2.0 PETROLEUM PRODUCTS

2.1 INTRODUCTION

When crude oil is subjected to refining processes, which are heating and distilling or a combination of cracking and distilling, in a fractionating column, it is separated into many different types of products by their various boiling temperature and is taken out at different heights of the column. By varying designs of the process and operating conditions, different types of products are produced.

Starting from the top of the fractionating column, different fractions, or different oils, derived from crude oil and the approximate ranges of boiling temperatures are:

Petroleum ether (largely pentanes and hexanes)	90°F to 170°F
Naptha (largely hexanes and heptanes)	90°F to 300°F
Gasoline	100°F to 400°F
Kerosene	300°F to 480°F
No. 2 Distillate	325°F to 750°F
No. 5 or 6 Fuel oil (also called residual or reduced crude)	600°F to 1000°F

Many of these products receive additional treatment to remove impurities and unwanted properties, but fuel oils do not. Figure 2-1 shows the simplified refinery processes and Figure 2-2 presents the refinery operations and their products. Table 2-1 briefly characterizes the petroleum refinery process streams, Table 2-2 presents a partial classification of fuels and Table 2-3 lists various refinery products and their applications.

2.2 GASOLINE

Briefly speaking, gasoline is a mixture of volatile hydrocarbons with a carbon number of four to twelve, has a boiling range of 38° to 204°C (100°- 400°F), and is generally derived from crude petroleum by a number of processes as indicated in Section 2.1. Synthetic gasolines may also be obtained by processing from other natural materials such as coal, shale, tar sands, etc. The hydrocarbons in the ordinary commercial grades of motor gasoline are paraffins, olefins, naphthenes, and aromatics, all in substantial concentrations.

2.2.1 Development of Gasolines

Gasolines are blended to satisfy diverse engine requirements; the composition of gasoline is an extremely complex mixture of hydrocarbons and specific additives. Additives may be used to provide certain functions or to enhance specific performance features. Because of this chemical complexity the properties which are generally used to describe and specify gasolines are those related to performance, not to the exact chemical composition. These properties include vapor pressure, distillation characteristics, octane number (antiknock quality index), lead content, sulfur content, specific gravity, gum formation or oxidation stability, and corrosion behavior.

Historically, automotive gasolines have been classified on the basis of antiknock quality; and leaded automotive gasolines have been classified into two grades--premium and regular--on the basis of octane number. Super-premium, intermediate, sub-regular, and blends of high and low octane grades have also been marketed. In high-altitude areas, octane levels have been somewhat lower than at sea level, because car octane requirements decrease with altitude.

With the exception of one premium gasoline marketed on the east coast and southern areas of the United States, all automotive gasolines until 1970 contained leaded antiknock compounds to increase antiknock quality. Leaded antiknock compounds were found to be detrimental to the performance of catalytic emission control systems under development at that time, also, some engines were designed to operate on unleaded fuel while others required leaded fuel or the occasional use of leaded fuel. Accordingly, during 1970 unleaded and low-lead gasolines were

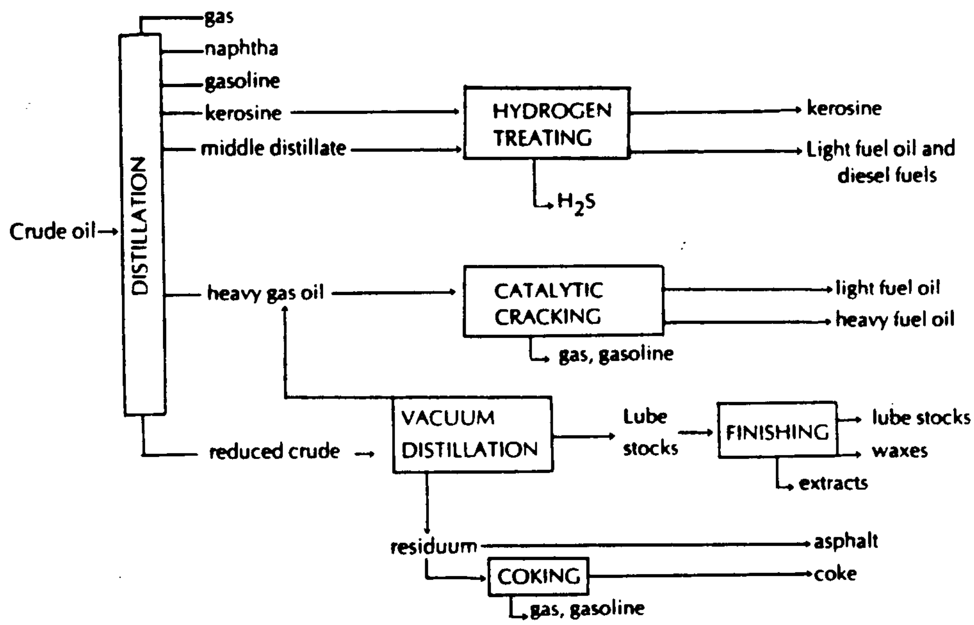


Figure 2-1 Processing Plan for Petroleum Refinery

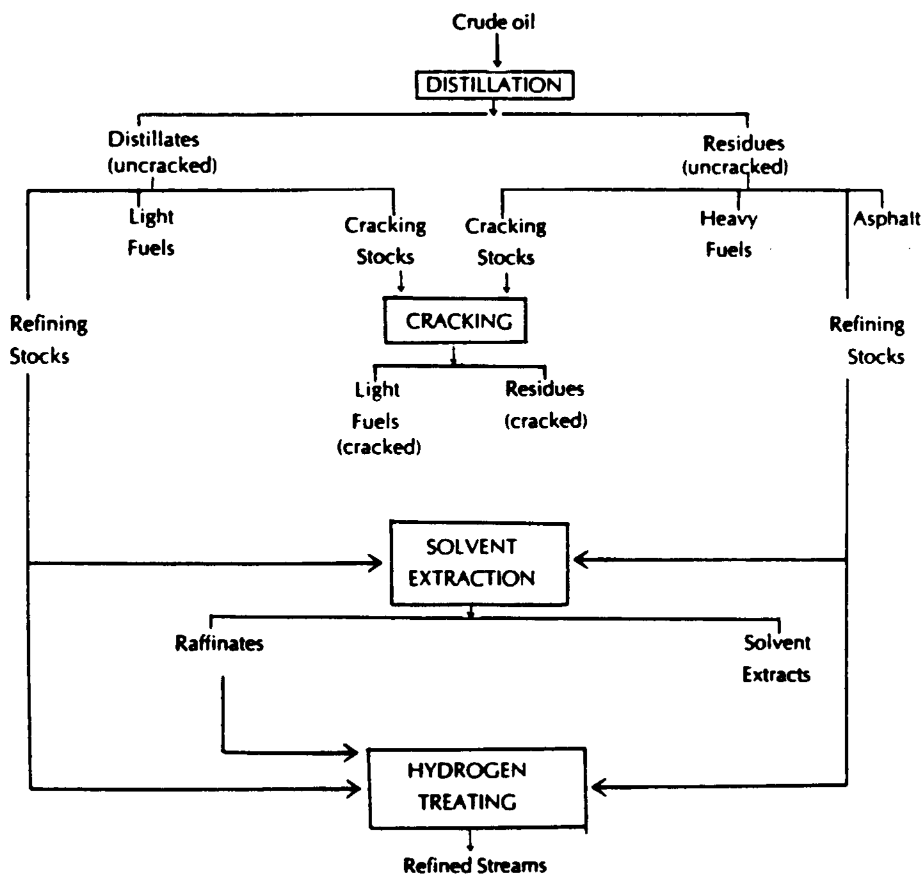


Figure 2-2 Major Petroleum Refinery Processes

Table 2-1 Petroleum Refinery Process Streams

Refinery Process Stream	Carbon Number	Boiling Range °C	Boiling Range °F
Straight Run Products of Atmospheric Distillation of Crude Oil			
Naphtha	4-12	<230	<446
Kerosine	9-16	150-290	302-554
Middle Distillate	11-20	205-345	401-653
Gas Oil	11-25	206-400	401-752
*Atmospheric Tower Residuum	>20	>350	>662
Products of Vacuum Distillation of Atmospheric Tower Residuum			
Vacuum Tower Condensate	11-25	205-400	401-752
Distillate	15-50		
Vacuum Gas Oil, Light	13-30	230-450	446-842
*Vacuum Gas Oil, Heavy	20-50	350-600	662-1112
Vacuum Residuum (Asphalt)	>34	>495	>923
Products of Cracking Processes (Catalytic Cracking, Thermal Cracking, Hydrocracking, Catalytic Reforming, etc.)			
Naphtha	4-12	<230	<446
Distillate			
Light	9-25	150-400	302-752
Intermediate	11-30	205-450	401-842
*Heavy (Catalytic, Thermal)	15-35	260-500	500-932
Hydrocracked	10-25	160-400	320-752
Residues			
*Catalytic Cracked Clarified Oil	>20	>350	>662
*Catalytic Reformer Fractionator Residue	10-25	160-400	320-752
Hydrocracked Residuum	>20	>350	>662
*Thermal Cracked Residuum	>20	>350	>662
Petroleum Coke			
*Steam Cracked Residuum	>14	>260	>500
Products of Extraction Processes (Solvent Refining, Deasphalting,Decarbonization, Acid Treatment, etc.)			
Raffinates			
Naphtha	5-12	<230	<446
Middle Distillate	9-20	150-345	302-653
Gas Oil	11-25	205-400	401-752
Distillate	15-50		
Residual Oil, Asphalt	>25	>400	>752
Extracts			
Naphtha	6-12	<220	<428
*Distillate (Light, Heavy)	15-50		
Gas Oil	13-25	230-400	446-752
Residual Oil	>25		
Products of Hydrotreating Processes			
Naphtha	4-13	<230	<446
Distillate	9-50		
Paraffin Wax	20-50		
*Vacuum Gas Oil	13-50	230-600	446-1112
Residual Oil	>25	>400	>752

* Likely to contain 5 wt. % or more of 4- to 6-membered condensed ring aromatic hydrocarbons.
Source: U.S. Environmental Protection Agency, 1978.

introduced to supplement the conventional gasolines already available.

Beginning in 1975, numerous new car models were equipped with catalytic exhaust treatment devices as one means of compliance with 1975 legal restriction in the U.S. on automobile emissions. The need for gasolines that do not adversely affect such catalytic devices has led to the large scale availability and growing use of

Table 2-2 Partial Classification of Fuels

Designation (Synonyms)	Uses	Refining History	Composition	Boiling Range
Gasolines	Automotive and Aviation fuels	Straight run, cracked distillates	C_4 - C_{11}	38-204°C (100-400°F)
Diesel fuels	Mobile and industrial engine fuels	Straight run distillates (paraffinic stocks)	30-35 % aromatics	
Mineral seal oil	Illuminating oil, solvent, insect spray	Straight run distillate	paraffinic	260-370°C (500-700°F)
Fuel oils	Liquid burner fuels			
No. 1(Kerosine, range oil)	Aviation and diesel fuels, illuminating oil, domestic heating oil, insect sprays	Straight run distillate	C_9 - C_{16} 15-20 % aromatics	171-293°C (340-560°F)
No. 2	Domestic heating oil	Straight run, cracked distillates	30-32 % aromatics 37-43 % paraffins 26-32 % naphthenes	177-343°C (360-650°F)
No. 4	Light industrial fuel (no preheating)	Heavier straight run, cracked distillates; light residual fuels		
No. 5	Industrial burners (some preheating)	Residual fuel, some distillates		
No. 6 (Bunker C)	Ships, industry, large scale heating (preheating)	Straight run, cracked residual		

Source: U. S. Bureau of Mines, 1975.

Table 2-3 High-Boiling Petroleum Products

Products	Applications
Distillates	
Heavy aromatic naphthas	Solvent, spraying oils, inks
Mineral seal oil	Illuminating oil
Distillate fuel oils	Diesel and turbine fuels
Refined Distillates	
Cutting and grinding oils	Metal working lubricants and coolants
Heat-treating oils	Metal quenching and tempering oils
Insulating oils	Transformer and cable oils
Automotive lubricant oils	Motor oils,transmission and parts lubricants
Hydraulic oils	Transmission fluids
Industrial lubricant oils	Machine, engine, and turbine lubricants; textile oils; printing oils
Technical white oils	Industrial lubricants, rubber extenders, spraying oils
Medicinal white oils	Medicinal preparations, food ingredients
Petrolatum	Medicinal and cosmetic preparations
Petroleum waxes	Coating for paper, food containers, and foods; rubber compounding ingredients; insulants; candles
Aromatic Extracts	
Solvents and extenders	In paints, varnishes, resins, natural and synthetic rubbers, foundry core oils, putty, printing ink vehicles, bituments; as pesticide solvents, fuel oil blending agents
Heat transfer oils	Heat transfer fluids
Heavy Aromatic Oils	
Residual fuel oils	Industrial heating and power fuels
Feedstocks	Manufacture of carbon black, petroleum pitch, and petroleum coke
Heat transfer oils	Heat transfer fluids
Residues	
Asphalt	Paving, roofing, and waterproofing materials
Petroleum pitch	Binder
Petroleum coke	Metallurgical electrodes

Source: Hobson, 1973

unleaded gasolines. Phosphorus also causes adverse effects on catalytic devices and consequently the phosphorus content of unleaded gasolines is restricted. Leaded gasoline has also been regulated by U.S. Environmental Protection Agency (EPA), which has set each manufacturer's averaged quarterly lead alkyl antiknock content at 0.10 g Pb per U.S. gallon (0.026 g Pb/L) (maximum) from January 1, 1986 onward.

Unleaded gasolines are defined as those to which no lead antiknock has been added deliberately. However, a small amount of lead pick up can occur in gasoline distribution. Since July 1, 1974 the EPA has required the widespread availability of unleaded gasoline containing no more than 0.05 g Pb per U.S. gallon (0.0013 g Pb/L) and no more than 0.005 g of phosphorus per U.S. gallon (0.0013 g P/L) and these limits are also contained in Federal Specification VVG-1690-C and in American Society for Testing and Materials (ASTM) D439. Some gasolines may contain manganese in the form of Methylcyclopentadienyl Manganese Tricarbonyl (MMT) for octane improvement. The EPA banned the use of MMT for unleaded gasoline in the U.S. effective October 27, 1978, because of adverse effects on exhaust hydrocarbon emissions.

2.2.2 Specification for Automotive Gasoline

As mentioned earlier in Section 2.2.1, the classification of gasolines is based on the requirements of performance, and a summarized specification is shown in Table 2-4. This specification, being under continuous review and revision, provides for an automatic variation of the volatility and antiknock index of gasoline in accordance with seasonal climatic changes at the locality where the gasoline is used. For details, see the publication of ASTM D439.

Table 2-4 Detailed Requirements for Gasoline

Volatility Class	Distillation Temperatures, °C(°F), at Percent Evaporated[A]: 10 Vol %, max	50 Vol %: min	50 Vol %: max	90 Vol %, max	End Point, max	Distillation Residue, Vol %, max	Vapor/Liquid Ratio (V/L)[A]: Test Temperature, °C (°F)	V/L, max
A	70 (158)	77 (170)	121 (250)	190 (374)	225 (437)	2	60 (140)	20
B	65 (149)	77 (170)	118 (245)	190 (374)	225 (437)	2	56 (133)	20
C	60 (140)	77 (170)	116 (240)	185 (365)	225 (437)	2	51 (124)	20
D	55 (131)	77 (170)	113 (235)	185 (365)	225 (437)	2	47 (116)	20
E	50 (122)	77 (170)	110 (230)	185 (365)	225 (437)	2	41 (105)	20

Volatility Class	Reid Vapor Pressure, max, kPa (psi)	Lead Content, max, g/L (g/gal): Unleaded[B]	Lead Content, max, g/L (g/gal): Leaded[C]	Copper Strip Corrosion, max	Existent Gum, max, mg/100 mL	Sulfur, max, Mass %: Unleaded	Sulfur, max, Mass %: Leaded	Oxidation Stability, Minimum, Minutes	Antiknock Index
A	62 (9.0)	0.013 (0.05)	1.1 (4.2)	No. 1	5	0.10	0.15	240	D
B	69 (10.0)	0.013 (0.05)	1.1 (4.2)	No. 1	5	0.10	0.15	240	D
C	79 (11.5)	0.013 (0.05)	1.1 (4.2)	No. 1	5	0.10	0.15	240	D
D	93 (13.5)	0.013 (0.05)	1.1 (4.2)	No. 1	5	0.10	0.15	240	D
E	103 (15.0)	0.013 (0.05)	1.1 (4.2)	No. 1	5	0.10	0.15	240	D

[A] At 101.3 kPa pressure (760 mm Hg).

[B] The intentional addition of lead or phosphorus compounds is not permitted. U.S. Environmental Protection Agency (EPA) regulations limit their maximum concentrations to 0.05 g of lead per gallon and 0.005 g of phosphorus per gallon (by Test Method D 3231), respectively.

[C] EPA regulations limit the lead concentration in leaded gasoline to no more than 0.5 g/gal (0.13 g/L), averaged for quarterly production of leaded gasoline. Effective Jan. 1, 1986, the EPA will require that the lead concentration of leaded gasoline be limited to 0.1 g/gal (0.026 g/L) averaged for quarterly production of leaded gasoline.

[D] See Table 3 of ASTM D439 publication.

2.2.3 Additives Used in Gasoline

Gasoline additives are used to enhance or provide various performance features related to the satisfactory operation of engines, as well as to minimize gasoline handling and storage problems. These compounds complement refinery processing in attaining the desired level of product quality. Table 2-5 summarizes various additives and their functions into nine categories.

Table 2-5 Commercial Gasoline Additives

Category	Function	Additive Type
1. Antiknock Compounds	improve motor octane quality or number	lead alkyls such as tetraethyllead, tetramethyllead, methylcyclopentadienyl manganese tricarbony (MMT)
2. Oxidation Inhibitors	inhibit oxidation and gum formation and precipitate formation; improve storage life	aromatic amines such as phenylenediamine, and alkyl phenol compounds (phenols, cresols)
3. Metal Deactivators	inhibit oxidation and gum formation catalyzed by certain metals, e.g., copper is a powerful oxidation catalysis	chelatingagent-N,N-disalicylidene-1,2-propanediamine
4. Corrosion Inhibitors	minimize corrosion of fuel systems and storage facilities	organic acids, amine salts, and derivatives of phosphoric acid. A widely used type is based on dimerized linoleic acid.
5. Detergents (carburetor/ injector)	prevent deposits in carburetor throttle bodies and port fuel injectors	amines and amine carbonxylates, phosphoric acids having surface active properties, some of which are polymeric
6. Deposit Control or Dispersants	remove and prevent deposit throughout carburetor, intake manifold, intake ports and valves	polybutene amines, polyether amines
7. Demulsifiers	improve water separation	polyglycol derivaties
8. Anti-icing	prevent icing in carburetor and fuel system	surfactants, alcohols, and glycols
9. Dyes	identification	azo and other oil-soluble compounds

Note: some materials may also be marketed as multifunctional or multipurpose additives, performing more than one of the functions described.

Some oxygenates, such as tert-butyl alcohol (TBA), ethyl tert-butyl ether (ETBE), methyl tert-butyl ether (MTBE), and other alcohols and ethers receiving attention as possible replacements for organometallic antiknock compounds are not additives, but rather blending agents.

The additives are not blended into gasoline all at once. At the refinery, the first additives to be blended are oxidation inhibitors, then metal deactivators and antiknock compounds. Dyes may also be added in the refinery blending operation. By law, leaded gasoline must contain dye to indicate the presence of lead alkyl compounds. Most refiners inject dye in at least one of the unleaded gasolines for grade indentification. Nearly

60% of all U.S. gasoline is shipped to the market by pipeline where it may receive another dose of corrosion inhibitors. All gasolines of a given grade which reach the distributing wholesaler or terminal have pretty much the same additive treatments. Detergent or deposit control additive is often added in at the time of loading into tank trucks for retailers.

2.2.4 Chemical Composition of Gasoline

There is not a single, general acceptable method for the determination of the entire chemical composition of gasoline at this time. But by far the most widely used method to determine the detailed hydrocarbon composition of gasoline is gas chromatography. The composition of gasolines also varies widely and depends on the sources of the crude oil and the refining processes. In addition to additives, 150 to 200 individual hydrocarbons have been identified, but this does not mean only that many compounds are contained in gasoline. In fact, one report indicated that there are 378 peaks (equivalent to 378 compounds or more) in the chromatogram of a gasoline sample obtained in that study. Figure 2-3 shows a chromatogram of a typical premium grade gasoline, and Table 2-6 in the appendix of this section is hydrocarbon identification of chromatographic peaks shown in Figure 2-3. Also in the appendix, Table 2-7 and Table 2-8 show two separate reports of hydrocarbon compositions in gasoline. This information may only reflect the result of the studied samples, whether or not they can represent all gasolines in the entire U.S. market is not known.

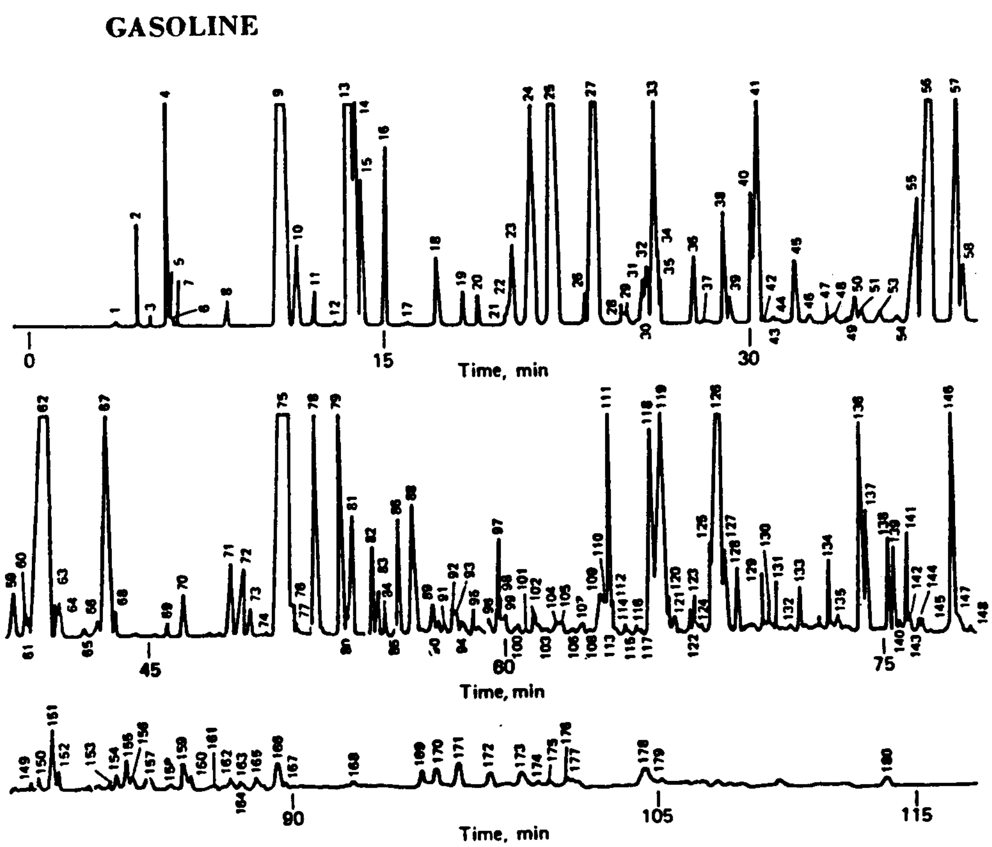


Figure 2-3 Chromatogram of a typical premium grade gasoline

<u>Hazardous Substances in Gasoline</u>--Of the identified compounds in gasoline there are thirteen chemicals (nine

Table 2-9 Physical and Chemical Properties of Toxic Gasoline Components

	Mass		Prevalence	Fate and Transport			Toxicity	
Compound	% Volume in Gasoline	% Weight[1] in Gasoline	% of Gasolines Containing Chemical	Water Solubility at 20°C (mg/L)	Vapor Pressure (torr)[2]	Degree of Biodegrad-ability	Final RQ (kg)[3]	Confidence in Data[4]
Benzene	1-2	0.81	> 99	1,780	75.0	Some	4.54	+
Toluene	4.0	12.02	> 99	515	22.0	Some	454.00	+
Xylene-M	5-8	3.83	> 99	175	5.0	Some	454.00	+
Xylene-O	5-8	1.93	> 99	162	6.0	Some	454.00	+
Xylene-P	5-8	1.58	> 99	198	6.5	Some	454.00	+
Ethylbenzene	2-5	1.70	> 99	152	7.0	Some	454.00	+
Naphthalene	0.7	0.10	> 90	31.1	1.0	Readily	45.40	+
Phenol	-	-	> 90	66,667	0.5	Readily	454.00	+
EDB	0.01	0.024	< 40	4,310	11.0	Some	4.54	0
EDC	0.01	< 0.024	< 40	8,690	61.0	Some	45.40	0
Tetraethyl Lead	-	-	< 40	0.08	0.2	Some	4.54	0
Dimethylamine	-	-	-	1×10^6	1,345.0	Readily	454.00	–
Cyclohexane	< 0.7	0.17	-	66.5	77.0	Some	454.00	–

[1] Source: Maynard and Sanders, 1969.
[2] At 20°C.
[3] The lower the RQ value, the more toxic the chemical is in pure product form.
[4] + = highly confident; 0 = somewhat confident; – = not confident.

hydrocarbons and four additives) which are regulated as hazardous substances under the Comprehensive Emergency Response, Compensation and Liability Act (CERCLA). These chemicals along with their physical and chemical properties are shown in Table 2-9.

2.3 KEROSENE

Kerosene is the distillate between gasoline and fuel oil fractions, also known as astral oil, coal oil and stove oil. Other common synonyms used are illuminating oil, kerosine, range oil, fuel oil No. 1, jet fuel JP-1. The distillate is further processed by hydrogen treatment and/or other chemicals to make commercial kerosene for different purposes. Kerosene appears as mobile, watery liquid in colorless to light brown.

The uses of kerosene are burner fuel, lamp fuel, solvent as degreasers and cleaner, gas turbine fuel (jet fuel), diesel fuel. The aviation fuels, Jet A, JP-5, GP-8, Thermally Stable (TS) jet fuel all are kerosene type fuel. By kerosene type fuel, it means the fuel has kerosene as its principal component.

2.3.1 Specification for Kerosene

The ASTM standard specification for kerosene (D3699-87) is based on the chemical and physical requirements listed in Table 2-10.

Table 2-10 Chemical and Physical Requirements for Kerosene

Property	ASTM Test Method[A]	Limit
Appearance:		
Color	D 156	+16 min
Composition:		
Mercaptan sulfur, ppm	D 1323	30 max[B]
Sulfur, wt %:	D 1266, D 2622	
No. 1-K		0.04 max
No. 2-K		0.30 max
Volatility:		
Distillation, °C(°F)	D 86	
10% recovered		205 (401) max
Final boiling point		300 (572) max
Flash point, °C(°F)	D 56, D 3243	38 (100) min
Fluidity:		
Freezing point, °C(°F)	D 2386	-30(-22) max
Viscosity at 40°C(104°F), cSt[C]	D 445	1.0 min/1.9 max
Combustion:		
Burning quality	D 187	pass (see 4.2)
Corrosion:		
Corrosion, 3 h at 100°C(212°F)	D 130	No. 3 max

A: The test methods indicated in this table are fully referenced in 2.1 of ASTM D3699. Where multiple test methods are shown, the first method listed is designated as the standard method for use in referee decisions.

B: The mercaptan sulfur determination may be waived if the fuel is considered sweet by the Doctor test described in 4.2.6 of Specification D 484.

C: 1 cST = 1 mm^2/s.

2.3.2 Properties and Hydrocarbon Contents of Kerosene

Some properties of kerosene were summarized in Table 2-11. The hydrocarbon composition of kerosene varies widely and as much as gasoline, and also depends on the sources of crude oil and their processing. Table 2-12 gives an idea of hydrocarbon contents in kerosene by broad category, and Table 2-13 indicates the aromatic hydrocarbons and polynuclear aromatic hydrocarbons in kerosene.

Table 2-11 Properties of Kerosene
(NIOSH, 1977; Mckeon and Stewart, 1982)

Properties	Value
Predominant molecular species	C_{10} - C_{16}
Boiling point range	300 - 550° F (175 - 325°C)
Kerosene - Deodorized	208 - 272°C
Molecular weight	170 - 180
Heating value	130,000 BTU/gal.
Flashing point	110 - 165°F
Ignition temperature	410 - 490°F
Sulfur content	0.04 - 0.3 %
Density	814.8 g/l
Specific Gravity (20/4°C)	0.8
Appearance	Water-white to straw(pale yellow)
Odor	Odorless to aromatic
Odor Threshold[a]	0.09 ppm (0.0006 mg/l) in air
Vapor pressure (mm Hg)	unknown
Vapor Density (air = 1)	4.5
Solubility	Insoluble in water; miscible with other petroleum solvents
Volatility[b]	More volatile than fuel oils; less volatile than gasoline

a: Carpenter et al., 1976 (also see BTSA, 1988d)
b: Gosselin et al., 1984

Table 2-12 Hydrocarbon Contents of Kerosene

Components	Deodorized (Carpenter et ai.,1976)	Non-deodorized (NIOSH, 1977)
	Percentage Weight	
Paraffins	55.2	37
n-paraffins	–	25
branched paraffins	–	12
Naphthenes	40.9	43
Monocycloparaffins	32.4	30
Dicycloparaffins	7.6	12
Tricycloparaffins	0.9	1
Alkylbenzenes	3.1	21
Monoaromatic	–	16
Diaromatic	–	5
Indan and Tetralins	0.8	–

–, not known

Table 2-13 Aromatic Hydrocarbons in Kerosene (Leseman, 1986)

Components	% Weight
Benzene	<0.2
Toluene	0.23 - 0.44
Ethylbenzene	0.36 - 0.38
Xylenes	0.62 - 1.3
n-propylbenzene	0.25 - 0.35
1, 3, 5-Trimethylbenzene	0.51 - 1.0
Naphthalene	0.3 - 0.6

Table 2-13 Polynuclear Aromatic Hydrocarbons in Kerosene (continued)
(Norris and Hill, 1974; Leseman, 1986)

Components	% Weight
Anthracene	0.4×10^{-5} - < 0.1×10^{-3}
Phenanthrene	0.2×10^{-1} - 0.3×10^{-1}
Methylanthracene	< 0.1×10^{-5}
Benz(a)anthracene	< 0.1×10^{-5}
Pyrene	< 0.16×10^{-4}
Fluorene	0.6×10^{-2} - 0.3×10^{-1}
Fluoranthene	0.9×10^{-5}
Chrysene	ND
Triphenylene	ND
Benzo(a)pyrene	< 0.1×10^{-5}
Benzo(e)pyrene	< 0.1×10^{-5}
Benzo(g, h, i)pyrene	< 0.1×10^{-5}

ND--Not detected.

2.4 DIESEL FUEL (DIESEL OIL)

Diesel fuels used in automobiles and railroad engines are commonly referred to as middle distillates, which have a boiling range of 325 to 700°F (163-371°C). Middle distillates represent products which have a higher boiling range than gasoline and are obtained from fractional distillation of crude oil or from streams from other refining processes. The makeup of finished diesel fuels is dependent on the requirements of engine design and type of service, and consists of various combinations of volatility, ignition quality, viscosity, sulfur level, gravity, and other characteristics. Additives may be used to impart special properties to the finished diesel fuel. Synonyms for diesel fuel are sometimes Fuel oil No. 2 or home heating oil.

2.4.1 Specifications for Diesel Fuel

To facilitate choice of an economical fuel that meets a given engine requirement, the ASTM has established three grades of classification to reflect their suitability for engine type and operating conditions. For ASTM specification (D975), see Table 2-14. Grade No. 1-D includes volatile fuel oils from kerosene to the intermediate distillates, which are recommended for high speed engines with frequent and fairly wide variations in load and speed. Grade No. 2-D contains distillate gas oil of lower volatility. This grade is suitable for use in high speed engines not subject to wide variations in load and speed. Grade No. 4-D consists of more viscous distillates and their blends with residual fuel oils, and is used for low and medium speed engines.

Table 2-14 **Detailed Requirements for Diesel Fuel Oils**[A,H]

Grade of Diesel Fuel Oil	Flash Point, °C (°F)	Cloud Point °C	Water and Sediment, vol %	Carbon Residue on, 10 % Residuum, %	Ash, weight %	Distillation Temperatures, °C (°F) 90 % Point		Viscosity Kinematic, cSt[G] at 40°C		Viscosity Saybolt, SUS at 100°F		Sulfur,[D] weight %	Copper Strip Corrosion	Cetane Number[E]
	Min	Max	Max	Max	Max	Min	Max	Min	Max	Min	Max	Max	Max	Min
No. 1-D A volatile distillate fuel oil for engines in service requiring frequent speed and load changes	38 (100)	[B]	0.05	0.15	0.01	...	288 (550)	1.3	2.4	...	34.4	0.50	No. 3	40[F]
No. 2-D A distillate fuel oil of lower volatility for engines in industrial and heavy mobile service.	52 (125)	[B]	0.05	0.35	0.01	282[C] (540)	338 (640)	1.9	4.1	32.6	40.1	0.50	No. 3	40[F]
No. 4-D A fuel oil for low and medium speed engines.	55 (130)	[B]	0.50	...	0.10	...	...	5.5	24.0	45.0	125.0	2.0	...	30[F]

[A] To meet special operating conditions, modifications of individual limiting requirements may be agreed upon between purchaser, seller, and manufacturer.

[B] It is unrealistic to specify low-temperature properties that will ensure satisfactory operation on a broad basis. Satisfactory operation should be achieved in most cases if the cloud point (or wax appearance point) is specified at 6°C above the tenth percentile minimum ambient temperature for the area in which the fuel will be used. The tenth percentile minimum ambient temperatures for the United States are shown in Appendix X2. This guidance is of a general nature; some equipment designs, use flow improver additives, fuel properties, or operations, or a combination thereof, may allow higher or require lower cloud point fuels. Appropriate low temperature operability properties should be agreed upon between the fuel supplier and purchaser for the intended use and expected ambient temperatures.

[C] When cloud point less than −12°C (10°F) is specified, the minimum viscosity shall be 1.7 cSt (or mm^2/s) and the 90 % point shall be waived.

[D] In countries outside the United States, other sulfur limits may apply.

[E] Where cetane number by Method D 613 is not available, Method D 976 may be used as an approximation. Where there is disagreement, Method D 613 shall be the referee method.

[F] Low-atmospheric temperatures as well as engine operation at high altitudes may require use of fuels with higher cetane ratings.

[G] 1 cSt = 1 mm^2/s.

[H] The values stated in SI units are to be regarded as the standard. The values in inch-pound units are for information only.

2.4.2 Additives Used in Diesel Fuels

Very much like gasoline, commercial diesel fuels may also contain a variety of additives to enhance or impart certain desirable properties. Those which may be found in diesel fuels are shown in Table 2-15.

Table 2-15 Commercial Diesel Fuel Additives - Function and Type

Class or Function	Common Additive Type
1. **Ignition Quality Improvers** - Raise Cetone Number thereby promoting faster starts and less white smoke.	Alkyl nitrates
2. **Oxidation Inhibitors** - Minimize oxidation and gum and precipitate formation, improve storage life.	Alkyl amines and amine containing complex materials.
3. **Biocides** - Inhibit the growth of bacteria and fungi which feed on hydrocarbons, help prevent filter clogging caused by these organisms.	Boron compounds, ethers of ethylene glycol, quaternary amine compounds.
4. **Rust Preventives** - Minimize rust formation in fuel systems and storage facilities.	Organic acids and amine salts. A widely used type is based on dimerized linoleic acid.
5. **Metal Deactivator** - Deactivates copper ions which are powerful oxidation catalysts.	N, N'-disalicylidene - 1,2-propane diamine.
6. **Pour Point Depressants** - Reduce the pour point and improve low-temperature fluidity properties by modifying the wax crystal growth, structure, and/or agglomeration.	Generally consist of polymeric materials such as polyolefins, polyacrylates, polymethacrylates, modified polystyrenes, ethylene-vinyl acetate copolymers, and ethylene-vinyl chloride copolymers.
7. **Demulsifiers and Dehazers** - Improve the separation of water from distillate fuels and prevent haze.	Surface active materials which increase the rate of water/oil separation. Usually quite complex mixtures.
8. **Smoke Suppressants** - Minimize exhaust smoke by catalyzing more complete combustion of carbonaceous materials or by helping to maintain fuel spray patterns.	Catalyst types are generally over-based barium compounds. Maintenance of spray patterns is helped by detergents.
9. **Detergent Dispersants** - Promote engine fuel system cleanliness, help prevent nozzle deposit formation and injector sticking, interfere with precipitate agglomeration, thus maintaining optimum filtration characteristics.	These are usually surface-active agents. They are often polymeric materials containing amines and other functional groups.
10. **Conductivity Improvers** - Improve dissipation of electrostatic charge.	Amine salts, metallic salts, and polymeric compounds.
11. **Dyes** - Various identification purposes including tax status.	Oil-soluble solid and liquid dyes.
12. **De-icers** - Reduce the freezing point of small amounts of water to prevent fuel line plugging.	Low molecular weight alcohols (ethanol, isopropanol, and/or methanol), and ethylene glycol monomethyl ether or di-ethylene glycol monomethyl ether.

Note: Some materials may also be marketed as multifunctional or multipurpose additives, performing more than one of the functions.

2.4.3 Properties and Composition of Diesel Fuel

Some general properties of diesel fuel are listed along with those of Fuel Oil No. 2 and Fuel Oil No. 6 in Table 2-14 and Table 2-16. The categoric composition and some characteristic components of diesel fuel are shown in Table 2-16, Table 2-17, and Table 2-19. Table 2-17 and Table 2-19 come from two different reports.

2.5 FUEL OIL

As there are many types of burners used in many different operations, from open hearths to small hot water heaters, there must be different grades of fuel oil to meet their needs. In order to keep the various grades on a uniform basis, the National Bureau of Standards and the American Society for Testing Materials have standardized five grades of fuel oils designated as No. 1,2,4,5, and 6. They are further explained below.

2.5.1 Specifications for Fuel Oil

The ASTM specifications (D396) for fuel oils are shown in Table 2-18. Fuel oil No. 1 is used almost exclusively for domestic heating, and as a solvent sometimes. The synonyms used with Fuel oil No. 1 are Jet fuel GP-1, kerosene, range oil, coal oil, etc. The fuel oil used in industries are grade No. 2,4,5, and 6. Fuel oil No. 2 is also called a gas oil or distillate oil, as it is capable of being distilled or vaporized at normal temperatures and pressures. Other synonyms for Fuel oil No. 2 are home heating oil, and diesel oil. Its common uses are

Table 2-16 General Properties and Composition of Diesel Fuel, Fuel Oil No. 2, and Fuel Oil No. 6 (Vandaveer, 1965; EPA, 1980; Conaway et al., 1983)

Properties, Components	Diesel Fuel	Fuel Oil No. 2	Fuel Oil No. 6
Properties:			
Boiling range	200 - 380°C (390 - 720°F)	177 - 343°C (360 - 650°F)	315 - 510°C (600 - 950°F)
Flashing point	52 - 96°C (120 - 203°F)	40 - 75°C (100 - 170°F)	>65°C (>150°F)
Ignition temp.	257°C	–	–
Relative Density	–	0.85 (15/4°C)	–
Gravity, °API	35 - 42	32 - 35	6 - 14
Viscosity, °F	34 -36[a]	34 - 36[a]	50 -300[b]
Vapor pressure	–	0.4 mm Hg (20°C)	–
Average MBtu/gal.	101 - 102	91	74
Distillation, °F			
10 %	390 -440°F	420 - 440°F	600 - 700°F
50 %	440 -510°F	490 - 530°F	850 - 950°F
90 %	490 - 600°F	580 - 620°F	–
Endpoint	510 - 660°F	630 - 660°F	–
Sulfur, wt%	<0.1 - 0.6	0.1 - 0.6	1 - 4
Components:			
C to H ratio	6.1 - 6.5	6.6 - 7.1	7.7 - 9.0
Carbon Type	C_{11} plus	C_9 plus	–
Paraffins[c], %	23 - 59	37 - 43	–
Naphthenes[c], %	50 - 53	26 - 32	–
Aromatics[c], %	24 - 35	30 - 32	–

a: Saybolt University Seconds at 100°F; b: Saybolt Furol Seconds at 122°F;
c: Approximate concentration; –: Not available

Table 2-17 Aromatic Components of Fuel Oils

Aromatic Hydrocarbons	Diesel Fuel (Norris & Hill, 1974) ppm	Fuel Oil No. 2 (Norris & Hill, 1974) ppm[a]	Fuel Oil No. 2 (Leseman, 1986) % wt[b]
Anthracene	2.9	1 - 4.2	0.013 - 0.017
Phenanthrene	ND	ND	0.02 - 0.3
Methylanthracene	9.3	6.6 - 20.7	–
Benz(a)anthracene	0.13	0.02 - 0.06	–
Pyrene	0.37	0 - 3.0	–
Fluorene	–	–	0.07 - 0.1
Fluoranthene	0.57	0 - 3.6	–
Chrysene	0.45	0.37 - 0.81	–
Triphenylene	3.3	0 - 1.2	–
Benzo(a)pyrene	0.07	0.01 - 0.05	–
Benzo(e)pyrene	0.18	0.01 - 0.02	–
Benzo(g, h, i)pyrene	0.03	0.01 - 0.07	–
Benzene	–	–	<0.2
Toluene	–	–	<0.2
Ethylbenzene	–	–	<0.2
Xylene	–	–	<0.2
n-Propylbenzene	–	–	<0.2
Trimethylbenzene	–	–	<0.2
Naphthalene	–	–	0.14 - 0.17

a: The range of values are from 4 different samples; b: The range of values are from 3 different samples;
ND: Not detected; –: Not available.

Table 2-18 Detailed Requirements for Fuel Oils[A]

Grade Description	No. 1	No. 2	No. 4 (Light)	No. 4	No. 5 (Light)	No. 5 (Heavy)	No. 6
	A distillate oil intended for vaporizing pot-type burners and other burners requiring this grade of fuel	A distillate oil for general purpose heating for use in burners not requiring No. 1 fuel oil	Preheating not usually required for handling or burning	Preheating not usually required for handling or burning	Preheating may be required depending on climate and equipment	Preheating may be required for burning and, in cold climates may be required for handling	Preheating required for handling and burning
Specific gravity, 60/60°F (deg API), max	0.8499 (35 min)	0.8762 (30 min)		...	...	...	...
Min	...	...	0.8762[G] (30 max)	...	...	...	...
Flash point, °C (°F) min	38 (100)	38 (100)	38 (100)	55 (130)	55 (130)	55 (130)	60 (140)
Pour point, °C, (°F) max	−18[C] (0)	−6[C] (20)	−6[C] (20)	−6[C] (20)	...	...	[H]
Kinematic viscosity, mm^2/s (cSt)[D]							
At 38°C (100°F) min	1.4	2.0[C]	2.0	5.8	>26.4	>65	...
max	2.2	3.6	5.8	26.4[F]	65[F]	194[F]	...
At 40°C (104°F) min	1.3	1.9[C]	...	5.5	>24.0	>58	...
max	2.1	3.4	...	24.0[F]	58[F]	168[F]	...
At 50°C (122°F) min	...	...	...	...	...	(42)	>92
max	...	...	...	...	...	(81)	638[F]
Saybolt Viscosity:[D]							
Universal at 38°C (100°F), min	...	(32.6)	(32.6)	(45)	(>125)	(>300)	(>900)
max	...	(37.9)	(45)	(125)	(300)	(900)	(9000)
Furol at 50°C (122°F) min	...	...	...	...	...	(23)	(>45)
max	...	...	...	...	...	(40)	(300)
Distillation Temperature, °C (°F)							
10 % Point max	215 (420)	...	...	...	...	...	...
90 % Point min	...	282[C] (540)	...	...	...	...	...
max	288 (550)	338 (640)	...	...	...	...	...
Sulfur content, % mass, max	0.5	0.5[B]	...	...	...	...	...
Corrosion copper strip, max	3	3	...	...	...	...	...
Ash, % mass, max	...	...	0.05	0.10	0.15	0.15	...
Carbon residue, 10 % b; % m, max	0.15	0.35	...	...	...	...	...
Water and sediment, % vol, max	0.05	0.05	(0.50)[E]	(0.50)[E]	(1.00)[E]	(1.00)[E]	(2.00)[E]

[A] It is the intent of these classifications that failure to meet any requirement of a given grade does not automatically place an oil in the next lower grade unless in fact it meets all requirements of the lower grade.

[B] In countries outside the United States other sulfur limits may apply.

[C] Lower or higher pour points may be specified whenever required by conditions of storage or use. When pour point less than −18°C (0°F) is specified, the minimum viscosity for grade No. 2 shall be 1.7 cSt (31.5 SUS) and the minimum 90 % point shall be waived.

[D] Viscosity values in parentheses are for information only and not necessarily limiting.

[E] The amount of water by distillation plus the sediment by extraction shall not exceed the value shown in the table. For Grade No. 6 fuel oil, the amount of sediment by extraction shall not exceed 0.50 weight %, and a deduction in quantity shall be made for all water and sediment in excess of 1.0 weight %.

[F] Where low sulfur fuel oil is required, fuel oil falling in the viscosity range of a lower numbered grade down to and including No. 4 may be supplied by agreement between purchaser and supplier. The viscosity range of the initial shipment shall be identified and advance notice shall be required when changing from one viscosity range to another. This notice shall be in sufficient time to permit the user to make the necessary adjustments.

[G] This limit guarantees a minimum heating value and also prevents misrepresentation and misapplication of this product as Grade No. 2.

[H] Where low sulfur fuel oil is required, Grade 6 fuel oil will be classified as low pour + 15°C (60°F) max or high pour (no max). Low pour fuel oil should be used unless all tanks and lines are heated.

Table 2-19 **Characteristic Componenets** of five petroleum fuels

Component	Regular Gasoline (Six Samples) % by weight	Unleaded Gasoline (Three Samples) % by weight	Aviation Gasoline (one Sample) % by weight	Kerosene (Three Samples) % by weight	Diesel No. 2 (Three Samples) % by weight
Benzene	0.47-3.6	<0.2-3.2	<0.2	<0.2	<0.2
Toluene	3.4-10	4.4-12	17	0.23-0.44	<0.2
Ethylbenzene	1.5-3.1	1.8-4.7	0.77	0.36-0.38	<0.2
Xylenes	5.4-11	7.4-16	1.6	0.62-1.3	<0.2
n-Propylbenzene	0.64-1.0	0.87-1.0	<0.2	0.25-0.35	<0.2
1,3,5-Trimethylbenzene	1.1-1.6	1.3-3.9	<0.2	0.51-1.0	<0.2
Naphthalene	0.1-0.6	0.2-0.5	0.006	0.3-0.6	0.14-0.17
Fluorene	<0.0003-0.02	<0.0003-0.007	0.0005	0.006-0.03	0.07-0.10
Phenanthrene	<0.0003-0.06	<0.0003-0.004	0.0004	0.02-0.03	0.26-0.30
Anthracene	<0.0001	<0.0001-0.0006	0.00002	<0.0001	0.013-0.017
Ethylenedibromide	0.015-0.02		0.054		
Lead	0.03-0.43		0.056		

Table 2-20 **Compositional Information** on a Bunker C fuel oil
(weight percent except where noted; Neff and Anderson 1981)

Sulfur	1.46
Nitrogen	0.94
Nickel	89 (ppm)
Vanadium	73 (ppm)
Saturates	21.1
Aromatics	34.2
Polars	30.3
Insolubles	14.4

Concentrations of C_{12} - C_{24} n-paraffins and aromatic hydrocarbons in a Bunker C fuel oil[a] (Neff and Anderson, 1981)

Compound	Concentration(mg/kg)
Total C_{12} -C_{24} n-paraffins	12,600
Benzene[b]	60,000
Naphthalene	1,000
1-Methylnaphthalene	2,800
2-Methylnaphthalene	4,700
Dimethylnaphthalenes	12,300
Trimethylnaphthalenes	8,800
Biphenyls[c]	<100
Fluorenes[c]	2,400
Phenanthrene	482
1-Methylphenanthrene	43
2-Methylphenanthrene	828
Fluoranthene	240
Pyrene	23
Benzo(a)anthracene	90
Chrysene	196
Triphenylene	31
Benzo(a)pyrene	44
Benzo(e)pyrene	10
Perylene	22
Total hydrocarbons analyzed	106,609

a: Only 10 % of the fuel is characterized.
b: Includes benzene, alkylbenzenes, tetralins, and dinaphthenobenzenes.
c: Includes the parent compounds and their alkyl homologs.

as a general purpose domestic and commercial fuel oil.

Some references are still made to industrial No. 2 and domestic No. 2 fuel oil. Sometimes there is a difference but many times these oils are the same. Domestic No. 2 distillates are usually lighter, while industrial No. 2 is heavier oil. Industrial burners can use both types satisfactorily, but domestic burners as a general rule, cannot.

Fuel oil No. 4 is a blended oil, usually of grade Nos. 2, 5, and 6. Synonyms of Fuel oil No. 4 are Residual fuel No. 4 and cat cracker feedstock. Its common uses are commercial and industrial burner fuel. No. 5 and No. 6 fuel oils are the heavy black residuals. Synonyms of No. 5 fuel oil are Residual fuel No. 5, NSFO, navy special fuel oil. Common uses of No. 5 fuel oil are fuel for power plants, ships, locomotives, and metallurgical operations. Another name for grade No. 6 fuel oil is "Bunker C" oil.

According to the standardized specifications for fuel oils, there is no grade No. 3. The No. 3 fuel oil was deleted and grade No. 2 substituted in these specifications in 1948. Due to habit and custom, some people still use No. 3, but to avoid confusion and misunderstanding, No. 2 and No. 3 can be accepted as meaning the same grade of oil.

2.5.2 <u>Properties and Composition of Fuel Oil</u>

The general properties of Fuel oil No. 2 and No. 6 are shown in Table 2-16, and Table 2-18 for all the fuel oils. Like gasoline or other oils, the composition of fuel oils varies widely; they are different as a result of their crude oil origins and processing procedures. Characteristic components in grade No. 2 and No. 6 fuel oil can be found in Table 2-16, Table 2-17, and Table 2-20.

2.6 GAS TURBINE FUEL OIL

The various grades of gas turbine fuel oil have to meet the limiting requirements shown in Table 2-21. As noted in the supplementary footnotes to Table 2-21, the requirements for Grade Nos. 1-GT and 2-GT conform

Table 2-21 Detailed Requirements for Gas Turbine Fuel Oils at Time and Place of Custody Transfer to User[F]

Designation[A]	Grade of Gas Turbine Fuel Oil	Flash Point, °C (°F)[B]	Pour Point, °C (°F)[B]	Water and Sediment, vol %	Carbon Residue on 10 % Residuum, wt %	Ash, wt %	Distillation Temperature, 90 % Point[B] °C (°F)		Kinematic Viscosity, cSt[C] at 40°C (104°F)		Kinematic Viscosity, cSt[C] at 50°C (122°F)	Saybolt Viscosity, S[B] Universal at 38°C (100°F)		Saybolt Viscosity, S[B] Furol at 50°C (122°F)	Specific Gravity 60/60°F (°API)[B]
		min	max	max	max	max	min	max	min	max	max	min	max	max	max
No. 0-GT	A naphtha or other low-flash hydrocarbon liquid.	[D]	...	0.05	0.15	0.01	...	...	[D]	...	...	...	...	...	...
No. 1-GT	A distillate for gas turbines requiring a fuel that burns cleaner than No. 2-GT.	38 (100)	−18[E] (0)	0.05	0.15	0.01	...	288 (550)	1.3	2.4	...	...	(34.4)	...	0.850 (35 min)
No. 2-GT	A distillate fuel of low ash suitable for gas turbines not requiring No. 1-GT.	38 (100)	−6[E] (20)	0.05	0.35	0.01	282 (540)	338 (640)	1.9	4.1	...	(32.6)	(40.2)	...	0.876 (30 min)
No. 3-GT	A low-ash fuel that may contain residual components.	55 (130)	...	1.0	...	0.03	...	...	5.5	...	638	(45)	...	(300)	...
No. 4-GT	A fuel containing residual components and having higher vanadium content than No. 3-GT.	66 (150)	...	1.0	...	...	...	...	5.5	...	638	(45)	...	(300)	...

[A] No. 0-GT includes naphtha, Jet B fuel, and other volatile hydrocarbon liquids. No. 1-GT corresponds in general to Specification D 396 Grade No. 1 fuel and Classification D 975 Grade No. 1-D diesel fuel in physical properties. No. 2-GT corresponds in general to Specification D 396 Grade No. 2 fuel and Classification D 975 Grade No. 2-D diesel fuel in physical properties. No. 3-GT and No. 4-GT viscosity range brackets Specification D 396 Grade No. 4, No. 5 (light), No. 5 (heavy), and No. 6 and Classification D 975 Grade No. 4-D diesel fuel in physical properties.

[B] Values in parentheses are for information only and may be approximate.

[C] 1 cSt = 1 mm^2/s.

[D] When flash point is below 38°C, or when kinematic viscosity is below 7.3 cSt at 40°C, or when both conditions exist, the turbine manufacturer should be consulted with respect to safe handling and fuel system design.

[E] For cold weather operation, the pour point should be specified 6°C below the ambient temperature at which the turbine is to be operated except where fuel heating facilities are provided. When a pour point less than −18°C is specified for Grade No. 2-GT, the minimum viscosity shall be 1.7 cSt, and the minimum 90 % point shall be waived.

[F] Gas turbines with waste heat recovery equipment may require sulfur limits in the fuel to prevent cold-end corrosion (see Appendix X2.4.1.11).

in most respects to corresponding Grade Nos. 1 and 2 fuels in Specification D396 (for Fuel oils), and to Grade Nos. 1-D and 2-D in Specification D975 (for Diesel fuel oils). The viscosity ranges of Grade Nos. 3-GT and 4-GT fuel cover the Grade Nos. 4,5, and 6 of fuel oil and Grade No. 4-D of diesel fuel. Fuels meeting the requirements of Fuel oils and Diesel fuels may also be supplied as gas turbine fuels if they meet the requirements of gas turbine fuel oil.

2.7 CHROMATOGRAMS OF VARIOUS FUELS

The chromatograms shown here only give a good idea about what the chromatograms for various fuels look like, and are not the standards. The pattern or profile (retention time and appearance of humps) of a chromatogram will be affected by the equipment used, equipment operating condition, and sample handling in addition to whatever components are in the sample.

Figure 2-4 shows chromatograms of gasoline, kerosene, diesel fuel, and fuel oil No. 2 from a column of 60 meters DB-1 (J+W) fused silica capillary and the programmed temperature of 0°C to 60°C at 4°C/min. to 250°C at 8°C/min. The difference of the chromatograms for the bottom three is not so much as the chromatograms of No. 2 fuel oil and kerosene are shown lying within the scope of that of diesel oil. Gasoline can be easily differentiated from the other three.

Figure 2-5 indicates chromatograms of kerosene and of fuel oils No. 2, 4, and 6. Differentiation of kerosene from the fuel oils and of fuel oil No. 6 from Nos. 4 and 2 is simple. Differentiation of fuel oil No. 2 from No. 4 is more difficult, particularly after the mixture has been spilled in natural waters. No. 2 has almost as much higher-boiling materials as No. 4 does, but No. 4 contains a small proportion of components with very long retention times.

Figure 2-6 displays chromatograms of three No. 2 fuel oil samples from different sources and Figure 2-8 presents chromatograms of three lubricating oils, No. 10, No. 20, and No. 30. Figure 2-7 exhibits chromatograms of transmission fluid and diesel oil.

Most of the positions of the humps in the chromatograms appear clustered in most of the cases. To overcome such problems, a gas chromatography can be computerized and programmed to choose any section of interest and to further display that section in better detail as shown in Figure 2-9.

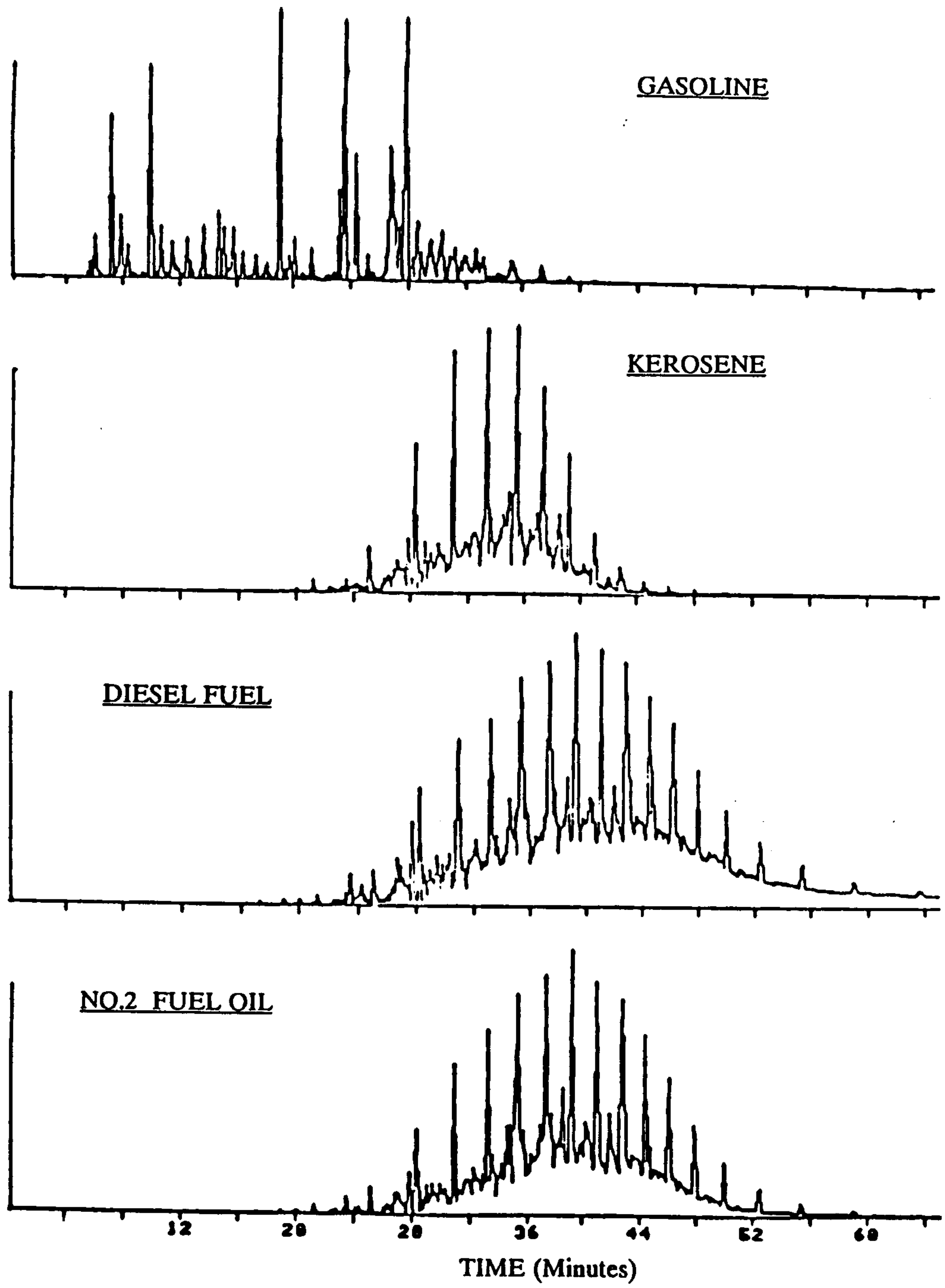
2.8 FATE OF THE SPILLED PETROLEUM PRODUCTS

When a petroleum product (hydrocarbons) is spilled into the environment, its components are then subjected not only to the physical process of diffusion, advection, volatilization, adsorption, and dissolution, but also to chemical processes. These processes are affected by the environment the spilled product is exposed to and the material the spilled substance comes in contact with. For those parameters of environmental media, see Section 1.0. The physical and chemical processes will be reviewed below.

2.8.1 <u>Adsorption</u>

As the petroleum moves downward and makes contact with soil, adsorption occurs through various mechanics, such as van der Waals forces, hydrophobic bonding, hydrogen bonding, ion exchange,...etc. The extent to which the petroleum adsorbs or is adsorbed to a specific soil or rock particles depend on the sorption potential of the chemicals; the organic carbon content of the particles; the texture, structure, and bulk density

Figure 2-4



Gas chromatograms (GC/MS) of four petroleum products. The column was a 60 m. DB - 1 (J + W) fused silica capillary. Temperature program is: 0° C to 60° C at 4° C/min. to 250° C at 8° C/min..

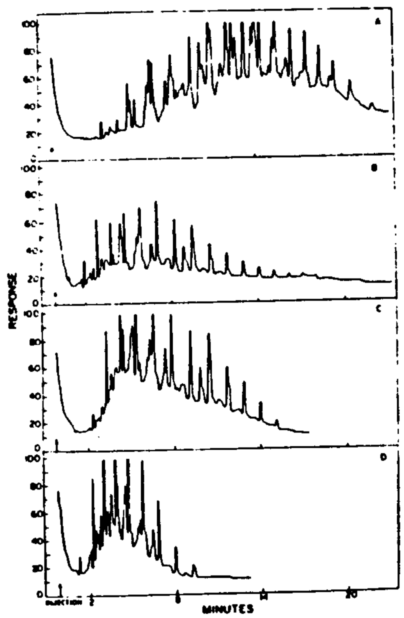


Figure 2-5 Chromatograms of fuel oils: A, No.6; B, No. 4; C, No. 2; and D, kerosine.

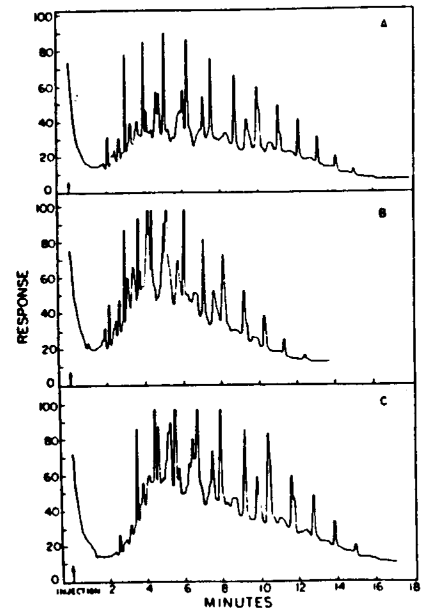


Figure 2-6 Chromatograms of three samples of fuel oil No. 2 from different manufacturers.

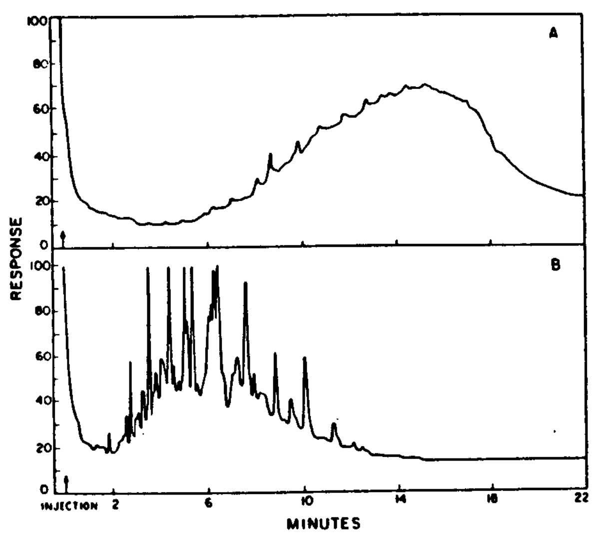


Figure 2-7 Chromatograms of transmission fluid, A, and diesel oil, B.

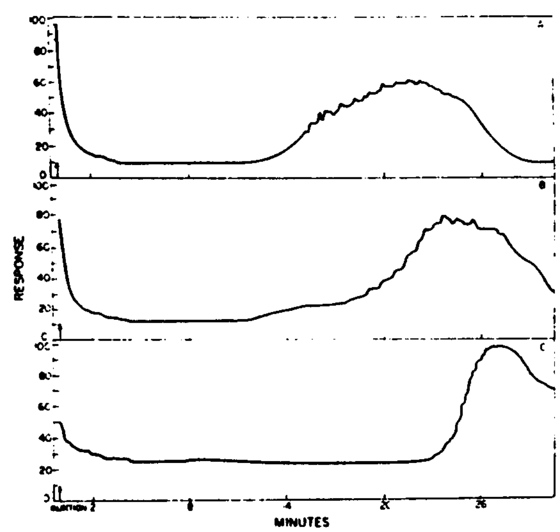
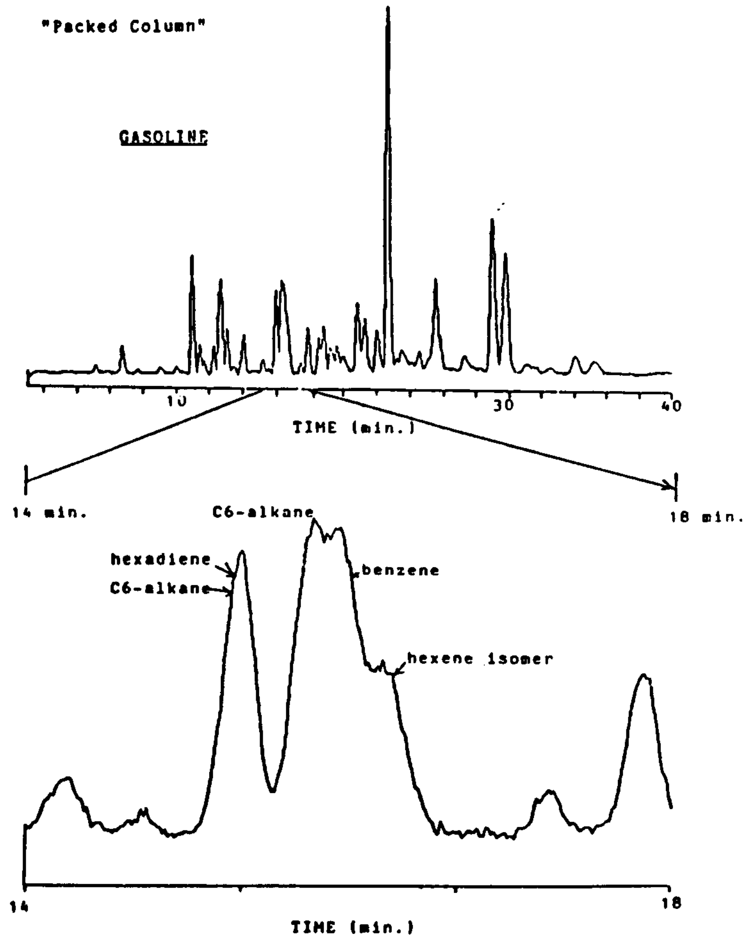


Figure 2-8 Chromatograms of lubricating oils: A, No. 10; B, No. 20; C, No. 30.

Figure 2-9 Total ion current chromatogram - method 8240 conditions



of the particles; clay and moisture content; cation ion exchange capacity; and pH. Table 2-22 lists adsorption

Table 2-22 Adsorption Coefficients for Gasoline Compounds

Chemical	K_{oc} Value
Tetraethyl Lead[1]	4,900 mL/g
(n) Heptane	2,361
(n) Hexane	1,097
Naphthalene[2]	976
(n) Pentane	568
Ethylbenzene[2]	565
Toluene	339
1-Pentane	280
(o) Xylene[2]	255
Benzene[2]	50
Phenol[2]	50
Ethylene Dibromide	44

Source: Lyman et al.(1982)

1: K_{oc} is a measure of the tendency for organic compounds to be adsorbed by soil. The higher the K_{oc} value for each compound, the lower the mobility and the higher the adsorption potential.

2: Also listed in Table 2-9 as a toxic compound.

coefficients for some gasoline compounds. Of the toxic compounds listed, tetraethyl lead and napthalene have relatively low mobility values and are likely to be adsorbed to the soil. Toluene, benzene, the xylenes, and phenol have high mobility values and, therefore, are more likely to appear in either the dissolved or gaseous phases.

2.8.2 Diffusion, Advection, and Volatilization

In order for a chemical to volatilize from a soil surface, the chemical within the soil must move to the soil surface and then move away from the soil surface into the atmosphere. These two events directly depend upon diffusion and advection. Diffusion is the mass transport that results from the random motion of vapor or gas molecules and is generally away from areas of high concentration toward areas of low concentration. Advection results from changes in the total pressure gradient and is the net downgradient migration of gases. The diffusion, in turn, is affected by soil nature, soil moisture, and the presence of dissolved higher molecular weight organics in soil water.

Volatilization of petroleum compounds to air or soil air depends upon the potential volatility of the compounds and on soil and environmental conditions which affect the vapor pressure of the chemicals. Factors which influence vapor pressure and, consequently, volatility include: soil parameters such as water content, clay content, and surface area; and environmental parameters, such as temperature, wind speed, evaporation rate, and precipitation.

2.8.3 Dissolution

The potential for dissolution of petroleum compounds into water is a function of each compound's chemical property which is expressed by the term solubility. The property of solubility determines the extent to which a contaminant will dissolve, it also affects other fate mechanisms. For example, a highly soluble substance often has a relatively low adsorption coefficient and also tends to be more readily degradable by micro-organisms. Solubility of some toxic gasoline compounds is shown in Table 2-9.

2.8.4 Chemical Processes

The chemical process of the spilled petroleum can be further divided into biotic and abiotic chemical transformations.

Abiotic Chemical Transformations are reactions, not performed by living organisms that decrease contaminant concentrations by degrading the chemicals into other products. The most important chemical transformations are hydrolysis and oxidation/reduction reactions. Hydrolysis refers to a reaction of a compound with water, usually resulting in the net exchange of some leaving functional group with OH^- at a reaction center which forms an alcohol product and other chemical. In water, hydrolysis may be promoted or catalyzed mainly by hydronium (H_3O^+, of H^+) or hydroxyl ions (OH^-), but in moist soil, loosely complexed metal ions may also be important catalysts for certain types of chemical reactions. Oxidation/Reduction reactions take place during chemical processes where reactive electron-deficient species, called oxidants, remove electrons from other, more electron-rich molecules called reductants. Oxidation/reduction reactions may be catalyzed by soils and clays, and are affected by factors such as water content, oxygen activity in the soil, and pH.

Biotic Chemical Transformation has two forms: biodegradation and biotransformation. Biodegradation is the decomposition of a contaminant by micro-organisms such as bacteria, fungi, and yeasts. The end products of biodegradation are water, carbon dioxide, and energy for cellular growth and reproduction. Bio-transformation is the partial biodegradation of compounds. In bio-transformation, contaminants are particularly degraded to simpler compounds which may be more or less soluble or toxic than the original compounds. Biodegradation occurs under aerobic and anaerobic conditions in the subsurface; however, the decay rates of most petroleum compounds are greater under aerobic conditions. Other factors that can influence the rate of degradation are: soil moisture content, compound availability, oxidation/reduction potential of the compounds, ambient temperature, pH of soil, inorganic nutrients, and concentration of micro-organisms.

Degradation is often the result of the combined effects of chemical transformation and biodegradation. For example, the oxidation/reduction of complex hydrocarbons can produce simple compounds such as peroxides, primary alcohols, and monocarboxylic acids. These compounds can then be further degraded by bacteria, leading to the formation of carbon dioxide, water, and new bacterial cell materials.

Table 2-6: Hydrocarbon Identification of Chromatographic Peaks Shown in Figure 2-3

Peak Number	Component*	Boiling Point °C	Peak Number	Component*	Boiling Point °C
1	propane	-42.07	44	2,4-dimethyl-1-pentene	81.64
2	isobtuane	-11.73	45	1-methylcyclopentene	75.8
3	isobutylene	- 6.90		+ 2 methyl-cis-3-hexene	86
	+ butene-1	- 6.26	46	2,4-dimethyl-2-pentene	83.28
4	n-butane	- 0.50		+ 3-ethyl-1-pentene	84.11
5	trans-2-butene	0.88		+ 3-methyl-1-hexene	84
6	neopentane	9.50	47	2,3-dimethyl-1-pentene	84.28
7	cis-2-butene	3.72	48	2-methyl-trans-3-hexene	86
8	3-methyl-1-butene	20.26		+ 5-methyl-1-hexene	85.31
9	isopentane	27.85	49	3,3-dimethylpentane	86.06
10	pentene-1	29.97	50	cyclohexane	80.74
11	2-methyl-1-butene	31.16		+(4-methyl-cis-2-hexene)	87.31
12	2-methyl-1,3-butadiene	34.07	51	4-methyl-1-hexene	86.73
13	n-pentane	36.07		+ 4-methyl-trans-2-hexene	87.56
14	trans-2-pentene	36.35	52	3-methyl-2-ethyl-1-butene	86.1
15	cis-2-pentene	36.94	53	5-methyl-trans-2-hexene	88.11
16	2-methyl-2-butene	38.57	54	cyclohexene	82.98
17	3,3-dimethyl-1-butene	41.24	55	2-methylhexane	90.05
18	2,2-dimethylbutane	49.74		+ (5-methyl-cis-2-hexene)	89.5
19	cyclopentene	44.24	56	2,3-dimethylpentane	89.78
20	3-methyl-1-pentene	54.14		+ (1,1-dimethylcyclopentane)	87.85
	+ 4-methyl-1-pentene	53.88		+(3,4-deimthyl-cis-2-pentene)	87.9
21	4-methyl-cis-2-pentene	56.30	57	3-methylhexane	91.85
22	2,3-dimethyl-1-butene	55.67	58	1-cis-3-dimethylcyclopentane	91.73
23	cyclopentane	49.26		+ 2-methyl-1-hexene	91.95
24	2,3-dimethylbutane	57.99		+ 3,4-dimethyl-trans-2-	
	+ (4-methyl-trans-2-pentene)*	58.55		pentene	90.5
25	2-methylpentane	60.27	59	1-trans-3-dimethylcyclopentane	90.77
26	2-methyl-1-pentene	60.72		+ heptene	93.64
27	3-methylpentane	63.28		+ 2-ethyl-1-pentene	94
	+ (hexene-1)	63.49	60	3-ethylpentane	93.48
	+ (2-ethyl-1-butene)	64.66		+ 3-methyl-trans-2-hexene	94
28	cis-3-hexene	66.47	61	1-trans-2-dimethylcyclopentane	91.87
29	trans-3-hexene	67.08	62	2,2,4-trimethylpentane	99.24
30	3-methylcyclopentene	65.0		+ (trans-3-heptene)	95.67
31	2-methyl-2-pentene	67.29	63	cis-3-heptene	95.75
32	3-methyl-cis-2-pentene	67.70	64	3-methyl-cis-3-hexene	95.33
33	n-hexane	68.74		+ 2-methyl-2-hexene	95.44
	+ (4,4-dimethyl-1-pentene)	72.49		+ 3-methyl-trans-3-hexene	93.53
34	trans-2-hexene	67.87	65	3-ethyl-2-pentene	96.01
35	cis-2-hexene	68.84	66	trans-2-heptene	97.95
36	3-methyl-trans-2-pentene	70.44	67	n-heptane	98.43
37	4,4-dimethyl-trans-2-pentene	76.75		+ (3-methyl-cis-2-hexene)	94
38	methylcyclopentane	71.81	68	2,3-dimethyl-2-pentene	97.40
	+ 3,3-dimethyl-1-pentene	77.57		+ cis-2-heptene	98.5
39	2,2-dimethylpentane	79.20	69	1-cis-2-dimethylcyclopentane	99.57
	+ 2,3-dimethyl-2-butene	73.21	70	methylcyclohexane	100.93
	+ (2,3,3-trimethyl-1-butene)	77.87		+ 2,2-dimethylhexane	106.84
40	benzene	80.10		+ 1,1,3-trimethylcyclopentane	104.89
41	2,4-dimethylpentane	80.50	71	2,5-dimethylhexane	109.10
42	4,4-dimethyl-cis-2-pentene	80.42		+ ethylcyclopentane	103.47
43	2,2,3-trimethylbutane	80.88	72	2,4-dimethylhexane	109.43

(continued)

Table 2-6 (Continued)

Peak Number	Component*	Boiling Point °C
73	2,2,3-trimethylpentane	109.84
74	1-trans-2-cis-4-trimethyl-	
	cyclopentane	109.29
75	toluene	110.63
76	3,3-dimethylhexane	111.97
77	1-trans-2-cis-3-trimethyl-	
	cyclopentane	110.2
78	2,3,4-trimethylpentane	113.47
79	2,3,3-trimethylpentane	114.76
80	1,1,2-trimethylcyclopentane	113.73
81	2,3-dimethylhexane	115.61
	+ 2-methyl-3-ethylpentane	115.65
82	2-methylheptane	117.65
83	4-methylheptane	117.71
84	3,4-dimethylhexane	117.73
	+ (1-cis-2-trans-4-	
	trimethylcyclopentane)	116.73
85	3-ethylhexane	118.53
86	3-methylheptane	118.93
	+ (3-methyl-3-ethylpentane)	118.26
87	1,1,3-trans-4-tetramethyl-	
	cyclopentane	121.6
88	2,2,5-trimethylhexane	124.08
	+ (1-cis-2-cis-4-trimethyl-	
	cyclopentane)	118
89	1,1-dimethylcyclohexane	119.54
	+ 1-trans-4-dimethyl-	
	cyclohexane	119.35
90	1-cis-3-dimethylcyclohexane	120.09
91	1-methyl-trans-3-ethyl-	
	cyclopentane	120.8
92	2,2,4-trimethylhexane	126.54
93	1-methyl-trans-2-ethyl-	
	cyclopentane	121.2
	+ 1-methyl-cis-3-ethyl-	
	cyclopentane	121.4
94	cycloheptane	118.79
95	1-methyl-1-ethylcyclopentane	121.52
96	1-trans-2-dimethylcyclohexane	123.42
	+ 1-cis-2-cis-3-trimethylcyclo-	
	pentane	123.0
97	n-octane	125.67
98	1-cis-4-dimethylcyclohexane	124.32
99	1-trans-3-dimethylcyclohexane	124.45
100	2,4,4-trimethylhexane	130.65
101	isopropylcyclopentane	126.42
102	2,3,5-trimethylhexane	131.34
103	2,2-dimethylheptane	132.69
104	1-methyl-cis-2-ethylcyclopentane	128.05
105	2,4-dimethylheptane	133.5
	+ 2,2,3-trimethylhexane	133.6
106	2,2-dimethyl-3-ethylpentane	133.83
	+ 2 methyl-4-ethylhexane	133.8
107	2,6-dimethylheptane	135.21
	+ (1-cis-2-dimethyl-	
	cyclohexane)	129.73
108	n-propylcyclopentane	130.95
109	ethylcyclohexane	131.78
110	2,5-dimethylheptane	136.0
	+ 3,5-dimethylheptane	136.0
111	ethylbenzene	136.19
112	2,4-dimethyl-3-ethylpentane	136.73
113	3,3-dimethylheptane	137.3
114	1,1,3-trimethylcyclohexane	136.63
115	2,3,3-trimethylhexane	137.68
116	1-cis-3-cis-5-trimethyl-	
	cyclohexane	138.41
117	2-methyl-3-ethylhexane	138.0
118	p-xylene	138.35
119	m-xylene	139.10
	+ (3,3,4-trimethylhexane)	140.46
120	2,3-dimethylheptane	140.5
121	3,4-dimethylheptane	140.6
122	4-methyloctane	142.48
123	2-methyloctane	143.26
124	3-ethylpehtane	143.0
125	3-metyloctane	144.18
126	o-xylene	144.41
	+ (2,2,4,5-tetramethyl-	
	hexane)	147.8
127	2,2,4-trimethylheptane	147.88
128	2,2,5-trimethylheptane	148
	+ 2,2,6-trimethylheptane	148
129	2,5,5-trimethylheptane	152.80
	+ 2,4,4-trimethylheptane	153
130	isopropylbenzene	152.39
131	n-nonane	150.80
132	3,3,5-trimethylheptane	155.68
133	2,4,5-trimethylheptane	157
	+ 2,3,5-trimethylheptane	157
134	n-propylbenzene	159.22
135	2,2,3,3-tetramethyhexane	160.31
	+ 2,6-dimethyloctane	158.54
136	1-methyl-3-ethylbenzene	161.31
137	1-methyl-4-ethylbenzene	161.99
138	3,3,4-trimethylheptane	164
	+ 3,4,4-trimethylheptane	164
	+ 3,4,5-trimethylheptane	164
139	1-methyl-2-ethylbenzene	165.15
	+ 5-methylnonane	165.1
140	4-methylnonane	165.7
141	1,3,5-trimethylbenzene	164.72

(continued)

Table 2-6: (Continued)

Peak Number	Component*	Boiling Point °C	Peak Number	Component*	Boiling Point°C
142	2-methylnonane	166.8	161	2-methylindane	184
143	tert-butylbenzene	169.12	162	1,4-dimethyl-2-ethylbenzene	186.91
144	unidentified C_{10}alkylate peak		163	1-methylindane	186.5
145	3-methylnonane	167.8	164	1-methyl-3-tert-butylbenzene	189.26
146	1,2,4-trimethylbenzene	169.35		+ unidentified C_{11} alkylate	
147	sec-butylbenzene	173.31		peak	
148	isobutylbenzene	172.76	165	1,3-dimethyl-4-ethylbenzene	188.41
149	1-methyl-3-isopropylbenzene	175.14	166	1,3-dimethyl-2-ethylbenzene	190.01
150	n-decane	174.12		+ 1,2-dimethyl-4-ethyl-	
151	1,2,3-trimethylbenzene	176.08		benzene	189.75
	+ 1-methyl-4-isopropyl-		167	1-methyl-4-tert-butylbenzene	192.76
	benzene	177.10	168	1,2-dimethyl-3-ethylbenzene	193.91
152	1-methyl-2-isopropylbenzene	178.15	169	n-undecane	195.89
	+ indane	177	170	1,2,4,5-tetramethylbenzene	196.8
153	1,3-diethylbenzene	181.10	171	1,2,3,5-tetramethylbenzene	198.0
154	unidentified C_{11} alkylate peak		172	isopentylbenzene	198.9
155	1-methyl-3-n-propylbenzene	181.80	173	5-methylindane	199
156	n-butylbenzene	183.27	174	4-methylindane	203
157	1,2-diethylbenzene	183.42	175	n-pentylbenzene	205.46
	+ 1,4-diethylbenzene	183.30	176	1,2,3,4-tetramethylbenzene	205.4
	+ 1-methyl-4-n-propyl		177	tetralin	205.57
	benzene	183.75	178	naphthalene	217.96
158	1-methyl-2-n-propylbenzene	184.80	179	1,3-dimethyl-5-tert-butylbenzene	205.1
159	1,3-dimethyl-5-ethylbenzene	183.75	180	n-dodecane	216.28
160	unidentified C_{11} alkylate peak				

* - Chemical name in parenthesis indicates a minor component also present in the peak.

Table 2-7: **Hydrocarbon Compositions of Typical Premium and Regular Grade Gasolines[a b]**

Component	wt% regular grade	wt% premium grade
propane	0.14	0.01
isobutane	0.30	0.37
isobutylene + butene-1	0.02	0.04
n-butane	3.93	4.29
trans-2-butene	0.16	0.20
neopentane	0.02	0.04
cis-2-butene	0.13	0.17
3-methyl-1-butene	0.08	0.12
isopentane	7.88	10.17
pentene-1	0.34	0.45
2-methyl-1-butene	0.35	0.22
n-pentane	7.27	5.75
trans-2-pentene	0.52	0.90
cis-2-pentene	0.43	0.67
2-methyl-2-butene	1.09	0.96
2,2-dimethylbutane	0.17	0.46
cyclopentene	0.13	0.18
2-methyl-1-pentene + 4-methyl-1-pentene	0.16	0.18
4-methyl-cis-2-pentene	0.05	0.04
2,3-dimethyl-1-butene	0.10	0.08
cyclopentane	0.58	0.51
2,3-dimethylbutane	0.59	1.55
4-methyl-trans-2-pentene	0.30	0.18
2-methylpentane	3.85	3.76
2-methyl-1-pentene	0.22	0.22
3-methylpentane + (hexene-1) + (2-ethyl-1-butene)	2.72	2.23
cis-3-hexene	0.13	0.11
trans-3-hexene	0.15	0.12
3-methylcyclopentene	0.08	0.04
2-methyl-2-pentene	0.32	0.27
3-methyl-cis-2-pentene	0.45	0.37
n-hexane + (4,4-dimethyl-1-pentene)	3.50	1.51
trans-2-hexene	0.36	0.18
cis-2-hexene	0.24	0.15
3-methyl-trans-2-pentene	0.44	0.34
4,4-dimethyl-trans-2-pentene	Trace	Trace
methylcyclopentane + 3,3-dimethyl-1-pentene	1.50	0.62
2,2-dimethylpentane + 2,3-dimethyl-2-butene + 2,3,3-trimethylbutane	0.20	0.14
benzene	1.35	0.81
2,4-dimethylpentane	0.32	1.71
2,2,3-trimethylbutane	Trace	0.04
4,4-dimethyl-cis-2-pentene	0.02	Trace
2,4-dimethyl-1-pentene	Trace	0.03
1-methylcyclopentene + 2-methyl-cis-3-hexene	O.37	0.32
2,4-dimethyl-2-pentene + 3-ethyl-1-pentene + 3-methyl-1-hexene	0.05	0.05
2,3-dimethyl-1-pentene	0.01	0.02
2-methyl-trans-3-hexene + 5-methyl-1-hexene	0.05	0.04
3,3-dimethylpentane	Trace	0.02
cyclohexane + 4-methyl-cis-2-hexene	0.36	0.17
4-methyl-1-hexene + 4-methyl-trans-2-hexene	0.08	0.09
3-methyl-2-ethyl-1-butene + 5-methyl-trans-2-hexene	0.03	0.04
cyclohexene	0.03	0.03
2-methylhexane + (5-methyl-cis-2-hexene)	1.25	1.48
2,3-dimethylpentane + (1,1-dimethylcyclopentane) + (3,4-dimethyl-cis-2-pentene)	0.47	4.17
3-methylhexane	1.41	1.77
1-cis-3-dimethylcyclopentane+ 2-methyl-1-hexene + 3,4-dimethyl-trans-2-pentene	0.41	0.27
1-trans-3-dimethylcyclpentane + 1-heptene + 2-ethyl-1-pentene	0.40	0.27
3-ethylpentane + 3-methyl-trans-2-hexene	0.25	0.16
1-trans-2-dimethycyclopentane	0.20	0.16
2,2,4-trimethylpentane + (trans-3-heptene)	0.32	4.58
cis-3-heptene	0.17	0.16
3-methyl-cis-3-hexene + 2-methyl-2-hexene + 3-methyl-trans-3-hexene	0.35	0.31
3-ethyl-2-pentene	0.04	0.04
trans-2-heptene	0.10	0.06
n-heptane + (3-methyl-cis-2-hexene)	1.92	1.96
2,3-dimethyl-2-pentene + cis-2-heptene	0.14	0.12
1-cis-2-dimethylcycopentane	0.13	0.09
methylcyclohexane + 2,2-dimethylhexane + 1,1,3-trimethylcyclopentane	0.61	0.31
2,5-dimethylhexane	0.24	0.42
ethylcyclopentane	0.14	0.18
2,4-dimethylhexane	0.34	0.50
2,2,3-trimethylpentane	Trace	0.23
1-trans-2-cis-4-trimethyl-cyclopentane	0.16	0.04

(continued)

Table 2-7: (Continued)

Component	wt% regular grade	wt% premium grade
Toluene + (3,3-dimethylhexane)	5.92	12.30
1-trans-2-cis-3-trimethylcyclopentane	0.25	0.06
2,3,4-trimethylpentane	0.11	2.26
2,3,3-trimethylpentane	0.05	2.28
1,1,2-trimethylcyclopentane	0.11	0.09
2,3-dimethylhexane + 2-methyl-3-ethylpentane	0.39	0.60
2-methylheptane	1.05	0.48
4-methylheptane	0.52	0.22
3,4-dimethylhexane + (1-cis-2-trans-4-trimethylcyclopentane)	0.20	0.16
3-ethylhexane	Trace	0.01
3-methylheptane + (3-methyl-3-ethylpentane)	1.54	0.63
2,2,5-trimethylhexane + (1-cis-2-cis-4-trimethylcyclopentane)	0.17	0.74
1,1-dimethylcyclohexane + 1-trans-4-dimethylcyclohexane + 1 cis-3-dimethylcyclohexane	0.27	0.17
1-methyl-trans-3-ethylcyclopentane	0.12	0.06
2,2,4-trimethylhexane	0.18	0.11
1-methyl-trans-2-ethylcyclopentane + 1-methyl-cis-3-ethylcyclopentane	0.13	0.07
cycloheptane + 1-methyl-1-ethylcyclpentane	0.11	0.05
1-trans-2-dimethylcyclohexane + 1-cis-2-cis-3-trimethylcyclopentane	0.18	0.12
n-octane + (1-cis-4-dimethylcyclohexane)	1.43	0.42
1-trans-3-dimethylcyclohexane	0.12	0.08
2,4,4-trimethylhexane	0.04	0.02
isopropylcyclopentane	0.02	0.01
2,3,5-trimethylhexane	0.05	0.15
2,2-dimethylheptane	0.08	0.01
1-methyl-cis-2-ethylcyclopentane	0.11	0.07
2,4-dimethylheptane + 2,2,3-trimethylhexane	0.24	0.08
2,2-dimethyl-3-ethylpentane + 2-methyl-4-ethylhexane	0.09	0.02
2,6-dimethylheptane + (1-cis-2-dimethylcylohexane)	0.20	0.07
n-propylcyclopentane	0.06	0.01
ethylcyclohexane	0.36	0.17

Component	wt% regular grade	wt% premium grade
2,5-dimethylheptane + 3,5-dimethylheptane	0.14	0.16
ethylbenzene	2.70	1.70
2,4-dimethyl-3-ethylpentane	0.05	0.03
3,3-dimethylheptane	0.08	0.04
2,3,3-trimethylhexane	0.12	0.05
2-methyl-3-ethylhexane	0.13	0.04
p-xylene	1.54	1.58
m-xylene + (3,3,4-trimethylhexane)	3.87	3.83
2,3-dimethylheptane	0.39	0.13
3,4-dimethylheptane	0.33	0.07
4-methyloctane	0.55	0.11
2-methyloctane	0.62	0.14
3-ethylheptane	0.16	0.02
3-methyloctane	0.85	0.60
o-xylene + (2,2,4,5-tetramethylhexane)	2.05	1.94
2,2,4-trimethylheptane	0.12	0.17
2,2,5-trimethylheptane + 2,2,6-trimethylheptane	0.07	0.27
2,5,5-trimethylheptane + 2,4,4-trimethylheptane	0.06	0.21
isopropylbenzene	0.23	0.10
n-nonane	0.83	0.14
3,3,5-trimethylheptane	0.05	0.02
2,4,5-trimethylheptane + 2,3,5-trimethylheptane	0.07	0.17
n-propylbenzene	0.72	0.24
2,6-dimethyloctane + (2,2,3,3-tetramethylhexane)	0.12	0.06
1-methyl-3-ethylbenzene	1.84	0.83
1-methyl-4-ethylbenzene	1.00	0.42
3,3,4-trimethylheptane + 3,4,4-trimethylheptane + 3,4,5-trimethylheptane	0.08	0.35
1-methyl-2-ethylbenzene + 5-methylnonane	0.90	0.34
4-methylnonane	0.26	0.04
1,3,5-trimethylbenzene	0.76	0.39
2-methylnonane	0.41	0.06
3-methylnonane	0.32	0.06
1,2,4-trimethylbenzene	2.83	1.61
sec-butylbenzene	0.13	0.01
isobutylbenzene	0.06	0.01
1-methyl-3-isopropylbenzene	0.12	0.03
n-decane	0.50	0.08
1,2,3-trimethylbenzene + 1-methyl-4-isopropylbenzene	0.68	0.32

(continued)

Table 2-7 (continued)

Component	wt% regular grade	wt% premium grade
1-methyl-2-isopropylbenzene + indane	0.35	0.15
1,3-diethylbenzene	0.25	0.08
1-methyl-3-n-propylbenzene	0.48	0.16
n-butylbenzene	0.25	0.05
1,2-diethylbenzene + 1,4-diethylbenzene + 1-methyl-4-n-propylbenzene	0.44	0.09
1-methyl-2-n-propbylbenzene	0.16	0.05
1,3-dimethyl-5-ethylbenzene	0.42	0.18
2-methylindane	0.10	0.02
1,4-dimethyl-2-ethylbenzene	0.36	0.09
1-methylindane	0.17	0.07
1-methyl-3-tert-butylbenzene	0.11	0.03
1,3-dimethyl-4-ethylbenzene	0.27	0.13
1,3-dimethyl-2-ethylbenzene + 1,2-dimethyl-4-ethylbenzene	0.50	0.19
1-methyl-4-tert-butylbenzene	0.13	0.04
1,2-dimethyl-3-ethylbenzene	0.09	0.03
n-undecane	0.22	0.07
1,2,4,5-tetramethylbenzene	0.21	0.10
1,2,3,5-tetramethylbenzene	0.42	0.17
isopentylbenzene	0.17	0.07
5-methylindane	0.30	0.11
4-methylindane	0.16	0.03
n-pentylbenzene	0.14	0.03
1,2,3,4-tetramethylbenzene	0.19	0.03
tetralin	0.14	0.02
naphthalene	0.24	0.10
1,3-dimethyl-5-tert-butylbenzene	0.16	0.02
n-dodecane	0.09	0.05
total saturates identified	56.38	62.30
total olefins identified	7.69	7.50
total aromatics identified	32.91	28.50
total components unidentified	3.02	1.70
total	100.00	100.0

a: Trace components less than 0.01 wt%.

b: Chemical name in parenthesis indicates a minor component also present in the peak.

Table 2-8: CHEMICAL COMPOSITION OF GASOLINE

Compound	Number of Carbons	Concentration (Weight Percent) (a)	Reference
Straight Chain Alkanes			
Propane	3	0.01 - 0.14	8, 10
n-Butane	4	3.93 - 4.70	8, 10, 11
n-Pentane	5	5.75 - 10.92	8, 10, 11
n-Hexane (d)	6	0.24 - 3.50	8, 10, 11
n-Heptane	7	0.31 - 1.96	10, 11
n-Octane	8	0.36 - 1.43	10
n-Nonane	9	0.07 - 0.83	10
n-Decane	10	0.04 - 0.50	10
n-Undecane	11	0.05 - 0.22	10
n-Dodecane	12	0.04 - 0.09	10
Branched Alkanes			
Isobutane	4	0.12 - 0.37	8, 10
2,2-Dimethylbutane	6	0.17 - 0.84	10
2,3-Dimethylbutane	6	0.59 - 1.55	8, 10, 11
2,2,3-Trimethylbutane	7	0.01 - 0.04	10
Neopentane	5	0.02 - 0.05	10
Isopentane	5	6.07 - 10.17	8, 10, 11
2-Methylpentane	6	2.91 - 3.85	8, 10, 11
3-Methylpentane	6	2.4 (vol)	8, 10, 11
2,4-Dimethylpentane	7	0.23 - 1.71	8, 10, 11
2,3-Dimethylpentane	7	0.32 - 4.17	8, 10, 11
3,3-Dimethylpentane	7	0.02 - 0.03	10
2,2,3-Trimethylpentane	8	0.09 - 0.23	10, 11
2,2,4-Trimethylpentane	8	0.32 - 4.58	8, 10
2,3,3-Trimethylpentane	8	0.05 - 2.28	10
2,3,4-Trimethylpentane	8	0.11 - 2.80	10, 11
2,4-Dimethyl-3-ethylpentane	9	0.03 - 0.07	10
2-Methylhexane	7	0.36 - 1.48	10
3-Methylhexane	7	0.30 - 1.77	10, 11
2,4-Dimethylhexane	8	0.34 - 0.82	10
2,5-Dimethylhexane	8	0.24 - 0.52	10
3,4-Dimethylhexane	8	0.16 - 0.37	10
3-Ethylhexane	8	0.01	10
2-Methyl-3-ethylhexane	9	0.04 - 0.13	10
2,2,4-Trimethylhexane	9	0.11 - 0.18	10
2,2,5-Trimethylhexane	9	0.17 - 5.89	10
2,3,3-Trimethylhexane	9	0.05 - 0.12	10
2,3,5-Trimethylhexane	9	0.05 - 1.09	10
2,4,4-Trimethylhexane	9	0.02 - 0.16	10
2-Methylheptane	8	0.48- 1.05	10
3-Methylheptane	8	0.63 - 1.54	10

Table 2-8: (continued)

Compound	Number of Carbons	Concentration (Weight Percent) (a)	Reference
4-Methylheptane	8	0.22 - 0.52	10
2,2-Dimethylheptane	9	0.01 - 0.08	10
2,3-Dimethylheptane	9	0.13 - 0.51	10
2,6-Dimethylheptane	9	0.07 - 0.23	10
3,3-Dimethylheptane	9	0.01 - 0.08	10
3,4-Dimethylheptane	9	0.07 - 0.33	10
2,2,4-Trimethylheptane	10	0.12 - 1.70	10
3,3,5-Trimethylheptane	10	0.02 - 0.06	10
3-Ethylheptane	10	0.02 - 0.16	10
2-Methyloctane	9	0.14 - 0.62	10
3-Methyloctane	9	0.34 - 0.85	10
4-Methyloctane	9	0.11 - 0.55	10
2,6-Dimethyloctane	10	0.06 - 0.12	10
2-Methylnonane	10	0.06 - 0.41	10
3-Methylnonane	10	0.06 - 0.32	10
4-Methylnonane	10	0.04 - 0.26	10
Cycloalkanes			
Cyclopentane	5	0.19 - 0.58	8, 10
Methylcyclopentane	6	Not qualified	8
1-Methyl-cis-2-ethylcyclopentane	8	0.06 - 0.11	10
1-Methyl-trans-3-ethylcyclopentane	8	0.06 - 0.12	10
1-cis-2-dimethylcyclopentane	7	0.07 - 0.13	10
1-trans-2-dimethylcyclopentane	7	0.06 - 0.20	10
1,1,2-trimethylcyclopentane	8	0.06 - 0.11	10
1-trans-2-cis-3-trimethylcyclopentane	8	0.01 - 0.25	10
1-trans-2-cis-4-trimethylcyclopentane	8	0.03 - 0.16	10
Ethycyclopentane	7	0.14 - 0.21	10
n-Propylcyclopentane	8	0.01 - 0.06	10
Isopropylcyclopentane	8	0.01 - 0.02	10
1-trans-3-dimethylcyclohexane	8	0.05 - 0.12	10
Ethylcyclohexane	8	0.17 - 0.42	10
cis-2-butene	4	0.13 - 0.17	10
trans-2-butene	4	0.16 - 0.20	10
Pentene-1	5	0.33 - 0.45	10
cis-2-pentene	5	0.43 - 0.67	8, 10
trans-2-pentene	5	0.52 - 0.90	10, 11
cis-2-hexene	6	0.15 - 0.24	10
trans-2-hexene	6	0.18 - 0.36	10
cis-3-hexene	6	0.11 - 0.13	10
trans-3-hexene	6	0.12 - 0.15	10
cis-3-heptene	7	0.14 - 0.17	10, 11
trans-2-heptene	7	0.06 - 0.10	10
Branched Alkenes			
2-Methyl-1-butene	5	0.22 - 0.66	8, 10, 11
3-Methyl-1-butene	5	0.08 - 0.12	10

Compound	Number of Carbons	Concentration (Weight Percent) (a)	Reference
2-Methyl-2-butene	5	0.96 - 1.28	8, 10, 11
2,3-Dimethyl-1-butene	6	0.08 - 0.10	10
2-Methyl-1-pentene	6	0.20 - 0.22	10, 11
2,3-Dimethyl-1-pentene	7	0.01 - 0.02	10
2,4-Dimethyl-1-pentene	7	0.02 - 0.03	10
4,4-Dimethyl-1-pentene	7	0.6 (vol)	11
2-Methyl-2-pentene	6	0.27 - 0.32	10, 11
3-Methyl-cis-2-pentene	6	0.35 - 0.45	10
3-Methyl-trans-2-pentene	6	0.32 - 0.44	10
4-Methyl-cis-2-pentene	6	0.04 - 0.05	10
4-Methyl-trans-2-pentene	6	0.08 - 0.30	10
4,4-Dimethyl-cis-2-pentene	7	0.02	10
4,4-Dimethyl-trans-2-pentene	7	Not qualified	10
3-Ethyl-2-pentene	7	0.03 - 0.04	10
Cycloalkenes			
Cyclopentene	5	0.12 - 0.18	10
3-Methylcyclopentene	6	0.03 - 0.08	10
Cyclohexene	6	0.03	10
Alkyl Benzenes			
Benzene (d)	6	0.12 - 3.50	6, 7, 8, 9, 10, 11, 12
Toluene (d)	7	2.73 - 21.80	5, 6, 7, 8, 9, 10, 11, 12
o-Xylene (d)	8	0.68 - 2.86	6, 9, 10, 12
m-Xylene (d)	8	1.77 - 3.87	10
p-Xylene (d)	8	0.77 - 1.58	10
1-Methyl-4-ethylbenzene	9	0.18 - 1.00	10
1-Methyl-2-ethylbenzene	9	0.19 - 0.56	6
1-Methyl-3-ethylbenzene	9	0.31 - 2.86	6, 9, 10, 11
1-Methyl-2-n-propylbenzene	10	0.01 - 0.17	6, 9, 10
1-Methyl-3-n-propylbenzene	10	0.08 - 0.56	9,10
1-Methyl-3-isopropylbenzene	10	0.01 - 0.12	10
1-Methyl-3-t-butylbenzene	11	0.03 - 0.11	10
1-Methyl-4-t-butylbenzene	11	0.04 - 0.13	10
1,2-Dimethyl-3-ethylbenzene	10	0.02 - 0.19	6, 10
1,2-Dimethyl-4-ethylbenzene	10	0.50 - 0.73	6
1,3-Dimethyl-2-ethylbenzene	10	0.21 - 0.59	6, 9
1,3-Dimethyl-4-ethylbenzene	10	0.03 - 0.44	6, 10
1,3-Dimethyl-5-ethylbenzene	10	0.11 - 0.42	6, 10
1,3-Dimethyl-5-t-butylbenzene	12	0.02 - 0.16	10
1,4-Dimethyl-2-ethylbenzene	10	0.05 - 0.36	6, 10
1,2,3-Trimethylbenzene	9	0.21 - 0.48	6
1,2,4-Trimethylbenzene	9	0.66 - 0.30	6, 9, 10, 11
1,3,5-Trimethylbenzene	9	0.13 - 1.15	6, 9, 10
1,2,3,4-Tetramethylbenzene	10	0.02 - 0.19	6, 10
1,2,3,5-Tetramethylbenzene	10	0.14 - 1.06	6, 9, 10
1,2,4,5-Tetramethylbenzene	10	0.05 - 0.67	6, 10
Ethylbenzene(d)	8	0.36 - 2.86	6, 9, 10, 11, 12
1,2-Diethylbenzene	10	0.57	9

Table 2-8: (continued)

Compounds	Number of carbons	Concentration (Weight Percent) (a)	Reference
1,3-Diethylbenzene	10	0.05 - 0.38	6, 9, 10
n-Propylbenzene	9	0.08 - 0.72	6, 9, 10
Isopropylbenzene	9	<0.01 - 0.23	6, 9, 10, 12
n-Butylbenzene	10	0.04 - 0.44	6, 9, 10
Isobutylbenzene	10	0.01 - 0.08	9, 10
sec-Butylbenzene	10	0.01 - 0.13	9 10
t-Butylbenzene	10	0.12	9
n-Pentylbenzene	11	0.01 - 0.14	10
Isopentylbenzene	11	0.07 - 0.17	10
Indan	9	0.25 - 0.34	6
1-Methylindan	10	0.04 - 0.17	10
2-Methylindan	10	0.02 - 0.10	10
4-Methylindan	10	0.01 - 0.16	10
5-Methylindan	10	0.09 - 0.30	10
Tetralin	10	0.01 - 0.14	10
<u>Polynuclear Aromatic Hydrocarbons</u>			
Napthalene(d)	10	0.09 - 0.49	6, 10
Pyrene	16	Not quantified	6
Benz(a)anthracene	18	Not quantified	6
Benz(a)pyrene	20	0.19 - 2.8 mg/kg	6
Benzo(e)pyrene	20	Not quantified	6
Benzo(g,h,i)perylene	21	Not quantified	6
<u>Elements</u>			
Bromine		80 - 345 ug/g	3
Cadmium		0.01 - 0.07 ug/g	1
Chlorine		80 - 300 ug/g	3
Lead(b)		530 - 1120 ug/g	8
Sodium		<0.6 - 1.4 ug/g	3
Sulfur(c)		0.10 - 0.15(ASTM)	
Vandadium		<0.02 - 0.001 ug/g	2, 3
<u>Additives</u>			
Ethylene dibromide(d)		0.7 - 177.2 ppm	4
Ethylene dichoride(d)		150 - 300 ppm	8
Tetramethyl lead			
Tetraethyl lead			

a. Conversion from other units assumed 0.75 specific gravity.

b. ASTM specfication, maximum, unleaded gasoline, 0.013 g/l maximum, conventional grade gasoline, 1.1 g/l. Title 13, GAC, Section 2253.2, maximum, leaded gasoline other than leaded high octane gasoline, 0.8 g/gallon maximum, leaded high octange gasoline, 1.0 g/gallon. Federal standards, January 1, 1986, maximum 0.1 g/gallon.

c. ASTM maximum, unleaded gasoline, 0.10 weight percent. Conventional grade gasoline, 0.15 weight percent, Title 13, GAC, Section 2252, maximum 300 ppm by weight.

d. Compounds for which AALs are being developed.

References

1. American Petroleum Institute, 1985a. Cadmium: Environmental and Community Health Impact. Washington, D.C. EA Report API 137C.

2. American Petroleum Institute, 1985b. Vanadium: Environmental and Community Health Impace. Washington, D.C. EA Report API 37D.

3. C. Block and R. Dams, 1978. Concentration Data of Elements in Liquid Fuel Oils as Obtained by Neutron Activation Analysis. Journal of Radioanalytical Chemistry 46, 137-144.

4. Clifford J. Bruell and George E. Hoag. Capillary and Packed Column Gas Chromatography of Gasoline Hydrocarbons and EDB, in Proceedings of the NWWA/API Conference on Petroleum Hydrocarbons and Organic Chemicals in Ground Water; Prevention, Detection and Restoration, NWWA, Worthington, Ohio pp. 234-266.

5. W. Emile Coleman, Jean W. Munch, Robert P. Streicher, H. Paul Ringhand, and Federick C. Kopfler, 1984. The Identification and Measurement of Components in Gasoline, Kerosene, and No. 2 Fuel Oil that Partition into the Aqueous Phase After Mixing. Arch. Environ. Conta. Toxicol. 13, 171-178.

6. George P. Gross, 1971. Gasoline Composition and Vehicle Exhaust Gas Polynuclear Aromatic Content. Esso Research and Engineering Co., Linden, N.J. 124 p. PB 200 266.

7. Harold E. Guard, James Ng, and Roy B. Loughlin, Jr., 1983. Characterization of Gasolines, Diesel Fuels and Their Water Soluble Fractions. Naval Biosciences Laboratory, Oakland CA, September 1983.

8. H.J. McDermott and S.E. Killiany, 1978. Quest for a Gasoline TLV. Am. Ind. Hyg. Assoc. J. 39, 110-117, February 1978.

9. National Research Coucil, 1981. The Alkyl Benzenes. National Academy Press, Washington, D.C.

10. W.N. Sanders and J.B. Maynard, 1968. Capillary Gas Chromatographic Method for Determining the C3-C12 Hydrocarbons in Full-Range Motor Gasolines. Analytical Chemistry 40(3), 527-535.

11. Mark E. Myers, Jr., Janis Stollsteiner, and Andrew M. Wims, 1975. Determination of Hydrocarbons-Type Distribution and Hydrogen/Carbon Ratio of Gasolines by Nuclear Magnetic Resonance Spectrometry. Analytical Chemistry 47(12), 2010-2015.

12. L. L. Stavinoha and F. M. Newman, 1972. The Isolation and Determination of Aromatics in Gasoline by Gas Chromatography. Journal of Chromatogarphic Science 10(9), 583-589.