
	(ppm)	(ng/Nm <sup>3</sup> )	(ng/Nm <sup>3</sup> )	(ng/Nm <sup>3</sup> )	(ng/Nm <sup>3</sup> )
Plant 1	62	0.53	33.9	1.53	67.1
Plant 2	1.5	0.067	60.2	3.02	146
Plant 3	9.8	0.81	618	37.1	1,651

In a plant that recycled used oils, PCDD/PCDF analyses gave the results as shown in Table 3. The building had a rotary kiln and used heavy used oils and related wastes such as oils, acis resins, used tyres, *etc.* as fuels. It should be noted that the high PCDD/PCDF concentrations mainly were caused by the operation of the process (Fiedler *et al.* 1995).

<sup>&</sup>lt;sup>3</sup> According to the Association of the Chemical Industry, Germany, 5 to 60 tons of PCP and PCP-Na was sold annually to the mineral oil industry during the years 1979 and 1984.

Table 3:PCDD/PCDF concentrations in building materials from a waste oil recycling<br/>plant; concentrations in ng/kg (Fiedler *et al.* 1995)

Material	ΣPCDD	ΣPCDF	BGA-TEQ
Concrete floor (surface, down to 10 mm)	8,100	2,200	143
Concrete floor (interior 10-100 mm)	630	300	14
Wall brick (depth 1-10 mm)	90	50	17
Wall brick (inside 10-100 mm)	51	34	7
Chimney brick (40 m high, outer surface)	12	ND.	(0.1)

# 7 SELECTED COUNTRY SITUATION

The most common causes of oil pollution are inadequate storage and deliberate disposal down drains. This applies both to waste oil and to virgin oil. The Regulations are likely to affect all industrial, commercial and institutional users who accumulate oil in containers larger than 200 liters (DTI 2001).

## 7.1 European Union

## 7.1.1 Legislation

Waste oil is classified as hazardous waste (in chapter 12 and 13 of the hazardous waste list). The waste terminology in Directive 75/439/EEC on waste oils (such as disposal, processing, regeneration and combustion) differs from the framework Directives and the Waste Management Strategy. Thus "disposal of waste oil" means any treatment (processing, destruction, storage and tipping) whereas "disposal of waste" means operations listed in Annex II A such as incineration without energy recovery or landfilling.

The terminology of the Directive 87/101/EEC on waste oils differs from the terminology of the earlier Directive 75/442/EEC. The present Directive includes a definition of "waste oil" and waste oil management terminology such as disposal (any treatment/handling), processing (regeneration and combustion), regeneration (refining into base oils), combustion (use as fuel) and collection (ref. Article 1). The main objectives of the 1987 Directive is One of the main axes of the directive 75/439/EC on Waste Oils (WO), amended in 1987, is that, among the different options for recovery, priority is given to the regeneration of WO over their incineration.

The main provisions of Directive 75/439/EEC on waste oil and its amendment 87/101/EEC are as follows:

- The general objective of the waste oils management is to avoid any damage to man or the environment (Article 2);
- Hierarchy of waste oils management: priority is given to the processing of waste oils by regeneration; otherwise waste oils have to be burned under environmentally acceptable conditions; safe destruction and controlled storage or tipping when both other options are not feasible (Article 3);

- Prohibition of: discharge of waste oils into waters, discharge harmful to the soil and uncontrolled discharge, processing exceeding existing emission levels (Article 4);
- Public information and promotional campaigns to ensure appropriate storage and collection as far as possible; undertakings may carry out collection and/or disposal; Member States may decide to allocate the waste oils to any of the types of processing (Article 5);
- Permit requirement for undertakings, provisions for processing, provisions for combustion (emission values for plants with a thermal input of 3 MW and more, adequate control for plants with less thermal input) (Articles 6, 7, 8);
- Specific requirements with regard to PCB/PCT (Article 10);
- Requirement to keep records, convey of information to competent authorities, periodic inspections, examination of technical development and adaptation of permits (Articles 11, 12, 13).

## 7.1.2 European Union – Country Situation

The current situation of waste oil (WO) management in Europe can be summarized as shown below; however, it should be noticed that the data quality if poor.

- About 4,930 kt of base oils were consumed in Europe in 2000, among which about 65 % of automotive oils and less than 35 % of industrial oils.
- About 50 % of consumed oils are lost during use (combustion, evaporation, residues left in the container, etc.). The remaining 50 % represent the collectable WO.
- Engine oils represent more than 70 % of 2,400 kt of the collectable WO (black industrial oils about 5 % and light industrial oils less than 25 %).
- Engine oils (and to a lower extent black industrial oils) are potentially suitable for regeneration, whereas light industrial oils, clean, join an independent recovery circuit.
- The average WO collection rate reached about 70 %-75 % in the EU in 2000.
   Approximately 1,730 kt of WO were collected. The remaining 675 kt (25 %-30 %) are accounted as illegally burnt or dumped in the environment. It still vary from country to country.
- The efficiency of the WO collection systems is often very high for engine oils (more than 80 %) and low for black industrial oils (less than 10 %).

The WO collection rate in the year 2000 for the EU Member States is shown in Figure 3.

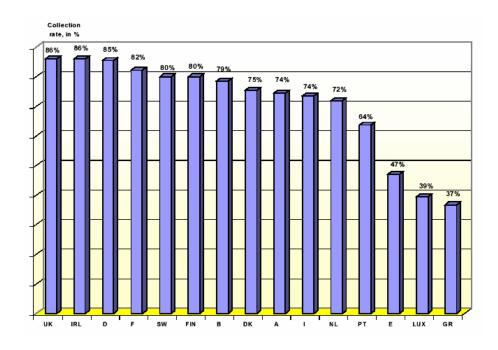


Figure 3: WO collection rate in EU Member States for 2000 (EC 2001)

- Appropriate collection and disposal arrangements for WO from industrial or automotive origin (garages, etc.) are generally well established in Europe. However, WO from "Do-it-Yourself" (DIY) oil changes are less likely to be collected and so present the greatest risk of improper disposal. Today, a lot of treatment processes exist (or are under development) in Europe. The most important are listed in Table 4.
- An average of 25 % of the collectable WO (and 33 % of the collected WO) would have entered a regeneration plant in the EU in 1999.
- About 50 % of WO were energetically used in the E.U., in 1999.
- Cement kilns play an important role in the energetic use of WO: about 400 kt of WO are burnt in cement kilns, which represents about 17 % of the total WO and 35 % of the WO burnt. Cement kilns are the major treatment route in France, Germany, and Sweden, and the only routes in Austria, Belgium, Italy, and the United Kingdom
- About 25 % of WO were still illegally disposed of in 1999.

Type of WO	Type of Treatment	Products
Clean WO	Reuse	<ul> <li>Hydraulic or cutting oils by: electricity companies, shipping industry, major engineering companies;</li> <li>Mould or base oil for the production chain saw oil</li> </ul>
Engine WO + clean WO	Regeneration or refining	Lubricant base oil
All types of WO including synthetic oils	Thermal cracking	<ul> <li>Distillate gas oil products, <i>e.g.</i>,</li> <li>gas oil (also called heating oil, diesel oil, furnace oil);</li> <li>de-metallized fuel oil;</li> <li>marine gas oil;</li> <li>re-refined light base oil.</li> </ul>
Mixed wastes	Gasification	Synthetic gas: hydrogen, methanol
All types of WO, especially heavy polluted ones	Severe re-processing	De-metallized fuel oil (or heavy distillate): marine diesel oil, fuel oil for heating
	Mild re-processing then burning	Replacement fuel, used in road stone plants, cement kilns, large marine engines, pulverized power stations, <i>etc</i> .
	Direct burning in waste incinerators, cement kilns, greenhouses, workshops, <i>etc</i> .	

#### Table 4: Treatment processes of WO applied in EU Member States

The following consolidated report is based on the questionnaire adopted by Commission Decision 94/741/EC of 24 October 1994. According to Directive 91/692/EEC Member States were obliged to submit their reports; however, the consolidated report only refers to eleven Member States.

The eleven Member States (two regions of Belgium, Denmark, Germany, France, Ireland, Luxembourg, the Netherlands, Austria, Finland, Sweden and the United Kingdom)<sup>4</sup>, which submitted their reports on the period 1995 to 1997 by 30 September 1998, confirmed that they have provided the Commission with details of the current laws and regulations in force to incorporate the Directive 75/439/EEC on the disposal of waste oils as amended into national law.

The provisions regarding the regeneration of waste oil include that Member States shall take the necessary measures to ensure that the operation of the regeneration plant does not cause avoidable damage to the environment (Article 7 (a)). In addition Member States ensure that base oils derived from regeneration do not constitute a hazardous waste and do not contain PCB/PCT in concentration beyond the limits of 50 part per million (ppm) (Article 7 (b)).

<sup>&</sup>lt;sup>4</sup> Greece, Italy, Portugal, and Spain did not send their reports

Status	Country	Domestic Waste Oil Regeneration
No report submitted	Greece, Italy, Portugal, and Spain	No information
No legislation in	Belgium – Walloon Region, Ireland,	No
place	the Netherlands	
	Austria	Yes
	France	Yes
Legislation in place	Denmark, Finland, and Sweden	No
	Germany (Federal Immission Control	Yes
	Act and Waste Oil Ordinance of	
	1987)	
	Luxemburg (Grand-Ducal Regulation	No
	of 30 November 1989)	
	United Kingdom (Environmental	Yes
	Protection Act 1990; Regulations on	
	Environmental protection	
	(Procedures and substances) 1991	
	Belgium – Flemish Region	No information

The report showed the following:

The Directive in Article 16 opens for more stringent national measures for the purpose of environmental protection. With the exception of France, Ireland, and the United Kingdom all reporting Member States indicated that they have taken more stringent measures than provided by the Directive for the purpose of environmental protection. These measures differ between stricter priority for regeneration (Luxembourg), stricter emission limit values (Germany), stricter values for the PCB content (the Netherlands). Remaining countries did not specify their measures.

#### 7.1.3 <u>Waste Oils Management</u>

In the years 1994/1995 and in the European Union, the mean rates of waste oil generated was 48 % and waste oil collected was 74.6%; the percentage share of regeneration was 36 % and of combustion was 64 %. The Commission considers the refining route as "regeneration" and the route untreated oil and the use after limited treatment for energetic use as well as the reprocessing into fuel oil as "combustion". It was found that the figures for waste oil generated differed widely between 33 and 66 % of the oil launched on the market.

#### 7.1.4 <u>Waste Oil Hierarchy</u>

According to Article 3 (1) and (2) Member States shall give the first priority to the regeneration of waste oils and second priority to the combustion of waste oils under environmentally acceptable conditions where technical, economic and organizational constraints so allow. Where the constraints do not allow regeneration or combustion, Member States shall take the necessary measures to ensure the safe destruction or controlled storage of waste oils (Article 3 (3)).

### 7.1.5 Limit Values and Other Obligations

According to Article 8 (1) Member States shall ensure that the emission values for combustion plants with a thermal input of more than 3 MW (Annex) are being observed. Member States may at any time set more stringent limit values or set limit values for other substances and parameters. Austria, Denmark, Finland and Germany implemented stricter limit values. Austria determined limit values for additional substances

The limit values for sulphur dioxide and dust, which had to be set by Member States, vary between 50 and 1,700 mg/Nm<sup>3</sup> for sulphur dioxide and between 10 and 100 mg/Nm<sup>3</sup> for dust.

According to Article 11 each Member State has to specify the quantity of waste oils (which must be below 500 liters per year) which oblige any establishment (producing, collecting and/or disposing of waste oil) to keep records. These records have to be conveyed on request to the competent authorities. Germany set a minimum quantity of 100 litres of waste oil.

#### 7.1.6 <u>Technical and Economic Analysis of WO Regeneration</u>

There is no major technical bottleneck for regeneration development since the technologies exist and the quality of base stocks produced is comparable to virgin base oils (Group I and even Group II when a severe hydro or solvent treatment is used for the finishing step). However, it remains to be seen whether the latest technical advances in regeneration prove to be sufficiently flexible to handle the changing composition of WO over the next 10 years and the possible increase of bio-lubricants consumption.

The above mentioned uncertainty generates risks for investors in regeneration facilities.

The economic bottleneck is obvious. In most of the cases, a regeneration plant is not economically self sufficient from the beginning<sup>5</sup>. At the tail end, potential users of re-refined base oils, in the automotive or industrial sector, are still reluctant to use regenerated products.

## 7.2 Germany

In Germany, plants for the distillation, raffination or further treatment of crude oil or crude oil products in mineral oil, waste oil or lube oil refineries need a permit according to the German Law on Immissions (BImSchG) and the 4<sup>th</sup> Ordinance on Immissions (4<sup>th</sup> BImSchV).

#### 7.3 United States of America

API: More than 640 million gallons of motor oil were sold in 1997; 345 million gallons of that was sold to do-it-yourselfers (those that change their own oil), with the remaining going

<sup>&</sup>lt;sup>5</sup> It would need to receive between 10 and 100 Euros for each ton delivered to the plant, depending on the technology, the capacity and the market conditions.

to the do-it-for-me service industry. Many service stations with repair facilities and oil change shops will accept your used oil for no charge

Reprocessing is the most common method of recycling used oil in the U.S. Each year processors treat approximately 750 million gallons of used oil. However, it seems that the U.S. have a definition of "recycling" different from other countries. The report states that seventy-five percent of used oil is being reprocessed and marketed to:

- 43 % asphalt plants;
- 14 % industrial boilers (factories);
- 12 % utility boilers (electric power plants for schools, homes, etc.);
- 12 % steel mills;
- 5 % cement/lime kilns;
- 5 % marine boilers (tankers or bunker fuel);
- 4 % pulp and paper mills;
- >1 % commercial boilers (generating heat for school, offices, *etc.*);
- 5 % other.

## 8 **REFERENCES**

API: American Petroleum Institute, USA. WebPage http://www.recycleoil.org/

Bröker G. (1980): Altölraffination – ein sinnvolles Recyclingverfahren? Schriftenreihe der Landesanstalt für Immissionsschutz des Landes NRW, Heft **50**, 7-16

Bröker G. And H. Gliwa (1986): Dioxin- und Furanemissionen bei der Verbrennung von Altöl. Staub – Reinh. Luft **46**, 435-438

DTI (2001): Waste Oil Recycling. Information sheet by Department of Trade and Industry, London, UK

EC (2001): Critical Review of Existing Studies and Life Cycle Analysis on the Regeneration and Incineration of WO. Study 20 AW 83–5 prepared by Taylor Nelson Sofres Consulting for European Commission, DG Environment A2 – Sustainable Resources Consumption and Waste, Brussels, Belgium, December 2001

EU (1975): Directive 75/439/EEC on waste oils. Commission of the European Community OJ L 194, 25.07.1975, pp 31

EU (1987): Directive 87/101/EEC = amendment to Directive 75/439/EEC. OJ L 42, 22.12.1986, pp 43

Fiedler H., C. Lau, G. Rippen, H.F. Wesp, O. Hutzinger, F. Vahrenholt, S. Sievers, P. Friesel, B. Gras, T. Reich, U. Schacht, and R. Schwörer (1996): Dioxin-Bilanz für Hamburg. *in:* Rippen – Handbuch Umweltchemikalien, 37.-41. Erg. Lfg. 12/96 ff (320 pages). ecomed Verlagsgesellschaft, Landsberg, Germany

Hagenmaier H. and H. Brunner (1986): Bestimmung polychlorierter Dibenzodioxine und polychlorierter Dibenzofurane in Motorölen, Altölen und Zweitraffinaten. Fresenius Z. Anal. Chem. **324**, 23-26