

Principles of Energy Conversion

Part 9. Chemical Energy & Fuels

March 8, 2018

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Article 15

Fuels

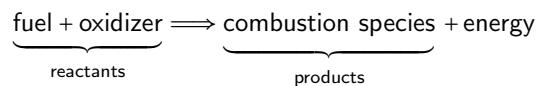
I believe that the great Creator has put ores and oils on this earth to give us a breathing spell. As we exhaust them, we must be prepared to fall back on our farms, which is God's true storehouse and can never be exhausted. We can learn to synthesize material for every human need from things that grow.

George Washington Carver [1864 - 1943]

15.1 Introduction to Fuels

The term *fuel* almost always indicates a source of chemical energy to be combusted for conversion to thermal energy. Fuels may also be used to produce light (electromagnetic energy) and electrical energy through electrochemical devices such as batteries and fuel cells. Sources of chemical energy for direct conversion to electrical energy are commonly referred to as *reactants*. The most commonly used combustible fuels are fossil fuels; coal, petroleum and natural gas. The most common combustible elements in these fuels are carbon (C), hydrogen (H), and sulfur (S). Hydrocarbon fuels are comprised of carbon atoms bonded in a chain with side bonds of hydrogen.

Combustion is the conversion of a fuel into combustion products and energy release. The energy released is nearly always in the form of heat (transient thermal energy). Combustion requires a chemical reaction between a fuel and an oxidizer. Oxygen is the most common oxidizer and most often the source of oxygen is air. The amount of energy released can be measured using a calorimeter.



Fuels are commonly divided into solid, liquid and gaseous forms. Solid fuels, such as coal, are generally specified in terms of the mass fraction of chemical elements. Carbon (C), hydrogen (H₂), and sulfur (S) are three common combustible elements found in fuels. Carbon oxidation is slower and more difficult than hydrogen or sulfur. It is a common assumption that both H₂ and S will burn completely in a fuel before any carbon burns. Liquid fuels, such as gasoline, are specified in terms of the mass fraction of hydrocarbon compounds (butane, octane, 2,2,4-trimethylpentane). Gaseous fuels, such as natural gas, are generally specified in terms of mole fractions of chemical compounds (methane, propane, isobutane). All three forms of fuel, solid, liquid and gaseous, are found naturally and can be synthesized or manufactured.

15.2 Solid Fuels

In the United States, solid fuels are predominantly coal, wood and biowaste from farming. In many parts of the world manure or peat are the most common solid fuels.

15.2.1 Coal & Coal Classifications

Using the American Society for Testing Materials standard ASTM D 388 [1], coal is ranked by carbon and volatile (light hydrocarbons) composition. The hardest coal is anthracite, followed by semi-anthracite, semi-bituminous, bituminous and lignite. Figure 15.1 illustrates the ranking of coals based on fixed carbon content and heating value. Fixed carbon indicates carbon not contained in volatiles. Volatiles are light hydrocarbons that are released from the coal with slight heating. Generally, volatiles are not considered when determining the heating value of a coal since these compounds have usually been driven off with heating prior to combustion. Coal ranks vary widely in hardness, carbon content, volatile matter content, and mineral content. The mineral content is not combustible and becomes the left over residue known as ash.

anthracite: This type of coal is hard, smoke-free that is low in volatile matter and high in carbon. Within this rank are three distinct groups of coal. Metaanthracite is the hardest and has the highest carbon content with greater than 98% fixed carbon. Anthracite has the next highest fixed carbon equal or greater than 92% and Semianthracite has a fixed carbon content equal or greater than 86%.

bituminous: This type of coal is less hard than anthracite, lower in fixed carbon and higher in volatiles. Within this type are Low-volatile bituminous, Medium-volatile bituminous, High-volatile A bituminous, High-volatile B bituminous, and High-volatile C bituminous. The primary differences are in the fixed carbon content and volatile content.

sub-bituminous: This type of coal is soft and sometimes referred to as black lignite. It is characterized by high volatile content and low fixed carbon. Heating values are relatively low relative to the preceding coal ranks and it pulverizes easily. Sub-bituminous A, Sub-bituminous B, and Sub-bituminous C are groups within this type with decreasing heating values, respectively.

lignite: This coal is brown with a woody structure and generally has a high moisture content. Lignite A and Lignite B are the two major groups with heating values between 6300 - 8300 Btu/lbm and less than 6300 Btu/lbm, respectively.

brown coal:

peat: Peat is semi-carbonized vegetable matter that must be dried before burning. It has a low heating value. Peat is created by partial decomposition of organic matter in water, where there is little to no oxygen present.

cannel coal: This type of coal does not fall under any particular system of classification. It is bituminous, but with an extra high hydrogen content. Often it is used in the manufacture of gas.

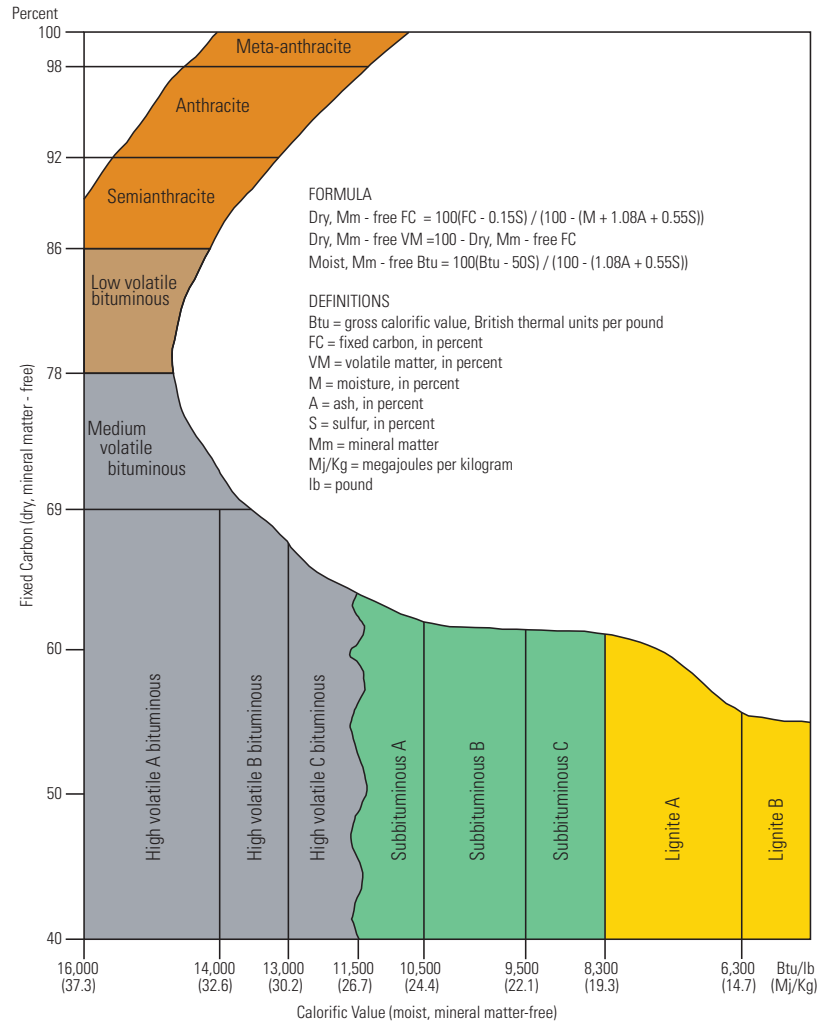


Figure 15.1. General coal ranks; from East [2]

US Demonstrated Reserve Base (DRB)

- anthracite; 1.5% of DRB; concentrated in northeastern Pennsylvania
- bituminous; 53% of DRB;
- subbituminous; 37% of DRB; all located west of the Mississippi River
- lignite; 9% of DRB; mostly found in Texas, Montana, and North Dakota
 [from US Energy Information Agency]

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Class	Group	Fixed carbon limits, % (dry, mineral-matter-free basis)		Volatile matter limits, % (dry, mineral-matter-free basis)		Calorific value limits, Btu/lb (moist, ^b mineral-matter-free basis)		Agglomerating character
		Equal or greater than	Less than	Greater than	Equal or less than	Equal or greater than	Less than	
I. Anthracitic	1. Metaanthracite	98	2	Nonagglomerating
	2. Anthracite	92	98	2	8	
	3. Semianthracite ^c	86	92	8	14	
II. Bituminous	1. Low-volatile bituminous coal	78	86	14	22	Commonly agglomerating ^e
	2. Medium-volatile bituminous coal	69	78	22	31	
	3. High-volatile A bituminous coal	...	69	31	...	14,000 ^d	
	4. High-volatile B bituminous coal	13,000 ^d	14,000	
	5. High-volatile C bituminous coal	11,500 ^d	13,000	
III. Subbituminous	1. Subbituminous A coal	10,500	11,500	Nonagglomerating
	2. Subbituminous B coal	9,500	10,500	
	3. Subbituminous C coal	8,300	9,500	
IV. Lignitic	1. Lignite A	6,300	8,300	Nonagglomerating
	2. Lignite B	6,300	

^a This classification does not include a few coals, principally nonbanded varieties, which have unusual physical and chemical properties and which come within the limits of fixed carbon or calorific value of the high-volatile bituminous and subbituminous ranks. All of these coals either contain less than 48 percent dry, mineral-matter-free fixed carbon or have more than 15,500 Btu/lb on the moist, mineral-matter-free basis.

water on the surface of the coal.

^b If agglomerating, classify in low-volatile group of the bituminous class.

^c Coals having 69 percent or more fixed carbon on the dry, mineral-matter-free basis shall be classified according to fixed carbon, regardless of calorific value.

^e It is recognized that there may be nonagglomerating varieties in these groups of the bituminous class, and there are notable exceptions in the high-volatile C bituminous group.

$$\text{Dry, Mm-free FC} = \frac{\text{FC} - 0.15S}{100 - (M + 1.08A + 0.55S)} \times 100 \quad \%$$

$$\text{Dry, Mm-free VM} = 100 - \text{dry, Mm-free FC} \quad \%$$

$$\text{Moist, Mm-free Btu} = \frac{\text{Btu} - 50S}{100 - (1.08A + 0.55S)} \times 100 \quad \text{per lb}$$

where Mm = mineral matter
 Btu = heating value per lb
 FC = fixed carbon, %
 VM = volatile matter, %
 M = bed moisture, %
 A = ash, %
 S = sulfur, %

All are for coal on a moist basis.

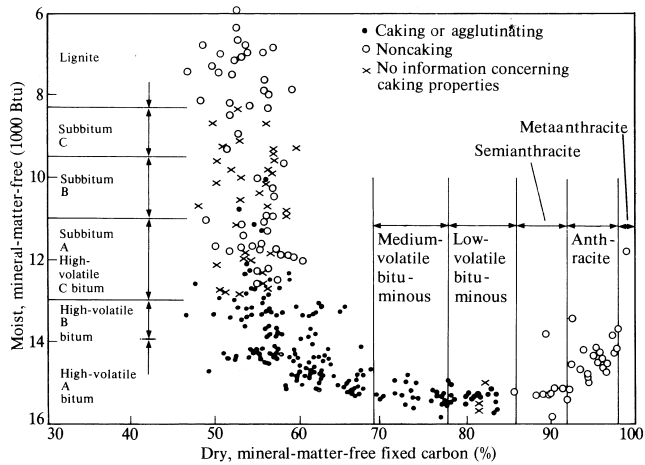


Figure 15.2. Classification of coals by rank, ASTM D 388. [3]

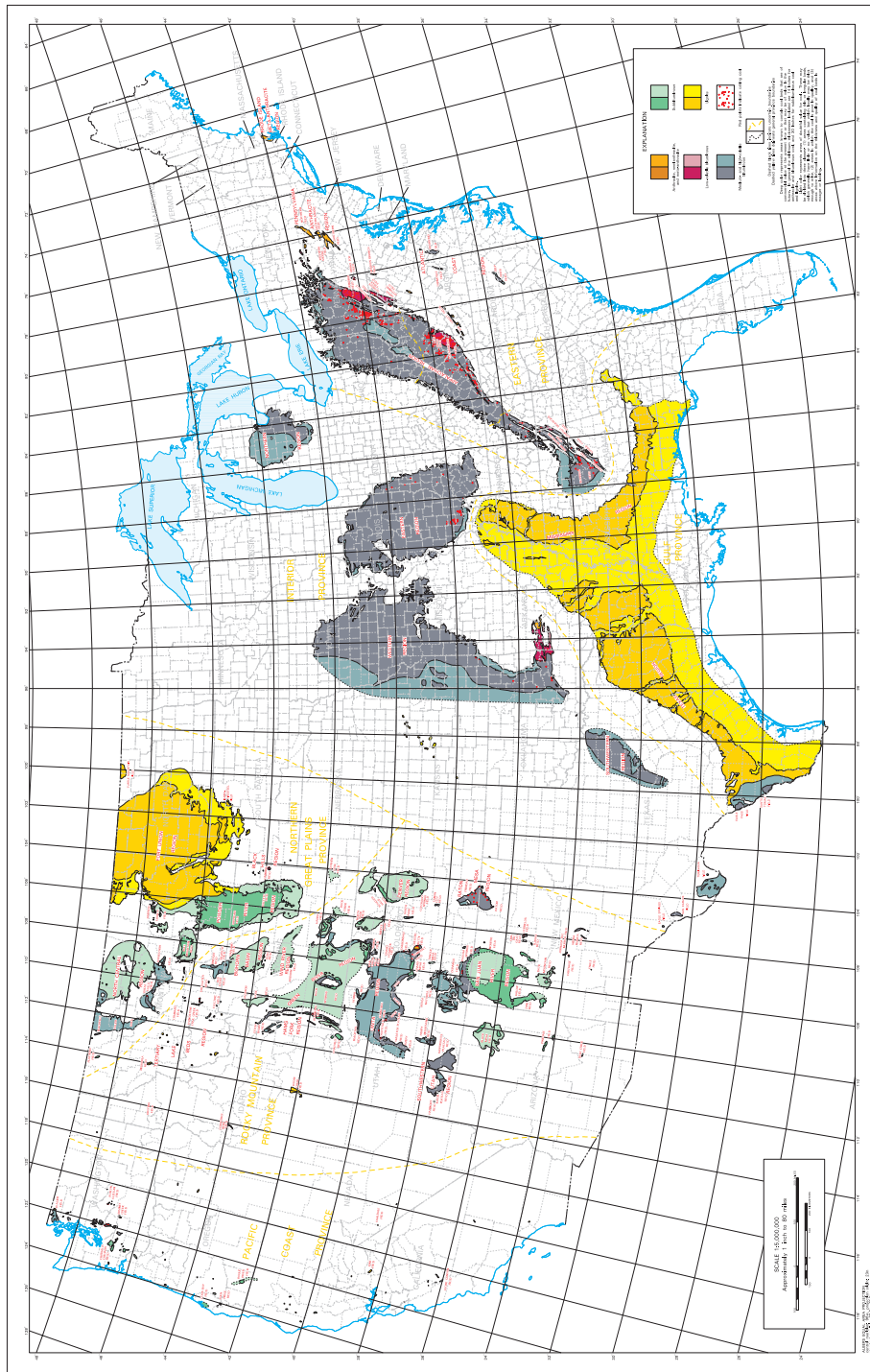


Figure 15.3. U.S. coal field map from USGS Open-File Report OF 96-92. [2]

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15.2.2 Biomass

- wood
- peat; often classified with coal

15.2.3 Manufactured

- torrefication (bio-coal)
- wood pellets

15.2.4 Refuse

- garbage
- manure

15.3 Analysis of Solid Fuels

not completed yet

15.3.1 Proximate Analysis

not completed yet

15.3.2 Ultimate Analysis

not completed yet

15.4 Hydrocarbon Chemistry

Many fuels are classified as hydrocarbons, which are composed of carbon and hydrogen. Hydrogen has a single electron (in the K shell) and needs to share an additional electron. This is why hydrogen gas is always found as H₂. Carbon atoms have 6 electrons, two in the K shell and four in the L shell, leaving the L shell 4 electrons short of being full. As such carbon can share four electrons with other elements. The simplest hydrocarbon is methane, CH₄, in which 4 hydrogen atoms all share a single electron with a carbon atom.

As the number of atoms increases, the fraction of hydrogen to carbon decreases and the hydrocarbon compound becomes less volatile. Extremely long hydrocarbon chains form solids. Fuels are generally a mixture of hydrocarbons. Crude oil (petroleum) may have millions of different hydrocarbon compounds.

Hydrocarbon compounds are divided into three major groups referred to as **aliphatic**, **alicyclic**, and **aromatic**. Aliphatic hydrocarbon compounds form carbon-atom “chains” and are the primary makeup of fossil fuels. Alicyclic and aromatic hydrocarbon compounds form carbon-atom “rings”; the difference between the two has to do with the structure of the ring. Aromatic hydrocarbons form benzene rings. A hydrocarbon compound may be *saturated* or *unsaturated*. Saturated hydrocarbons have a single bond, that is share a single electron, between each carbon atom of the chain or ring. Unsaturated hydrocarbons have at least two carbon atoms with multiple bonds, that is sharing two or three electrons. The chemical and physical properties may be extremely different for hydrocarbon compounds having the same number of carbon and hydrogen atoms but with different structures.

15.4.1 Aliphatic Hydrocarbons

Aliphatic hydrocarbons are naturally found in all fossil fuels and are in the form of carbon “chains”. The chain may be a single line of carbon atoms or there may be branches of carbon chains. There are three subgroups of the aliphatic hydrocarbons: **alkanes**, **alkenes**, & **alkynes**.

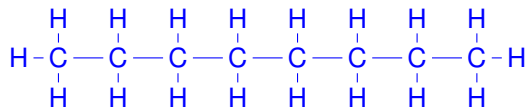
Alkanes, also known as paraffins, are saturated hydrocarbons with the number of carbon and hydrogen atoms corresponding to C_nH_{2n+2}. Common examples include:

Methane, CH ₄	Hexane, C ₆ H ₁₄	.
Ethane, C ₂ H ₆	Heptane, C ₇ H ₁₆	.
Propane, C ₃ H ₈	Octane, C ₈ H ₁₈	.
Butane, C ₄ H ₁₀	Nonane, C ₉ H ₂₀	Hexadecane, C ₁₆ H ₃₄
Pentane, C ₅ H ₁₂	Decane, C ₁₀ H ₂₂	.

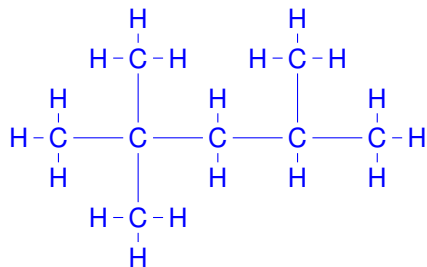
Normal alkanes, prefixed with “n-”, are saturated hydrocarbons in which the carbon atoms are connected in a single chain. Alkanes with carbon-atom branches, typically in the form of a methyl group (CH₃), are prefixed with “iso-”. The n- and iso- forms of octane (C₈H₁₈) are:

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n-octane: C_8H_{18}



iso-octane: C_8H_{18}



This particular arrangement of iso-octane is technically known as

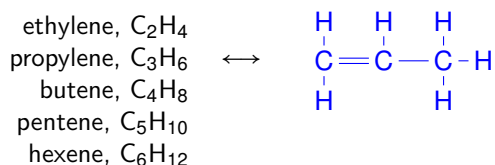
2,2,4-trimethylpentane.

There are 3 methyl groups (CH_3) attached to a pentane backbone at the 2nd, 2nd, and 4th carbon atom positions.

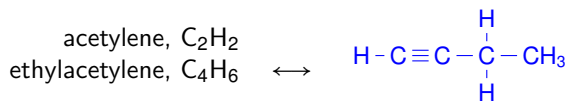
If one hydrogen atom in an alkane is replaced by OH^- , the hydrocarbon becomes an alcohol. For example:

methyl alcohol, methanol: CH_3OH
ethyl alcohol, ethanol: C_2H_5OH
propyl alcohol, propanol: C_3H_7OH
butyl alcohol, butanol: C_4H_9OH

Alkenes, also known as olefins, are unsaturated hydrocarbons with one double bond between two carbon atoms, C_nH_{2n}

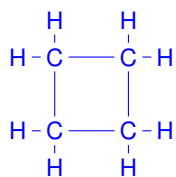
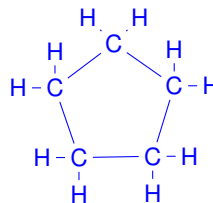


Alkynes, also known as acetylenes, are unsaturated hydrocarbons with one triple bond between two carbon atoms, $C_nH_{2(n-1)}$



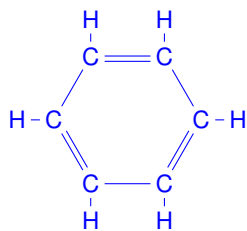
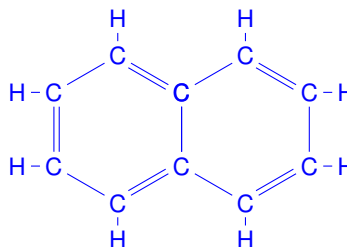
15.4.2 Alicyclic Hydrocarbons

Alicyclic hydrocarbons are saturated carbon atom “rings” with two hydrogen atoms for every carbon atom, C_nH_{2n} , which is the same as the alkene subgroup of aliphatic hydrocarbons but without any double carbon bonds and now in a ring structure. The alicyclic name is the same as the alkene group preceded by “cyclo”. Common examples include cyclopropane (C_3H_6), cyclobutane (C_4H_8), and cyclopentane (C_5H_{10}).

cyclobutane, C_4H_8 cyclopentane, C_5H_{10}

15.4.3 Aromatic Hydrocarbons

Aromatic hydrocarbons are composed of benzene “rings”, which are formed from six carbon atoms with a double bond every other atom. Single-ring molecules have a C-H ratio of C_nH_{2n-6} . Double-ring molecules have a C-H ratio of C_nH_{2n-12} . Common examples include benzene (C_6H_6), toluene (C_7H_8), xylene (C_8H_{10}), and naphthalene ($C_{10}H_8$). New hydrocarbon compounds can be created by adding methyl groups (CH_3) to the ring(s) in place of a hydrogen atom.

benzene, C_6H_6 naphthalene, $C_{10}H_8$

15.5 Liquid Fuels - Petroleum

Crude oil contains a nearly infinite number and variety of hydrocarbons. The range of hydrocarbon molecular weights ranges from very light gaseous hydrocarbons (low-C-to-H ratio) to heavy tar-like liquids and waxes (high-C-to-H ratio). The latter may have 83-87% carbon (11-14% H₂). There may also be sulfur, nitrogen, water, O₂, CO₂, and mineral impurities. Petroleum (crude oil) is separated into groups of similar hydrocarbons to create products for specific applications.

Table 2.3 PRODUCTS OF PETROLEUM DISTILLATION

Fraction	Molecular Size Range	Boiling Point Range		Typical Uses
		Degrees Celsius		
Gas	C ₁ -C ₅	- 164 to 30		Gaseous fuel
Petroleum ether	C ₅ -C ₇	30 to 90		Solvent, dry cleaning
Straight-run gasoline	C ₅ -C ₁₂	30 to 200		Motor fuel
Kerosene	C ₁₂ -C ₁₆	175 to 275		Fuel for stoves, diesel, and jet engines
Gas oil or fuel oil	C ₁₅ -C ₁₈	Up to 375		Furnace oil
Lubricating oil	C ₁₆ -C ₂₀	350 and up		Lubrication
Greases	C ₁₈ -up	Semisolid		Lubrication
Paraffin (wax)	C ₂₀ -up	Melts at 52-57		Candles
Pitch and tar	High	Residue in boiler		Roofing, paving

Source: Spencer L. Seager and H. Stephen Stoker, *Chemistry: A Science for Today* (San Francisco: Scott, Foresman, 1973), p. 299.

Table 2.4 THE ALKANE SERIES OF HYDROCARBONS^a

<i>n</i>	Molecule	Name	Primary Use
1	CH ₄	Methane	Natural gas
2	C ₂ H ₆	Ethane	Natural gas
3	C ₃ H ₈	Propane	Bottled gas
4	C ₄ H ₁₀	Butane	Bottled gas
5	C ₅ H ₁₂	Pentane	Gasoline
6	C ₆ H ₁₄	Hexane	Gasoline
7	C ₇ H ₁₆	Heptane	Gasoline
8	C ₈ H ₁₈	Octane	Gasoline

^a The heat of combustion for these hydrocarbons ranges from about 53,000 Btu/kg for methane to 45,000 Btu/kg for octane.

Figure 15.4. Hydrocarbon molecular weights for various petroleum products [4].

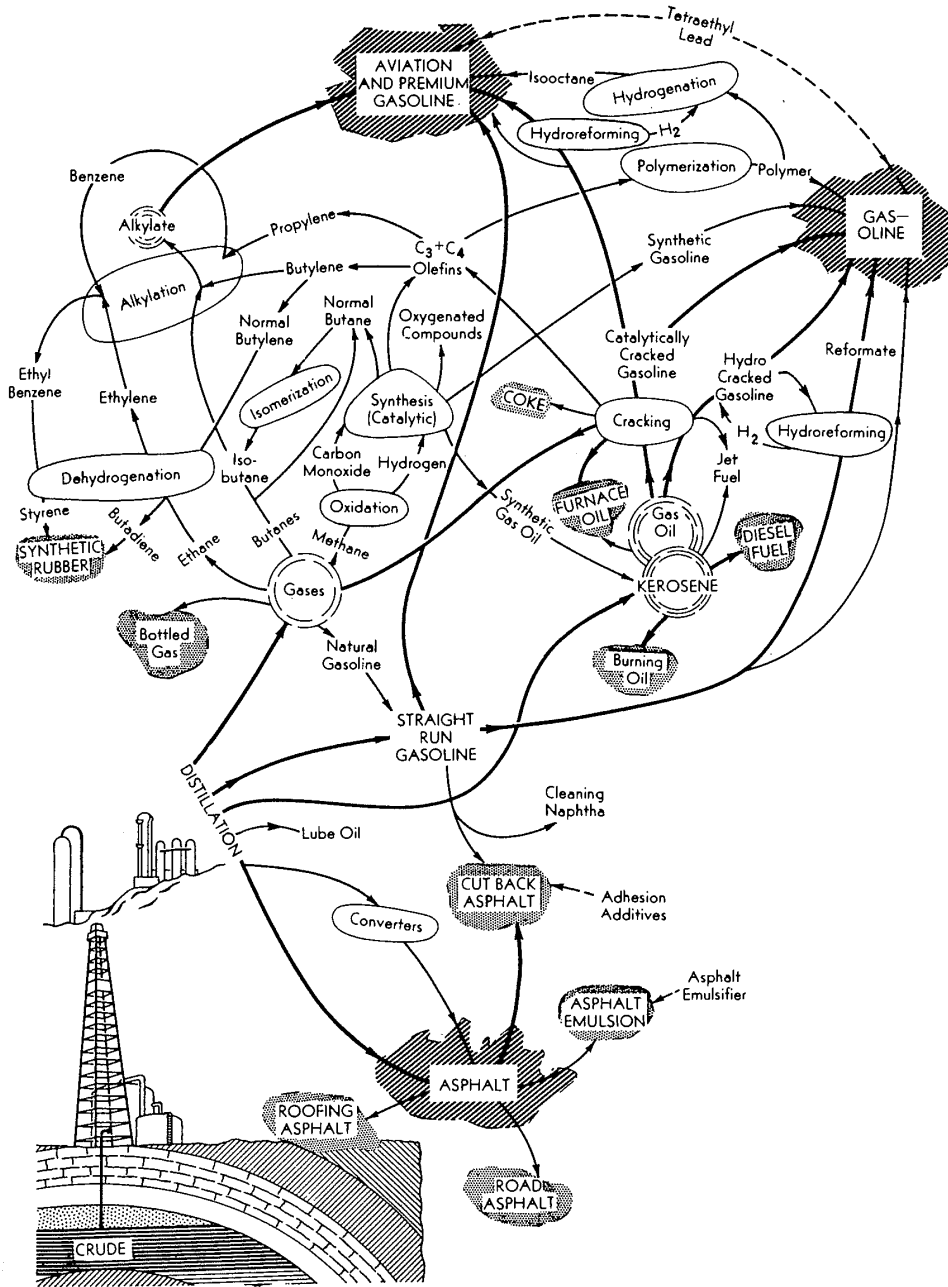


Figure 15.5. Petroleum products [5].

15.5.1 Petroleum Refining

Refining of crude petroleum consists of four basic processes:

1. **separation** of similar weight hydrocarbons
2. **conversion** of hydrocarbons – from heavy-to-light or light-to-heavy
3. **cleaning** of undesirable impurities such as sulfur
4. **blending** of hydrocarbons for creation of specific products

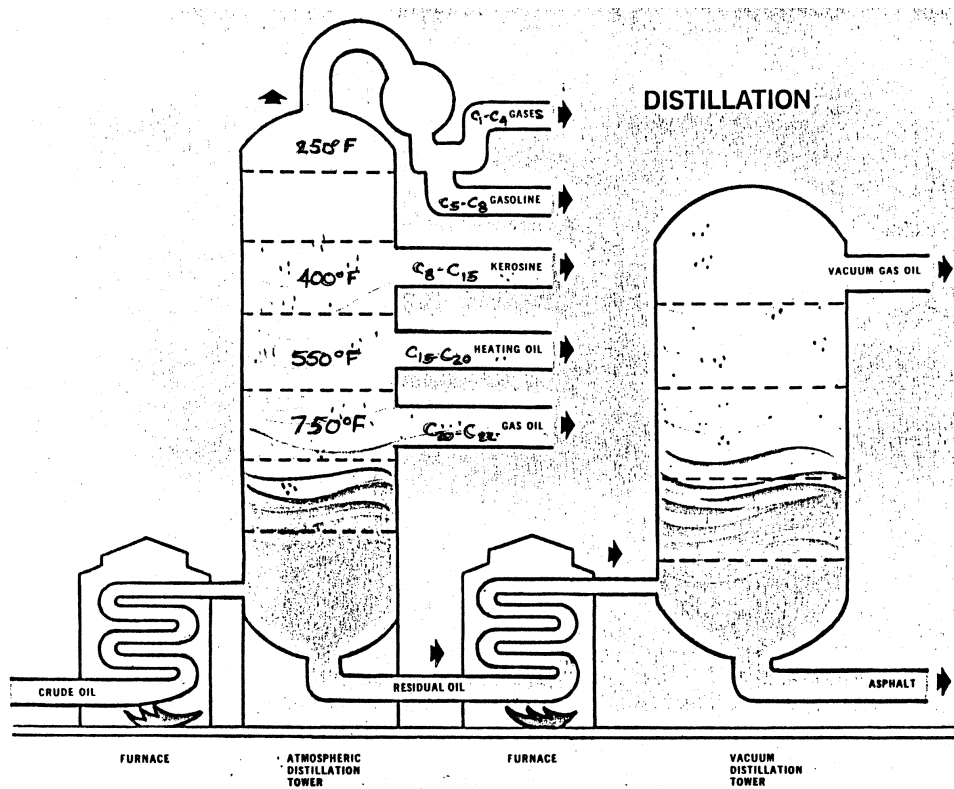


Figure 15.6. Distillation (separation) of light hydrocarbons from crude. Fractioning tower distills at atmospheric pressure to separate gases, gasolines, kerosenes, heating oils and gas oils from crude feed stock. Vacuum distillation tower removes additional gases (gas oils) from residual crude. The remaining residual is used for asphalts, heavy fuel oil, and feed stock to the Delayed Coker. [6]

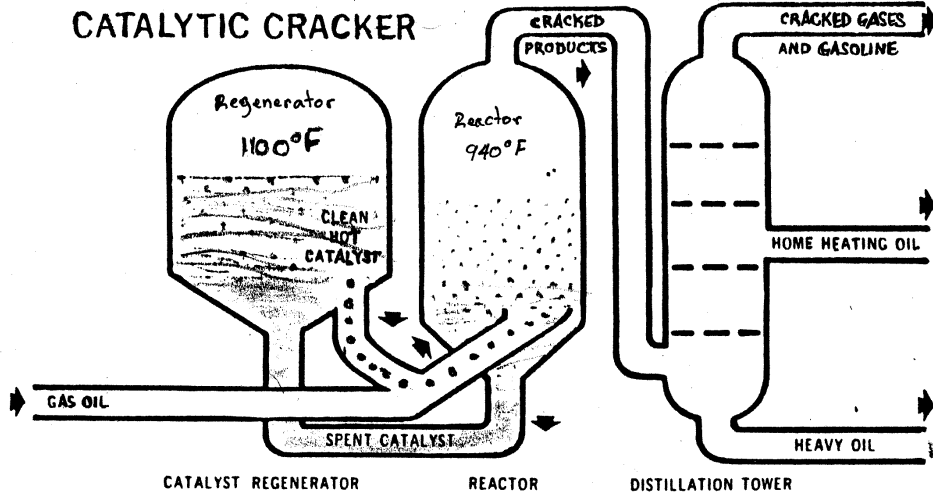


Figure 15.7. Cracking large hydrocarbon molecules into small molecules. Products include refinery fuel gas, liquefied petroleum gases, chemical feed stocks, light grades of home heating oil, and heavy fuel oil. [6]

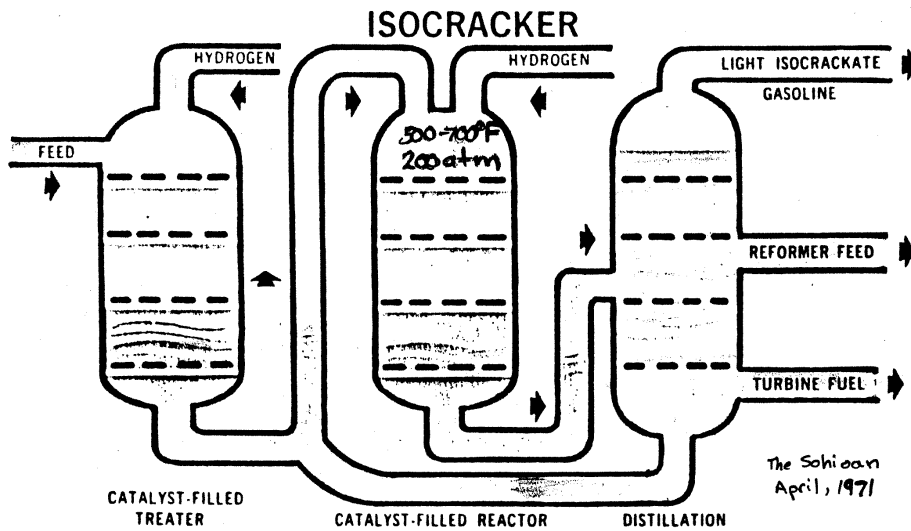


Figure 15.8. Cracking long hydrocarbons. Output can be adjusted from 100% gasoline to aviation fuel in response to market demand. [6]

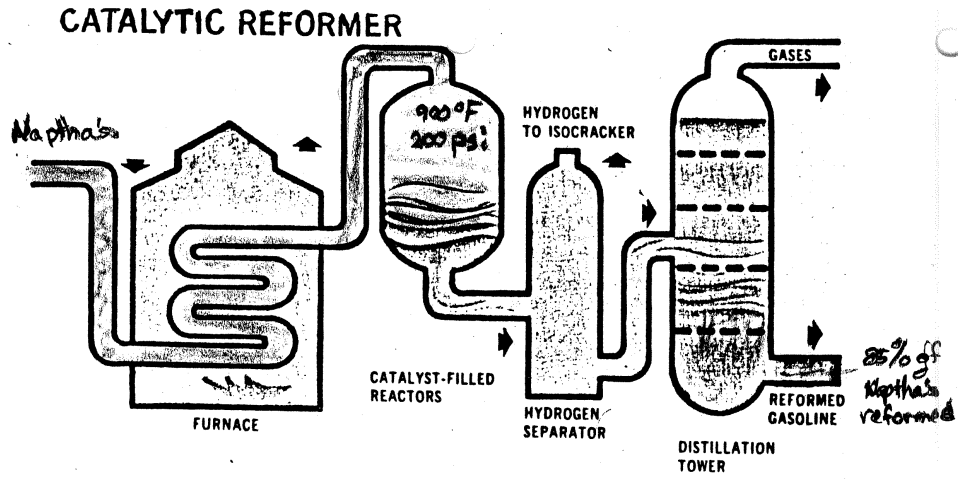


Figure 15.9. Combining small hydrocarbon molecules (naphtha) into high octane gasolines. Dry cleaning fluid is 50 octane naphtha. [6]

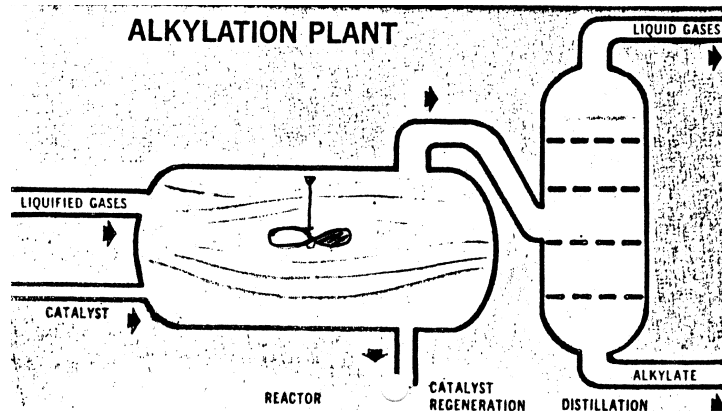


Figure 15.10. Combines short hydrocarbons to form long hydrocarbons. The *alkylate* has an octane greater than 100. [6]

15.6 Rating Liquid Fuels for Internal Combustion

After refining, liquid fuels are rated for combustion. The two most common ratings are the **Octane Number** used for spark-ignition engines and the **Cetane Number** used for compression-ignition engines.

15.6.1 Octane

The octane # of an unknown fuel is determined using a Cooperative Research Engine (CFR engine), which is a single-cylinder spark-ignition engine with an adjustable compression ratio from approximately 4:1 to 14:1. The engine is run with the fuel while the compression ratio is slowly increased until “knock” (detonation) is detected. The octane number of a fuel is the percent volume of 2,2,4-trimethylpentane that knocks at the same compression ratio. Typical gasolines are between 85 and 90 octane. Some gasolines are rated at octane numbers greater than 100 because of the addition of lighter hydrocarbons, alcohols or other additives.

- 100-octane fuel → 2,2,4-trimethylpentane, C_8H_{18} (isooctane)
“hard to break” & resists detonation
- 0-octane fuel → n-heptane, C_7H_{16}

15.6.2 Cetane

The cetane # is the %v of n-hexadecane which has the same combustion characteristics in a CFR engine. Typical diesel fuels are between 30 and 60 cetane.

- 100-cetane fuel → n-hexadecane, $C_{16}H_{34}$ (n-cetane)
- 0-cetane fuel → alpha-methyl naphthalene, $C_{11}H_{10}$
1 H atom in α -position; on one of 4 C-atoms closest to common C-atoms for both rings

15.7 Rating Liquid Fuels for Power Production

Distillates: No. 1, No. 2, No. 4

- No. 4 is low in sulfur, H_2O , dirt & low viscosity

Residual Oils: No. 5 (light), No. 5 (heavy), No. 6

- No. 5 heavy is high in sulfur, H_2O & high viscosity

Crude most suitable for direct firing is called **sweet**; low sulfur content.

15.8 Petroleum-Like Liquid Fuels

shale oil: Shale oil is a substance known as kerogen trapped in marlstone. Kerogen is a wax-like solid hydrocarbon in which the hydrocarbon molecules are heavily cross linked. Typically there is a significant sulfur and nitrogen content.

tar sands:

15.8.1 Liquid Bio-Fuels

- vegetable oil
- palm oil
- algae oil
- whale oil

15.8.2 Manufactured Liquid Fuels

- coal-to-liquid (CTL)
- ethanol
- methanol
- bio-diesel

15.8.3 By-Products from Industrial Processes

- black liquor

15.9 Gaseous Fuels

15.9.1 Natural Gas

Natural gas is a mixture of light hydrocarbons and nitrogen with traces of other gases. The majority hydrocarbon in natural gas is methane. The typical higher heating value of natural gases is approximately 1000 Btu/ft³

15.9.2 Manufactured Gaseous Fuels

- propane via distillation
- butane via distillation
- hydrogen
- syngas - from solid fuels
- town gas - from coal

15.9.3 By-Products of Natural & Industrial Processes

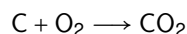
- anerobic & aerobic digesters – methane

Article 16

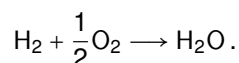
Conserving Mass in Chemical Reactions

16.1 Chemical Reactions

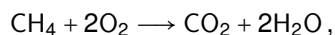
Complete combustion of carbon and hydrogen requires a mole balance of each element. One mole of carbon dioxide (CO_2) is formed from one mole of carbon and one mole of oxygen gas (O_2).



One mole of water is formed from one mole of hydrogen gas (H_2) and one-half mole of oxygen gas (O_2), or 2 moles of atomic hydrogen (H) and 1 mole of atomic oxygen (O).



Molecules are chemically being split and recombined in different forms so both mass and species must be conserved. The number atoms of each element must be balanced in and out of the device. For methane reacting with oxygen, the chemical balance is:



which shows 1 mole of methane (CH_4) being reacted with 2 moles of oxygen (O_2) to form 1 mole of carbon dioxide (CO_2) and 2 moles of water (H_2O). There is 1 mole of carbon in both the reactants and in the products. Similarly, there are 4 moles of hydrogen in the reactants and the products. The integer coefficients that balance the reactant and product elements are the molar proportions for which the species react. For combustion of a fuel such as methane with exactly the correct amount of oxygen, the coefficients are known as *stoichiometric coefficients*.

16.2 Mol and Mass Balances

A mole is directly related to the mass of a substance through the molecular mass, also known as the molecular weight. One *mole* is the number of parts in a substance that is equal to the number of atoms per 12 grams of carbon-12. For example, the molecular mass of carbon-12¹ is 12.00000 g/gmol. A gmol of H_2 is equivalent to 2.016 g. Thus, the mass of a substance is equal to the number of moles times the molecular mass.

$$\text{mass} = \text{mols} \times \text{molecular mass} \quad m = nM$$

¹The 12 indicates the isotope of carbon which is identified by the number of nuclear particles (6 neutrons and 6 protons) in the nucleus. Carbon-14 is another carbon isotope that has 14 nucleons (6 protons, 8 neutrons) and is radioactive.

Article 16 Conserving Mass in Chemical Reactions

Note the use of *gmol* instead of the common abbreviation *mol*. This is to indicate the mass relationship. Similarly,

$$\begin{aligned} \text{kmol, kmol} &\equiv 12 \text{ kg of carbon-12} \\ \text{lbmol} &\equiv 12 \text{ lbm of carbon-12} \\ \text{slugmol} &\equiv 12 \text{ slug of carbon-12} \\ \text{mol, gmol} &\equiv 12 \text{ g of carbon-12} \end{aligned}$$

Typically, 1 mol refers to 1 gmol. However, in the U.S. power industry 1 mol often refers to 1 lbmol. And these are not equivalent; 1 lbmol = 453.59237 gmol. Always be certain of the unit system within which you are working!

Another useful measure is *molal volume*; which is the volume per mol occupied by a gas. As an example, at 60 °F and 1 atm, the specific volume of oxygen is $v_{O_2} = 11.819 \text{ ft}^3/\text{lbm}$. On a molar basis, the specific molar volume (molal volume) is:

$$\bar{v}_{O_2} = \left(32 \frac{\text{lbm}}{\text{lbmol}} \right) \left(11.819 \frac{\text{ft}^3}{\text{lbm}} \right) = 378.21 \frac{\text{ft}^3}{\text{lbmol}}$$

The bar over the volume symbol indicates volume on a per mole basis. In a similar fashion, the molal volume of hydrogen at 60 °F and 1 atm is:

$$\bar{v}_{H_2} = \left(2.016 \frac{\text{lbm}}{\text{lbmol}} \right) \left(187.723 \frac{\text{ft}^3}{\text{lbm}} \right) = 378.45 \frac{\text{ft}^3}{\text{lbmol}}$$

Notice the similarity in molal volumes. A good approximation of volume of any gas at 60 °C and 1 atm is 379 ft³/lbm.

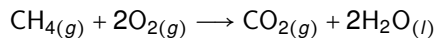
The number of particles in 1 gmol is fixed and defined as Avagadros number, N_A .

$$N_A = 6.02214129 \times 10^{23} \text{ particles/gmol}$$

The particles may be anything – atoms, molecule, electrons, neutrons, etc.

16.2.1 Conservation of Mass

While the total number of moles may not be conserved, the total mass of the reactants and products is conserved though not by species or elements. For example, complete combustion of methane is



Using the molecular masses of the reactants and the number of moles per species, the total mass of reactants ($\text{CH}_4 + 2\text{O}_2$) is:

$$\left(\frac{12 \text{ kg}}{\text{kmol}} \text{ C} \right) \left(1 \text{ kmol C} \right) + \left(\frac{1 \text{ kg}}{\text{kmol}} \text{ H} \right) \left(4 \text{ kmol H} \right) + \left(\frac{16 \text{ kg}}{\text{kmol}} \text{ O} \right) \left(4 \text{ kmol O} \right) = 80 \text{ kg}$$

The total mass of the products ($\text{CO}_2 + 2\text{H}_2\text{O}$) is:

$$\begin{aligned} \left(\frac{12 \text{ kg}}{\text{kmol}} \text{ C} \right) \left(1 \text{ kmol C} \right) + \left(\frac{16 \text{ kg}}{\text{kmol}} \text{ O} \right) \left(2 \text{ kmol O} \right) + 2 \left(\frac{1 \text{ kg}}{\text{kmol}} \text{ H} \right) \left(2 \text{ kmol H} \right) \\ + 2 \left(\frac{16 \text{ kg}}{\text{kmol}} \text{ O} \right) \left(1 \text{ kmol O} \right) = 80 \text{ kg} \end{aligned}$$

16.3 Equivalent Hydrocarbon

Many fuels are composed of multiple combustible compounds the fraction of which varies depending upon the source of the fuel. This is particularly true for natural gases and biofuels. Table 17.4 shows the range of molar composition for selected U.S. natural gases. From the molar fractions, the total enthalpy of reaction can be determined. A convenient method for these calculations is to derive an equivalent hydrocarbon for the multi-compound fuel.

Consider the following gaseous fuel comprised of methane, ethane and propane,

compound	% volume	mol fraction	carbon	hydrogen
methane, CH _{4(g)}	67.4	0.674	0.674	2.696
ethane, C ₂ H _{6(g)}	16.8	0.168	0.336	1.008
propane, C ₃ H _{8(g)}	15.8	0.158	0.474	1.264
total		1.000	1.484	4.968

the equivalent hydrocarbon is C_{1.484}H_{4.968}. The molar mass of this fuel can be determined using the equivalent hydrocarbon.

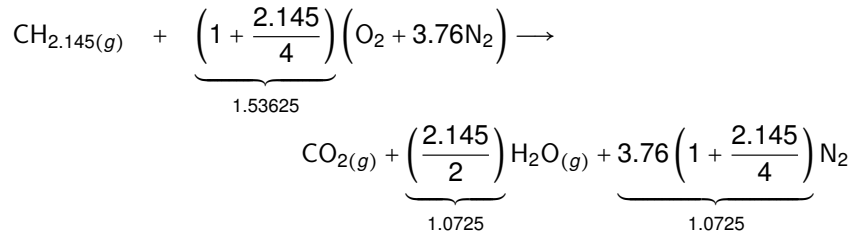
$$\left(\frac{1.484 \text{ kgmol C}}{\text{kgmol fuel}}\right)\left(\frac{12.01 \text{ kg}}{\text{kgmol C}}\right) + \left(\frac{4.968 \text{ kgmol H}}{\text{kgmol fuel}}\right)\left(\frac{1.008 \text{ kg}}{\text{kgmol H}}\right) = \frac{22.83 \text{ kg}}{\text{kg fuel}}$$

The mass fraction of hydrogen to carbon is:

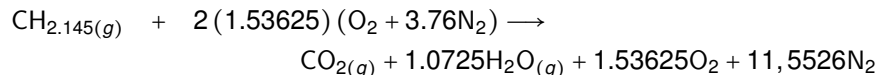
$$\frac{m_H}{m_C} = \frac{4.968(1.008)}{1.484(12.01)} = 0.281 \frac{\text{kg H}}{\text{kg C}}$$

16.3.1 Equivalent Hydrocarbon for Natural Gas Turbines

A commonly used approximation for natural gases combusted in a power generating Brayton cycle is CH_{2.145} [?], which for stoichiometric combustion balances as:



At 200% theoretical air, the reaction equation becomes

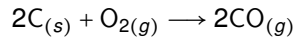


16.4 Combustion

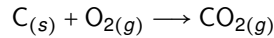
When there is just enough oxygen to react with all of the fuel, the reaction occurs under stoichiometric conditions. There is no excess oxygen or combustible species

Article 16 Conserving Mass in Chemical Reactions

remaining in the products. For example, a non-stoichiometric reaction is:



There is insufficient oxygen for complete combustion of carbon. The product is carbon monoxide which is still combustible. Stoichiometric conditions for carbon combustion are:



The subscripts (s), (g), (v), (l) indicate the species is in a solid, gaseous, vapor or liquid form, respectively. The amount of oxygen required for complete combustion of carbon is:

$$\frac{(32 \text{ kg O}_2/\text{kmol O}_2)(1 \text{ kmol O}_2)}{(16 \text{ kg C}/\text{kmol C})(1 \text{ kmol C})} = \frac{2.66 \text{ kg O}_2}{\text{kg C}} = \frac{2.66 \text{ lbm O}_2}{\text{lbm C}} \equiv \frac{1 \text{ kmol O}_2}{\text{kmol C}}$$

Thus for each kg of carbon in a fuel, 2.66 kg of oxygen is required for complete oxidation.

16.5 Complete Combustion in Air

The most common source of oxygen for combustions is air. Table 16.1 gives the percent composition of dry air. For the purposes of combustion, the inert components (CO₂, argon, neon) are combined with and treated as nitrogen.

Table 16.1. Composition of dry air

	% by volume	% by mass
O ₂	20.99	23.15
N ₂	78.03	76.85
inert	0.98	–

The respective mass and mole fractions with oxygen, nitrogen and air are:

$$\frac{\text{lbmol air}}{\text{lbmol O}_2} = \frac{1 \text{ ft}^3 \text{ air}}{0.2099 \text{ ft}^3 \text{ O}_2} = 4.76$$

$$\frac{\text{lbmol N}_2}{\text{lbmol O}_2} = \frac{0.7901 \text{ ft}^3 \text{ N}_2}{0.2099 \text{ ft}^3 \text{ O}_2} = 3.76$$

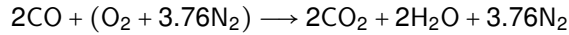
$$\frac{\text{lbm air}}{\text{lbm O}_2} = \frac{1 \text{ lbm air}}{0.2315 \text{ lbm O}_2} = 4.32$$

$$\frac{\text{lbm N}_2}{\text{lbm O}_2} = \frac{0.7685 \text{ lbm N}_2}{0.2315 \text{ lbm O}_2} = 3.32$$

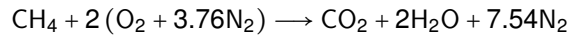
equivalent molecular mass of air

16.5 Complete Combustion in Air

Thus, stoichiometric combustion of carbon monoxide (CO) in air is:

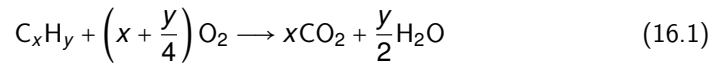


and complete (stoichiometric) combustion of methane (CH₄) is:

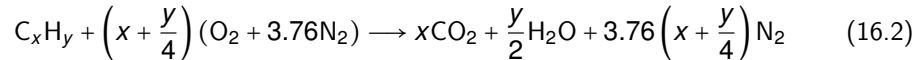


16.5.1 Complete (stoichiometric) Combustion of Hydrocarbon

Complete combustion of a hydrocarbon in oxygen follows a general reaction of the form:



In air, stoichiometric combustion of a hydrocarbon becomes:



The amount of dry air required for the stoichiometric reaction is:

$$\frac{\text{mols of dry air}}{\text{mols of C}_x\text{H}_y} = \frac{(x + y/4)(1 + 3.76)}{1} = \frac{x + y/4}{0.21} \quad (16.3)$$

16.5.2 Theoretical and Excess Air

More air than necessary for stoichiometric combustion may be used during combustion. Describing the amount of air per quantity of fuel used during combustion varies with the type of fuel (solid, liquid, gaseous) and the application (internal combustion, external combustion). The most commonly used measures of the amount of air are *theoretical air*, *excess air*, *air-fuel ratio*, and *equivalence ratio*.

Theoretical Air is the amount of air required for complete combustion; in other words stoichiometric conditions. The percent excess air is:

$$\% \text{ excess air} = \left(\frac{\text{air supplied} - \text{theoretical required}}{\text{theoretical required}} \right) \times 100$$

and

$$\% \text{ theoretical air} = \% \text{ excess air} + 100$$

The air-fuel ratio, A/F, is defined as the mass of air to the mass of fuel. For a stoichiometric reaction the air-fuel ratio becomes:

$$A/F^\circ = \left(\frac{m_{\text{air}}}{m_{\text{fuel}}} \right)_{\text{stoich}} = \frac{4.76(x + y/4)}{1} \cdot \frac{M_{\text{air}}}{M_{\text{fuel}}}$$

where the \circ -superscript indicates stoichiometric, or 100% theoretical, and M is the molecular mass. Using the air-fuel ratio, theoretical and excess air are:

$$\% \text{ theoretical air} = 100 \left\{ \frac{A/F}{A/F^\circ} \right\}$$

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$$\% \text{ excess air} = 100 \left\{ \frac{A/F - A/F^\circ}{A/F^\circ} \right\}$$

The last measure of air to be discussed is the *equivalence ratio*, Φ , which is the actual fuel-to-air ratio divided by the theoretical fuel-to-air ratio.

$$\Phi \equiv \frac{F/A}{F/A^\circ} = \frac{A/F^\circ}{A/F}$$

Theoretical and excess air can be expressed in terms of the equivalence ratio.

$$\% \text{ theoretical air} = \frac{100}{\Phi}$$

$$\% \text{ excess air} = \left(\frac{1 - \Phi}{\Phi} \right) \times 100$$

When the equivalence ratio is equal to one ($\Phi = 1$), then the combustion reaction occurs under stoichiometric conditions. If the equivalence ratio is greater than one ($\Phi > 1$), then the fuel-air mixture is considered *rich*; that is, there is insufficient air for complete combustion and some fuel components will appear in the products of the chemical reaction. If the equivalence ratio is less than one ($\Phi < 1$), then the fuel-air mixture is considered *lean*.

Article 17

Enthalpy Change in Chemically Reacting Flow

When a single species is flowing through a device, such as liquid or gas flowing through a heat exchanger, then conservation of energy reduces to the First Law of Thermodynamics.

$$\dot{Q} - \dot{W} = \dot{E}|_{\text{out}} - \dot{E}|_{\text{in}} . \quad (17.1)$$

In the absence of significant changes in kinetic energy (inertial potential) or gravitation potential the change in fluid energy becomes the change in fluid enthalpy, $\dot{H}_{\text{out}} - \dot{H}_{\text{in}}$.

When there is multiple species flowing through the energy converter, then the change in enthalpy for each species must be considered. For example, if air and water are co-flowing through a device, then conservation of energy becomes:

$$\dot{Q} - \dot{W} = \sum_{\text{out}} (\dot{m}h|_{\text{air}} + \dot{m}h|_{\text{water}}) - \sum_{\text{in}} (\dot{m}h|_{\text{air}} + \dot{m}h|_{\text{water}}) , \quad (17.2)$$

assuming negligible changes in any other fluid energies besides enthalpies. Conservation of mass is applied to each species separately.

17.0.1 Sensible Heat

The fluid flowing out is chemically identical to the fluid flowing in; that is the same gas, vapor or liquid, then the change in enthalpy is known as a *sensible heat*, $\Delta\dot{H}_s$. On a per mass basis, sensible heat is the difference in the enthalpy relative to the enthalpy of a reference state. The most common reference state is 298 K (25 °C, 77 °F) and 1 atm.

$$h_s = h(T) - h(T_{\text{ref}}) \quad (17.3)$$

All measures of energy (internal energy, enthalpy, etc) are relative to a reference state. Consider the case of steam (water vapor) being cooled as shown in Figure 17.1a. Water vapor at 582 °C, 1 atm is cooled to 100 °C, 1 atm and remains in the vapor state.

$${}_2\dot{Q}_3 = \dot{H}_3 - \dot{H}_2 = \dot{m}(h_{s,3} - h_{s,2}) ,$$

where

$$h_{s,2} = h_2 - h(298K) = 3666 \text{ kJ/kg} - 104.8 \text{ kJ/kg}$$

and

$$h_{s,3} = h_3 - h(298K) = 2676 \text{ kJ/kg} - 104.8 \text{ kJ/kg} .$$

For non-reacting species such as water vapor, the reference temperature enthalpies cancel out. The resulting change in specific enthalpy is -989.8 kJ/kg. This cancellation will not be true for reacting mixtures.

Article 17 Enthalpy Change in Chemically Reacting Flow

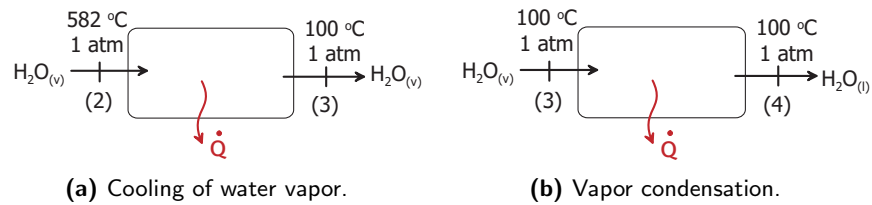


Figure 17.1. Heat transfer by sensible and latent heat cooling of combustion product.

17.0.2 Latent Heat

If the heat is further extracted from the water vapor as shown in Figure 17.1b, condensation will occur without a change in fluid temperature until all of the vapor has become liquid. The enthalpy change for this process, $H_{\text{vapor}} - H_{\text{liquid}}$, is known as *latent heat*.

$${}_3\dot{Q}_4 = \dot{m}(h_4 - h_3)$$

where

$$h_3 = h_g(373K) - h(298K) = 2676 \text{ kJ/kg} - 104.8 \text{ kJ/kg}$$

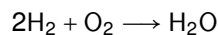
and

$$h_4 = h_f(373K) - h(298K) = 419.1 \text{ kJ/kg} - 104.8 \text{ kJ/kg}.$$

The reference temperature enthalpies cancel because the fluid remains the same species (H_2O). The resulting change in enthalpy, or latent heat, is $h_{fg} = -2257 \text{ kJ/kg}$.

17.1 Enthalpy of Formation

During a chemical reaction the species change during conversion of energy. Consider the formation of water vapor by the combustion of hydrogen with oxygen.



For this type of process, the change in fluid energies must include a chemical and a thermal component. For hydrogen and oxygen at the reference state, 298 K and 1 atm, the enthalpy entering the process must include the chemical energy of each species plus the sensible heat plus the latent heat.

$$h_{\text{total}} = h_f^\circ + h_s + h_{fg}$$

where h_f° is the *enthalpy of formation*.¹ The $^\circ$ -superscript indicates the value at the standard state, which is typically 298 K and 1 atm.²

¹This is also referred to as the constant pressure heat of formation and heat of formation. There are many different symbolic representations for the enthalpy of formation; Δh_f° , $\Delta h_{f,T_R}^\circ$, h_{f,T_R}° , ...

²Exercise caution when looking up values for the enthalpy of formations. The standard state is not the same for all sources of tabulated data.

17.1 Enthalpy of Formation

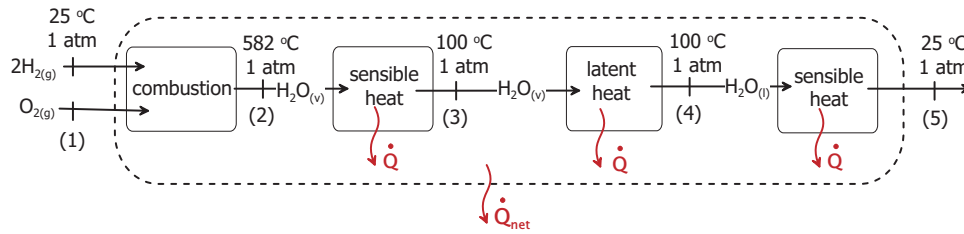


Figure 17.2. Combustion of hydrogen and cooling the combustion product (water) back to the reference state.

Enthalpies of formation are determined by chemically reacting species and then adding or subtracting thermal energy until the products are returned to the standard state. Enthalpy of formation is also referred to as constant pressure heat of formation. As an example, Figure 17.2 shows the sequence of processes for the combustion of hydrogen to form water vapor and then cooling and condensing the water vapor back to the reference temperature. The net heat extracted is:

$$\begin{aligned}\dot{Q}_{\text{net}} &= \dot{H}_{\text{out}} - \dot{H}_{\text{in}} \\ &= \dot{m}_{\text{H}_2\text{O}} \left[h_{f,\text{H}_2\text{O}(l)}^\circ + (h_5 - h_{\text{H}_2\text{O},298\text{K}}) \right] \\ &\quad - \dot{m}_{\text{H}_2} \left[h_{f,\text{H}_2(g)}^\circ + (h_{1,\text{H}_2} - h_{\text{H}_2,298\text{K}}) \right] \\ &\quad - \dot{m}_{\text{O}_2} \left[h_{f,\text{O}_2(g)}^\circ + (h_{1,\text{O}_2} - h_{\text{O}_2,298\text{K}}) \right]\end{aligned}$$

Table 17.1 lists values of enthalpy of formation on a per mass basis for various compounds at a standard state of 25°C (298 K) and 1 atm. The enthalpy of formation for elements such as carbon (C) and sulfur (S) are zero. Gases in their base state such as hydrogen (H₂), oxygen (O₂), and nitrogen (N₂) also have an enthalpy of formation of zero. Table 17.1 lists the enthalpy of formations on a per mass basis for a number of compounds with a standard state of 298 K and 1 atm. To convert from a mass to a molar basis, multiply by the molecular mass of the compound. For convenience, Table 17.2 lists from another source enthalpies of formation on a per mole basis. The enthalpy of formation at temperatures other than the reference temperature are found by including the change in sensible heat, $h(T) - h(T_{\text{ref}})$. Table 17.3 lists enthalpies of formation on a per mass basis for various gases at 1 atm and various temperatures.

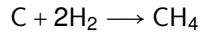
Returning to the energy balance described by Figure 17.2, the inlet and exit conditions are at the reference state. Therefore the difference in sensible heat change is zero for each of the species; e.g. $h_5 - h_{\text{H}_2\text{O},298\text{K}} = 0$, resulting in:

$$\dot{Q}_{\text{net}} = \dot{H}_{\text{out}} - \dot{H}_{\text{in}} = \dot{m}_{\text{H}_2\text{O}} h_{f,\text{H}_2\text{O}(l)}^\circ$$

The measured value of the enthalpy of formation for liquid water is -15 875.5 kJ/kg. For water vapor, $h_{f,\text{H}_2\text{O}(v)}^\circ = -13 430.8$ kJ/kg; the difference between the liquid water and water vapor enthalpy of formations is the latent heat of vaporization.

17.1.1 Example – Enthalpy of Formation: Methane

A change in temperature accompanies chemical conversion. The temperature may increase (exothermic process) or decrease (endothermic process). As an example, consider methane which is a hydrocarbon compound formed from 1 mole of carbon and 4 moles of elemental hydrogen or 2 moles of H₂.



If the reactants (C and H₂) are initially at the standard state (25°C) and the methane formed is brought back to the standard state, the heat transfer is the resulting enthalpy of formation, $H_{f,298K}^\circ$.

$$Q = \left\{ H_{f,298K,\text{CH}_4}^\circ + \left[H_{\text{CH}_4}(T) - H_{\text{CH}_4}(298K) \right] \right\} \\ - \left\{ H_{f,298K,\text{C}}^\circ + \left[H_{\text{C}}(T) - H_{\text{C}}(298K) \right] \right\} \\ + \left\{ H_{f,298K,\text{H}_2}^\circ + \left[H_{\text{H}_2}(T) - H_{\text{H}_2}(298K) \right] \right\}$$

The sensible heats, $H(T) - H(298K)$, equal zero for all reactants and products because the temperature begins and ends at the reference state. Also the enthalpies of formation for the carbon and hydrogen are zero, resulting in:

$$Q = H_{f,298K,\text{CH}_4}^\circ$$

The enthalpy of formation is tabulated on a per mass or per mol basis.

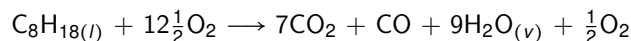
$$Q = n_{\text{CH}_4} \bar{h}_{f,298K,\text{CH}_4}^\circ = m_{\text{CH}_4} h_{f,298K,\text{CH}_4}^\circ$$

17.2 Enthalpy of Reaction

The enthalpy of reaction, $\bar{h}_{r,298K}^\circ$, is the heat transferred for 1 mole of a specific compound reaction with the reactants and products at the standard state. The enthalpy of reaction is the difference in total enthalpy of the products and reactants.

17.2.1 Example – Enthalpy of Reaction: Octane

For example, incomplete combustion of octane could result in the production of CO₂, CO, H₂O. Carbon monoxide (CO) is also combustible so this combustion process is considered incomplete. Complete combustion would leave only carbon dioxide (CO₂) and water (H₂O).



17.3 Enthalpy of Combustion

With all reactants and products at 298 K and 1 atm, conservation of energy for this scenario reduces to:

$$Q = H_{\text{products}} - H_{\text{reactants}}$$

On a per mole basis:

$$\bar{q} = \left\{ \left(7 \frac{\text{mol CO}_2}{\text{mol C}_8\text{H}_{18}} \right) \bar{h}_{f,\text{CO}_2}^\circ + \left(1 \frac{\text{mol CO}}{\text{mol C}_8\text{H}_{18}} \right) \bar{h}_{f,\text{CO}}^\circ + \left(9 \frac{\text{mol H}_2\text{O}}{\text{mol C}_8\text{H}_{18}} \right) \bar{h}_{f,\text{H}_2\text{O}(v)}^\circ + \left(1 \frac{\text{mol O}_2}{2 \text{mol C}_8\text{H}_{18}} \right) \bar{h}_{f,\text{O}_2}^\circ \right\} \\ - \left\{ \left(1 \frac{\text{mol C}_8\text{H}_{18}}{\text{mol C}_8\text{H}_{18}} \right) \bar{h}_{f,\text{C}_8\text{H}_{18}}^\circ + \left(\frac{12.5 \text{ mol O}_2}{\text{mol C}_8\text{H}_{18}} \right) \bar{h}_{f,\text{O}_2}^\circ \right\}$$

For these product species, the enthalpy of reaction for combustion of octane is:

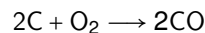
$$\bar{q} = \left\{ 7 \left(-393\,520 \frac{\text{J}}{\text{mol}} \right) + 1 \left(-110\,525 \frac{\text{J}}{\text{mol}} \right) + 9 \left(-241\,818 \frac{\text{J}}{\text{mol}} \right) + 0.5 \left(0 \frac{\text{J}}{\text{mol}} \right) \right\} \\ - \left\{ 1 \left(-249\,957 \frac{\text{J}}{\text{mol}} \right) + 12.5 \left(0 \frac{\text{J}}{\text{mol}} \right) \right\} \\ = -4\,791\,570 \text{ J/mol C}_8\text{H}_{18}$$

17.3 Enthalpy of Combustion

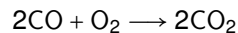
Enthalpy of Combustion, $h_{c,298\text{K}}^\circ$, is the heat transferred when 1 mole of a compound is completely combusted and the products cooled back to the standard state. Complete combustion at stoichiometric conditions is what distinguishes the enthalpy of combustion from enthalpy of reaction.

17.3.1 Example – Enthalpy of Combustion: Carbon

Carbon burns as a solid. In analyzing carbon oxidation, the carbon is assumed to first completely oxidize to carbon monoxide (CO),



then to carbon dioxide (CO₂) provided sufficient oxygen is present.



Measuring the heat extracted from the reactor (combustion vessel) to return the products to the standard state temperature provides the change in chemical potential energy.

Article 17 Enthalpy Change in Chemically Reacting Flow

Applying conservation of energy on a per mole basis,

$$\begin{aligned} \bar{q}_{\text{CO}} = & 2 \left[\bar{h}_{f,298\text{K},\text{CO}}^{\circ} + \left(\bar{h}(298\text{K}) - \bar{h}(T_{\text{ref}}) \right)_{\text{CO}} \right] \\ & - 2 \left[\bar{h}_{f,298\text{K},\text{C}}^{\circ} + \left(\bar{h}(298\text{K}) - \bar{h}(T_{\text{ref}}) \right)_{\text{C}} \right] \\ & - \left[\bar{h}_{f,298\text{K},\text{O}_2}^{\circ} + \left(\bar{h}(298\text{K}) - \bar{h}(T_{\text{ref}}) \right)_{\text{O}_2} \right] \end{aligned}$$

The heat of formation for Carbon (C) and Oxygen (O₂) are zero. And since the final temperature is equal to the reference temperature there is no change in sensible heat. Oxidation of two moles of carbon produces two moles of carbon monoxide. On a per mole basis, the heat released is

$$\bar{q} = \bar{h}_{f,298\text{K},\text{CO}}^{\circ} = -110\,530 \text{ kJ/kmol CO}.$$

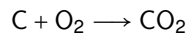
The heat released during combustion of CO to CO₂ can be similarly examined.

$$\begin{aligned} q_{\text{CO}_2} = & 2 \left[h_{f,298\text{K},\text{CO}_2}^{\circ} + \left(h(298\text{K}) - h(T_{\text{ref}}) \right)_{\text{CO}_2} \right] \\ & - 2 \left[h_{f,298\text{K},\text{CO}}^{\circ} + \left(h(298\text{K}) - h(T_{\text{ref}}) \right)_{\text{CO}} \right] - \left[h_{f,298\text{K},\text{O}_2}^{\circ} + \left(h(298\text{K}) - h(T_{\text{ref}}) \right)_{\text{O}_2} \right] \end{aligned}$$

With the reactants and products at the standard state on a per mole basis, the heat released from oxidation of CO is

$$\bar{q} = \bar{h}_{f,298\text{K},\text{CO}_2}^{\circ} - \bar{h}_{f,298\text{K},\text{CO}}^{\circ} = -282\,990 \text{ kJ/kmol CO}.$$

Carbon dioxide is the final oxidization state of carbon. The complete chemical balance combustion of carbon is



with a subsequent heat of formation equal to the sum of the heats released during oxidation of carbon and then of carbon monoxide.

$$\underbrace{(-110\,530 \text{ kJ/kmol})}_{[\text{C-to-CO}]} + \underbrace{(-282\,990 \text{ kJ/kmol})}_{[\text{CO-to-CO}_2]} = -393\,520 \text{ kJ/kmol CO}_2$$

17.4 Heating Values

Under stoichiometric conditions with air and when the reactants products are at a standard state, the heat released is known as a *heating value* (HV) for the fuel. The heating value of CO₂ is equal to the heat of formation for complete (stoichiometric) combustion of carbon in air.

Heating values are the enthalpy difference between the products and the reactants with all compounds brought back to the standard state.

$$\text{HV} = \left[\sum_{\text{products}} (n\bar{h}_f) - \sum_{\text{reactants}} (n\bar{h}_f) \right]_{\text{standard state}}$$

The heating value is often qualified as the higher heating value (HHV) or the lower heating value (LHV). Higher heating value is the enthalpy released due to the reaction in which the water vapor is condensed. The latent heat released during condensation is included in the total heat of reaction. Lower heating value is the total enthalpy change when the product water remains in the vapor state.

$$\text{HHV} = \text{LHV} + m_{\text{water}} h_{fg}$$

17.5 Adiabatic Flame Temperature

Adiabatic flame temperature is determined by isolating the chemical reaction from any heat or work exchange with the environment.

$$Q = 0 = \Delta H_{\text{total}} \implies \sum_{\text{products}} (n\bar{h}_f) = \sum_{\text{reactants}} (n\bar{h}_f)$$

The temperature at which the total enthalpy of the products equals the total enthalpy of the reactants is the adiabatic flame temperature. This temperature will change depending on the stoichiometric conditions. For example, the adiabatic flame temperature will be higher for a compound completely combusted in oxygen as compared to air. The nitrogen present in the air has a thermal capacitance that results in a lower temperature of the reactants. This is referred to as a dilution effect. Similarly, a lean combustion mixture (> 100% theoretical air) will have a lower temperature than a stoichiometric or rich combustion mixture due to dilution effects.

Table 17.1. Enthalpies of Formation per mass at 25°C (77°F) and 1 atm. [7]

Substance	Formula	M	State	h_f°	
				Btu/lbm	kJ/kg
carbon	C	12.011	solid	0	0
oxygen	O ₂	32.000	gas	0	0
hydrogen	H ₂	2.016	gas	0	0
nitrogen	N ₂	28.016	gas	0	0
sulfur	S	32.060	solid	0	0
carbon monoxide	CO	28.011	gas	-1697.6	-3948.3
carbon dioxide	CO ₂	44.011	gas	-3846.7	-8946.8
water	H ₂ O	18.016	liquid	-6825.7	-15,875.5
			vapor	-5774.6	-13,430.8
methane	CH ₄	16.043	gas	-2007.8	-4669.8
ethane	C ₂ H ₆	30.070	gas	-1211.3	-2817.3
propane	C ₃ H ₈	44.097	gas	-1013.1	-2356.3
butane	C ₄ H ₁₀	58.124	gas	-933.7	-2171.6
octane	C ₈ H ₁₈	114.230	liquid	-941.4	-2189.5
			vapor	-785.1	-1826.0
nitric oxide	NO	30.008	gas	-1298.8	-3020.8
nitrogen dioxide	NO ₂	46.008	gas	-315.3	-733.3
sulfur dioxide	SO ₂	64.060	gas	-1992.0	-4632.8

17.5 Adiabatic Flame Temperature

Table 17.2. Enthalpy of Formation per mole at 25 °C (77 °F) and 1 atm. [8]

Compound	Formula	Formula Weight	State	Constant-Pressure Heat of Formation, ΔH_f	
				(Btu/lb-mol)	(J/mol)
Argon	Ar	39.948	Gas	0	0
Carbon (graphite)	C	12.0112	Solid	0	0
Carbon monoxide	CO	28.0106	Gas	-47,517	-110,525
Carbon dioxide	CO ₂	44.0100	Gas	-169,179	-393,510
Methane	CH ₄	16.0430	Gas	-32,162	-74,809
Ethane	C ₂ H ₆	32.0701	Gas	-36,408	-84,685
Propane	C ₃ H ₈	44.0976	Gas	-44,647	-103,849
<i>n</i> -Butane	C ₄ H ₁₀	58.1248	Liquid	-63,480	-147,655
<i>n</i> -Heptane	C ₇ H ₁₆	100.2064	Liquid	-96,471	-224,392
<i>n</i> -Octane	C ₈ H ₁₈	114.2336	Liquid	-107,462	-249,957
Hydrogen atom	H	1.0080	Gas	93,708	217,965
Hydrogen	H ₂	2.0159	Gas	0	0
Water	H ₂ O	18.0153	Gas	-103,963	-241,818
Helium	He	4.0026	Gas	0	0
Nitrogen atom	N	14.0067	Gas	203,226	472,704
Nitrogen	N ₂	28.0134	Gas	0	0
Nitric oxide	NO	30.0061	Gas	38,800	90,249
Nitrogen dioxide	NO ₂	46.0055	Gas	14,264	33,178
Ammonia	NH ₃	17.0306	Gas	-19,823	-46,108
Oxygen atom	O	15.9994	Gas	107,124	249,170
Oxygen	O ₂	31.9988	Gas	0	0
Hydroxyl	OH	17.0074	Gas	16,747	38,954

*Values from *Selected Values of Chemical Thermodynamic Properties*, National Bureau of Standards Technical Note 270-3, 1968, and F. D. Rossini, *Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds*, Carnegie Press, Pittsburgh, Pa., 1953.

Table 17.3. Enthalpies of formation [Btu/lbm] at various temperatures and 1 atm. [7]

Temperature, K	CO ₂	CO	H ₂ O	O ₂	H ₂	N ₂
298	-3846.7	-1697.6	-5774.6	0	0	0
400	-3807.5	-1651.9	-5692.2	40.7	631.4	52.8
500	-3765.4	-1606.5	-5609.4	81.8	1255.5	90.8
600	-3720.4	-1560.2	-5524.0	124.3	1880.4	136.5
700	-3673.1	-1513.0	-5435.9	168.1	2506.9	183.3
800	-3623.7	-1464.5	-5345.0	213.0	3137.4	231.0
900	-3572.6	-1415.0	-5251.1	258.8	3773.3	279.8
1000	-3520.2	-1364.5	-5154.3	305.3	4414.2	329.5
1100	-3466.5	-1313.1	-5054.3	352.5	5062.5	380.2
1200	-3411.9	-1261.0	-4951.4	400.2	5717.8	431.6
1300	-3356.4	-1208.2	-4845.7	448.4	6381.9	483.7
1400	-3300.2	-1154.8	-4737.2	497.0	7055.6	536.5
1500	-3243.4	-1100.9	-4626.2	546.0	7739.1	590.8
1600	-3186.1	-1046.6	-4512.8	595.3	8434.0	643.5
1700	-3128.3	-992.0	-4397.1	646.0	9136.4	697.6
1800	-3070.1	-937.0	-4279.6	694.9	9848.2	752.2
1900	-3011.6	-881.7	-4160.1	745.3	10568	807.0
2000	-2952.8	-826.1	-4038.9	795.9	11296	862.1
2100	-2893.6	-770.3	-3916.1	846.8	12031	917.5
2200	-2834.2	-714.3	-3791.8	899.3	12774	973.1
2300	-2774.6	-658.2	-3666.2	949.6	13523	1028.9
2400	-2713.1	-601.8	-3539.4	1001.5	14279	1084.9
2500	-2654.9	-545.3	-3411.5	1053.7	15043	1141.1

* To convert to kJ/kg multiply by 2.32584.

Table 17.4. Molar composition of selected U.S. fuel gases. [1, App. H]

Fuel gases	Higher heating value, [†] kJ/m ³ ‡	Composition, in percentage by volume or mole								
		CH ₄	C ₂ H ₄	C ₂ H ₆ sp	H ₂	CO	O ₂	N ₂	CO ₂	H ₂ O
Natural gases:										
Alabama	36,140	97.6						2.1	0.3	
Arkansas	36,730	99.2						0.6	0.2	
California-A	39,080	77.5		16.0					6.5	
California-B	40,880	83.4		15.4				0.5	0.7	
Illinois	35,400	95.6						3.9	0.5	
Indiana	43,110	75.4		23.4				1.2		
Kansas	36,290	98.0						0.8	1.2	
Kentucky	43,350	75.0		24.0				1.0		
Louisiana-A	34,760	78.8	9.5				0.3	11.3	0.1	
Louisiana-B	36,570	90.0		5.0				5.0		
Missouri	35,490	84.1		6.7				8.4	0.8	
New York	40,840	84.0		15.0				1.0		
Ohio-A	35,000	93.3	0.3		1.8	0.5	0.3	3.4	0.2	0.2
Ohio-B	35,060	93.4	0.4		1.6	0.4	0.4	3.4	0.4	
Oklahoma-A	39,160	73.5		18.4				8.1		
Oklahoma-B	35,490	84.1		6.7				8.4	0.8	
Pennsylvania-A	39,170	90.0		9.0				0.8	0.2	
Pennsylvania-B	41,140	83.4		15.8				0.8		
West Virginia	43,040	76.8		22.5				0.7		

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