

U.S. EPA HPV Challenge Program
Category Assessment Document for
Reclaimed Petroleum Hydrocarbons:
Residual Hydrocarbon Wastes from Petroleum Refining

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Summary

The following category assessment examines residual hydrocarbon wastes recovered when crude oil is refined into fuels and other downstream products. These waste streams are all complex substances that are reflective of the crude oils and product streams generated within an oil refinery. Because waste streams are not uniform and are often mixed and combined in a tank or other containment structure, the composition of the wastes are not static, but change rapidly as they are collected and stored for processing. Typically they contain hydrocarbons boiling over 350 degrees Fahrenheit and may contain significant amounts of polycyclic aromatic compounds (PAC).

Many, but not all, of these waste streams are generated, 1) when process wastewater undergoes primary treatment, 2) inside storage tanks as accumulated sludges or sediments, and 3) as a result of the recovery and reuse of intermediate products or wastes. The wastes can either exist as oily liquids, aqueous emulsions, or sludges depending on their source within the refinery, the type of crude being processed, and the degree of recovery and reuse the wastes have undergone. They all generally contain some water and solids, which can alter their appearance and method of disposal.

Many physical property differences between waste oils, emulsions, and sludges can be explained by differences in hydrocarbon content. Properties such as polarity and molecular weight will impact other related properties in a very predictable fashion. However, the actual properties of these waste materials are dictated by their overall composition, which in most cases is too complex to allow an accurate determination using an estimation routine. This is consistent with available information showing that the boiling range for many waste samples can span 800 °F (less than 200 °F to greater than 1000 °F).

If released to the environment, the constituents within these complex substances will partition, distribute, and degrade in accordance with their own chemical properties. Because these substances contain a high percentage of hydrophobic substances, direct releases to water bodies will result in soil and sediment accumulation and little aqueous dissolution. Vaporization is also possible for those chemical constituents with measurable vapor pressure. Available information shows that the hydrocarbons in these wastes will eventually degrade in the environment by biological means.

The information available for residual fuel oils are believed to provide an adequate surrogate for assessing the ecotoxicity of the hydrocarbon wastes in this category. The lethal and effective loading rates (EL₅₀) from studies on residual fuel oils indicate that the acute aquatic toxicities to rainbow trout and daphnia were greater than 100 mg/L. In algae (*Raphidocelis subcapitata*) the 72-hour inhibitory effect EL₅₀ levels falls in between 30 and 100 mg/L (30<EC50<100).

The acute health effects of residual hydrocarbon waste surrogates demonstrate that the acute oral toxicity of these streams is expected to be greater than 5000 mg/kg and the acute dermal toxicity greater than 2000 mg/kg. Positive in vitro mutagenicity assays have been reported for many residual hydrocarbon waste surrogates. The in vivo mutagenicity assay results

are equivocal. Subchronic studies and reproduction/developmental studies are available for two different types of hydrocarbon waste. The findings from dermal studies show that the systemic effects of a DAF float blend were greater than those observed following treatment with a sample of API separator sludge. Other studies on hydrocarbon waste surrogates support a relationship between PAC content of the mixture and the subchronic and developmental effects observed following the dermal treatment of rats.

1. Introduction

All of the substances in this category are derived from the refining of petroleum crude oil.

Table 1. Residual Hydrocarbon Waste Streams Included in the Category Assessment

CAS #	CAS Name	CAS Definition
68476-53-9	Hydrocarbons, C more than 20, petroleum wastes	A complex combination of hydrocarbons produced as waste material from slop oil, sediments, and water. It consists of hydrocarbons having a carbon number predominantly greater than C ₂₀ and boiling above approximately 350 °C (662 °F).
68477-26-9	Waste, petroleum	The waste products from any petroleum refinery or production process which has been dewatered. It is commonly called slop oil.
68918-73-0	Residues (petroleum), clay-treating filter wash	A complex residuum from the solvent washing of clay-treating filters. It consists predominantly of unsaturated hydrocarbons having carbon numbers predominantly greater than C ₂₀ and boiling above approximately 350°C (662 °F).

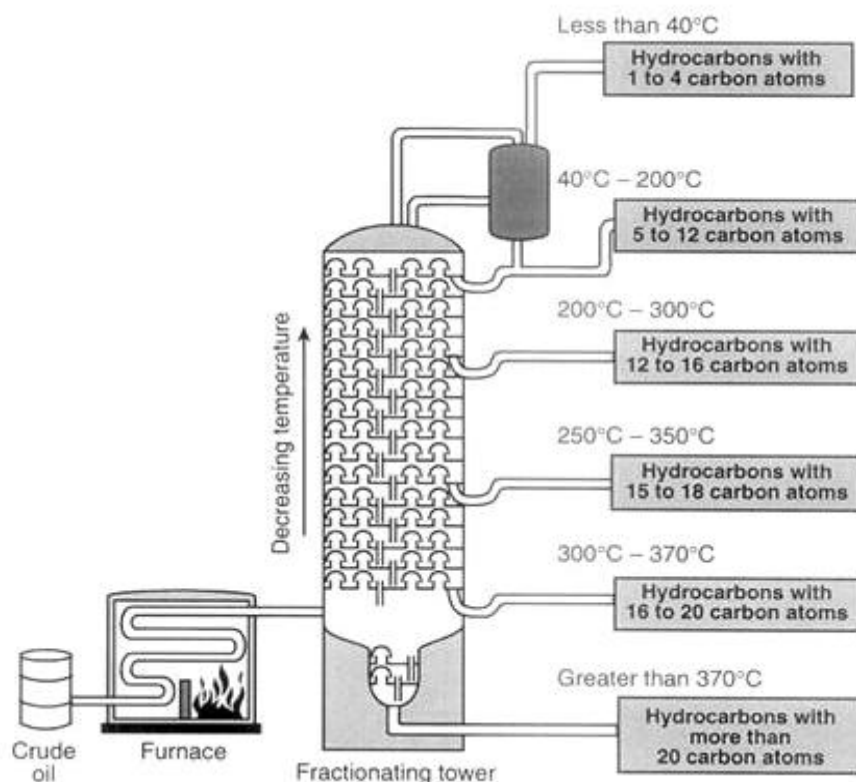


Figure 1. Crude Oil Distillation Process

As shown in Figure 1, the refining of crude oil into petroleum products uses distillation as well as chemical treatment, catalysts, and pressure to separate and combine the basic types of hydrocarbon molecules into petroleum streams, which have the characteristics needed for blending commercial petroleum products. As is the case for many industrial processes, the refining of petroleum products produces a number of unintentional byproducts, wastes, and other hydrocarbon-containing process streams that are not typically sold as products. For example, oil is recovered from wastewater streams and the catalysts, filters and other materials in contact with oil are washed to recover hydrocarbons. The oil that is occasionally spilled and the oil recovered from wastewater treatment are generally recycled back into the refinery. Table 2 shows the different waste stream categories that can be found within a modern oil refinery. API (American Petroleum Institute) separator sludge, DAF (Dissolved Air Flotation) floats, and FFU (Flotation-Flocculation Unit) sludges are of particular interest because they are generated in the greatest volume within a refinery (Haverhoek, 1987). All of these hydrocarbon wastes have been incorporated into this category assessment.

Table 2. Types of Refinery Waste*

Hydrocarbon Wastes	Spent Catalysts
API separator sludge	Fluid cracking catalyst
Dissolved air flotation float	Hydroprocessing catalyst
Slop oil emission solids	Spent inorganic clays

Tank bottoms	Miscellaneous spent catalysts
Other separator sludges	
Pond sediment	Chemical/Inorganic Wastes
FFU sludges	Spent caustic
Desalter bottoms	Spent acids
Waste oils/solvents	Waste amines
Miscellaneous oil sludges	Miscellaneous inorganic waste
Contaminated Soils and Solids	Aqueous Waste
Heat exchanger bundle cleaning sludge	Biomass
Waste coke/carbon/charcoal	Oil contaminated water (not wastewater)
Waste sulfur	High/low pH water
Miscellaneous contaminated soils	Spent sulfidic solutions

* taken from Bush and Levine, 1992

2. Hydrocarbon Waste Disposal

More than 80% of the hydrocarbons waste generated within a refinery is reused, reclaimed, or recycled with the remaining 20% eliminated by an acceptable disposal method. From a disposal perspective, the waste materials generated at different unit operations within a refinery can be conveniently segregated into two groups: oily waste or sludge waste. This distinction is somewhat artificial since both waste types often coexist, with the sludge wastes often containing sizable amount of oil and the oil wastes containing noticeable amounts of sludge (Brown *et al.*, 1985). The main difference between oily waste and sludge waste is related to the amount of organic and inorganic solids in the waste stream. Those hydrocarbon wastes with high suspended solids will often be disposed of differently than those having high oil content (Hess, 1979). Unlike these two categories, oily emulsions are classified as a type of waste that is processed into oily waste and sludge only after the water has been removed.

Many, but not all, oily hydrocarbon wastes are listed as hazardous under RCRA (USEPA, 1995). The following definition of hazardous waste applies to those wastes generated by oil refineries in the United States. Hazardous hydrocarbon wastes are described as:

Any sludge and/or float generated from the physical and/or chemical separation of oil/water/solids in process wastewaters and oily cooling wastewaters from petroleum refineries. Such wastes include, but are not limited to, sludges and floats generated in: induced air flotation units, tanks and impoundments, and all sludges generated in DAF units. Sludges generated in stormwater units that do not receive dry weather flow, sludges generated from non-contact once-through cooling waters segregated for treatment from other process or oily cooling waters. Sludges generated in aggressive biological treatment units including sludges and floats generated in one or more additional units after wastewaters have been collected.

The following industry waste streams from petroleum refining have been designated as hazardous under RCRA:

- Dissolved air flotation float

- Slop oil emulsion solids
- Heat exchanger bundle cleaning sludge
- API separator sludge
- Petroleum refinery primary oil/water/solids sludge
- Petroleum refinery secondary (emulsified) oil/water/solids separation sludge
- Clarified slurry oil storage tank sediment

The 1984 Hazardous and Solid Waste Amendments (HSWA) to the Resource Conservation and Recovery Act (RCRA) established strict standards for the handling, storage and disposal of all regulated hydrocarbon wastes. As part of the regulations, all surface impoundments which treat or store hazardous wastes must either be double lined or taken out of service. In addition, hazardous materials within surface impoundments and contaminated soil beneath the impoundments must be removed and disposed of in secure landfills or treated and properly disposed of on-site. This regulation, in effect, eliminated the storage of oily sludge in unregulated surface impoundments or lagoons (Bhattacharyya and Shekdar, 2003). Whereas, the oily wastes isolated from wastewater and other unit operations are generally combined and sent to the slop oil tank for temporary storage, sludges generally find their way to storage basins before being processed. The disposal methods for these two waste types are somewhat different given the high percentage of reusable material in oily waste and the large amount of unusable solids in sludges.

A. Oily waste

Slop oil is any petroleum product that does not meet product specifications and cannot be used or distributed without further processing (WDEQ, 1991). The slop oil system includes a marshalling operation aimed at eliminating the discharge of usable product into wastewater. Slop oil systems are comprised of collection points that are situated at all of the major sources where wastes are generated. If a small volume of oily waste is generated, the slop oil system may simply be a collection drum. If facilities generate large volumes of waste product, they will be directly piped from the generation point to the marshalling area.

The ultimate fate of slop oils is dictated by the amount of bottom sediment and water (BS&W) it contains, which can be determined analytically using an ASTM method. Slop oil with a BS&W less than 1% is an ideal candidate for reprocessing and reuse. It is far more common, however, to find slop oils with a BS&W ranging from 5 to 60% and a solids content of nearly 20% (Rhodes, 1994). Unless slop oil has a sufficiently low BS&W content, indiscriminate recycling by addition to the distillation unit desalter will cause excessive corrosion in the downstream equipment. The primary disposal methods of oily waste include:

- re-refined in the distillation unit
- direct use as a fuel
- shipment off-site for hydrocarbon recovery
- deep well injection
- landfilling in a regulated and approved site

B. Sludge

There are a variety of disposal methods for the sludge emanating from refinery operations (USEPA, 1996). Each refinery tends to use a particular method based on economic

considerations, historical preferences, and the local geography (Alshammari *et al.*, 2008). New environmentally friendly disposal methods are continuously being developed and tested, but many lose favor due to cost concerns, environmental issues, or less than expected efficiencies (Marks *et al.*, 1992; Stepnowski *et al.*, 2002). A major concern in the disposal of both waste oils and sludges is the PAC concentration, which is major factor in determining the intrinsic health and environmental hazards associated with each waste stream (Kothandaraman *et al.*, 1992).

The sludge disposal methods found to be in greatest use today include:

- landfilling in a regulated and approved site
- use as a starting material in the delayed cokers, which cracks the heavy long chain hydrocarbon molecules into smaller molecular gas and oil products, as well as petroleum coke
- use as a starting material for the production of bitumen
- incineration in a rotary kiln

3. Residual Hydrocarbon Waste Composition

Petroleum crude is a complex substance containing thousands of different organic hydrocarbon molecules. It contains 83-87% carbon, 11-15% hydrogen, and 1-6% sulfur. Three types of hydrocarbons predominate: paraffins (saturated chains), naphthenes (saturated rings), and aromatics (unsaturated rings). In many respects, the chemical composition of waste oils and sludges provides a snapshot of individual crude oil components at any particular stage of the refining process. This method of characterizing the individual waste streams is somewhat imprecise. Because individual wastes are not uniform and are often mixed and combined in a tank or other containment structure, the composition of the wastes are not static, but change rapidly as they are collected and stored for processing. For this reason, the compositional information described in the following paragraphs should not be viewed as an absolute characterization, but rather as a general picture that is subject to change depending on the type of crude being refined and wastes being collected.

Information regarding the composition of waste oils and sludges can be located in many sources. Much of this work, however, is rather simplified and rudimentary and often applies to one particular type of slop oil or sludge (Bojes and Pope, 2007). There has been no systematic attempt at characterizing the chemical composition of all the hydrocarbon waste types from a refinery operation. Published data does show, however, that these wastes often contain variable amounts of sulfides, phenols, heavy metals, aliphatic hydrocarbons, and aromatic hydrocarbons along with sizable amounts of PAHs. The lack of specific information on all of the waste types covered in this category assessment is not considered to be major concern, since each of the wastes undoubtedly contains a wide variety of aliphatic, aromatic, and 2-7 ring PACs, which are the constituents of greatest concern when evaluating potential health and environmental hazards. The results from several key studies have been summarized in the following paragraphs. The summary is intended to show the variability and chemical complexity associated with hydrocarbon waste streams and to characterize the different types of hydrocarbons that may be present.

As shown in Table 3, the sludge from a DAF unit contained appreciably high amounts of aliphatic hydrocarbons as well as PAHs, naphthalene, fluorine, and phenanthrene. The results revealed considerable batch to batch variation, as seen from the high standard deviations and the large spread in measured values.

Table 3. Hydrocarbon Concentrations for Flocculation-Flotation Unit Sludge*

Constituent	Number of Rings	Concentration Mean	Standard Deviation	Range
Total petroleum hydrocarbon (g/kg)	---	145	21.2	130 – 160
Nonpolar aliphatic hydrocarbon	---	63.67	16.7	54 – 83
Nonpolar aromatic hydrocarbon (g/kg)	---	0.08	0.04	0.04 – 0.12
Total extractable aliphatic hydrocarbon (g/kg)	---	69.33	24.8	55 – 98
Total extractable aromatic hydrocarbon (g/L)	---	0.08	0.04	0.04 – 0.12
Acenaphthylene (mg/kg)	3	2.28	0.6	1.5 – 2.8
Acenaphthene (mg/kg)	3	9.75	5.9	1 – 14
Fluorene (mg/kg)	3	27.25	10.0	17 – 41
Phenanthrene (mg/kg)	3	43.75	18.4	25 – 69
Anthracene (mg/kg)	3	3.25	2.0	1.5 – 5
Fluoranthene (mg/kg)	4	2.63	0.6	1.9 – 3.4
Pyrene (mg/kg)	4	6.33	3.8	0.8 – 9.3
Benzo[a]anthracene (mg/kg)	4	2.95	0.9	2.2 – 4.1
Chrysene (mg/kg)	4	9.88	3.3	5.7 – 13.0
Benzo[b&k]fluoranthene (mg/kg)	5	1.74	0.8	1.0 – 2.8
Benzo[a]pyrene (mg/kg)	5	0.89	0.3	0.6 – 1.2
Indo[1,2,3-c,d]pyrene (mg/kg)	5	0.60	0.4	0.1 – 1.0
Dibenzo[a,h]anthracene (mg/kg)	5	0.66	0.3	0.3 – 1.0
Benzo[g,h,i]perylene (mg/kg)	6	0.83	0.2	0.5 – 1.0

* taken from Kriipalu *et al.*, 2008; sample size is 3-4 for each analyses

Similarly, the bottom sludge from a crude oil storage tank was shown to contain a number of 4, 5, and 6 ring PAHs that were present over a 10-20-fold concentration range (Li *et al.* 1995).

In many instances, attention has been focused on the analysis of those PAHs and PACs typically found in waste streams, since these chemicals are an important determinant of the overall hazard. Table 4 provides a revealing comparison of the hydrocarbon constituents in slop oil and wastewater sludges from a Midwestern refinery (Burks and Wagner, 1982). The hydrocarbon concentrations in the slop oil and sludge from an API separator and the sludge from

a DAF unit were determined using a RCRA approved method. Although the method was capable of distinguishing between a large number of aromatic and polyaromatic compounds, it was not able to uniquely identify isomeric forms of substituted PAHs or some aromatic structures with the same number of rings. Consequently, isomeric ring structures such as chrysene and benzanthracene could not be unambiguously separated. The results showed that both the waste oil and sludge contained relatively high amounts of various PAHs, with the sludge samples containing a higher concentration of 4 and 5 ring PAHs.

Table 4. Chemical Composition of Slop Oil and Sludges from an Oil Refinery*

Constituent	API Slop Oil Emulsion	API Sludge	DAF Floating Solids
Toluene (mg/L)	5.78	2.72	5.72
Xylene (mg/L)	0.10	---	0.53
Trimethylbenzene (mg/L)	0.31	0.06	0.11
Methylethylbenzene (mg/L)	0.10	---	---
Methylpropylbenzene (mg/L)	0.06	---	---
Dimethylethylbenzene (mg/L)	0.21	---	---
Tetramethylbenzene (mg/L)	0.29	0.04	0.24
C ₅ – benzene (mg/L)	1.16	---	---
Dihydroindene (mg/L)	0.04	---	---
Methyl dihydroindene (mg/L)	0.04	1.00	---
C ₂ – dihydrindene (mg/L)	0.60	---	---
Naphthalene (mg/L)	1.61	0.15	0.32
Methyl naphthalene (mg/L)	9.83	1.20	2.58
Dimethyl naphthalene (mg/L)	15.98	3.19	5.35
Ethyl naphthalene (mg/L)	1.08	0.57	0.45
C ₃ – naphthalene (mg/L)	11.73	2.44	4.48
C ₄ – naphthalene (mg/L)	1.61	0.84	0.70
Tetrahydrohaphthol (mg/L)	0.26	---	---
Dimethyldihydronaphthalene (mg/L)	0.14	---	---
Methyl tetralol (mg/L)	0.20	---	---
Dimethyl thianidene (mg/L)	0.08	---	0.11
Biphenyl (mg/L)	0.56	---	0.18
Acenaphthene(mg/L)	0.13	---	0.32
Methyl (acenaphthene/biphenyl) (mg/L)	5.11	0.58	1.43
C ₂ – (acenaphthene/biphenyl) (mg/L)	1.58	---	0.50
C ₃ – (acenaphthene/biphenyl) (mg/L)	---	---	0.46
Fluorene (mg/L)	1.25	0.14	0.26
Methyl fluorene (mg/L)	1.48	0.76	0.36
C ₂ – fluorene (mg/L)	1.18	0.40	0.97
C ₃ – fluorene (mg/L)	0.52	0.11	0.58
Naphthol thianaphthene (mg/L)	---	0.84	1.31
Dibenzothiophene (mg/L)	0.56	0.50	0.62
Methyl dibenzothiophene (mg/L)	1.36	1.00	1.62
C ₂ – dibenzothiophene (mg/L)	0.24	2.10	3.72
C ₃ – dibenzothiophene (mg/L)	---	0.82	---
Anthracene/phenanthrene (mg/L)	5.14	3.57	6.23
Methyl (anthracene/phenanthrene) (mg/L)	11.64	13.85	21.90

C ₂ – (anthracene/phenanthrene) (mg/L)	8.60	16.36	22.54
C ₃ – (anthracene/phenanthrene) (mg/L)	2.23	5.67	4.20
C ₄ – (anthracene/phenanthrene) (mg/L)	---	1.90	1.44
C ₅ – (anthracene/phenanthrene) (mg/L)	---	0.22	
Pyrene/fluoranthene (mg/L)	1.65	9.43	10.16
Methyl (pyrene/fluoranthene) (mg/L)	2.13	---	11.47
C ₂ – (pyrene/fluoranthene) (mg/L)	0.51	6.04	6.30
C ₃ – (pyrene/fluoranthene) (mg/L)	---	16.86	---
Chrysene/benzanthracene (mg/L)	1.51	14.90	15.26
Methyl (chrysene/benzanthracene) (mg/L)	0.35	13.84	9.67
Benzopyrene/benzofluoranthene (mg/L)	2.86	22.71	11.43

* taken from Burks and Wagner, 1983

The aromatic ring class (ARC) content of some petroleum waste samples has been determined by analyzing an organic extract of the waste stream using a gas chromatography/flame ionization detection technique (Roy *et al.*, 1988). This approach focuses on the distribution of aromatic ring class (ARC) and allows easy identification of those samples containing a particular PAC profile. This is important for both environmental and human health hazard determinations, where studies have shown that the ring class can have an impact on fate and potency (Neff *et al.*, 2005; ATSDR, 1995, TERA, 2008, API, 2008). Table 5 shows the distribution of aromatic ring classes for the PACs found in some hydrocarbon waste samples submitted by Petroleum HPV member companies (PRR, 2009).

Table 5. Compositional Analysis of Wastes, Petroleum (CAS 68477-26-9)

Samples of CAS 68477-26-9	Boiling Range (°F) (T10-T90)	DMSO (%) *	ARC 1 (%)#	ARC 2 (%)	ARC 3 (%)	ARC 4 (%)	ARC 5 (%)	ARC 6 (%)	ARC 7 (%)
WASTES, PETROLEUM	339 – 585	15.7	1.6	9.4	3.1	0.3	0.0	0.0	0.0
WASTES, PETROLEUM	407 – 1051	5.2	0.2	2.6	1.0	0.5	0.4	0.3	0.0
WASTES, PETROLEUM (SLOP OIL)	342 – 715	16.2	3.2	6.5	3.2	1.5	1.1	1.0	0.0
WASTES, PETROLEUM (SLOP OIL)	314 – 834	15.9	1.6	8.0	3.2	1.0	0.8	1.0	0.0
WASTES, PETROLEUM (SLOP OIL)	212 – 957	16.4	1.6	6.6	4.9	1.6	1.1	1.3	0.0
WASTES, PETROLEUM (SLOP OIL)	217 – 1033	12.7	0.6	8.9	3.8	0.3	0.0	0.0	0.0
WASTES, PETROLEUM (SLOP OIL, DEWATERED)	216 – 971	1.8	0.0	1.4	0.4	0.0	0.0	0.0	0.0
WASTES, PETROLEUM (SLOP OIL, DEWATERED)	212 – 757	0.3	0.0	0.1	0.2	0.0	0.0	0.0	0.0
WASTES, PETROLEUM	404 – 874	4.1	1.2	2.9	0.2	0.0	0.0	0.0	0.0
WASTES, PETROLEUM	218 – 935	1.7	0.1	0.9	0.5	0.1	0.1	0.0	0.0
WASTES, PETROLEUM	262 – 960	15.7	1.6	9.4	3.1	0.3	0.0	0.0	0.0
WASTES, PETROLEUM	82 – 1126	5.2	0.2	2.6	1.0	0.5	0.4	0.3	0.0

Aromatic ring class (ARC) is the is the weight percent of PACs that have the state number aromatic rings within the total sample.

* Percent of DMSO-extractable polycyclic aromatic compounds (PACs) as determined by PAC 2 Method as described by API (2008).

4. Category Justification

These waste streams are all complex substances that are reflective of the crude oils and product streams generated within an oil refinery. Because wastes streams are not uniform and are often mixed and combined in a tank or other containment structure, the composition of the wastes are not static, but change rapidly as they are collected and stored for processing. Typically they contain hydrocarbons boiling over 350 degrees Fahrenheit and may contain significant amounts of polycyclic aromatic compounds (PAC). All exist as liquids, emulsions, or suspensions at room temperature with variable solution densities and viscosities. Although the toxicity of individual hydrocarbon wastes has not been extensively studied, much can be surmised by looking at hydrocarbon substances of similar composition. Thus, refinery streams and products from other HPV petroleum categories can serve as surrogate substances and provide toxicity hazard information for these waste streams.

5. Physical Chemical Properties

Although hydrocarbon wastes are generally categorized as either oils or sediments, they can actually exist in three physical forms: simple oil, an emulsion, or sludge. All three forms contain crude oil components and also include three individual ingredients in varying proportions: oil, water, and solids. In fact, the primary difference between the three waste forms is the ratio of water and solids within the oily matrix. Simple waste oils generally contain less water than sludges, which are highly viscous and contain a high percentage of solids.

Waste oil emulsions, commonly known as the rag layer, are particularly unique and have physical properties quite different from oils and sludges. This uniqueness is highlighted in Figure 2. Whereas, oily wastes and sludges exist as dark brown to greenish black liquids, waste emulsions are lighter in color. The small dispersed oil drops in emulsions are affected by gravity and surface tension, which causes them to coalesce into larger drops that rise to the top of the water. This process ultimately causes the hydrocarbon emulsion to separate into an aqueous layer and an oily top layer. Depending on how the emulsion is formulated and the physical environment, the physical separation may take minutes, months, or years.



dissolved oil emulsified oil separated oil

Figure 2. Appearance of Oil/Water Mixtures

Because of the amorphous and highly variable nature of these three waste streams, there has been no systematic attempt to determine their chemical and physical properties. The boiling point, melting point, volatility, octanol/water partition coefficient, and water solubility are all affected to a large degree by both their coarse composition and by the nature of the chemical constituents in the oil phase. Consequently, property measurements associated with one waste stream cannot be applied to another stream or to another sample of the same waste collected on a different day or different location.

Despite these limitations, there are some general facts that can be offered regarding the physical properties of these residual hydrocarbon waste streams. As shown below in Table 6, the oil, water, and solids content of different wastes can vary significantly, with the oil content sometimes approaching 50% of the total composition. Slop oils tend to contain somewhat less water because they are recovered earlier in the waste accumulation process before a substantial amount of mixing has occurred. In contrast, tanks bottoms sludge contains a higher percentage of the solids that will settle upon storage.

Table 6. Physical Characteristics of Representative Hydrocarbon Waste Streams*

Type of Waste	Appearance	Oil (%)	Water (%)	Solids (%)
Slop oil	emulsion	48	40	12
API separator sludge	suspension	23	53	24
DAF float	liquid	13	84	3
Tank bottoms	suspension	48	13	39

* taken from (Bider and Hunt, 1982)

Property testing of these materials is complicated by the myriad of possible hydrocarbon combinations that are possible. In fact, these materials possess such extreme

property values, especially for K_{ow} and water solubility that any analytical determination will likely exceed the limits of the assay, at least for some types of waste. For this reason, only general property estimates can be provided. These data can be used along with standard physical property compilations for the hydrocarbons found in petroleum products to estimate the behavior of a particular waste type when the composition is known (Heath *et al.*, 1993).

Table 7. Relative Change in the Key Properties of Different Waste Forms

Waste Form	Solids	Avg. Mol. Weight	PAH Content	Boiling Point	Volatility	Water Solubility
oily waste	↓ increases	↓ increases	↓ increases	↓ increases	↓ decreases	↓ decreases
Emulsions						
Sludges						

Many physical property differences between waste oils, emulsions, and sludges can be explained by differences in hydrocarbon content. As shown in Table 7, properties such as polarity and molecular weight will impact other related properties in a very predictable fashion. These changes are consistent with the increased amounts of high molecular weight PACs found in sludges versus oily wastes. It is important to recognize, however, that the actual properties of these waste materials are dictated by their overall composition, which in most cases is too complex to allow an accurate determination using an estimation routine. This is consistent with available information showing that the boiling points for many wastes range from less than 93 °C (200 °F) to greater than a 538 °C (1000 °F) (see Table 5). Similarly, information generated in freeze thaw experiments with oily emulsions indicate that many of these wastes will freeze at temperatures of -20 °C (-4 °F); but the range of values for individual wastes has not been determined (Jean *et al.*, 1999).

Although it is difficult to predict the properties associated with any particular hydrocarbon waste due to the vagaries of chemical composition and water content, it is possible to empirically estimate how each property will change as the oil, water, and solids content changes. A key factor affecting each of these properties is the polarity and molecular weight of the constituents. As the solids content of the waste increases so will the relative concentration ratios and molecular size of the individual components. This change will in turn affect the overall boiling point, water solubility, vapor pressure, and soil sorption coefficients of the wastes in the direction noted in Table 8. The values show that the aliphatic constituents found in hydrocarbon wastes have a lower boiling point, lower water solubility, and higher vapor pressure than the aromatic constituents. The variability associated with these property values can span several orders of magnitude.

Table 8. Representative Physical Properties for TPH Fractions*

Fraction	Boiling Point (°C)	Water Solubility (mg/L)	Vapor Pressure (atm)	Log K _{oc}
Aliphatic				
EC ₅ – EC ₆	51	36	0.35	2.9
EC _{>6} – EC ₈	96	5.4	0.063	3.6
EC _{>8} – EC ₁₀	150	0.43	0.0063	4.5
EC _{>10} – EC ₁₂	200	0.034	0.00063	5.4
EC _{>12} – EC ₁₆	260	0.00076	0.000048	6.7
EC _{>16} – EC ₃₅	320	0.0000025	0.0000011	8.8
Aromatic				
EC ₅ – EC ₇	80	220	0.11	3.0
EC _{>7} – EC ₈	110	130	0.035	3.1
EC _{>8} – EC ₁₀	150	65	0.0063	3.2
EC _{>10} – EC ₁₂	200	25	0.00063	3.4
EC _{>12} – EC ₁₆	260	5.8	0.000048	3.7
EC _{>16} – EC ₂₁	320	0.65	0.0000011	4.2
EC _{>21} – EC ₃₅	340	0.066	0.00000000044	5.1

* Determined by establishing empirical relationships between the equivalent carbon number (EC) and available physical property information for the chemicals in each carbon fraction (API, 1992). The values were calculated using the EC value in the midpoint of the group as an independent variable in the regression equations (Gustafson *et al.*, 1997).

6. Environmental Fate

Residual hydrocarbon wastes bear a strong resemblance to crude oil when released into the environment. Given the compositional similarity and the plethora of information on the distribution and ultimate fate of the crude oil parent, it provides a more than adequate surrogate for examining many of the fate characteristics of hydrocarbon wastes.

Several component categories of crude oil, particularly aliphatics, aromatics, and PACs, provide a reasonable basis by which to gauge how the wastes will behave in the environment (Ward *et al.*, 2003). As these hydrocarbon categories display distinct differences in key physical and chemical properties that can affect their distribution and biodegradation in the environment,

it is not surprising that a range of environmental behaviors would be observed, especially when comparing aliphatics and aromatics. For example, the rate of biodegradation by microbes in the environment is expected to show a preferential sequence of hydrocarbon utilization so that discrete hydrocarbon types will disappear from a complex mixture in a predictable order. In addition, it is important to recognize that while all hydrocarbons have an innate ability to be used by microbes as an energy source and are inherently biodegradable from a practical standpoint; these substances would not likely pass standard ready biodegradability tests.

Reliable information sources are available on key, high profile components found in appreciably high amounts in hydrocarbon wastes. For instance, the Agency for Toxic Substances and Disease Registry (ATSDR) has developed detailed toxicological profiles for Total Petroleum Hydrocarbons (TPH) as well as PAHs. Although not specifically summarized as part of this category assessment, the information in these profiles can be used, if needed, to gain additional insight into the overall behavior of TPHs in the environment.

Since crude oil contains an abundance of hydrocarbons with densities less than that of water, these lighter non-aqueous phase liquids will float and pose less risk of groundwater contamination than more highly water solubility chemicals. Likewise, because these non-aqueous phase liquids are relatively insoluble in water the threat to aquatic organisms is related to their miscibility. The biodegradability of hydrocarbon wastes has been the subject of considerable interest since it provides one of the best possible choices for the disposal of waste oils and sludges (Jack *et al.*, 1994). Bioremediation of wastes by land treatment has been shown to be effective if the application rate and soil conditions are properly managed (Salanitro *et al.*, 1997). Studies indicate that 60-70% of the hydrocarbons in an oily sludge can be degraded within 2-3 years following land application (Loehr *et al.*, 1992).

About a hundred individual species of bacteria and fungi are able to use oil components to sustain their growth and metabolism (Atlas, 1995). The degrees and rates of degradation for hydrocarbon waste depend, first of all, upon the structural class of the target TPH. For instance, structure activity determinations reveal that the pattern of hydrocarbon degradation decreases in the following order: *n*-alkanes; isoalkanes; alkenes; single-ring alkylbenzenes (e.g. BTEX); polycyclic hydrocarbons; and high molecular weight cycloalkanes (Bartha and Atlas, 1977; Potter and Simmons, 1998). With increasing structural complexity and molecular weight, the rate of microbial decomposition will typically decrease. In addition, the rate of biodegradation will depend on the physical state of the waste, including the degree of aqueous dispersion. The most important environmental factors influencing hydrocarbon biodegradation are temperature, concentration of nutrients and oxygen, and, of course, species composition and abundance of TPH-degrading microorganisms. Experiments have shown that 90% of the alkanes and monocyclic saturates and 50-70% of aromatic compounds of C₄₄ or less could be environmentally biodegraded under ideal conditions (Huesemann, 1997).

Although there is some good general information on the biodegradation of hydrocarbons waste under both laboratory and under field conditions, the same is not true for the other fate parameters of interest. The only practical way to consider these other endpoints of interest is to look at surrogates or key chemical constituents. Table 9 displays the estimated environmental properties of several aliphatic, cycloaliphatic, aromatic, and polycyclic chemicals that can be

found in crude oil and hydrocarbon wastes. As expected, there is a regular and predictable relationship between these properties, influenced heavily by the relative change in molecular weight. It also is important to recognize that the composition and fate characteristics of the waste will change as the material ages and weathers to form oxidation products that have appreciably different properties from the parent substance. In fact, a relatively large number of physical processes can affect the fate of hydrocarbon waste components following their environmental release. These include physical transport by wind and currents, aqueous dissolution in accordance with the relative solubility of the constituents, emulsification, especially of the high molecular weight fractions in marine environments, photooxidation reactions in both the vapor and liquid phases, slow sedimentation, and the aggregation of small droplets into globules.

Table 9. Fate Estimates for a Group of Representative Chemicals Found in Hydrocarbon Waste*

Fraction/ Example Hydrocarbon	CAS #	Photooxidation ($t_{1/2}$ days)	Biodegradation ($t_{1/2}$ days)	Hydrolysis	Level III Fugacity			
					Air	Water	Soil	Sediment
Aliphatic								
EC ₅ – EC ₆ hexane	110-54-3	2.0	4.7	NA	35.6	55.9	4.8	3.7
EC _{>6} – EC ₈ octane	111-65-9	1.3	6.4	NA	14.3	31.5	21.5	32.7
EC _{>8} – EC ₁₀ nonane	111-84-2	1.1	7.4	NA	6.8	18.3	27.7	47.3
EC _{>10} – EC ₁₂ dodecane	112-40-3	0.8	11.8	NA	3.5	12.2	21.5	62.8
EC _{>12} – EC ₁₆ hexadecane	544-76-3	0.5	21.7	NA	0.6	5.7	29.9	63.8
EC _{>16} – EC ₃₅ eicosane	112-95-8	0.4	39.9	NA	0.3	3.7	27.8	68.1
Aromatic								
EC ₅ – EC ₇ benzene	71-43-2	5.5	4.5	NA	37.6	48.1	14.1	0.2
EC _{>7} – EC ₈ ethylbenzene	100-41-4	1.8	5.0	NA	12.8	32.7	53.8	0.7
EC _{>8} – EC ₁₀ naphthalene	91-20-3	0.5	5.6	NA	0.9	11.5	86.6	1.0
EC _{>10} – EC ₁₂ methylnaphthalene	90-12-0	0.2	8.9	NA	0.8	17.3	80.3	1.7
EC _{>12} – EC ₁₆ anthracene	120-12-7	0.3	123.0	NA	0.2	9.3	79.0	11.6

EC _{>16} – EC ₂₁ chrysene	218-01-9	0.2	343.8	NA	0.1	4.3	47.6	78.0
EC _{>21} – EC ₃₅ coronene	191-07-1	0.2	643.2	NA	<0.1	0.7	42.4	56.9

* All parameters calculated using subroutines in the USEPA (EPI) Suite (v 4.0) program.

Conclusions

If released to the environment, the constituents within these complex substances will partition, distribute, and degrade in accordance with their own chemical properties. Because these substances contain a high percentage of hydrophobic substances, direct releases to water bodies will result in soil and sediment accumulation and little aqueous dissolution. Vaporization is also possible for those chemical constituents with measurable vapor pressure. Available information shows that the hydrocarbons in these wastes will eventually degrade in the environment by biological means.

7. Ecotoxicity

Although the ecotoxicity of individual hydrocarbon wastes has not been extensively studied, much can be surmised by reference to hydrocarbon substances of similar composition. Thus, refinery streams and products from other HPV petroleum categories can serve as surrogate substances and provide ecotoxicity hazard information for these waste streams. Any consideration of the ecotoxicity of hydrocarbon wastes must also recognize that there is wide variation in chemical composition and the fact that PAC content, although important, is not the only determinant of toxicity for these waste substances (Barron *et al.*, 1999).

The importance of carbon number, molecular structure, and molecular weight in determining the overall toxicity of a particular hydrocarbon waste necessitated a search for reasonable surrogates that represented of the various hydrocarbon wastes in this category. The petroleum products showing the closest resemblance to residual hydrocarbon wastes are residual fuel oils (ASTM D 396), specifically fuel oils No. 4, 5, and 6. .

Residual fuel oils are blended from several different refinery operations including atmospheric distillation, vacuum distillation, catalytic cracking, visbreaking and others. Similar to many wastes, they have a high-boiling range (flash points above 55 Centigrade) and contain a significant number of high molecular weight compounds. Residual fuel oil, like many analogous hydrocarbon wastes, can also contain high concentrations of PACs.

Residual fuel oils have been examined in variety ecotoxicity assays. The procedure generally used for testing substances with limited water solubility involves the preparation of a water accommodated fraction (WAF), which is a water sample that has been equilibrated with the oily test material of interest. WAFs are defined by the loading fraction, which is the ratio of oil to water used to generate the WAF samples. Loading rates are important because hydrocarbons vary in their relative water solubility and the higher the loading rate, the greater the percentage of water soluble materials in solution.

In Table 10, a series of WAF studies are summarized on the acute toxicity of two residual fuel oil samples to fish, daphnia, and algae (Shell, 1997a, b, c, d, e, f). The lethal and effective loading rates (EL₅₀) from these studies indicate that the acute aquatic toxicities to rainbow trout and daphnia were greater than 100 mg/L. In algae (*Raphidocelis subcapitata*) the 72-hour inhibitory effect EL₅₀ levels falls in between 30 and 100 mg/L (30<EC₅₀<100).

Table 10. Summary of Aquatic Toxicity Studies Performed with Residual Fuel Oils

Species	Material	Test Procedure	Effect	Concentration	Reference
Rainbow trout (<i>Oncorhynchus mykiss</i>)	Light residual fuel oil	WAF	96 hr LL50	>1000mg/L	Shell, 1997a
Rainbow trout (<i>Oncorhynchus mykiss</i>)	Heavy residual fuel oil	WAF	96 hr LL50	>100, <1000mg/L	Shell, 1997b
<i>Daphnia magna</i>	Light residual fuel oil	WAF	48 hr EL50	>1000mg/L	Shell, 1997c
<i>Daphnia magna</i>	Heavy residual fuel oil	WAF	48 hr EL50	>220, <460mg/L	Shell, 1997d
<i>Raphidocelis subcapitata</i>	Light residual fuel oil	WAF	72 hr E150 SGR 72 hr E150 AUC	>100, <300 mg/L >3, <10 mg/L	Shell, 1997e
<i>Raphidocelis subcapitata</i>	Heavy residual fuel oil	WAF	72 hr E150 SGR 72 hr E150 AUC	>30, <100 mg/L >30, <100 mg/L	Shell, 1997f

Other studies have also been performed to evaluate the sublethal effects of residual fuel oils on aquatic organisms by a variety of different methods (not included in the robust summaries). Reductions in serum glucose and slight damage to gill morphology were observed following an exposure of rainbow trout (*Salmo gairdneri*) with Bunker C fuel oil at concentrations up to 200 mg/L for 96 hours (McKeown and March, 1978a). Sheepshead minnow (*Cyprinodon variegatus*) exposed to Bunker C heavy fuel oil showed a difference in respiratory rate and a depression of oxygen consumption (Anderson, 1974). The intermolt time period for juvenile horseshoe crabs (*Limulus polyphemus*) showed a proportional increase with increasing exposure concentrations to Bunker C fuel oil (Strobel and Brenowitz, 1981). American oysters (*Crassostrea virginica*) showed an ability to close their shell to minimize Bunker C exposure (Anderson and Anderson, 1976).

Conclusions

The information available for residual fuel oils are believed to provide an adequate surrogate for assessing the ecotoxicity of the hydrocarbon wastes in this category. The test results observed using these surrogate substances are in good relative agreement with the results observed with selected waste types.

8. Health Effects

The health effects of residual hydrocarbon wastes has been primarily assessed by read-across to several residual fuel oil blending streams with available test data. Measured test data are available on two residual hydrocarbon wastes for characterizing the subchronic effects and

the reproductive/developmental effects following repeated dermal exposures in rats: DAF float sludge and API separator sludge.

A. Acute toxicity

The acute health effects of hydrocarbon waste surrogates are presented in Tables 11-15. These residues and distillates are all complex substances having carbon numbers greater than C₂₀ and with a PAC content sometimes greater than 5%. A more complete description of these residual materials is presented in the HPV Test Plan for Heavy Fuel Oils (API, 2004). As seen below in Tables 12 and 13, the acute oral toxicity of these streams is generally greater than 5000 mg/kg and the acute dermal toxicity is greater than 2000 mg/kg.

Table 11. A Comparison of the Acute Oral Toxicity of Heavy Fuel Oil Residues and Slop Oil

Sample Type	LD ₅₀ value	Observations	References
Residual fuel oils [‡]	5.13 - >25 mL/kg	Lethargy; grease on fur	API 1980a,b,c,d
Atmospheric residue	>5000 mg/kg	Stained coats; dark red areas in lung lobes	UBTL 1990b
Vacuum distillate [‡]	>5000 mg/kg	↓ Activity; chromorhinorrhea, ↓ fecal output; urogenital staining; ↓ urine	Mobil 1988b,c Mobil 1992a
Cracked residue	4320 mg/kg (♀) 5270 mg/kg (♂)	Mortalities; hypoactivity; piloerection; staining around mouth, nose, urogenital; hair loss; weight loss; intestinal mucosa damage	API 1982
Cracked distillate	>5000 mg/kg	Oral, nasal discharge; lethargy; abnormal stools; pale & mottled kidneys	UBTL 1988
Slop oil	> 4300 mg/kg	---	Houston Refining, 2006

* all studies performed in rats

‡ number of fuel oils tested = 4 and number of vacuum distillates tested = 3

Table 12. Acute Dermal Toxicity of Heavy Fuel Oil Residues

Sample Type	LD ₅₀ value	Observations	References
Residual fuel oils [‡]	>5 mL/kg	Erythema; slight congestion of liver	API 1980a,b,c,d
Atmospheric residue	>2000 mg/kg	Abnormal stool; dark red areas in lung	UBTL 1992b
Vacuum distillate [‡]	>2000 mg/kg	↓ Food consumption; soft stool; ↓ fecal output	Mobil 1988a,b,c Mobil 1992a

Cracked residue	>2000 mg/kg	No signs systemic toxicity; no gross findings	API 1982
Cracked distillate	>2000 mg/kg	Erythema & edema; mottled kidneys	UBTL 1989a UBTL 1992a

* all studies performed in rabbits

‡ number of fuel oils and vacuum distillates tested = 4

The dermal and ocular irritation potential shown in Table 13 and 14 indicate that these residues have a slight to moderate capacity to cause some degree of primary inflammation of exposed tissue. These findings for fuel oil residues are entirely consistent with the mild to moderate ocular and dermal irritancy of slop oil containing a high percentage (> 67%) of C₂₀ or greater hydrocarbons (Houston Refining, 2006).

Table 13. A Comparison of the Ocular Irritation of Heavy Fuel Oil Residues and Slop Oil

Sample Type	Irritation Indices*	Observations	Reference
Residual fuel oils‡	2.67 – 7.67 rinsed 0 – 1.33 rinsed 4.0 – 7.33 un-rinsed 0.0 – 1.33 un-rinsed	Minimal – mild irritant	API 1980a,b,c,d
Atmospheric residue	0.0 & 0.0 un-rinsed only	Not irritating	UBTL 1991
Vacuum residue	5.7 & 4.7 rinsed 5.0 & 4.7 un-rinsed	Un-rinsed - not irritating Rinsed - minimal irritant	UBTL 1989g
Vacuum distillate‡	2.0 – 10.3 1.7 – 3.3 [#]	Un-rinsed only	Mobil 1988a,b,c Mobil 1992a
Cracked residue	2.0 & 0 rinsed & un-rinsed	Minimal irritant	API 1982
Cracked distillate	5.7 & 0.0 un-rinsed 5.3 & 0.0 rinsed	Un-rinsed - not irritating Rinsed – not irritating	UBTL 1989f
Slop oil	---	Mild to moderate	Houston Refining, 2006

* 24 & 72 hr studies in rabbits

48 hr score

‡ number of fuel oils and vacuum distillates tested = 4

Table 14. A Comparison of the Dermal Irritation of Heavy Fuel Oil Residues and Slop Oil

Sample Type	Irritation Index	Observations	References
Residual fuel oils‡	0.27 – 1.54	Minimal – slight irritant	API 1980a,b,c,d
Atmospheric residue	3.5	Moderately irritating	UBTL 1992d

Vacuum residue	0.18	Not irritating	UBTL 1989e
Vacuum distillate [‡]	1.2 – 3.6	-	Mobil 1988a,b,c Mobil 1992°
Cracked residue	0.2	-	API 1982
Cracked distillate	5.6	Moderately irritating	UBTL 1989d
Slop oil	---	Minimal to mild	Houston Refining, 2006

* all studies performed in rabbits

‡ number of fuel oils and vacuum distillates tested = 4

The results in Table 15 reveal that residual fuel oil blending streams may have some small capability to cause dermal sensitization in guinea pigs. Similarly, dermal sensitization was observed with a slop oil sample tested in guinea pigs by the Buehler method (Houston Refining, 2006).

Table 15. A Comparison of the Dermal Sensitization of Heavy Fuel Oil Residues and Slop Oil

Sample Type	Challenge Response	Observations	References
Residual fuel oils [‡]	-	3 samples non-sensitizer, 1 sample mild sensitizer	API 1980a,b,c,d
Atmospheric residue	0/10	Non-sensitizer	UBTL 1992c
Vacuum residue	0/10	Non-sensitizer	UBTL 1989c
Vacuum distillate [‡]	1/10	Non-sensitizer	UBTL 1990c
Cracked residue	0/10	Non-sensitizer	API 1984
Cracked distillate	0/10	Non-sensitizer	UBTL 1989b
Slop oil	---	Sensitizer	Houston Refining, 2006

* all studies performed in guinea pigs

‡ number of fuel oils and vacuum distillates tested = 4

B. Repeated dose toxicity

Subchronic studies are available for two different types of hydrocarbon waste. A 90-day subchronic dermal toxicity study was performed in male Sprague-Dawley rats treated with API separator sludge that contained approximately 22% water, 9% soil and 69% solids (Mobil, 1990a). The test material was applied once per week for 13 weeks to the shaved backs of

animals at dose levels of 0, 2500, or 10,000 mg/kg. No deaths were associated with this study, nor were there clinical signs indicative of systemic toxicity. After six weeks of treatment, slight to moderate chronic deterioration of the skin was observed in some animals.

No significant body weight changes were observed during the study. A small, but statistically significant, increase in segmented neutrophils was observed along with decreases in lymphocytes at 5 and 13 weeks for animals treated at the high dose level. Statistically significant reductions were also observed at 5 and 13 weeks for serum total bilirubin at the low dose level. No differences were found in absolute and relative organ weights. Necropsy revealed adhesions to and from adjacent internal organs (liver, heart and lung) in all treatment groups including controls. These adhesions were not treatment-related and were the result of pressure applied to these and other organs by the wrapping procedure employed to keep the test material in contact with the skin. An examination of testicular epididymal sperm showed no differences between the treatment groups. No other adverse effects were noted during the course of the study. The toxicological significance of an increase in segmented neutrophils and a decrease in lymphocytes in the 10,000 mg/kg animals was questioned. Based on the results of this study, the no observed adverse effect level for API separator sludge was 10,000 mg/kg.

A second dermal study was performed in male and female Sprague-Dawley rats treated with a DAF float blend at dose levels of 0, 60, 250, or 1000 mg/kg/day (Mobil, 1995). Analytical characterization of the DAF float blend showed it to contain 33% organics with the remainder being water and other polar materials (Mobil, 1992d). In addition, the sample contained 16.0% non-aromatics (paraffins and aliphatics), 11.5% aromatic PACs of 2 rings or more, and 5.2% mono aromatics. Animals were treated with this material for 13 weeks at 5 days/week by application of the test material to the shave dorsal trunk without an occlusive wrap (animals wore Elizabethan style collars to prevent ingestion). Minimal to moderate skin irritation was observed in the treated groups, particularly in the high dose group. After 13 weeks, male and females in the high dose group gained significantly less weight than the controls.

After 5 and 13 weeks of treatment, elevated levels of ketone bodies and protein appeared in the urine of female rats at the mid and high dose and in males treated at the high dose. Statistically significant decreases were reported in red blood cell parameters including RBC count in male rats, and hemoglobin and hematocrit for male and female rats treated at the mid and high dose. Platelet counts were also significantly decreased at the high dose in both sexes. White blood cell counts were significantly increased at the mid dose in females and high dose in males.

At 13 weeks, blood glucose, urea nitrogen, sodium and chloride levels were significantly altered in male rats and blood urea nitrogen, cholesterol, uric acid and potassium were affected in female rats. At 5 weeks, uric acid and potassium were significantly different in males at the 250 mg/kg/day level, and calcium at the 1000 mg/kg level. Absolute and relative liver weights were increased in both sexes. An increase in the absolute liver weights was observed in males at the mid dose and females at the high dose. The relative liver weights were significantly increased for males at all dose levels and for females at the mid and high dose. A significant decrease was seen in the absolute and relative thymus weights for both sexes at the high dose and in the

absolute thymus weight of the mid dose males. Significant decreases were also observed in the final body weights and in the absolute weights of the epididymides, kidneys, and prostate of high dose males and in the absolute brain weight of high dose females. Significant increases were seen in the relative weights of the adrenals, brain, heart and testes of high dose group males.

Histopathologic examination of the tissues showed generally moderate epidermal hyperplasia and slight hyperkeratosis in the treated skin with surprisingly minimal chronic inflammation and without ulceration. It also revealed significant bone marrow hypocellularity, liver necrosis and hepatocellular hypertrophy, thymic atrophy, hemorrhage/hemosiderosis in lymph nodes, epithelial hyperplasia in the distal airways of the lungs, myofiber degeneration/myocytolysis in the heart, increased tubular basophilia in kidneys, minor mucosal irritation at the limiting ridge of the stomach, and acinar cell degeneration in the pancreas. No differences were observed between the treatment groups for any of the testicular sperm measurements. However, epididymal parameters showed possible treatment-related effects which included significantly lower cauda epididymal weights with subsequent lower epididymal sperm counts. Based on observed results, a NOAEL for DAF Float Blend could not be definitively established since the LOAEL of 60 mg/kg/day was the lowest dose tested. The treatment-related effects on the skin, liver, kidneys and lymph nodes were of greatest significance.

The findings from preceding two dermal studies show that the systemic effects of the float blend were greater than those observed following treatment with API separator sludge. Furthermore, when the target organ toxicity of the DAF float is compared with the results obtained with a variety of residual fuel oil blending streams, many similarities can be observed. As shown in Table 16, many of the blending streams used in residual fuel oils caused notable effects in the liver, thymus, and bone marrow. These same target tissues were also affected to some degree after the dermal exposure of rats to DAF float waste. These results are not particularly surprising, since previous studies with refinery streams has shown a relationship between the PAC content of the mixture and the subchronic and developmental effects observed following the dermal treatment of rats (Feuston *et al.*, 1994, TERA 2008, API, 2008). Those mixtures containing PACs composed of 3-7 rings were able to cause a decrease in thymus weight, aberrant hematology, and altered clinical chemistry results. The compositional analysis shown in Table 5 reveals that 3-7 ring PACs are common in hydrocarbon wastes. These data confirm that the health effects induced by residual fuel oil blending streams and hydrocarbon waste are similar.

Table 16. Summary of Subchronic Dermal Studies with Heavy Fuel Oil Residues

Sample Type	Species and Route	Dose	Treatment Regimen	Major Findings	Histopathology	Reference
Residual fuel oil	rat/dermal	0.5, 1.0, 2.5 496 992 2480 ml/kg/d	5x/week for 4 weeks	♂ - ↓ eosinophils at mid and high dose; ↓ SGPT at low and high dose; ↑ glucose at high dose; ↓ total protein at low dose; ↓ hemoglobin at high dose; ↑ relative liver weight at all doses ↑ relative spleen weight at high dose ♀ - ↓ SGPT at low and high dose; ↑ glucose at mid and high dose; ↑ relative liver weight at all doses ↑ relative spleen weight at low and mid dose	Hyperkeratosis(minimal severity at application site)	UBTL, 1987
Atmospheric residue	rat/dermal	0.01, 0.25, 1.00 ml/kg/d 9, 231 928 mg/kg/d	5x/week for 4 weeks	♂ - ↔ normal necropsy, hematology, clinical chemistry; ♀ - ↔ normal necropsy, hematology, clinical chemistry	acanthosis, hyperkeratosis	UBTL, 1990a
Atmospheric distillate	rat/dermal	30, 125, 500 mg/kg/d	5x/week for 13 weeks	♂, ♀ - numerous hematology and clinical chemistry changes at mid and high doses ↑ liver size at necropsy ↓ thymus size at necropsy	♂, ♀ - ↓ hematopoiesis and thymic lymphocytes at high dose; focal liver necrosis and liver hyper-trophy at high dose;	Mobil, 1992c
Vacuum distillate	rat/dermal	30, 125, 500, 2000 mg/kg/d	5x/week for 13 weeks	♂ - ↓ growth rate at high dose; ↓ erythrocytes & platelet counts at high dose; ↑ cholesterol at mid and high dose ♀ - ↓ growth rate at high dose; ↓ erythrocytes & platelet counts at mid and high dose; ↓ serum glucose at mid and high dose mid and high doses	♂ - ↓ erythropoiesis and thymic lymphocytes; bone marrow fibrosis at high dose ♀ - ↓ thymic lymphocytes	Mobil, 1988d
Cracked residue	rat/dermal	8, 30, 125, 500,	5x/week for 13 weeks	♂, ♀ - several hematology and clinical chemistry parameters affected ↓ body weight	♂, ♀ - lesions observed in liver, thymus, and bone marrow	Mobil, 1985b Cruzan et al., 1986

		2000 mg/kg/d		↑ mortality at high dose		
Cracked distillate	rat/dermal	8, 30, 125 mg/kg/d	5x/week for 13 weeks	♂ - ↔ normal necropsy, hematology, clinical chemistry; and sperm measurements ♀ - ↔ normal necropsy, hematology, clinical chemistry	♂, ♀ - skin thickening with subcutis inflam- mation, parakeratosis, ↑ mitosis in basal epidermal cells	Mobil, 1992b Feuston et al., 1994

C. Mutagenicity

Studies have shown a relationship between the mutagenicity of petroleum streams and the concentrations of PACs containing more than 2 rings (Roy *et al.*, 1988). The results from an optimized Ames Salmonella assay showed a relationship with the PAC ring content (3-7) in 21 different petroleum substances. In general, hydrocarbon waste mixtures containing an appreciable PAC concentration will be genotoxic in *in vitro* test systems. Tables 17 and 18 describe the results obtained with residual fuel oil blending streams and a sample of slop oil. The studies show that all but two of the *in vitro* assays (cytogenetic assay and bacterial forward mutation assay) produced positive results with fuel oil distillates or residues. These results are consistent with the optimized Ames assay results for extracts from a combined API separator/slop oil emulsion sample that tested positive in *S. typhimurium* strain TA 98 with metabolic activation, in a repair proficient strain of *B. subtilis*, and in the diploid form of *A. nidulans* (Donnelly *et al.*, 1985; Brown *et al.*, 1986). The positive findings are consistent with those for with slop oil, which was found to be genotoxic in a mouse lymphoma assay and a CHO sister chromatid exchange test (Houston Refining, 2006).

Table 17. *In Vitro* Genotoxicity Assays Performed with Residual Fuel Oil Blending Streams and Slop Oil

Sample Type	Assay	Results	Reference
Vacuum distillate	Optimized Ames CHO cell cytogenetic assay	Positive with activation Negative with/without activation	Mobil 1985a Mobil 1987a
Cracked residue	Standard Ames Mouse lymphoma Sister chromatid exchange Cell transformation Unscheduled DNA synthesis Mammalian forward mutation assay	Pos. with/without activation Pos. with/without activation Pos. with/without activation Pos. only with activation Positive Neg. with/without activation	API 1986b API 1985e API 1985f API 1986a API 1985b API 1985°
Slop Oil	Mouse lymphoma assay CHO sister chromatid exchange	Positive Positive	Houston Refining, 2006

The optimized Ames test differs from the Standard Ames test in that petroleum samples are extracted with DMSO to concentrate the PAC fraction, hamster liver replaces rat liver homogenate, and co-factors in the activation mixture are increased to facilitate metabolism of PAC.

In vivo mutagenicity assays have yielded somewhat different results depending on the type of assay employed. Residual fuel oil blending streams produced generally negative results in rat cytogenetic and micronucleus assays, but mouse sister chromatid exchange and rat unscheduled DNA repair assays were positive. These data on residual fuel oil blending streams provide a basis for evaluating the genotoxicity of hydrocarbon wastes. The diversity and merit of the genotoxicity assays employed are believed to provide an adequate basis for the evaluating the mutagenicity of all the hydrocarbon wastes in this category.

Table 18. *In Vivo* Genotoxicity Assays Performed with Heavy Fuel Oil Residues

Sample Type	Assay	Species	Results	Reference
Vacuum distillate	Micronucleus	Rat (♀, ♂)	Negative at up to 2000 mg/kg/day; 5x/week for 13 weeks via dermal route	Mobil, 1987b
Cracked residue	Cytogenetic Assay	Rat (♀, ♂)	Negative at up to 1 g/kg/day by gavage for 6 days	API, 1985e
	Sister Chromatid Exchange	Mice (♀, ♂)	Single IP dose positive at 4.0 (♀, ♂) & 2.0 (♂) g/kg; negative at 0.4 g/kg	API, 1985d
	Unscheduled DNA Synthesis	Rat (♂)	Positive at 100 & 1000 mg/kg by gavage; negative at 50 mg/kg	API, 1985c

D. Reproductive and developmental toxicity

Reproductive/developmental screening assays have been performed on samples of API separator sludge and DAF float blend. The samples used in the test were similar to those used in the subchronic dermal toxicity studies described above. The study with API separator sludge was performed in pregnant Sprague-Dawley rats that were treated dermally at dose levels of 0, 500, or 2000 mg/kg/day on days 0 through 19 of gestation (Mobil, 1990b). Each animal was sacrificed on day 20 and standard measures of maternal and fetal pathology were performed; including an examination of the number of corpora lutea, implantations, and resorptions, along with evidence of fetal soft tissue and skeletal malformations. A majority of the clinical findings appeared to result from the handling stress.

Overall, the treated groups consumed less food than the control group. The difference in food consumption was statistically significant in the low and high dose groups during the mid to latter part of gestation. No findings attributable to the test material were observed at the time of maternal necropsy. There was a dose-related increase in the percent resorptions and the percentage of dams with resorptions. There was also a corresponding dose-related decrease in viable litter size. The increase in resorptions and the decrease in viable litter size were biologically significant at the 500 mg/kg/day level and statistically significant at the high dose level. In addition, although mating was confirmed for all females, the percentage of pregnant females which were implanted was markedly decreased at the 2000 mg/kg/day dose level.

A significant reduction in fetal weight was seen in the high dose group. At the time of external fetal examination, microphthalmia was noted in seven fetuses; two in the control group, two in the 500 mg/kg/day group, and three in the 2000 mg/kg/day group. The incidence of skeletal malformations was comparable among the treated and the control groups. In general, the malformations appeared as isolated occurrences and did not appear to be related to test material administration. Fetal visceral examination revealed a significant increase in the total number of

malformations seen in the high dose group; individual malformations were not statistically significant. Among the findings noted were: microphthalmia, anophthalmia, right-sided esophagus (one), heart (septal) defect (one), and ectopic testes. Microphthalmia and ectopic testes were also seen in the control fetuses. A NOAEL for dermal exposure to API separator sludge was not achieved for either maternal or developmental toxicity. In both cases, the LOAEL was determined to be 500 mg/kg/day.

The study with the DAF float blend was performed similarly except that a separate group received single oral exposure to the test material (Mobil 1990c). Pregnant Sprague-Dawley rats were treated dermally at dose levels of 125, 500, or 1000 mg/kg/day on days 0-19 of gestation or orally at 2000 mg/kg on day 13 of gestation. Treatment at the high dermal dose was discontinued on day 15 because of a suspected high incidence of resorptions as indicated by severe red vaginal discharge in several animals. No treatment related clinical signs were noted during the study except for a dose-related increase in the incidence of moderate to severe skin irritation at the site of dosing. Other treatment related findings included red vaginal discharge observed in females exposed at dose levels greater than 125 mg/kg/day.

Mean maternal body weights were significantly reduced throughout most of the gestation period for animals in the mid and high dose groups. At study termination on day 20, gravid uterine weight, carcass weight, and net maternal body weight gain were also reduced at the mid and high dose levels. The low dose group gained significantly less weight during the initial stages of dermal treatment, but maintained a weight gain comparable to the control group for the remainder of gestation. In general, animals exposed to the DAF float blend at dose levels of 500 and 1000 mg/kg/day consumed significantly less food than the control group throughout most of gestation.

At necropsy, enlarged lymph nodes (in the auxiliary, brachial, lumbar, and thymic region) were observed in the mid and high dose animals. The wall of the stomach mucosa of two females appeared thickened following the oral treatment. A reduction in thymus size was observed in females from all groups; however, this finding was noted most frequently following dermal treatment at the mid and high dose. These same groups also showed a significant reduction in both absolute and relative thymus weights. In general, the liver weights were higher than those of control animals; but the only statistically significant change occurred in the relative liver weights of animals treated at the low dose.

Several reproductive parameters were affected by the DAF float blend treatment including: the mean number/percent resorptions, litter size, and the number of dams with resorptions. Increased resorptions were observed at all dermal treatment levels, but not in the orally treated animals. Fetuses from dams exposed to dose levels of 500 and 1000 mg/kg/day weighed significantly less than control fetuses. A significant increase in incomplete ossification of various skeletal structures was noted at the mid and high dose, suggesting fetal growth retardation. Fetal rib malformations were significantly increased at the high dose level. Overall, the incidence of fetal malformations increased with increasing dose level.

Statistically significant decreases in RBC count, hemoglobin and hematocrit were observed at the high dose. Platelets were also significantly reduced at the mid dose only. Aberrant serum chemistry values were obtained for serum glucose, urea nitrogen, aspartate aminotransferase, creatinine, cholesterol, triglycerides, total protein, albumin, albumin/globulin ratio, sodium and calcium. The serum changes suggested some degree of hepatotoxicity and renal dysfunction. A NOAEL for dermal exposure to DAF float blend was not determined and a maternal and developmental LOAEL 125 mg/kg/day was established based on the red vaginal discharge in the dams and the visceral and skeletal anomalies in the fetuses. No significant adverse effects were noted in the group receiving a single oral dose.

The developmental effects observed with these two hydrocarbon waste samples are not dissimilar from those shown to occur with different types of heavy fuel oil. An examination of the results in Table 19 reveals that the fuel oils have a similar pattern of reproductive and developmental effects as do the hydrocarbon wastes. These data are not surprising since all of these samples contain appreciable amounts of PACs that are known to cause development effects (TERA, 2008 and API, 2008).

Table 19. Summary of Reproductive/Developmental Studies with Heavy Fuel Oil Residues

Sample Type	Species and Route	Dose Levels	Treatment Regimen	Major Findings	NOAEL	Reference
Atmospheric residue	rat/dermal;	50, 333, 1000 mg/kg/d	0-20 gestation	↔ no deaths or treatment-related clinical change ↓ body weight at high dose ↑ gestation length at high dose ↓ pup body weight	333 mg/kg (maternal) 333 mg/kg (developmental)	UBTL, 1994
Atmospheric distillate	rat/dermal	8, 30, 125, 500 mg/kg/d	0-19 gestation	↔ no deaths or treatment-related clinical change ↓ body weight at high dose ↓ absolute/relative thymus weight at two high doses ↑ gestation length at high dose ↓ fetal body weight ↑ resorptions at high dose ↑ skeletal malformations two highest doses	30 mg/kg (maternal) 30 mg/kg (developmental)	Mobil, 1991
Vacuum distillate	rat/dermal	30, 125, 500, 1000 mg/kg/d	0-19 gestation	↓ clinical chemistry values at high dose ↓ absolute/relative thymus weight ↑ relative liver weight at the two highest dose levels ↓ fetal body weight at two highest dose levels ↑ visceral and skeletal malformations at 500 mg/kg	125 mg/kg (maternal) 125 mg/kg (developmental)	Mobil, undated
Crack Residue (Clarified slurry oil)	rat/dermal	0.05, 1, 10, 50, 250 mg/kg/d	0-19 gestation	↔ no deaths or premature deliveries ↓ food consumption and gravid uterus weight in dams ↔ no increase in fetal malformations ↓ number of live fetuses and fetal body weights at maternally toxic doses ↑ number of resorptions at maternally toxic doses ↑ number of reversible visceral Variations	0.05 mg/kg (maternal) 0.05 mg/kg (developmental)	Hoberman <i>et al.</i> , 1995

Table 19 (con't). Summary of Reproductive/Developmental Studies with Residual Fuel Oil Blending Streams

Sample Type	Species and Route	Dose Levels	Treatment Regimen	Major Findings	NOAEL	Reference
Cracked Residue (Cracked clarified oil)	rat/dermal	0.05, 10, 250 mg/kg/d	one week prior to mating thru day 20 gestation, litters examined from day 0 – 4 of lactation	↔ no deaths ↑ vaginal discharge at high dose ↓ body weights, body weight change and food consumption in dams at mid and high dose ↓ thymus size at high dose ↓ no litter delivered at the high dose ↔ no adverse effect on pups in mid and low dose groups	0.05 mg/kg (maternal) 10 mg/kg (developmental)	UBTL,1994
Cracked distillate	rat/dermal	8, 30, 125, 250 mg/kg/d	0-19 gestation	↑ dermal erythema scabbing and eschar ↑ vaginal discharge at three highest dose levels ↓ mean body weight dams ↓ absolute thymus weight ↑ absolute liver weight ↓ decreased litter size at mid & high dose ↑ increased resorptions at mid & high dose 50% litters with total resorptions at high dose ↑ developmental abnormalities with shortened jaw length and an esophageal displacement two highest dose levels ↑ malformation of the vertebral column	30 mg/kg (maternal) 30 mg/kg (developmental)	Mobil, 1987c

No reproductive toxicity studies were identified for hydrocarbon wastes. However, male and female reproductive studies of another petroleum substance (clarified slurry oil) indicated that reproductive endpoints (e.g., fertility and sperm production) were unaffected at doses at which fetal survival was severely compromised in a developmental toxicity study that extended to postnatal day 4 (Hoberman *et al.*, 1995). Assuming that clarified slurry oil, which has a high PAC content, is representative of other PAC-containing petroleum streams, it can be reasonably assumed that reproductive effects, such as fertility and sperm production, would not be sensitive effects of PAC-containing materials compared to developmental toxicity effects. In addition, the potential for PAC-containing petroleum streams, including a hydrocarbon waste (DAF Float), to affect reproductive organs was assessed via 13 week repeat-dose studies in which the testes, accessory sex organs, and epididymides were weighed in males, and the potential for pathological changes was evaluated in microscopic examinations. There was little evidence of reproductive organ effects in the repeat-dose studies of DAF Float or other petroleum streams evaluated (Mobil 1990c, API 2008).

Across a number of developmental toxicity studies that examined embryonal and fetal development, the effects most commonly observed, and statistically significant at the lowest levels, were related to fetal/pup survival and weight gain. There was little evidence of teratogenicity (i.e. malformations) in any of the conventional developmental toxicity studies. As expected, increased incidences of skeletal variations (i.e., delayed ossification) were often observed at dose levels producing decreased fetal/pup body weight. Based on the results of a large number of repeat-dose studies and developmental toxicity studies, as well as the two reproductive toxicity screening studies of carbon black oil, the most sensitive endpoints related to reproductive and developmental toxicity appear to be those associated with the survival and growth of fetuses and offspring; effects on fertility, sperm production and reproductive organ effects do not appear to be sensitive endpoints for assessment of the potential hazards of PAC-containing petroleum substances.

Conclusions

Available test data with residual fuel oil blending streams and two types of waste hydrocarbons indicate that the substances are systemic and developmental toxicants following repeated dermal exposure. These findings are not surprising considering their potential PAC content and the recognized health hazards from this class of chemicals.

9. Exposure

The substances in the residual hydrocarbon waste category are typically recycled within the refinery to recover the hydrocarbon content. Any off-site transfer would be to a regulated hazardous waste disposal site or for another industrial application (i.e., cement kiln). There are no consumer uses or uses that would result in exposure to children. These substances are regulated by EPA under Resources Conservation and Recovery Act (USEPA, 1982, 1995, 1996). Potential exposure to refinery workers would be minimized by OSHA Hazard Communication regulations and the basic industrial hygiene practices observed at petroleum refineries.

10. References

- Alshammari, J.S., Gad, F.K., Elgibaly, A.A.M., and Khan, A.R. (2008). Solid waste management in petroleum refineries. *American Journal of Environmental Sciences* **4**,353-361.
- Anderson, J.W., Neff, J.M., Cox, B.A., Tatem, H.E., and Hightower, G.M. (1974) The effects of oil on estuarine animals: toxicity, uptake and depuration, respiration. In: *Pollution and Physiology of Marine Organisms*, F.J. Vernberg and W.B. Vernberg (eds.), p.p. 285-310. Academic Press, New York, NY.
- Anderson, R.D. and Anderson, J.W. (1976) Oil bioassays with the American oyster, *Crassostrea virginica* (*Gmelin*). *Proceedings of the National Shellfisheries Association* **65**,38-42.
- API (1980a). Acute toxicity tests API 78-6 #6 Heavy fuel oil (API gravity 11.7/2.7%S. API Med. Res. Publ. 27-32814, American Petroleum Institute. Washington, DC.
- API (1980b). Acute toxicity tests API 78-7 #6 Heavy fuel oil (API gravity 17.1/0.8%S. API Med. Res. Publ. 27-32774, American Petroleum Institute. Washington, DC.
- API (1980c). Acute toxicity tests API 78-8 #6 Heavy fuel oil (API gravity 23.1/0.2%S. API Med. Res. Publ. 27-32816, American Petroleum Institute. Washington, DC.
- API (1980d). Acute toxicity tests API 79-2 #6 Heavy fuel oil (API gravity 5.2/1.2%S. API Med. Res. Publ. 27-32813, American Petroleum Institute. Washington, DC.
- API (1982). Acute toxicity studies catalytically cracked clarified oil Sample 81-15. API Med. Res. Publ. 30-31854. American Petroleum Institute. Washington, DC.
- API (1984). Dermal sensitization study in guinea pigs closed patch technique Catalytic cracked clarified oil API sample 81-15. API Med. Res. Publ. 31-31417. American Petroleum Institute. Washington, DC.
- API (1985a). CHO/HGPRT Mammalian cell forward gene mutation assay of API 81-15. API Med. Res. Publ. 32-32118, Washington, DC.
- API (1985b). Evaluation of the potential of RO-1, 81-15 and PS8-76D5-SAT to induce unscheduled DNA synthesis in primary rat hepatocyte cultures. API Med. Res. Publ. 32-32407. American Petroleum Institute. Washington, DC.
- API (1985c). Evaluation of the potential of RO-1, 81-15, and PS8-76D-SAT to induce unscheduled DNA synthesis in the in vivo-in vitro hepatocyte DNA repair assay. API Med. Res. Publ. 32-32406. American Petroleum Institute. Washington, DC.
- API (1985d). In vivo sister chromatid exchange assay API 81-15, catalytically cracked clarified oil (CAS 64741-62-4). API Med. Res. Publ. 32-32254. American Petroleum Institute. Washington, DC.
- API (1985e). Mutagenicity evaluation studies in the rat bone marrow cytogenetic assay in the mouse lymphoma forward mutation assay catalytic cracked clarified oil API sample 81-15. API Med. Res. Publ. 32-30534. American Petroleum Institute. Washington, DC.

-
- API (1985f). Sister chromatid exchange assay in Chinese Hamster Ovary (CHO) cells. Catalytic cracked clarified oil; API sample 81-15 CAS 64741-62-4. API Med. Res. Publ. 32-32750. American Petroleum Institute. Washington, DC.
- API (1986a). Morphological transformation of BALB/3T3 Mouse embryo cells API 81-15, Catalytically cracked clarified oil (CAS 64741-62-4). API Med. Res. Publ. 33-32638. American Petroleum Institute. Washington, DC.
- API (1986b). Salmonella/Mammalian-microsome plate incorporation mutagenicity assay (Ames test). API Med. Res. Publ. 33-30599. American Petroleum Institute. Washington, DC.
- API (1992). Technical Data Book – Petroleum Refining, 5th Edition, American Petroleum Institute. Washington, DC.
- API (2004). Heavy Fuel Oil Category Test Plan and Robust Summaries Submitted to the U.S. EPA, June 17, 2004. American Petroleum Institute. Washington, DC. <http://www.petroleumhvp.org/index.html>
- API (2008). The Relationship between the Aromatic Ring Class Content and Selected Endpoints of Repeat-dose and Developmental Toxicity of High-boiling Petroleum Substances. PAC Analysis Task Group. American Petroleum Institute. Washington, DC.
- Atlas, R.M. (1995). Bioremediation of petroleum pollutants. *International Biodeterioration & Biodegradation* **35**,317-327.
- ATSDR (1995). Toxicological Profile for Polycyclic Aromatic Hydrocarbons. U.S. Dept. Health and Human Services. Agency for Toxic Substances and Disease Registry. Atlanta, GA.
- Barron, M.G., Podrabsky, T., Ogle, S., and Ricker, R.W. (1999). Are aromatic hydrocarbons the primary determinant of petroleum toxicity to aquatic organisms? *Aquatic Toxicology* **46**, 253-268.
- Bartha, R. and Atlas, R.M. (1977) The microbiology of aquatic oil spills. *Advances in Applied Microbiology* **22**,225-266.
- Bhattacharyya, J.K. and Shekdar, A.V. (2003). Treatment and disposal of refinery sludges: Indian scenario. *Waste Management Research* **21**,249-261.
- Bojes, H.K., and Pope, P.G. (2007). Characterization of EPA's 16 priority pollutant polycyclic aromatic hydrocarbons (PAHs) in tank bottom solids and associated contaminated soils at oil exploration and production sites in Texas. *Regulatory Toxicology and Pharmacology* **47**,288-295.
- Brown, K.W., Deuel, L.E., and Thomas, J.C. (1985). Distribution of inorganic constituents in soils following land treatment of refinery wastes. *Water Air and Soil Pollution* **25**, 285-300.
- Brown, K.W., Donnelly, K.C., Thomas, J.C., Davol, P., and Scott, B.R. (1986). Mutagenic activity of soils amended with two refinery wastes. *Water Air and Soil Pollution* **29**, 1-13.
- Burks, S.L. and Wagner, J. (1983). Characterization and Treatment of Aqueous Wastes and Residue from Petroleum Refineries. US Environmental Protection Agency, R.S. Kerr Environmental Research Laboratory. EPA-600/2-83-086. Ada, OK.

-
- Bush, B., and Levine, G. (1992). The generation and management of wastes and secondary materials in the CONCAWE (1998). Heavy Fuel Oils. Product dossier no. 98/109. Conservation of Clean Air and Water in Europe. Petroleum products and health management group. Brussels, Belgium.
- Côté, R.P. (1976). The Effects of Petroleum Refinery Liquid Wastes on Aquatic Life, with Special Emphasis on the Canadian Environment. National Research Council of Canada, Pub. No. 15021. Ottawa, Canada.
- Cruzan, G., Low, L. K., Cox, G. E., Meeks, J. R., Mackerer, C. R., Craig, P. H., Singer, E. J. and Mehlman, M. A. 1986. Systemic toxicity from subchronic dermal exposure, chemical characterization, and dermal penetration of catalytically cracked clarified slurry oil. *Tox. and Ind. Health* Vol 2, No. 4, pp 429-444.
- Dave, H., Ramakrishna, C., Bhatt, B.D., and Desai, J.D. (1994). Biodegradation of slop oil from a petrochemical industry and bioreclamation of slop oil contaminated soil. *World Journal of Microbiology & Biotechnology* **10**,653-656.
- Donnelly, K.C., Brown, K.W., Thomas, J.C., Davol, P., Scott, B.R., and Kampbell, D. (1985). Evaluation of the hazardous characteristics of two petroleum refinery wastes. *Hazardous Waste & Hazardous Materials* **2**,191-208.
- Ferrari, M.D., Neirotti, E., Albornoz, C., Mostazo, M.R., and Cozzo, M. (1996). Biotreatment of hydrocarbons from petroleum tank bottom sludges in soil slurries. *Biotechnology Letters* **18**, 1241-1246.
- Feuston, M.H., Low, L.K., Hamilton, C.E., and Mackerer, C.R. (1994). Correlation of systemic and developmental toxicities with chemical component classes of refinery streams. *Fundamental and Applied Toxicology* **22**, 622-630.
- FWPCA (1967). Petroleum Refining Industry Wastewater Profile. In: *The Cost of Clean Water, Volume III Industrial Waste Profile No. 5*. Federal Water Pollution Control Administration. Washington, DC.
- Gulyas, H., and Reich, M. (1995). Organic compounds at different stages of a refinery wastewater treatment plant. *Water Science and Technology* **32**,119-126.
- Gustafson, J.B., Tell, J.G., and Orem, D. (1997). Selection of Representative TPH Fractions Based on Fate and Transport Considerations. Volume 3. Total Petroleum Hydrocarbon Criteria Working Group Series. Amherst Scientific Publishers. Amherst, MA.
- Haverhoek, S. (1987). Management of hazardous wastes in the oil refinery industry. In: *Management of Hazardous and Toxic Wastes in the Process Industries*. S.T. Kolaczowski and B.D. Crittenden, (eds.). pp. 95-103. Elsevier Applied Science. London, England.
- Heath, J.S., Koblis, K., and Sager, S.L. (1993). Review of chemical, physical, and toxicologic properties of components of total petroleum hydrocarbons. *Journal of Soil Contamination* **2**,1-25.
- Hess, L.Y. (1979). Disposal practices. In: *Reprocessing and Disposal of Waste Petroleum Oils*, pp. 162-169. Noyes Data Corporation, Park Ridge, NJ.

- Hoberman, A.M., Christian, M.S., Roth, L.R., and Koschier, F. (1995). Developmental toxicity of clarified slurry oil (CSO) in the rat. *Fundamental and Applied Toxicology* **28**,34-40.
- Houston Refining (2006). Slop oil. Material Safety Data Sheet, AP 1170. Houston Refining. Houston, TX.
- Huesemann, M.H. (1997). Incomplete hydrocarbon biodegradation in contaminated soils: Limitations in bioavailability or inherent recalcitrance? *Bioremediation Journal* **1**,27-39.
- Jack, T.R., Francis, M.M., and Stehmeier, L.G. (1994). Disposal of slop oil and sludges by biodegradation. *Research in Microbiology* **145**,49-52.
- Jean, D.S., Lee, D.J., and Wu, J.C.S. (1999). Separation of oil from oily sludge by freezing and thawing. *Water Research* **33**,1756-1759.
- Kothandaraman, S., Ahlert, R.C., Venkataramani, E.S., and Andrews, A.T. (1992). Supercritical extraction of polynuclear aromatic hydrocarbons from soil. *Environmental Progress* **11**,220-222.
- Kriipsalu, M., Marques, M., and Maastik, A. (2008). Characterization of oily sludge from a wastewater treatment plant flocculation-flotation unit in a petroleum refinery and its treatment implications. *Journal of Material Cycles and Waste Management* **10**,79-86.
- Leemann, J.E. (1988). Hazardous waste minimization .5. Waste minimization in the petroleum industry. *International Journal of Air Pollution Control and Hazardous Waste Management* **38**,814-823.
- Li, C.T., Lee, W.J., Mi, H.H., and Su, C.C. (1995). PAH emission from the incineration of waste oily sludge and PE plastic mixtures. *Science of the Total Environment* **170**, 171-183.
- Loehr, R.C., Martin, J.H., and Neuhauser, E.F. (1992). Land treatment of an aged oily sludge – organic loss and change in soil characteristics. *Water Research* **26**,805-815.
- Marks, R.E., Field, S.D., Wojtanowicz, A.K., and Britenbeck, G.A. (1992). Biological treatment of petrochemical wastes for removal of hazardous polynuclear aromatic hydrocarbon constituents. *Water Science and Technology* **25**,213-220.
- McKeown, B.A. and March, G.L. (1978). The acute effect of Bunker C oil and an oil dispersant on: part 1 - serum glucose, serum sodium and gill morphology in both freshwater and seawater acclimated rainbow trout (*Salmo gairdneri*). *Water Research* **12**,157-163.
- Mobil (1985a). A modified Ames pre-incubation mutagenesis assay for determination of specific mutagenicity of the DMSO extract of heavy vacuum gas oil. Study No. 52261. Mobil Environmental and Health Science Laboratory. Princeton, NJ.
- Mobil (1985b). Thirteen-week toxicity study by dermal application of clarified slurry oil (CSO) to rats. Study No. 20525. Mobil Environmental and Health Science Laboratory. Princeton, NJ.
- Mobil (1987a). Metaphase analysis of Chinese hamster ovary (CHO) cells treated in vitro with a DMSO extract of heavy vacuum gas oil (a screening assay). Study No. 52262. Mobil Environmental and Health Science Laboratory. Princeton, NJ.

Mobil (1987b). Micronucleus assay of bone marrow red blood cells from rats treated via dermal administration of heavy vacuum gas oil. Study No. 61591. Mobil Environmental and Health Science Laboratory. Princeton, NJ.

Mobil (1987c). Developmental toxicity screen in rat exposed dermally to Heavy coker gas oil-2. Report of study No. 50431. Mobil Environmental and Health Science Laboratory. Princeton, NJ.

Mobil (1988a). Consolidated acute test report on heavy vacuum gas oil. Study Nos. 62443, 62444, 62445. Mobil Environmental and Health Science Laboratory. Princeton, NJ.

Mobil (1988b). Consolidated acute test report on V/breaker HGO. Study Nos. 62496, 62497, 62498, 62499. Mobil Environmental and Health Science Laboratory. Princeton, NJ.

Mobil (1988c). Consolidated acute test report on visbreaker gas oil VIBRA. Study Nos. 62500, 62501, 62502, 62503. Mobil Environmental and Health Science Laboratory. Princeton, NJ.

Mobil (1988d). Thirteen-week dermal administration of heavy vacuum gas oil to rats. Study No. 61590. Mobil Environmental and Health Science Laboratory. Princeton, NJ.

Mobil (1990a). Thirteen-week Dermal Administration of API Separator Bottom Sludge to Rats. Study Number 63036. Mobil Oil Corporation. Princeton, NJ.

Mobil (1990b). Developmental Toxicity Study in Rats Exposed Dermally to API Separator Bottom Sludge. Study Number 63239. Mobil Oil Corporation. Princeton, NJ.

Mobil (1990c). Developmental Toxicity Study in Rats Exposed Dermally to DAF Float Blend. Study Number 63264. Mobil Oil Corporation. Princeton, NJ.

Mobil (1991). Developmental toxicity study in rats exposed dermally to heavy atmospheric gas oil. Study No. 64146. Mobil Environmental and Health Science Laboratory. Princeton, NJ.

Mobil (1992a). Consolidated acute test report on V.B. Mittelol. Study Nos. 64635, 64636, 64637, 64638. Mobil Environmental and Health Science Laboratory. Princeton, NJ.

Mobil (1992b). Thirteen-week dermal administration of visbreaker gas oil to rats. Study No. 63237. Mobil Environmental and Health Sciences Laboratory. Princeton, NJ.

Mobil (1992c). Thirteen-week dermal administration of heavy atmospheric gas oil to rats. Study No. 63456. Mobil Oil Corporation Environmental and Health Sciences Laboratory. Princeton, NJ.

Mobil (1992d). Chemical Characterization Studies of DAF Float Blend (CRU No. 89106). Study Number 63786. Mobil Oil Corporation. Princeton, NJ.

Mobil (1995). Thirteen-week Dermal Administration of DAF Float Blend to Rats. Study Number 63266. Mobil Oil Corporation. Princeton, NJ.

Mobil (undated). Developmental toxicity screen in rats exposed dermally to heavy vacuum gas oil (HVGO): Final report. Study No. 61801. Mobil Environmental and Health Sciences Laboratory. Princeton, NJ.

-
- NCEL (1985). The Physical, Chemical, and Toxicological Properties of Navy Oily Sludge. Report N-1739. Naval Civil Engineering Laboratory Port Hueneme, CA.
- Neff, J.M., Stout, S.A., and Gunster, D.G. (2005). Ecological risk assessment of polycyclic aromatic hydrocarbons in sediments: Identifying sources and ecological hazards. *Intergrated Environmental Assessment and Management* **1**,22-33.
- Pak, A., and Mohammadi, T. (2008). Wastewater treatment of desalting units. *Desalination* **222**,249-254.
- Peterson, D.R. 1994. Calculating the Aquatic Toxicity of Hydrocarbon Mixtures. *Chemosphere* **29**,2493-2506
- PRR (2009) Characterization and quantitation of polynuclear aromatic compounds (PAC) in HPV kerosene, gas oil, heavy fuel oil and hydrocarbon waste samples by PRR ("Mobil" method 2) PAC. Port Royal Research 2009-0102.
- Potter, T.L. and Simmons, K.E. (1998). Composition of Petroleum Mixtures. Selection of Representative TPH Fractions Based on Fate and Transport Considerations. Volume 2. Total Petroleum Hydrocarbon Criteria Working Group Series. Amherst Scientific Publishers. Amherst, MA.
- REMPEC (2004). Port Reception Facilities for Collecting Ship-Generated Garbage, Bilge Water and Oily Wastes. Activity B Optimum Solutions for Collecting, Treatment and Disposal of Relevant Ship-Generated Solid and Liquid Wastes. Regional Marine Pollution Emergency Response Centre for the Mediterranean Sea. The Hague, Netherlands.
- Rhodes, A. (1994). New process effectively recovers oil from refinery waste streams. *Oil & Gas Journal* **92**,92-94.
- Roy, T.A. Johnson, S.W., Blackburn, G.R., Deitch, R.A., Schreiner, C.A., and Mackerer, C.R. (1988). Estimation of mutagenic and dermal carcinogenic activities of petroleum fractions based on polynuclear aromatic hydrocarbon content. In: *Polynuclear Aromatic Hydrocarbons: A Decade of Progress*. M. Cooke and A.J. Dennis (eds.), pp. 809-825. Battelle Press. Columbus, OH.
- Salanitro, J.P., Dorn, P.B., Husemann, M.H., Moore, K.O., Rhodes, I.A., Jackson, L.M.R., Vipond, T.E., Western M.M., and Wisniewski, H.L. (1997). Crude oil bioremediation and soil ecotoxicity assessment. *Environmental Science and Technology* **31**,1769-1776.
- Seneviratne, M. (2007). Oil refining. In: *A Practical Approach to Water Conservation for Commercial and Industrial Facilities*. Chpt 14., pp 330-342. Elsevier. Oxford, UK.
- Shell. 1997a. Light fuel oil: Acute toxicity of water accomodated fractions to *Oncorhynchus mykiss*. Study OP.97.47001, Shell Research and Technology Centre, Thornton, UK.
- Shell. 1997b. Heavy fuel oil: Acute toxicity of water accomodated fractions to *Oncorhynchus mykiss*. Study OP.97.47002. Shell Research and Technology Centre, Thornton, UK.
- Shell. 1997c. Light fuel oil: Acute toxicity of water accommodated fractions to *Daphnia magna*. Study OP.97.47001. Shell Research and Technology Centre, Thornton, UK.

- Shell. 1997d. Heavy fuel oil: Acute toxicity of water accommodated fractions to *Daphnia magna*. Study OP.97.47002. Shell Research and Technology Centre, Thornton, UK.
- Shell. 1997e. Light fuel oil: Acute toxicity of water accommodated fractions to *Raphidocelis subcapitata*. Study OP.97.47001. Shell Research and Technology Centre, Thornton, UK.
- Shell. 1997f. Heavy fuel oil: Acute toxicity of water accommodated fractions to *Raphidocelis subcapitata*. Study OP.97.47002. Shell Research and Technology Centre, Thornton, UK.
- Speight, J.G. (2005). Refinery wastes. In: *Environmental Analysis and Technology for the Refining Industry*. Chpt. 4. pp. 87-121. John Wiley & Sons. Hoboken, NJ.
- Stepnowski, P., Siedlecka, E. M., Behrend, P., and Jastorff, B. (2002). Enhanced photo-degradation of contaminants in petroleum refinery wastewater. *Water Research* **36**,2167-2172.
- Strobel, C.J. and Brenowitz, A.H. (1981) Effects of Bunker C oil on juvenile horseshoe crabs (*Limulus polyphemus*). *Estuaries* **4**,157-159.
- TERA (2008). "Peer Consultation on Relationship between PAC Profile and Toxicity of Petroleum Substances" (API Report), <http://www.tera.org/peer/API/APIWelcome.htm>, accessed 28 Oct 2009 and "Report of the Peer Consultation on Relationship between PAC Profile and Toxicity of Petroleum Substances Volume I" (TERA peer review) <http://www.tera.org/peer/API/PAC MEETING REPORT Final.pdf>, accessed 28 Oct 2009
- UBTL (1986). Dermal sensitization study in guinea pigs administered heavy fuel oil. Report No. ATX-85-0158. Utah Biomedical Testing Laboratory Inc. Salt Lake City, UT.
- UBTL (1987). 28 day dermal toxicity study in rats on Watson Heavy Fuel Oil. Report No. ATX-86-0008. (Utah Biomedical Testing Laboratory Inc. Salt Lake City, UT.
- UBTL (1988). Acute oral toxicity study in rats administered F-97-01. Report No. ATX-88-0086, study No. 64707. Utah Biomedical Testing Laboratory Inc. Salt Lake City, UT
- UBTL (1989a). Acute dermal toxicity study (limit test) in rabbits administered test article F-97-01. Study No. 64834. Report No. ATX-88-0087. Utah Biomedical Testing Laboratory Inc. Salt Lake City, UT
- UBTL (1989b). Dermal sensitization study in guinea pigs administered test article F-97-01 (Coker heavy gas oil). Study No. 64838. Report No. ATX-88-0090. Utah Biomedical Testing Laboratory Inc. Salt Lake City, UT.
- UBTL (1989c). Dermal sensitization study in guinea pigs administered test article F-98-01 (Vacuum tower bottoms. Study No. 65066. Report No. ATX-88-0097. Utah Biomedical Testing Laboratory Inc. Salt Lake City, UT.
- UBTL (1989d). Primary dermal irritation study in rabbits administered test article F-97-01 (Coker heavy gas oil). Study No. 64782. Report No. ATX-88-0089. Utah Biomedical Testing Laboratory Inc. Salt Lake City, UT.

- UBTL (1989e). Primary dermal irritation study in rabbits administered test article F-98-01 (Vacuum tower bottoms). Study No. 65054. Report No. ATX-88-0096. Utah Biomedical Testing Laboratory Inc. Salt Lake City, UT.
- UBTL (1989f). Primary eye irritation study in rabbits administered test article F-97-01 (Coker heavy gas oil). Study No. 64831. Report No. ATX-88-0088. Utah Biomedical Testing Laboratory Inc. Salt Lake City, UT.
- UBTL (1989g). Primary eye irritation study in rabbits administered test article F-98-01 (Vacuum tower bottoms). Study No. 65042. Report No. ATX-88-0095. Utah Biomedical Testing Laboratory Inc. Salt Lake City, UT.
- UBTL. (1990a). 28 day dermal toxicity study in rats. Report No. ATX-90-0066. Utah Biomedical Testing Laboratory Inc. Salt Lake City, UT.
- UBTL (1990b). Acute oral toxicity study in rats administered test article F-132. Report No. ATX-90-0059. Utah Biomedical Testing Laboratory Inc. Salt Lake City, UT.
- UBTL (1990c). Dermal sensitization study in albino guinea pigs administered test article F-113-01 (Heavy Vacuum Gas Oil). Report No. ATX-89-0035. Utah Biomedical Testing Laboratory Inc. Salt Lake City, UT.
- UBTL (1991). Primary eye irritation study in rabbits administered test article F-132 (Atmospheric tower bottoms). Study No. 65833. Report No. ATX-90-0061. Utah Biomedical Testing Laboratory Inc. Salt Lake City, UT.
- UBTL (1992a). Acute dermal toxicity study (limit test) in rabbits administered test article F-136. Study No. 65989. Report No. ATX-90-0092. Utah Biomedical Testing Laboratory Inc. Salt Lake City, UT.
- UBTL (1992b). Acute dermal toxicity study in rabbits administered test article F-132. Study No. 65893. Report No. ATX-90-0060. Utah Biomedical Testing Laboratory Inc. Salt Lake City, UT.
- UBTL (1992c). Dermal sensitization study in guinea pigs administered test article F-132 (Atmospheric tower bottoms). Study No. 65849. Report No. ATX-90-0063. Utah Biomedical Testing Laboratory Inc. Salt Lake City, UT.
- UBTL (1992d). Primary dermal irritation study in rabbits administered test article F-132 (Atmospheric tower bottoms). Study No. 65841. Report No. ATX-90-0062. Sa Utah Biomedical Testing Laboratory Inc. Salt Lake City, UT.
- UBTL (1994). A developmental toxicity screen in female rats administered F-228 dermally during gestation days 0 to 20. Study No. 66479. Report No. ATX-91-0267. Utah Biomedical Test Laboratory, Inc. Salt Lake City, UT.
- USEPA (1982). Development Document for Effluent Limitations, Guidelines and Standards for the Petroleum Refining Point Source Category, EPA-440/1-82-014. U.S. Environmental Protection Agency. Washington, DC.

- USEPA (1995). Hazardous Waste Management System; Identification of Hazardous Waste: Petroleum Refining Process Wastes; Land Disposal Restrictions for Newly Identified Wastes; and CERCLA Hazardous Substance Designation and Reportable Quantities. *Federal Register* **60**,57747-57800.
- USEPA (1996). Study of Selected Petroleum Refining Residuals: Industry Study. US Environmental Protection Agency, EPA530-R-96-018. Office of Solid Waste. Washington, DC.
- Van Wezel, A.P. and Opperhuizen, A. (1995). Narcosis Due to Environmental Pollutants in Aquatic Organisms: Residue-Based Toxicity, Mechanisms, and Membrane Burdens. *Critical Reviews in Toxicology* **25**,255-279.
- WDEQ (1991). Pollution Prevention: Petroleum Refining and Petroleum Distribution Systems. Wyoming Department of Environmental Quality. Cheyenne, WY.
- Ward, O., Singh, A., and Van Hamme, J. (2003), Accelerated biodegradation of petroleum hydrocarbon waste. *Journal of Industrial Microbiology and Biotechnology* **30**,260-270.
- Wong, J.M. and Hung, Y.-T. (2005). Treatment of oilfield and refinery wastes. In: *Waste Treatment in the Process Industries*. L.K. Wang, Hung, Y.-T., Lo, H.H., and Yapijakis, C (eds.). CRC Press. Boca Raton, FL.

Annex 1

Background Information

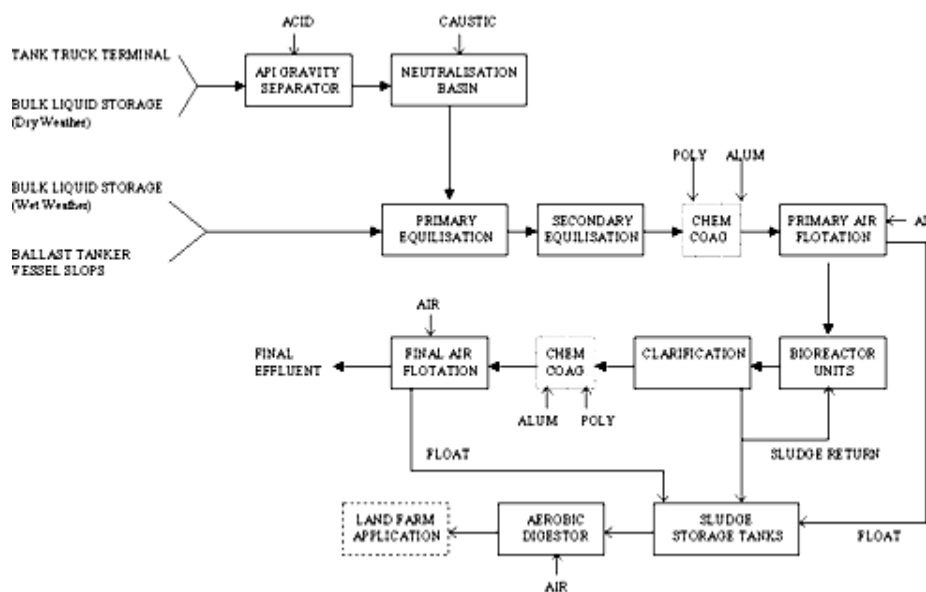
Residual Hydrocarbon Waste Generation

The waste streams in this category represent a diverse group of waste oils and waste materials generated at various stages of the crude oil refining process. The substances are all complex hydrocarbon mixtures that may contain varying amounts of sulfidic, phenolic, and heavy metal components depending on their specific source and the methods of removal and isolation from the process stream (Wong and Hung, 2005). These wastes, generally known as either slop oils or sludges, can contain a range of hydrocarbons with a chain length as high as C₃₅ or greater.

Two of the three substances specifically addressed in this category originate from refinery wastewater and the remaining substance, clay-treating filter wash, is so similar in chemical characteristics that it can reasonably be lumped with the other wastewater residues (USEPA, 1996). For the purposes of this category assessment document, residual hydrocarbon wastes have been assigned the following description:

Hydrocarbon wastes are complex substances consisting of free oil, oily sludge, solvents, emulsified oil, solids, and water that can either originate from crude oil stock or processed streams. These substances are created when individual waste streams, including those from the five HPV substances addressed in this assessment document, are accumulated and temporarily stored in basins or slop tanks before being recycled or disposed of in an acceptable manner.

Upon initial generation, many hydrocarbon wastes contain an appreciable quantity of water even though they may have originated from an operation designed to separate an oily waste from water. In fact, wastewater processing is a major source of many oily waste streams. As shown below, wastewater from a variety of sources needs to undergo a primary and intermediate treatment to remove as much oil and sludge as possible before secondary treatment can take place at a wastewater treatment plant.



Hydrocarbon Waste Generation during Wastewater Treatment

The oils in wastewater may arrive for initial primary treatment either as free oil emulsions (i.e. suspensions of small oil droplets dispersed in water), or as a stable emulsion. Unlike a free oil suspension, stable emulsions are very small oil droplets formed by the mechanical shearing that occurs when pumping or transferring an oil-water mixture. Such waste emulsions, known also as a rag layer, may be stable for some periods of time and do not separate quickly, but may coalesce over time into larger oil droplets that can be collected. Oily wastes of this type have a density less than water and will rise to the water surface to form a floating layer of oil, whereas the high density sludges and sediments will settle to the bottom. Stable hydrocarbon emulsions do not coalesce or separate spontaneously and need to be broken up through the use of coagulants, flocculants, and demulsifiers to separate the oil particles from the water.

To fully understand and appreciate the complexity and inherent diversity of the hydrocarbon wastes that can be generated within a refinery, it is helpful to discuss the processes leading to their formation and separation from solid waste and wastewater. Crude oil refining consumes and re-uses an estimated 65-90 gallons of water for every barrel of crude oil that is refined (Seneviratne, 2007). Much of this water is used on a continuous basis either as a coolant, as a carrier solvent, or as a steam source. The last two uses are particularly relevant since they involve direct contact with crude oil and the resultant formation of a wastewater stream that is composed in part of an oily emulsion.

The wastewaters generated in a petroleum refinery are of four different types: process wastewater, surface water runoff, and cooling water. The first type of waste water is of greatest concern and is responsible for the generation of the largest amount of hydrocarbon waste. Process wastewater emanates from many different sources within a refining operation; however, only a few of these processes give rise to an appreciable quantity of oil or an oily aqueous emulsion (Speight, 2005). As shown below, four operations: crude oil storage, crude oil desalting,

distillation, and catalytic cracking, generate the largest percentage of oily wastewaters (USEPA, 1982).

Wastewaters and Hydrocarbon Wastes Generated by Various Refinery Processes

Production Process	Wastewater flow	Biological Oxygen Demand	Chemical Oxygen Demand	Free Oil	Emulsified Oil	Suspended Solids
Crude Oil Storage	XX	X	XXX	XXX	XX	XX
Crude Oil Desalting	XX	XX	XX	X	XXX	XXX
Crude Distillation	XXX	X	X	XX	XXX	X
Thermal Cracking	X	X	X	X	---	X
Catalytic Cracking	XXX	XX	XX	X	X	X
Hydrocracking	X	---	---	---	---	---
Polymerization	X	X	X	X	0	X
Alkylation	XX	X	X	X	0	XX
Isomerization	X	---	---	---	---	---
Reforming	X	0	0	X	0	0
Solvent Refining	X	---	X	---	X	---
Asphalt Blowing	XXX	XXX	XXX	XXXX	---	---
Dewaxing	X	XXX	XXX	---	0	---
Hydrotreating	X	X	X	---	0	0
Drying and Sweetening	XXX	XXX	X	0	X	XX

XXX – Major contribution XX – Moderate contribution X – Minor contribution 0 – No contribution --- No data

The degree of wastewater contamination from these major refining operations is determined by the length of contact with the crude oil, the temperatures involved, and the volume of water utilized.

1. Crude oil storage

Crude oil is stored in tanks of varying size to ensure adequate feedstock for the refinery and to provide a supply for intermediate processing units. Generally, the crude oil is stored long enough for the separation of water and suspended solids. The wastewater from stored crude is mainly in the form of free and emulsified oil and suspended solids. The water layer accumulates below the oil, forming a bottom sludge (Ferrari *et al.*, 1996). When the water layer is drawn off, emulsified oil present at the oil-water interface is removed as well and treated as a waste requiring initial treatment.

2. Desalting

Crude oil can contain inorganic salts, suspended solids, and water-soluble trace metals that must be removed to reduce corrosion and prevent process unit catalysts from being poisoned (Pak and Mohammadi, 2008). The two most often used methods of crude-oil desalting, chemical and electrostatic separation, use hot water as the extracting agent. In chemical desalting, water and a surfactant are added to the crude, which is then heated so that salts and other impurities dissolve in the water and settle out at the bottom of the tank. Electrical desalting requires the application of an electrostatic charge to agglomerate suspended water globules in the bottom of the settling tank. The wastewater and associated contaminants are discharged from the bottom of the settling tank to the primary treatment facility. The desalted crude is continuously drawn from the top of the settling tanks and sent to the crude distillation tower.

3. Distillation

The wastewater generated at the distillation tower represents one of the largest sources of hydrocarbon wastes from process water. The wastewater from crude oil fractionation generally comes from four or five different sources depending on the configuration of the system (Alva-Argáez *et al.*, 2007). These include collection at over accumulators prior to the transfer of hydrocarbons to other fractionators, at oil sampling line discharge lines, from barometric condensers used to create vacuum conditions, and at the overhead reflex drum where the stripping steam is condensed. The wastewaters from these sources contain oily emulsions along with sulfides, phenols, and heavy metals.

4. Catalytic cracking

Fluidized catalytic cracking breaks down heavy hydrocarbon fractions into lower molecular weight substances that can be more effectively utilized. This process is dependent on the use of a finely powdered catalyst, which produces large volumes of high-octane gasoline stocks, furnace oils, and other useful middle molecular weight distillates. The catalyst is usually heated and lifted into the reactor area by the incoming oil feed which, in turn, is immediately vaporized upon contact. Vapors from the reactors pass upward through a cyclone separator which removes most of the entrained catalyst. The wastewater from catalytic cracking originates with the steam strippers and overhead accumulators used with the fractionators that recover and separate the various hydrocarbon fractions.

Annex 2

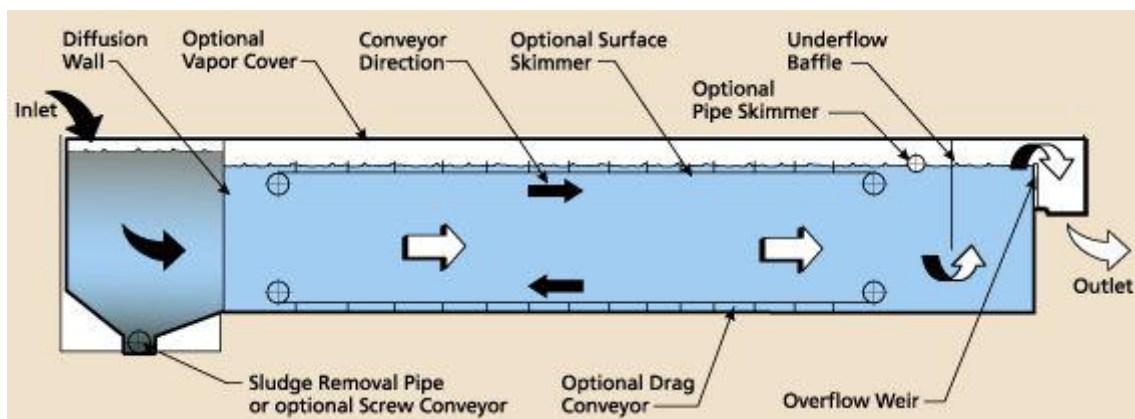
Background Information

Hydrocarbon Waste Separation

As stated previously, although the four refining operations described above make a substantial contribution to the overall load of hydrocarbon waste, other less prominent processes may also contribute. These remaining refinery processes may dramatically impact the composition and overall characteristics of the waste streams that are processed for oil recovery. Before delivery to the wastewater treatment plant, the hydrocarbon-containing wastewaters from these operations undergo an initial primary treatment to remove the bulk of free and emulsified oil and oily sediment. Any of a variety of primary treatment techniques can be used to break-up the oil-water emulsion to yield a hydrocarbon layer that can be separated or skimmed off and collected for final recovery. The treatment plant influent that is generated following this initial primary treatment still contains a large number of hydrocarbons that are often digested in an activated sludge process (Gulyas and Reich, 1995). The following five primary treatment options can be employed in various combinations to separate hydrocarbons wastes from process water. The operating principles and efficiencies of these techniques are described in more detail below.

1. API separator

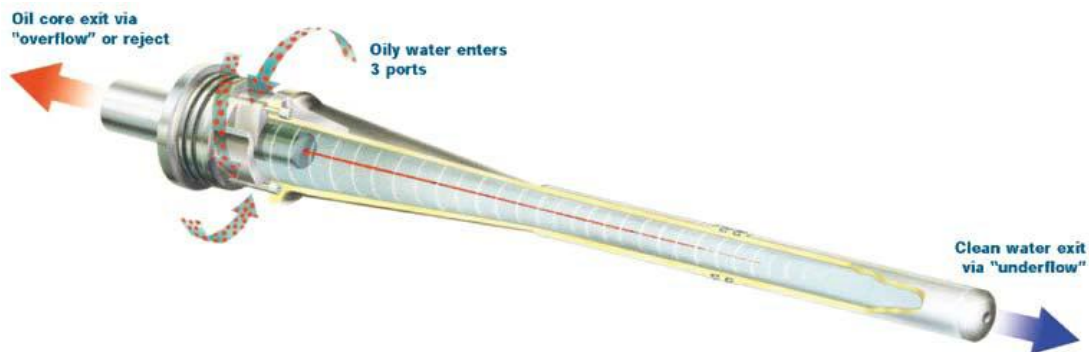
An API separator is a rectangular basin often constructed of concrete that uses gravity to achieve separation of wastewater components. The separator is in essence a retention basin that allows sufficient time for the separation of lighter oils and heavier sediments which accumulate as either a floating hydrocarbon layer or as a sediment that settles out as bottom sludge. Fractions are removed using a mechanical scraping for bottom sludge and a skimmer for oily surface scum. API-separators are commonplace at refineries and oil terminals that process large volumes of wastewater.



API Separator Operation

2. Hydrocyclone

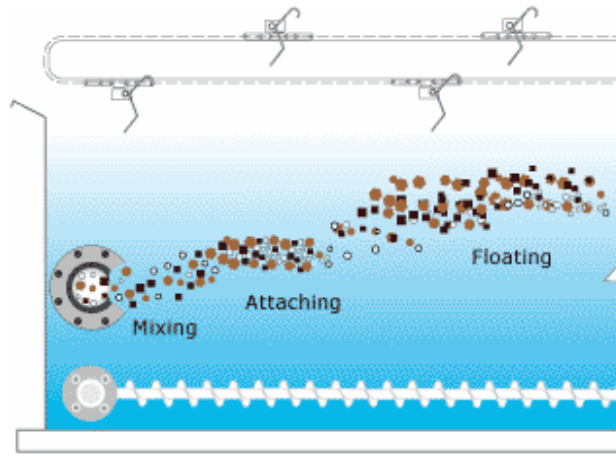
Hydrocyclones are enhanced gravity separators that use centrifugal force to achieve wastewater separation. The device consists of an inverted cone that imparts an angular momentum to the wastewater by forcing a tangential entry at the bottom of the cyclone. The resulting spinning motion forces solids against the wall where they accumulate as a hydrocarbon waste that can be collected and removed. Hydrocyclones are classified by the size of the cone that separates the solid particles in different size ranges. Hydrocyclones are generally used for the separation of wastewater from solids, but when operated in a horizontal manner they can also be used for the separation of wastewater and oil. The higher the density difference between oil and water or the solids and water, the better is the separation efficiency of the hydrocyclone. A typical horizontal hydrocyclone for oil water separation is shown below.



Operation of a Hydrocyclone for the Treatment of Refinery Wastewaters

3. Induced air flotation

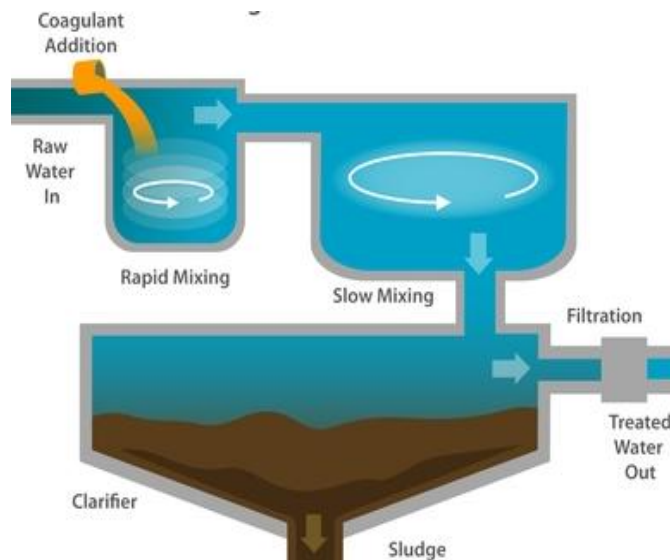
Induced air flotation relies on the dispersion of air bubbles, which act as magnets and adhere to free oil droplets and suspended solids in the wastewater. The treated oil and solids rise to the surface as a hydrocarbon waste product that is collected and removed by a mechanical scraper. The collected sludge has a high water content, often greater than 90%, and needs further treatment to separate the oil and water before final disposal. Induced air flotation is normally accomplished without adding chemicals to the water, and is a frequently employed as a primary treatment in refineries with high wastewater flow rates. The process will not break-up finely-dispersed oily emulsions.



Operation of an Induced Air Flotation Unit

4. Chemical coagulation and flocculation

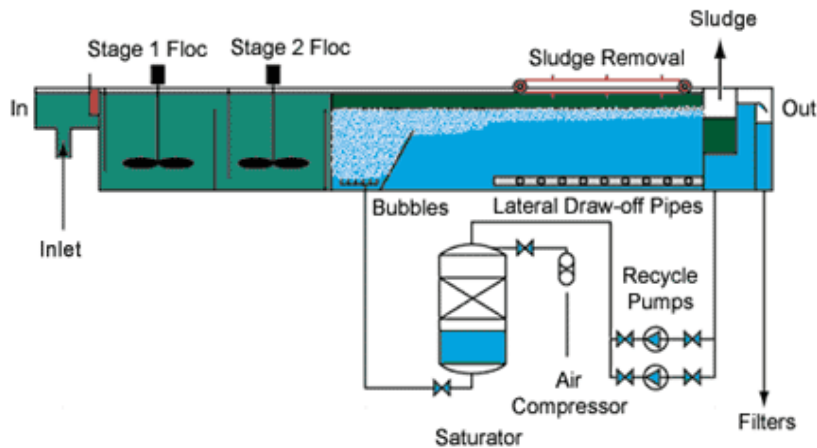
The breakdown of oily emulsions can be accomplished using a combination of coagulation and flocculation. This process uses chemical coagulants such as alum, ferric chloride, ferrous sulfate, lime, sodium hydroxide or organic polymers to break up the colloidal suspensions and suspended sediments. The emulsified oil particles and solids form larger hydrocarbon flocs, which are subsequently separated following sedimentation. The chemicals are mixed with the raw wastewater in coagulation/flocculation tanks, in-line mixers, or pipe-flocculators. The flocculation procedure may also be integrated into a flotation unit that separates the hydrocarbons waste by flotation instead of sedimentation.



Hydrocarbon Wastes from the Operation of a Coagulation-Flotation Unit

5. Dissolved air flotation

Dissolved air flotation (DAF) utilizes air bubbles to break down emulsions that are substantially smaller in size. Very fine air bubbles provide higher separation efficiency of the hydrocarbon waste. The bubbles are generated by saturating a small continuous flow of pressurized clean water with compressed air. The pressurized air/water feed is then injected into the flotation tank where the sudden pressure drop causes the release of very fine air bubbles. The air bubbles attach to the flocculated oils and solids and rise to the water surface and form a floating layer of hydrocarbon waste. The figure below shows how a scraper/skimmer then removes the scum to a discharge hopper.



Wastewater Treatment Using a Dissolved Air Flotation Unit

The operating efficiency of these five primary wastewater treatment methods differ somewhat. As shown below, DAF is capable of removing far more emulsified oil than the other methods. All five methods are capable of removing free oil and suspended sediment at approximately equal efficiencies. Use of these devices in series will result in enhanced removal efficiencies for all forms of waste.

Hydrocarbon Waste Removal Efficiencies for Wastewater Treatment Units*

Separation Method	Free Oil	Emulsified Oil	Suspended Solids
API Separator			
removal efficiency (%)	90 – 95	0	80 – 85
effluent quality (mg/L)	15 – 20	NA	20 – 30
Hydrocyclone			
removal efficiency (%)	80 – 90	0	90 – 95
effluent quality (mg/L)	20 – 30	NA	5 – 10
Induced Air Flotation			
removal efficiency (%)	80 – 90	0	90 – 98
effluent quality (mg/L)	5 – 10	NA	5 – 10
Chemical Coagulation/Flocculation			
removal efficiency (%)	NA	NA	NA
effluent quality (mg/L)	NA	NA	NA
Dissolved Air Flotation			
removal efficiency (%)	95 – 98	95 – 98	95 – 98
effluent quality (mg/L)	5 – 10	5 – 10	56 – 10

* taken from REMPEC, 2004

In most refineries, wastewater is treated in a centralized fashion with all waste streams converging at a central station (FWPCA, 1967). The first step in the treatment process typically involves flow through an API separator, which performs the initial separation of solids and oils from the water. Solids that settle in the API separator are called API separator sludge, whereas the floating layer is termed slop oil. In many refineries, the next step involves treatment at a DAF unit, which removes additional oil and solids. If warranted, the effluent from these processes may be subject to further primary treatment by any of the processes described above, or by a secondary biological treatment before discharge to surface waters. The oil recovered from the API or DAF treatment will often be stored in slop oil tanks, where it is again separated into oil, water, and sediment. The oil is returned to the desalting unit for reprocessing and the wastewater is again recycled back to the API separator.

Annex III – Data Matrix

	Category Member	Category Member	Category Member	Category Member	Category Member	Supporting Material	
CASRN	68477-26-9	68477-26-9	68477-26-9	68476-53-9	68918-73-0	68476-33-5	Read Across Range to Untested Category Members
CAS Name	Wastes, Petroleum	Wastes, Petroleum	Wastes, Petroleum	Hydrocarbons, C _{>=20} , petroleum wastes	Residues (petroleum), clay-treating filter wash	Fuel oil, residual	
Waste Sample Type	DAF Float Blend	API Separator Sludge					
Endpoint							
PHYSICAL-CHEMICAL PROPERTIES							
Melting Point (°C)							not relevant
Pour Point (°C)						-2 to 35	-2 to 35
Freezing Point (°C)							not relevant
Boiling Point (°C)			typically > 100 °C	>350 °C (662 °F).	> 350 °C (662 °F).	340 - 1239	highly variable
Vapor Pressure			0.00000000044 - 0.35 (atm)			9x10 ³ to 5x10 ¹⁷ Pa	highly variable
Partition Coefficient Log Kow			2.9 - 8.8			1.7 - 25	highly variable
Water Solubility ¹ (mg/L)			0.0000025 - 220			0.4 - 6.3	highly variable
ENVIRONMENTAL FATE							
Photodegradation, OH ⁻ reaction T _{1/2} ¹ (h or d)			0.2 - 0.5 days				0.2 to 0.5
Stability in Water			"stable", hydrolysis unlikely				stable

Environ. Distribution ¹			distribution depends on HC class and compound MW. Air <6.1% Water < 82.5% Soil <86.6%				distribution depends on HC class and compound MW. Air <6.1% Water < 82.5% Soil <86.6%
Biodegradation classification						inherently biodegradable	inherently biodegradable
ENVIRONMENTAL EFFECTS							
Acute Fish LL50 (mg/L WAF loading rate)						100 - >1000	100 - >1000
Acute Daphnia EL50 (mg/L WAF loading rate)						220 - >1000	220 - >1000
Algae EL50 (mg/L WAF loading rate)							
EL50 SGR						>30, < 300	>30, < 300
EL50 AUC						>3, <100	>3, <100
HEALTH EFFECTS							
Rat Acute Oral (mg/kg)						LD50 >5000	LD50 >5,000
Rat Acute Dermal (mg/kg)						LD50 >2000	LD50 >2,000
Dermal Rat Repeated-Dose (mg/kg/d)	NOAEL <60	NOAEL = 10,000					NOAEL <60
Genotoxicity, <i>in vitro</i>						Positive	Positive
Genotoxicity, <i>in vivo</i>						Equivocal	Equivocal
Dermal Developmental toxicity (mg/kg/d)	NOAEL <125	NOAEL <500					NOAEL <125

blank cells = no data; value will be read across range

¹ Level 1 fugacity model output. Range of values based upon characteristics of potential individual hydrocarbon constituents.

Annex IV. Robust Summaries (Separate Document)