

Maritime Transportation, Chemistry and Oil

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Introduction

Nowadays the most important natural product on the human being's life is crude oil, the impact being higher for more industrialized countries. Petroleum products are present in all aspects of our lives, in fact as happened in the recent past, abrupt changes in its price provoked economical instability with the corresponding loss of citizens' quality of life.

According to the Review of Maritime Transport 2009, a yearly report of UNCTAD,¹ crude oil and petroleum products represents one third of the total world seaborne trade for the year 2008 (see Figure 1). Shipping reveals, on a per ton basis, as the most efficient and environmentally way of transportation over long distances.

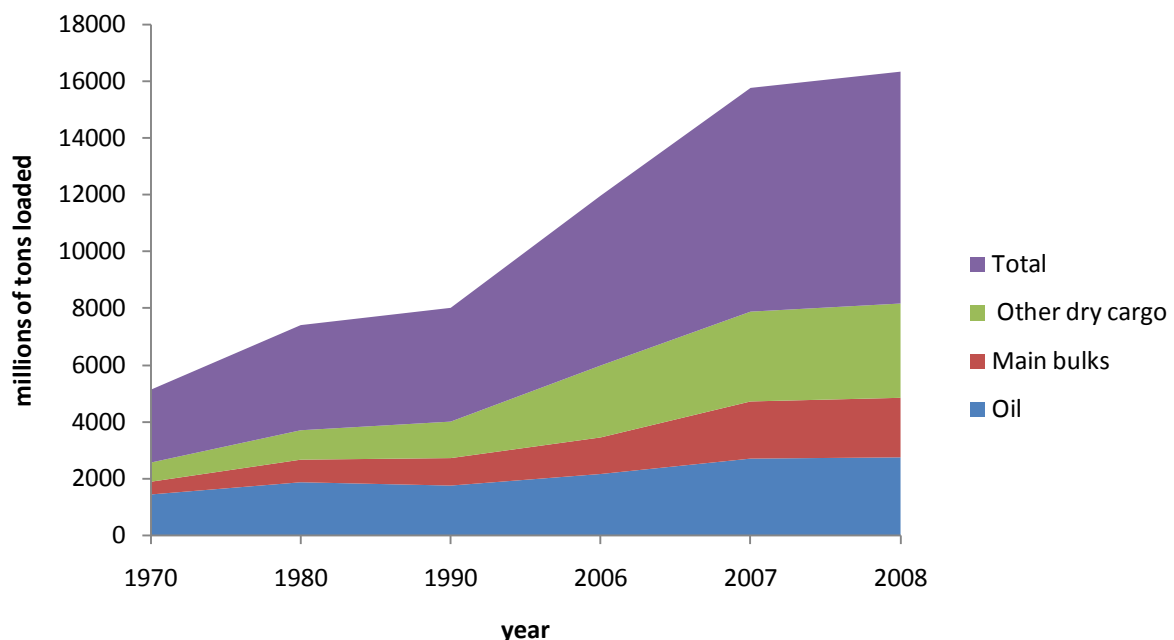


Figure 1. International seaborne trade (Source: Review of Maritime Transport 2009)

Crude oil (or petroleum²) a natural product, usually obtained by drilling wells from beneath the surface of earth's surface, is a flammable liquid composed mainly of hydrocarbons. Chemical composition of petroleum is strongly dependent on the source, which in practice means different physical properties, e.g., the appearance of crude oil varies greatly with its composition, its colour going from heavy black (mainly), to brown, red, amber, and even nearly colourless.

¹ UNCTAD: UNITED NATIONS CONFERENCE ON TRADE AND DEVELOPMENT (<http://www.unctad.org>)

² Petroleum comes from Greek *πετρέλαιον*, literally "rock oil"

Petroleum is used mostly as "primary energy" source, nearly of the 85% of crude oil is converted in petroleum-based fuels (gasoline, diesel, jet, heating, ...), the remaining being used as raw material for production of a lot of chemicals also omnipresent in our lives (plastics, synthetic textiles, fertilizers, pesticides, solvents, paints, cosmetics, additives, pharmaceuticals, etc.).

As reported in the Review of Maritime Transport 2009, in 2008 global oil production increased by 0.4 percent (380,000 barrels per day) to reach 81.8 mbd, whereas the share of tanker trade in the total world seaborne trade amounted to 33.7 per cent, and world shipments of tanker cargoes reached 2.75 billion tons, two thirds of which were crude oil. Crude oil seaborne shipments increased by an estimated 1.1 per cent, to reach 1,83 billion tons, and world shipments of petroleum products are estimated to have increased by 2.7 per cent, to reach 915.3 million tons (see Figure 2)³.

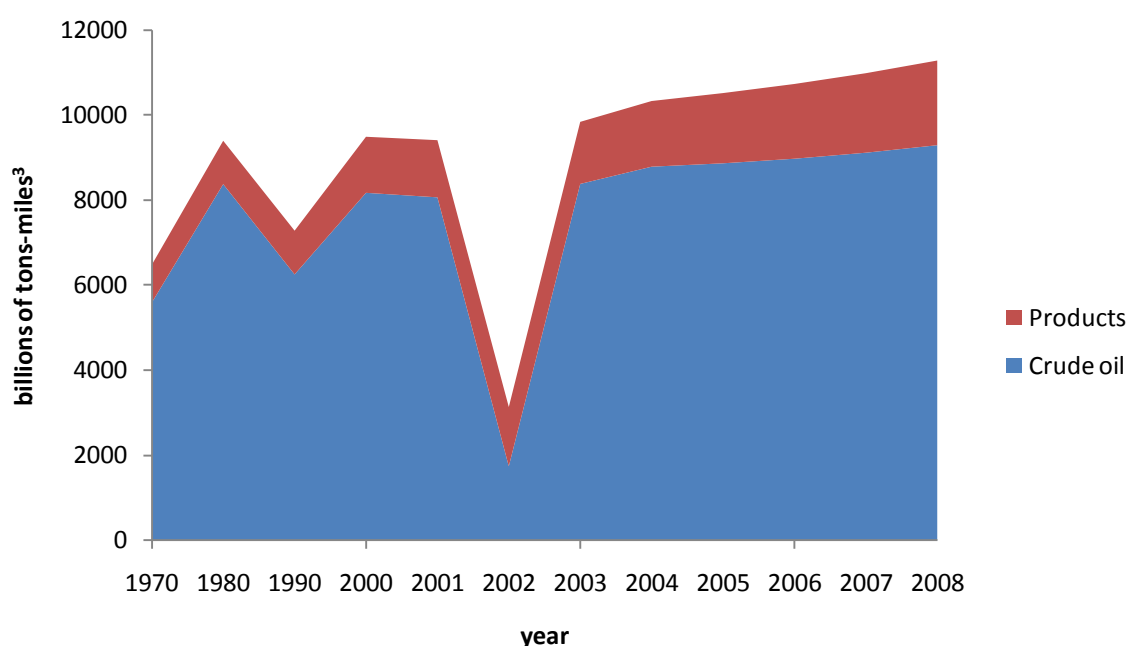


Figure 2. World seaborne trade of crude oil and petroleum products
(Source: Review of Maritime Transport 2009)

Crude oil and petroleum products, in addition to being transport commodities, are also the main source of fuel which propels ships, which means vessels are a source of air pollution, carbon dioxide and other combustion products are released to the atmosphere thus increasing the concentration of greenhouse gases (GHGs), which are considered to cause global

³ Ton-mile is a unit of freight transportation equivalent to a ton of freight shipped one mile.

warming, and as a consequence climate change. According to the Second IMO GHG Study (2009),⁴ using year 2007 as reference, near of 300 million of tonnes of fuel were burnt by international shipping, which implies c.a. 900 million of tonnes of CO₂ entering the atmosphere, such amount will increase 20% by 2020, and grow by a factor of 2 to 3 by 2050 as a result of the growth in maritime transportation.

Although those figures seem impressive, shipping is one of the lowest emitting freight transport options (Figure 3), and within ships, tankers being more polluting (Figure 4).

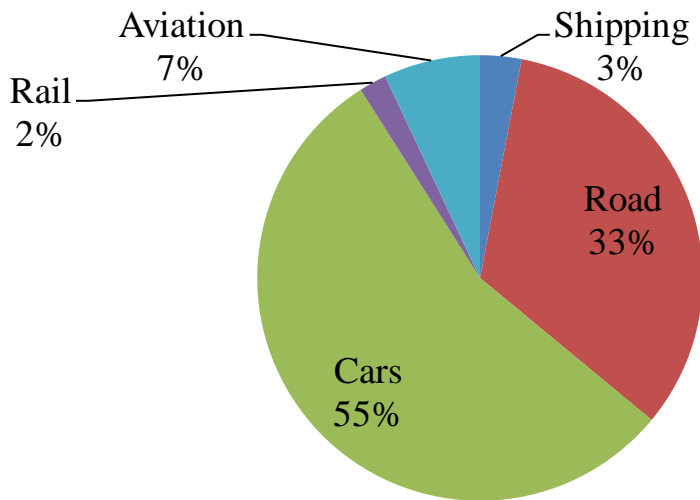


Figure 3. Percent CO₂ emissions from transport by mode

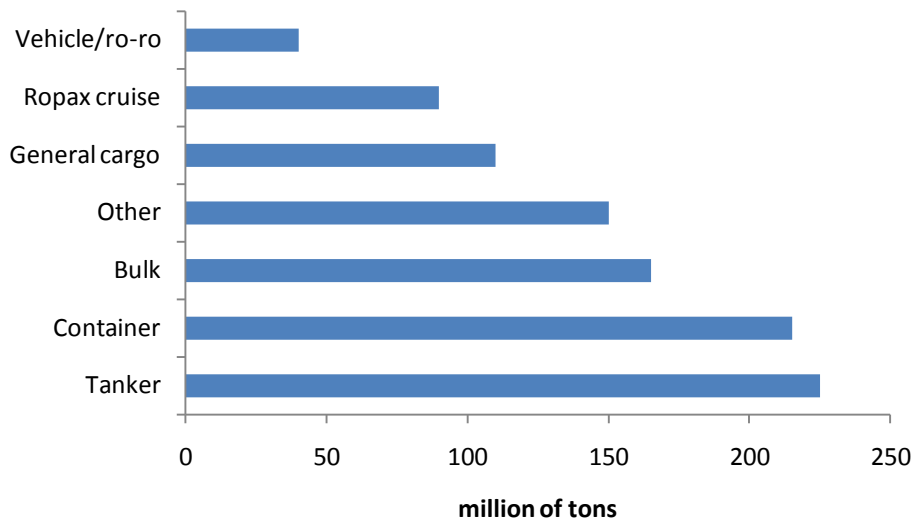


Figure 4. Estimation of CO₂ emissions by cargo carriers
(Source: Review of Maritime Transport 2009)

⁴ http://www.imo.org/Environment/mainframe.asp?topic_id=1823

Components of crude oil are separated by fractional distillation at an oil refinery as shown in the following figure together with its common usage:

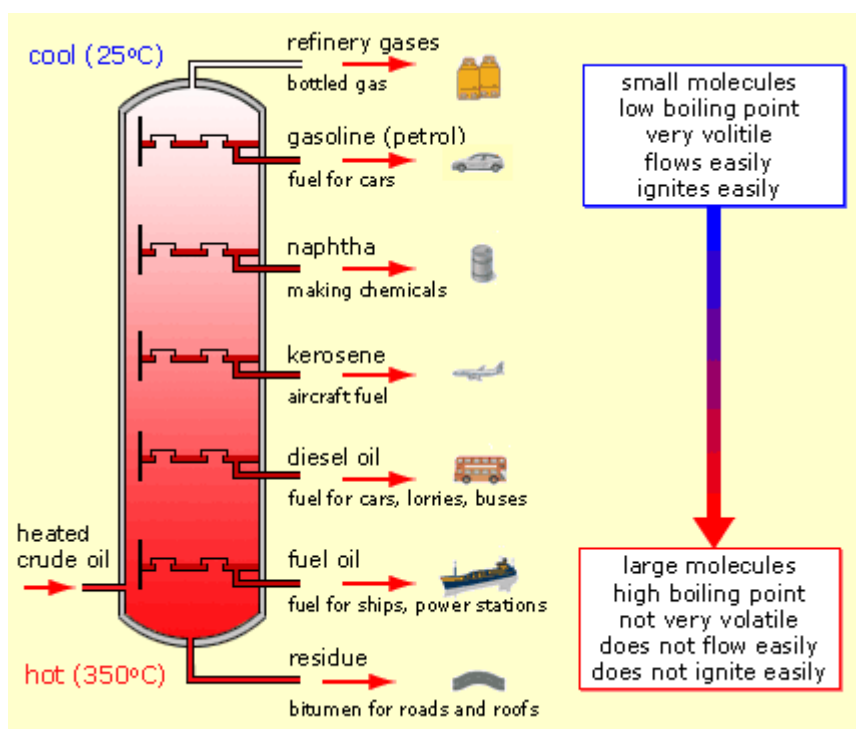


Figure 5. Components of crude oil obtained by fractional distillation⁵

Separation of the petroleum compounds is based on its different boiling point; those with lower boiling point leave the fractioning column from top (e.g. liquefied petroleum gas – LPG–, gasoline, naphtha), whereas those having higher boiling point leave it at the bottom (e.g. fuel oil, lubricating oils, wax and tar), and in the middle distillates compounds like kerosene and diesel. Sometimes oils are classified considering the amount of each the distillation fraction present in crude oil.

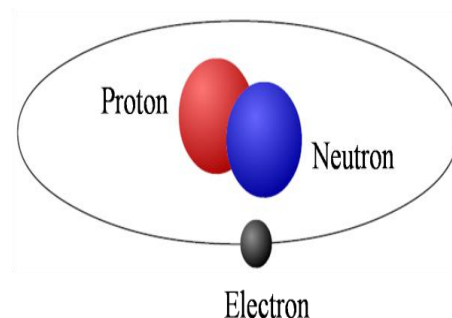
A bit of chemistry

Generally speaking matter is a mixture of so called (chemical) elements, which are substances that cannot be broken down by chemical means., i.e., they cannot be separated into simpler substances; till now 118 elements have been observed, of which 94 occur naturally on Earth.

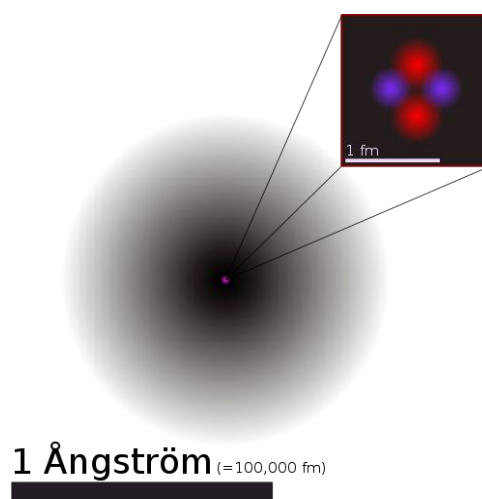
⁵ Image taken from http://1.bp.blogspot.com/_UWDSu9sy7fA/R71AWz0y1SI/AAAAAAAAANI/OhXtwcWCBJw/s320/pds_fractional_dist_1.gif

Elements can be classified in several ways, the most popular being the periodic table of (chemical) elements, which, as appearing in Wikipedia,⁶ can be found in the [Appendix](#); there links to some periodic tables at Internet are also provided. Roughly speaking, elements in the same column share similar chemical reactivity.

The smallest component of an element having its chemical properties is called an atom, which could be described in terms of the subatomic particles: protons, neutrons, and electrons. One of simplest way to visualize an atom is to consider it as a small solar system, i.e., electrons (planets) orbiting around the nucleus (sun), the latter containing protons and neutrons (see the Figure at right).



Although modern physicochemical theories describe the atom as an entity comprising a nucleus surrounded by electron clouds (or shells like in an onion), the simplest description of chemical reactivity uses electrons as point particles (like planets in the solar system analogy). In the accompanying figure the modern view of the helium atom is shown: nucleus (pink) and electron cloud (black-grey);⁷ the upper right is a magnification of the protons and the neutrons in the nucleus.



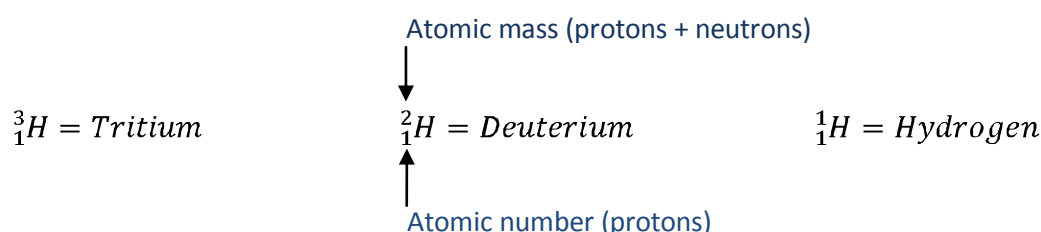
At this stage two fundamental physicochemical magnitudes should be considered: mass and electric charge. Proton and neutron are nucleons, both having almost the same mass, which is nearly 2000 times the mass of the electron; on the other hand, the proton bears +1 elementary electrical charge, the same but negative the electron, and the neutron carries no charge. Elements are neutral as a consequence of having the same number protons and electrons; in fact the order in the periodic table depends on this number, called atomic number. This number is usually written as a subscript before the symbol of the element, e.g., ${}^1\text{H}$, ${}^{12}\text{C}$, ${}^{16}\text{O}$.

⁶ http://en.wikipedia.org/wiki/Periodic_table

⁷ Image taken at http://en.wikipedia.org/wiki/File:Helium_atom_QM.svg [1 Ångstrom (Å) = 10^{-10} m]

A related term is mass number, which is the total number of protons and neutrons in the atom. Chemical elements consist of atoms with the same number of protons (and electrons, of course). Chemical elements ordering in the periodic table is based on the atomic number as well as their reactivity, which is related with the number of electrons in the different shells, mainly in the more external (the valence shell).

Atoms with different number of neutrons and the same atomic number, known as isotopes, are considered to be the same elements, for example hydrogen has three isotopes, in this case specific names are given (see below); isotopes distinguish by its atomic mass, e.g., oxygen-16 (O-16), oxygen-18 (O-18). Natural elements are mixture of the corresponding isotopes, commonly used atomic masses are a weighted average of their atomic masses according to their natural abundance.



Although the unified atomic mass unit (u),⁸ is the mass unit used to express atomic masses, usually it is easy to handle mass of elements in grams, then the term mol enters in scene, which is the number of atoms in exactly 12 grams of carbon-12, such number being known as the Avogadro's constant ($N_A = 6.022 \cdot 10^{23}$), i.e., a mol of atoms contains $6.022 \cdot 10^{23}$ atoms. Mass numbers at the periodic table of (chemical) elements have both meanings: atomic masses expressed in unified atomic mass (u), and the grams corresponding to a mol of each element.

Chemical substances are combination of two or more elements (atoms of different elements at the molecular level). Compounds containing lighter elements show more differences in chemical reactivity when different isotopes are involved.

A chemical reaction is the transformation of one set of chemical compounds (or elements) to another, which is symbolized by the corresponding chemical equation as shown in Figure 6.

⁸ For short, the unified atomic mass (u), or Dalton (Da), is defined as one twelfth of the mass of an isolated atom of carbon-12, which means $1 \text{ u} = 1.660 \cdot 10^{-27} \text{ kg}$ (<http://goldbook.iupac.org/U06554.html>)

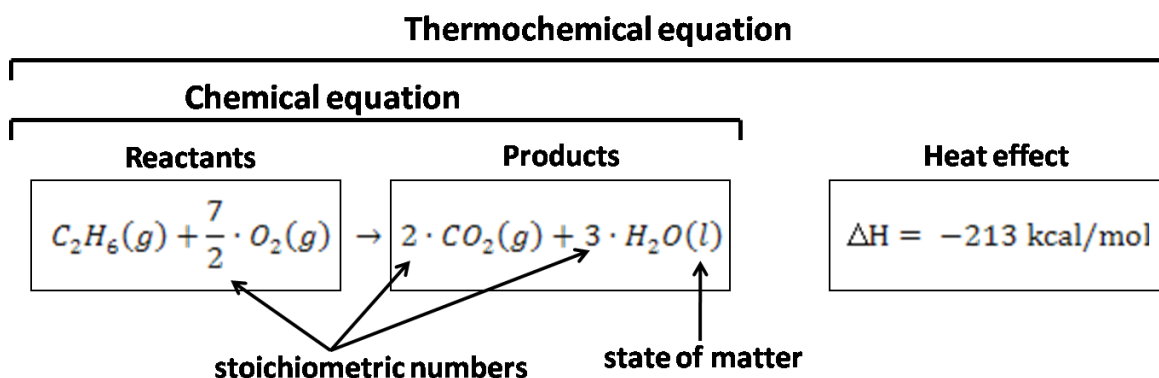


Figure 6. Items of the (thermo)chemical equation⁹

The chemical equation should read: 1 mol of ethane (30 g), in the gas phase, reacts with 7/2 moles (112 g-3.5x32-) of oxygen, also in the gas phase, forming 2 moles (88 g-2x44-) of carbon dioxide, in the gas phase, and 3 moles (54 g-3x18-) of liquid water, and at the same time 213 kcal per mol of ethane are evolved.^{10,11} Actually chemical equation expresses the ratio reactants should be mixed up, and the corresponding relative amounts of products to be obtained.

Sometimes state of matter is omitted, and also a compound (a catalyst) or other information, like temperature or pressure conditions, is written over/down the arrow. Catalyst speeds up the reaction rate; and the stated conditions, if any, are required to the reaction proceed.

Chemical equations must be balanced; the same type and number of atoms of each element must appear on both sides of the arrow, which is an expression of the mass law conservation. A single arrow has to do with the chemical reaction going to completion, i.e., at least one of the reactants completely disappears at the end of the reaction. Not always reactants are in stoichiometric amounts, the relative quantities dictated by the chemical equation; in fact it is common all are in excess but one, the limiting reagent.

Sometimes two opposite arrows (\rightleftharpoons) are used in a chemical equation in which both reactants and products are present at the end of the reaction, chemical equilibrium is used to refer to.

⁹ 1 Btu (British thermal unit) = 1.06 kJ (kilojoules) = 0.25 kcal (kilocalories).

¹⁰ The number of moles corresponding to a given mass of a compound is obtained dividing this mass by its molecular weight (both in the same units).

¹¹ Usually enthalpy (H) is the thermodynamic state function used to describe heat effects.

Chemical substances are symbolized by its chemical formula, a way of expressing the type and number of the atoms of chemical elements present in each compound; the corresponding molecular weight (M_w)¹² calculated as the sum of the atomic masses of its composing elements, number of atoms of the same element should be taken into account, e.g., the molecular weight of C_2H_6 is $2 \times 12 + 6 \times 1 = 30$ (for sake of simplicity approximate rounded atomic masses were used).

Chemical reactions do not only form different chemical compounds, usually there are also associated heat effects, as indicated in Figure 6. Chemical processes releasing heat are named exothermic, the contrary endothermic; by convention in chemistry, minus sign being used for the former, and positive for the latter. The actual energy effect, as well the amount of product(s), depends on the mass of the reactants participating in the reaction, e.g., in the example given in Fig. 6, the heat release will be in proportion to 213 kcal for each 30 g (1 mol) of ethane (assuming oxygen is present at least in stoichiometric ratio). Although many chemical reactions are spontaneous, often coming about only after the input of energy (heat, light, electricity, even mechanical).

In chemical reactions electronic, and usually atomic, rearrangement take place giving different chemical substance(s), this means, roughly speaking, in a chemical reaction atoms assemble in a different way, i.e., bonds between them should be broken and formed.

Main types of chemical bonds are:

- Covalent: pairs of electrons are shared between bonded atoms, usually two. Figure 7 illustrates the modern view of the chemical bond.

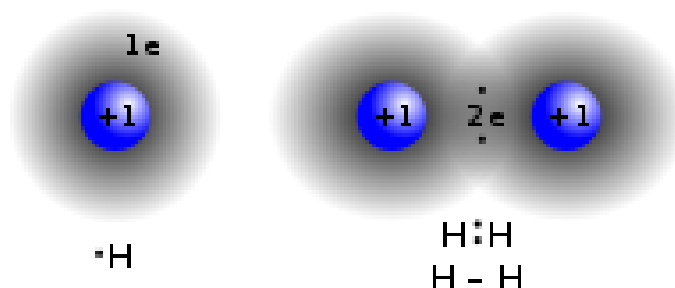


Figure 7. Electron clouds overlap to form the covalent bond in hydrogen molecule¹³

¹² Also called relative molecular mass (M_r) (<http://goldbook.iupac.org/R05271.html>).

¹³ Image taken from http://en.wikipedia.org/wiki/File:Covalent_bond_hydrogen.svg

For sake of simplicity chemical bonds, and even chemical reactions, often are described by representing electrons by dots around the atomic symbols, in particular valence electrons, i.e., those in the outer shell (Figure 8).

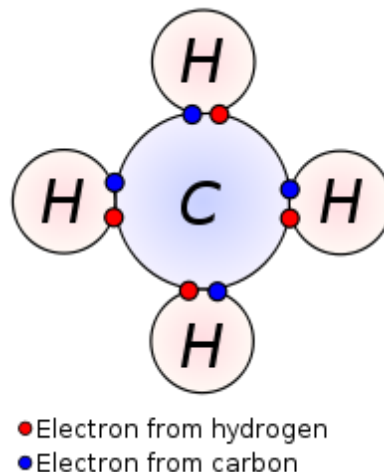


Figure 8. Lewis dot structure of the four covalent bonds in methane¹⁴

Methane consists of four single carbon-hydrogen covalent bonds, each one represented by a dash “–” located between the bonded atoms (Figure 9); in multiple bonds, double or triple, the number of piled dashes is the bond order (Figure 9), e.g., the oxygen molecule (O_2) involves a double bond ($O=O$), and a triple bond occurs in the nitrogen molecule, N_2 , ($N\equiv N$). The higher the order, the stronger the bond.

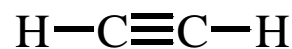
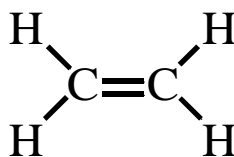
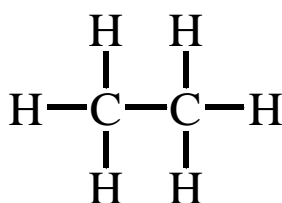


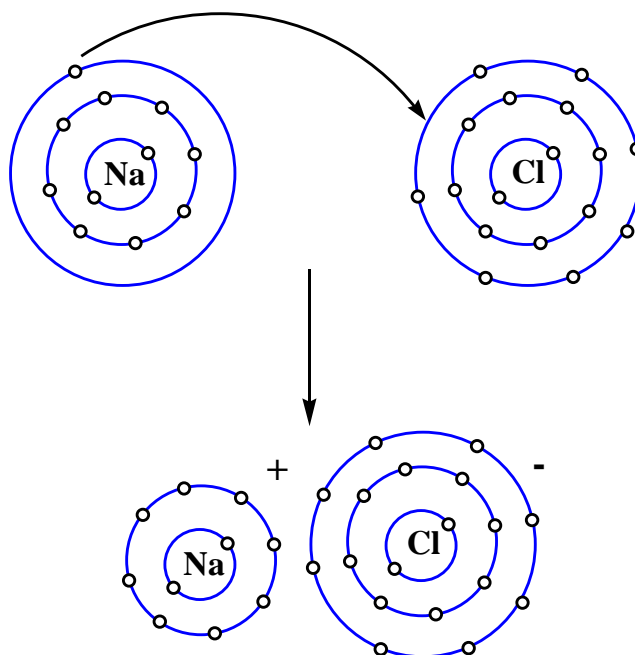
Figure 9. Single, double and triple bonds involving two carbon atoms

In a simple way, although shared electrons “belong” to both atoms. In many compounds bonding electron are more time, in average, orbiting one of the atoms, then

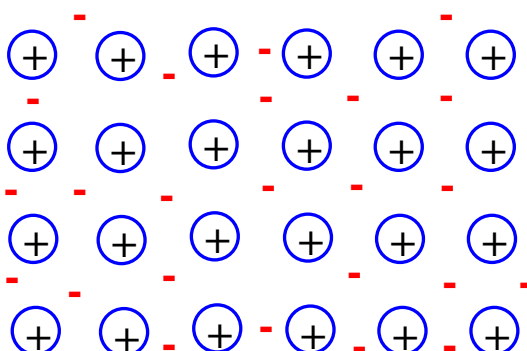
¹⁴ Image taken from <http://en.wikipedia.org/wiki/File:Covalent.svg>

the molecule can be described, from the electrostatic point of view, behaving as an electric dipole, and the molecule is said to be polar.

- Ionic: atoms (or groups of them) loss/gain electron(s) to give positive and negative charged entities (ions),¹⁵ then the compound is formed as the result of the electrostatic interaction of a huge amount of those ions.



- Metallic: the simplest pictorial model is as a collection of positive charges (nucleus) in a sea of electrons (-).

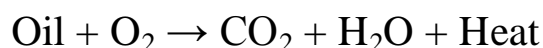


¹⁵ Cation: a positive charged ion, whereas Anion is used to refer to a negatively charged ion.

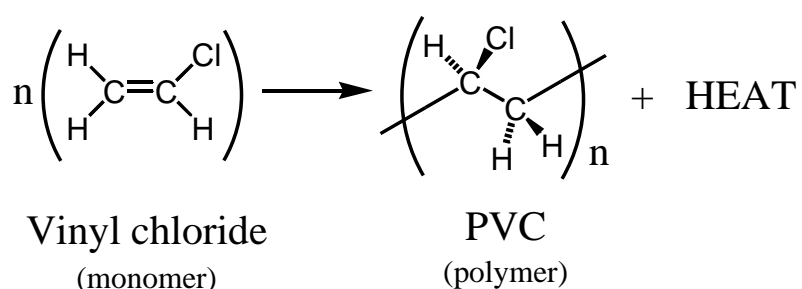
Molecules interact to each other, hydrogen bonding being the stronger of the intermolecular interactions. Many properties of liquid and solid water (ice) are only explained by taking into account hydrogen bonding.

Oil might suffer a myriad of chemical reactions, two of them relevant with regard to maritime transportation of oil: combustion and polymerization; the former essential when energy is needed for propelling the ship, and highly dangerous in case of accident, and the latter to be inhibited during transportation.

Combustion: is a redox reaction, in which crude oil (or petroleum products) combines with oxygen to ideally produce carbon dioxide, water and heat:



Polymerization: a chemical process in which small molecules (monomers, all alike or different) react to form a very large chainlike or network molecule (polymer), for example, polymerization of vinyl chloride to give the universally spread polyvinylchloride –PVC–:



The rate of the chemical reactions¹⁶ depends on several factors: reactants concentration, temperature, pressure, state of matter, surface area available for contact between the reactants when they are in condensed immiscible phases, presence or absence of catalysts, and sometimes UV or Vis radiation. Chemical reactions are represented as colliding spheres, with only few molecules having enough energy to yield the reaction product(s); this is why usually they require input energy to proceed, spontaneous reactions also. Molecules should be activated to produce the chemical change, and the minimum energy to be achieved is known as the activation energy. Chemical reactions usually involve several steps in going from reactants to the final products, where some species (intermediates) appear and vanish. The sequence of such steps is known as the reaction mechanism.

¹⁶ The simplest definition of the rate of a reaction, or reaction rate, is how fast it takes place.

Any factor increasing the probability of “collision” between reactants (more concentrated solutions, higher pressure) or its energy (temperature raise) speeds up the reaction rate. In heterogeneous reactions the higher the surface area, the faster the reaction, e.g., oxidation of iron shavings is much faster than that of an iron bar of the same mass.

Catalysts, substances not destroyed during the chemical reaction, provide alternative step(s) for the reaction occur with lower activation energy, thus increasing its reaction rate. On the other side, inhibitors are substances capable to decrease, even block, the rate of the chemical reactions; they play a role when transporting chemicals in bulk able to polymerize, e.g. butadiene.

A bit of physics

When crude oil and petroleum products are transported in bulk some physical properties should be taken into account:

Density: mass per unit volume of a substance. Density is temperature-dependent. Common units are: g/mL (or g/cm³), and kg/m³. It is a relevant magnitude as it relates to buoyancy. Oils and petroleum products float on water as their density is less than that of the water, but bitumens and certain residual fuel oils having densities greater than 1.0 g/mL. As a consequence of the evaporation of the more volatile components of spilled oil its density may increase enough for the oils to submerge below the water surface.

Specific gravity and American Petroleum Institute (API) gravity are density-related properties of oils often used:

Specific gravity (or relative density) is the ratio, **at a specified temperature**, of the oil density to the density of pure water.

$$\text{specific gravity} = \frac{\text{oil density at specified temperature (T)}}{\text{pure water density at specified temperature (T)}}$$

API gravity (⁰API) is calculated as:

$$^{\circ}\text{API} = \frac{141.5}{\text{specific gravity } \left(\frac{60}{60} \text{ }^{\circ}\text{F}\right)} - 131.5$$

The API gravity scale arbitrarily assigns an API gravity of 10° to pure water.

Crude oil is classified as light, medium or heavy, according to its measured API gravity:¹⁷

- Light crude oil is defined as having an API gravity higher than 31.1 °API.
- Medium oil is defined as having an API gravity between 22.3 °API and 31.1 °API.
- Heavy oil is defined as having an API gravity below 22.3 °API.
- Extra heavy oil is defined with API gravity below 10.0 °API.

The price of a crude oil is usually based on its API gravity, with high gravity oils commanding higher prices.

In the oil industry, quantities of crude oil are often measured in metric tons. One can calculate the approximate number of barrels per metric ton for a given crude oil based on its API gravity:¹⁷

$$\text{barrels of crude oil per metric ton} = \frac{1}{\frac{141.5}{^\circ\text{API} + 131.5} \cdot 0.159}$$

Density dependence on temperature has capital relevance when huge amounts of crude oil and/or petroleum products, any liquid in general, are considered. A change in the temperature of the oil cargo implies a change in its volume, so volume correction factors (VCFs) are used to correct observed volumes to equivalent volumes at a standard temperature and pressure; this is the way to use volumetric measures equitably in general commerce. The VCF is a factor used for converting volumes at an observed temperature and gravity or density to a standard temperature (60 °F or 15 °C). In addition of published tables, there are several utilities to calculate VCF, some commercial^{18,19} and other freely usable on Internet.²⁰

Viscosity: a measure of a fluid's resistance to flow. Viscosity is also temperature-dependent; as temperature decreases, viscosity increases. This magnitude can be expressed in two ways, the more usual: dynamic viscosity (also known as absolute viscosity), and kinematic viscosity, both being related:

¹⁷ http://en.wikipedia.org/wiki/API_gravity

¹⁸ See for example http://rofa-products.com/products/ASTMD1250_04_pc.php

¹⁹ See for example <http://www.peteng.com/jmm/api01.html>

²⁰ <http://www.ior.com.au/ecfdensity.html>, <http://www.alaska.net/~jlanders/PetEng/APIConvert.htm>;
<http://widman.biz/English/Calculators/DegreesAPI.html>; <http://cargotek.com/util.html#VCF54A>

$$\text{Kinematic viscosity} = \frac{\text{Absolute viscosity}}{\text{density}}$$

The SI unit of dynamic viscosity is the millipascal-second (mPa·s),²¹ whereas Stokes, actually centistokes (cSt) is used for kinematic viscosity.

Viscosity is a relevant property of oils because it affects the rate at which spilled oil will spread, the degree to which it will penetrate shoreline substrates, and determines the selection of mechanical spill countermeasures equipment.

Pour Point: the lowest temperature at which the oil will just flow under standard test conditions, it gives a rough indication of the lowest temperature at which oil is readily pumpable. In the case of residual fuel oils, pour points may be influenced by the thermal history of the sample, that is, the degree and duration of heating and cooling to which the sample has been exposed.

Interfacial Tension: the force of attraction between the molecules at the interface of two fluids; surface tension is called when an air/liquid interface is involved. The SI unit for interfacial tension is millinewton per meter (mN/m).²²

Both oil viscosity and surface tension affect the rate at which an oil spill spreads. Air/oil and oil/water interfacial tensions can be used to calculate the spreading coefficient as:

$$\text{Spreading coefficient} = S_{WA} - S_{OA} - S_{WO}$$

which provides an indication of the tendency for the oil to spread. S_{WA} is water/air surface tension, S_{OA} is oil/air surface tension, and S_{WO} is water/oil interfacial tension. The higher the spreading coefficient, the faster the spreading will occur. Oils having spreading coefficients greater than zero spread to a thin slick. Contrary to viscosity and density interfacial tensions of crude oils and petroleum products do not show systematic variations with temperature and degree of evaporation.

Vapour pressure: the pressure that a vapour, in thermodynamic equilibrium with its condensed phase, exerts on a closed container. Vapour pressure is temperature-dependent; it

²¹ This is equivalent to the former unit centipoise (cP).

²² It is equivalent to dyne/cm.

increases with temperature (see Figure 9),²³ and can be used as an indirect measure of the evaporation rate of a liquid. Any pressure unit can be used.

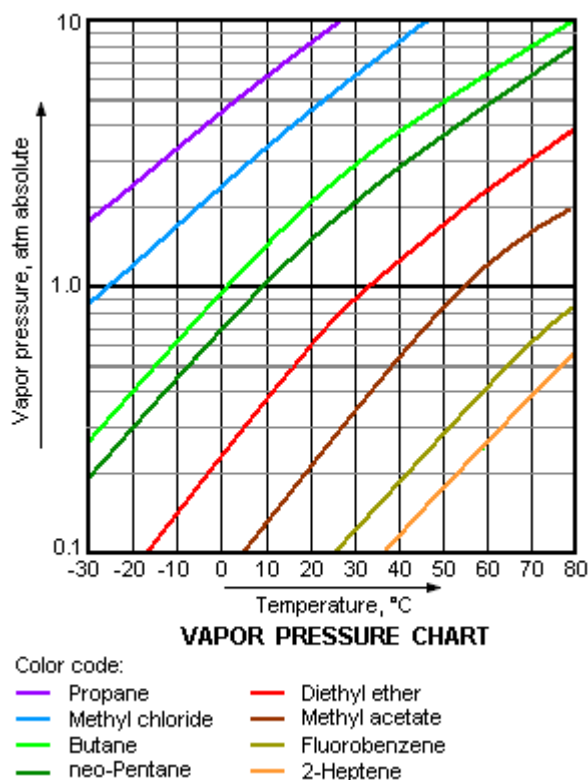


Figure 9. Dependence of vapour pressure on temperature for selected hydrocarbons²⁴

Several methods are at disposal to measure vapour pressure: isoteniscopic, dynamic, static, **Reid**, vapour pressure balance, ...; a commonly used method for crude oils is the Reid vapour pressure –RVP–, as determined by ASTM method D 323 - Standard Test Method for Vapour Pressure of Petroleum Products (Reid Method).

RVP method determines vapour pressure at 37.8°C (100°F) of petroleum products and crude oils *with initial boiling point above 0°C (32°F)* by saturating a known volume of oil in an air chamber of known volume and measuring the equilibrium pressure which is then corrected to one atmosphere (101.3 kPa); this method does not apply to liquefied petroleum gases (LPG).

Boiling point is related to vapour pressure, it is the temperature at which the vapour pressure of a liquid equals the external pressure, boiling points should be referred to given pressure, commonly 1 atm or 1 bar.

As stated in the Introduction, crude oil separates into fractions by fractional distillation (Figure 5), fractions having lower boiling points leave the fractionating column at its top.

²³ Vapour pressure dependence on temperature is described by the Clausius-Clapeyron equation.

²⁴ Image taken from http://en.wikipedia.org/wiki/File:Vapor_Pressure_Chart.png

Typical petroleum fractions and their corresponding true boiling point (TBP) cut points are shown in Table 1.

Table 1. True boiling point (TBP) cut points of typical crude oil fractions²⁵

Product	TBP Cut Points, °C	TBP Cut Points, °F
Light straight-run gasoline	(C5)-70	(C5)-158
Light naphtha	70-100	158-212
Medium naphtha	100-150	212-302
Heavy naphtha	150-190	302-374
Light kerosene	190-235	374-455
Heavy kerosene	235-265	455-536
Atmospheric gas oil	265-343	536-650
Vacuum gas oil	343-565	650-1049
Atmospheric residue	>343	>650
Vacuum residue	>565	>1049

Boiling range distributions provide an indication of volatility and component distribution; they are useful in modelling oil spills, and in predicting evaporative loss.

Odour Threshold: the lowest concentration in air that humans can detect by smell, it cannot be used to prevent overexposure because sensitivity to odours varies over wide limits; moreover, some chemicals cannot be smelled at toxic concentrations, odours can be masked by other odours, and some compounds, like hydrogen sulphide (H₂S), rapidly deaden the sense of smell.

*Empirical equations for the thermal properties of petroleum products.*²⁶ The following equations allow a gross prediction of thermal conductivity,²⁷ specific heat,²⁸ and latent heat of vaporization²⁹ of crude oil and petroleum products:

²⁵ Data taken a pdf file formerly accessible at www.etcentre.org/spills (Web page out of service)

²⁶ Equations taken from <http://en.wikipedia.org/wiki/Petroleum>

²⁷ Ability to conduct heat

Property	Equation (t = ⁰ F temperature)	Equation (t = ⁰ Celsius temperature)
Thermal Conductivity	$K = \frac{0.813}{d} [1 - 0.0003(t - 32)]$ K units: BTU · hr ⁻¹ ft ⁻²	
Specific heat	$c = \frac{1}{\sqrt{d}} (0.388 + 0.00045t)$ c units: BTU/lbm·°F	$c = \frac{1}{\sqrt{d}} (0.402 + 0.00081t)$ c units: kcal/kg°C
Latent heat of vaporization	$L = \frac{1}{d} (110.9 - 0.09t)$ L units: BTU/lbm	$L = \frac{1}{d} (194.4 - 0.162t)$ L units: kcal/kg
where d is the <i>specific gravity</i> at 60 ⁰ F (15 ⁰ C)		

Adhesion: defined as the mass of oil per unit area that will remain on a standard test surface; oils tend to adhere to surfaces to a greater or lesser degree .A semi-quantitative measure of it is obtained , after dipping and draining oil for 30 minutes, under prescribed conditions.

Oil and Chemistry

Crude oil is mainly a complex mixture of a very large number of different hydrocarbons, i.e., substances mainly composed by hydrogen and carbon, their simplest chemical composition denoted by C_nH_m (with m ≤ 2·n+2); therefore they are organic compounds as carbon is the main element in their molecular structure.³⁰ Organic compounds containing nitrogen, oxygen, sulphur, and trace amounts of metals (vanadium, nickel, copper, iron,...) are also present in petroleum (Table 2); collectively these atoms, other than C & H, are called heteroatoms.

Table 2. Elementary composition, by weight, of crude oil

Element	Carbon	Hydrogen	Nitrogen	Oxygen	Sulphur	Metals
Range	83 - 87%	10 - 14%	0.1 - 2%	0.1 - 1.5%	0.5 - 6%	less than 1000 ppm ³¹

²⁸ Heat capacity of a substance per unit mass (Heat capacity is the ability of a body to store heat as it changes in temperature).

²⁹ Amount of energy absorbed by a liquid chemical substance when is converted to vapour at its boiling point, i.e., temperature remains constant during the phase transition (liquid → gas).

³⁰ There are also inorganic carbon compounds like carbon monoxide (CO), carbon dioxide (CO₂), carbonates and bicarbonates.

³¹ ppm = parts per million, denotes one part per 1,000,000 parts, e.g., 1 ppm of metals means one gram of metals per a million of grams (1 metric ton) of crude oil.

Each petroleum variety has a unique composition, which define its physical and chemical properties. Hydrocarbons (C_nH_m) in crude oils can be grouped in (see Figure 10):

- saturates (paraffins and naphthenes, waxes are also included)
- aromatics
- asphaltics (resins & asphaltenes)

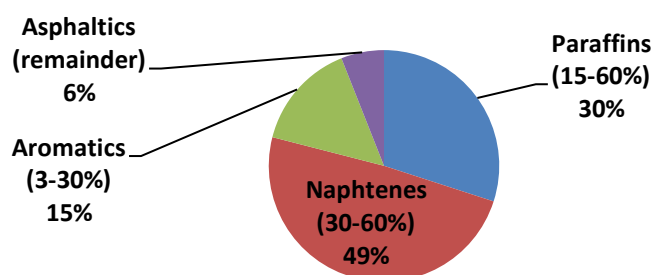


Figure 10. Average relative ratios, by weight, of hydrocarbons in crude oil (values in brackets indicate range)³²

The basic classification of hydrocarbons is shown below:

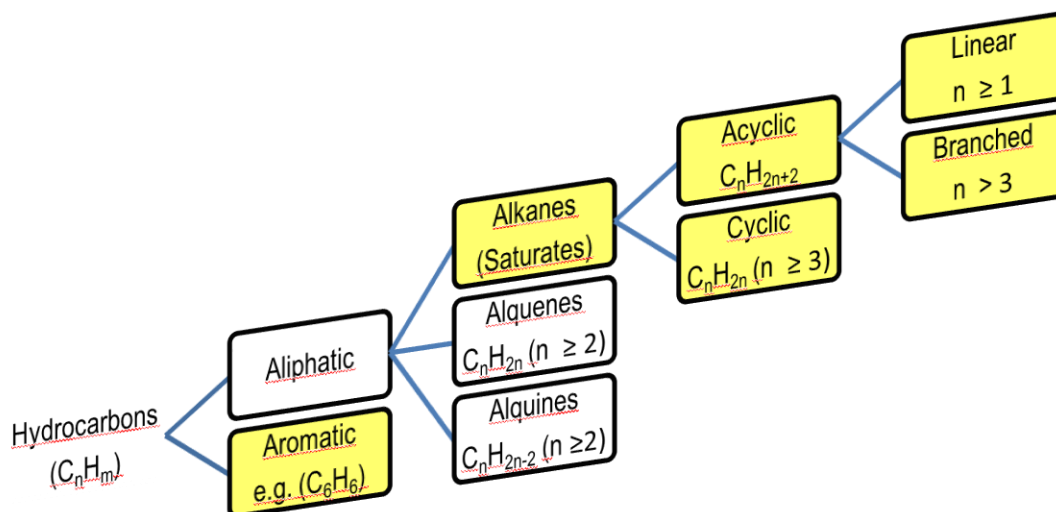


Figure 11. Basic types of hydrocarbons (those in yellow boxes are main components of crude oil)

³² Values taken from <http://en.wikipedia.org/wiki/Petroleum>

The ability of carbon to form single, and multiple –up to three–, stable carbon-carbon bonds allows the potential formation of an almost infinite number of organic compounds, even cyclic. Molecular formulas in the figure refer to the simplest compounds of each class, but for linear and branched alkanes where it always applies; for example molecular formula for cycloalkanes with more than one ring changes to $C_nH_{2(n+1.r)}$, where r is the number of rings.

Saturates belong to the aliphatic hydrocarbons family, they are alkanes. The term “saturates” refers to all bonds between pairs of atoms (C&H and C&C) are single bonds, therefore each carbon atom must have four covalent bonds (either C-C or C-H bonds), and each hydrogen joins to a carbon atom. On the other hand, unsaturates implies the existence of at least one double, or triple, carbon-carbon covalent bond in the molecule; the degree of unsaturation increasing with the number of such bonds.³³

Depending on the carbon atoms arrangement in the carbon backbone,³⁴ alkanes can be classified as acyclic (**paraffins**)³⁵ and cyclic (**naphthenes**); paraffins also divide in linear, where carbon atoms are joined in a snake-like structure, or branched. Linear, also named *n*-alkanes, and branched alkanes with the same number of carbon atoms are isomers, i.e., molecules having the same the molecular formula,³⁶ here C_nH_{2n+2} ; the number of carbon atoms is often used to define the size of the alkane (e.g., C2-alkane). From Table 3 it follows that, at room temperature and pressure, *n*-alkanes up to four carbon atoms are gases, from five to 16 liquids, and solids those with more carbon atoms.³⁷ Branched-chain alkanes have lower boiling points than their straight-chain counterparts, and the contrary applies to naphthenes (cycloalkanes). Figure 12 shows general structures and specific examples of hydrocarbons. There are several ways to name organic compounds, the most widely used is that proposed by IUPAC³⁸, although sometimes alternative names are used.

In organic chemistry the symbol R is widely used to represent any organic fragment joined to the carbon skeleton, the simplest those derived from alkanes are named alkyl groups, e.g., methyl (CH_3-), ethyl (CH_3-CH_2-), butyl ($CH_3-CH_2-CH_2-CH_2-$), etc.

³³ http://en.wikipedia.org/wiki/Degree_of_unsaturation

³⁴ Also known as carbon skeleton.

³⁵ Paraffin waxes have between 20 and 40 carbon atoms.

³⁶ Molecular formula: how many atoms of each type are in the molecule (e.g. C_2H_6), which not always coincides with the empirical formula (the simplest ratio of the elements present in the molecule, CH_3).

³⁷ In organic chemistry the members of a homologous series by a constant relative molecular mass of 14, i.e., by CH_2 .

³⁸ <http://www.iupac.org/>

Table 3. Physical properties of selected n-alkanes³⁹

n-Alkane	Formula	Boiling point [°C]	Melting point [°C]	Density [g·cm ⁻³] (at 20°C)
Methane	CH ₄	-162	-183	gas (0.666·10 ⁻³) ^a
Ethane	C ₂ H ₆	-89	-181.76	gas (1.25·10 ⁻³) ^a
Propane	C ₃ H ₈	-42	-188	gas (1.83·10 ⁻³) ^a
Butane	C ₄ H ₁₀	-0.5	-135	gas (2.41·10 ⁻³) ^a
Pentane	C ₅ H ₁₂	36	-130	0.626
Hexane	C ₆ H ₁₄	69	-95	0.659
Heptane	C ₇ H ₁₆	98	-91	0.684
Octane	C ₈ H ₁₈	126	-57	0.703
Nonane	C ₉ H ₂₀	151	-54	0.718
Decane	C ₁₀ H ₂₂	174	-30	0.730
Undecane	C ₁₁ H ₂₄	196	-26	0.740
Dodecane	C ₁₂ H ₂₆	216	-10	0.749
triacontane	C ₃₀ H ₆₂	343	37	solid

^a Value calculated assuming the ideal gas model ($P \cdot V = n \cdot R \cdot T$), and $P = 1$ atm.

In organic structures X and/or Y, called substituents, stand for atoms or groups of atoms attached to the carbon backbone, for example halogens (Cl, Br, I). One feature of organic chemistry is that the all organic compounds can be derived from methane (CH₄) either by full or partial substitution of its hydrogens by heteratom(s) or alkyl radical derivatives –also obtained from methane as the starting point–, and/or changing the degree of bonding between carbons e.g., ethane (CH₃–CH₃) coming from the replacement of one hydrogen atom of methane by the methyl radical.

The rather limited chemical reactivity of alkanes is enhanced by increasing its degree of unsaturation, or by the substitution of its hydrogens with heteroatom(s), thus providing the molecule with characteristic chemical reactivity. A group of atoms responsible for a

³⁹ Adapted from <http://en.wikipedia.org/wiki/Alkane>

characteristic chemical reaction is known as **functional group**,⁴⁰ showing similar reactivity in all organic compounds, although it could be affected by nearby functional groups.

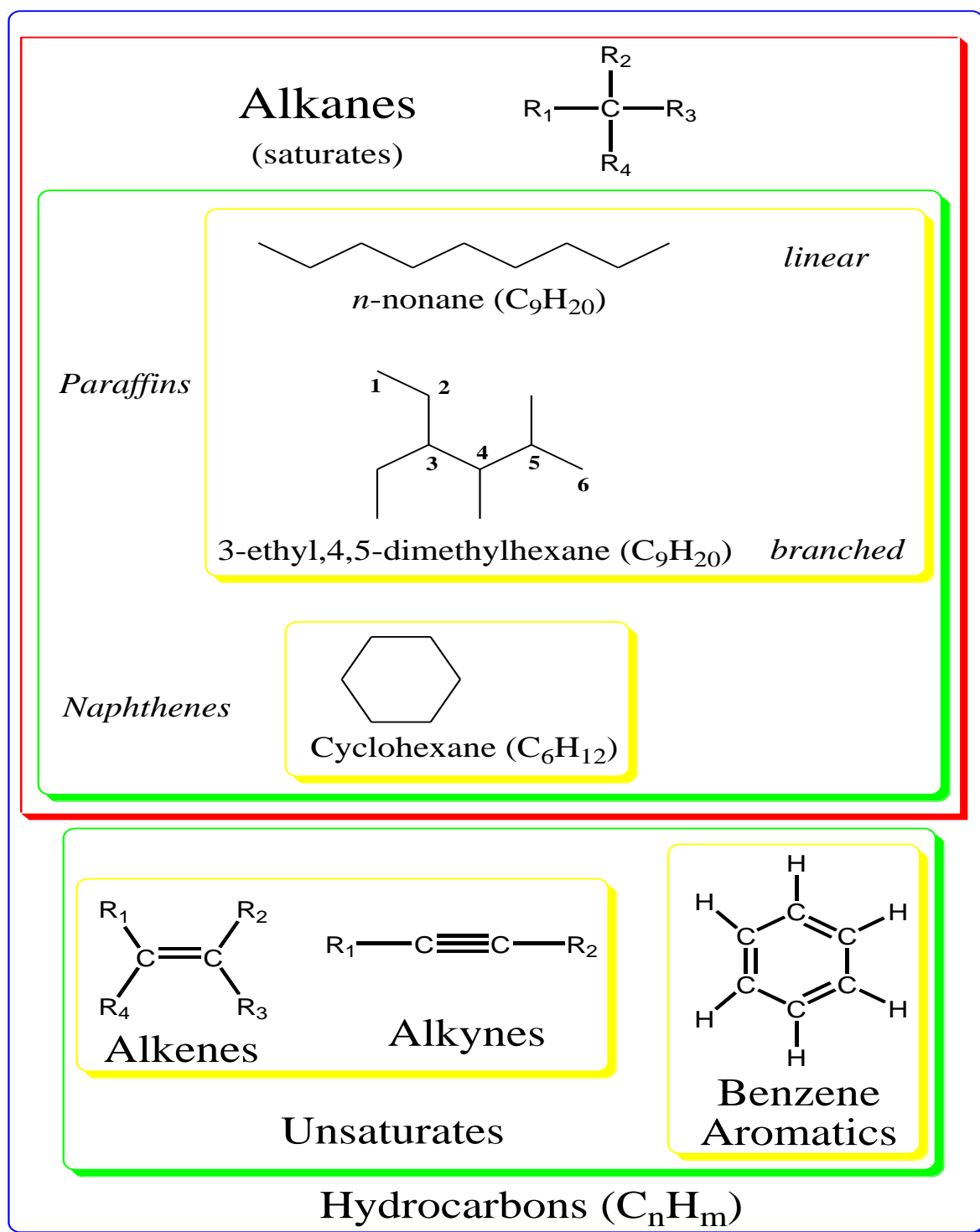


Figure 12. Basic examples of hydrocarbons

⁴⁰ http://en.wikipedia.org/wiki/Functional_group

Next figure shows different ways to represent organic chemical compounds, sometimes hydrogens are omitted by sake of simplicity.

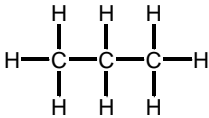
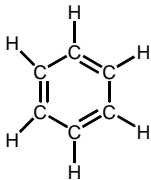
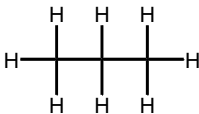
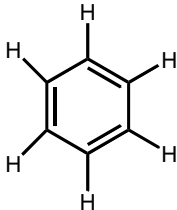

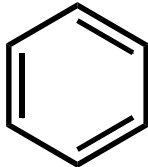
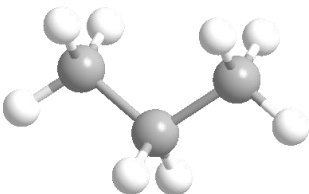
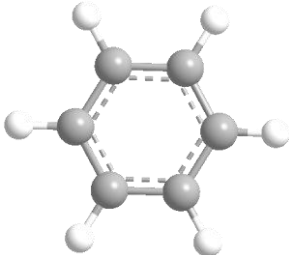
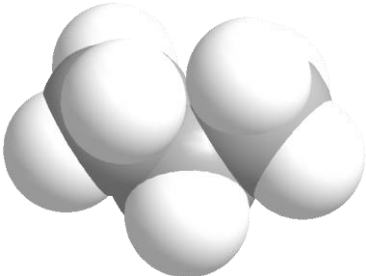
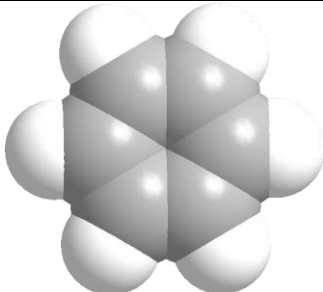
Propane		Benzene
	Structural formula	
		
		
CH ₃ CH ₂ CH ₃ CH ₃ -CH ₂ -CH ₃	Condensed formula	
C ₃ H ₈	Molecular formula	C ₆ H ₆
	Ball & stick model ⁴¹	
	Space filling model ⁴²	

Figure 13. Pictorial molecular models of chemical compounds

⁴¹ http://en.wikipedia.org/wiki/Ball-and-stick_model.

⁴² In space-filling model, also known as CPK model, atoms are represented by spheres where atoms radii and distances are all in the same scale. Colors are used to differentiate elements. (See http://en.wikipedia.org/wiki/Space-filling_model).

Waxes are composed by n-alkanes (the predominant species and crude specific), iso-alkanes, alkyl cyclic compounds and alkyl aromatics. Short-branched chains are the next most common. It is generally accepted that n-alkanes from C18 to C40 represent waxy material. In waxes *cloud point* refers to the temperature below which wax form a cloudy appearance.⁴³

Aromatics (AH) are compounds that have at least one benzene ring as part of their chemical structure. They include mono-, di-, and polynuclear aromatic hydrocarbons (PAHs) with and without alkyl side chains. Phenyl group (or ring), denoted as Ph (or ϕ), refers to the functional group C_6H_5- , whereas any functional group derived from a simple aromatic ring is named as Aryl (Ar).

Benzene, toluene, ethyl benzene, and xylenes (BTEX), and substituted benzenes are the most common aromatic compounds in petroleum, making up to a few percent of the total mass of some crude oils (Figure 14). BTEX are hazardous carcinogenic and neurotoxic compounds usually classified as priority pollutants.⁴⁴

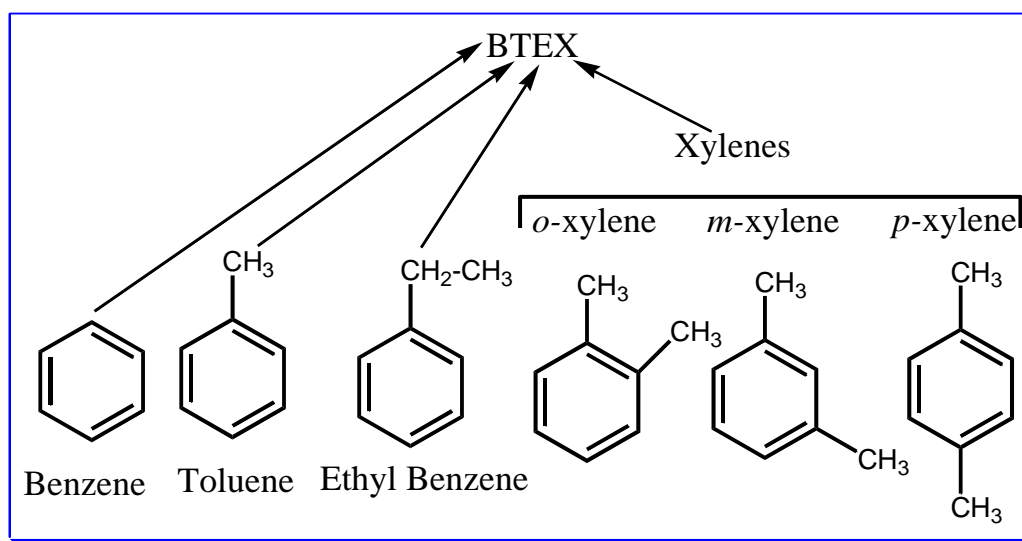


Figure 14. BTEX are volatile organic compounds (VOCs⁴⁵)

PAHs contain two or more fused benzene rings (Figure 15), and are also compounds of environmental concern.^{46,47}

⁴³ Wax appearance temperature (WAT) and wax precipitation temperature (WPT) are synonymous of cloud point.

⁴⁴ <http://www.sepa.org.uk/default.aspx>.

⁴⁵ http://en.wikipedia.org/wiki/Volatile_organic_compound.

⁴⁶ http://en.wikipedia.org/wiki/Polycyclic_aromatic_hydrocarbon.

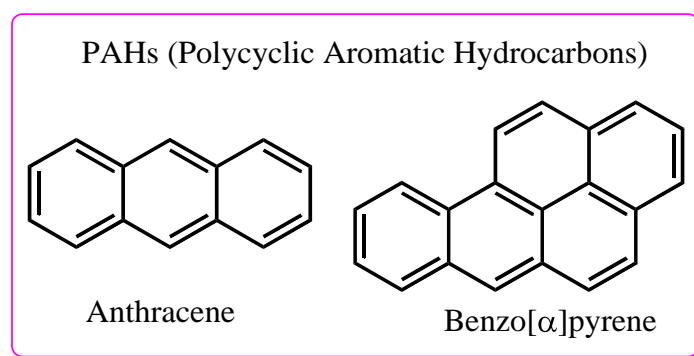


Figure 15. Examples of polycyclic aromatic hydrocarbons (PAHs)

Asphaltenes and resins are separated by the so-called SARA method, which takes its name from the fractions produced, namely saturates (S), aromatics (A), resins (R), and asphaltenes (A).

Asphaltenes consist mainly of carbon and hydrogen (C:H ratio is approximately 1:1.2), and nitrogen, oxygen, sulphur, and trace amounts of vanadium and nickel are also present (Figure 16). They have a distribution of molecular masses in the range of 400 u to 1500 u (maximum around 750 u).⁴⁸ Asphaltenes are defined operationally as the n-heptane (C₇H₁₆)-insoluble, toluene (C₆H₅CH₃)-soluble component of crude oil.⁴⁹ Resins are similar to asphaltenes, and contain aggregates with a multitude of building blocks such as sulfoxides, amides, thiophenes, pyridines, quinolines, and carbazoles.

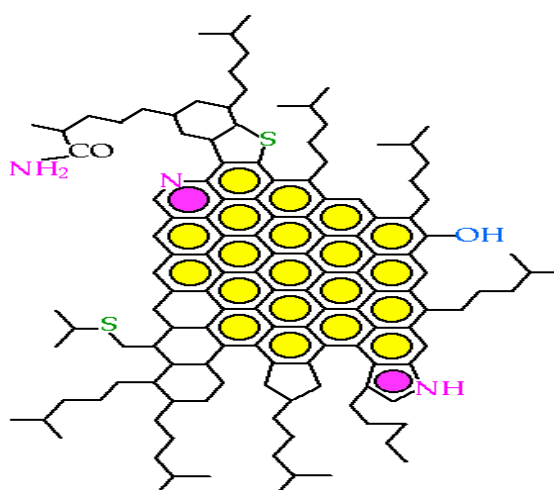


Figure 16. A typical asphaltene⁵⁰

⁴⁷ http://ec.europa.eu/environment/air/pdf/pp_pah.pdf.

⁴⁸ <http://en.wikipedia.org/wiki/Asphaltene>

⁴⁹ Also applies to bitumen or coal.

⁵⁰ Image taken from http://tigger.uic.edu/~mansoori/Asphaltene.Molecule_html

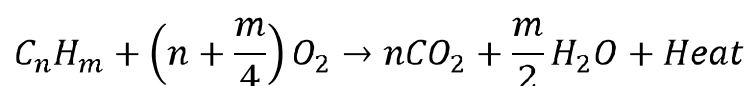
In the oil market the amount of sulphur present in crude oil determines its price, sweet crude, with sulphur content less than 0.5%, being preferred, as it requires less refining to meet sulphur standards imposed on fuels in consuming countries, which implies fewer environmental problems. Sour crude refers to crude oil with sulphur content exceeding that limit.

Concerning maritime transportation the chemical reactivity is divided in four groups:

1. Reactivity with water.
2. Reactivity with air.
3. Self-reactivity, i.e., polymerization.
4. Reactivity with other substances.

When crude oil and petroleum products are considered, reactivity with air, i.e. combustion, deserves special attention; polymerization may occur carrying some oil derivatives, so an inhibitor should be added.

Combustion is relevant in two ways, it provides the way to propel the ship, and care should be taken to avoid it as out of control fire on board. The simplest chemical equation representing hydrocarbons combustion is:



The exothermical process described by this chemical equation is the ideal one in oxygen atmosphere; in practice nitrogen oxides (NO_x⁵¹), carbon monoxide and soot appear. Furthermore, when heteroatoms like S are present sulphur oxides (SO_x⁵²) are also formed. The heat of combustion, at a constant volume, of a petroleum product can be approximated as follows:

$$Q_v = 12,400 - 2,100 \cdot d^2$$

where Q_v is the released heat measured in cal/gram, and d is the specific gravity at 60°F.

Concerning uncontrolled fires, fire triangle provides a simple model for understanding the ingredients involved in a fire (Figure 17).⁵³

⁵¹ <http://en.wikipedia.org/wiki/NOx>.

⁵² <http://www.epa.gov/nonroad/marine/ci/420r07009.pdf>.

⁵³ http://en.wikipedia.org/wiki/Fire_triangle.



Figure 17. Fire triangle⁵⁴

Removal of any of the ingredients prevents or extinguishes fire. The presence of oxygen, fuel and heat is not enough; flammable substances produce fire when its vapours are in the appropriate proportions with air: flammable or explosive limits (Figure 18).⁵⁵

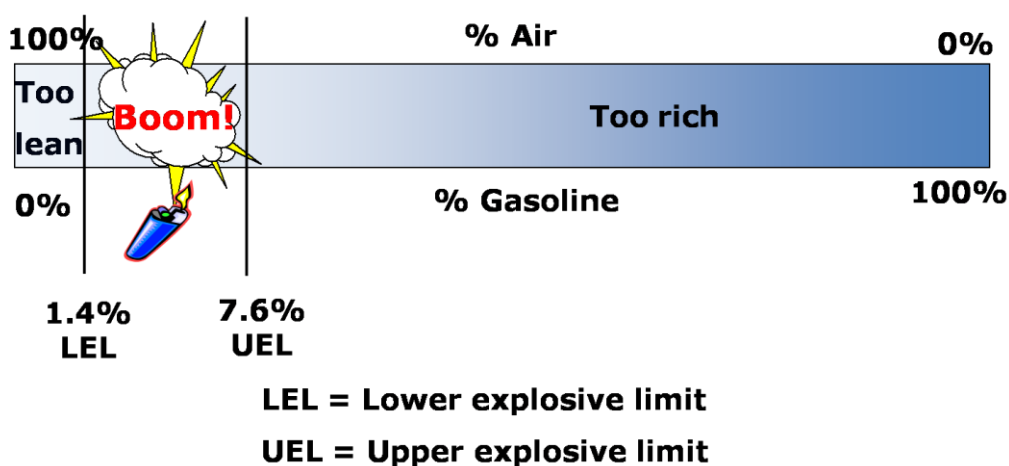


Figure 18. Flammable limits of gasoline

The Lower Explosive Limit⁵⁶ (LEL) is the lowest percent concentration in air (by volume) of a gas or a vapour in air capable of producing a flash of fire in presence of an ignition source; the Upper Explosive Limit (UEL)⁵⁷ being the corresponding highest percent concentration in air (by volume). The flammable (or explosive range) is broadened as temperature rises, while greater pressure increases both values. LEL and UEL of selected compounds are collected in Table 4.

⁵⁴ Image taken from http://en.wikipedia.org/wiki/File:Fire_triangle.svg.

⁵⁵ http://en.wikipedia.org/wiki/Flammability_limit.

⁵⁶ Also known as Lower Flammable Limit (LFL).

⁵⁷ Upper Flammable Limit (UFL) is also used.

Usually the flammable range is rather small for many organic compounds; only within this range conditions are given to keep the combustion running with the participation of transient species in chain reactions.⁵⁸ The need of such conditions, between LEL and UEL, changes the fire triangle into the fire tetrahedron (see below). Safe transportation of flammable products implies the carriage of such goods outside the explosive range.

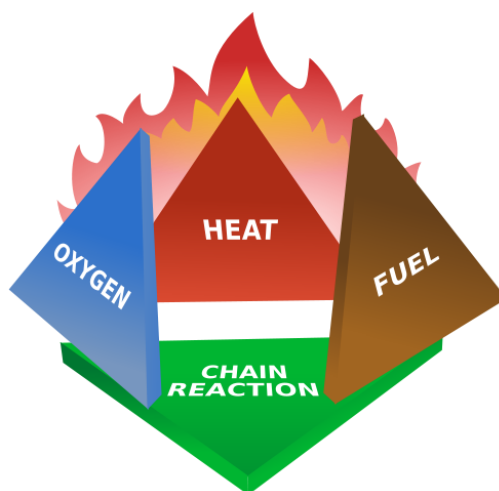


Figure 18. Fire tetrahedron⁵⁹

Relevant temperature values related with flammability are: flash point, fire point and autoignition point, the former often provided on info sheets of crude oil and petroleum products characteristics.

The flash point of a liquid is the lowest temperature at which it vaporizes to form an ignitable mixture in air in presence of an ignition source (spark, flame, etc.); at the flash point, the vapour may cease to burn when the source of ignition is removed. Various international standards define flammable liquids those with a flash point less than 43°C, and combustible liquids those having a flash point above it. Flash points of selected compounds are shown in Table 4.

The minimum temperature at which the application of a test flame to the oil sample surface causes the vapour of the oil to ignite and burn for at least five seconds is the **Fire point**; it is higher than the flash point, sometimes slightly like in gasoline, or up to 30°C above for ordinary commercial lubricating oils. Neither the flash point nor the fire point is related to the much higher temperature of the burning liquid.

⁵⁸ <http://en.wikipedia.org/wiki/Combustion>.

⁵⁹ Image taken from http://en.wikipedia.org/wiki/File:Fire_tetrahedron.svg.

Table 4. LEL, UEL, flash point and autoignition point of selected substances⁶⁰

Compound	LEL in % by volume of air	UEL in % by volume of air	Flash point (°C)	Autoignition point (°C)
Benzene	1.2	7.8	-11	560
Carbon monoxide	12	75	-191 Flammable gas	609
Cyclopentane	1.5 - 2	9.4	- 37 to -38.9	361
Decane	0.8	5.4	46.1	210
Diesel fuel	0.6	7.5	>62	210
Gasoline	1.4	7.6	< -40	246 - 280
Hydrogen	4	75	Flammable gas	
Hydrogen sulphide	4.3	46	Flammable gas	
Kerosene	0.6 - 0.7	4.9 - 5	>38	210

Autoignition point is the lowest temperature at which the material will ignite without the existence of any ignition source.⁶¹ Autoignition points of selected compounds are collected in Table 4.

As stated before flammable range is narrow for many organic compounds, for sake of comparison the corresponding range of very explosive gases, like carbon monoxide and hydrogen, is given. Flash point and autoignition point do not correlate, e.g., at typical ambient temperature gasoline (flash point < -40°C) in the presence of an ignition source ignites whereas diesel fuel (flash point > 62°C) does not; on the other hand, in absence of any source of ignition diesel fuel ignites first (210°C –diesel fuel– vs. > 245°C –gasoline–).

Properties of many oils can be found in the oil spill modelling program ADIOS2, freely available at the Web site of the NOAA's NATIONAL OCEAN SERVICE - OFFICE OF

⁶⁰ Data adapted from http://en.wikipedia.org/wiki/Flammability_limit.

⁶¹ Sometimes ignition point is used as synonymous of autoignition point.

RESPONSE AND RESTORATION: (<http://response.restoration.noaa.gov/index.php>), in the following table properties for the oil BELRIDGE HEAVY are given.

Product type	Crude	Oil Class Group	4
Location	San Joaquin Valley, California		
API	13.6	Pour point	2 °C
Density			
	g/cc	°C	% Evaporated
	0.9849	0	0
	0.9746	15	0
	0.9871	0	3
	0.9770	15	3
Viscosity			
	g/cc	°C	% Evaporated
Dynamic (cP)		0	0
	92600.00	15	0
	12610.00	0	3
	156200.00	15	3
	17105.00	15	3
Distillation cuts			
Weight %	Vapour Temp °C	Weight %	Vapour Temp °C
1	160	52	450
2	200	62	500
9	250	71	550
17	300	79	600
28	350	86	650
39	400	91	700
Flash point	90 °C	Adhesion	0.88 g/m ²
Maximum water content of the emulsion	-	Emulsification constant	-
Interfacial tension (Dynes/cm)			
Oil-Water	25.10 (15°C)	Oil-Seawater	20.00 (15°C)
Metals (ppm)			
Nickel	70.00	Vanadium	86.00

Group Analysis (weight %)			
Aromatics	39	Polars	-
Asphaltenes	3	Resins	30
Benzene	-	Saturates	28
Naphthenes	-	Sulphur	1
Paraffins	-	Wax	1

Table 5. Main properties of BELRIDGE HEAVY oil⁶²

From the top of the table (upmost right) it follows that BELRIDGE HEAVY belongs to the 4 Oil Class, such classification of transported oils is done according to their specific gravity as follows:⁶³

Table 6. Oil classes according their specific gravity

Group	Specific gravity	Examples
Group I	> 0.8	Gasoline, Kerosene
Group II	0.8 - 0.85	Gas Oil, Abu Dhabi Crude
Group III	0.85 - 0.95	Arabian Light Crude, North Sea Crude Oils (e.g Forties)
Group IV	> 0.95	Heavy Fuel, Venezuelan Crude Oils

This classification relates to the behaviour of oil when it is released in the environment.

Metals in crude oil

Metal content in crude oils provides useful information about its origin, which also could help in identifying the source of oil spills. Nickel and vanadium content in oil is of relevance as both metals have detrimental effects on catalysts used in cracking and desulphurization processes.

⁶² Data taken from the ADIOS2 program

[http://response.restoration.noaa.gov/type_topic_entry.php?RECORD_KEY%28entry_topic_type%29=entry_id,topic_id,type_id&entry_id\(entry_topic_type\)=181&topic_id\(entry_topic_type\)=1&type_id\(entry_topic_type\)=3](http://response.restoration.noaa.gov/type_topic_entry.php?RECORD_KEY%28entry_topic_type%29=entry_id,topic_id,type_id&entry_id(entry_topic_type)=181&topic_id(entry_topic_type)=1&type_id(entry_topic_type)=3)

⁶³ Data courtesy of ITOPF (<http://www.itopf.com/marine-spills/fate/models/>)

Oil Spills

Oil spills at sea can cause significant damage to the environment and impact commercial activities such as fishing, aquaculture, and tourism,

Oil tanker pollution shows two different aspects: one related to routine ship operation, and other relative to accidents occurring from time to time with accidents. Sea water pollution comes from tank washes and engine room effluent discharges, whereas air pollution results from emissions of fuel combustion.

Reduction of harmful emissions from ships to the atmosphere is regulated by the directives of the International Maritime Organization⁶⁴ contained in the MARPOL Annex VI.⁶⁵ IMO proposes a progressive reduction in sulphur oxides (SOx) and nitrogen oxides (NOx) emissions from ships.

In spite of such “routine ship pollution” should be kept in mind, main environmental impact relates to accidental oil spills, also known as black tides. The remainder of this material will be devoted to oil spills. The IMO’s annex related to Prevention of Pollution by Oil is MARPOL Annex I.⁶⁶

According to the work of Jacqueline Michel,⁶⁷ crude oil is the complex mixture of three types of components: heavy-weight, medium-weight, and light-weight, each one with the following characteristics:

- *Heavy-weight components*
 - Hydrocarbon compounds containing more than 20 carbon atoms.
 - Almost no loss by evaporation.
 - Almost no water-soluble fraction.
 - Potential for bioaccumulation, via sorption onto sediments, otherwise not highly bioavailable.
 - Potential for chronic toxicity, because they contain PAHs (phenanthrene, anthracene, etc.)
 - Most of the components are waxes, asphaltenes, and polar compounds which do not have any significant bioavailability or toxicity.

⁶⁴ <http://www.imo.org>

⁶⁵ http://www.imo.org/Environment/mainframe.asp?topic_id=233

⁶⁶ http://www.imo.org/environment/mainframe.asp?topic_id=231

⁶⁷ http://response.restoration.noaa.gov/book_shelf/678_Chapter2.pdf

- Long-term persistence in sediments, as tar balls, or asphalt pavements.
- These heavier components pose little acute toxicity risks, except that due to smothering, because of the very low solubility of the individual compounds.
- They are the most persistent components of oil, their degradation rates being very slow.
- *Medium-weight components*
 - Hydrocarbon compounds containing between 10 and 22 carbon atoms.
 - A boiling range from about 150 to 400°C.
 - Evaporation rates of up to several days, although there will be some residue which does not evaporate at ambient temperatures.
 - Low water-soluble fraction (at most a few mg/L).
 - Moderate acute toxicity because they contain diaromatic hydrocarbons (naphthalenes) which are toxic in spite of their low solubility.
 - Moderate potential for bioaccumulation and chronic toxicities associated with the diaromatic hydrocarbons.
 - Alkanes which are readily degraded.
 - They pose the greatest environmental risks to organisms because the compounds are more persistent, they are biologically available, and the PAHs have high toxicity.
- *Light-weight components*
 - Hydrocarbon compounds containing up to ten carbon atoms.
 - A boiling range up to 150° C.
 - Rapid and complete evaporation, usually within a day.
 - High water solubility; usually contributes >95% of water-soluble fraction.
 - High acute toxicity because they contain the aromatic hydrocarbons (BTEX) which are soluble and toxic. Even though these aromatic compounds have solubility of over 1,000 mg/L, evaporation rapidly removes them from solution.
 - No potential for bioaccumulation (they evaporate instead).
 - Mostly composed of alkanes and cycloalkanes which have relatively low solubility, and thus low acute toxicity potential.
 - They do not persist in the environment due to their fast evaporation.

Refined petroleum products, in contrast to crude oil, have only a very narrow range of components, and they are characterized according to boiling range fractions.

The behaviour of crude oil at sea is dominated by the proportion of each component present in the spilled oil. The main features of the previously defined oil classes (Table 6) being as follows:

Oil class I — Very Light Oils (e.g. Jet Fuels, Gasoline)

- Highly volatile (should all evaporate within 1-2 days).
- High concentrations of toxic (soluble) compounds.
- Result: localized, severe impacts to water column and intertidal resources.
- Duration of impact is a function of the resource recovery rate.
- No dispersion necessary.
- No cleanup necessary.

Oil class II —Light Oils (e.g. Diesel, No. 2 Fuel Oil, Light Crudes)

- Moderately volatile; will leave residue (up to one-third of spill amount) after a few days.
- Moderate concentrations of toxic (soluble) compounds, especially distilled products.
- Will "oil" intertidal resources with long-term contamination potential.
- Has potential for subtidal impacts (dissolution, mixing, sorption onto suspended sediments).
- No dispersion necessary.
- Cleanup can be very effective.

Oil class III —Medium Oils (Most Crude Oils)

- About one-third will evaporate within 24 hours.
- Maximum water-soluble fraction 10-100 ppm.
- Oil contamination of intertidal areas can be severe and long-term.
- Oil impacts to waterfowl and fur-bearing mammals can be severe.
- Chemical dispersion is an option within 1-2 days.
- Cleanup most effective if conducted quickly.

Oil class IV —Heavy Oils (e.g. Heavy Crude Oils, No. 6 Fuel Oil, Bunker C)

- Heavy oils with little or no evaporation or dissolution.
- Water-soluble fraction is less than 10 ppm.
- Heavy contamination of intertidal areas likely.
- Severe impacts to waterfowl and fur-bearing mammals (coating and ingestion).
- Long-term contamination of sediments possible.
- Weathers very slowly.

- Chemical dispersion seldom effective.

Small saturates (<C18) are the most dispersible components, whereas large saturates (waxes) can produce anomalous evaporation, dispersion, emulsification, and flow behaviour. As stated before, one and two rings aromatics are fairly soluble in water, but also evaporate rapidly; larger aromatics show neither of these behaviours to any extent, complex PAHs are particularly resistant to biodegradation. Asphaltenes and resins do not appreciably evaporate, disperse, or degrade, and both stabilize water-in-oil emulsions when its content in oil is greater than 3%

During oil spills, the sulphur content should be taken into account as it becomes a health and safety concern for cleanup personnel; dangerous levels of sulphur dioxide are produced when high sulphur oils burn.

The International Maritime Organization defines⁶³ **non-persistent oil** (*those belonging to Group 1*) as a petroleum based oil that consists of hydrocarbon fractions:

- at least 50% of which by volume, distil at a temperature of 340°C (645°F); and
- at least 95% of which by volume, distil at a temperature of 370°C (700°F).

and **persistent oil** all oils which are not within the category of “non-persistent oil”.

The fate of spilled oil in water bodies, also known as **weathering** (Figure 19), is governed by physical, chemical, and biological processes that depend on the oil properties, hydrodynamics, meteorological and environmental conditions.

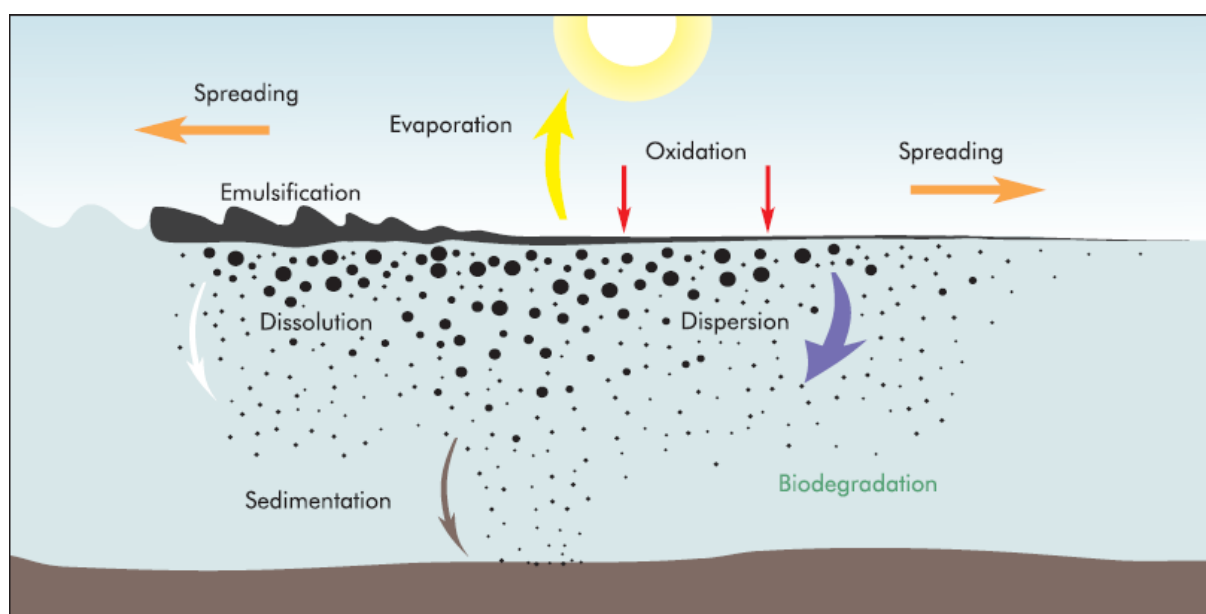


Figure 19. Oil weathering pathways⁶⁸

⁶⁸ Courtesy of ITOPF (http://www.itopf.com/_assets/documents/tip2.pdf)

Spreading, evaporation, dispersion, and emulsification rapidly change oil properties after the oil spill; some oils being able to form water-in-oil emulsions. Oil weathering varies dramatically due to the influence of air and sea temperature, wind speed, and sea state. The more severe the conditions, the more rapid the spreading and breaking up of the oil.

Just after oil spills, it spreads out covering extensive areas of the sea surface; low viscosity oils spreading faster than those with high viscosity. Initially a single slick is formed, but after a few hours it breaks up due to waves, water currents, tidal streams and winds; narrow bands or windrows parallel to the wind direction are formed (Figure 20). Movement of the oil patches depends on currents, tide and wind, having similar speed as the water body (Figure 21); it takes place till spilled oil remains on the sea surface.



Figure 20. Scattered patches of heavy fuel oil⁶⁹

Spreading depends on the spreading coefficient⁷⁰, which is a function of the water/air surface tension, the oil/air surface tension, and the water/oil interfacial tension. Oil patches are rarely uniform, and large variations in their thickness are typical. Visual appearance and thickness of the oil spilled roughly relates to its type and to the amount released (Table 7), this fact is used in aerial observation of oil spills. Thickness varies from millimetres to several centimetres in water-in-oil emulsions and viscous oils. Spreading is time dependent, the table below shows the change of thickness with time after a 100 m³ oil spill of Iranian crude oil:

Time (sec)	100	1000	10000	100000
Thickness (cm)	0.327	0.070	0.011	0.003

⁶⁹ Courtesy of ITOPF (http://www.itopf.com/_assets/documents/tip1.pdf).

⁷⁰ See page 15.

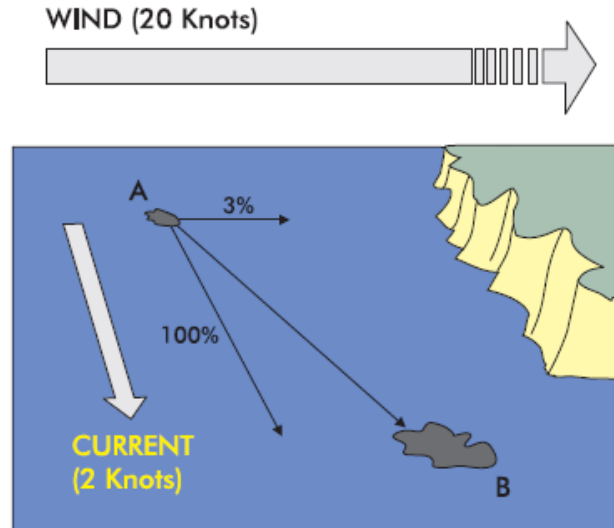


Figure 21. Movement of an oil slick at sea due to the wind and the current⁶⁹

Table 7. Visual appearance, thickness and volume of floating oil⁶⁹

Oil Type	Appearance	Approximate Thickness	Approximate Volume (m ³ /km ²)
Oil Sheen	Silver	>0.0001mm	0.1
Oil Sheen	Iridescent	>0.0003mm	0.3
Crude and Fuel Oil	Brown to Black	>0.1mm	100
Water-in-oil Emulsions	Brown/Orange	>1mm	1000

Only ten minutes after a spill of 1 ton of oil, the oil can disperse over a radius of 50 m, forming a slick 10-mm thick.

Evaporation is the most important weathering process in the first several days of an oil spill (Figure 22); it removes 100 percent of the light oils within a very short time. Medium crude oils evaporate between 20% and 30% within the first day, whereas such numbers lowers to 5 – 10% for heavy oils. This process even removes the dissolved hydrocarbons.

The rate of evaporation is speeded up by environmental factors like air temperature and solar radiation, wind speed and water surface roughness, and area of slick exposed; on the other hand, formation of emulsions dramatically slows down it.

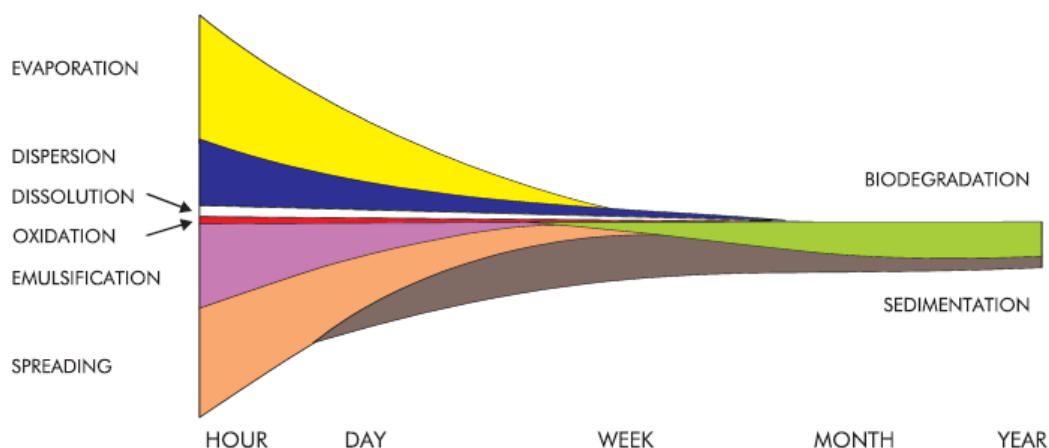


Figure 22. Time dependence of weathering processes of a crude oil spill (the width of each band states their relevance of the process⁶⁸

Dispersion takes place when the slick breaks up into fragments and droplets of varying sizes due to waves and turbulence at the sea surface; it encourages other natural processes such as dissolution, biodegradation and sedimentation to occur. Dispersion is faster for light oils and of low viscosity, and if the sea is very rough.

Larger droplets tend to rise back to the surface, there they may either coalesce with other droplets reforming a slick, or spread out forming a very thin film; on the other hand, some of the smaller droplets may remain suspended in the sea water, this part of oil having greater surface area than before dispersion occurred.

Dissolution. Dissolution of oil hydrocarbons into the water column poses risks to aquatic organisms because of the acute toxicity of the compounds that have significant water solubility. The monoaromatics show the highest solubility, 50 fold than that of similar molecular weight alkanes; benzene being the most soluble in sea water. However, these compounds are also those first to be lost through evaporation, a process which is 10 -100 times faster than dissolution. The term *solubility* as applied to oils is being replaced by the technically more precise term *water-soluble fraction*.

Emulsification. A water-in-oil emulsion is a stable dispersion of small droplets of water in oil (Figure 23), which occurs by physical mixing promoted by turbulence at the sea surface, and shows very different characteristics from their parent crude oils. This has important implications for the fate and behaviour of the oil and its subsequent cleanup.

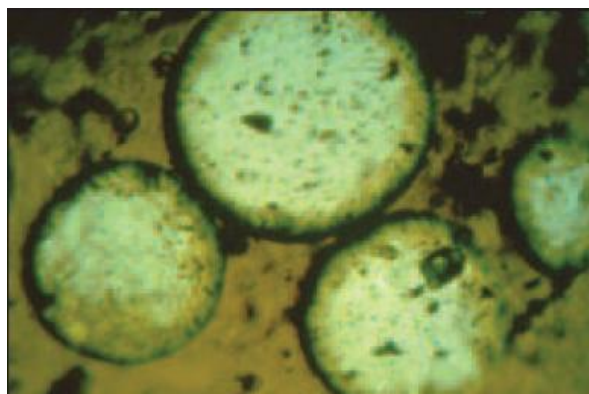


Figure 23. Image (x1,000) of a water-in-oil emulsion (water droplets surrounded by oil).⁶⁸

Formation of emulsions affects the behaviour of an oil spill in many ways. First, weathering rates are much slower. The oil is more viscous and sticky, and is often referred to as chocolate mousse because of its appearance. Most recovery equipment works very poorly on mousse.

The volume of oil is increased by a factor of 2-3, because the emulsion is up to 70 percent water. Tendency to emulsify and emulsion stability is very closely related to the asphaltene content. Laboratory and field experience point out that stable emulsions are likely to form for: high viscosity heavy crudes, crudes and refined products having high asphaltene content ($\geq 5\%$), and crudes with high content of heteroatoms (oxygen, nitrogen and sulphur). On the contrary, emulsification hardly occurs during spills of gasoline, kerosene, and diesel fuels (except under very cold conditions).

Oxidation. Chemical transformations of oil in the water column and on the water surface start the day after the oil spill. They are mainly photochemical oxidations promoted by sunlight - mainly UV-, its extent depending on the type of oil and the way of exposure. These processes are catalyzed by some trace elements like vanadium, and inhibited by compounds containing sulphur. Photo-oxidation increases the viscosity of the spilled oil, and promotes the formation of solid oil aggregates (tar balls), which may be as large as pancakes (photo at right⁷¹), although most are coin-sized; however, this process is very slow. The



⁷¹ Image taken from NOAA:

[http://response.restoration.noaa.gov/topic_subtopic_entry.php?RECORD_KEY%28entry_subtopic_topic%29=entry_id,subtopic_id,topic_id&entry_id\(entry_subtopic_topic\)=154&subtopic_id\(entry_subtopic_topic\)=8&topic_id\(entry_subtopic_topic\)=1](http://response.restoration.noaa.gov/topic_subtopic_entry.php?RECORD_KEY%28entry_subtopic_topic%29=entry_id,subtopic_id,topic_id&entry_id(entry_subtopic_topic)=154&subtopic_id(entry_subtopic_topic)=8&topic_id(entry_subtopic_topic)=1)

products of oxidation usually have increased solubility in sea water, and their toxicity as well. The formation of tar balls is caused by the oxidation of thick layers of high viscosity oils or emulsions, forming an outer protective coating of heavy compounds and increasing the persistence of the oil as a whole.

Sedimentation. Part of the oil, up to 10-30%, is adsorbed on the suspended material and sinks; it is relevant near the coastal zone and in shallow waters where particulates are abundant and water is subjected to intense mixing. Sedimentation of oil (except for the heaviest fractions) is an extremely slow process in areas far from the shore. The oxidation processes slow down under conditions in the bottom of the sea. The heavy oil fractions accumulated inside the sediments can be preserved for years. Simultaneously, biosedimentation takes place.

Biodegradation. The suspended forms of oil and its components undergo intense biological decomposition in the water column. The fate of most substances of an oil spill at sea is ultimately dependent on the microbial activity. About a hundred known species of bacteria and fungi are able to use oil components to sustain their growth and metabolism, each one degrades a particular group of compounds; however, some compounds in oil are not biodegradable. The biodegradation rate depends upon the structure of the corresponding molecule. Alkanes biodegrade faster than naphthenic and aromatic compounds; the rate of microbial decomposition usually slows down when complexity of molecular structure increases, i.e., the number of carbon atoms and degree of chain branching. In addition, this rate depends on the physical state of the oil, including the degree of its dispersion. The most important environmental factors, apart organisms themselves, influencing biodegradation include temperature, concentration of nutrients and oxygen.

Response to oil spills would involve logistics of transporting the spill recovery equipment and personnel to the spill source, recover spilled oil until the spill source is stopped and develop systems and processes to render the recovered oil sellable, thus minimizing the environmental damage and the economic impact of the black tide. Unfortunately, the technology does not exist to totally recover all the oil that is spilled at sea.

An essential element of effective response to marine oil spills is aerial reconnaissance;⁶⁹ it assesses the location and extent of oil contamination, and verifies predictions of the movement and fate of oil slicks at sea.

There are three main ways to fight against black tides at sea (Fig. 24):

- Containment and recovery⁷²
- Disperse it
- In-situ burning

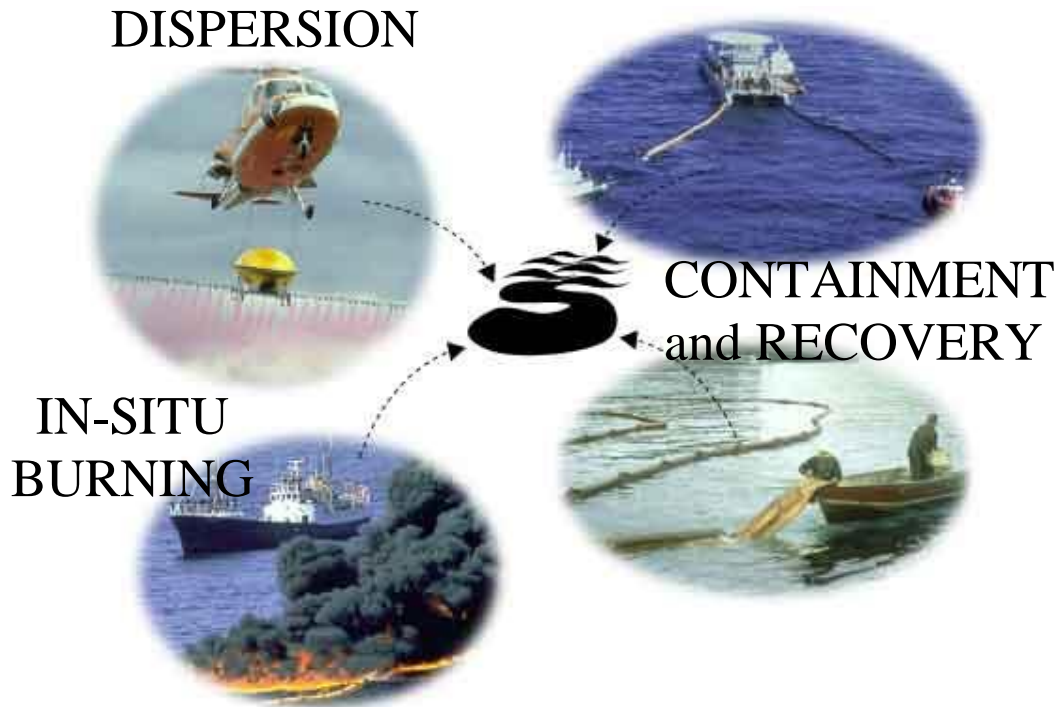


Figure 24. Oil spill cleanup procedures⁷³

Containment and recovery. Its aim is to remove the pollutant from the sea surface, at sea and near the coastline, before it hits the shore. Booms and skimmers are used.

There are several types of booms, all sharing the following main features:

- freeboard to prevent or reduce splash over;
- a sub-surface skirt to prevent or reduce escape of oil under the boom;
- longitudinal tension member to provide strength to withstand the effects of winds, waves and currents.

Booms should be flexible to conform to wave motion yet sufficiently rigid to retain as much oil as possible. No boom is capable of containing oil against currents greater than 0.7 knot at right angles to the boom, irrespective of boom size or skirt depth.

⁷² <http://www.itopf.com/spill-response/clean-up-and-response/containment-and-recovery/>

⁷³ Image taken from NOAA:

[http://response.restoration.noaa.gov/topic_subtopic_entry.php?RECORD_KEY%28entry_subtopic_topic%29=entry_id,subtopic_id,topic_id&entry_id\(entry_subtopic_topic\)=160&subtopic_id\(entry_subtopic_topic\)=8&topic_id\(entry_subtopic_topic\)=1](http://response.restoration.noaa.gov/topic_subtopic_entry.php?RECORD_KEY%28entry_subtopic_topic%29=entry_id,subtopic_id,topic_id&entry_id(entry_subtopic_topic)=160&subtopic_id(entry_subtopic_topic)=8&topic_id(entry_subtopic_topic)=1)

Towing booms at sea, for example in U (photo at right⁷⁴) or J configurations, is a difficult task requiring specialised vessels.

Various types of weir, oleophilic and suction skimmers currently exist for recovering oil from the sea surface. The use of each type is determined by the specific environmental conditions and oil/oil emulsion properties. The



simplest skimmers are suction devices which remove oil from the water surface directly or via a weir, although these pick up a lot of water at the same time. More complex units rely on the adhesion of oil to metal or plastic disks, or oleophilic belts or ropes; natural or man-made floating debris reduces the efficiency of the recovery.

Low temperature, high waves, strong winds as well as the formation of water-in-oil emulsion dramatically change oil slick properties within a short period following the spill, leading to a decrease in the mechanical recovery efficiency.

Dispersion. The effectiveness of mechanical response techniques varies and depends on the nature, size, and location of the spill as well the environmental conditions under it is carried out. Dispersants may help to break up the oil slick when containment and recovery are not enough or possible, or to avoid the contact of the oil with sensitive habitats and resources.

Dispersants are chemical agents (surfactants⁷⁵) that reduce interfacial tension⁷⁶ between oil and water thus enhancing the natural process of dispersion, i.e., the break-up of slicks on the surface into a multitude of smaller droplets dispersed in the water column is facilitated. The dispersed oil droplets do not merge into larger droplets, avoiding the reformation of surface slicks.

The mode of action of dispersants is shown in Fig. 25.⁷⁷ The dispersant (solvent plus surfactant) if sprayed onto the oil (A); then the solvent carries the surfactant into the oil (B). The molecules of the surfactant attach to the oil (C), reducing the interfacial tension between oil and water breaking up the oil slick (D).

⁷⁴ Image courtesy of ITOPF (<http://www.itopf.com/spill-response/clean-up-and-response/containment-and-recovery/>)

⁷⁵ Surfactants molecules are made up of two parts: a oil-compatible (oleophilic) part, and a water-compatible (hydrophilic) part.

⁷⁶ See page 15.

⁷⁷ Image courtesy of ITOPF (http://www.itopf.com/_assets/documents/tip4.pdf)

Finally, the so formed small droplets disperse in the water column by turbulent mixing (E), i.e., the suspended small droplets spread in three dimensions (the water column) instead of two (sea surface). This facilitates the breakdown of the hydrocarbons by bacteria naturally present in sea water (Figure 26), and the local toxic effect of spilled oil is reduced.

There are three main types of dispersants:⁷⁸

- Type 1: based on hydrocarbon solvents with between 15% to 25% surfactant. They are sprayed neat onto the oil as pre-dilution with sea water renders them ineffective. Typical dose rates are between 1:1 and 1:3 (dispersant:oil).
- Type 2: dilutable concentrate dispersants which are alcohol or glycol (i.e. oxygenated) solvent based with a higher surfactant concentration. Dilution is normally 1:10 with sea water.
- Type 3: concentrate dispersants with a similar formulation to type 2 dispersants, which are designed to be used neat and typical dose rates are between 1:5 and 1:30.

Commercial formulations of modern chemical dispersants usually comprised two or more surfactant molecules having different solubility in both water and oil; dispersants are usually applied by airplane (for handling large off-shore spills) or helicopter (for dispersing smaller spills near shore areas), and also by boat (for treating minor spills in harbours or confined waters).

The use of dispersants is limited by technical factors. They must be used in precise proportions and conditions. Dispersion remains inefficient on viscous or weathered oil with viscosities greater than 2000 centistokes, and calm waters (Fig. 26).

The use of dispersants is an option when the type and properties of the oil favour chemical dispersion and:

- the black tide threatens a sensitive coastal area and mechanical recovery is not feasible
- waves are able to break up the surface slick
- there is sufficient potential for rapid dilution of the dispersed oil

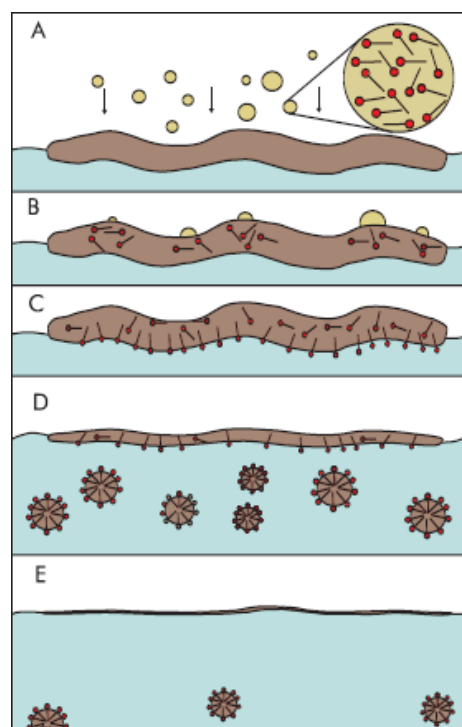


Figure 25. Dispersion of an oil slick

⁷⁸ <http://www.itopf.com/spill-response/clean-up-and-response/dispersants/>

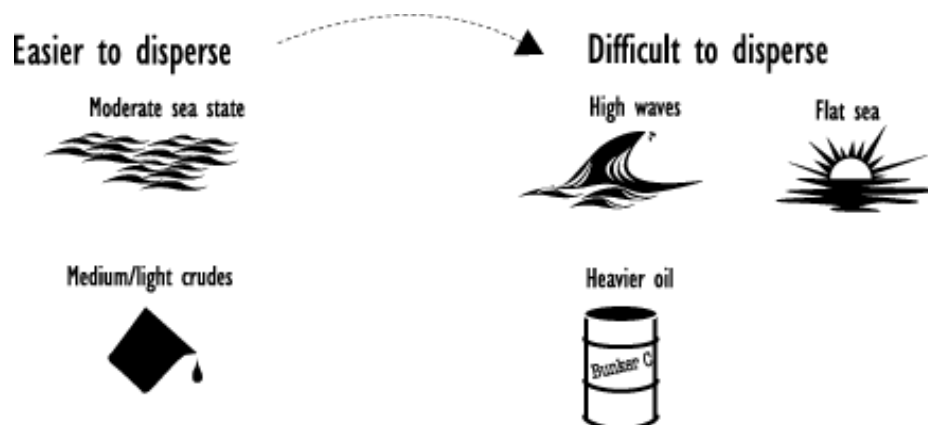


Figure 26. Ideal conditions for dispersing oil spills⁷⁹

The dispersed oil droplets are colonized by bacteria that then begin to degrade them; next, organisms like protozoans and nematodes join the colonies, and finally the some products are incorporated the food web (Figure 27).

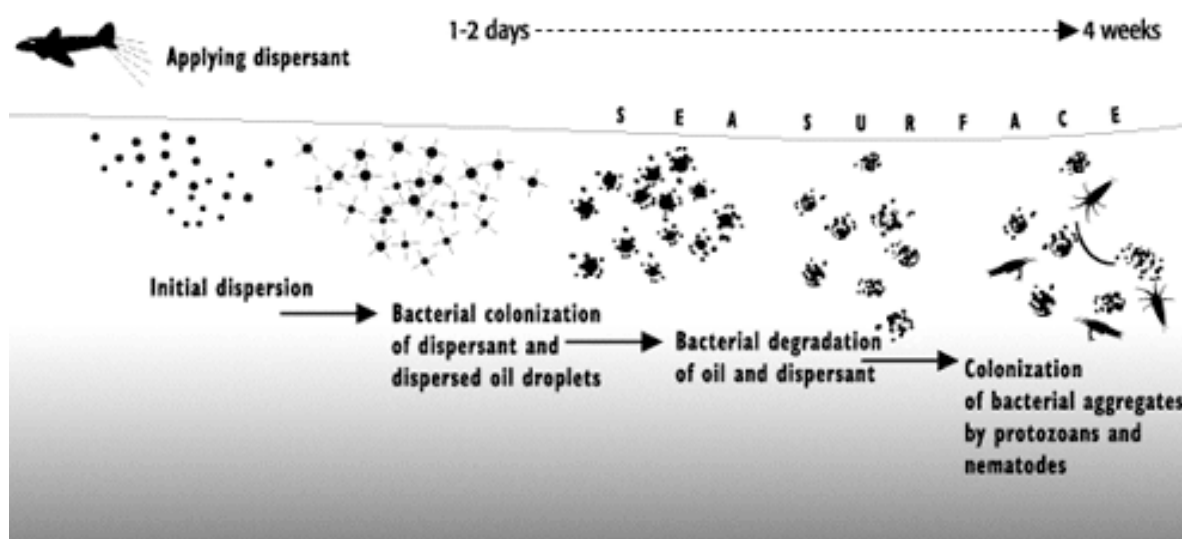


Figure 27. Biodegradation of dispersed oil droplets⁷⁸

Contrary to what happens in the open ocean, where significant biological effects are improbable, in the proximity to sensitive areas like water intakes, mariculture facilities or fish spawning areas the cost-effectiveness and conflicting priorities for protecting different resources from pollution damage should be careful analyzed. The main disadvantage of dispersion of oil is the localized and temporary increase in oil in water concentration that

⁷⁹ Image taken from NOAA:

[http://response.restoration.noaa.gov/topic_subtopic_entry.php?RECORD_KEY%28entry_subtopic_topic%29=entry_id,subtopic_id,topic_id&entry_id\(entry_subtopic_topic\)=158&subtopic_id\(entry_subtopic_topic\)=8&topic_id\(entry_subtopic_topic\)=1](http://response.restoration.noaa.gov/topic_subtopic_entry.php?RECORD_KEY%28entry_subtopic_topic%29=entry_id,subtopic_id,topic_id&entry_id(entry_subtopic_topic)=158&subtopic_id(entry_subtopic_topic)=8&topic_id(entry_subtopic_topic)=1)

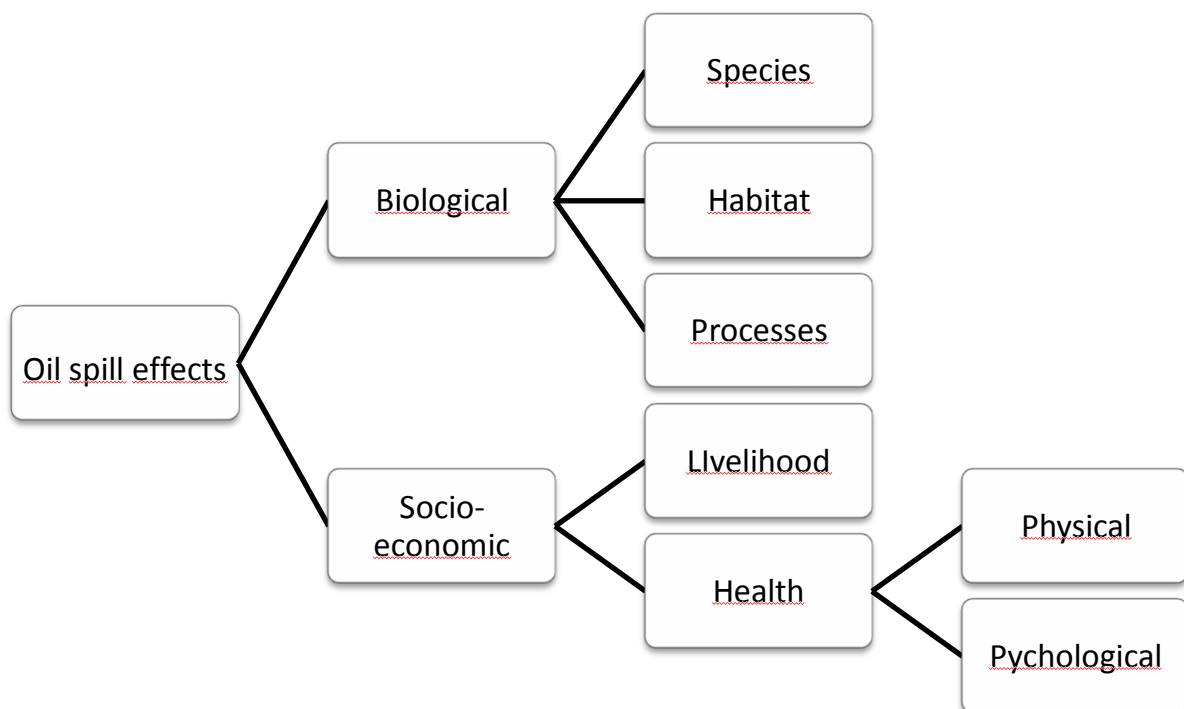
could have an effect on the marine life within the immediate vicinity of the dispersant operation.

In-situ burning is the controlled burning of oil slicks at sea, or close to the site where the spill occurred. For spilled oils on open waters, the oil must be collected and held by fire-resistant booms to ensure that the boomed oil achieves the minimum thickness to be ignited and sustain burning. The advantages of *in-situ* burning include rapid removal of oil and, at the same time, it avoids oil recovery, transport, storage, and disposal. On the other hand, the generation of large quantities of smoke, and the formation and possible sinking of extremely viscous and dense residues are the main disadvantages.

Although it is not a proper cleanup procedure, lightering (transfer the cargo of oil from a stricken vessel into another vessel or a barge) helps in reducing the amount of oil to be spilled.

The use of chemical dispersants, as well as *in-situ* burning, revolves around changing the fate of spilled material within the environment, as opposed to attempting recovery of that material, the latter being the preferred option from the environmental point of view.

Effects of oil spills. The following scheme shows the basic effects of oil spills.



Oil spills could harm to wildlife through physical contact, ingestion, inhalation and absorption. Floating oil can contaminate plankton, which includes algae, fish eggs, and the larvae of various invertebrates thus entering in the web food, therefore bigger fish, birds, terrestrial mammals, and even humans may finally become affected.

The biological effect of oil spilled depends on its type and quantity, the season and weather, the type of shoreline, and the type of waves and tidal energy in the area of the black tide. The animals and plants most at risk are those that could come into contact with a contaminated sea surface. Physical smothering is one of the main threats posed to living resources by the persistent residues of spilled oils and mousse.

Oil spill modelling. After an oil spill the first and primary concern of response planners is to determine the direction of the slick, its speed, and to know its weathering and spreading characteristics under the influence of prevailing currents and weather conditions. In this sense oil spill modelling can be vital in both oil spill preparedness and response activities.

There are many oil spill modelling software, here two interesting tools merits a comment: **GNOME** and **ADIOS2**. Both programs are freely downloadable from the NOAA's NATIONAL OCEAN SERVICE - OFFICE OF RESPONSE AND RESTORATION web site.⁸⁰ According to the information provided by the **GNOME**⁸¹ is a trajectory model able to (i) estimate the trajectory of spills (user should provide data on wind and weather conditions, circulation patterns, river flow, and the type of oils spilled); (ii) predict the trajectories that can result when there is inexactness (uncertainty) in current and wind observations and forecasts; (iii) use weathering algorithms to make simple predictions about the changes the oil will undergo while it is exposed to the environment; (iv) quickly be updated and re-run with new information; and (v) provide trajectory output (including uncertainty estimates) in a geo-referenced format that can be used as input to GIS (geographic information system) programs. **GNOME** can provide the needed trajectory, and **ADIOS2** can provide the detailed mass balance.

GNOME uses a simplistic weathering algorithm, a more complex algorithm is implemented in the **ADIOS2** program.⁶² Automated Data Inquiry for Oil Spills (**ADIOS2**) is an initial oil spill response tool for emergency spill responders and contingency planners to use on either a

⁸⁰ NOAA's web site: http://response.restoration.noaa.gov/resource_catalog.php

⁸¹ GNOME information can be found at:

[http://response.restoration.noaa.gov/type_subtopic_entry.php?RECORD_KEY%28entry_subtopic_type%29=entry_id,subtopic_id,type_id&entry_id\(entry_subtopic_type\)=292&subtopic_id\(entry_subtopic_type\)=8&type_id\(entry_subtopic_type\)=3](http://response.restoration.noaa.gov/type_subtopic_entry.php?RECORD_KEY%28entry_subtopic_type%29=entry_id,subtopic_id,type_id&entry_id(entry_subtopic_type)=292&subtopic_id(entry_subtopic_type)=8&type_id(entry_subtopic_type)=3)

Macintosh or Windows-compatible computer. **ADIOS2** integrates a library of approximately one thousand oils with a short-term oil fate and cleanup model to help you estimate the amount of time that spilled oil will remain in the marine environment, and to develop cleanup strategies. **ADIOS2** calculations combine real-time environmental data entered by the user, such as wind speed, with carefully researched chemical and physical property information in its oil library. The program provides a best-guess answer and also calculates possible ranges in the values of estimated spill properties.

Table 8 shows the result of 100000 barrels oil spill involving the different types of oil, as modelled in **GNOME**, somewhere at the San Diego Bay.

Table 8. Oil spills modeled by **GNOME**

	Evaporated/Dispersed	Beached	Floating	Off map
Gasoline	100000	0	0	0
Kerosene	92000	6800	1200	0
Diesel	62700	33000	4300	0
Fuel oil 4	49700	43900	6400	0
Medium	39700	53300	7000	0
Fuel oil 6	30600	62000	7400	0
Non weathering	0	87800	12200	0

The corresponding files and Quicktime⁸² movies are provided as accompanying material, as well as an example of the **ADIOS2** output of the weathering of 100000 barrels of BELRIDGE HEAVY oil.

In addition to **GNOME** and **ADIOS2**, it is worth to mention the NOAA Unit Converter for Oil Spills (**NUCOS**) and the *Spill Tools* software, also freely available from the NOAA's Ocean Service Office of Response and Restoration Web site. **NUCOS**⁸³ is a simple desktop

⁸² <http://www.apple.com/es/quicktime/download/>

⁸³ NOAA's NATIONAL OCEAN SERVICE - OFFICE OF RESPONSE AND RESTORATION:
[http://www.response.restoration.noaa.gov/type_subtopic_entry.php?RECORD_KEY\(entry_subtopic_type\)=entry_id,subtopic_id,type_id&entry_id\(entry_subtopic_type\)=717&subtopic_id\(entry_subtopic_type\)=8&type_id\(entry_subtopic_type\)=3](http://www.response.restoration.noaa.gov/type_subtopic_entry.php?RECORD_KEY(entry_subtopic_type)=entry_id,subtopic_id,type_id&entry_id(entry_subtopic_type)=717&subtopic_id(entry_subtopic_type)=8&type_id(entry_subtopic_type)=3)

tool that converts basic units of velocity, mass, length, etc., but more specifically, converts units that are unique to oil spill response. *Spill Tools*⁸⁴ is a collection of three tools to assess how effectively spilled oil can be recovered (**Mechanical Equipment Calculator**), removed (**In Situ Burn Calculator**), or dispersed (**Dispersant Mission Planner**). All three *Spill Tools calculators* need an estimate of the thickness of the specified oil slick, which could be calculated from the **ADIOS2** program.

Mechanical Equipment Calculator⁸⁵ allows the estimation of the rates at which mechanical equipment, such as skimmers, can recover oil from a specified slick. By using user's information the program determines how reconfiguring the skimmer operation might affect how quickly oil could be recovered.

In Situ Burn Calculator⁸⁵ estimates how much fire boom it is needed to burn a specified amount of spilled oil or section of an oil slick; how many burns should be conducted, and the concentrations within the smoke plume that would be generated by the burn.

The Dispersant Mission Planner⁸⁵ calculates how much dispersant should be applied to completely treat a specified amount of oil, given a particular dispersant-to-oil ratio. To use the planner, in addition to the oil thickness, the area covered by the spilled oil to be treated.

DMP2⁸⁶ is an update to the **Dispersant Mission Planner** that was originally part of the *Spill Tools* software collection.

⁸⁴ NOAA's NATIONAL OCEAN SERVICE - OFFICE OF RESPONSE AND RESTORATION:

[http://response.restoration.noaa.gov/topic_subtopic_entry.php?RECORD_KEY\(entry_subtopic_topic\)=entry_id,subtopic_id,topic_id&entry_id\(entry_subtopic_topic\)=355&subtopic_id\(entry_subtopic_topic\)=8&topic_id\(entry_subtopic_topic\)=1](http://response.restoration.noaa.gov/topic_subtopic_entry.php?RECORD_KEY(entry_subtopic_topic)=entry_id,subtopic_id,topic_id&entry_id(entry_subtopic_topic)=355&subtopic_id(entry_subtopic_topic)=8&topic_id(entry_subtopic_topic)=1)

⁸⁵ NOAA's NATIONAL OCEAN SERVICE - OFFICE OF RESPONSE AND RESTORATION:

[http://response.restoration.noaa.gov/topic_subtopic_entry.php?RECORD_KEY%28entry_subtopic_topic%29=entry_id,subtopic_id,topic_id&entry_id\(entry_subtopic_topic\)=466&subtopic_id\(entry_subtopic_topic\)=8&topic_id\(entry_subtopic_topic\)=1](http://response.restoration.noaa.gov/topic_subtopic_entry.php?RECORD_KEY%28entry_subtopic_topic%29=entry_id,subtopic_id,topic_id&entry_id(entry_subtopic_topic)=466&subtopic_id(entry_subtopic_topic)=8&topic_id(entry_subtopic_topic)=1)

⁸⁶ NOAA's NATIONAL OCEAN SERVICE - OFFICE OF RESPONSE AND RESTORATION:

[http://response.restoration.noaa.gov/topic_subtopic_entry.php?RECORD_KEY%28entry_subtopic_topic%29=entry_id,subtopic_id,topic_id&entry_id\(entry_subtopic_topic\)=552&subtopic_id\(entry_subtopic_topic\)=8&topic_id\(entry_subtopic_topic\)=1](http://response.restoration.noaa.gov/topic_subtopic_entry.php?RECORD_KEY%28entry_subtopic_topic%29=entry_id,subtopic_id,topic_id&entry_id(entry_subtopic_topic)=552&subtopic_id(entry_subtopic_topic)=8&topic_id(entry_subtopic_topic)=1)

Complementary material

- PowerPoint file: *ships_terms_oer.ppsx*
- Self evaluation tests: *mar_trans_chem_en_test_oer (WinRAR Zip)*
- Oil spill modelling using GENOME⁸¹

pdf file	Quicktime movie ^a
gasoline_oer.pdf	SpillMovie_oer_gasoline_gnome.mov
kerosene_oer.pdf	SpillMovie_oer_kerosene_gnome.mov
diesel_oer.pdf	SpillMovie_oer_diesel_gnome.mov
fuel_oil_4_oer.pdf	SpillMovie_oer_fuel_oil_4_gnome.mov
medium_oer.pdf	SpillMovie_oer_medium_crude_gnome.mov
fuel_oil_6_oer.pdf	SpillMovie_oer_fuel_oil_6_gnome.mov
non_weathering_oer.pdf	SpillMovie_oer_non_weathering_gnome.mov

a <http://www.apple.com/es/quicktime/download/>

- Oil spill modelling using ADIOS2⁶²: **belridge_heavy_ADIOS2.pdf**
- Software allowing the Volume Correction Factor (VCF) -EXCEL spreadsheets formerly available at INTERNET -:
 - VCF_1.xls
 - VCF_2.xls

Further reading

Review of Maritime Transport 2009

(downloadable at http://www.unctad.org/en/docs/rmt2009_en.pdf)

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YouTube videos

Atomic structure: <http://www.youtube.com/watch?v=Gsf7jhWr6ng&feature=related>

Ionic bond: http://www.youtube.com/watch?v=xTx_DWboEVs

Convalent bond: http://www.youtube.com/watch?v=1wpDicW_MQQ&NR=1

Ionic & covalent bond: <http://www.youtube.com/watch?v=QqjcCvzWwww&feature=related>

Very interesting links:

- NOAA's NATIONAL OCEAN SERVICE - OFFICE OF RESPONSE AND RESTORATION: <http://response.restoration.noaa.gov/index.php>
- CEDRE - Centre de Documentation, de Recherche et d'Expérimentations sur les pollutions accidentelles des eaux: <http://www.cedre.fr/>
- ITOPF – The International Owner Pollution Federation Limited: <http://www.itopf.com/>
- INTERTANKO – The International Association of Independent Tanker Owners <http://www.intertanko.com/>
- Black tides: <http://www.black-tides.com/>
- MOUSSE formation: <http://www.pcs.gr.jp/doc/EMousse/text.htm>

Books

- Crude Oil Waxes, Emulsions, and Asphaltenes. Becker, J. R. Pennwell Books (1997)
- Fundamentals of Petroleum Refining. Fahim, M.A., Elkilani, A. Elsevier Science (2009)
- Interfacial Properties of Petroleum Products (Chemical Industries). Pillon, L. Z. CRC Press (2007)
- Oil: A Beginner's Guide (Beginner's Guides). Smil, V. Oneworld Publications (2008)
- Oil Spill Dispersants: Efficacy and Effects. National Academies Press (2005) (freely readable on-line http://www.nap.edu/catalog.php?record_id=11283)
- Petroleum Spills in the Marine Environment: Chemistry and Formation of Water-in-Oil Emulsions and Tar Balls. Payne, J.R., Philips, C.R. Lewis Publishers (1985).
- Principles of Environmental Chemistry (2nd edition). Girard, J. E. Jones & Bartlett Publishers (2009)
- The Basics of Oil Spill Cleanup (2nd edition). Fingas, M. CRC Press (2000).

Appendix - Periodic Table of the Elements

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Links to some periodic tables of (chemical) elements at Internet

http://en.wikipedia.org/wiki/Periodic_table (WIKIPEDIA)

<http://www.chemicalelements.com/>

<http://www.webelements.com/>

<http://www.chemicool.com/>

<http://education.jlab.org/itselemental/>

<http://periodictable.com/> (photographs)

<http://www.rsc.org/chemsoc/visualelements/PAGES/pertable fla.htm>

<http://www.uky.edu/Projects/Chemcomics/> (the periodic table of comic books)

<http://www.periodicvideos.com/> (the periodic table of videos -University of Nottingham-)

<http://chemistry.about.com/library/blperiodictable.htm>

http://old.iupac.org/reports/periodic_table/IUPAC_Periodic_Table-22Jun07b.pdf

<http://www.ptable.com/> (very complete information on chemical elements –drawback: is in Spanish, although it has some links to web pages in English –).

Group #	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Period	<div>Back to: Text Table of contents</div>																	
1	1 H																	2 He
2	3 Li	4 Be	Periodic Table of the Elements										5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	57 La*	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	89 Ac**	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Uut	114 Uug	115 Uup	116 Uuh	117 Uus	118 Uuo
* Lanthanoids			58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu		
** Actinoids			90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr		

<u>Element categories</u> in the periodic table										
<u>Metals</u>						<u>Nonmetals</u>				
<u>Alkali metals</u>	<u>Alkaline earth metals</u>	<u>Inner transition elements</u>		<u>Transition elements</u>	<u>Other metals</u>	<u>Metalloids</u>	<u>Other nonmetals</u>	<u>Halogens</u>	<u>Noble gases</u>	(Unknown)
		<u>Lanthanides</u>	<u>Actinides</u>							
<u>Atomic number</u> colors show <u>state</u> at <u>standard temperature and pressure</u> (0 °C and 1 atm)					Borders show natural occurrence					
Solids	Liquids	Gases	Unknown		<u>Primordial</u>	<u>From decay</u>	<u>Synthetic</u>	(Undiscovered)		

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