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HIGH PRODUCTION VOLUME (HPV) CHEMICAL CHALLENGE PROGRAM

**TEST PLAN
HEAVY FUEL OILS CATEGORY**

Submitted to the US EPA

By

The Petroleum HPV Testing Group

www.petroleumhvp.org

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PLAIN LANGUAGE SUMMARY

The Heavy Fuel Oils (HFOs) category includes both finished products (residual fuels) and the primary refinery streams from which they are blended. Members of the heavy fuel oil category are a diverse group of substances encompassing hydrocarbons with a wide range of molecular weights, carbon numbers (C_7 to C_{50}) and boiling points (250 – 1112 °F (121 to 600 °C)). In addition to petroleum hydrocarbons they contain heterocyclic compounds containing sulfur, nitrogen, and oxygen, and organo-metallic compounds. The residual fuels are low-grade fuels primarily used in industrial boilers and other direct source heating applications (e.g., blast furnaces) and as a principal fuel in marine applications. The finished heavy fuels (residual fuels) are products that consist primarily of the residuum of the refining process after virtually all of the higher-quality hydrocarbons have been distilled, cracked, or catalytically removed from crude oil feedstock. To produce a residual fuel of a specified viscosity, the high viscosity of the residual streams is reduced by adding a diluent (cutter stock) that is typically a lower quality distillate stream. The choice of the distillate cutter stock is itself variable and largely a function of availability at any given time within the refinery and the viscosity specifications of the product being manufactured. For instance, in refineries with catalytic cracking units, catalytically cracked cycle oils are common fuel diluents (CONCAWE, 1998). Because residual fuels are blended from a variety of different residual and distillate materials, the specifications for residual fuel oils are very general, with viscosity being the controlling specification. The exact blend used for a specific residual fuel is determined largely by the desired viscosity of the finished fuel and specifications set by ASTM (2002). As a result, the composition of residual fuel oils can vary widely and will depend on the refinery configuration, the crude oils being processed and the overall refinery demand.

The Testing Group is proposing to perform a repeat-dose/reproductive/developmental screening study (OECD 422) on a representative sample of a reformer residue. A representative sample of a residual fuel oil will be tested using the reproductive/developmental screening protocol (OECD 421). *In-vitro* genotoxicity assays (modified Ames & chromosomal aberration) will also be performed on samples of an atmospheric residue, atmospheric distillate, cracked distillate, reformer residue and a residual fuel oil.

The environmental fate characteristics of the materials in this category are due in large part to the physico-chemical parameters of the individual component hydrocarbons. Where physico-chemical data did not exist or were impractical to obtain, calculated physico-chemical and environmental data for selected constituents of category members has been developed using the EPIWIN[®] computer model.

When released to the environment, the dispersion of heavy fuel oil depends upon the severity of the weathering elements. High-energy environments will tend to disperse substances more quickly than low energy environments. During weathering, low molecular weight fractions will dissolve in the water column or volatilize to the air, whereas intermediate fractions will float and/or spread out on water or soil where they tend to form emulsions or adsorb to soil and sediment particles. The viscous high molecular weight components will agglomerate and float or sink depending upon the density of the substance. Volatile components are not expected to persist in the atmosphere due to their capacity to undergo direct and/or indirect photodegradation. Hydrocarbons are regarded as being inherently biodegradable, and the low molecular weight fraction that dissolves in water will rapidly biodegrade. The limited water solubility and bioavailability of the heavy fractions reduces their capacity for biodegradation. These substances will biodegrade, although at a much slower rate.

For the assessment of the ecotoxicity of heavy fuel oils, the category substances are considered as a single group, and the potential for any category member to elicit adverse effects in aquatic organisms is attributed to the solubility of the constituent hydrocarbons in that member. This is valid because petroleum hydrocarbons elicit effects through a common mode of toxicity termed nonpolar narcosis (van Wezel and Opperhuizen, 1995), which is produced by the soluble hydrocarbon fractions in aqueous preparations. Fuels having molecular weight hydrocarbons predominately higher than the solubility "cut-off" for acute toxicity show no measurable acute toxicity (CONCAWE 2001). The solubility cut-off varies with the hydrocarbon structure; thus, for paraffinic hydrocarbons the solubility cut-off occurs at about C_{10} , while for alkylbenzenes it is about C_{14} (CONCAWE, 2001). Other individual components contribute to toxicity, but as molecular weight increases, both solubility and toxicity decline.

Existing aquatic toxicity data show heavy fuel oil related refinery streams to have moderate to no aquatic toxicity depending upon species and test substance. Algae have exhibited a greater sensitivity than fish or invertebrates to heavy fuel oil exposure, and different substances have produced different toxicity in the same species. Because substances in the Heavy Fuel Oil category include a wide range of molecular weight hydrocarbons, existing data may not represent the ecotoxicity of some category members based on their distillation and carbon number ranges. However, the Testing Group believes the combination of existing residual fuel oil ecotoxicity data and data on kerosene and gas oil streams sufficiently covers what would be expected for the ecotoxicity of all members of the heavy fuel oil category. Kerosene and gas oils are composed of similar hydrocarbon constituents as in heavy fuel oils and have similar molecular weights as the light components of category members with low initial boiling points. Therefore, because the light-end components of the heavy fuel category members are expected to be the most toxic components, the ecotoxicity of the kerosene and gas oils represent a conservative estimate of the ecotoxicity for those heavy fuel oil category members. No additional ecotoxicity testing of heavy fuel oil is proposed.

DESCRIPTION OF THE HEAVY FUEL OILS CATEGORY

The Heavy Fuel Oils (HFOs) category includes both finished products (residual fuels) and the primary refinery streams from which they are blended. The residual fuels are low-grade fuels primarily used in industrial boilers and other direct source heating applications (e.g., blast furnaces) and as a principal fuel in marine applications. The residual fuels are products that consist primarily of the residuum of the refining process after virtually all of the higher-quality hydrocarbons have been distilled, cracked, or catalytically removed from crude oil feedstock. Historically, fuel oils were based on residues from the atmospheric column. However, the increasing demand for transportation fuels such as gasoline, kerosene and diesel has led to an increased value for the atmospheric residue as a feedstock for vacuum distillation and for cracking processes. As a consequence, most heavy fuel oils are currently based on vacuum residues and residues from thermal and catalytic cracking operations (CONCAWE, 1998). These high viscosity residual streams may in turn be "cut" with lower quality, lighter weight distillates to produce a finished residual fuel of a specified viscosity. The choice of the distillate cutter stock is itself variable and largely a function of availability at any given time within the refinery and the viscosity specifications of the fuel being manufactured. While the materials most frequently used as cutter stocks are included in this category, other streams may occasionally be used, e.g., kerosene and gas oils. These other materials are characterized in other API HPV Test Plans. The exact blend used for a specific residual fuel is determined largely by the desired viscosity of the finished fuel and specifications (ASTM, 2002). Some of the refinery streams in the category that have lower viscosities and lower polyaromatic compound (PAC) levels have low-volume, specialty applications such as cutter stock in cutback asphalt, synfuel binders and carbon electrode production.

Members of the heavy fuel oils category are a diverse group of substances that encompass hydrocarbons with a wide range of molecular weights, with carbon numbers ranging from C_7 to C_{50} and boiling points between 250 – 1112 °F (121 to 600 °C). However, "typical" heavy fuel oils are C_{20} - C_{50} with the low carbon numbers and boiling temperatures being associated with lighter weight "cutter" streams (CONCAWE, 1998). All the category members are complex mixtures, containing variable amounts of alkanes, cycloalkanes, aromatics, olefins, asphaltenes, and hetero-molecules containing sulfur, oxygen, nitrogen and organo-metals. Because they are complex mixtures composed of relatively high molecular weight compounds, the materials in this category are difficult to characterize in detail. Consequently, they are typically not defined by detailed compositional information but instead by process history, physical properties, and product use specifications (ASTM, 2003). Since viscosity is the controlling specification, and other limiting requirements - notably boiling point ranges - are unspecified, there is significant variation in the chemical composition of the resulting fuel products (Uhler, 2002; IARC, 1989).

Because the process history of a refinery stream determines its chemical composition, the Testing Group expects that streams that have undergone similar processing will have similar physical/chemical/biologic properties and environmental fate and transport characteristics. The refinery streams within the heavy fuels category can therefore be grouped into seven subcategories based on their process histories. As shown in Figure 1, the major processes used to produce the refinery streams included in the heavy fuel oils category are:

Atmospheric distillation

Heavy fuel oil related streams produced by atmospheric distillation comprise fractions of crude oil separated by heating (650-700 degrees °F) at atmospheric pressure. They include atmospheric distillates (heavy gas oils) and the heavier residual materials. The distillate HFO streams are similar to some of the refinery streams covered in the API HPV Gas Oils category, albeit of higher molecular weight. Some of these streams may be further hydrotreated or desulfurized to remove sulfur, nitrogen, and other impurities. Most atmospheric distillates undergo further processing in order to convert them into higher value fuels (diesel, kerosene). However, a portion of the heavier distillate streams may be used as blending stocks to reduce the viscosity of the residual streams. The residual refinery streams comprise a heterogeneous group of poorly defined, viscous, high boiling hydrocarbon streams that usually contain suspensions of resin/asphaltene complexes. These streams often have high levels of heterocyclic aromatic and naphthenic compounds. Varying percentages of sulfur, nitrogen, oxygen, and other elements are present as heterocyclic inclusions, primarily in the aromatics fraction. These residual streams often have a PAC content over 5%, but the content can be much higher depending on the processing the stream has undergone. As shown in

Figure 1, there are eight refinery streams in the heavy fuel oils category that are produced by atmospheric distillation (two distillate and six residual streams). See Appendix A for a more detailed description of each of these streams.

Vacuum distillation

The residuum from the atmospheric distillation unit is heated at higher temperatures to further separate heavier molecules. This is done under reduced pressure to prevent thermal cracking. In addition to producing lube oils, various vacuum distillates (vacuum gas oils) and vacuum residues are produced. Similar to the atmospheric distillates, some of the vacuum distillates may be hydrotreated or desulfurized to remove sulfur, nitrogen, and other impurities. Most vacuum distillates undergo further processing in order to convert them into higher value fuels (diesel, kerosene). However, a portion of the heavier vacuum distillate streams may be used as blending stocks to reduce the viscosity of the residual streams. The vacuum residual refinery streams comprise a heterogeneous group of poorly defined, viscous, high boiling hydrocarbon streams that usually contain suspensions of resin/asphaltene complexes. These streams often have high levels of heterocyclic aromatic and naphthenic compounds. Varying percentages of sulfur, nitrogen, oxygen, and other elements are present as heterocyclic inclusions, primarily in the aromatics fraction. These residual streams often have a PAC content over 5%, but the content can be much higher depending on the processing the stream has undergone. As shown in Figure 1, there are nine refinery streams in the heavy fuel oils category that are produced by vacuum distillation (seven distillate and two residual streams). See Appendix A for a more detailed description of each of these streams.

Cracking

Many of the distillate and residual streams used to blend heavy fuel oils are derived from cracking processes. Cracking is a process that breaks ("cracks") the heavier, higher boiling petroleum streams produced by atmospheric or vacuum distillation into lighter molecular weight materials such as gasoline, diesel fuel, jet fuel and kerosene. Often, after cracking, streams may be hydrotreated (reduces nitrogen and aromatic content) or undergo desulfurization.

There are two basic types of cracking processes, those using heat and pressure (thermal cracking) to break molecular bonds, and those using a catalyst (catalytic cracking) to facilitate the cracking process. Both thermal and catalytic cracking are used to produce refinery streams that are used for blending heavy fuel oils.

Visbreaking, coking and steam cracking are types of thermal cracking. In visbreaking, the heavy feedstock is heated under pressure to crack the molecules in the stream. Coking is a severe method of thermal cracking. In steam cracking, the hydrocarbon stream is diluted with steam and then briefly heated (>900 °C) in a furnace. Light hydrocarbon feeds produce streams rich in the lighter alkenes, including ethylene, propylene and butadiene. Heavier hydrocarbon feeds give some of these, but also give products rich in aromatic hydrocarbons. Petroleum pitch, sold as a product for various applications, is a high aromatic residual material produced from either thermal cracking or catalytic cracking.

Catalytic cracking and hydrocracking are two types of catalytic cracking. Catalytic cracking is similar to thermal cracking except a catalyst facilitates conversion of the heavier to lighter products and requires less severe operating conditions than thermal cracking. Catalytic cracking converts heavy paraffins to light paraffins and olefins, heavy naphthenes to light naphthenes and olefins, and heavy aromatics to light aromatics, naphthenes and olefins. As noted above, petroleum pitch is a high aromatic residual material from either catalytic cracking or thermal cracking.

Hydrocracking is a combination of catalytic cracking and hydrogenation, using high pressure, high temperature, a catalyst, and hydrogen. It is typically used for feedstocks that are difficult to process by either catalytic cracking or reforming. When the feedstock has a high paraffin content, the primary function of hydrogen is to prevent formation of PACs. Hydrocracking converts sulfur and nitrogen compounds to hydrogen sulfide and ammonia.

The Testing Group thinks the refinery streams produced by the various cracking processes can be considered as a single subcategory since they represent a continuum in the severity of the cracking process.

All the cracking processes produce refinery streams that are similar from a physical-chemical perspective, being differentiated from each other primarily by the ratio of their unsaturated and saturated hydrocarbon content. While the ratio of the saturated and aromatic hydrocarbons may vary between subcategory members, the saturated and aromatic hydrocarbons species that make up the subcategory members are similar. For instance, refinery streams that are produced by catalytic cracking (most severe) have high levels of aromatics. In contrast, hydrocracked (least severe) streams have relatively low amounts of aromatics, since hydrocracking introduces hydrogen into the cracking process that results in saturation of aromatic compounds. As shown in Figure 1, there are eleven refinery streams in the heavy fuel oils category that are produced by cracking (five distillate and six residual streams). See Appendix A for a more detailed description of each of these streams.

Reforming

Catalytic reforming employs a catalyst to facilitate the structural rearrangement of hydrocarbon molecules in order to increase the aromatic content of a refinery stream, ultimately leading to a gasoline with a higher octane. During reforming, olefins are saturated to form paraffins, which are then converted to shorter paraffins, isoparaffins, and naphthenes. The naphthenes are converted to aromatics by dehydrogenation (Gary and Handwerk, 1994). As shown in Figure 1, there are two refinery streams in the heavy fuel oils category that are produced as residues of reforming. See Appendix A for a more detailed description of each of these streams.

Residual Fuel Oils

In addition to the process streams discussed above, the heavy fuel oil category also includes two blended residual fuel oils. These two fuel oils are most often produced by blending any combination of the distillate and residual streams contained in the seven process subcategories, provided the finished fuel meets the appropriate product specifications. Less frequently, the residual fuels can be blended using residual streams from this category, but petroleum distillates (cutter stocks) covered in other API HPV Test Plans. See Appendix A for a more detailed description of each of these two residual fuel oils.

Analytical data for representative materials in this category are shown in Table 1.

Table 1. Composition of Representative Samples of the HFO Category

Endpoint	Atmospheric Residue	Vacuum Distillate	Cracked Distillate	Cracked Residue	Residual Fuel Oil
CAS No.	64741-45-3	64741-57-7 ¹	64741-81-7	64741-62-4	68476-33-5
Specific gravity	0.9698	0.9285	0.9383	1.0725	0.8491
Refractive index	1.5132	1.515	1.5259	Too dark	1.6306
Distillation (°F)					
IBP	531	548	411	395	340
End point	1041	1131	831	952	1239
Non-aromatics	32.18	40.03	49.6	41.7	55.8
Aromatics (wt %)	67.82	59.97	50.4	58.3	44.2
API, 1987; CONSCI 1992a,b; DataChem 1990					

Composition of Heavy Fuel Oil Blending Streams

While detailed compositional information is limited, general compositional information can be inferred from a refinery stream's physical properties and the type of processing it has undergone. For instance, the higher the boiling temperature range of a stream, the higher the molecular weight of the oil's components, the higher the levels of PACs, polycycloparaffins and hetero-atoms (N, O, S, and metals) increase, and the lower the levels of paraffins (see Figure 2). Furthermore, since "cracking" raises the olefin and aromatic content of refinery streams, streams that have been "cracked" have higher olefin and aromatic hydrocarbon content than "straight run" streams that have undergone a limited amount of additional processing. For example, catalytically cracked clarified oil has been reported to contain 58% three to five ring aromatic hydrocarbons (IARC, 1989). Thus, a

residual fuel blended using primarily catalytically cracked or steam cracked components will have a higher PAC content (may approach 20%) than a fuel blended primarily of a non-cracked stream, i.e. heavy vacuum gas oil (CONCAWE, 1998). If on the other hand, the blending stocks are predominantly atmospheric or vacuum distillates or residues, the concentration of three to seven ring aromatic hydrocarbons is likely to be of the order of 6-8% (IARC, 1989). The types and levels of PACs found in a specific fuel will depend on the processing the residual portion of the fuel has undergone, and the nature of the blending stream ("cutter" stock) that is used to adjust the viscosity of the finished fuel.

Figure 1. HFO Process Diagram

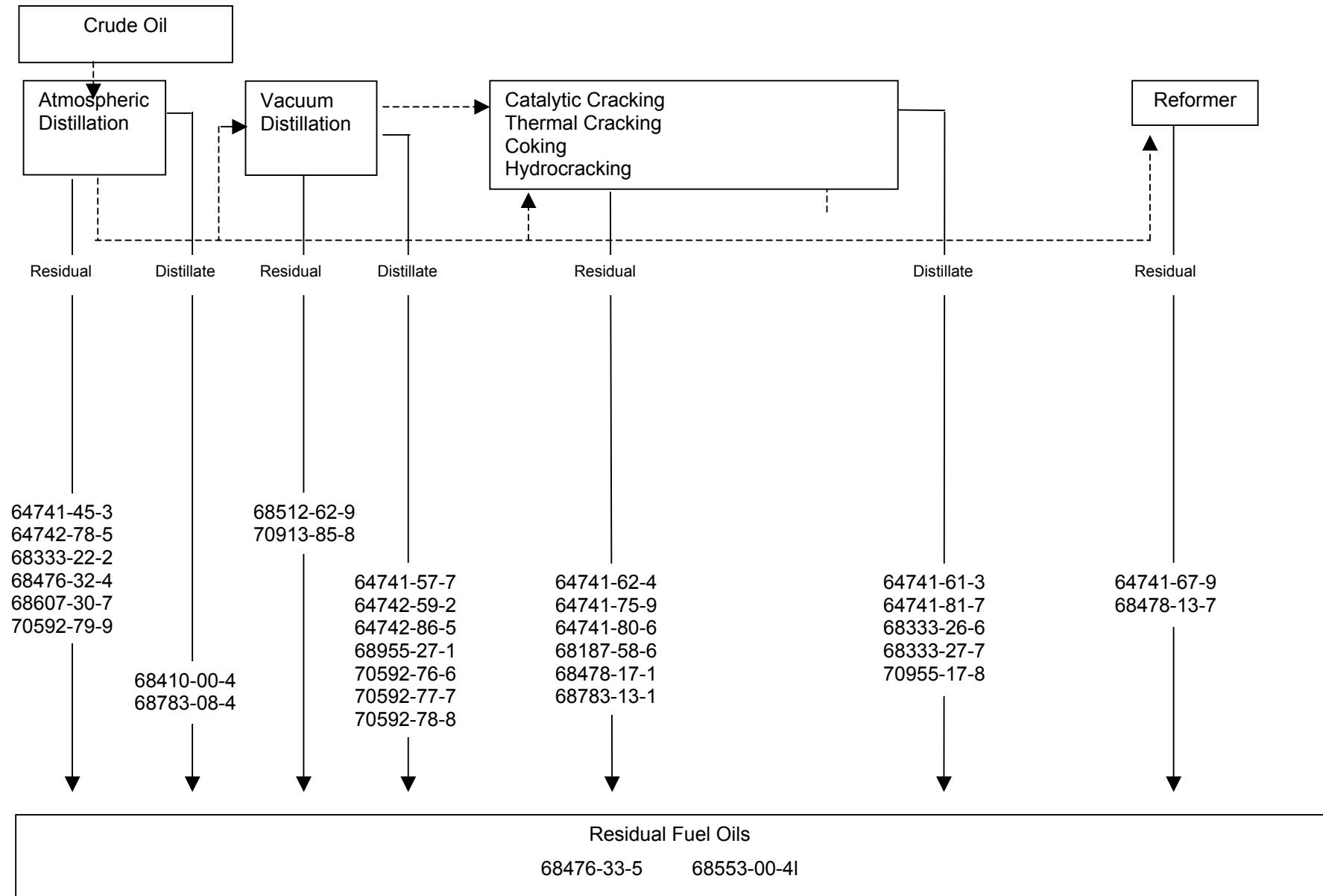
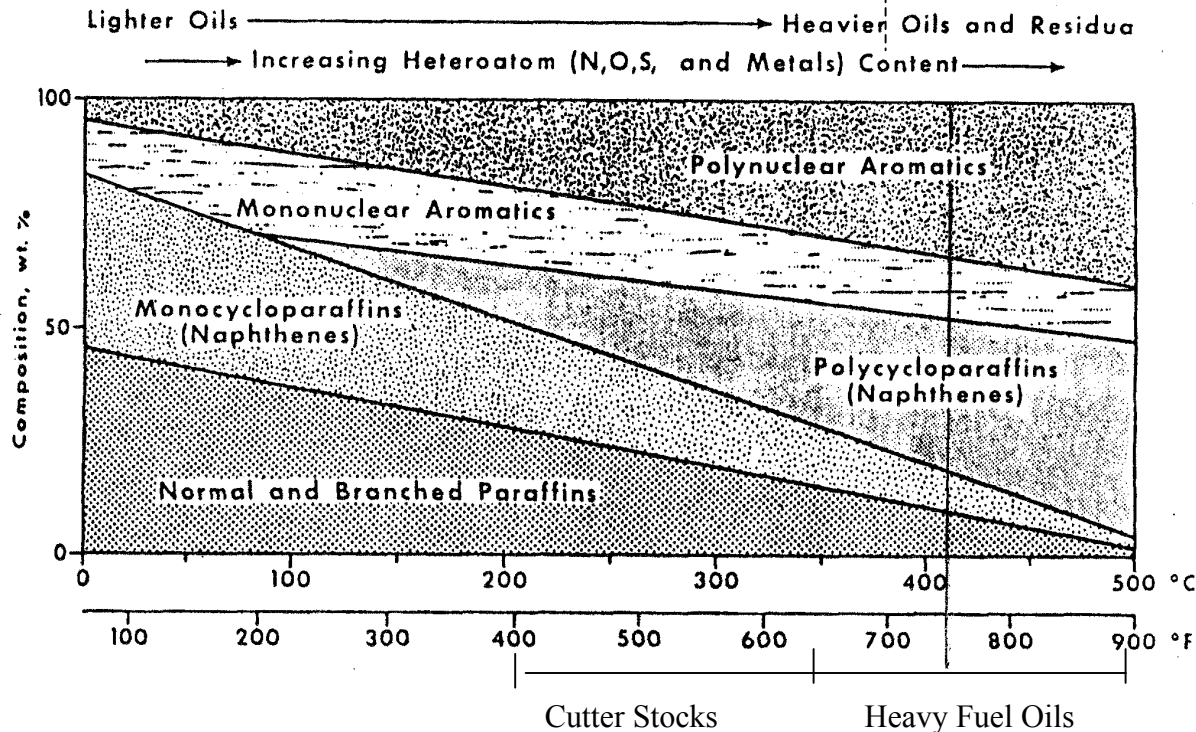


Figure 2. Refinery Stream Composition – Boiling Range vs. General Composition



Speight, 1998

Links to additional resources on refining processes and petroleum-related glossaries are presented in Appendix B.

CATEGORY RATIONALE AND TEST MATERIAL DESCRIPTION

With regard to mammalian toxicity, when analyzing the existing data, proposing testing and identifying potential test materials the Testing Group considered the following:

- The HFO category consists of finished products (residual fuels) and the primary refinery streams from which they are blended;
- The refinery streams in this category that are blended to produce finished heavy fuels can be grouped into seven subcategories according to their process history;
- Refinery streams within a process subcategory are similar from a process and physical/chemical perspective, and are expected to have similar biologic, environmental fate and transport characteristics;
- The range of toxicity of the materials in each process subcategory can be characterized by characterizing representative materials within each subcategory;
- The toxicity of the finished products (Residual Fuel Oils) will fall within the range of toxicities exhibited by the streams blended to produce the finished fuel;
- Because of compositional overlaps and similarities, other API HPV test programs involving gas oils, aromatic extracts, jet fuel/kerosene and asphalt will produce data that will assist in characterizing the materials in this category.

With regard to ecotoxicity, when analyzing the existing data, the Testing Group proposes that a material's solubility (i.e. carbon chain length) determines the degree of ecotoxicity. This is valid and consistent with the current theory on the mode of toxic action for non-polar organic molecules (such as petroleum hydrocarbons) to aquatic organisms (Peterson, 1994; van Wezel and Opperhuizen, 1995). Thus, the category substances are

considered as a single group. Furthermore, the streams and products in the heavy fuel oil category are composed of constituent hydrocarbon compounds that also are represented in other petroleum product HPV categories that have substantial ecotoxicity data. Therefore, the Testing Group has employed data from other categories as read across to describe potential ecotoxicity for all streams and products in the heavy fuel oil category.

Because the compositions of the materials in this category vary over time, it is not possible to specify in this Test Plan the exact chemical makeup of the test samples that will be used in the mammalian testing. Specific analytical data on the test samples will be developed and made available when the samples are obtained. For a both the process subcategories and the residual fuel, the Testing Group will attempt to select test sample(s) that are thought to have the highest potential toxicities.

EVALUATION OF EXISTING HEALTH EFFECTS DATA AND PROPOSED TESTING

General Evaluation

Reviews of this category of fuels have been published by two expert panels (CONCAWE, 1998; IARC, 1989). In preparing this Test Plan, the approach of the Testing Group has been to review the available toxicology studies and include in the robust summary a detailed description(s) of the one study or a small number of studies that best address each SIDS Level 1 endpoint. Other studies are cited in the appropriate "Remarks" section of the Robust Summary and are intended to supplement the readers' knowledge.

The Test Plan addresses the health effects endpoints of the category by:

- Evaluating the toxicology database for the heavy fuel oil related refinery streams and products,
- Using read-across information whenever possible among category members, and other API HPV categories, and
- Proposing selected testing on representative samples.

HEALTH EFFECTS

Acute Toxicity

The following acute toxicity results have been reported on representative samples of the seven heavy fuel oil subcategories:

Acute Oral Toxicity	LD₅₀ value	Species	Observations
Residual Fuel Oils (4 samples)	5.13 - >25 ml/kg _{bw}	Rat	Lethargy; grease on fur
Process Subcategories			
Atmospheric residue	>5000 mg/kg _{bw}	Rat	Stained coats; dark red areas in lung lobes
Atmospheric distillate	No studies available	-	-
Vacuum residue	Data on two vacuum residuum samples (CAS no. 64741-56-6, API samples 81-13 and 81-14) are presented in the API HPV Asphalt Test Plan	-	-
Vacuum distillate (3 samples)	>5000 mg/kg _{bw}	Rat	↓ Activity; chromorhinorrhea, ↓ fecal output; urogenital staining; ↓ urine
Cracked residue	4320♀ 5270♂ mg/kg _{bw}	Rat	Mortalities; hypoactivity; piloerection; staining around mouth, nose,

			urogenital; hair loss; weight loss; intestinal mucosa damage
Cracked distillate	>5000 mg/kg _{bw}	Rat	Oral, nasal discharge; lethargy; abnormal stools; pale & mottled kidneys
Reformer residue	No studies available	-	-
UBTL, 1988,1990b; API, 1980a-d, 1982; Mobil, 1988b,c, 1992a			

Acute Dermal Toxicity	LD ₅₀ value	Species	Observations
Residual Fuel Oils (4 samples)	>5 ml/kg _{bw}	Rabbit	Erythema; slight congestion of liver
Process Subcategories			
Atmospheric residue	>2000 mg/kg _{bw}	Rabbit	Abnormal stool; dark red areas in lung
Atmospheric distillate	No studies available	-	-
Vacuum residue	Data on two vacuum residuum samples (CAS no. 64741-56-6, API samples 81-13 and 81-14) are presented in the API HPV Asphalt Test Plan	-	-
Vacuum distillate (4 samples)	>2000 mg/kg _{bw}	Rabbit	↓ Food consumption; soft stool; ↓ fecal output
Cracked residue	>2000 mg/kg _{bw}	Rabbit	No signs systemic toxicity; no gross findings
Cracked distillate	>2000 mg/kg _{bw}	Rabbit	Erythema & edema; mottled kidneys
Reformer residue	No studies available	-	-
API, 1980a-d, 1982; UBTL 1989a, 1992a,b			

Dermal Irritation	Irritation Index	Species	Observations
Residual Fuel Oils (4 samples)	0.27 – 1.54	Rabbit	Minimal – slight irritant
Process Subcategories			
Atmospheric residue	3.5	Rabbit	Moderately irritating
Atmospheric distillate	No studies available	-	-
Vacuum residue	0.18	Rabbit	Not irritating
Vacuum distillate (4 samples)	1.2 – 3.6	Rabbit	-
Cracked residue	0.2	Rabbit	-
Cracked distillate	5.6	Rabbit	Moderately irritating
Reformer residue	No studies available	-	-
UBTL, 1989d,e, 1992 d; API 1980a-d, 1982; Mobil, 1988a,b c, 1992a			

Eye Irritation	Irritation Indices	Species	Observations
	24 & 72 hr		
Residual Fuel Oils (4 samples)	2.67 – 7.67 & 0 – 1.33 rinsed 4.0 – 7.33 & 0.0 – 1.33 un-rinsed	Rabbit	Minimal – mild irritant
Process Subcategories			

Atmospheric residue	0.0 & 0.0 un-rinsed only	Rabbit	Not irritating
Atmospheric distillate	No studies available	-	-
Vacuum residue	5.0 & 4.7 un-rinsed 5.7 & 4.7 rinsed	Rabbit	Un-rinsed - not irritating – Rinsed - minimal irritant
Vacuum distillate (4 samples)	2.0 – 10.3 & 1.7* – 3.3*	Rabbit	Un-rinsed only * 48 hr score
Cracked residue	2.0 & 0 rinsed & un-rinsed	Rabbit	Minimal irritant
Cracked distillate	5.7 & 0.0 un-rinsed 5.3 & 0.0 rinsed	Rabbit	Un-rinsed - not irritating Rinsed – not irritating
Reformer residue	No studies available	-	-
UBTL, 1989f,g, 1991 API, 1980a-d, 1982; Mobil, 1988a,b, c, 1992a			

Sensitization	Challenge Response	Species	Observations
Residual Fuel Oils (4 samples)	-	Guinea Pig	3 samples non-sensitizer 1 sample mild sensitizer
Process Subcategories			
Atmospheric residue	0/10	Guinea Pig	Non-sensitizer
Atmospheric distillate	No studies available	-	-
Vacuum residue	0/10	Guinea Pig	Non-sensitizer
Vacuum distillate	1/10	Guinea Pig	Non-sensitizer
Cracked residue	0/10	Guinea Pig	Non-sensitizer
Cracked distillate	0/10	Guinea Pig	Non-sensitizer
Reformer residue	No studies available	-	-
API, 1980a-d, 1984; UBTL, 1986,1989b,c; 1990c, 1992c			

Summary: No additional testing is planned. Multiple acute toxicity studies have been reported on a number of representative samples of the heavy fuel oil refinery streams as well as on finished residual fuels. These data and data from the other 12 API HPV Test Plans show the acute toxicity of a wide-array of petroleum hydrocarbon streams is consistently low, with many oral LD50's greater than 5 g/kg, and dermal LD50s greater than 2 g/kg. While no data is presented for the vacuum residue process subcategory, the Testing Group thinks existing acute toxicity data on two vacuum residuum samples (CAS no. 64741-56-6, API samples 81-13 and 81-14) presented in the API HPV Asphalt Test Plan support the Group's position that this subcategory of materials would have low acute toxicities. Similarly, although no data is presented for the atmospheric distillate or reformer residue subcategories, materials produced by these processes have been considered in other API HPV Test Plans that have consistently shown the acute toxicities of the materials to be low. Consequently, the Testing Group thinks the acute toxicities of these materials can be characterized by "Read Across" from materials other API HPV Test Plans.

Repeat-Dose Toxicity

Studies of up to 13 weeks duration have been reported for representative streams in a number of the process subcategories within the heavy fuel oil category. In instances where there were multiple studies available for a subcategory, only the study of the longest duration was fully summarized in the attached Robust Summary (Appendix C).

Residual Fuel Oils

Dose levels of 0.5 (496 mg), 1.0 (992 mg), or 2.5 (2480 mg) ml/kg_{bw}/day of a heavy fuel oil (CAS no. 668476-33-5) were applied undiluted to the skin of male and female rats (UBTL, 1987). The test material was applied 5x/week for 4 weeks. The test material produced minimal reversible dermal irritation at all dose levels. Daily observations of the animals found no compound-related effects other than staining at the site of application. Similarly, there were no compound-related findings at necropsy other than the staining of the skin produced by the test article.

Eosinophil counts were significantly lower for the mid-dose and high-dose males. SGPT levels were significantly lower for the low- and high-dose females and the high-dose males. Glucose levels were significantly higher for the mid- and high-dose females and high-dose males. Total protein levels were significantly lower for the low-dose males. Hemoglobin levels were significantly lower for the high-dose males. Upon comparison and review of historic data, the study directors concluded the significant values obtained from the hematology or clinical chemistry assays were within normal limits and did not exhibit any clear dose-related trends.

Relative liver weights were significantly higher for the females in all dose groups and in the high-dose males. With the exception of the liver/brain weight ratios in the low-dose males, liver/body weight and liver/brain weight ratios were significantly higher for both sexes in all dose groups. The liver weight changes were thought by the study directors to be compound-related. Spleen/body weight ratios were significantly higher for the low and mid-dose females and the high-dose males. The spleen/brain weight ratios were significantly higher for the low-dose females and the high-dose males. The changes in relative spleen weights were not thought to be dose-related by the study directors.

Microscopic examination of selected tissues from the control and high dose groups found no compound-related effects other than hyperkeratosis (minimal severity) at the test compound application site.

Process Subcategories

Atmospheric Residue

Dose levels of 0.01 (9 mg), 0.25 (231 mg) or 1.0 (927.9 mg) ml/kg_{bw}/day of an atmospheric residue (CAS no. 64741-45-3) were applied undiluted to the skin of male and female rats (UBTL, 1990a). The test material was applied 5x/week for 4 weeks. There were no clinical observations made that were considered to be treatment-related. The only treatment-related finding at gross necropsy was a dark staining of the treated skin site. There were no compound-related effects on either hematology or clinical chemistry values. Nor were there any treatment-related differences in body weights or organ weights or organ/body weight ratios. The only treatment-related histopathological findings occurred in the skin and these consisted of trace to mild acanthosis and trace to moderate hyperkeratosis in the high dose animals. The study authors concluded that there were no systemic effects at the highest dose level tested.

Atmospheric Distillates

Dose levels of 30, 125 or 500 mg/kg_{bw}/day of a heavy atmospheric gas oil (CAS no. 68783-08-4) were applied undiluted to the skin of male and female rats (Mobil, 1992c). The test material was applied 5x/week for 13 weeks. To assess male reproductive health, a satellite group of 10 males was administered 500 mg/kg_{bw}/day of the gas oil. At the end of the study the epididymides and testes from the male rats in the control and 125 mg/kg_{bw}/day groups were given an in-depth histopathology examination, including spermatid (testes) and spermatozoa (epididymides) counts. In general, application of the test material produced only "slight" skin irritation. One of ten high dose males was sacrificed *in extremis*, the investigators considered the death to be treatment-related. There were treatment-related changes in a number of serum chemistry and hematological parameters in the rats in the mid- and high dose groups. At necropsy, treatment-related macroscopic findings in both sexes included increased liver size, decreased thymus size, thickening of the limiting ridge between the non-glandular and glandular sections of the stomach and enlarged and reddened lymph nodes. There were some organ weight (absolute and relative) differences in the 125 and 500 mg/kg_{bw}/day groups. The histopathology examination found treatment-related changes only in animals in the 500 mg/kg_{bw}/day groups. These changes included a severe reduction in hematopoiesis in the bone marrow; liver hypertrophy and connective tissue formation; increased areas of hematopoiesis, focal necrosis and individual cell death in the liver; and a reduction in the numbers of lymphocytes in the thymus glands. There were no treatment-related effects on any of the epididymal sperm or testicular spermatid parameters. The investigators concluded the no-observable-effect level (NOAEL) for the study was 30 mg/kg_{bw}/day.

Vacuum Residue

Data on repeat-dose toxicity studies in rabbits on two vacuum residuum samples (CAS no. 64741-56-6, API samples 81-13 and 81-14) are presented in the API HPV Asphalt Test Plan.

Vacuum Distillate

An undiluted heavy vacuum gas oil (CAS no. 64741-57-7) was applied to the skin of male and female rats 5 days each week for 13 weeks (Mobil, 1988d). Dose levels were 30, 125, 500 & 2000 mg/kg_{bw}/day. The unscheduled deaths of two of ten males in the high dose group were considered to be compound-related. Growth rates of males and females in the highest dose group were reduced compared to controls. At five and thirteen weeks, the 2000 mg/kg_{bw}/day dose group had reduced erythrocytes and platelets. Similar reductions were also found in the 500 mg/kg_{bw}/day females. Changes in several clinical chemistry values were also seen in the 2000 mg/kg_{bw}/day dose group. In addition in females dosed with 500 mg/kg_{bw}/day had reduced serum glucose levels, while in the 500 mg/kg_{bw}/day males, cholesterol was increased.

At gross necropsy, in the 500 and 2000 mg/kg_{bw}/day dose groups, relative thymus weights were reduced while relative liver weights were increased. Histological examination revealed decreased erythropoiesis and fibrosis of the bone marrow in the 2000 mg/kg_{bw}/day males. There was a reduction in thymic lymphocytes in both sexes in the 2000 mg/kg_{bw}/day group. Examination of the testes of animals in the 2000 mg/kg_{bw}/day dose group found no compound-related effect on sperm morphology. The investigators found the NOEL for both males and females was 125 mg/kg_{bw}/day.

Cracked Residue

Dose levels of 8, 30, 125, 500 and 2000 mg/kg_{bw}/day of a clarified slurry oil (CAS no. 64741-62-4) were applied undiluted to the skin of male and female rats (Cruzan et al., 1986; Mobil, 1985b). The test material was applied 5x/week for 13 weeks. There was an adverse, dose-related effect on mortality, with none of the rats in the highest dose group (2000 mg/kg/day) surviving past the second week of the study. Compound-related effects were observed on body weights, and several hematology and clinical chemistry parameters. Based on these changes, and histopathology findings, the target organs of toxicity were judged by the study directors to be the liver, thymus and bone marrow. The investigators concluded that none of the dose levels used in the study represented a no-observable-adverse- effect level (NOAEL).

Cracked Distillate

Dose levels of 8, 30 and 125 mg/kg_{bw}/day of a visbreaker gas oil (CAS no. 68471-81-7) were applied undiluted to the skin of male and female Sprague-Dawley rats (Feuston et al., 1994; Mobil, 1992b). The test material was applied 5x/week for 13 weeks. There were no deaths during the study. No clinical signs of toxicity were observed, with the exception of dose-related skin irritation. There were no compound-related effects on body weights or hematology and clinical chemistry values. Urinalysis found no treatment-related effects. At necropsy, the only treatment-related findings were effects on the skin and enlarged lymph nodes (the latter predominantly in the higher dose groups). Microscopic examination of the skin revealed thickened epidermis with parakeratosis, chronic inflammation in the subcutis, ulcers and increased mitosis in the epidermal basal cells. The skin changes were more severe in females than the males. Lymph nodes were enlarged in the high dose animals and in most instances, microscopic examination revealed non-specific reactive hyperplasia. Epididymides and testes from the male rats in the control and 125 mg/kg_{bw}/day groups were given an in-depth histopathology examination, including spermatid (testes) and spermatozoa (epididymides) counts. Treatment with visbreaker gas oil did not cause any changes in testicular spermatid or epididymal spermatozoa count nor in sperm morphology. The investigators concluded the NOAEL in the study was > 125 mg/kg_{bw}.

Reformer Residue

No studies available.

Carcinogenicity

In addition to the repeat-dose studies discussed above, several dermal carcinogenicity studies on samples of cracked residual streams have been reported (API, 1989; McKee et al., 1990; Smith et al., 1951). Although carcinogenicity is not a required endpoint of the HPV program, the Testing Group believes the results may be useful in evaluating the repeated-dose endpoint. A tabulation of these studies can be found in section 5.7 of the attached Robust Summary (Appendix C).

Summary: The Testing Group proposes to test a representative sample of a reformer residue stream by the dermal route of administration using a 28-day repeated-dose/reproductive/developmental toxicity

screening protocol (OECD Test Guideline 422). No repeat dose information exists on the reformer residue streams. While no data is available for the vacuum residue process subcategory, the Testing Group thinks these materials can be characterized by “read across” from the data on the vacuum residue streams found in the API HPV Asphalt Test Plan.

In-Vitro (Mutagenicity)

Subcategory	Assay	Results
Residual Fuel Oils	No studies to report	-
Process Subcategories		
Atmospheric residue	No studies to report	-
Atmospheric distillate	No studies to report	-
Vacuum residue	Mouse lymphoma - data on two vacuum residuum samples (CAS no. 64741-56-6, API samples 81-13 and 81-14) are presented in the API HPV Asphalt Test Plan	Weakly positive with activation
Vacuum distillate	Modified Ames–	Positive with activation
	Cytogenetic assay with Chinese Hamster Ovary cells	Negative with/without activation
Cracked residue	Modified Ames	Positive with/without activation
	Mouse lymphoma	Positive with/without activation
	Sister chromatid exchange	Positive with/without activation
	Cell transformation	Negative without activation Positive with activation
	Unscheduled DNA synthesis	Positive
	Bacterial forward mutation	Negative with/without activation
Cracked distillate	No studies to report	-
Reformer residue	No studies to report	-
API, 1985a,b, e, f, 1986b,c; Mobil, 1985a, 1987e		

Summary: The Testing Group is proposing to perform a modified Ames and chromosomal aberration (OECD 473) assays on representative samples of a residual fuel oil, atmospheric residue, atmospheric distillate, cracked distillate and reformer residue.

In-Vivo (Chromosomal Aberrations)

Subcategory	Assay	Species	Results
Residual Fuel Oils	No studies to report	-	-
Process Subcategories			
Atmospheric residue	No studies to report	-	-
Atmospheric distillate	No studies to report	-	-
Vacuum residue	Cytogenetic Assay - data on two vacuum residuum samples (CAS no. 64741-56-6, API samples 81-13 and 81-14) are presented in the API HPV Asphalt Test Plan	Rat (♀, ♂)	Negative at up to 3 g/kg/day by gavage for 5 days
Vacuum distillate	Micronucleus	Rat (♀, ♂)	Negative at up to 2000 mg/kg _{bw} /day; 5x/week for 13 weeks via dermal route
Cracked residue	Cytogenetic Assay	Rat (♀, ♂)	Negative at up to 1 g/kg/day by

			gavage for 5 days
	Sister Chromatid Exchange	Mice (♀, ♂)	Single IP dose - positive at 4.0 (♀, ♂) & 2.0 (♂) g/kg _{bw} ; negative at 0.4 g/kg _{bw}
	Unscheduled DNA Synthesis	Rat (♂)	Positive at 100 & 1000 mg/kg _{bw} by gavage; negative at 50 mg/kg _{bw}
Cracked distillate	No studies to report	-	-
Reformer residue	No studies to report	-	-
API, 1985c,d, e; Mobil, 1987f			

Summary. No additional *in-vivo* testing is planned. Adequate studies exist on the vacuum distillate and cracked residue subcategories. The Testing Group thinks results from the API HPV Gas Oils test plan can be “read across” to the atmospheric distillate subcategory given the similar process history. Similarly, the Testing Group thinks results on vacuum residue streams from the API HPV Asphalt test plan can be “read across” to characterize the vacuum residue subcategory. Given the high aromatic content of the cracked distillates and reformer residues, the Testing Group would expect these types of materials would produce positive results in the Ames assays. Other materials with high PAC content (aromatic extracts) have produced negative results in *in vivo* chromosomal aberration assays. If the *in vitro* assays are positive, the Testing Group will consider additional *in vivo* testing.

Reproductive/Developmental Toxicity

Residual Fuel Oils

No studies to report.

Process Subcategories

Atmospheric Residue

In a developmental screening study, dose levels of 50, 333, & 1000 mg/kg_{bw}/day of an atmospheric residue (CAS no. 64741-45-3) were applied to the skin of presumed-pregnant female rats on days 0-20 of gestation (UBTL, 1994). There were no deaths or treatment-related clinical effects amongst the dams. The study directors considered decreased body weight changes and the increase in gestation length at a dose of 1,000 mg/kg to be signs of compound-related maternal toxicity. Signs of developmental toxicity considered by the study directors to be compound-related included decreased pup body weights on Lactation Days 0 and 4 at a dose of 1,000 mg/kg. The report authors concluded that for maternal toxicity and signs of developmental toxicity the no-observable-adverse-effect level (NOAEL) was 333.0 mg/kg_{bw}/day.

Atmospheric Distillate

A developmental toxicity screening study has been reported on a heavy atmospheric gas oil (CAS no. 68783-08-4) (Mobil, 1991). Undiluted test material was applied daily on days 0 to 19 of gestation to the clipped skin of resumed-pregnant female rats. Dose levels included 8, 30, 125 and 500 mg/kg_{bw}/day. Signs of maternal toxicity considered by the study director to be related to administration of the test material included effects on body weights, body weight gain, food consumption, thymus weights (absolute & relative), liver weights (relative), and a number of clinical chemistry and hematological parameters. A red vaginal discharge (normally indicative of litter resorption) was observed in 7/11 animals in the 500 mg/kg_{bw}/day group and two females dosed with 125 mg/kg_{bw}/day. The investigators could not decide if the vaginal discharge was treatment-related since a similar observation had been noted in control animals. Evaluation of reproductive parameters in the 8 and 30 mg/kg_{bw} found no compound-related effects. Statistically insignificant differences in preimplantation losses were seen in both the 125 and 500 mg/kg_{bw}/day groups. There was a significant increase in the mean number/percent resorptions in the 500 mg/kg_{bw}/day group. Mean fetal body weights were significantly decreased for all viable fetuses in the 500 mg/kg_{bw}/day group and in the male pups of the 125 mg/kg group. There was a significant increase in incomplete ossification of a number of skeletal structures (nasal bones, thoracic centra, caudal centra, sternbrae, metatarsal and pubis) in the 125 and 500 mg/kg_{bw}/day groups. There were no treatment-related abnormalities found in the soft tissues. Exposure to gas oil did not adversely affect pup survival or development. The investigators

concluded the no-observable-adverse-effect levels (NOAELs) for both maternal toxicity and teratogenicity were 30 mg/kg_{bw}/day.

Vacuum Residue

No studies to report.

Vacuum Distillate

In a developmental screening study, dose levels of 30, 125, 500 and 1000 mg/kg_{bw}/day of a heavy vacuum gas oil (HVGO, CAS no. 64741-57-7) were applied to the skin of presumed-pregnant female rats (Mobil, Undated). The test material was administered on days 0 to 19 of gestation. All animals were euthanized on day 20. Clinical signs of maternal toxicity considered by the study authors to be compound-related were seen primarily in the 1000 mg/kg_{bw}/day dose group. In the dams, the only treatment-related findings seen at necropsy were lungs that had a pale appearance (500 and 1000 mg/kg_{bw}/day) and a reduction in thymus size. Organ weight data confirmed that the thymus weights in the highest dose group were reduced and furthermore, relative liver weights were increased in the 500 and 1000 mg/kg_{bw}/day animals. A number of reproductive parameters were affected by treatment with HVGO. Fetuses of dams in both the 500 and 1000 mg/kg_{bw}/day dose groups had treatment-related decreases in body weights. Upon external examination, one fetus in the 1000 mg/kg_{bw}/day group was found to be edematous, pale in color, with both hind paws malformed. Malformations of the vertebral columns were observed in several fetuses, but only in the 500 mg/kg_{bw}/day group. While a variety of skeletal malformations were observed in both treated and control groups, the degree of malformation was more severe in the HVGO-exposed groups. Visceral malformations were restricted to two fetuses in the 500 mg/kg_{bw}/day group. Of the two fetuses, one had microphthalmia and the other had a diaphragmatic hernia that displaced the heart from the left- to right-hand side. The study authors concluded the no-observable-adverse-effect levels (NOAELs) for both maternal and fetal toxicity were 125 mg/kg_{bw}/day.

Cracked Residue

A developmental toxicity screening study has been reported on a clarified slurry oil (CSO, CAS no. 64741-62-4) (Hoberman et al., 1995). Undiluted test material was applied daily on days 0 to 19 of gestation to the clipped skin of resumed-pregnant female rats. Dose levels included 0.05, 1.0, 10, 50 or 250 mg/kg_{bw}/day. No deaths occurred among the dams and no dam aborted or prematurely delivered a litter. Neither maternal toxicity nor fetal developmental effects were seen at the 0.05 mg/kg_{bw}/day dose level. Nor were any fetal malformations or variations observed in the 0.05 mg/kg_{bw}/day group. Dose-related signs of maternal toxicity were seen at dose levels greater than 0.05 mg/kg_{bw}/day. The effects included decreased food consumption and decreased body and gravid uterine weights, and the occurrence of red vaginal exudates. Fetal developmental effects, as measured by number of live fetuses, total resorptions, early resorptions, % dead or resorbed conceptuses/litter and fetal body weights were seen at doses that were maternally toxic. There were no treatment-related incidences of fetal malformations. However, increased incidences of fetal variations that are generally interpreted as reversible delays in development associated with significant decreases in body weight were produced in fetuses in the 1.0, 10 and 50 mg/kg_{bw}/day dose groups. These variations included moderate dilation of the renal pelvis, slight dilation of the lateral ventricles of the brain, bifid thoracic vertebral centrum and decreased average numbers of ossified caudal vertebrae, metacarpals and hindpaw phalanges. The study authors concluded the no-observable-adverse-effect levels (NOAELs) for both maternal and fetal toxicity were 0.05 mg/kg_{bw}/day.

To determine potential effects on gonadal function, reproductive organs and mating behavior, 0.1, 1, 10, 50 & 250 mg/kg/day of a clarified slurry oil (CAS no. 64741-62-4) were applied dermally to male rats for 70 days before a seven-day cohabitation period with untreated virgin female rats (Argus, 1992). Female rats were examined daily for viability and clinical observations, and body weights were recorded on days 0, 6 and 14 of presumed gestation. On day 14 of presumed gestation, the female rats were sacrificed by carbon dioxide asphyxiation, and a gross necropsy of the thoracic and abdominal viscera was performed. The uterus of each rat was examined for pregnancy, number and distribution of implantations, early resorptions and live and dead embryos. No deaths and no skin reactions were caused by the test material. All absolute and relative organ weights were comparable among the six dosage groups. There were compound-related effects on body weights, body weight gains, and food consumption. Mating and fertility parameters were unaffected at any of the dose levels. There were no compound-related effects on any testicular parameter.

Litter averages for corpora lutea, implantations, and live embryos and resorptions did not significantly differ among females mated with male animals from the six dosage groups. There were no dead embryos, and no dam resorbed all conceptuses. The study directors concluded that the paternal no-observable-adverse-effect-level (NOAEL) was 1 mg/kg/day. The reproductive NOAEL for the male rats was >250 mg/kg/day (no mating, fertility or testicular parameters in the male rats were affected by the highest dosage tested).

In a reproductive/developmental toxicity screen, female Sprague-Dawley rats were administered catalytically cracked clarified oil (CAS no. 64741-62-4) at dose levels of 0.05, 10, 250 mg/kg/day (UBTL, 1994). The test material was administered one week prior to the initiation of mating, throughout mating, and through Day 20 of gestation. Male rats to which the females were mated were not administered test compound. Food consumption and body weights were recorded throughout the premating, mating and gestation periods. On Day 4 of lactation, each female was sacrificed and the ovaries and uterine horns examined to determine the number of corpora lutea and implantation sites, respectively. Litters were observed during Days 0 –4 of lactation for signs of toxicity and mortality. Pups were examined daily for external abnormalities. On Days 0 and 4 of lactation, each pup was weighed and its sex was determined. On day 4 of lactation, all surviving pups were examined externally, sacrificed and discarded. No deaths occurred during the study. The study directors considered the following signs of maternal toxicity to be related to administration of the test material: a higher incidence of vaginal discharge at a dose of 250 mg/kg; decreased body weights, body weight changes, and food consumption at doses of 10 and 250 mg/kg; and decreased thymus size at a dose of 250 mg/kg. Signs of developmental toxicity considered to be compound-related were limited to the 250 mg/kg dose group; none of the females in this dose level delivered a litter. The study directors concluded the no-observable-adverse-effect levels (NOAEL) were 0.05 mg/kg for maternal toxicity and 10 mg/kg for signs of developmental toxicity.

Cracked Distillate

Doses of 8, 30, 125 and 250 mg/kg_{bw}/day of a heavy coker gas oil (CAS no. 64741-81-7) were applied daily to the skin of resumed-pregnant female rats in a developmental screening study (Mobil, 1987d). Animals were dosed on days 0-19 of gestation. All animals were euthanized on day 20. Treatment-related clinical observations in the dams consisted of erythema, flaking, scabbing, edema, eschar and fissuring and the occurrence of a red vaginal discharge. Eschar and fissuring occurred in the highest two dose groups only. Vaginal bleeding was seen in the groups receiving doses of 30 mg/kg_{bw}/day and higher. There was a dose-related decrease in mean body weight gains over the course of the experiment. At necropsy, the only treatment-related observation in the dams was an apparent reduction in thymus size, which was noted at all treatment levels. Absolute thymus weights were decreased, while absolute liver weights were increased. A number of clinical chemistry values were affected, but only at the highest dose of 250 mg/kg_{bw}/day. Select reproductive parameters were adversely affected, but only in the 125 and 250 mg/kg_{bw}/day groups. Viable and non-viable fetuses from these two dose levels were observed to have signs of abnormal external development, including reduced (shortened) lower jaws and edema. Visceral anomalies seen in these same two dose groups included displacement of esophagus from a left-sided to a right-sided position and distension of the ureters. Malformations of the vertebral column were restricted to fetuses of dams exposed to the test material. Although signs of aberrant development were observed in control animals, the degree of the observed effects was not as severe in the control groups as the groups exposed to test material. The authors concluded that the no-observable-adverse-effect-level for maternal and fetal toxicity was 30 mg/kg_{bw}/day.

Reformer Residue

No studies to report

Summary: The Testing Group proposes to test a representative sample of a residual fuel oil by the dermal route of administration using a reproductive/developmental toxicity screening protocol (OECD Testing Guideline 421). The Testing Group proposes to test a representative sample of a reformer residue by the dermal route of administration using a 28-day repeat-dose/reproductive/developmental toxicity screening protocol (OECD Test Guideline 422). The Testing Group thinks the existing data on refinery streams in the process subcategories allows the developmental toxicity of these materials to be characterized. While no data exists for the vacuum residue subcategory, the Testing Group believes the physical nature of these materials (very viscous) will limit the

bioavailability of any potentially biologically significant components. Furthermore, data is available for atmospheric residuum, a similar material, which because of its lower boiling point will contain higher levels of these potentially biologically significant components. Therefore, the Testing Group is not proposing any testing for this subcategory of materials. No reproductive or developmental data is available for the reformer residue streams. However, the Testing Group has already proposed a repeat-dose study on a reformer residue. The Testing Group is proposing to maximize the utility of the study by conducting a 28-day repeated-dose/reproductive/developmental toxicity screen (OECD Test Guideline 422). This will provide data not only on the repeat-dose toxicity of this subcategory of materials, but also on their reproductive/developmental toxicity thereby adding to the extensive database that exists on these materials.

While none of the developmental studies summarized in this test plan provide data on pre-mating exposure of males or females, the existing data adequately characterize the reproductive endpoint for these materials. Repeat-dose studies on samples of atmospheric distillates, vacuum distillates, and cracked distillates have included an in-depth histopathological examination of reproductive organs. Furthermore, studies have been reported on catalytically cracked clarified oil (cracked residue) in which pre-mating exposures of males or females were conducted. Catalytically cracked clarified oil has produced the lowest maternal no-observed-adverse-effect-level (NOAEL) in the developmental screens that have been performed. The Testing Group expects the reproductive toxicity of the other materials in this category to be less than that of catalytically cracked clarified oil.

The lack of reproductive/developmental toxicity data on a finished residual fuel suggests the need for a reproductive/developmental screen on a representative sample of a residual fuel. The Testing Group is proposing a reproductive/developmental toxicity screen (OECD Test Guideline 421) of a residual fuel in order to develop a complete data set on a finished product and to test its hypothesis that the toxicity of the finished fuel will fall within the range of the toxicities of the streams from which the fuel is blended. To that end, the Testing Group will select a residual fuel test sample that is well characterized with respect to the components from which it was blended. The goal will also be to select a residual fuel oil sample that has a significant portion of cracked residues since these streams appear to show the highest potential for toxicity within this category.

EVALUATION OF EXISTING PHYSICO-CHEMICAL AND ENVIRONMENTAL FATE DATA AND PROPOSED TESTING

The physicochemical endpoints for the EPA HPV chemical program include melting point, boiling point, vapor pressure, octanol/water partition coefficient ($\log K_{ow}$), and water solubility. Environmental fate endpoints include photodegradation, hydrolysis, environmental transport and distribution (fugacity), and biodegradation. Although some data for products in this category exist, not all of these endpoints are defined and a consensus database for chemicals that represent products in this category does not exist. Therefore, calculated and measured data have been identified and a technical discussion provided, where appropriate. The EPIWIN[®] (EPA, 2001) computer model, as discussed in the U.S. EPA document entitled "The Use of Structure-Activity Relationships (SAR) in the High Production Volume Chemicals Challenge Program" has been used to calculate physical-chemical properties of representative constituents of heavy fuel oils (EPA, 1999).

The substances covered under this HPV testing plan are mixtures of differing compositions. Because of the diversity of compounds encompassing heavy fuel oils, it is not feasible to model the physicochemical endpoints for each potential compound. Where modeling was necessary to fulfill an endpoint, such estimates were made for common hydrocarbon structures (e.g., saturated, aromatic, olefinic and heterocyclic hydrocarbons) and range of molecular weight hydrocarbons (i.e., number of carbon atoms) known to be represented in heavy fuel oil mixtures. Since molecular weight and structural conformation determine in large part many of the physicochemical and fate processes, the modeled estimates for these isomeric structures are expected to represent potential ranges of values for all substances in the heavy fuel oil category.

Physico-Chemical Data

Melting Point

For complex mixtures like petroleum products, melting point may be characterized by a range of temperatures reflecting the melting points of the individual components. To better describe the physical phase or flow characteristics of petroleum products, the pour point is routinely used. The pour point is the lowest temperature at which movement of the test specimen is observed under prescribed conditions of the test (ASTM, 1999).

Measured pour points ranged from $-2\text{ }^{\circ}\text{C}$ to $35\text{ }^{\circ}\text{C}$ (CONSCI, 1992a,b; CONSCI, 1993a-d; Jokuty et al., 2002; NIPER, 1993a,b). Those values are consistent with the review by CONCAWE (1998), which stated pour points for these products are typically $<30\text{ }^{\circ}\text{C}$. The differences in flow characteristics of heavy fuels are related to the composition of the crude oil from which they are produced, the variety of refining practices that result in products that go into heavy fuels, and the practice of adding a lighter "cutter stock" to heavy fuel oils to improve their flowable characteristics at low temperatures. Based on the cited data, heavy fuel oil streams and products will exist at ambient temperatures as dense, viscous oil. Those category members with the highest pour points will be characteristically solid to semi-solid substances, while those with the lowest pour points will have the greatest liquefaction.

Summary: No additional testing is proposed. The pour points of various heavy fuel oils have been adequately measured.

Boiling Point

For complex petroleum mixtures, boiling points are expressed as ranges (i.e., distillation ranges) that are governed by the individual constituent hydrocarbons within the mixtures. Constituent molecules have individual boiling points, and boiling points increase as molecular weight increases. Streams within the Heavy Fuel Oil HPV category are highly diverse mixtures, and are produced from a variety of refining processes; processes including both atmospheric and vacuum distillation; therefore, the boiling ranges of the streams also would be expected to vary widely. Based on CAS definitions for the refining streams in this category, boiling points can range from 121 to $600\text{ }^{\circ}\text{C}$ (EPA, 2004). Actual boiling ranges for any of the heavy fuel oil streams will depend upon source of the feedstock and the refining process. Boiling ranges reported in various literature sources such as material safety data sheets (Sinclair Oil Corp; Total UK Ltd., 2003; and TFMM, 2001), government-sponsored databases (ECB, 2000; Jokuty et al., 2002), and the American Petroleum Institute (API, 1987) lend support to the CAS-defined boiling range.

Summary: No additional testing is proposed. Products within this category vary with respect to their distillation ranges and specific ranges depend upon the hydrocarbon composition of the feedstocks from which they are produced. Values cited provide typical ranges for the distillation of these materials.

Vapor Pressure

Few vapor pressure measurements are available for heavy fuel oils; therefore, the EPIWIN (EPA, 2001) computer model was used to estimate vapor pressures for representative components of these substances. For heavy fuel oil mixtures, the total vapor pressure is the sum of the partial pressures of the individual components (Dalton's Law of Partial Pressures), while the partial pressure of an individual constituent is a product of the vapor pressure of the pure material times its mole fraction in the mixture (Raoult's Law). Therefore, for complex mixtures such as heavy fuel oils, the partial pressures of individual constituents may be quite low.

The heavy fuel oil category is composed of many different refining streams, and the vapor pressures of such substances will vary with the source of the crude and the refining method used. Measured values of $<100\text{ Pa}$ (Total UK Ltd, 2003) and $>500\text{ Pa}$ (ECB, 2000) for two heavy fuel oil streams reflected this variability. Vapor pressure estimates made using EPIWIN[®] version 3.10 (EPA, 2001) for constituent hydrocarbons representing paraffinic, olefinic, naphthenic, aromatic, and polar/heterocyclic components in heavy fuel streams bounded the measured data. Vapor pressure estimates of low molecular weight hydrocarbons ($\text{C}_7 - \text{C}_{11}$) of varying isomeric structures ranged from 7 Pa to $9 \times 10^3\text{ Pa}$. As molecular weights increased, vapor pressure estimates decreased. Estimates for the high molecular weight constituents ($\text{C}_{38} - \text{C}_{50}$) ranged from $2 \times 10^{-7}\text{ Pa}$ to $5 \times 10^{-17}\text{ Pa}$. The modeled data represent a potential vapor pressure range for the hydrocarbon constituents expected to occur in all subcategories of heavy fuel oils.

Summary: No additional testing is proposed. The vapor pressures of representative hydrocarbon constituents of heavy fuel oils have been adequately characterized. Measured data reflect the variability expected for substances in this category.

Partition Coefficient

In mixtures such as the heavy fuel oils, the percent distribution of the hydrocarbon groups (i.e., paraffins, naphthenes, olefins, aromatics, polar/heterocyclics) and the carbon chain lengths determines in-part the partitioning characteristics of the mixture. Generally, hydrocarbons with fewer carbon atoms tend to have lower partition coefficients than those with higher carbon numbers (CONCAWE, 2001). However, due to their complex composition, unequivocal determination of the log K_{ow} of the hydrocarbon mixtures cannot be made. Rather, partition coefficients of representative hydrocarbon types covering the range of carbon atoms found in substances in this category were modeled using the EPIWIN[®], version 3.10 computer model (U.S. EPA, 2001).

The isomeric structures and numbers of carbon atoms were selected because they are representative of the types and molecular weights of hydrocarbon compounds found in heavy fuel oils. Therefore, the estimated values represent the potential range of values for partition coefficient for hydrocarbon constituents in this category. The estimates show log K_{ow} values to range from 1.7 to 25. Standardized methods for measuring partition coefficient are analytically limited to substance up to log Kow ~4, or occasionally 5 (OECD, 1995). An estimation method is available for log Kow up to 6 (OECD, 1989). Based on the estimated values determined by EPIWIN[®], available analytical methods begin to fail for hydrocarbon compounds that contain roughly 15 to 20 carbon atoms. The modeled data represent a potential log Kow range for the hydrocarbon constituents expected to occur in all subcategories of heavy fuel oils.

Summary: No additional modeling is proposed. Partition coefficients (K_{ow}) of 1.7 to 25 were calculated for representative hydrocarbon components of heavy fuel oils.

Water Solubility

When released to water, dissolution of the water-soluble constituents in heavy fuel oils will depend upon environmental factors affecting the mixing and weathering of the substance. Lower molecular weight components that have the highest solubilities also have appreciable vapor pressures and thus would tend to both dissolve and volatilize from the surface. Under controlled conditions with minimal opportunity for volatilization, the water solubility of heavy fuel oil no. 6 was measured to be 6.26 mg/l (Shiu et al., 1990). Additional supporting data gave a range of water solubilities from 0.4 to 6.3 mg/l (Suntio et al., 1986; Anderson et al., 1974; MacLean and Doe, 1989). Because blended fuels are composed of the refining streams from which they are produced, these solubility values are expected to approximate the water solubility for all substances within the heavy fuel oil subcategories. Specific solubility values for heavy fuels oils and the refining streams are dependent upon the composition of the crude oil and the refining process that it undergoes. Calculated and measured water solubilities differ for individual components of complex petroleum substances. At any particular loading rate, aqueous concentrations of each component are a function of relative volume of aqueous and petroleum phases, partition coefficient between phases, amount of component present and the maximum water solubility of each component.

Summary: No testing modeling is proposed. Reported water solubility values for heavy fuel oils ranged from 0.4 to 6.3 mg/l.

Environmental Fate Data

Photodegradation

The direct aqueous photolysis of an organic molecule occurs when it absorbs sufficient light energy to result in a structural transformation. Only light energy at wavelengths between 290 and 750 nm can result in photochemical transformations in the environment, although absorption is not always sufficient for a chemical to undergo photochemical degradation. Saturated and one-ring aromatic hydrocarbons do not show absorbance in the 290 to 800 nm range and would not be expected to be directly photo-degraded. Polyaromatic hydrocarbons (PAHs), on the other hand, have shown absorbance of the 290 to 800 nm range of light energy and are capable of being degraded by ultraviolet radiation (Fasnacht and Blough, 2002). The degree and rate at which these compounds photo-degrade depends upon whether conditions allow penetration of light with

sufficient energy to effect a change. In laboratory experiments, ultraviolet illumination of thin films of heavy fuel oil led to disappearance of polyaromatic compounds (Garrett et al., 1998). The loss was more pronounced for larger polycyclic species and the more alkylated forms of the parent hydrocarbon. This pattern of loss also was demonstrated *in situ*, where disappearance of PAHs on painted granite panels placed in an intertidal marine location was greatest for larger and more alkylated species (Jezequel, et al. 2003).

Hydrocarbon components in heavy fuel oils are subject to indirect photodegradation within the tropospheric layer of the atmosphere. Indirect photodegradation is the reaction with photosensitized oxygen in the atmosphere in the form of hydroxyl radicals (OH) and other oxygen containing radicals (e.g., NO₃). The potential to undergo indirect photodegradation estimated using the atmospheric oxidation potential (AOP) model subroutine (AOPWIN V1.90) in EPIWIN[®] (EPA, 2001), which calculates a chemical half-life and an overall OH reaction rate constant based on a 12-hour day and a given OH concentration. Atmospheric oxidation half-lives were calculated for the various molecular weight and isomeric structures representing constituent hydrocarbons (paraffins, naphthenes, olefins, aromatics, and polar/heterocyclics) in heavy fuel oils. Structures and molecular weights of selected constituents were chosen on the basis of carbon number as identified in the category substances and known hydrocarbon composition of heavy fuel oils. Therefore, the estimated values identify a potential AOP range for substances in the heavy fuel oil category. AOP half-lives for heavy fuel oil hydrocarbon constituents ranged from <0.1 day to 5.2 days. The modeled data represent a potential range of photodegradation half-lives for the hydrocarbon constituents expected to occur in all substances in the heavy fuel oil category.

Summary: No additional modeling is proposed. Atmospheric half-lives of <0.1 to 5.2 days have been calculated for representative hydrocarbon components of heavy fuel oils.

Stability in Water

Chemicals that have a potential to hydrolyze include alkyl halides, amides, carbamates, carboxylic acid esters and lactones, epoxides, phosphate esters, and sulfonic acid esters (Harris, 1982). Because heavy fuel oils do not contain significant levels of these functional groups, materials in the heavy fuel oils category are not subject to hydrolysis.

Summary: Computer modeling will not be conducted for materials in the heavy fuel oils category because they do not undergo hydrolysis.

Chemical Transport and Distribution in the Environment (Fugacity Modeling)

Fugacity-based multimedia modeling provides basic information on the relative distribution of chemicals between selected environmental compartments (e.g., air, water, soil, sediment, suspended sediment and biota). The US EPA has agreed that computer-modeling techniques are an appropriate approach to estimating chemical partitioning (fugacity is a calculated, not measured endpoint). A widely used fugacity model is the EQC (Equilibrium Criterion) model (Trent University, 1999). The EQC model is a Level 1 (i.e., steady state, equilibrium, closed system and no degradation) model that utilizes the input of basic chemical properties including molecular weight, vapor pressure, and water solubility to calculate distribution within a standardized regional environment. EPA cites the use of this model in its document "Determining the Adequacy of Existing Data" that was prepared as guidance for the HPV chemicals program (U.S. EPA, 1999).

Based on the physical-chemical characteristics of component hydrocarbons in heavy fuel oils, the lower molecular weight components are expected to have the highest vapor pressures and water solubilities, and the lowest partition coefficients. These factors enhance the potential for distribution in the environment. To gain an understanding of the potential transport and distribution of heavy fuel oil components, the EQC model was used to characterize the environmental distribution of hydrocarbons having different molecular weight and isomeric structures. Structures and molecular weights of selected constituents were chosen on the basis of carbon number as identified in the category substances and known and estimated hydrocarbon composition of heavy fuel oils (Potter and Simmons, 1998; Quann and Jaffe, 1992; Saeger and Jaffe, 2002). Therefore, the estimated values identify the potential environmental distribution for component hydrocarbons in the Heavy Fuel Oil Category.

Partitioning behavior of constituent hydrocarbons of substances in the Heavy Fuel Oil Category depends largely on molecular weight, with smaller compounds (e.g., 7 to 12 carbon atoms) partitioning to the air or water according to their vapor pressure or water solubility properties. In the atmosphere they are expected to degrade rapidly via indirect photodegradation processes, while water soluble components are subject to biodegradation. Once hydrocarbons attain a size of approximately 20 carbon atoms, their low vapor pressure and water solubility prevent their partitioning to air or dissolving in water. Much real-world information has been gained from studies on heavy fuel oil spills (Fuel oil #6 or Bunker C) since this oil is carried by all cargo ships and is the most frequently spilled oil (Jezequel et al. 2003). When spilled on water, heavy fuel oil usually spreads into thick, dark colored slicks that will often breakup into discrete patches and tar balls (NOAA, 2004). Only the lowest molecular weight fractions would be expected to disperse into the water column, and only 5-10% of the material is expected to evaporate within the first few hours of a spill. The specific gravity of a particular fuel oil may vary from 0.95 to 1.03; thus, spilled oil can float, suspend, or sink (NOAA, 2004). Small changes in water density may dictate whether the oil will sink or float. With time and the effects of weathering, heavy fuel oil attains a tar-like consistency, and these fractions will become incorporated into soil or bottom sediments where they will undergo slow to moderate biodegradation. Overall, the principle routes of weathering of spilled heavy fuel include physical removal, dissolution, photo-oxidation, and biodegradation (Jezequel, et al. 2003).

Summary: No further modeling is proposed. Fugacity-based computer modeling has been done for representative constituent hydrocarbon components of heavy fuel oils.

Biodegradation

Extensive research on oil degradation in marine environments indicates that virtually all kinds of oil are susceptible to microbial oxidation. When a heavy fuel oil is spilled, shoreline microbial communities respond quickly to the oiling, with numbers of hydrocarbon-degrading microbes and mineralization potentials increasing after exposure (Leahy and Colwell, 1990). The rate of mineralization is influenced by microbial characteristics (e.g., species), and environmental factors such as available nutrients, oxygen, temperature and degree of dispersion (Mulkins-Phillips and Stewart, 1974; Rashid, 1974; Prince, 2002; Garrett, et al., 2003). In marine systems, degradation is most enhanced by the addition of nutrients (nitrogen and phosphorus), as these are considered most limiting in seawater (Richmond et al., 2001). In general, due to the high viscosity of heavy fuels, their tendency to slowly weather into discrete tar balls, and the eventual incorporation of those substances into soil/sediment can physically isolate and prevent dispersion and microbial attack (Richmond et al., 2001; Prince et al., 2003). However, over time, component hydrocarbons are depleted through selective biodegradation (Lee, et al. 2003). This structure-related trend shows hydrocarbons in order of increasing difficulty for biodegradation to be: 1) n-alkanes, 2) isoalkanes, 3) alkenes, 4) monoaromatic alkylbenzenes, 5) polyaromatic compounds, and 6) high molecular weight cycloalkanes (Bartha and Atlas, 1977; Potter and Simmons, 1998). Less is known about the biodegradability of polar components in oils, which are collectively known as asphaltenes and resins. Many of these have molecular weights of 2000 to 5000 and show little degradation; hence they can persist in the environment for a long time (Prince, 2002; Prince et al., 2003). In standard 28-day studies, heavy fuel oils would not be expected to be readily biodegradable. In one study, Walker et al. (1975) measured an 11% biodegradation of Bunker C fuel oil over 28 days when incubated with a mixed culture of estuarine bacteria in a nutrient medium. Based on the current understanding of hydrocarbon biodegradability, constituents in heavy fuel oils would be expected to biodegrade over time.

Summary: No additional testing is proposed. A technical discussion of hydrocarbon biodegradation based on reviews of available literature was incorporated in a robust summary format.

EVALUATION OF EXISTING ECOTOXICITY DATA AND PROPOSED TESTING

Various ecotoxicity studies on heavy fuel oils have been reported using different means of test substance exposures. These have been reviewed and reported by CONCAWE (1998). For the assessment of ecotoxicity of poorly water soluble mixtures of hydrocarbons as found in petroleum products, the generally accepted procedure is to report results expressed in terms of the "loading rate" (OECD, 2000). The loading rate is defined as the amount of the product that is equilibrated with the aqueous test medium, and the aqueous phase at equilibrium is termed the water-accommodated fraction (WAF) for the specific loading rate. Toxicological endpoints such as the LL50 or EL50 are used to express the loading rate of the product lethal to or produce a specific effect in 50% of the test organisms. Exposures may be prepared as oil-water dispersions (OWDs),

where the insoluble petroleum fractions remain in the exposure solutions. This method also results in an expression of the concentration of the applied product (i.e., mg test substance/l), but the methodology does not prevent potential adverse effects to the organisms due to physical entrapment. Small species appear to be more susceptible than large species. Water-soluble fractions (WSFs) and their dilutions also may be reported in ecotoxicity studies. Ecotoxicity endpoints based on water-soluble fractions have been reported to range from 0.9 mg/l to >4.5 milligrams total petroleum hydrocarbons (TPH)/l (MacLean and Doe, 1989; Jokuty et al., 2002). These preparations are expressed in terms of the measured concentrations of hydrocarbons in solution but do not allow the ecotoxicity of the product to be expressed in terms of the amount of that product required to produce a particular effect. Such results are not comparable to results obtained under WAF or OWD preparation methods.

For the assessment of the ecotoxicity of heavy fuel oils, the category substances are considered as a single group, and the potential for any category member to elicit adverse effects in aquatic organisms is attributed to the solubility of the constituent hydrocarbons in that member. This is valid because petroleum hydrocarbons elicit effects through a common mode of toxicity termed non-polar narcosis (Peterson, 1994; van Wezel and Opperhuizen, 1995), which is produced by the soluble hydrocarbon fractions in aqueous preparations. Fuels having molecular weight hydrocarbons predominately higher than the solubility "cut-off" for acute toxicity show no measurable acute toxicity (CONCAWE, 2001). The solubility cut-off varies with the hydrocarbon structure; thus, for paraffinic hydrocarbons the solubility cut-off occurs at about C10, while for alkylbenzenes it is about C14 (CONCAWE, 2001). Other individual components contribute to toxicity, but as molecular weight increases, solubility declines, as does toxicity.

Petroleum streams in the heavy fuel oil category generally consist of hydrocarbon molecules having 20 to 50 carbon atoms, although some streams in this category have low-end carbon atoms from 7 to 15. Heavy fuel oils also may be blended with gas oils or similar low viscosity fuels to meet market specifications. This makes a highly heterogeneous group of petroleum substances that spans a wide range of molecular weight fractions. Based on distillation and carbon number ranges of the category members, existing data on heavy fuel oil ecotoxicity may not represent the ecotoxicity of category members that contain a relatively high proportion of hydrocarbons below the solubility cut-off for acute toxicity (i.e., those having hydrocarbons with low-end carbon numbers of 7 to 15 and low initial boiling points). In spite of the heterogeneity of the heavy fuel oil category, the constituents in heavy fuels are generic hydrocarbon structures (e.g., saturates, aromatics, etc.) represented in other petroleum HPV categories. Therefore, the Testing Group proposes to use ecotoxicity data from the following HPV categories to read-across to cover the lightest heavy fuel oil streams:

- Referenced data cited in the Kerosene/Jet Fuel Test Plan and robust summaries (API, 2003a),
- Referenced data cited in the Gas Oils Test Plan and robust summaries (API, 2003b), and
- Data generated from the proposed testing of select gas oils streams high in saturated and aromatic hydrocarbons.

Kerosenes and jet fuels are composed of saturated and aromatic hydrocarbon compounds having structures and molecular weights similar to the light-end components in heavy fuel oils. Hence, the ecotoxicity of those substances provides conservative estimates of the ecotoxicity of the lightest heavy fuel oils. Blended heavy fuel oils also contain a fraction of heterocyclic compounds that show solubility and molecular weight relationships similar to other hydrocarbons (i.e., solubility decreases with increasing molecular weight). These compounds may contribute to aquatic toxicity, and their contribution is integrated in the current heavy fuel oil test data. When all ecotoxicity data sets are combined, the ranges of endpoint values are expected to cover the potential ecotoxicity of all category members of the heavy fuel oil category that contain various fractions of saturated, aromatic, and heterocyclic compounds.

Robust summaries for kerosene and gas oils ecotoxicity data cited below may be found in the HPV submissions for Kerosenes/Jet Fuel Test Plan (API, 2003a) and Gas Oils Test Plan (API, 2003b).

Acute Toxicity to Fish

Data for heavy fuel oils showed slight or no acute toxicity to fish when tested as either WAFs or OWDs. Shell (1997a,b) tested WAFs of a "light" and a "heavy" residual fuel oil (CAS No. 68476-33-5) and found the 96-hour LL50s for exposures to rainbow trout (*Oncorhynchus mykiss*) to be between 100 mg/l and 1000 mg/l for the

“heavy” residual fuel oil and >1000 mg/l for the “light” residual fuel oil. Mobil (1987a) obtained a 96-hour LL50 of >10,000 mg/l when bluegill (*Lepomis macrochirus*) were exposed to OWDs of No. 6 fuel oil.

Fish LL50 values for kerosene/jet fuel tested as WAFs were between 10 mg/l and 100 mg/l (API, 2003a). LL50 values for distillate fuels cited in the gas oil HPV test plan ranged from 3.2 to 65 mg/l (API, 2003b).

Acute Toxicity to Aquatic Invertebrates

Data for invertebrates (*Daphnia magna*) showed a similar range of sensitivities as fish. In testing WAFs of the “light” and “heavy” residual fuels, Shell (1997c,d) found the EL50 of the “light” to be >1000 mg/l while that of the “heavy” to be between 220 mg/l and 460 mg/l. Mobil (1987b) exposed daphnids to solutions in which oil was coated on the inside surface of the test vessels. Exposures done in this manner resulted in no immobilized daphnids at the maximum loading rate of 10,000 mg/l.

Invertebrate EL50 values for kerosene/jet fuel tested as WAFs were ranged 1.4 mg/l to <89 mg/l (API, 2003a). EL50 values for distillate fuels cited in the gas oil HPV test plan ranged from 2.0 to <300 mg/l (API, 2003b).

Toxicity to Algae

Shell (1997e,f) reported the EL50 values based on growth rate and biomass for 72-hour exposures of *Raphidocelis subcapitata* to a “light” and a “heavy” residual fuel oil. Tests were run in sealed vessels without headspace. For the “light” material, the ELr50 (rate-based) was concluded to lie between 100 mg/l and 300 mg/l while the ELb50 (biomass-based) was between 3 mg/l and 10 mg/l. This contrasted somewhat with toxicity endpoints for the “heavy” residual fuel oil. Those tests gave ELr50 and ELb50 values of between 30 mg/l and 100 mg/l. Mobil (1987c) coated the surface of test flasks with No. 6 fuel oil and measured algal (*R. subcapitata*) biomass over 96 hours. Tests vessels were plugged with cotton, but otherwise allowed air exchange. Growth inhibition at the maximum loading rate of 10,000 mg/l was 47.5%, but the authors concluded that the ELb50 was >5,000 mg/l. Inhibition of 22% to 27% occurred in the lowest three test levels, and the authors suggested physical obstruction of light penetration may have affected cell growth.

In 96-hour exposures using WAFs of kerosene, EL50 values ranged from 5.0 to 6.2 mg/l when based on inhibition of growth rate, and ranged from 5.9 mg/l to 11 mg/l when based on biomass (API, 2003a). In 72-hour WAF exposures, EL50 values based on growth rate and biomass fell within the range of 10 mg/l to 30 mg/l (API, 2003a).

Algae exposed to WAFs of distillate fuels produced 72-hour EL50 values based on growth rate that ranged from 2.2 to <46 mg/l, while values based on algal biomass ranged from 1.8 to 25 mg/l (API, 2003b).

The heavy fuel oil, kerosene, and gas oil ecotoxicity data described above are listed in the following Table 2. Together, these data encompass values that represent the potential toxicity of all members in the Heavy Fuel Oil HPV category.

Table 2. Ecotoxicity Data for Heavy Fuel Oil, Kerosene/Jet Fuel Oil, and Gas Oil.

Species	Material	Exposure	Effect / concentration	Reference
		Type	(mg/l)	
<u>FISH</u>				
Heavy Fuel Oil				

Rainbow trout (Oncorhynchus mykiss)	CAS No. 68476-33-5 (light) residual fuel oil	WAF	96-h LL50 = >1000	Shell, 1997a
Rainbow trout (O. mykiss)	CAS No. 68476-33-5 (heavy) residual fuel oil	WAF	96-h LL50 = 100 – 1000	Shell, 1997b
Bluegill (Lepomis macrochirus)	No. 6 fuel oil	OWD	96-h LL50 = >10,000	Mobil, 1987a
Kerosene/Jet Fuel				
Various species	Various	WAF	96-h LL50 = 18 20 10 – 100 25	API, 2003a
Gas Oil				
Various species	Distillate fuels	WAF	96-h LL50 = 57 3.2 6.6 57 21 65	API, 2003b
<u>INVERTEBRATES</u>				
Heavy Fuel Oil				
Daphnia magna	CAS No. 68476-33-5 (light) residual fuel oil	WAF	48-h EL50 = >1000	Shell, 1997c
D. magna	CAS No. 68476-33-5 (heavy) residual fuel oil	WAF	48-h EL50 = 220 – 460	Shell, 1997d
D. magna	No. 6 fuel oil	OWD	48-h EL50 = >10,000	Mobil, 1987b
Kerosene/Jet Fuel				
D. magna	Various	WAF	48-h EL50 = 21 1.4 40 – 89 1.9	API, 2003a
Gas Oil				

D. magna	Distillate fuels	WAF	48-h EL50 =	API, 2003b
			7.8	
			5.3	
			14	
			42	
			2.0	
			210	
			68	
			13	
			100 – 300	
			13	
			6.4	
			36	
			9.6	
<u>ALGAE</u>				
Heavy Fuel Oil				
Raphidocelis subcapitata	CAS No. 68476-33-5 (light) residual fuel oil	WAF	96-h ELr50 = 100 – 300 96-h ELb50 = 3 – 10	Shell, 1997e
R. subcapitata	CAS No. 68476-33-5 (heavy) residual fuel oil	WAF	96-h ELr50 = 30 – 100 96-h ELb50 = 30 – 100	Shell, 1997f
R. subcapitata	No. 6 fuel oil	OWD	96-h ELb50 = >5,000	Mobil, 1987c
Kerosene/Jet Fuel				
R. subcapitata	Various	WAF	96-h ELr50 = 6.2 5.0 96-h ELb50 = 11 5.9 72-h ELr50 = 10 – 30 72-h ELb50 = 10 – 30	API, 2003a

Gas Oil				
R. subcapitata	Distillate fuels	WAF	72-h ELr50 =	API, 2003b
			2.9	
			2.2	
			78	
			22	
			22 – 46	
			72-h ELb50 =	
			1.8	
			2.2	
			25	
			10	
			10 – 22	

WAF = Water Accommodated Fraction

OWD = Oil-Water Dispersion

Summary. No further testing is proposed. The ecotoxicity data for heavy fuel oils combined with data for kerosene/jet fuel and gas oils HPV categories provides a range of ecotoxicity endpoints expected to encompass the ecotoxicity of all members of the heavy fuel oils HPV category.

	REFINERY Streams Subcategories							Finished Residual Fuels
TEST	Atmospheric Residue	Atmospheric Distillate	Vacuum Residue	Vacuum Distillate	Cracked Residue	Cracked Distillate	Reformer Residue	Residual Fuel Oil
Physical/Chemical Properties⁷								
Melting Point	Ad							
Boiling Point	Ad							
Vapor Pressure	Ad							
Water Solubility	Ad							
Partition coefficient (log Kow)	Ad							
Ecotoxicity⁷								
Algae Growth Inhibition	RA ⁹							
Acute Freshwater Invertebrate	RA ⁹							
Acute Freshwater Fish	RA ⁹							
Environmental Fate⁷								
Biodegradation	Ad							
Stability in Water	NA							
Photodegradation (estimate)	Ad							
Transport and Distribution	Ad							
Mammalian Toxicity								
Acute	Ad	RA ¹	RA ²	Ad	Ad	Ad	RA ³	Ad
Repeat-dose	Ad	Ad	Ad ²	Ad	Ad	Ad	Test ⁵	Ad
Reprod/Develop	Ad	Ad	Ad	Ad	Ad	Ad	Test ⁵	Test ⁶
Genotoxicity, in vitro	Test ⁸	Test ⁸	Ad	Ad	Ad	Test ⁸	Test ⁸	Test ⁸
Genotoxicity, in-vivo	RA ⁴	RA ¹	RA ²	Ad	Ad	RA ⁴	RA ⁴	RA ⁴

Ad = Adequate, indicates adequate existing data.
NA = Not Applicable, *the endpoint is not applicable" due to inherent physical and/or chemical properties. A technical discussion was developed to address such endpoints.*

¹ read across from API HPV Gas Oils Test Plan
² read across from API HPV Asphalt Test Plan
³ read across from API HPV Aromatic Extracts Test Plan Test Plan
⁴ read across from *in-vitro* genotoxicity assay
⁵ OECD 422 repeat dose/reproductive/developmental screen
⁶ OECD 421 reproductive/developmental screen
⁷ For the assessment of the physical/chemical properties, ecotoxicity, and environmental fate, the category substances are considered as a single group, and the potential for any category member to elicit adverse effects in aquatic organisms is attributed to the solubility of the constituent hydrocarbons in that member
⁸ Modified Ames & in vitro chromosomal aberration (OECD 473).

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APPENDIX A.

CAS Numbers and Definitions of Category Members

The CAS numbers and definitions of refinery streams, including those in the heavy fuel oils category, were developed in response to Section 8(b) of the Toxic Substances Control Act. This section of TSCA required identification and registration with the Environmental Protection Agency before July 1979 of each "chemical substance" being manufactured, processed, imported or distributed in commerce. Due to analytical limitations and known variability in refinery stream composition, identification of every specific individual molecular compound in every refinery process stream under all processing conditions was impossible. Recognizing these problems, the American Petroleum Institute (API) recommended to the EPA a list of generic names for refinery streams consistent with industry operations and covering all known processes used by refiners. The list, including generic names, CAS numbers and definition of each stream, was published by the EPA as "Addendum I, Generic Terms Covering Petroleum Refinery Process Streams."

Because of the variability inherent in the processing of petroleum materials, the definitions API developed for the CAS numbers are qualitative in nature, written in broad, general terms. The definitions often contain only ranges of values for carbon numbers, with little if any quantitative analytical information or concern for possible compositional overlaps. As a result, the CAS descriptions are not useful in determining the exact composition of any specific refinery stream.

Residual Fuel Oils

68476-33-5

Fuel oil, residual

The liquid product from various refinery streams, usually residues. The composition is complex and varies with the source of the crude oil.

68553-00-4

Fuel oil, no. 6

A distillate oil having a minimum viscosity of 900 SUS at 37.7°C (100°F) to a maximum of 9000 SUS at 37.7°C (100°F).

Process Subcategories

Atmospheric Residual

64741-45-3

Residues (petroleum), atm. Tower

A complex residuum from the atmospheric distillation of crude oil. It consists of hydrocarbons having carbon numbers predominantly greater than C20 and boiling above approximately 350 °C (662°F). This stream is likely to contain 5 wt % or more of 4- to 6-membered condensed ring aromatic hydrocarbons.

64742-78-5

Residues (petroleum), hydrosulfurized atmospheric

A complex combination of hydrocarbons obtained by treating an atmospheric tower residuum with hydrogen in the presence of a catalyst under conditions primarily to remove organic sulfur compounds. It consists of hydrocarbons having carbon numbers predominantly greater than C20 and boiling above approximately 350°C (662°F). This stream is likely to contain 5 wt % or more of 4- to 6-membered condensed ring aromatic hydrocarbons.

68333-22-2

Residues (petroleum), atmospheric

A complex residuum from atmospheric distillation of crude oil. It consists of hydrocarbons having

carbon numbers predominantly greater than C11 and boiling above approximately 200°C (392°F). This stream is likely to contain 5 wt.% or more of 4- to 6-membered condensed ring aromatic hydrocarbons.

68607-30-7

Residues (petroleum), topping plant, low-sulfur

A low-sulfur complex combination of hydrocarbons produced as the residual fraction from the topping plant distillation of crude oil. It is the residuum after the straight-run gasoline cut, kerosene cut and gas oil cut have been removed.

70592-79-9

Residues (petroleum), atm. tower, light

A complex residuum from the atmospheric distillation of crude oil. It consists of hydrocarbons having carbon numbers predominantly greater than C11 and boiling above approximately 200°C (392°F). This stream is likely to contain 5 wt % or more of 4- to 6-membered condensed ring aromatic hydrocarbons.

68476-32-4

Fuel oil, residues-straight-run gas oils, high-sulfur

NONE

Atmospheric Distillate

68410-00-4

Distillates (petroleum), crude oil

A complex combination of hydrocarbons produced by distillation of crude oil. It consists of hydrocarbons having carbon numbers predominantly in the range of C11 through C50 and boiling in the range of approximately 205°C to greater than 495°C (401°F to above 923°F).

68783-08-4

Gas oils (petroleum), heavy atmospheric

A complex combination of hydrocarbons obtained by the distillation of crude oil. It consists of hydrocarbons having carbon numbers predominantly in the range of C7 through C35 and boiling in the range of approximately 121°C to 510°C (250°F to 950°F),
Residual

Vacuum Residual

68512-62-9

Residues (petroleum), light vacuum

A complex residuum from the vacuum distillation of the residuum from the atmospheric distillation of crude oil. It consists of hydrocarbons having carbon numbers predominantly greater than C13 and boiling above approximately 230°C.

70913-85-8

Residues (petroleum), solvent-extd. vacuum distilled atm residuum

A complex residuum produced by the solvent extraction of the vacuum distillate of the complex residuum from the atmospheric distillation of crude oil.

Vacuum Distillate

64741-57-7

Gas oils (petroleum), heavy vacuum

A complex combination of hydrocarbons produced by the vacuum distillation of the residuum from atmospheric distillation of crude oil. It consists of hydrocarbons having carbon numbers

predominantly in the range of C20 through C50 and boiling in the range of approximately 350°C to 600°C (662°F to 1112°F). This stream is likely to contain 5 wt. % or more of 4- to 6-membered condensed ring aromatic hydrocarbons.

64742-59-2

Gas oils (petroleum), hydrotreated vacuum

A complex combination of hydrocarbons obtained by treating a petroleum fraction with hydrogen in the presence of a catalyst. It consists of hydrocarbons having carbon numbers predominantly in the range of C13 through C50 and boiling in the range of approximately 230°C to 600°C (446°F to 1112°F). This stream is likely to contain 5 wt % or more of 4- to 6-membered condensed ring aromatic hydrocarbons.

64742-86-5

Gas oils (petroleum), hydrodesulfurized heavy vacuum

A complex combination of hydrocarbons obtained from a catalytic hydrodesulfurization process. It consists of hydrocarbons having carbon numbers predominantly in the range of C20 through C50 and boiling in the range of approximately 350°C to 600°C (662°F to 1112°F). This stream is likely to contain 5 wt. % or more of 4- to 6-membered condensed ring aromatic hydrocarbons.

68955-27-1

Distillates (petroleum), petroleum residues vacuum

A complex combination of hydrocarbons produced by the vacuum distillation of the residuum from the atmospheric distillation of crude oil.

70592-76-6

Distillates (petroleum), intermediate vacuum

A complex combination of hydrocarbons produced by the vacuum distillation of the residuum from atmospheric distillation of crude oil. It consists of hydrocarbons having carbon numbers predominantly in the range of C14 through C42 and boiling in the range of approximately 250°C to 545°C (482°F to 1013°F). This stream is likely to contain 5 wt.% or more of 4- to 6-membered condensed ring aromatic

70592-77-7

Distillates (petroleum), light vacuum

A complex combination of hydrocarbons produced by the vacuum distillation of the residuum from atmospheric distillation of crude oil. It consists of hydrocarbons having carbon numbers predominantly in the range of C11 through C35 and boiling in the range of approximately 250°C to 545°C (482°F to 1013°F).

70592-78-8

Distillates (petroleum), vacuum

A complex combination of hydrocarbons produced by the vacuum distillation of the residuum from atmospheric distillation of crude oil. It consists of hydrocarbons having carbon numbers predominantly in the range of C15 through C50 and boiling in the range of approximately 270°C to 600°C (518°F to 1112°F). This stream is likely to contain 5 wt.% or more of 4- to 6-membered condensed ring aromatic hydrocarbons.

Cracked Residual

64741-62-4

Clarified oils (petroleum), catalytic cracked (also listed in Olefins Panel Fuel Oils Category)

A complex combination of hydrocarbons produced as the residual fraction from distillation of the products from a catalytic cracking process. It consists of hydrocarbons having carbon numbers predominantly greater than C20 and boiling above approximately 350°C (662°F). This stream is likely to contain 5 wt % or more of 4- to 6-membered condensed ring aromatic hydrocarbons.

64741-75-9

Residues (petroleum), hydrocracked

A complex combination of hydrocarbons produced as the residual fraction from distillation of the products of a hydrocracking process. It consists of hydrocarbons having carbon numbers predominantly greater than C20 and boiling above approximately 350°C (662°F).

64741-80-6

Residues (petroleum), thermal cracked

A complex combination of hydrocarbons produced as the residual fraction from distillation of the product from a thermal cracking process. It consists predominantly of unsaturated hydrocarbons having carbon numbers predominantly greater than C20 and boiling above approximately 350°C (662°F). This stream is likely to contain 5 wt % or more of 4- to 6-membered condensed ring aromatic hydrocarbons.

68187-58-6

Pitch, petroleum, arom

The residue from the distillation of thermal cracked or steam-cracked residuum and/or catalytic cracked clarified oil with a softening point from 40 degree C to 180 degree C (104 degree F to 356 degree F). Composed primarily of a complex combination of three or more membered condensed ring aromatic hydrocarbons.

68478-17-1

Residues (petroleum), heavy coker gas oil and vacuum gas oil

A complex combination of hydrocarbons produced as the residual fraction from the distillation of heavy coker gas oil and vacuum gas oil. It predominantly consists of hydrocarbons having carbon numbers predominantly greater than C13 and boiling above approximately 230°C (446°F).

68783-13-1

Residues (petroleum) coker scrubber condensed-ring-aromatic-containing

A very complex combination of hydrocarbons produced as the residual fraction from the distillation of vacuum residuum and the products from a thermal cracking process. It consists predominantly of hydrocarbons having carbon numbers predominantly greater than C20 and boiling above approximately 350°C (662°F). This stream is likely to contain 5 wt. % or more of 4- to 6-membered condensed ring

Cracked Distillate

64741-61-3

Distillates (petroleum), heavy catalytic cracked

A complex combination of hydrocarbons produced by the distillation of products from a catalytic cracking process. It consists of hydrocarbons having carbon numbers predominantly in the range of C15 through C35 and boiling in the range of approximately 260 °C to 500°C (500°F to 932°F). This stream is likely to contain 5 wt. % or more of 4- to 6-membered condensed ring aromatic hydrocarbons.

64741-81-7

Distillates (petroleum), heavy thermal cracked

A complex combination of hydrocarbons from the distillation of the products from a thermal cracking process. It consists predominantly of unsaturated hydrocarbons having carbon numbers predominantly in the range of C15 through C36 and boiling in the range of approximately 260°C to 480°C (500°F to 896°F). This stream is likely to contain 5 wt. % or more of 4- to 6-membered condensed ring aromatic hydrocarbons.

68333-26-6

Clarified oils (petroleum), hydrosulfurized catalytic cracked

A complex combination of hydrocarbons obtained by treating catalytic cracked clarified oil with

hydrogen to convert organic sulfur to hydrogen sulfide which is removed. It consists of hydrocarbons having carbon numbers predominantly greater than C20 and boiling above approximately 350°C (662°F). This stream is likely to contain 5 wt. % or more of 4- to 6-membered condensed ring aromatic hydrocarbons.

68333-27-7

Distillates (petroleum), hydrodesulfurized intermediate catalytic cracked

A complex combination of hydrocarbons obtained by treating intermediate catalytic cracked distillates with hydrogen to convert organic sulfur to hydrogen sulfide which is removed. It consists of hydrocarbons having carbon numbers predominantly in the range of C11 through C30 and boiling in the range of approximately 205°C to 450°C (401°F to 842°F). It contains a relatively large proportion of tricyclic aromatic hydrocarbons.

70955-17-8

Aromatic hydrocarbons, C12-20

A complex combination of hydrocarbons obtained from the distillation of biphenyl and naphthalene feedstocks. It consists predominantly of hydrocarbons having carbon numbers predominantly in the range of C12 through C20, such as alkylbenzenes, alkylnaphthalenes, indans, fluorenes, acenaphthalenes, phenanthrenes and anthracenes, and boiling in the range of approximately 282.degree.C to 427.degree.C (540.degree.F to 800.degree.F).

Reformer Residual

64741-67-9

Residues (petroleum), catalytic reformer fractionator

A complex combination of hydrocarbons produced as the residual fraction from distillation of the product from a catalytic reforming process. It consists of predominantly aromatic hydrocarbons having carbon numbers predominantly in the range of C10 through C25 and boiling in the range of approximately 160 °C to 400°C (320°F to 725°F). This stream is likely to contain 5 wt. % or more of 4- or 6-membered condensed ring aromatic hydrocarbons.

68478-13-7

Residues (petroleum), catalytic reformer fractionator residue distn.

A complex residuum from the distillation of catalytic reformer fractionator residue. It boils approximately above 399°C (750°F).

APPENDIX B.

Links to Additional Resources

Refining Processes: General Descriptions

http://www.chevron.com/about/learning_center/refinery
<http://www.lubrizol.com/lubetheory/default.htm>
<http://www.orionrefining.com/flow.htm>
http://www.osha-slc.gov/dts/osta/otm/otm_toc.html
http://www.shellglobalsolutions.com/base_oils/library/library.htm
<http://www.shell-lubricants.com/learningcenter/aboutoil.html>
http://www.shellus.com/welcome/history/hist_oil_main.html
<http://www.epa.gov/compliance/resources/publications/assistance/sectors/notebooks/petrefsnpt1.pdf>
http://www.mts.net/~dbrad1/base_oil.htm

Petroleum Related Glossaries

http://www.caltex.com.au/products_glo.asp
<http://www.citgo.com/CommunityInvolvement/Classroom/Glossary.jsp>
<http://www.epplp.com/gloss.html>
http://www.prod.exxon.com/exxon_productdata/lube_encyclopedia/
http://www.hellenic-petroleum.gr/english/glossary/gl_main.htm
http://www.prod.exxon.com/exxon_productdata/lube_encyclopedia/
<http://www.oilanalysis.com/dictionary>
<http://www.orionrefining.com/glossary.htm>
<http://www.gedolbear.com/glossary.htm>
http://www.shellglobalsolutions.com/base_oils/glossary/a_g.htm
http://www.ursa-texaco.com/English/glossary_a.html
http://www.eia.doe.gov/pub/oil_gas/petroleum/data_publications/petroleum_marketing_annual/current/pdf/glossary.pdf

APPENDIX C.

Robust Summary

(Separate document)