

NOAA Technical Memorandum ERL MESA-17



CHEMICAL AND PHYSICAL PROPERTIES OF REFINED PETROLEUM PRODUCTS

Herbert Curl, Jr.
Kevin O'Donnell

Marine Ecosystems Analysis Program
Boulder, Colorado
October 1977

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NATIONAL OCEANIC AND
ATMOSPHERIC ADMINISTRATION

Environmental
Research Laboratories

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CHEMICAL AND PHYSICAL PROPERTIES OF REFINED PETROLEUM PRODUCTS

Herbert Curl, Jr. and Kevin O'Donnell

1. INTRODUCTION

1.1 Composition of Fuel Oils

As a nation grows, its demand for oil also increases. If supplies of oil are not available within a country, then oil must be imported. With the increased traffic in oil comes the increased risk of major spills. The purpose of this paper is to examine the chemical, physical, and toxic properties of the refined petroleum products.

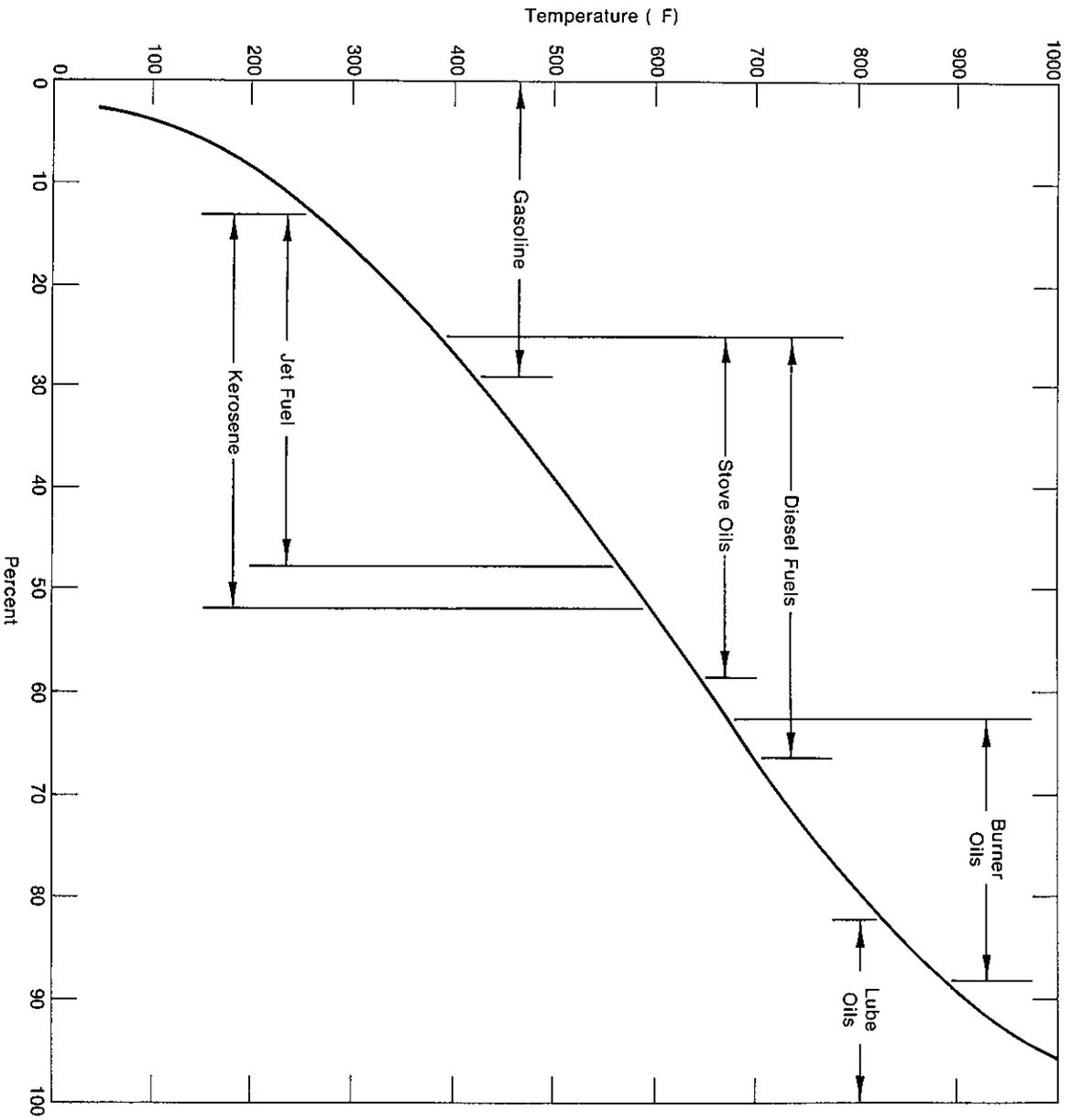
Crude oil is an extremely complex mixture of hydrocarbons. (Compounds containing only the elements carbon and hydrogen). In crude oil, the number of carbon atoms per molecule ranges from 4 to more than 40. The fewer carbon atoms that a hydrocarbon has, the lower its molecular weight and the greater its volatility. The various kinds of fuel oil (labeled Fuel Oil #1 through Fuel Oil #6) are obtained by distilling crude oil, and removing the different fractions (see Fig. 1). After distillation of some of the very volatile fractions such as naphtha and benzene, the first fuel oil fraction is labeled Fuel Oil #1 or kerosene. The number of carbon atoms per molecule lies between 10 and 16. The fraction that remains after distillation, Fuel Oil #6, is very viscous, being composed mainly of the heavy molecular weight hydrocarbons.

The chemical composition of fuel oils varies greatly. Petroleum fuels consist primarily of n-paraffins, isoparaffins (paraffin = alkane = saturated hydrocarbon chain), naphthenes (= cyclic, saturated hydrocarbon rings) and aromatics (= cyclic, unsaturated hydrocarbon, i.e., benzene or toluene). Olefins (= alkenes = unsaturated hydrocarbon chain) are not normally present, except under conditions of severe cracking or refining, although olefins may account for 30 percent of the weight of gasoline.

1.2 Solubility in Water

No exact numbers can be given for solubilities of fuel oil in water because the composition of a fuel oil varies from one refinery to another, although certain generalizations can be made about the solubility of the components of fuel oil (See graph 1). Hydrocarbons of a lower molecular weight are more soluble than those of a higher molecular weight. Branching of a hydrocarbon isomer (two hydrocarbons with the same formula, but different molecular arrangement) tends to increase solubility. For a particular carbon number, ring formation tends to increase solubility in water. An unsaturated hydrocarbon ring is more

FIGURE 1



soluble in water than a saturated ring of the same carbon number. Aromatic rings are more soluble than cyclic-alkanes or cyclic alkenes. Alkenes are more soluble than alkanes, and alkynes are more soluble than either (although they are very rare in fuel oils). The solubility of a hydrocarbon in sea water is less than in fresh water, because of a "salting out" effect. An increase in temperature of the water will greatly increase the amount of hydrocarbons dissolved in the water. Turbulence will also increase the rate of solution of hydrocarbons into the water.

1.3 Evaporation and Weathering

Under normal conditions of wind, waves, and temperature on an open sea, the evaporation rate of spilled oil may be quite significant. Most hydrocarbons with 4 or less carbon atoms are in the gas phase at room temperature, and are not present in fuel oils. Oil components with 5 or 6 carbon atoms per molecule will almost totally evaporate after only 1 hour exposure because of their low boiling points. After 5 hours, components with up to 8 carbons may evaporate. After 3 days, the fractions with less than 11 carbon atoms may disappear. After 10 days, fractions up to 15 carbon atoms may disappear. Part of the loss may be due to solubility of the components in the water, but most is due to evaporation. In the case of the spill of Kuwait crude oil from the TORREY CANYON in 1967, the volume of oil had decreased by 30 to 40 percent after several days of evaporation (Nelson-Smith 1973).

As the lighter components of an oil evaporate, the density of the remaining oil increases. For example, Kuwait crude oil has a density of 0.869 g/ml at 16°C (60.8°F). After 9 percent (by weight) is lost to evaporation, the density becomes 0.895 g/ml. After evaporation of 38.1 percent by weight, the density is 0.955 g/ml (Smith 1968). This is what occurred in the TORREY CANYON spill and corresponds to evaporation of fractions up to about 15 carbon atoms. It should be noted that the density of sea water at this temperature is 1.02 g/ml. It is not uncommon for higher boiling fuel oils and crude oils to form fairly inert "tar balls", composed of hydrocarbons with 16 to 40 carbon atoms, after loss of the more volatile components. The density of these balls may exceed that of the water, especially if they have collected suspended sand and sediment from the surrounding waters. In this case, the oil may sink to the bottom of the ocean.

When considering evaporation, we must also consider the thickness of the slick as a function of time. In the case of crude oil, a spill of 100 cubic meters of oil on calm water would create a slick that would be about 2 to 3 mm thick after 100 seconds. After 13 minutes, the slick would be about 0.5 to 0.7 mm thick. In 2 hours, it would be about 0.10 to 0.15 mm, and after about 1 day, it would be about 0.02 to 0.03 mm thick (Berridge et al. 1968).

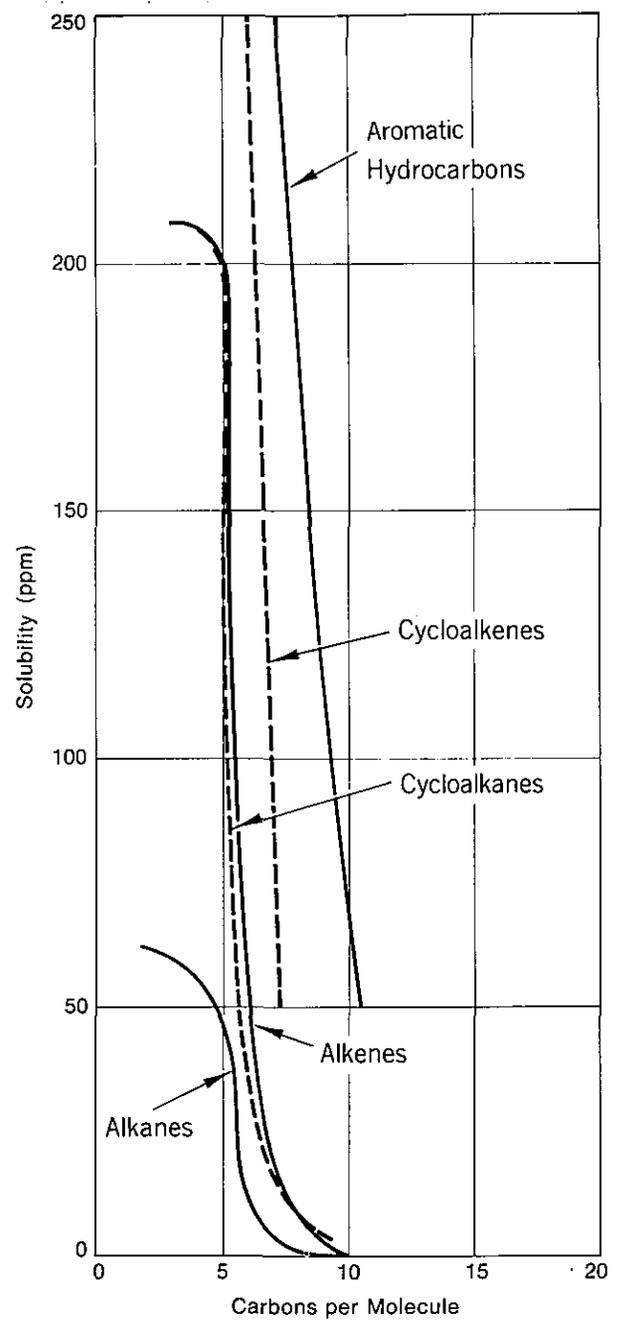


FIGURE 2

1.4 Toxicity

The most toxic components of fuel oils are the aromatics which are relatively highly soluble in water. These include benzene, toluene, xylene, naphthalene and others. Studies on small mammals indicate that death can occur by skin contact of 1.2 grams of benzene per kilogram body weight (International Technical Information Institute 1975-6). A good measure of the toxicity of a fuel oil is the percent of low boiling fractions, especially the aromatics. After the aromatic fractions, the toxicity decreases from olefins through naphthenes to paraffins. Within each group, the hydrocarbons of lesser molecular weight tend to be more toxic. Octane (8-carbon paraffin) and decane (10-carbon paraffin) are relatively toxic; dodecane (12-carbon paraffin) and paraffins of higher carbon number are nearly non-toxic. Olefins in the 12-carbon range are considered quite toxic, and 12-carbon aromatics even more so. Newly spilled oil is more toxic than weathered oil, because weathering removes much of the more volatile, toxic fractions. After about 10 days of weathering, some crude oils may assume the properties of a #6 fuel oil. Bunker C (F.O. #6) is virtually non-toxic in 4-day trials on lobsters, salmon and flatfish; lethal concentration to kill 50 percent is greater than 10,000 parts per million, because of its lack of volatile toxic components (Clark 1971).

In evaluating the toxicity of oil, a number of parameters must be considered including, the type of oil, the type of biological species used, concentration of oil, and length of time of contact. In choosing a biological species for toxicity testing, it should be noted that certain species are more resistant to oil than others. Although fuel oil #6 has little effect on most fish, it is one of the worst oils for birds, its effect being not toxic, but disabling, causing feathers to become matted down, making flight impossible and decreasing resistance to cold temperatures.

Of the various fuels, the most toxic is probably gasoline because of its high content of aromatics and other low-boiling hydrocarbons. Toxicity decreases as the type of fuel oil becomes less volatile. Thus, fuel oil #1 and #2 are moderately toxic. Toxicity decreases along the series F.O. #4, #5, with F.O. #6 being least toxic.

2. REFINED PETROLEUM PRODUCTS*

2.1 Gasoline

Physical Description: A clear, volatile liquid.

Chemical Description: A complex mixture of hydrocarbons, averaging 5-10 carbon atoms per molecule.

Virgin gasoline usually contains:

- 50 percent alkanes (paraffins).
- 40 percent cyclic alkanes (naphthenes).
- 10 percent aromatics.

Blended gasolines are mixtures of virgin gasoline, catalytically cracked gasoline, and thermally reformed gasolines, and may contain up to 30 percent alkenes (olefins).

Constants: Flash point: -45°F . (-43°C).

Density: 0.66 to 0.70.

Auto-ignition temperature: 495°F (257°C).

Vapor density: 3 to 4 times that of air.

Explosion limits of vapor in air:

- Upper: 7.6 percent.
- Lower: 1.4 percent.

Viscosity: Slightly less than water (see graph 2.)

Average boiling range: $90-363^{\circ}\text{F}$ ($32-184^{\circ}\text{C}$).

*Chemical and Physical Properties Data are from American Society for Testing and Materials (1974) and Sax (1968).

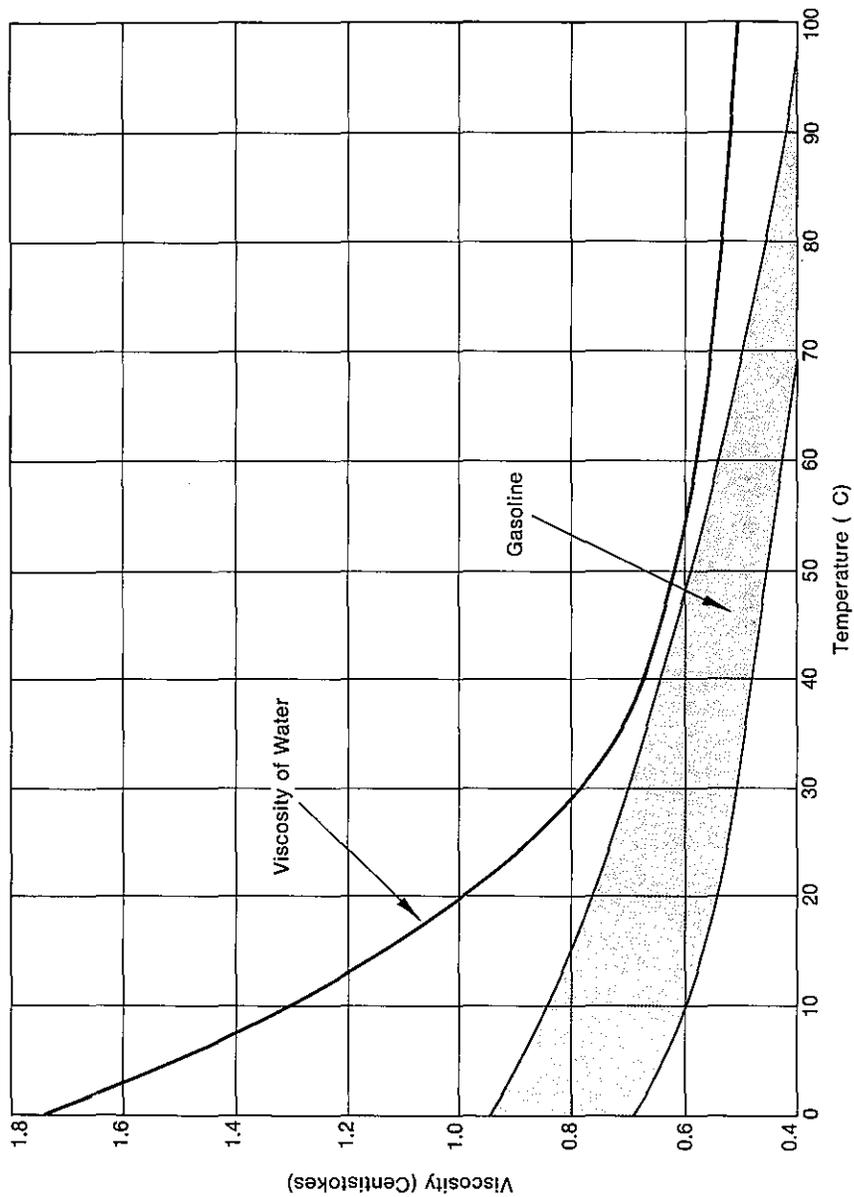


FIGURE 3

2.2 Fuel Oil Number 1 (Kerosene)

- Physical Description: A pale yellow or clear oily liquid.
- Chemical Description: A complex mixture of hydrocarbons, usually containing 10 to 16 carbon atoms per molecule with the average being 12. The average chemical composition by percent is:
- 35 percent alkanes (paraffins).
 - 60 percent cyclic alkanes (naphthenes).
 - 15 percent aromatics.
- A.S.T.M. Definition: A light distillate intended for use in burners of the vaporizing type in which the oil is converted to a vapor by contact with a heated surface or by radiation. High volatility is necessary to ensure that evaporation proceeds with a minimum of residue.
- Constants:
- Flash point: 100⁰-165⁰F (38-74⁰C).
 - Auto-ignition temperature: 444⁰F (229⁰C).
 - Density range: 0.80 to 0.875 (see graph 3).
6.879 to 7.085 pounds per gallon.
 - Explosion limits of vapor in air:
 - Upper: 5.0 percent.
 - Lower: 0.7 percent.
 - Vapor density: 4.5 times that of air.
 - Pour point: 0⁰F (-18⁰C).
 - Viscosity: See graph 4.
 - Average boiling range: 345-510⁰F (174-266⁰C).

See also Jet Fuels which are similar to Fuel Oil Number 1.

2.3 Fuel Oil Number 1 (Jet Fuels)

Jet Fuels similar to Fuel Oil Number 1 (Kerosene).

- J.P.-1: Flash point: 95⁰ to 145⁰F (35-63⁰C).
Auto-ignition temperature: 44⁰F (228⁰C).
- J.P.-4: Flash point: -10⁰ to 30⁰F (-23 - -1⁰C).
Auto-ignition temperature: 468⁰F (242⁰C).
Composition: 65 percent gasoline.
35 percent light petroleum distillates.
- J.P.-5: Flash point: 95⁰ to 145⁰F (35-63⁰C).
Auto-ignition temperature: 475⁰F (246⁰C).
Composition: Specially refined kerosene.
- J.P.-6: Flash point: 100⁰F (38⁰C).
Auto-ignition temperature: 435⁰F (224⁰C).
Composition: A higher kerosene cut than J.P.-4 with fewer impurities.

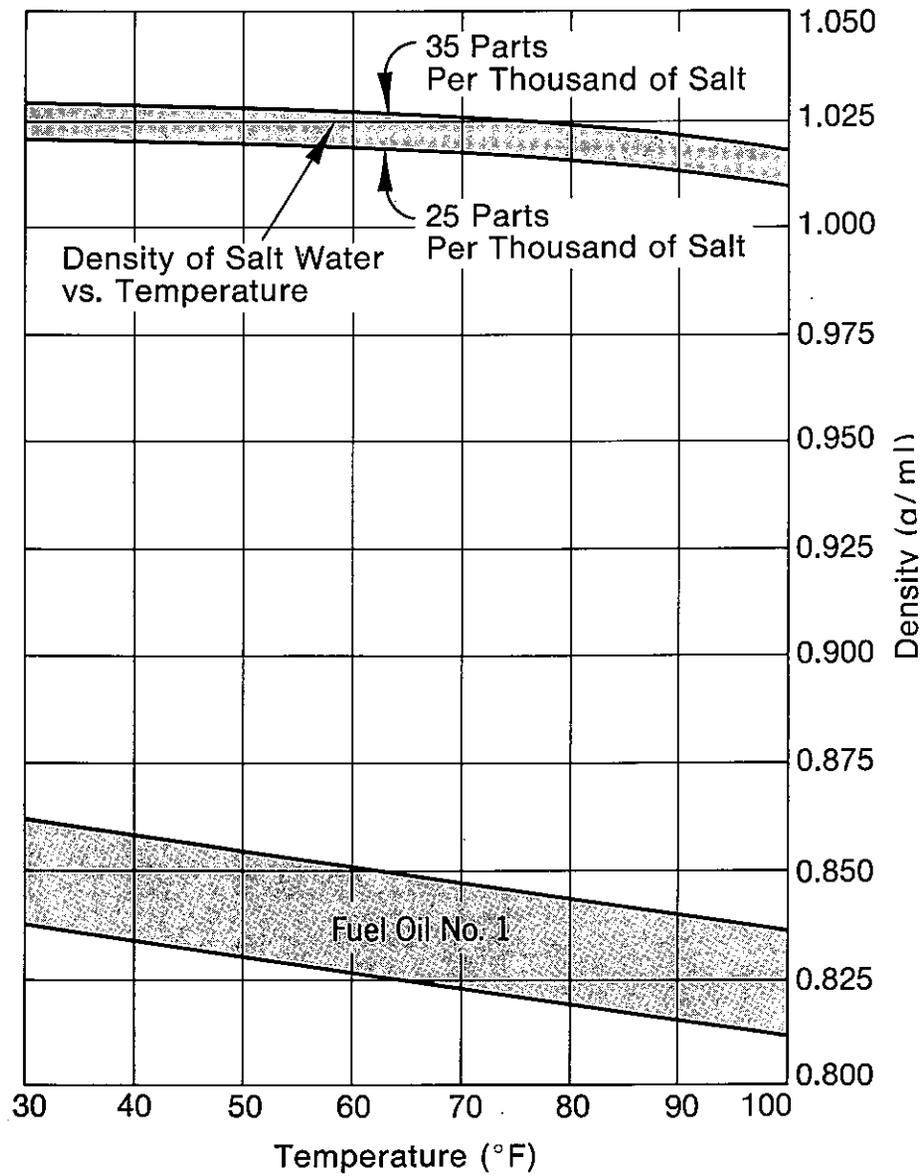


FIGURE 4

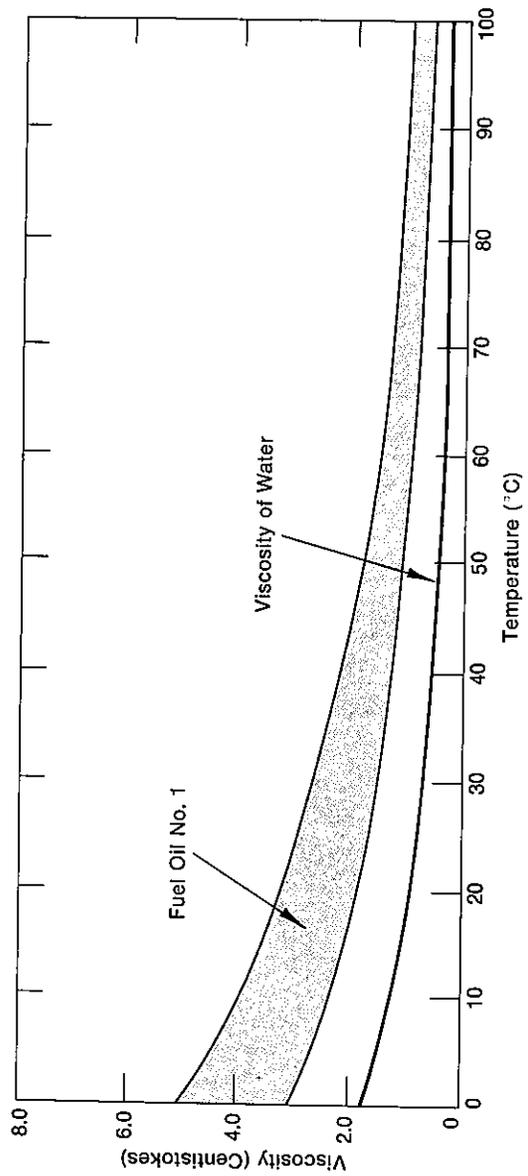


FIGURE 5

2.4 Fuel Oil Number 2 (Diesel Oil)

Physical Description: A yellow viscous liquid.

Chemical Description: A complex mixture of hydrocarbons with 12 to 20 carbon atoms per molecule, with the average being 15. The average chemical composition, by percent, is:

30 percent alkanes (paraffins).
45 percent cyclic alkanes (naphthenes).
25 percent aromatics.

A.S.T.M. Definition: A heavier distillate than Fuel Oil Number 1. It is intended for use in atomizing type burners which spray the oil into a combustion chamber where tiny droplets burn while in suspension. This grade of oil is used in most domestic burners and in many medium capacity commercial-industrial burners where its ease of handling and ready availability sometimes justify its higher cost over the residual fuel oils.

Constants: Flash point: 100⁰F (38⁰C).
Auto-ignition temperature: 494⁰F (257⁰C).
Pour point: 20⁰F (-7⁰C).
Boiling range: 93-365⁰F (34-185⁰C).
Density range: 0.825 to 0.925 (see graph 5).
7.128 to 7.490 pounds per gallon.
Viscosity: See graph 6.

Types of Number 2 Fuel Oil:

- No. 1-D A volatile distillate for engines in service requiring frequent speed and load changes.
- No. 2-D A distillate of lower volatility for engines and heavy mobile service.
- No. 4-D A fuel for low and medium speed engines.

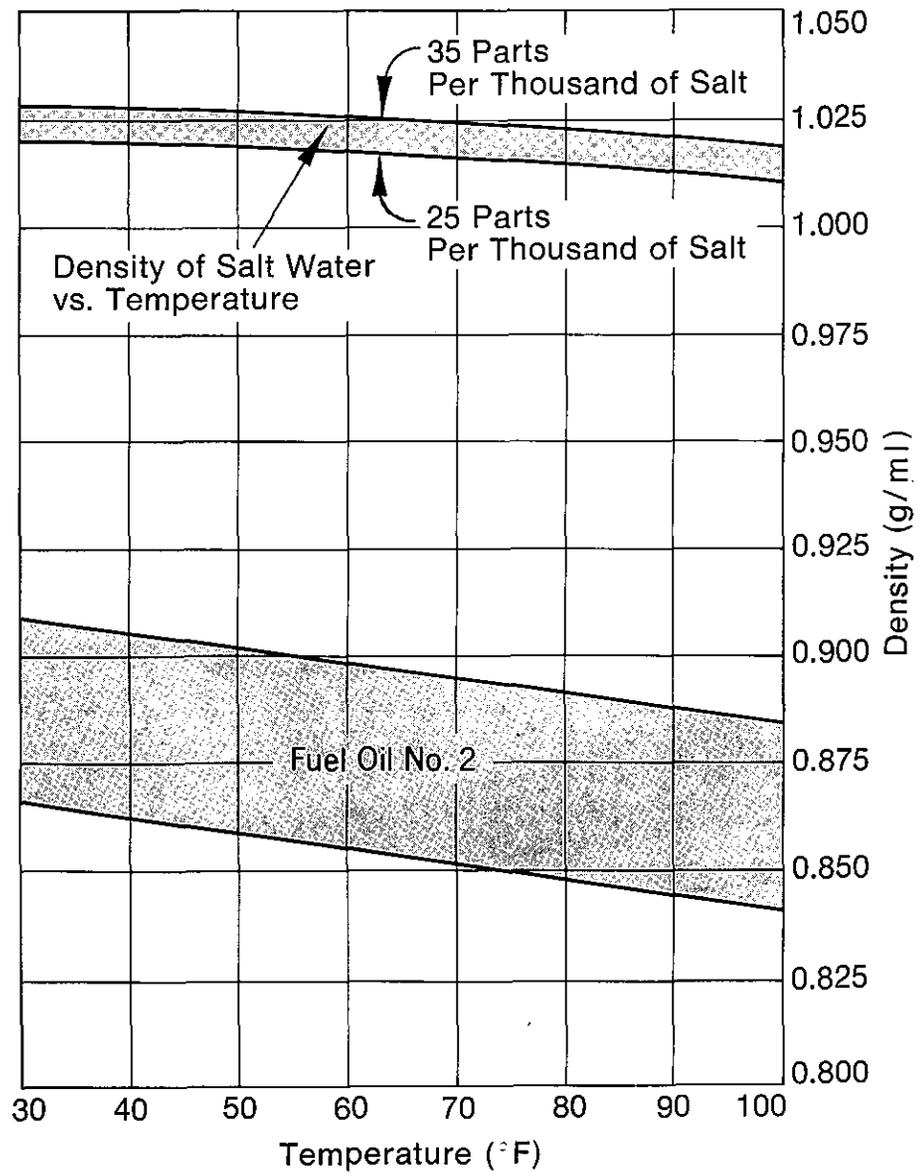


FIGURE 6

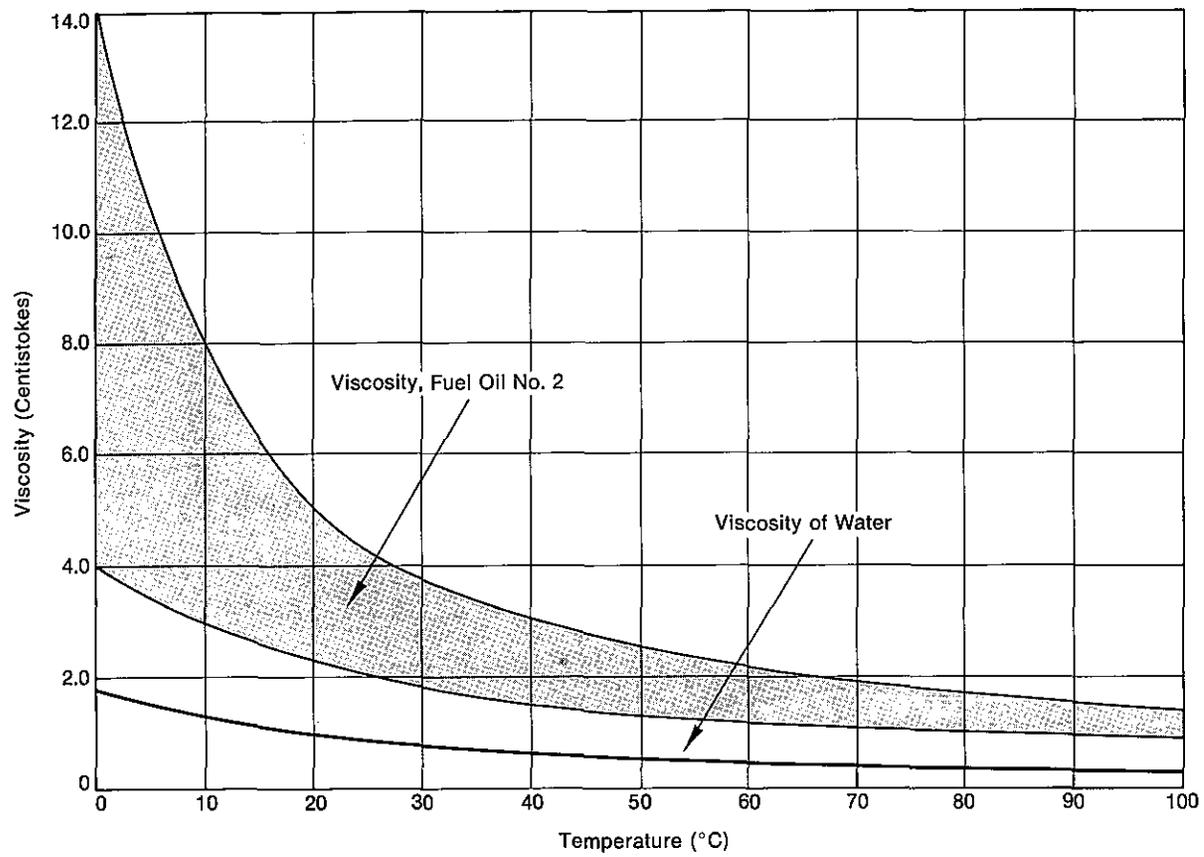


FIGURE 7

2.5 Fuel Oil Number 3

Formerly a distillate oil for use in burners requiring a low viscosity fuel, now incorporated as part of Fuel Oil Number 2.

2.6 Fuel Oil Number 4

Physical Description: Can be prepared by combining 40 percent Fuel Oil Number 2 and 60 percent Fuel Oil Number 6, or, may be a high-boiling-distillate or light residual of the crude oil.

A.S.T.M. Definition: Fuel Oil Number 4 is intended for use in burners that atomize oils of higher viscosity than domestic burners can handle. Its permissible viscosity ranges allow it to be pumped and atomized at relatively low storage temperatures. Thus, in all but extremely cold weather, it requires no preheating for handling.

Constants: Flash point: 130⁰F (54⁰C).
Auto-ignition temperature: 505⁰F (263⁰C).
Pour point: 20⁰F (-7⁰C).
Density range: 7.538 to 7.587 pounds per gallon (see graph 7).
Viscosity: See graph 8.

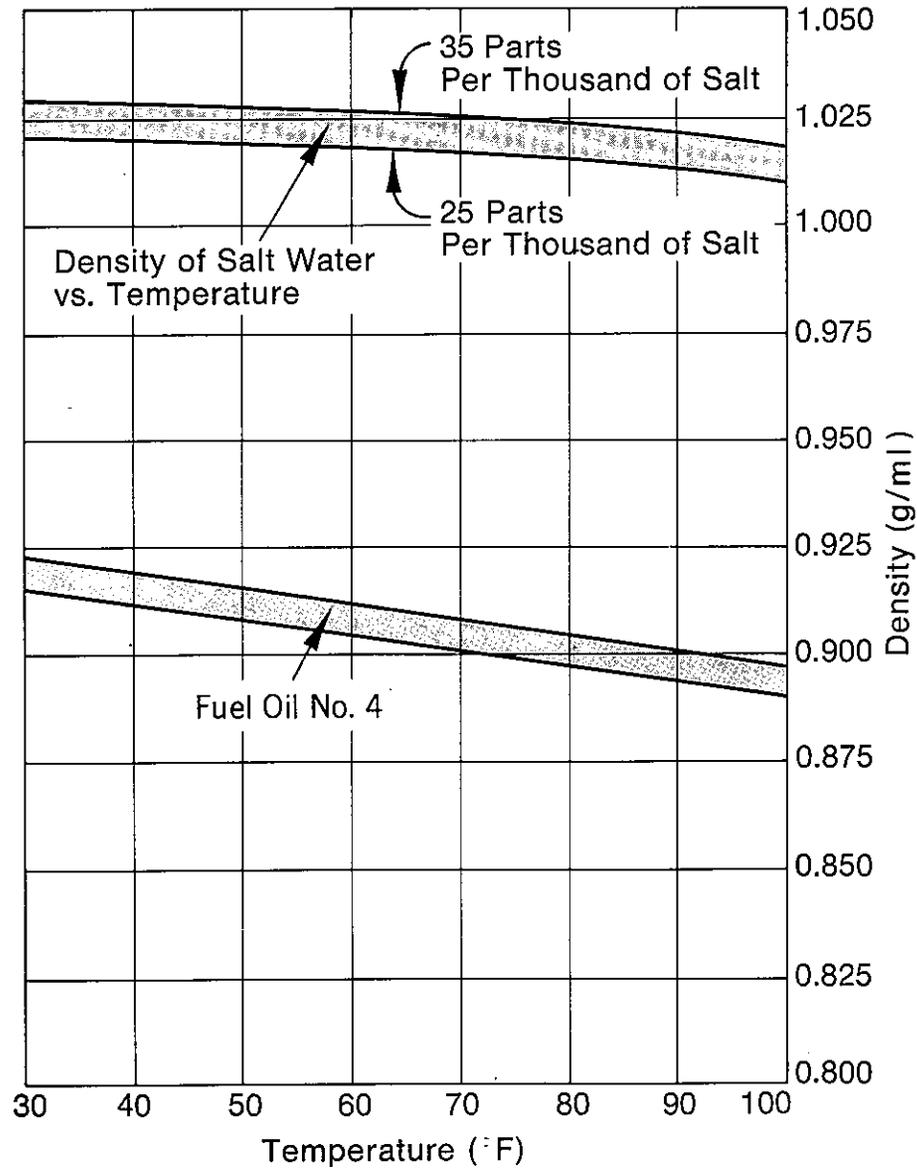


FIGURE 8

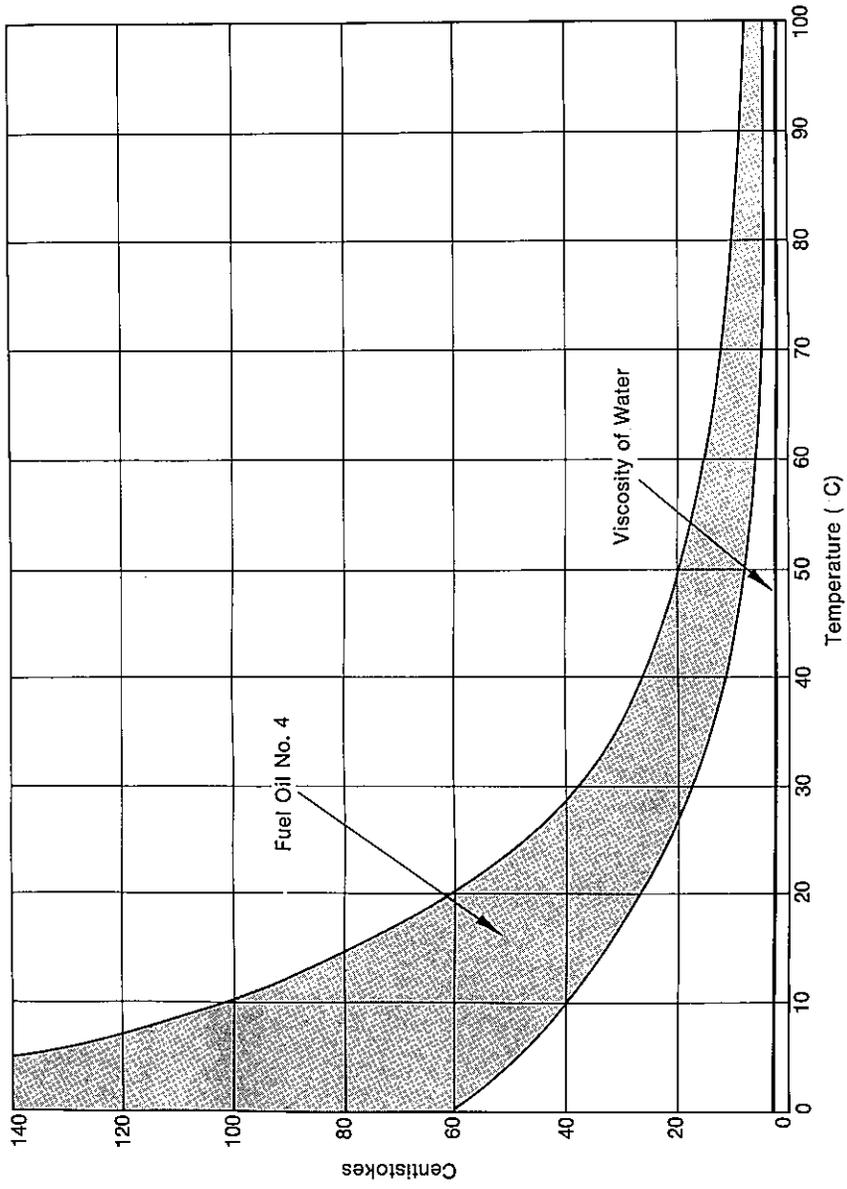


FIGURE 9

2.7 Fuel Oil Number 5 (Navy Special or Bunker 'B')

Physical Description: May be prepared by adding 20 to 25 percent of Fuel Oil Number 2 to 75 to 80 percent of Fuel Oil Number 6.

A.S.T.M. Definitions:

- A) Light: A residual oil of intermediate viscosity for burners capable of handling fuel more viscous than Fuel Oil Number 4 without preheating. Preheating may be necessary in some types of equipment for burning and in colder climates for handling.
- B) Heavy: A residual fuel oil more viscous than grade Number 5 (light) and is intended for use in similar service. Preheating to 170-220^oF (77-104^oC) is recommended before handling or use.

Flash point: over 130^oF (over 54^oC).

Density: 7.686 to 7.891 pounds per gallon (see graph 9).

Viscosity: See graph 10.

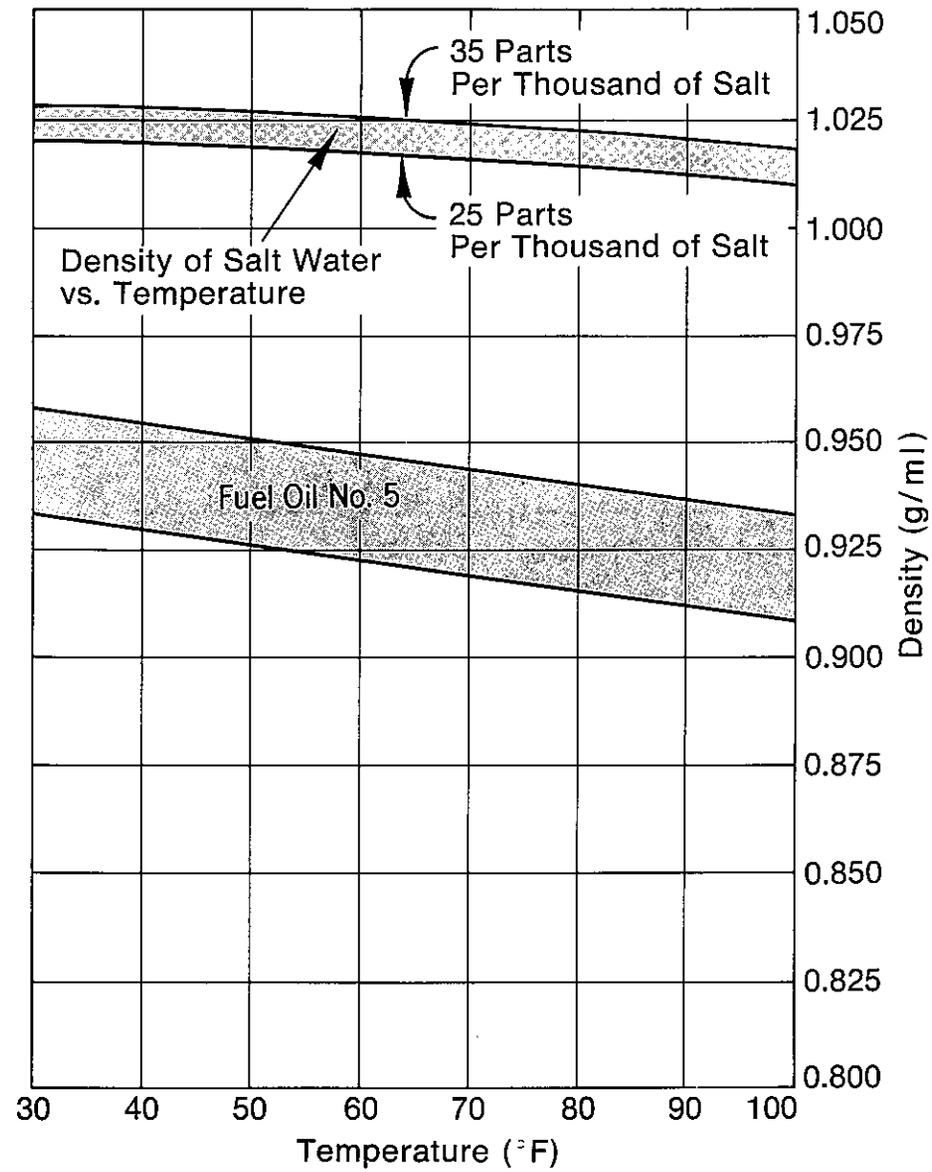


FIGURE 10

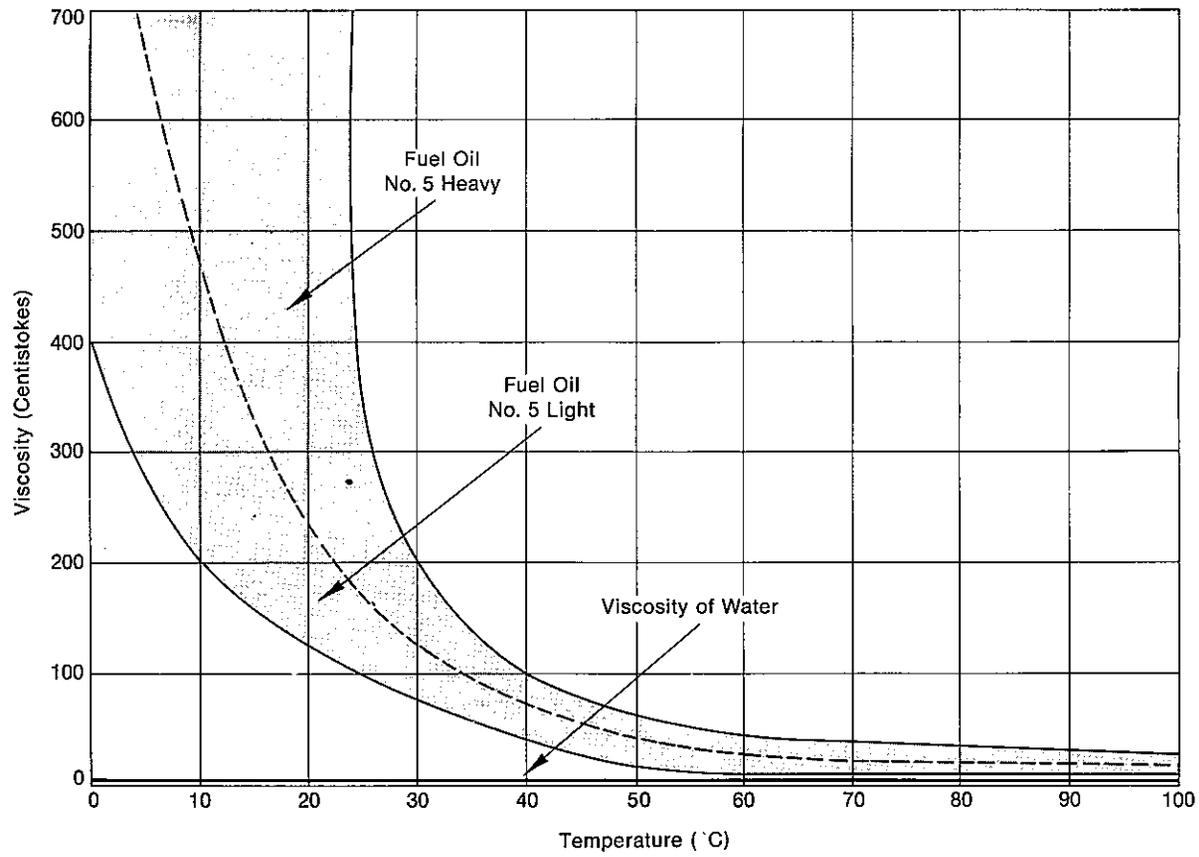


FIGURE 11

2.8 Fuel Oil Number 6 (Bunker 'C')

Physical Description: Very viscous, dark colored liquid.

Chemical Description: A complex mixture of heavy molecular weight hydrocarbons, averaging about 30 carbon atoms per molecule. The average chemical composition is:

15 percent alkanes (paraffins).

15 percent polar compounds, containing nitrogen, oxygen, or sulfur.

25 percent aromatics.

45 percent cyclic alkanes (naphthenes).

A.S.T.M. Definition: A high viscosity oil used mostly in commercial and industrial heating. It requires preheating to 220-260^oF (104-127^oC) to permit pumping and atomizing. The additional equipment and maintenance required to handle this fuel usually preclude its use in small installations.

Constants: Flash point: Above 150^oF (66^oC).

Density: 7.998 to 8.108 pounds per gallon (see graph 11).

Auto-ignition temperature: 765^oF (407^oC).

Pour point: Low pour = 60^oF maximum (16^oC max).

High pour = no maximum.

Viscosity: See graph 12.

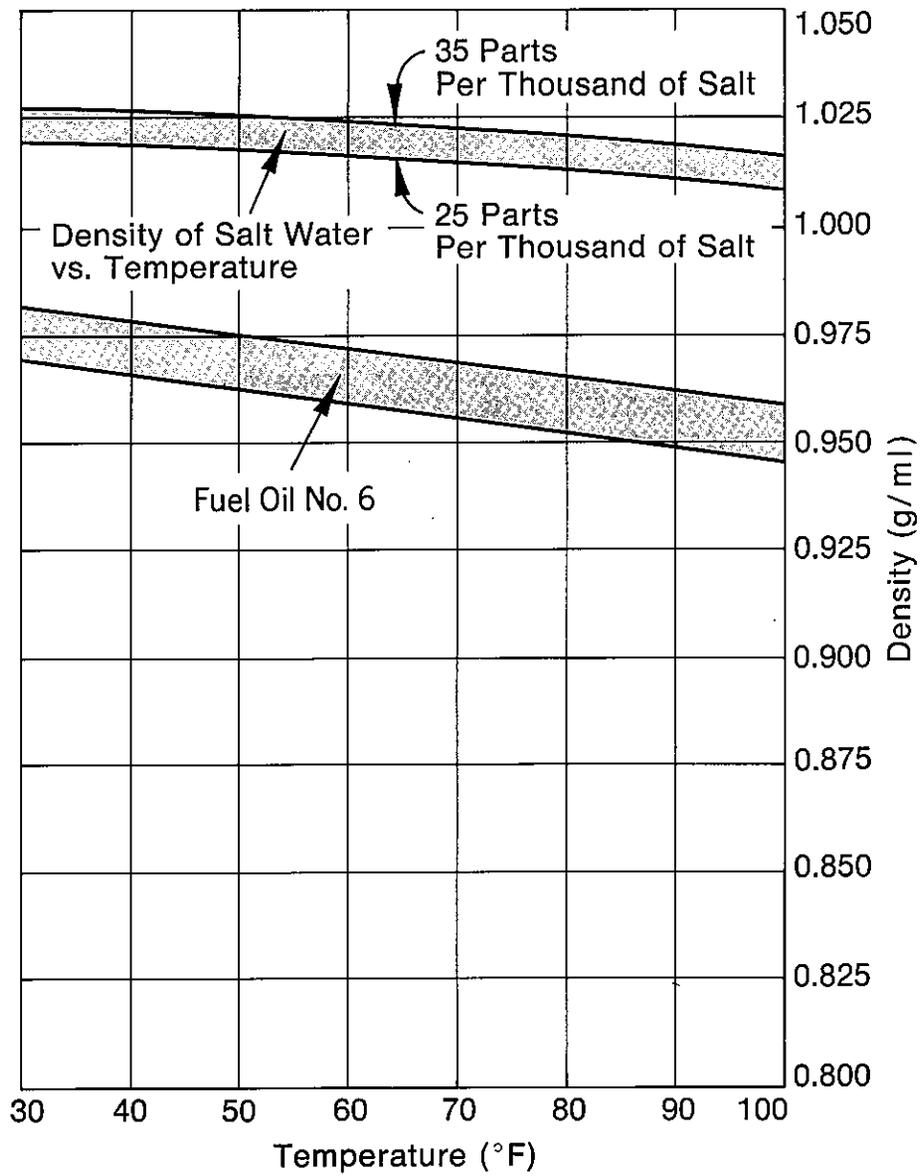


FIGURE 12

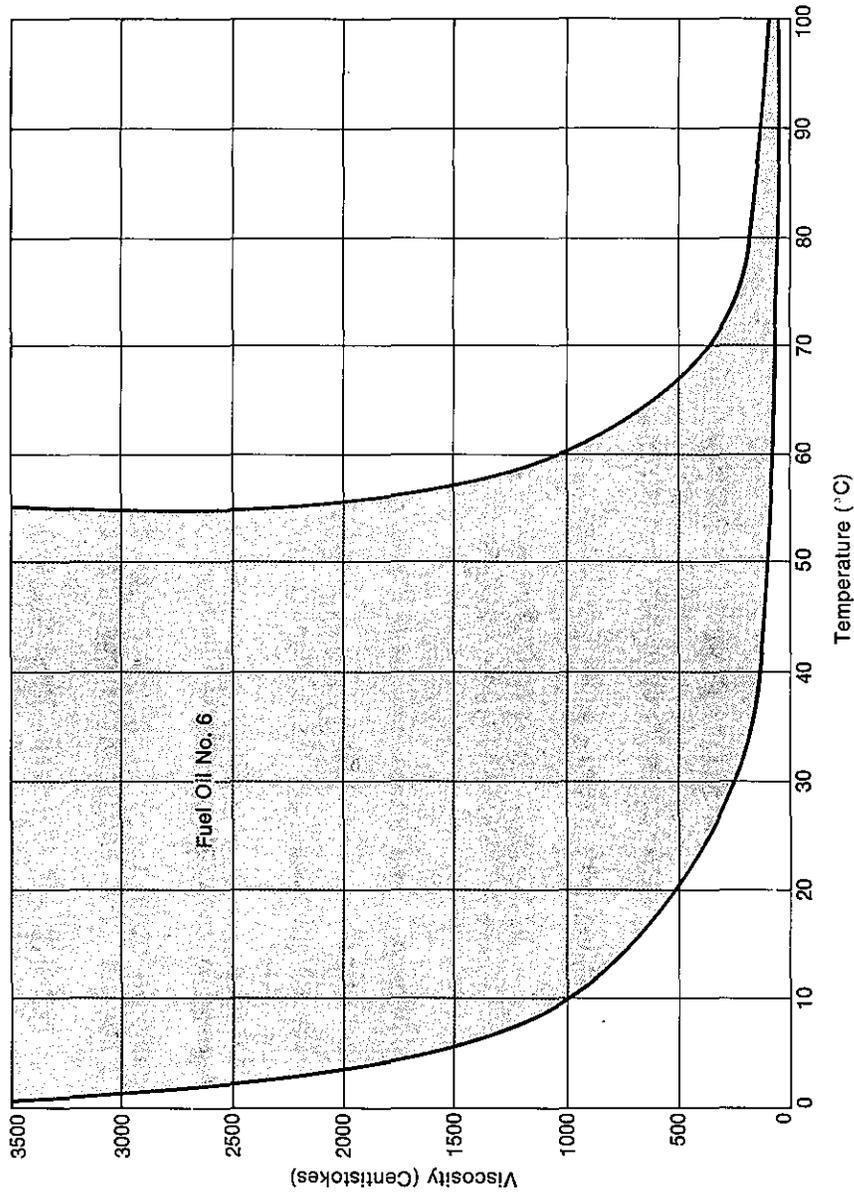


FIGURE 13

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Appendix A

ESTIMATES OF SPILL VOLUMES ON WATER (Hornstein 1973)

The color that is reflected by oil on water is related to the thickness of the oil slick. By observing the color of the slick (and thus, the thickness) and estimating the number of square miles covered by the oil, we can get a fairly accurate estimate of the volume of oil that is spilled. For example, oil with a thickness of 3×10^{-6} inches appears as a silvery sheen. If this silvery sheen is visible over an area of 1 square mile, then the volume of oil is 1.2×10^4 cubic inches, or 6.97 cubic feet of oil. By knowing that there are 7.481 gallons per cubic feet, we can conclude that there were

$$1 \text{ sq. mile} \times \frac{6.97 \text{ cubic feet}}{1 \text{ sq mile}} \times \frac{7.481 \text{ gallons}}{1 \text{ cubic foot}} = 52 \text{ gallons of oil on that 1 sq. mile surface.}$$

APPEARANCE OF OIL ON WATER	THICKNESS (inches)	VOLUME (gal/sq.mi)
1. Barely visible under most favorable light conditions. (Need to compare with clear water to observe)	1.5×10^{-6}	25
2. Visible as silvery sheen	3×10^{-6}	50
3. First trace of color may be observed (yellow, bronze, deep violet or purple)	6×10^{-6}	100
4. Bright bands of color are visible (purple, blue to green)	12×10^{-6}	200
5. Colors begin to turn dull (brick red, turquoise, trace of white, or pale yellow)	40×10^{-6}	670
6. Colors are much darker	80×10^{-6}	1300+

Appendix B

A SAMPLING OF THE WORLD'S MAJOR OIL SPILLS

TYPE OF OIL SPILL	YEAR OF SPILL																							Total Per Type
	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77		
Gasoline														1	1		1	2	4				9	
Jet Fuel												1						1					2	
F.O. #1																	1	1	1				3	
F.O. #2		1											1	2				4	7				15	
F.O. #4														1					1				2	
F.O. #5																		1	1				2	
F.O. #6	1				1		1			1			2	4	3		1	4	13	3			34	
Crude Oil						1	2				1	2	7	6	6		5	6	21	5			62	
TOTAL PER YEAR	1	1	0	0	1	1	3	0	0	1	1	3	10	14	11		8	18	48	8*				

*To up until April 17, 1975.

Appendix C

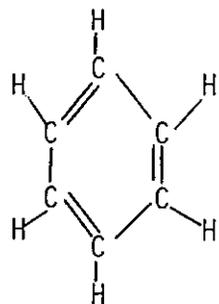
DEFINITIONS

Alkanes or Paraffins: Hydrocarbons with the formula $C_N H_{2N+2}$, where N is an integer greater than zero, i.e., $CH_3 - CH_2 - CH_2 - CH_2 - CH_3 = C_5 H_{12}$.

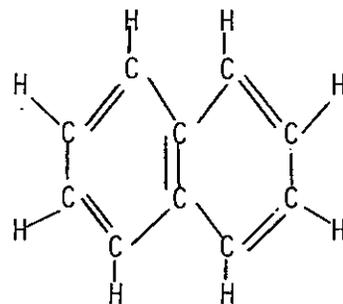
Alkenes or Olefins: Unsaturated Hydrocarbon: One with a double bond between two carbons:
 $CH_3 - HC = CH_2$ Propene (double bond)

Aromatic Hydrocarbons: A very stable cyclic hydrocarbon with alternating single and double bonds between carbons, and $4N + 2$ carbons per cyclic part of molecule ($N = 1, 2, 3, \dots$).

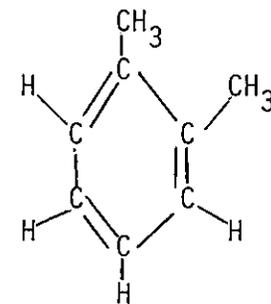
Examples:



Benzene

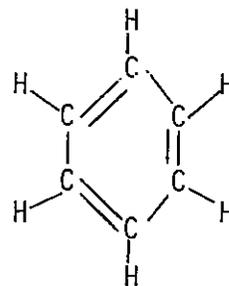


Naphthalene



ortho-Xylene

Often, an aromatic compound is shown without the hydrogens and with a circle in the middle to represent the double bonds, so benzene,



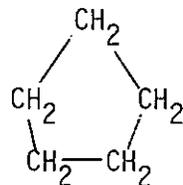
would be represented as



Auto-Ignition Temperature: The lowest temperature at which a substance will ignite, in absence of an open flame.

Barrel: 42 U.S. gallons of petroleum.

Cyclic Alkanes: or Naphthenes: Cyclic, saturated hydrocarbons, i.e.:



cyclopentane C₅H₁₀

Flash Point: The lowest temperature at which a substance gives off sufficient vapor to ignite in an open flame.

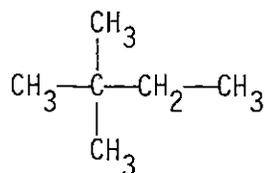
Fuel Oil: Any liquid or liquefiable petroleum product burned for generation of heat in a firebox or furnace, or for the generation of power in an engine, exclusive of oils with a flash point below 100^oF (38^oC) and oils burned in cotton or woolwick burners.

Fuel oils in common use fall into one of these four classes:

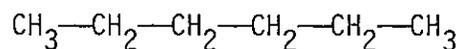
- Residual fuel oil that is a topped crude petroleum (crude oil with the more volatile components distilled off) or viscous residuals.
- Fuel oils that are distillates derived directly or indirectly from crude petroleum.
- Crude petroleum and weathered crude petroleum of very low commercial value.
- Blended fuel. Mixtures of two or more of the preceding classes.

Isomer: Different compounds with same chemical formula but different molecular arrangement.

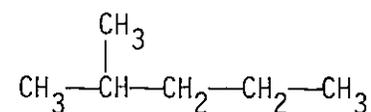
Three Isomers of Formula C₆H₁₄:



neo-Hexane



Normal Hexane



iso-Hexane

Naphthenes: See Cyclic Alkanes.

Olephins: See Alkenes.

Paraffins: See Alkanes.

Pour Point: The lowest temperature to which a solid substance must be heated in order for it to flow.

Saturated Hydrocarbon: An organic compound that contains no double or triple bonds (alkanes are saturated).

Saturated Compound:
$$\text{H}_3\text{C}-\text{CH}_2-\text{CH}_3$$

Propane

Unsaturated Hydrocarbon: An organic compound that contains one or more double or triple bond(s).

Unsaturated Compound:
$$\text{H}_3\text{C}-\text{CH}=\text{CH}_2$$

Propene

Appendix D

CONVERSIONS

	To Convert From:	To:	Multiply by
Amount of Oil			
A) Volume			
	Barrels	Gallons	42.0
	Gallons	Barrels	0.0238
	Tons of Fuel Oil #1	Gallons	280-290
	Fuel Oil #2	Gallons	267-280
	Fuel Oil #4	Gallons	263-265
	Fuel Oil #5	Gallons	253-260
	Fuel Oil #6	Gallons	246-250
B) Weight			
	Pounds	Tons	0.0005
	Tons	Pounds	2000
	Gallons of Fuel Oil #1	Pounds	6.879 to 7.085
	Fuel Oil #2	Pounds	7.128 to 7.490
	Fuel Oil #4	Pounds	7.538 to 7.587
	Fuel Oil #5	Pounds	7.686 to 7.891
	Fuel Oil #6	Pounds	7.998 to 8.108
Temperature			
	Fahrenheit	Centigrade	See table 1
	Centigrade	Fahrenheit	See table 1

6. Table 1. Temperature Conversions

$^{\circ}\text{C}$	$^{\circ}\text{F}$	$^{\circ}\text{C}$	$^{\circ}\text{F}$
0°C	32 $^{\circ}\text{F}$		
1	33.8	20	68.0
2	35.6	21	69.8
3	37.4	22	71.6
4	39.2	23	73.4
5	41.0	24	75.2
6	42.8	25	77.0
7	44.6	26	78.8
8	46.4	27	80.6
9	48.2	28	82.4
10	50.0	29	84.2
11	51.8	30	86
12	53.6	31	87.8
13	55.4	32	89.6
14	57.2	33	91.4
15	59.0	34	93.2
16	60.8	35	95.0
17	62.6	36	96.8
18	64.4	37	98.6
19	66.2	37.8	100.0

Formula for $^{\circ}\text{F}$ to $^{\circ}\text{C}$:

$$(^{\circ}\text{F}-32) \times \frac{5}{9} = ^{\circ}\text{C}$$

Formula for $^{\circ}\text{C}$ to $^{\circ}\text{F}$:

$$(^{\circ}\text{C} \times \frac{9}{5}) + 32 = ^{\circ}\text{F}$$