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HIGH PRODUCTION VOLUME (HPV) CHEMICAL CHALLENGE PROGRAM

TEST PLAN
CRUDE OIL CATEGORY

Submitted to the US EPA

by

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Petroleum HPV Testing Group

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TEST PLAN

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PLAIN LANGUAGE SUMMARY

This test plan addresses the potential for mammalian and environmental toxicity resulting from exposure to crude petroleum. Crude oils are naturally occurring substances derived from decomposition of plant and animal matter under high temperature and pressure for thousands of years. Crude oil is a complex combination of hydrocarbons consisting predominantly of aliphatic, alicyclic and aromatic hydrocarbons covering the carbon number range from C1 to C60+. It also contains sulfur, oxygen and nitrogen compounds, organometallic complexes notably of sulfur and vanadium, and dissolved gases such as hydrogen sulfide (CONCAWE, 2001). In appearance, crude oils range from thin, light colored oils consisting mainly of gasoline-quality stock to heavy, thick tar-like materials. The chemical composition of crude oils from different producing regions, and even from within a particular formation, can vary tremendously. Crude oils are identified by the predominant proportion of similar hydrocarbon molecules. Paraffinic crude oils are rich in straight chain and branched paraffins, have a high API gravity, low density and viscosity, and contain a higher concentration of gasoline grade naphtha. Naphthenic crude oils contain mainly cycloparaffins and aromatic hydrocarbons, have low API gravity, higher density and viscosity and contain residual materials and heteroatoms (e.g. sulfur, nitrogen, oxygen-containing hydrocarbon analogs).

Mammalian Toxicity Summary

The petroleum crude category contains only CAS Number 8002059 to identify all conventional crude oils and those derived from tar sands, regardless of source or hydrocarbon distribution. Crude oils tested demonstrated similar and relatively low acute toxicity. Crude oils have induced gene mutation in bacteria only after solvent extraction to concentrate biologically active aromatic hydrocarbons in the test fraction. Crude oils tested in rat and mouse micronucleus assays yielded negative results, although one crude did induce sister chromatid exchange in mice. Limited repeat dose studies performed by the oral or dermal routes demonstrated similar effects on hematologic endpoints, enlargement of the liver and thymic atrophy, with some skin irritation from thirteen weeks of dermal exposure. Three developmental toxicity studies suggest that in general, crude oils cause fetal death, decreased fetal weight and delayed skeletal ossification at doses that are maternally toxic. An occurrence of decreased pup viability at Day 4 of lactation was observed from maternal exposure to a heavy crude oil.

Although studies on crude oils are relatively few by comparison to some other petroleum categories, there is a substantial body of data on products derived from crude oils, such as gasoline, diesel fuels, kerosene and jet fuels, lubricating oils and white oils, which are subjects of other HPV test plans. Extrapolation from these studies provides insight into biologically active components of crude oils. Occurrence and severity of toxic effects appear correlated with concentration of polynuclear aromatic hydrocarbons (PAH) and PAH-containing nitrogen or sulfur heteroatoms (PAC). In addition there are significant data developed from monitoring effects of unintentional oil spills, providing “real world” environmental information.

Environmental Summary

Due to their complex composition, crude oils vary widely in their physical/chemical properties. The melting point, boiling point, vapor pressure, partition coefficient and water solubility characteristics of crude oils can differ between oil producing regions as well as within a specific production field. Despite these wide-ranging physical and chemical characteristics, some generalizations can be made regarding the environmental behavior of crude oil. When a release to the environment occurs, components of crude oil will partition into various environmental compartments. The lower molecular weight components may dissolve in water or volatilize to the atmosphere, intermediate fractions may float and spread out on water where they may form emulsions and/or adsorb to soil and sediment, and the viscous, heavy components may agglomerate and float or sink in water or adhere to soil and sediment. The rate at which partitioning occurs depends not only on the nature of the crude but also on the severity of the weathering processes it encounters.

When components of crude oil disperse, they may undergo further chemical and physical transformations. Constituents that partition to the air interact with hydroxyl radicals in the atmosphere and thus are subject to indirect photodegradation. Atmospheric half-lives range from 0.4 days (e.g., n-dodecane) to 6.5 days (e.g., benzene). Crude oils are subject to biodegradation, but biodegradation rates vary considerably, and no crude oils would be considered to be readily biodegradable in standard tests. Low molecular weight components may readily biodegrade, but as molecular weight increases, hydrocarbons become increasingly insoluble in water, so that their bioavailability is limited. In general, hydrocarbons are regarded as being inherently biodegradable, although the degradation rates of the more complex high molecular weight fractions may be very slow.

Crude oil is, in general, harmful to aquatic organisms. In both marine and freshwater environments, a spill event may cause extensive mortality to non-motile susceptible species such as phytoplankton, crustaceans and larvae or eggs of fish and invertebrates. In contrast, spills of crude oil may not acutely affect highly mobile species such as adult fish, and mollusks and polychaete worms have an apparent tolerance to oil contamination. Acute aquatic toxicity of crude oil ranged from 10 to >100 mg/l in studies of whole oil dispersions in water or as water-accommodated fractions (WAFs) (CONCAWE, 2001). Acute toxicity is attributed to those water-soluble hydrocarbon components that are either saturates (aliphatic and alicyclic) or mono- and di-aromatics. Polyaromatic hydrocarbons (PAHs) in crude oil are not expected to contribute significantly to acute aquatic toxicity due to limited bioavailability. However, their partition coefficients (log Kow 3 to >6) indicate they have the potential to bio-accumulate, thus chronic toxicity of PAHs may be a concern.

Other risks to aquatic species, semi-aquatic birds, and sea mammals include physical fouling of plumage, fur, gills etc, by floating oil product. This results in loss of buoyancy, insulation and smothering of inter-tidal animals. Ingestion of oil resulting from attempts by animals to clean contaminated body parts may result in severe enteritis and toxicity.

Spills in freshwater environments have been shown to adversely affect the aquatic macro-invertebrate community, with the observed effects associated with oil sorption and substrate coating. Recovery of such communities in some habitats may be rapid (e.g., riffle areas of streams/rivers), while impacts to backwater areas may persist for months.

Ultimately, the type of crude oil and the local conditions and habitats will dictate the potential and extent to which crude oil persists and cause effects in the environment.

As a result of crude oil spills and continuous long-term release of crude oil components, a plethora of real-world data is available on the acute and chronic effects of crude oil. In summary, there is adequate literature on most of the physical/chemical properties, transformation (fate) processes and aquatic and terrestrial effects endpoints. Where there is not specific 'data', a technical discussion has been prepared to characterize crude oil behavior/impact with respect to the required endpoint based upon information of those products and their components derived from refining of crude oil (e.g. gasoline, lubricating oils, diesel fuels, kerosene, jet fuels, white oils and waxes). Therefore, it is not necessary to propose any further testing for crude oil to satisfy the basic data set requirements for physical/chemical properties, transformation processes or environmental toxicity.

The strategy of this test plan is to provide more definitive data on hazards from crude oil by selecting samples that compositionally reflect the extremes of hydrocarbon distribution. Proposed samples are a light crude oil (high API gravity, high paraffinic, lower aromatic content) and a heavy crude oil (lower API gravity, higher naphthenic and aromatic content) to be tested by the dermal route of exposure in a Combined Repeat Dose Toxicity Study with the Reproductive/Developmental Toxicity Screening Test (OECD protocol 422).

The currently available data on crude oils and refinery streams and the proposed testing outlined in Table 4, combined with chemical characterization, will provide sufficient information to profile mammalian and environmental toxicity for a wide range of naturally occurring crude oils.

Description of the Category

Crude oils are naturally occurring substances formed millions of years ago from the remains of tiny aquatic plants and animals that settled with mud and silt into the bottoms of ancient seas, and the remains of fish and terrestrial animals trapped in swamps and bogs. Successive layers built up, subjecting the remains to high pressures and temperature and causing chemical transformation to hydrocarbons and other crude oil constituents. In many areas crude oil migrated and accumulated in porous rock formations overlaid by impervious rock formations that prevented further travel, geologically speaking, the petroleum trap. Usually a layer of salt water underlies the oil pool.

Among the earliest known uses of natural crude oil and tar, collected from swamps and seepage, was for waterproofing and medicinal purposes. The "fiery furnace of Nebuchadnezzar" is believed to have been an oil seepage that caught fire. In the 1850s, it became known that crude petroleum could be distilled to produce kerosene for illumination, a cheaper and better source of light than whale oil. The industry began with the successful drilling of the first commercial well near Titusville, Pennsylvania in 1859 and the opening of the first refinery in 1862 to process crude into kerosene by atmospheric distillation. Development of the internal combustion engine led to production of gasoline and diesel fuel, and the advent of the airplane created the need for high-octane aviation fuel. A brief chronology of the development of refining processing is found in Appendix 2, Table A2-1 (OSHA, 1993; Mobil, 1997).

Although petroleum in the United States was originally found in Pennsylvania, Texas, California and Louisiana with their offshore fields are now the largest producers of crude oil. Oil reserves also exist in Alaska. The large oil fields of the Middle East provide substantial crude and supplies also come from Canada and South America. Access to oil bearing strata may require drilling as deep as 5 miles underground. Crude oil frequently comes to the surface under great pressure and in combination with large volumes of gas. Gas is separated from oil and processed to remove additional liquids of high volatility to form "natural gasoline" for blending into motor gasoline. The remaining "dry gas" is sold for fuel or recycled back to the underground formations to maintain pressure in the oil pool and thus increase recovery of crude oil. Steam is sometimes injected under pressure into wells to force out remaining oil from a depleted pool.

Types and composition:
Crude oils range from thin, light colored oils consisting mainly of gasoline to thick, black oil similar to melted tar, varying in appearance and composition from one oil field to another. An "average" crude contains 84% carbon, 14% hydrogen, 1-3% sulfur, and approximately 1.0% nitrogen, 1.0% oxygen and 0.1% minerals and salts. Crude oils are composed of paraffinic, naphthenic (cycloparaffinic) and aromatic compounds, and are identified based on the predominant proportion of similar hydrocarbon molecules. Paraffinic crude oils are rich in straight chain and branched paraffins; naphthenic crude oils contain mainly naphthenic and aromatic hydrocarbons. Mixed base crude oils have varying amounts of each type of hydrocarbon. Table 1 provides examples of various crude oil compositions.

Most of these oils would be considered light crude (=33^0 API). The heavy crude oils = 28^0 API) are Prudhoe Bay, Saudi Heavy, Venezuela Heavy, Belridge Heavy. Mid-range crude oils are Kuwait, Venezuela Light, USA West Texas sour.

Table 1: Properties of Whole Crude Oils

Crude Source	Paraffins % vol	Naphthenes % vol	Aromatics % vol	Sulfur % wt.	API gravity (^{0}API)
Light Crude oils					
Saudi Light	63	18	19	2.0	34
South Louisiana	79	45	19	0.0	35
Beryl	47	34	19	0.4	37
North Sea Brent	50	34	16	0.4	37
Nigerian Light					
Lost Hills Light	Non-aromatics 50%		50	0.9	-
USA Mid Contint. sweet	-	-	-	0.4	40
Mid range Crude oils					
Venezuela Light	52	34	14	1.5	30
Kuwait	63	20	24	2.4	31
USA West Texas sour	46	32	22	1.9	32
Heavy Crude oils					
Prudhoe Bay	27	36	28	0.9	28
Saudi Heavy	60	20	15	2.1	28
Venezuela Heavy	35	53	12	2.3	24
Belridge Heavy	Non-aromatics 37%		63	1.1	-

IARC, 1989, Mobil, 1997; OSHA, 1993

Appendices 1 and 2 describe hydrocarbon chemistry and the distribution of products from processing of crude oil. From 1927-1967, the American Petroleum Institute sponsored research in petroleum composition that resulted in the isolation of 266 hydrocarbons from the gaseous, gasoline, kerosene, light gas oil, heavy gas oil, and light lubricant portions of a Ponca Oklahoma crude oil (King, 1988).

Crude oils are further classified by viscosity, specific gravity (density) and by API gravity. API gravity is an indication of the gasoline potential of crude oil; $^0\mathrm{API} = \frac{141.5}{\mathrm{Sp.Gr.}} - 131.5$.

The higher the API gravity (the lower the specific gravity), the more valuable is the crude. A crude with a high API gravity (=33^0API, Platts, 2003), and high % hydrogen usually contains a higher concentration of naphtha, which can be processed readily to make gasoline and is considered a light crude. Crude oils with high % carbon and low %

hydrogen are usually rich in aromatics and tend to contain more residual material (e.g. asphalts) and heteroatoms (e.g. sulfur, nitrogen, oxygen-containing hydrocarbon analogs). The “heavy crude oils” require more steps in processing, and are more costly to refine (Appendix 2, Fig. A2-1).

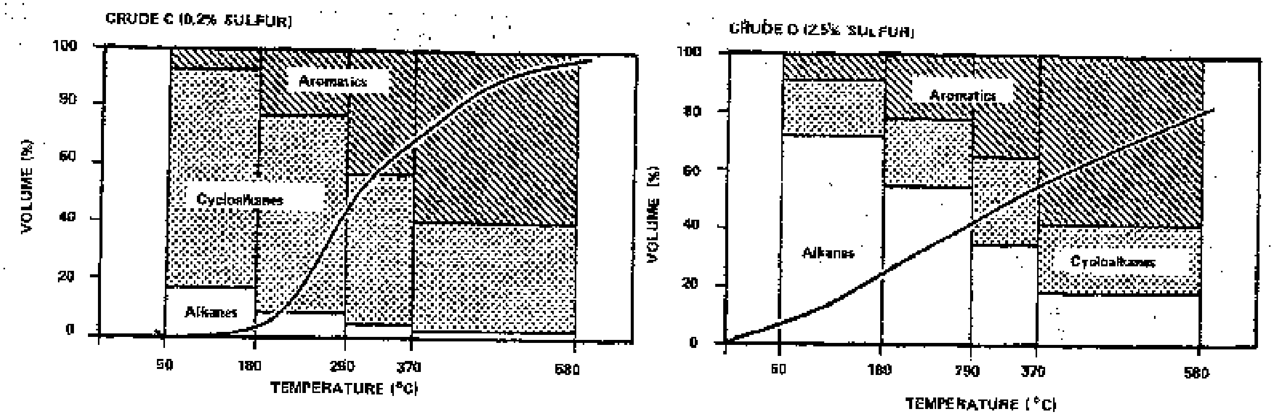
Crude oils also contain varying amounts of non-hydrocarbon sulfur, nitrogen, oxygen and trace metals. Sulfur is present as hydrogen sulfide (H_2S), as thiols, mercaptans, sulfides, benzothiophenes, polysufides, or as elemental sulfur. As a rule, the proportion, stability and complexity of sulfur compounds are greater in heavier crude oil fractions. H_2S is a primary contributor to corrosion in refinery process units and combustion of sulfur-containing petroleum products can produce undesirable byproducts such as sulfuric acid and sulfur dioxide. Total sulfur contents of crude oils spans a range of <0.1% - 5.0% by elemental analysis. In general, as API gravity decreases, sulfur content increases. For example, a light US crude (Rodessa, Louisiana has an API gravity of 42.8 and a sulfur content of 0.28%, while an extremely heavy crude from Venezuela has an API gravity of 9.5 and contains 5.25% sulfur (Dickey, 1981; IARC, 1989). Crude oils high in sulfur are designated “sour crude oils”, and those low in sulfur are “sweet crude oils”. Sulfur is removed during refining by catalytic hydrotreating or by caustic wash (sweetening) processes. Nitrogen types include anilines, pyridines, quinolines, pyrols, carbazoles, benzonitrils and amides. Nitrogen is found in lighter fractions as basic compounds and in heavier fractions as non-basic compounds. Total nitrogen varies from <0.01% -1.0% by elemental analysis. Oxygen compounds are generally phenols, ketones and carboxylic acids. Metals found in crude oil include nickel, iron, vanadium, and arsenic in small quantities. These are removed during refining to avoid poisoning of catalysts, and when burning heavy fuel oils, to minimize deposits of vanadium oxide, and nickel oxide in furnace boxes, ducts and tubes. Inorganic salts such as magnesium chloride or calcium chloride are suspended as minute crystals in crude oil or dissolved in entrained water (brine). These salts are removed or neutralized prior to processing to prevent catalyst poisoning, equipment corrosion and fouling.

CATEGORY RATIONALE

The petroleum crude category contains only one CAS number to identify all crude oil regardless of source. The definition for Crude Petroleum, CAS #8002-05-9 on the TSCA Inventory (1985) is “a complex combination of hydrocarbons consisting predominantly of aliphatic, alicyclic and aromatic hydrocarbons. It may also contain small amounts of nitrogen, oxygen, and sulfur compounds. This category encompasses light, medium and heavy petroleum, as well as the oils extracted from tar sands.” Oil extracted from tar sands undergoes upgrading at or near the production site to produce a higher quality, lighter material referred to as synthetic crude oil.

All petroleum crude oils reach the refinery in a natural state, except for the removal of some contaminants (e.g. sediment, water, mineral salts) at the wellhead. Crude oils with very similar boiling ranges may differ considerably in other physical properties, hydrocarbon composition and distribution of paraffinics, naphthenics and aromatics and sulfur content. These variations are illustrated in Figure 1 for two typical crude oils from the American Petroleum Institute (API): Crude C, a naphthenic crude with low sulfur content, and Crude D, a paraffinic crude with higher sulfur content.

Fig. 1. Characteristics of two samples of crude oil



IARC, 1989

Synthetic crude oil, from upgraded tar sands, is compositionally similar to high quality conventional crude oil (>33^{0}API). The conventional technologies such as delayed and fluid coking, hydrotreating, and hydrocracking, used to upgrade heavy crude oils and bitumens, are used to convert tar sands into an essentially “bottomless” crude, consisting of blends of hydrotreated naphthas, diesel and gas oil without residual heavier oils. Table 2 presents side by side comparative data for a Canadian Synthetic crude oil and a high quality Light Louisiana Sweet Crude, showing the similarity in paraffin, naphthene and aromatic content over the gasoline boiling range and a lower sulfur and metal [nickel, vanadium] content in the synthetic crude oil. This information was supplied to EPA under the requirements of the 211(b) Fuel and Fuel Additives Test Rule [40CFR Part 79, 6/27/94) to support the position that tar sands-derived synthetic crude oil is comparable to conventional crude oils for health effects and environmental testing, a position with which EPA concurred.

TABLE 2. Specification Comparisons: Petroleum and Synthetic Crude Oils

	Canadian Synthetic Crude	Lt Louisiana Sweet Crude
^{0}API	32.2	35.3
Sulfur, (wt %)	0.16	0.49
Viscosity SUS@100^{0}F	38.6	41.8
Nickel ppm	4.1	7.7
Vanadium ppm	5.4	11.0
Hydrocarbons: Avg Vol % over gasoline boiling range [IBP-400^{0}F]		
Paraffinic (vol%)	69	72
Naphthenic	27	24
Aromatics	14	12

Courtesy of Marathon Ashland Petroleum LLC, 1994

Human exposure to petroleum crude oils is primarily through skin contact, however some airborne exposure to crude oil components, such as hydrogen sulfide, mercaptans and gaseous and volatile hydrocarbons can occur via explosive events at wellheads, during transport and in the refinery. Known carcinogens such as benzene, certain polycyclic aromatic hydrocarbons, nickel and arsenic compounds are found in crude oil. Environmental exposure to marine organisms by dermal and oral routes occurs from accidental spills or spillage during loading for transport. Exposure to terrestrial species also occurs due to spillage and tank leakage (IARC, 1989).

Review of existing health effects data indicates that acute toxicity is relatively low and similar over a range of crude oils: oral LD50 rats> 5.0g/kg, dermal LD50 rabbits> 2.0g/kg. Skin irritation was minimal and skin sensitization unlikely; some eye irritation has been observed with a heavy oil sample. Crude oils induced gene mutation in *Salmonella typhimurium* when extractions of polycyclic aromatic compounds (PAC) rich in 3-7 ring polynuclear aromatic hydrocarbons (PAH) and N- or S- containing heteroatoms, were tested with metabolic activation. Limited repeat dose studies performed by the oral and dermal routes demonstrated similar effects on hematological endpoints, enlarged liver and thymic atrophy. These effects were also reported in sea otters exposed to Prudhoe Bay crude from the Valdez oil spill (Alaskan Crude Oil Conference, 1989).

Although few large-scale studies have been performed with crude oils, significant resources have been committed to performing mammalian and environmental toxicity studies on products derived from refining of crude oil (e.g., gasoline, lubricating oils, diesel fuels, kerosene, jet fuels, white oils and waxes). Extrapolation from these refinery stream studies and from available data from mammalian studies with crude oil either in the laboratory or from mammals exposed to environmental spills indicates that crude oil-induced mammalian toxicity is correlated with increasing levels of aromatic components rich in 3-7-ring PAC. The lighter the crude oil, the lower the PAC levels, and the heavier the crude oil, the higher the PAC levels.

For environmental endpoints, the toxicity of crude oils does not correlate with levels of 3-7 ring PAC, but is defined by the range of components of crude oil in general. The majority of constituent chemicals are neutral organic hydrocarbons whose toxic mode of action to aquatic organisms is non-polar narcosis. Acute toxicity is attributed to those water-soluble components that are either saturates (aliphatic or alicyclic) or mono- or di-aromatics. Polyaromatic hydrocarbons (PAH) in crude oil are not expected to contribute significantly to acute aquatic toxicity due to limited bioavailability, but by bioaccumulating, may contribute to chronic effects on aquatic organisms, the benthic community and fish species. Bioaccumulation is species dependent, and many aquatic organisms have shown the capacity to metabolize PAHs and thus do not bioaccumulate to levels predicted by partitioning characteristics. The extent of bioaccumulation depends on the species as well as the type of PAH compound (Eisler 1987).

TEST MATERIALS

The Petroleum HPV testing program proposes to test a light crude oil (high ^{0}API, high paraffinic content), and a heavy crude oil (lower ^{0}API, higher naphthenic, aromatic content) by the most appropriate route of mammalian exposure (dermal administration) to cover the extremes of component composition of materials in this category. Results from these studies, combined with published data and environmental monitoring following accidental releases of crude, will be used to delineate the range of toxicity from petroleum crude oils.

EVALUATION OF EXISTING HEALTH EFFECTS DATA and PROPOSED TESTING

Results of studies from various crude oils are summarized in this section. Studies are comprised of both laboratory and environmental monitoring data collected from monitoring species exposed by unintentional oil spills. Detailed study information is available in the Robust Summaries organized in the IUCLID data set format employed by the European Union (Appendix 3). The currently available data submitted to the HPV program and any additional testing will be developed with the goal of facilitating international harmonization of hazard and risk characterization worldwide.

Mammalian Toxicity

Acute Toxicity

Acute oral and dermal toxicity and eye and skin irritation data from 5 crude oils [4 light crude oils and 1 heavy crude] are summarized in Table 3. Crude oils were not significantly toxic orally in rats or dermally in rabbits, and demonstrated minimal skin irritation. Only Lost Hills light crude induced substantial conjunctival irritation at 24 hours. In a separate study of 3 samples of crude oils, Smith (1981) reported oral toxicity in the mouse as LD_{50} ranging from >10.0g/kg (mixed petroleum crude oils) to >16.0g/kg (Wilmington crude 18^{0}API; Recluse crude).

Table 3. Acute Toxicity of Crude Oils

Sample	Oral LD_{50} (Rat) g/kg	Dermal LD_{50} (Rabbit) g/kg	Skin Irritation (Rabbit)[a] Erythema	Skin Irritation (Rabbit)[a] Edema	Eye Irritation (Rabbit 24hr) Conjunctiva
Beryl [36.5^{0}API]	>5.0	>2.0	ND	ND	1.7
Arab Lt [34.5 API]	>5.0	>2.0	0.9	0.1	1.3
Mid-Continent [40^{0}API]	>5.0	>2.0	ND	ND	0.3
Lost Hills Light	>5.0	>2.0	1.6	1.3	3.7
Belridge Heavy	>5.0	>2.0	0.6	0.8	0.8

a- Mean scores of reactions at 24, 48, and 72 hrs. Mobil (1984a, 1985, 1990a)

Evaluation of Lost Hills Light and Belridge Heavy for sensitization in the guinea pig (Bueler method) indicated that crude oils were unlikely to cause skin sensitization (Mobil, 1991a,b).

Summary: Crude oils show little toxicity from short duration exposure. **There are sufficient data to characterize acute toxicity endpoints for a range of light to heavy crude oils and no additional testing is proposed.**

Repeat Dose Toxicity

Three crude oils (Arab Light, 34.5^{0}API Prudhoe Bay, 28^{0}API, heavy; and South Louisiana. 35^{0}API, light) were administered orally to CD-1 mice once daily for 5 days (Leighton, 1990). Prudhoe Bay was administered at concentrations of 0, 2, 4, 8, 10, 12, or 16ml/kg/day; Arab Light and South Louisiana were given at 10ml/kg/day only. All three crude oils induced minor hematologic changes, liver enlargement and thymic and splenic atrophy without concurrent pathological effects on tissue structure. Liver enlargement was considered an adaptive, physiological response and thymic atrophy a non-specific, stress-related secondary effect.

Lost Hills Light (LHL- low viscosity, 50.0 wt% PAC, 0.86 wt% S) and Belridge Heavy (BH - high viscosity, 63 wt% PAC, 1.05 wt% S) crude oils were administered dermally to the clipped backs of male and female Sprague Dawley rats at dose levels of 0, 30, 125, and 500mg/kg/day for 13 weeks, 5 days/wk; sites were not occluded (Feuston et al., 1997b).
Effects of dermal exposure at 500mg/kg of heavy crude oil [Belridge Heavy] included reduced mean body wt gain in male rats only, depressed hemoglobin and hematocrit counts in both sexes and decreased red blood cell counts in females. Liver weight was increased and thymus weight decreased in both sexes at 500mg/kg and relative liver weight was increased in males of the 125mg/kg group. Microscopically, thymic atrophy was observed in most 500mg/kg rats (both sexes) but hypertrophy and hyperplasia of the thyroid was only observed in some 500mg/kg males and no females. Hyperplasia of treated skin was slightly less severe in BH treated rats than in those exposed to the light crude oil. Dermal exposure to the light crude oil [Lost Hills Light} at 500mg/kg did not affect body weight or body weight gain but did depress hemoglobin and hematocrit counts in male rats only. Increased liver weight was seen in both sexes at 500mg/kg but no significant weight changes were seen in the thymus. Microscopically, hyperplasia of treated skin was slightly more severe than with exposure to heavy crude oil. Thymic atrophy occurred in only a few rats compared to most rats treated with the heavy crude oil at 500mg/kg. Hypertrophy and hyperplasia of the follicular epithelium of the thyroid was seen in some male rats at all dose levels but not in females. LOAEL = 30mg/kg based on irritation and marginal thyroid effects, for both crude oils. However, Belridge Heavy, richer in 3-5 and 4-5 ring polynuclear aromatic compounds (PAC), demonstrated more severe toxicity in target systems than Lost Hills Light. These results correlated with data from similar studies performed on refinery streams which revealed a relationship between endpoints of general toxicity and increasing levels of 3-7 and 4-7 ring PAC (Feuston et al., 1994; Mobil, 1992a,b).

Summary: The available data from oral and dermal repeat dose toxicity studies on crude oils demonstrate similar toxic effects for both light and heavy crude oils (e.g. hematologic changes, liver enlargement and thymic atrophy) by either route. **These studies are adequate to define the repeated dose toxicity of crude oils.** However, additional systemic toxicity data on a light and a heavy crude will be collected as part of the OECD protocol 422 proposed to evaluate reproductive/developmental toxicity of crude oils.

In Vitro Genetic Toxicity

Gene mutation assays performed with *Salmonella typhimurium* with and without metabolic activation from rodent liver homogenate were negative when neat (unextracted) crude oils (Arab Light, 34.5^{0}API,light crude, Petrilli et al., 1980); Wilmington, 18^{0}API, heavy crude, Lockard et al., 1982) were tested. Solvent extraction of crude oils with dimethyl sulfoxide produced a polycyclic aromatic compound fraction enriched in 3-5 and 3-7 ring PAH and heteroatoms, which when tested in the modified Ames test with *S. typhimurium* strain TA98 with metabolic activation resulted in increased incidence of revertant colonies for several oils – light crude oils - Arab Light, Beryl, Mid-Continent, and Belridge Heavy. Lost Hills Light which contains less aromatic constituents was negative for bacterial mutagenesis (Mobil, 1984b, 1990b). *In vitro* studies employing mammalian cells did not demonstrate genetic damage from exposure of neat Belridge Heavy or Lost Hills Light to Chinese Hamster ovary cells (Mobil, 1991c,d), or transformation from exposure of Syrian Hamster ovary cells to Wilmington crude (Lockard et al., 1982). Wilmington crude also did not induce sister chromatid exchange *in vitro* (Lockard et al., 1982).

Summary: *In vitro* gene mutation has been demonstrated in bacterial assays for a variety of crude oil extracts. Where activity is present, it occurs with metabolic activation only and severity is correlated with higher ratios of PAC. *In vitro* tests with neat (unextracted) crude oils in bacterial or mammalian cells are negative, due to limited solubility of the whole oil in aqueous medium and possible competition of non-biologically active components for available metabolic sites. **There are sufficient data to characterize the *in vitro* genetic toxicity endpoint for crude oils and no additional testing is proposed.**

In Vivo Genetic Toxicology

Results of micronucleus assays in Sprague Dawley rats treated dermally with Lost Hills Light or Belridge Heavy crude oils at concentrations of 0, 30, 125 or 500 mg/kg for 13 wks demonstrated that these crude oils did not induce cytogenetic damage in bone marrow of treated rats (Mobil, 1990c;1991e). Administration of Wilmington [heavy] crude oil at the same doses and regime in ICR mice also produced negative results, but a single intra-peritoneal injection at doses of 1.8, 3.6 or 7.2g/kg did induce a slight increase in sister chromatid exchanges in mouse bone marrow, indicative of some DNA perturbation (Lockard et al., 1982).

Summary: The data available are sufficient to characterize the *in vivo* cytogenetic toxicity endpoint for crude oils. **No additional testing is proposed.**

Carcinogenicity:

A number of crude oil samples have been investigated for their potential to cause skin cancer in mouse skin painting studies of 104-110 wk duration. These samples include Naphthenic, Gulf Coast [API Crude C], Paraffinic, high sulfur [API Crude D] (Lewis et al., 1984), San Joaquin Valley [21^0API] (Clark et al., 1988), and Wilmington crude (Renne et al., 1981). All crude oils produced skin tumors in 33-100% of mice with latency periods of 40-76 wks, and are considered dermal carcinogens. Tumor incidence and latency depended on crude oil composition and dose. In a limited initiation study, mice were treated with a single dermal dose (50µl) of South Louisiana [light] crude, followed by treatment with a phorbol ester promoter for 180 days. Calkins et al (1981) concluded that South Louisiana crude oil was not a tumor initiator. Interestingly, this conclusion is not inconsistent with the skin painting results since compounds which induce tumors after fairly long latency periods to first tumor, are frequently assumed to act by promoting the expression of genetic events induced by initiating compounds rather than causing these events directly. In the International Agency for Research on Cancer (IARC, 1989) evaluation of carcinogenic risk to humans, crude oils were assigned to Group 3 – not classifiable as to carcinogenicity to humans, based on “inadequate evidence” for carcinogenicity in humans, and ‘limited evidence” for carcinogenicity in experimental animals.

Summary: These studies are summarized for information only and are beyond the scope of HPV testing. **No testing is proposed**

Reproductive and Developmental Toxicity

Prudhoe Bay crude oil (28^0API, heavy crude) was administered orally to Sprague Dawley pregnant rats in a single dose at levels up to 10ml/kg on specified days of gestation or as repeated doses up to 2ml/kg/day on gestation days (GD) 6-17 (Khan et al., 1987). Increased incidence of resorptions, increased fetal death and decreased fetal weight were observed with both treatment regimes at maternally toxic doses. NOEL maternal and developmental toxicity = 893mg/kg.

Lost Hills Light (LHL- low viscosity, 50 weight% PAC, 0.86 weight% S) and Belridge Heavy (BH- high viscosity, 63 wt%, 1.05 wt% S) were evaluated for pre- and post-natal developmental toxicity by the dermal route (Feuston et al., 1997a; Mobil, 1991f,g). LHL was applied to clipped backs of presumed pregnant rats at concentrations of 0, 125, 500, 1000 (postnatal group only) and 2000 (prenatal group only) mg/kg/day on GD 0-19. BH was applied under the same regimen at concentrations of 0, 30, 125, and 500mg/kg/day. Application sites were not occluded. Prenatal rats were killed on GD20; postnatal rats delivered naturally and remain, untreated, with their litters until sacrifice at 3-4wk postpartum. Both crude oils produced maternal and developmental toxicity. Maternal effects included slight (LHL) to moderate (BH) skin irritation, lower body weight gain and increased relative liver weights at concentrations = 500mg/kg for both crude oils. Parturition was delayed in the BH 500mg/kg group. A significant increase in resorptions with concomitant decrease in litter size was observed in animals exposed to LHL at 2000mg/kg and the BH at 500mg/kg. The 4-day pup viability index was decreased in all

BH exposed groups. Reductions in mean fetal body weights were observed at these doses and reduced ossification of skeletal elements were also reported. For the light crude oil, Lost Hills Light, developmental effects were observed at doses that were maternally toxic; NOEL maternal toxicity = 125mg/kg, NOEL developmental = 500mg/kg. The heavy crude oil, Belridge Heavy, induced reduction in the day 4 pup viability index at all dose levels; NOEL maternal = 125mg/kg, NOEL developmental could not be established. Generally, the greater severity of effects was seen in animals from groups exposed to Belridge Heavy, compositionally higher in aromatic compounds with 3-5 and 4-5 hydrocarbon rings. These results are consistent with results of studies performed with refinery products derived from these and other petroleum crude oils.

Sperm morphology was examined after 5 days intra-peritoneal injections of Wilmington crude [18^0API, heavy] to mice at levels up to 2.1g/kg/day. Evaluation of samples 35 days after exposure did not reveal any significant increase in the incidence of abnormal sperm (Lockard et al., 1982).

Summary: These studies demonstrate, in general, that petroleum crude oils induce developmental toxicity at doses which are also toxic to the dam and do not appear to be uniquely hazardous to the fetus. Sperm do not appear to be susceptible to crude oil induced toxicity. Decreases in viability at postnatal day 4 observed in pups from dams exposed to Belridge Heavy at both maternally toxic and non-toxic doses, may suggest the possibility of weakened systems and failure to thrive not expressed as overt toxicity at earlier stages of development. More severe effects correlated with higher levels of PAC in the crude sample. **To provide additional reproductive toxicity information, the Reproductive/Developmental Toxicity screen as part of a Repeat Dose systemic toxicity study (OECD protocol 422) is proposed.**

EVALUATION OF EXISTING PHYSICOCHEMICAL AND ENVIRONMENTAL FATE DATA

The physicochemical endpoints for the EPA HPV chemical program include melting point, boiling point, vapor pressure, water solubility, and octanol/water partition coefficient (Kow). Environmental fate endpoints include biodegradation, photodegradation, hydrolysis, and fugacity. Because the HPV substances covered under the testing plan are mixtures of differing compositions, it is not possible to measure or calculate a single numerical value for some of the physicochemical properties. For example, a product that is a mixture of chemicals does not have a melting point, but rather a melting point range. Melting point and boiling point ranges will be reported because these substances are complex mixtures. Where appropriate, values for PC properties will be represented as a range of values according to the product's component composition. Although some data for materials in this category exist, not all of these endpoints are defined and a consensus database for chemicals that represent materials in this category does not exist. Therefore, calculated and measured representative data were identified and a technical discussion provided where appropriate. The EPIWIN© computer model, as discussed in the US EPA document entitled "The Use of Structure-Activity Relationships (SAR) in the High

Production Volume Chemicals Challenge Program. " is used to calculate physical/chemical properties of representative PONA constituents of crude oils. Log P_{ow}, atmospheric oxidation half-lives and environmental media partitioning were calculated for individual hydrocarbon constituents identified previously in crude oils, and the range of these properties are summarized.

Summary: Where measured data does not exist and is impractical to develop, calculated physicochemical and environmental data for selected constituents of crude oils have been developed using the EPIWIN© computer model

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 phase or flow characteristics of petroleum products, the pour point is routinely used. The range of figures quoted in the robust summary, -30 - 30 ° C, are a typical range for the pour point as measured by a standard oil industry procedure (ASTM Method D97; ASTM 1991). Some low wax crude oils have pour points below -30 °C.

Summary: The pour point of various crude oils has been adequately characterized. **No additional testing is necessary**

Boiling point: Distillation temperatures for crude oil range from approximately -1 - 565 ° C at 1013 hPa. The ASTM D86 method measures the distillation range of petroleum products. The figures quoted represent the approximate range for crude oils and are based on (a) the boiling point of n-butane for the lower value and (b) an upper limit quoted by Speight (1990). In practice, atmospheric distillation of crude oil is not practiced above 275-300 °C, to avoid thermal decomposition of the residue. The residue is normally vacuum-distilled in a subsequent operation.

Summary: The distillation range for crude oil has been adequately described. **No additional testing is necessary**

Vapor pressure: The range of vapor pressures has been reported from 6 - 45 kPa (Jokuty, et al. 2002). Crude oil vapor pressure is a function of oil temperature and composition. Reported values represent vapor pressures of different crude oil types as reported in Environment Canada database.

Summary: The vapor pressure of various crude oils has been adequately measured. **No additional testing is necessary**

Partition Coefficient: The range of partition coefficients for constituent hydrocarbons in crude oil extend from 2 to > 6, based on the calculated log P_{ow} at 25^{0}C (European Chemicals Bureau, 2000). The calculation was done by the CLOGP Version 3.5 program (Calculation of LOG Partition coefficient octanol/water). The figures represent the spread of calculated and/or measured values for typical hydrocarbon components of crude oil. Calculated values for higher molecular weight hydrocarbons are above 6, but such values are notional, since no correlation has been established between calculated and experimental values.

Summary: The reported range of partition coefficients represents varied constituent hydrocarbons in different crude oils. **No additional testing is necessary**

Water Solubility: The aqueous solubilities of the main classes of hydrocarbons present in crude oil differ and increase in the order n-alkanes<isoalkanes< cycloalkanes< aromatics (McAuliffe, 1966). Solubilities of crude oil components may extend up to one or two percent individually, however, total solubility of all components will be dictated by component composition and loading rates of oil to water.

Summary: Calculated and measured water solubilities differ for individual components of complex petroleum substances. At any particular loading rate, aqueous concentrations of each component is 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. Aromatics represent the most abundant class of water-soluble hydrocarbons in crude oil. The water solubility of aromatics decreases with increasing number and size of alkyl substituents (McAuliffe, 1966). Although none of the components are appreciably water soluble, crude oils higher in aromatics and naphthenics demonstrate greater solubility than other oils. Available literature describing solubility determinations of components in crude oil are presented in robust summary formats. **No additional testing is necessary.**

Environmental Fate Data

Environmental fate endpoints include biodegradation, photodegradation, hydrolysis, and fugacity. Biodegradation data, available for several representative crude oils in this category, show that these materials can exhibit a moderate to rapid rate of biodegradation. For the photodegradation endpoint, data will be calculated. Most of the hydrocarbon components of crude oils are not subject to hydrolysis at measurable rates, therefore, hydrolysis is not a relevant endpoint for these materials.

A summary of fate processes indicates that most crude oil releases occur in seawater, where wind and wave action contribute significantly to the natural removal processes. Crude oil spreads as a film on the surface of water, facilitating the loss by volatilization of its lighter components. In air, the volatile hydrocarbons are photo-degraded by reaction with hydroxyl radicals, their half-lives varying from 0.5 day (e.g. for n-dodecane) to 6.5 days (e.g. for benzene). The water solubility of crude oil is low, with only the lower molecular weight aromatic hydrocarbons and some polar compounds showing low, but significant solubilities. The dissolved constituents gradually biodegrade in water. Some of the higher molecular weight compounds are removed by emulsification and these also slowly biodegrade; others adsorb to sediment and sink. A further removal process from the water column involving the heavier fraction is agglomeration to form tars, some of which are heavier than water and hence, sink (CONCAWE, 2001).

Equilibrium models are used to calculate chemical fugacity that can provide information on where a chemical is likely to partition in the environment. These data are useful in identifying environmental compartments that could potentially receive a released chemical. Fugacity data can only be calculated. In its guidance document for HPV data development, the US EPA states that it accepts Level I fugacity data as an estimate of chemical distribution values. The input data required to run a Level I model include basic physicochemical parameters; distribution is calculated as percent of chemical partitioned to the 6 environmental compartments within a unit world. Level I data are basic partitioning data that allow for comparisons between chemicals and indicate the compartment(s) to which a chemical is likely to partition in the environment. Calculated environmental partitioning behavior for selected constituents of the crude oils indicate that these chemicals will partition largely to the air, and therefore their fate in air is of environmental interest. The lower molecular weight components will mainly partition to air, with a maximum of about 1% of mono-aromatic hydrocarbons partitioning to water. As the molecular weights increase, there is less tendency for the hydrocarbons to partition to air, the environmental distribution being preferentially to soil and sediment. Collectively, the wide molecular weight range of the hydrocarbons in crude oil will mean that at equilibrium, distribution will be mainly to air and soil, with much less than 1.0% being present in water (European Chemicals Bureau, 2000).

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. In general, many component molecules in crude oils will undergo direct photolysis. Saturated hydrocarbons (paraffins and naphthenics), olefins with one double bond, and single ring aromatics, which constitute the majority of these components, do not absorb appreciable light energy above 290 nm. However, to a limited extent, some degradation of PAH molecules in crude oil in the environment may occur as the result of photo-oxidative processes, although PAHs bound to sediments are reported to be less susceptible to photo-oxidation. The persistence of PAHs in sediments may be due to lack of light for photo-oxidation. Therefore, this fate process will not contribute to a measurable degradative removal of chemical components in this category from the environment.

Atmospheric oxidation as a result of hydroxyl radical attack is not direct photochemical degradation, but rather indirect degradation. AOPs can be calculated using a computer model. Indirect photolysis can be estimated using models accepted by the US EPA and other authorities. An estimation method accepted by the US EPA includes the calculation of atmospheric oxidation potential (AOP). In air, the volatile hydrocarbon molecules in crude oils will undergo reaction with photosensitized oxygen in the form of hydroxyl radicals (OH-) (Atkinson, 1990). The computer program AOPWIN (atmospheric oxidation program for Microsoft Windows 1), used by the US EPA OPPTS (Office of Pollution

Prevention and Toxic Substances), calculates a chemical half-life based on an overall OH- reaction rate constant, a 12-hr day, and a given OH- concentration.

Atmospheric oxidation half-life values for typical hydrocarbon constituents of crude oils (European Chemicals Bureau, 2000):

Constituent	Half-life (days)
benzene	6.5
n-butane	3.2
n-hexane	1.4
toluene	1.3
cyclohexane	1.1
n-decane	0.69
n-tetradecane	0.42
naphthalene	0.37

Summary: Insufficient data are available to characterize the atmospheric oxidation potential of chemical components found in materials in this category. Therefore, representative components for this category are identified and their AOP values calculated. AOPWIN version 1.89 calculates atmospheric oxidation half-lives of hydrocarbons in contact with hydroxyl radicals in the troposphere, under the influence of sunlight and in contact with O_3, based on a 12-hour day at 25^0C. Hydrocarbons of carbon number greater than C20 will have little or no tendency to partition to air. **No additional modeling is necessary.**

Stability in Water:

Summary: Hydrolysis of an organic chemical is the transformation process in which a water molecule or hydroxide ion reacts to form a new carbon-oxygen bond. 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). The majority of chemical components in crude oils are hydrocarbons, which are not included in these chemical groups, and they are not subject to hydrolysis reactions with water. **No additional testing or modeling is necessary.**

Chemical Transport and Distribution in the Environment (Fugacity Modeling):

A widely used fugacity model is the EQC (Equilibrium Criterion) model. Level 1 is a steady state, equilibrium 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 (Mackay et al., 1992). Transport media are air, soil, water, biota, suspended sediment and sediment. Values representing the calculated range of distribution to environmental media of representative hydrocarbon components found in crude oils will be presented in a robust summary. Results for a range of percent distribution of typical hydrocarbons found in crude oils are shown in tabular form as follows, but a more exhaustive analysis of crude oil hydrocarbon partitioning is presented in the robust summary section.

	%Air	%Water	%Soil	%Sediment	%Susp. matter	%Biota
Propane	100.0	0	0	0	0	0
n-eicosane	0	0	97.7	2.2	0.1	0
benzene	98.8	1.1	0.1	0	0	0

Summary: Fugacity modeling for those constituents in crude oils indicates that, at steady state, the lower molecular weight components will mainly partition to air, with a maximum of about 1% of mono-aromatic hydrocarbons partitioning to water. As the molecular weights increase, there is less tendency for the hydrocarbons to partition to air, the environmental distribution being preferentially to soil and sediment. Collectively, the wide molecular weight range of the hydrocarbons in crude oil will mean that at equilibrium, distribution will be mainly to air and soil, with much less than 1.0% being present in water. These data are adequate to define environmental distribution of crude oil components. **No additional modeling is necessary for this endpoint.**

Biodegradation: Crude oil contains hydrocarbons of well-defined generic types that are biodegraded at different rates. n-Alkanes are readily degraded in seawater, since many Microorganisms can utilize them. Branched-chain or iso-alkanes are less readily biodegraded, but they do ultimately biodegrade. The degradation of cycloalkanes has not been extensively studied, but the ring structure is more resistant to biodegradation, and degrades more slowly. Aromatic hydrocarbons are also resistant to biodegradation, but a few microorganisms are able to utilize them. High molecular weight compounds, the tars and asphaltenes, show little to no degradation, and are persistent.

Few data are available on the biodegradation of samples of crude oils obtained under laboratory conditions. However, extensive research on oil degradation in marine environments indicates that virtually all kinds of oil are susceptible to microbial oxidation. The rate of oxidation is influenced by microbial characteristics, and environmental factors such as available nutrients, oxygen, temperature and degree of dispersion. Crude oil has been found to be equally well degraded in sea water and in fresh water, with the availability of nitrogen and phosphorous containing compounds especially important in determining rate of degradability. Adapted microorganisms are often found in ocean areas where crude oil spills are common. Zobell (1969) has calculated that where an adapted microbial population is available in well-aerated seawater at 20 to 30°C, the rate of crude oil oxidation ranges from 0.02 to 0.2 g of oil oxidized/m^2/day. The same author found experimentally that complete oxidation of 1.0 mg of hydrocarbon requires between 3 and 4 g of oxygen, i.e. it has a BOD of 3 to 4 mg oxygen/mg. Since the oxygen content of seawater is between 6 and 11 mg/liter, depending on salinity and temperature, this means that about 320,000 liters of seawater is required to oxidize one liter of crude oil. Five day respirometric tests run both in fresh water and in salt water at 30°C using a Kuwait crude oil resulted in 15% and 3% biodegradation, respectively (Bridie, A.L. and Bos, J., 1971). Biodegradation rates for crude oils will vary considerably, but in standard 28-day studies, none would be expected to be readily biodegradable. However, the evidence from spillages and from natural seepages is that most of the non-volatile constituents of crude oil are inherently biodegradable, but that some of the highest molecular weight components are persistent in water (CONCAWE, 2001).

Summary: A technical discussion of hydrocarbon degradation of crude oils and representative component molecules based on reviews of available literature will be incorporated in a robust summary format. **No additional testing is proposed.**

EVALUATION OF EXISTING ECOTOXICITY DATA AND PROPOSED TESTING

The HPV Chemical Test Program includes acute toxicity endpoints for a freshwater fish and invertebrate, and toxicity to a freshwater alga. The materials in the Crude Oil Category produce a similar range of toxicity for these three endpoints based on results of comparable studies using standard test methods and exposure solution preparation procedures. This is because crude oils are complex combinations of relatively similar series of homologous chemicals. Therefore, their short-termed toxicities are expected to fall within the range of toxicity demonstrated by the materials summarized in this test plan. Experimental studies of acute aquatic toxicity show values for crude oil samples in the range 10 to over 100 mg/l, which were evaluated as dispersions of the whole oil in water or as water accommodated fractions (WAFs) (CONCAWE 2001). These values are in accordance with the predicted aquatic toxicity of crude oils based on their hydrocarbon composition. This is expected because the majority of constituents in crude oil are neutral organic hydrocarbons, whose mode of action is non-polar narcosis, which is brought about by disruption of biological membrane function. Acute toxicity is attributed to those water-soluble hydrocarbon components that are saturates (paraffins or cyclics) and mono- and di-aromatics (Peterson, 1994; van Wezel and Opperhuizen, 1995; CONCAWE, 1996; Di Toro, et al., 2000). The differences between toxicities (i.e., LC/LL50, EC/EL50) can be explained by the differences between the target tissue-partitioning behaviors of the individual chemicals (Verbruggen et al., 2000).

Aquatic Toxicity

For the assessment of eco-toxicity of poorly water soluble mixtures of hydrocarbons as found in petroleum products, it is now generally accepted that results should be expressed in terms of the "loading rate" (OECD 2000). The "loading rate" may be 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 loading rate (OECD 2000). Toxicological endpoints such as the LL50 or EL50 are used to express the loading rate of the product that is lethal or produces a specific effect to 50% of the test organisms. Studies in which the results are expressed in terms of the measured concentrations of hydrocarbons in dilutions of "water soluble fractions (WSF)" do not allow the eco-toxicity of a product to be expressed in terms of the amount of that product required to produce a particular effect and, therefore, such results are not comparable to results obtained with other substances.

In spite of the variety of fish and invertebrate species that have been tested under a range of different laboratory methodologies, some consensus on sensitivity of aquatic species and different life stages can been made. In general, the larvae of fish and crustaceans appear to be most susceptible to the water-soluble fraction of crude oil. Exposures of plankton and algae have indicated that certain species of diatoms and green algae are inhibited, whereas micro-flagellates are less sensitive. For the most part, mollusks and most inter-tidal worm species appear to be tolerant of oil contamination (McAuliffe, 1966).

For the Crude Oil HPV Category, robust summaries were prepared for six acute eco-toxicity studies with a fish, an invertebrate, and an alga on samples of two crude oils. All exposure solutions were prepared as water accommodated fractions. Fish LL50 values were 21 and 41 mg/L, invertebrate EL50 values were 2.7 and 4.1, and alga LL50 values based upon germination of spores were 122 and 528 mg/L, while alga EL50 values based upon growth were 122 and 311 mg/L (EMBSI 2001a-e, 2002).

These summarized studies are supported by published data on aquatic toxicity of crude oils that show a wide variety in the response of organisms to oil exposures. Some of this variability may be due to using different methodologies such as WAFs and WSFs, as noted above, but overall, referenced data generally follows the information provided in the robust summaries. The following information summarizes published reliable representative aquatic toxicity data of crude oils.

LC50 values for rainbow trout of 350 and 310 mg/L were reported for nominal concentrations of Forties crude oil prepared as dispersions (Westlake, 1991). Although the test dispersions were prepared in closed jars, tests were run in open vessels, and significant evaporative losses of lower molecular weight hydrocarbons may have occurred. Therefore these data may reflect an underestimation of the acute toxicity. Similar open-system tests exposing fish species to either dispersions of crude oil and water, or to water soluble fractions of crude oil, indicate LC50 values as a function of loading rate ranged from 3.7 g/L to greater than 80 g/L (Anderson, et al., 1974). Since significant evaporative losses of lower molecular weight hydrocarbons may have occurred, the measured LC50 values potentially underestimate the true eco-toxicity. Forty-eight hour LC50 values for rainbow trout exposed to water-soluble fractions (WSF) of Norman Wells crude oil were 10.4 mg/l (open vessel) and 11.6 mg/l (closed vessel), based on measurements of dissolved hydrocarbons made at the beginning and end of the 48-hour period (Lockhart, et al., 1987).

The acute toxicity of nineteen crude oils to brown shrimp was assessed using whole-oil dispersions prepared by continuous stirring and gave LC50 values in the range 32 to 140 μl/L, equivalent to approximately 27 to 120 mg/L (Franklin and Lloyd, 1982). In tests with *Daphnia magna*, dispersions of Forties crude oil in water gave EC50 values of 43 and 51 mg/L (Westlake, 1991). Although the test dispersions were prepared in closed jars, tests were run in open vessels, significant evaporative losses of lower molecular weight hydrocarbons may have occurred and hence the measured EC50 values underestimate the true eco-toxicity. Lethal loading rate concentrations LL50 (96h) of 618 mg/l and 39 mg/L were determined for the test species, *Mysodopsis bahia,* and the kelp forest mysid, *Holmesimysis costata*, when exposed to water accommodated fractions of Kuwait crude oil (Bragin, et al., 1994).

Algal tests with *Anabaena doliolum* were run using WSF of Assam crude oil and using whole crude oil in equilibrium with the algal suspension medium. The WSF method gave a mean 15-day EC50 of 9.06 mg/l, and the direct loading (or whole oil) method gave a 15-day EC50 of 5.73 mg/l, both based on measured dissolved hydrocarbon concentrations in the aqueous phase (Gaur and Singh, 1989).

Significant effects were found at both 40% WSF (17ppm oil) and 50% WSF (21ppm oil) of Ekofisk crude oil on the development of the eggs of two sea urchin species, Strongylocentrotus pallidus and S. droebachiensis. At these levels, the larvae filled with degenerating cells, and differentiation of the intestine and skeletal growth were inhibited compared with the control larvae (Falk-Petersen, 1979).

Other risks to aquatic species, semi-aquatic birds, and sea mammals include physical fouling of plumage, fur, gills etc, by floating oil product. This results in loss of buoyancy, insulation and smothering of inter-tidal animals. Ingestion of oil resulting from attempts by animals to clean contaminated body parts may result in severe enteritis and toxicity.

Spills in freshwater environments have been shown to adversely affect the diversity and abundance of the aquatic macro-invertebrate community, with the observed effects associated with oil sorption and substrate coating (Poulton, et al., 1997; Poulton, et al., 1998). Recovery of such communities in some habitats may be rapid (e.g., riffle areas of streams/rivers), while impacts to backwater areas may persist for months. Ultimately, the type of crude oil and the local conditions and habitats will dictate the potential and extent to which crude oil persists and cause effects in the environment.

Summary: A range of measurements of aquatic toxicity has been obtained in laboratory studies of crude oils. Variability in results may be related in part to the source of the crude oil, or it may reflect different approaches to testing. However, those studies using dispersions of whole oil, employing water soluble fractions, and water accommodated fractions have generally given LC50 or EC50 values in the range 10-100 mg/L or greater when expressed in terms of oil loading rate. **No additional testing is proposed.**

TABLE 4. MATRIX OF AVAILABLE ADEQUATE DATA AND PROPOSED TESTING FOR THE PRIMARY TEST MATERIALS

	Petroleum Crude Oil CAS #8002-05-9
Melting Point	Adequate
Boiling Point	Adequate
Vapor Pressure	Adequate
Partition Coefficient	Adequate
Water Solubility	Adequate
Photodegradation	Adequate
Stability in Water	Adequate
Transport and Distribution	Adequate
Biodegradation	Adequate
Acute Toxicity to Fish	Adequate
Acute Toxicity to Aquatic Invertebrates	Adequate
Toxicity to Algae	Adequate
Acute Toxicity	Adequate
Repeated Dose	Adequate
Genotoxicity, in vitro	Adequate
Genotoxicity, in vivo	Adequate
Repro/Developmental	**Test [2 samples]**

Adequate	Indicates adequate existing data.
Test	Indicates proposed testing

TEST PROPOSAL

This study plan proposes a Combined Repeat Dose Toxicity Study with Reproductive/Developmental toxicity Screening Test (OECD protocol 422) for a selected light crude (high paraffinic, low aromatic, >33^{0}API) and heavy crude (low paraffinic, high aromatic, <28^{0}API) oil sample by the dermal route. Dermal and oral exposures have been shown to induce similar systemic effects (e.g. hematologic changes, liver enlargement and thymic atrophy) with light and heavy crude oils (Leighton, 1990; Khan et al., 1987; Feuston et al., 1997a,b). Dermal exposure has been selected as the most likely route of human exposure. Analytical characterization will be performed on the light and heavy crude oils selected for mammalian testing. Environmental effects of petroleum crude are well defined from laboratory studies and monitoring at spill sites and no further testing is proposed.

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Repeat Dose toxicity

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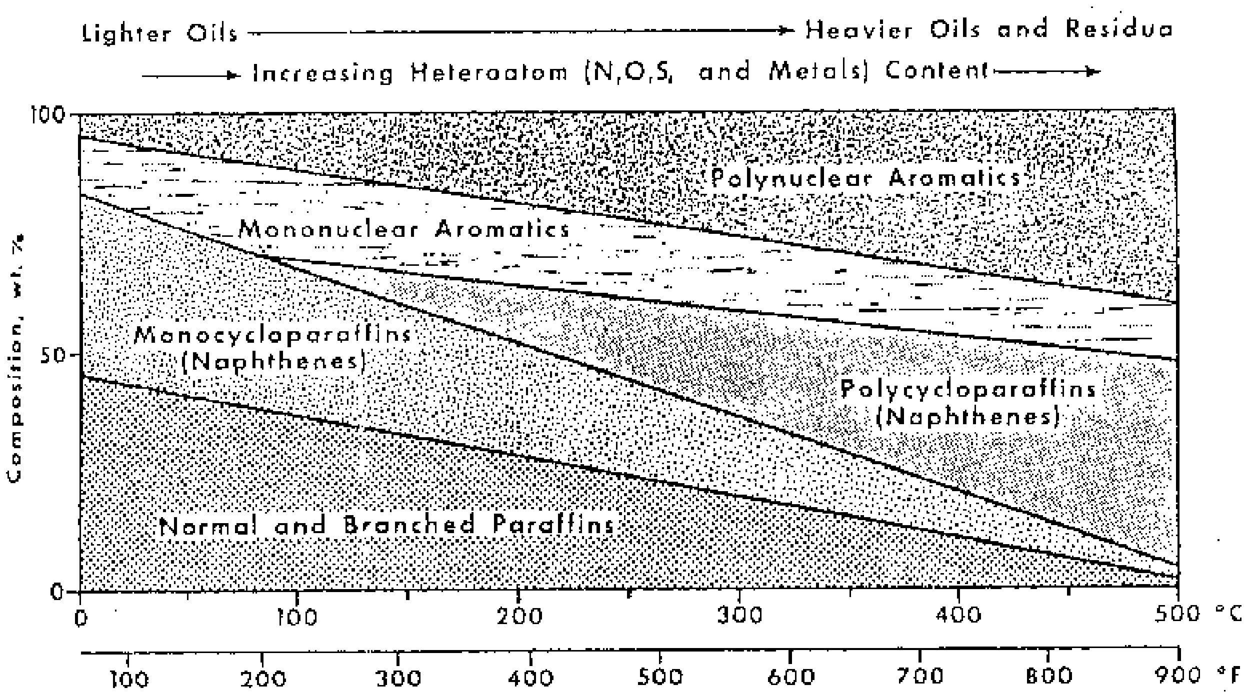
APPENDIX 1; Petroleum Chemistry and Crude Composition

The hydrocarbons that comprise crude oil – paraffins, naphthenes (cycloparaffins) and aromatics – share some structural features but differ in the ratio of hydrogen to carbon atoms and how those atoms are arranged. Olefins are not present in crude oils and are formed from rearrangement of atoms during the cracking process to produce gasoline-blending streams. Paraffins occur in higher concentrations in lower boiling fractions of crude oil while the concentration of naphthenes (cycloparaffins) and aromatics increase at higher boiling ranges (Fig A1-1)



Feedstock composition represented by the distribution of chemical types.

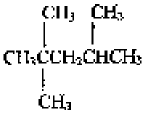
Mobil, 1997

Hydrocarbon molecules in crude oil may include from 1 to more than 50 carbon atoms at room temperature. When isolated, hydrocarbons containing 1-4 carbon atoms are gases, those with 5-19 carbon atoms are usually liquid, and those with 40 or more carbon atoms are solids.

Paraffins: C_nH_{2n+2} where n= number of carbon atoms.

Carbons are joined by single bonds (e.g. butane, $CH_3CH_2CH_2CH_3$). Paraffins with 4 or more C atoms may have 2 or more structural arrangements or structural isomers, for example:

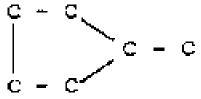
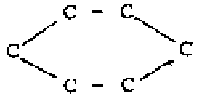
normal octane, $CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3$ or isooctane



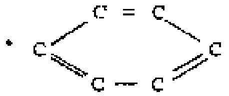
$CH_3\underset{CH_3}{\overset{CH_3}{C}}CH_2\overset{CH_3}{CH}CH_3$

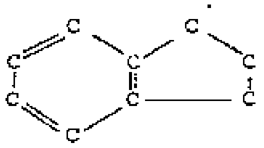
Normal paraffins occur in most crude oils but in varying total concentrations (King, 1983). As a rule, crude oils of older geological age contain higher quantities of n-paraffins. Occurrences relative to other hydrocarbon classes decrease as the boiling point of fractions distilled from crude oil increases. C_{12}-C_{16} n-paraffins have been identified as accelerators of skin carcinogenesis. Branched (iso) paraffins are found throughout the boiling range but do diminish with increasing boiling point. Certain lower molecular weight branched paraffins are capable of producing kidney damage in male rats (light hydrocarbon nephropathy).

<u>Naphthenes</u>: Cycloparaffins in gasoline have 5 or 6 carbon atoms arranged in a ring and belong to either a cyclopentane or cyclohexane series, for example:

C_6H_{12}	Methylcyclopentane	
C_6H_{12}	Cyclohexane	

Cycloparaffins constitute a substantial proportion of petroleum with 5- to 6-membered ring structure being the predominant type. Most individual cycloparaffins that have been isolated are in the boiling range of gasoline and kerosene. The cycloparaffin portion of lubricant fractions is a complex mixture of non-condensed and condensed 5- and 6-member rings. Polycycloparaffins may act as inhibitors in skin carcinogenesis.

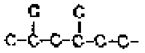
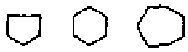
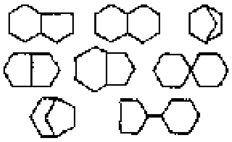
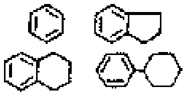
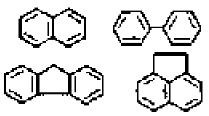
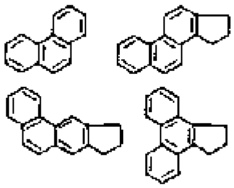
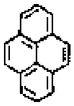
<u>Aromatics</u>: Some carbon atoms are arranged in a ring joined by aromatic bonds. for example: benzene, C_6H_6  . In polycyclic aromatics, some carbons are shared by 2 or more rings, for example, indane, C_9H_{10}



Aromatic hydrocarbon types appear to be present in the same relative proportions in different crude oils. Where several possibilities for alkyl substitution exist, the predominant isomers are generally those containing substituents with the smallest number of carbon atoms. In heavier, lubricant type fractions, mixed aromatic-cycloparaffin hydrocarbons

predominate, as mono-, di-, or trinuclear aromatic-cycloparaffin hydrocarbons. Certain polynuclear aromatics are associated with systemic toxicity and skin cancer.
Resins and asphaltenes are high molecular wt fractions (500-10,000)_containing N, S, and oxygen found in the residuum/bottoms of crude oils. They have high polarity, low solubility and limited bioavailability and toxicity. They may constitute from 10% in light paraffinic oil to up to 60% in heavy crude oils.
Much of the compositional information described above was derived from the extensive analysis of a Ponca Oklahoma crude, performed under the sponsorship of the American Petroleum Institute. Table A1-1 summarizes these findings (King, 1983).

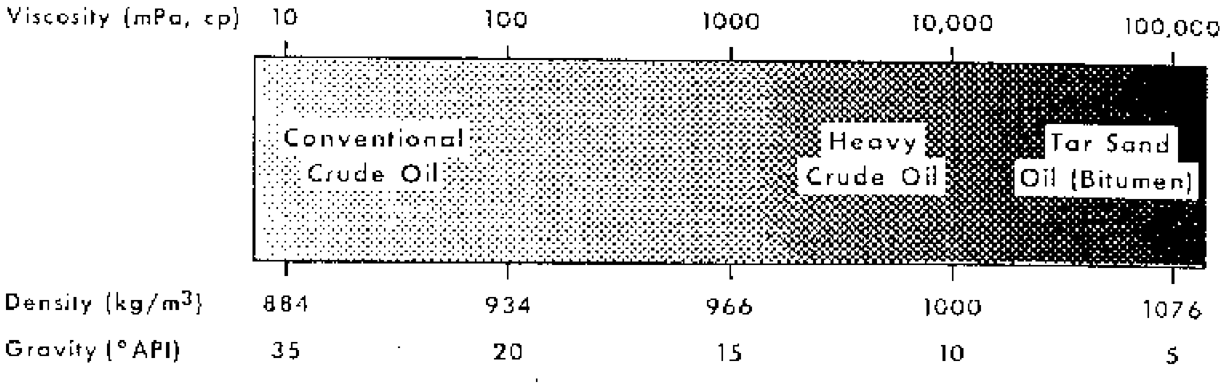
TABLE A1-1: Types of Hydrocarbons Isolated from Ponca Crude

HYDROCARBON TYPE	BASIC STRUCTURES	NUMBER ISOLATED	FRACTIONS WHERE FOUND
Paraffins			
n-Paraffins	C–C–C–C–C–C–	33	All Distillates
Branched Paraffins	 $C{-}\overset{C}{\overset{\mid}{C}}{-}C{-}\overset{C}{\overset{\mid}{C}}{-}C{-}C{-}$	41	Gasoline, Light Gas Oil
Cycloparaffins			
Monocycloparaffins		39	Gasoline, Kerosine
Bicycloparaffins		29	Gasoline, Kerosine
Tricycloparaffins		3	Gasoline, Kerosine
Aromatics			
Mononuclear Aromatics		48	Gasoline, Kerosine, Light Gas Oil
Dinuclear Aromatics		60	Kerosine, Light Gas Oil
Trinuclear Aromatics		10	Heavy Gas Oil-Light Lubricant
Tetranuclear Aromatics		3	Heavy Gas Oil-Light Lubricant

APPENDIX 2: Crude Product Potential

Crude oils are classified by viscosity, density and API gravity. API gravity was developed as a means to identify the gasoline production potential of a crude oil; the higher the API gravity, the more valuable the crude. Fig. A2-1 illustrated classification of crude oil by this density-gravity method.

Fig. A2-1



Type of Crude	Characteristics
1. Conventional or "light" crude	Density-gravity range less that 934kg/m^3 (>33^{0}API)
2. "Heavy" crude oil	Density-gravity range from 1000kg/m^3 to more than 934kg/m^3 (10^{0}API to <28^{0}API) Maximum viscosity of 10,000mPa.s(cp)
3. "Extra-heavy" crude oil; may also include atmospheric residua. (b.p.>340^{0}C; >650^{0}F)	Density-gravity greater than 1000kg/m^3 (<10^{0}API) Maximum viscosity of 10,000mPa.s(cp)
4. Tar sand bitumen [before upgrade]or natural asphalt; may also include vacuum residua. (b.p.>510^{0}C; >950^{0}F)	Density-gravity greater than 1000kg/m^3 (<10^{0}API) Viscosity greater than 10,000mPa.s(cp)

Mackerer and Biggs, AIHCE, 1996; Platts, 2003

Heavier crude oils have higher density-gravity values and higher viscosity, with lower API gravity, making them less suitable for gasoline stocks but better candidates for lubricant and heavy fuel production. Fig. A2-2 shows yield comparisons for 4 typical crude oils.

YIELD COMPARISON OF CRUDES

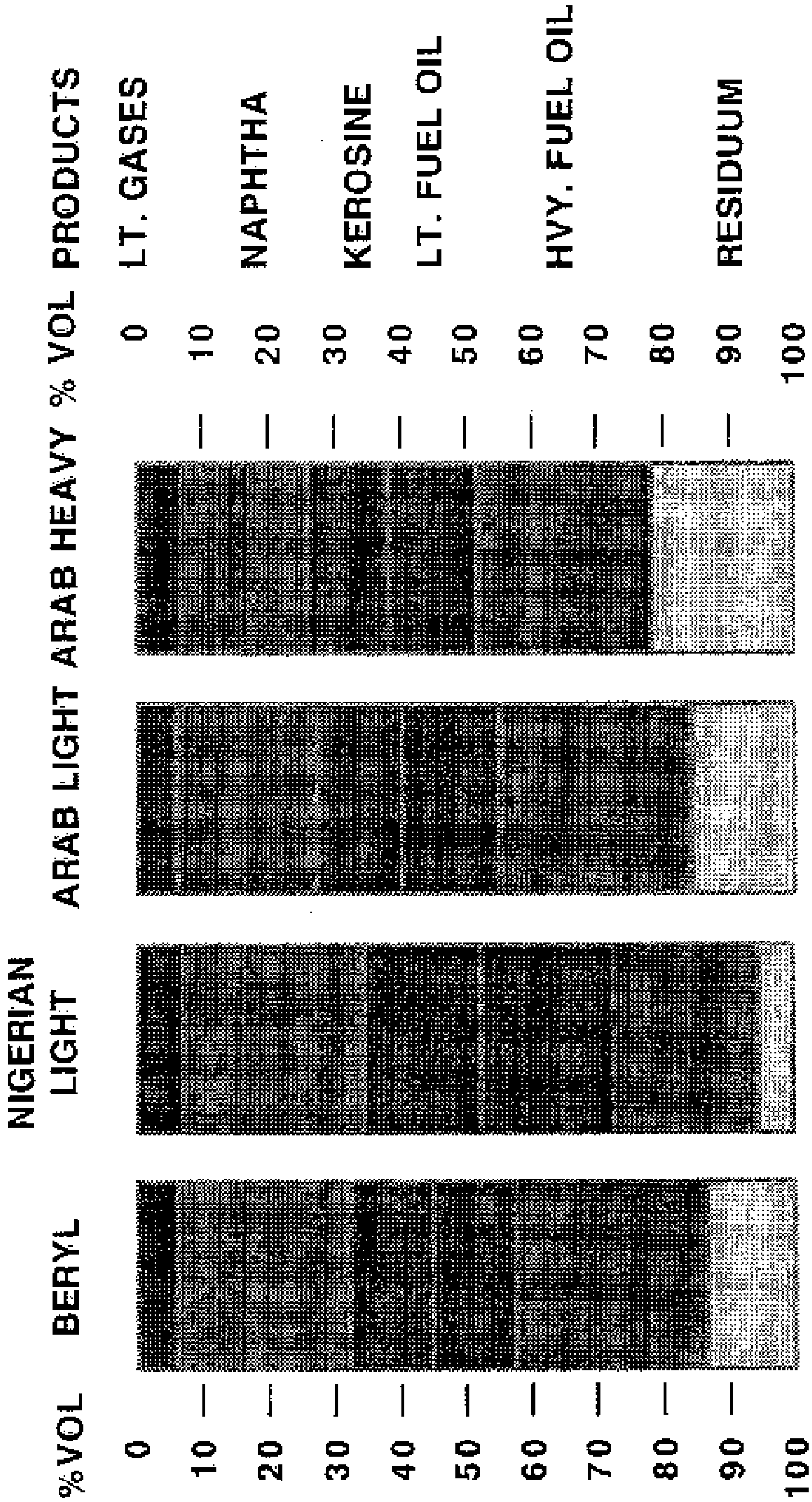


Table 2.1 BRIEF SUMMARY OF THE HISTORY OF REFINING PROCESSING

YEAR	PROCESS NAME	PROCESS PURPOSE	BYPRODUCTS, ETC.
1862	Atmospheric Distillation	Produce Kerosine	Naphtha, Tar, etc.
1870	Vacuum Distillation	Lubricants (original) Cracking feedstocks (1930's)	Asphalt, Residual Coker Feedstocks
1913	Thermal Cracking	Increase Gasoline	Residual, Bunker Fuel
1916	Sweetening	Reduce Sulfur	
1930	Thermal Reformation	Improve Octane Number	Residual
1932	Hydrogenation	Remove Sulfur	Sulfur
1932	Coking	Produce Light Products	Coke
1933	Solvent Extraction	Improve Lubricant Viscosity Index	Aromatics
1935	Solvent Dewaxing	Improve Pour Point	Waxes
1935	Cat. Polymerization	Improve Gasoline Yield & Octane No.	Petrochem Feedstocks
1937	Catalytic Cracking	Higher Octane Gasoline	Petrochem Feedstocks
1939	Visbreaking	Reduce Viscosity	Increased Distillate, Tar
1940	Alkylation	Increase Gasoline Octane & Yield	High Octane Aviation Gasolin
1940	Isomerization	Produce Alkylation Feedstock	Naphtha
1950	Deasphalting	Increase Cracking Feedstock	Asphalt
1952	Catalytic Reforming	Convert Low Quality Naphtha	Aromatics
1954	Hydrodesulfurization	Remove Sulfur	Sulfur
1956	Inhibitor Sweetening	Remove Mercaptans	
1957	Cat. Isomerization	Convert to Molecules w/High Oct. No.	Alkylation Feedstocks
1960	Hydrocracking	Improve Quality & Reduce Sulfur	Alkylation Feedstocks
1961	Fluid Cat. Cracking	Increase Gasoline Yield	Petrochem Feedstocks
1974	Catalytic Dewaxing	Improve Pour Point	
1975	Resid. Hydrocracking	Increase Gasoline Yield from Residual	

Table A2-1 summarizes the history of petroleum refining. Since the first refinery was established in 1862, processes have been developed and continually improved to maximize the yield and efficiency of production of high quality fuels, lubricants and petrochemicals from petroleum crude, and concomitantly to minimize or eliminate hazardous components, waste products and environmental contaminants.