
4 Combustion Basics

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4.1 INTRODUCTION

This chapter gives a brief overview of some basic combustion tenets, including:

- Principles of mass and energy conservation
- Concept of moles and molecular weight
- Energy, heat, and temperature
- Important flame properties
- Flame liftoff and flashback
- Diffusion and premix burners
- Natural and forced draft, NO_x and CO emissions

Where appropriate, brief examples reinforce these concepts and provide worked solutions.

4.1.1 CONSERVATION OF MASS

In chemical reactions, including combustion, mass is conserved. That is to say, mass is neither created nor destroyed during the combustion reaction: 100 kg of fuel + 1000 kilograms of air will generate 100 + 1000 (=1100) kg of products. Notwithstanding, the species will change. For example, one can write a reaction for methane (CH₄) combustion with oxygen as follows:



The subscripted numbers refer to the number of elements in a given molecule. Oxygen molecules are diatomic (comprising two oxygen atoms). The antecedent numbers refer to the number of molecular entities. A molecular entity with no antecedent number is presumed to refer to a single molecule. Hence, Equation 4.1 shows that one molecule of methane (CH₄) reacts with two molecules of oxygen (2O₂) to produce one molecule of carbon dioxide (CO₂) and two molecules of water (2H₂O).

Equation 4.1 is a *balanced* equation, meaning that the left and right sides of the equation comprise identical amounts of each element, C, H, and O. However, the molecular species have changed. On the left side, CH₄ and O₂ are present; on the right side, CO₂ and H₂O.

4.2 MOLES

A single molecule like CH₄ has an infinitesimal weight, so engineers deal with a more tractable quantity known as the *mole* (abbreviated *mol*). A mole is 6.02×10^{23} molecules. Table* 4.1 gives the mass for moles of the corresponding elements. The mass of a mole of an element is known as the *atomic weight*. The mass of a mole of molecules is known as the *molecular weight*.

Example 4.1

Calculate the molecular weight of CH₄.

Solution:

To calculate the molecular weight (M), one combines the atomic weights, e.g., $M_{\text{CH}_4} = M_{\text{C}} + 4M_{\text{H}} = 12.01 + 4(1.01) = 16.05$ g. Therefore, one mole of CH₄ has a mass of 16.05 g, which is the molecular weight.

Combustion engineers often work with British units, such as the pound (lb_m), where the subscript “m” is used to denote a pound mass (as opposed to a pound of force, lb_f — a fundamentally different quantity). A pound-mole (lbmol) has the same numerical value as the mol but is related to the lb_m rather than the gram. With this definition, a lbmol of CH₄ comprises 16.02 lb_m. For this reason, most atomic weights are listed as pure numbers. It is up to the combustion engineer to decide which basis to use — the mol (sometimes called the g-mol) or the lbmol.

4.3 MOLECULAR WEIGHT OF AIR

Air is comprised of two species — nitrogen (N₂) and oxygen (O₂) — in the approximate respective proportion of 79% and 21% by volume.

Example 4.2

Calculate the “molecular weight” of air.

* Table 4.1 in *The John Zink Combustion Handbook*, CRC Press, Boca Raton, FL, 2001, 36.

TABLE 4.1
Alphabetical List of Atomic Weights for Common Elements¹

Name	Symbol	At. No.	Atomic Weight	Footnotes	Name	Symbol	At. No.	Atomic Weight	Footnotes
Actinium	Ac	89	[227]		Europium	Eu	63	151.964(1)	
Aluminum	Al	13	26.981538(2)		Fermium	Fm	100	[257]	
Americium	Am	95	[243]		Fluorine	F	9	18.9984032(5)	
Antimony	Sb	51	121.760(1)	g	Francium	Fr	87	[223]	
Argon	Ar	18	39.948(1)	g r	Gadolinium	Gd	64	157.25(3)	g
Arsenic	As	33	74.92160(2)		Gallium	Ga	31	69.723(1)	
Astatine	At	85	[210]		Germanium	Ge	32	72.61(2)	
Barium	Ba	56	137.32(7)		Gold	Au	79	196.96655(2)	
Berkelium	Bk	97	[247]		Hafnium	Hf	72	178.49(2)	
Beryllium	Be	4	9.012182(3)		Hassium	Hs	108	[269]	
Bismuth	Bi	83	208.98038(2)		Helium	He	2	4.002602(2)	g
Bohrium	Bh	107	[264]		Holmium	Ho	67	164.93032(2)	
Boron	B	5	10.811(7)	g m r	Hydrogen	H	1	1.00794(7)	g m r
Bromine	Br	35	79.904(1)		Indium	In	49	114.818(3)	
Cadmium	Cd	48	112.411(8)	g	Iodine	I	53	126.90447(3)	
Calcium	Ca	20	40.078(4)	g	Iridium	Ir	77	192.217(3)	
Californium	Cf	98	[251]		Iron	Fe	26	55.845(2)	
Carbon	C	6	12.0107(8)	g r	Krypton	Kr	36	83.80(1)	g m
Cerium	Ce	58	140.116(1)	g	Lanthanum	La	57	138.9055(2)	g
Cesium	Cs	55	132.90545(2)		Lawrencium	Lr	103	[262]	
Chlorine	Cl	17	35.4527(9)	m	Lead	Pb	82	207.2(1)	g
Chromium	Cr	24	51.9961(6)		Lithium	Li	3	6.941(2)	g m r
Cobalt	Co	27	58.933200(9)		Lutetium	Lu	71	174.967(1)	g
Copper	Cu	29	63.546(3)	r	Magnesium	Mg	12	24.3050(6)	
Curium	Cm	96	[247]		Manganese	Mn	25	54.938049(9)	
Dubnium	Db	105	[262]		Meitnerium	Mt	109	[268]	
Dysprosium	Dy	66	162.59(3)	g	Mendelevium	Md	101	[258]	
Einsteinium	Es	99	[252]		Mercury	Hg	80	200.59(2)	
Erbium	Er	68	167.26(3)	g	Molybdenum	Mo	42	95.94(1)	g

(Continued)

TABLE 4.1
Alphabetical List of Atomic Weights for Common Elements¹ (Continued)

Name	Symbol	At. no.	Atomic Weight	Footnotes	Name	Symbol	At. no.	Atomic Weight	Footnotes
Neodymium	Nd	60	144.24(3)	g	Ruthenium	Ru	44	101.07(2)	g
Neon	Ne	10	20.1797(6)	g m	Rutherfordium	Rf	104	[261]	
Neptunium	Np	93	[237]		Samarium	Sm	62	150.36(3)	g
Nickel	Ni	28	58.6934(2)		Scandium	Sc	21	44.955910(8)	
Niobium	Nb	41	92.90638(2)		Seaborgium	Sg	106	[266]	
Nitrogen	N	7	14.00674(7)	g r	Selenium	Se	34	78.96(3)	
Nobelium	No	102	[259]		Silicon	Si	14	28.0855(3)	r
Osmium	Os	76	190.23(3)	g	Silver	Ag	47	107.8682(2)	g
Oxygen	O	8	15.9994(3)	g r	Sodium	Na	11	22.989770(2)	
Palladium	Pd	46	106.42(1)	g	Strontium	Sr	38	87.62(1)	g r
Phosphorus	P	15	30.973761(2)		Sulfur	S	16	32.066(6)	g r
Platinum	Pt	78	195.078(2)		Tantalum	Ta	73	180.9479(1)	
Plutonium	Pu	94	[244]		Technetium	Tc	43	[98]	
Polonium	Po	84	[209]		Tellurium	Te	52	127.60(3)	g
Potassium	K	19	39.0983(1)	g	Terbium	Tb	65	158.92534(2)	
Praseodymium	Pr	59	140.90765(2)		Thallium	Tl	81	204.3833(2)	
Promethium	Pm	61	[145]		Thorium	Th	90	232.0381(1)	g
Protactinium	Pa	91	231.03588(2)		Thulium	Tm	69	168.93421(2)	
Radium	Ra	88	[226]		Tin	Sn	50	118.710(7)	g
Radon	Rn	86	[222]		Titanium	Ti	22	47.867(1)	
Rhenium	Re	75	186.207(1)		Tungsten	W	74	183.84(1)	
Rhodium	Rh	45	102.90550(2)		Uranium	U	92	238.0289(1)	g m
Rubidium	Rb	37	85.4678(3)	g	Vanadium	V	23	50.9415(1)	

Xenon	Xe	54	131.29(2)	g	m	Zinc	Zn	30	65.39(2)	
Ytterbium	Yb	70	173.04(3)	g		Zirconium	Zr	40	92.224(2)	g
Yttrium	Y	39	88.90585(2)							

g – geological specimens are known in which the element has an isotopic composition outside the limits for normal material. The difference between the atomic weight of the element in such specimens and that given in the table may exceed the stated uncertainty.

m – modified isotopic compositions may be found in commercially available material because it has been subjected to an undisclosed or inadvertent isotopic fractionation. Substantial deviations in atomic weight of the element from that given in the table can occur.

r – range in isotopic composition of normal terrestrial material prevents a more precise atomic weight being given; the tabulated atomic weight value should be applicable to any normal material.

This table of atomic weights is reprinted from the 1995 report of the IUPAC Commission on Atomic Weights and Isotopic Abundances. The Standard Atomic Weights apply to the elements as they exist naturally on Earth, and the uncertainties take into account the isotopic variation found in most laboratory samples. Further comments on the variability are given in the footnotes.

The number in parentheses following the atomic weight value gives the uncertainty in the last digit. An entry in brackets indicates that mass number of the longest-lived isotope of an element that has no stable isotopes and for which a Standard Atomic Weight cannot be defined because of wide variability in isotopic composition (or complete absence) in nature.

REFERENCE

IUPAC Commission on Atomic Weights and Isotopic Abundances, Atomic Weights of the Elements, 1995, *Pure Appl. Chem.*, 68, 2339, 1996.

Source: Courtesy of CRC Press.¹

TABLE 4.2
Mass and Mole Balance for Hydrogen Combustion with Air

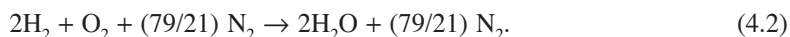
Species	IN		OUT	
	Moles In	Mass In	Moles Out	Mass Out
H ₂	200	404	0	0
O ₂	100	3,200	0	0
N ₂	376	10,536	376	10,536
H ₂ O	0	0	200	3,604
Totals	676	14,140	576	14,140

Note: Mass is conserved, but not moles.

Solution:

For convenience of calculation, combustion engineers often treat air as if it were a single entity having a “molecular weight” of 29. This weight is calculated from the molecular weights of nitrogen and oxygen as follows: $(0.79)(2)(14.01) + (0.21)(2)(16.00) = 29.0$.

Knowing the ratio of N₂ and O₂ in air, we can derive an equation for combustion of a fuel in air. For example, Equation 4.2 gives the balanced equation for hydrogen combustion with air.



Nitrogen is not significantly consumed in the reaction.

Example 4.3

Calculate the mass of fuel, air, and combustion products for hydrogen combustion of 100 lbmol of H₂.

Solution:

Equation 4.2 gives the molar proportions for hydrogen combustion. Table 4.2 derives the weights of each species in Equation 4.2. If there are 100 lbmol of O₂, then there must be (79/21) 100 lbmol N₂ = 376 lbmol N₂. Multiplying 376 lbmol N₂ by its molecular weight gives (2)(14.01)(376) = 10,536 lb_m. In a similar manner, Table 4.2 arrives at all quantities. The totals in Table 4.2 clearly show that mass is conserved, but moles are not.

4.4 THE IDEAL GAS LAW

One may have noticed that the volume percent and mole percent were presumed identical when calculating the molecular weight of air. This behavior is allowed for by the ideal gas law, which can be written as:

$$pV = nRT \quad (4.3)$$

where p is the pressure (psia), V is the volume (ft³), n is the number of lbmols, R is a universal constant, 10.73 psia-ft³/lbmol °R, and T is the absolute temperature (°R).

* Table 4.2, in *The John Zink Combustion Handbook*, CRC Press, Boca Raton, FL, 2001,164.

First, a word about some of the units. The ideal gas law requires temperature and pressure in absolute units. One such unit is the lb_f/in^2 absolute, or pounds per square inch, absolute, a.k.a. *psia*. One standard atmosphere of pressure exerts 14.7 psia. However, most pressure gages are calibrated to read “0” at atmospheric pressure (denoted as *psig*), where the “g” indicates that it is a gage pressure. So, a tire pressure gage reading 32 psig is equivalent to 46.7 psia ($32 + 14.7 = 46.7$).

Likewise, the ideal gas law references a temperature known as absolute zero. Once all the thermal energy is extracted from a substance, it can grow no colder. Absolute zero is approximately -460°F . To reference temperature above absolute zero, the Rankine temperature scale ($^\circ\text{R}$) was developed. To convert $^\circ\text{F}$ to $^\circ\text{R}$, add 460. Therefore, $70^\circ\text{F} \approx 530^\circ\text{R}$.

With this understanding, one can easily convert between mass, mols, and volume of gas. We have already shown that 100 lbmol O_2 has a mass of 3200 lbm. The volume can be calculated by rearranging Equation 4.3 and solving for V .

Example 4.4

Calculate the volume of 100 lbmol of any gas at standard atmospheric pressure and 32°F . How much volume would 1 lbmol of gas occupy under these conditions?

Solution:

$V = nRT/p = 100 \text{ [lbmol]} \cdot 10.73 \text{ [psia ft}^3/\text{lbmol R]} \cdot (32 + 460) \text{ [R]} / 14.7 \text{ [psia]} = 35,913 \text{ ft}^3$. Therefore, 1 lbmol of gas under the above conditions would occupy $\sim 359 \text{ ft}^3$.

From Equation 4.3 we can also see that n and V are proportional. Therefore, volume and mol percent are identical. The ideal gas law is quite accurate at all but very low temperatures and high pressures. Because industrial combustion is a high-temperature, low-pressure affair, the ideal gas law is perfectly suited to combustion calculations.

4.5 CONSERVATION OF ENERGY

Like mass, energy is also a conserved quantity for combustion reactions. Energy is stored in the chemical bonds that make up a molecular entity. Depicting Equation 4.2 graphically for the reacting species gives:



Molecular entities as depicted in Equation 4.4 are known as *structural formulas* because they reveal some elements of the structure of each molecule, where the single and double lines are known as *single* and *double* bonds, respectively. Hydrogen generally shares one bond, oxygen two, nitrogen three, and carbon four. If the products represent a lower energy state than the reactants, heat will be liberated and the reaction is known as an *exothermic reaction*. Fuels are, by definition, those entities that can produce heat (exothermic) upon reaction with oxygen. To calculate the heat of combustion, one can use a heat of combustion table. Table 4.3 gives the heats of combustion of several important fuels.

4.6 LOWER AND HIGHER HEATING VALUES

There are two possible ways to calculate a heating value. One way is to presume that the combustion exit gases are sufficiently hot that the water vapor from the combustion process does not condense. With this assumption, the heat released is known as the *net* or *lower heating value (LHV)*. In other cases — for example, a condensing turbine where the combustion products are cooled to the point of water condensation — one obtains the gross or *higher heating value (HHV)*.

TABLE 4.3
Physical Constants of Typical Gaseous Fuel Mixture Components

No.	Fuel Gas Component	Chemical Formula	Molecular Weight	Boiling Point 14.696 psia (°F)	Vapor Pressure 100°F (psia)	Specific Heat Capacity, C _p 14.696 psia (Btu/lb _m /°F)	Latent Heat of Vaporization 14.696 psia & Boiling Point (Btu/lb _m)	Heating Value				Unit Volume per Unit Volume of Combustible								Unit Mass per Unit Mass of Combustible								Flammability Limits (vol% in air mixture)							
								Gas Density Ideal Gas, 14.696 psia, 60°F			Btu/scf		Btu/lb _m		Required for Combustion				Flue Gas Products				Required for Combustion				Flue Gas Products				Theoretical Air Required (lb./10,000 Btu)				
								Specific Gravity (Air = 1)	Gas Density (lb./ft ³)	Specific Volume (ft ³ /lb _m)	LHV (Net)	HHV (Gross)	LHV (Net)	HHV (Gross)	O ₂	N ₂	Air	CO ₂	H ₂ O	N ₂	SO ₂	O ₂	N ₂	Air	CO ₂	H ₂ O	N ₂	SO ₂	Lower	Upper		No.			
Paraffin (alkane) Series (C _n H _{2n+2})																																			
1.	Methane	CH ₄	16.04	-258.69	—	0.5266	219.22	0.554	0.042	23.651	912	1,013	21.495	23.845	2.0	7.547	9.547	1.0	2.0	7.547	—	3.989	13.246	17.235	2.743	2.246	13.246	—	7.219	5.0	15.0				
2.	Ethane	C ₂ H ₆	30.07	-127.48	—	0.4097	210.41	1.038	0.079	12.618	1,639	1,792	20.418	22.323	3.5	13.206	16.706	2.0	3.0	13.206	—	3.724	12.367	16.092	2.927	1.797	12.367	—	7.209	2.9	13.0	2			
3.	Propane	C ₃ H ₈	44.10	-43.67	190	0.3881	183.05	1.522	0.116	8.604	2,385	2,592	19.937	21.669	5.0	18.866	23.866	3.0	4.0	18.866	—	3.628	12.047	15.676	2.994	1.624	12.047	—	7.234	2.1	9.5	3			
4.	n-Butane	C ₄ H ₁₀	58.12	31.10	51.6	0.3867	165.65	2.007	0.153	6.528	3,113	3,373	19.679	21.321	6.5	24.526	31.026	4.0	5.0	24.526	—	3.578	11.882	15.460	3.029	1.550	11.882	—	7.251	1.8	8.4	4			
5.	Isobutane	C ₄ H ₁₀	58.12	10.90	72.2	0.3872	157.53	2.007	0.153	6.528	3,105	3,365	19.629	21.271	6.5	24.526	31.026	4.0	5.0	24.526	—	3.578	11.882	15.460	3.029	1.550	11.882	—	7.268	1.8	8.4	5			
6.	n-Pentane	C ₅ H ₁₂	72.15	96.92	15.57	0.3883	153.59	2.491	0.190	5.259	3,714	4,017	19.507	21.095	8.0	30.186	38.186	5.0	6.0	30.186	—	3.548	11.781	15.329	3.050	1.498	11.781	—	7.267	1.4	8.3	6			
7.	Isopentane	C ₅ H ₁₂	72.15	82.12	20.44	0.3827	147.13	2.491	0.190	5.259	3,705	4,017	19.549	21.047	8.0	30.186	38.186	5.0	6.0	30.186	—	3.548	11.781	15.329	3.050	1.498	11.781	—	7.283	1.4	8.3	7			
8.	Neopentane	C ₅ H ₁₂	72.15	49.10	35.9	0.3666	135.58	2.491	0.190	5.259	3,692	3,994	19.390	20.978	8.0	30.186	38.183	5.0	6.0	30.186	—	3.548	11.781	15.329	3.050	1.498	11.781	—	7.307	1.4	8.3	8			
9.	n-Hexane	C ₆ H ₁₄	86.18	155.72	4.956	0.3664	143.95	2.975	0.227	4.403	4,415	4,767	19.415	20.966	9.5	35.846	45.346	6.0	7.0	35.846	—	3.527	11.713	15.240	3.064	1.463	11.713	—	7.269	1.2	7.7	9			
Napthene (cycloalkane) Series (C _n H _{2n})																																			
10.	Cyclopentane	C ₅ H ₁₀	70.13	120.60	9.917	0.2712	137.35	2.420	0.180	5.556	3,512	3,764	19.005	20.368	7.5	27.939	35.180	5.0	5.0	28.939	—	3.850	11.155	14.793	3.146	1.283	11.155	—	7.262	—	—	10			
11.	Cyclohexane	C ₆ H ₁₂	84.16	177.40	3.267	0.2901	153.25	2.910	0.220	5.545	4,180	4,482	18.849	20.211	9.0	33.528	42.970	6.0	6.0	33.528	—	4.620	13.386	17.750	3.146	1.283	11.155	—	7.848	1.3	8.4	11			
Olefin Series (C _n H _{2n})																																			
12.	Ethene (Ethylene)	C ₂ H ₄	28.05	-154.62	—	0.3622	207.57	0.969	0.074	13.525	1,512	1,613	20.275	21.636	3.0	11.320	14.320	2.0	2.0	11.320	—	3.422	11.362	14.784	3.138	1.284	11.362	—	6.833	2.7	34.0	12			
13.	Propene (Propylene)	C ₃ H ₆	42.08	-53.90	226.4	0.3541	188.18	1.453	0.111	9.017	2,185	2,336	19.687	21.048	4.5	16.980	21.480	3.0	3.0	16.980	—	3.422	11.362	14.784	3.138	1.284	11.362	—	7.024	2.0	10.0	13			
14.	1-Butene (Butylene)	C ₄ H ₈	56.11	20.75	63.05	0.3548	167.94	1.937	0.148	6.762	2,885	3,086	19.493	20.854	6.0	22.640	28.640	4.0	4.0	22.640	—	3.422	11.362	14.784	3.138	1.284	11.362	—	7.089	1.6	9.3	14			
15.	Isobutene	C ₄ H ₈	56.11	19.59	63.4	0.3701	169.48	1.937	0.148	6.762	2,868	3,069	19.376	20.730	6.0	22.640	28.640	4.0	4.0	22.640	—	3.422	11.362	14.784	3.138	1.284	11.362	—	7.129	1.6	—	15			
16.	1-Pentene	C ₅ H ₁₀	70.13	85.93	19.115	0.3635	154.46	2.421	0.185	5.410	3,585	3,837	19.359	20.727	7.5	28.300	35.800	5.0	5.0	28.300	—	3.422	11.362	14.784	3.138	1.284	11.362	—	7.135	1.4	8.7	16			
Aromatic Series (C _n H _{n-6})																																			
17.	Benzene	C ₆ H ₆	78.11	176.17	3.224	0.2429	169.31	2.697	0.206	4.857	3,595	3,746	17.421	18.184	7.5	28.300	35.800	6.0	3.0	28.300	—	3.072	10.201	13.274	3.380	0.692	10.201	—	7.300	1.38	7.98	17			
18.	Toluene	C ₇ H ₈	92.14	231.13	1.032	0.2598	154.84	3.181	0.243	4.118	4,296	4,497	17.672	18.501	9.0	33.959	42.959	7.0	4.0	33.959	—	3.125	10.378	13.504	3.340	0.782	10.378	—	7.299	1.28	7.18	18			
19.	o-Xylene	C ₈ H ₁₀	106.17	291.97	0.264	0.2914	149.1	3.665	0.280	3.574	4,970	5,222	17.734	18.633	10.5	39.619	50.119	8.0	5.0	39.619	—	3.164	10.508	13.673	3.316	0.848	10.508	—	7.338	1.18	6.48	19			
20.	m-Xylene	C ₈ H ₁₀	106.17	282.41	0.326	0.2782	147.2	3.665	0.280	3.574	4,970	5,222	17.734	18.633	10.5	39.619	50.119	8.0	5.0	39.619	—	3.164	10.508	13.673	3.316	0.848	10.508	—	7.338	1.18	6.48	20			
21.	p-Xylene	C ₈ H ₁₀	106.17	281.05	0.342	0.2769	144.52	3.665	0.280	3.574	4,970	5,222	17.734	18.633	10.5	39.619	50.119	8.0	5.0	39.619	—	3.164	10.508	13.673	3.316	0.848	10.508	—	7.338	1.18	6.48	21			
Additional Fuel Gas Components																																			
22.	Acetylene	C ₂ H ₂	26.04	-119	—	0.3966	—	0.899	0.069	14.572	1,448	1,499	20.769	21.502	2.5	9.433	11.933	2.0	1.0	9.433	—	3.072	10.201	13.274	3.380	0.692	10.201	—	7.300	2.5	80	22			
23.	Methyl alcohol	CH ₃ OH	32.04	148.1	4.63	0.3231	473	1.106	0.084	11.841	767	868	9.066	12.158	1.5	5.660	7.160	1.0	2.0	5.660	—	4.498	4.974	6.482	1.373	1.124	4.974	—	6.309	6.72	36.5	23			
24.	Ethyl alcohol	C ₂ H ₅ OH	46.07	172.92	2.3	0.3323	367	1.590	0.121	8.236	1,449	1,600	11.918	13.261	3.0	11.320	14.320	2.0	3.0	11.320	—	2.084	6.919	9.003	1.911	1.173	6.919	—	6.841	3.28	18.9	24			
25.	Ammonia	NH ₃	17.03	-28.2	212	0.5002	587.2	0.588	0.045	22.279	364	441	7.966	9.567	0.75	2.830	3.582	—	1.5	3.330	—	1.409	4.679	6.008	—	1.587	5.502	—	6.298	15.50	27.00	25			
26.	Hydrogen	H ₂	2.02	-423.0	—	3.4080	193.9	0.070	0.005	188.217	274.6	325.0	51.625	61.095	0.5	1.887	2.387	—	1.0	1.887	—	7.936	26.323	34.290	—	8.937	26.353	—	5.613	4.00	74.20	26			
27.	Oxygen	O ₂	32.00	-297.4	—	0.2186	91.6	1.15	0.084	11.858	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	27		
28.	Nitrogen	N ₂	29.16	-320.4	—	0.2482	87.8	0.972	0.074	13.472	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	28		
29.	Carbon monoxide	CO	28.01	-313.6	—	0.2484	92.7	0.967	0.074	13.546	321.9	321.9	4.347	4.347	0.5	1.877	2.387	1.0	—	1.887	—	—	1.897	2.468	1.571	—	1.870	—	5.677	12.50	74.20	29			
30.	Carbon dioxide	CO ₂	44.01	-109.3	—	0.1991	238.2	1.519	0.116	8.621	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	30		
31.	Hydrogen sulfide	H ₂ S	34.08	-76.6	394.0	0.2380	235.6	1.177	0.090	11.133	595	646	6.537	7.097	1.5	5.660	7.160	—	1.0	5.680	1.0	1.410	4.682	6.093	—	0.529	4.682	1.880	8.585	4.30	45.50	31			
32.	Sulfur dioxide	SO ₂	64.06	14.0	88	0.1450	166.7	2.212	0.169	5.923	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	32		
33.	Water vapor	H ₂ O	18.02	212.0	0.9492	0.4446	970.3	0.622	0.047	21.061	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	33		
34.	Air	—	29.97	-317.6	—	0.2400	92	1.000	0.076	13.099	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	34		

Example 4.5

Calculate the heat release rate (LHV) for 1000 ft³/hr of CH₄

Solution:

The LHV is given directly in Table 4.2 for CH₄ as 912 Btu/ft³. For 1000 ft³/hr of CH₄, the total heat release rate becomes:

$$1000 \text{ [ft}^3\text{/hr]} \times 912 \text{ [Btu/ft}^3\text{]} = 912,000 \text{ Btu/hr}$$

(or 0.91 million Btu/hr, often abbreviated as 0.91 MMBtuh).

In the hydrocarbon, petroleum, and chemical process industries, the usual convention is to use the LHV. In boilers, the usual convention is HHV, although most boilers do not condense the water in the combustion products. For these reasons, it is important to state the basis clearly and use it consistently throughout the calculation.

4.7 ENTHALPY AND LATENT HEAT

When energy is absorbed by a gas, the gas increases in temperature and expands. The contribution of the internal energy stored in the gas plus the energy required to expand the gas is termed *enthalpy*. Because combustion reactions are typically carried out at constant pressure, a change in temperature will always be accompanied by an expansion, according to the ideal gas law.

Remarkably, in some cases, adding heat to a substance does not change its temperature. For example, adding heat to water at the boiling point transforms it to steam at the same temperature. Combustion engineers refer to this heat as *latent* heat because it is stored in the gas as internal energy rather than expressed as a temperature increase. The latent heat of water vapor is ~970 Btu/lb_m. This means that for every lb_m of steam condensed at the boiling point, one will liberate 970 Btu.

4.8 SENSIBLE HEAT AND HEAT CAPACITY

Sensible heat is the energy stored as a temperature rise. It is termed “sensible heat” because the absorption of energy results in a temperature rise, a common-sensical phenomenon. The proportionality constant between the energy absorbed and the temperature rise is known as the *heat capacity*. It has units of energy per mass per degree. For example, the heat capacity of liquid water is approximately 1 Btu/lb_m °F. A basic formula used to relate the enthalpy to the heat capacity and temperature is:

$$\Delta H = C_p \Delta T \quad (4.5)$$

where ΔH is the difference in enthalpy between the two states (Btu/lb_m), C_p is the heat capacity at constant pressure (Btu/lb_m °F), and ΔT is the temperature difference (°F or °R).

Example 4.6

Find the energy required to heat liquid water from its freezing point (32°F) to its boiling point (212°F)

Solution:

From Equation 4.4, the energy necessary to heat liquid water from its freezing point at 32°F to its boiling point at 212°F is:

$$\Delta H = 1 \text{ [Btu/lb}_m \text{ °F]} (212 - 32) \text{ [°F]} = 180 \text{ Btu/lb}_m$$

Example 4.7

Find the energy required to change liquid water to steam at the boiling point.

Solution:

The latent heat to change phase from liquid water to steam is $\Delta H = 970 \text{ Btu/lb}_m$. Therefore, the required heat to convert liquid water at the freezing point to steam is the sum of the sensible and latent heats, or:

$$\Delta H = (970 + 180) [\text{Btu/lb}_m] = 1150 \text{ Btu/lb}_m$$

Note that most of the energy requirement to generate steam is the latent heat requirement. It cannot be neglected!

As enthalpy can be expressed in various units (e.g., Btu/lb_m , Btu/lbmol , Btu/ft^3), so heat capacity can also be expressed on a mass, molar, or volume basis. One can convert from one form to another by making use of molecular weights and the ideal gas law (in the case of gases). Enthalpy for liquids is not typically expressed volumetrically. However, if desired, one can easily convert between volumetric- and mass-based units for liquids if the liquid density $[\text{lb}_m/\text{ft}^3]$ is known.

4.9 SOME PROPERTIES OF FLAMES

Combustion typically results in an intense luminous zone of fuel oxidation known as a *flame*. One important property related to a flame is the *ignition temperature*. Table* 4.4 lists the ignition temperatures and other important properties of some common fuels. Once ignition takes place, there is more than enough energy liberated from the fuel combustion to ignite other fuel molecules. Thus, combustion, once started, is self-sustaining. If the ignition temperature is not achieved, sufficient fuel molecules cannot combust to ignite others. By extracting sufficient energy from the flame, the reaction may be *quenched*, that is, extinguished.

4.9.1 FLAMMABILITY LIMITS

Another very important requirement for sustained combustion is that the fuel and air be within certain limits known as *flammability limits*. Table 4.4 also gives lower and upper flammability limits for various fuels. The *upper flammability limit (UFL)* is the maximum fuel volume concentration that will sustain a flame. As the fuel concentration increases, more air is required to combust the fuel. However, because the fuel and air must sum to 100%, the fuel concentration can only be increased at the expense of reducing the available air. As the air becomes limiting, not all of the fuel can combust completely. Ultimately, a limit is reached where sufficient fuel cannot react with air to sustain the reaction. This is the upper flammability limit.

The *lean or lower flammability limit (LFL)* represents the opposite case. When the LFL is reached, there is insufficient fuel to release sufficient energy to sustain combustion, and the flame goes out. The ideal fuel/air mixture is determined by constructing a balanced equation for the fuel/air mixture (e.g., Equation 4.2). However, because fuel and air cannot be perfectly mixed, *excess air* is required as a good combustion practice to ensure complete combustion. For many fuels, 3% excess air (1.03 times more air than theoretically necessary) is usually sufficient. However, the actual excess air requirement is dependent on some unique factors of the equipment and fuel, and is ultimately determined from experience.

* Table 4.4, in *The John Zink Combustion Handbook*, CRC Press, Boca Raton, FL, 2001, 45.

TABLE 4.4
Combustion Data for Hydrocarbons

Hydrocarbon	Formula	Higher Heating Value (vapor) (Btu lb _m ⁻¹)	Theor. Air/Fuel Ratio, by Mass	Max. Flame Speed, (ft s ⁻¹)	Adiabatic Flame Temp. (in air) (°F)	Ignition Temp. (in air) (°F)	Flash Point (°F)	Flammability Limits (in air) (% by volume)	
Paraffins or Alkanes									
Methane	CH ₄	23875	17.195	1.1	3484	1301	Gas	5.0	15.0
Ethane	C ₂ H ₆	22323	15.899	1.3	3540	968–1166	Gas	3.0	12.5
Propane	C ₃ H ₈	21669	15.246	1.3	3573	871	Gas	2.1	10.1
<i>n</i> -Butane	C ₄ H ₁₀	21321	14.984	1.2	3583	761	−76	1.86	8.41
<i>iso</i> -Butane	C ₄ H ₁₀	21271	14.984	1.2	3583	864	−117	1.80	8.44
<i>n</i> -Pentane	C ₅ H ₁₂	21095	15.323	1.3	4050	588	<−40	1.40	7.80
<i>iso</i> -Pentane	C ₅ H ₁₂	21047	15.323	1.2	4055	788	<−60	1.32	9.16
Neopentane	C ₅ H ₁₂	20978	15.323	1.1	4060	842	Gas	1.38	7.22
<i>n</i> -Hexane	C ₆ H ₁₄	20966	15.238	1.3	4030	478	−7	1.25	7.0
Neohexane	C ₆ H ₁₄	20931	15.238	1.2	4055	797	−54	1.19	7.58
<i>n</i> -Heptane	C ₇ H ₁₆	20854	15.141	1.3	3985	433	25	1.00	6.00
Triptane	C ₇ H ₁₆	20824	15.151	1.2	4035	849	—	1.08	6.69
<i>n</i> -Octane	C ₈ H ₁₈	20796	15.093	—	—	428	56	0.95	3.20
iso-Octane	C ₈ H ₁₈	20770	15.093	1.1	—	837	10	0.79	5.94
Olefins or Alkenes									
Ethylene	C ₂ H ₄	21636	14.807	2.2	4250	914	Gas	2.75	28.6
Propylene	C ₃ H ₆	21048	14.807	1.4	4090	856	Gas	2.00	11.1
Butylene	C ₄ H ₈	20854	14.807	1.4	4030	829	Gas	1.98	9.65
iso-Butene	C ₄ H ₈	20737	14.807	1.2	—	869	Gas	1.8	9.0
<i>n</i> -Pentene	C ₅ H ₁₀	20720	14.807	1.4	4165	569	—	1.65	7.70

(Continued)

TABLE 4.4
Combustion Data for Hydrocarbons (Continued)

Hydrocarbon	Formula	Higher Heating Value (vapor) (Btu lb _m ^{−1})	Theor. Air/Fuel Ratio, by Mass	Max. Flame Speed, (ft s ^{−1})	Adiabatic Flame Temp. (in air) (°F)	Ignition Temp. (in air) (°F)	Flash Point (°F)	Flammability Limits (in air) (% by volume)	
Aromatics									
Benzene	C ₆ H ₆	18184	13.297	1.3	4110	1044	12	1.35	6.65
Toluene	C ₇ H ₈	18501	13.503	1.2	4050	997	40	1.27	6.75
<i>p</i> -Xylene	C ₈ H ₁₀	18663	13.663	—	4010	867	63	1.00	6.00
Other Hydrocarbons									
Acetylene	C ₂ H ₂	21502	13.297	4.6	4770	763–824	Gas	2.50	81
Naphthalene	C ₁₀ H ₈	17303	12.932	—	4100	959	174	0.90	5.9

Note: Based largely on: “Gas Engineers’ Handbook,” American Gas Association, Inc., Industrial Press, 1967. For heating value in J kg⁻¹, multiply the value in Btu lb_m⁻¹ by 2324. For flame speed in ms⁻¹, multiply the value in fts⁻¹ by 0.3048.

REFERENCES

- American Institute of Physics Handbook*, 2nd ed., D.E. Gray, Ed., McGraw-Hill Book Company, 1963.
Chemical Engineers’ Handbook, 4th ed., R.H. Perry, C.H. Chilton, and S.D. Kirkpatrick, Eds., McGraw-Hill Book Company, 1963.
Handbook of Chemistry and Physics, 53rd ed., R.C. Weast, Ed., The Chemical Rubber Company, 1972; gives the heat of combustion of 500 organic compounds.
Handbook of Laboratory Safety, 2nd ed., N.V. Steere, Ed., The Chemical Rubber Company, 1971.
Physical Measurements in Gas Dynamics and Combustion, Princeton University Press, 1954.

4.9.2 LAMINAR FLAME SPEED

An important property related to flame propagation is the flame speed (see [Table 4.4](#)). Consider a large open container of fuel and air, intimately mixed in ideal proportions. If the fuel is ignited at one end of the container, the flame will flash or propagate to the other end at a particular velocity. This is a measure of the kinetics of the flame — that is, how fast can the fuel and air react and pass its energy on to the adjacent but unreacted fuel/air mixture? The *laminar flame speed* is one such measure of the kinetics of the flame. [Table 4.4](#) gives laminar flame speeds for several fuels. Most hydrocarbons have a similar flame speed. But hydrogen, owing to its high enthalpy per mole and its low viscosity and rapid diffusion, has a flame speed more than triple most hydrocarbon fuels.

4.10 LIFTOFF AND FLASHBACK

One can envision two scenarios for a propagating flame. In the first scenario, already discussed, the air and fuel are premixed and stationary. The flame then propagates within the quiescent mixture. In such a case, the mixture is stationary and the flame is moving. Another scenario is to move the fuel and air, and allow the flame to remain stationary. The typical industrial burner functions in this way, having moving reactants and a stationary flame. A stationary flame confined to the burner and certain portions of the furnace is critical. Otherwise, the high flame temperatures of wayward flames would be destructive to boilers and process tubes.

If the reactants are metered at a velocity exceeding the flame speed, the flame will begin to move in the direction of the reactant flow. This condition is known as *lift-off*. If the flame is carried to a region downstream of the burner, combustion products within the furnace may dilute the fuel/air mixture below the LFL. This would extinguish the flame and result in a very dangerous condition — uncombusted fuel may accumulate and later find an ignition source. This could result in an explosion.

If the reactants are metered at a velocity much lower than the flame speed, the flame moves opposite the direction of the reactant flow. In the case of premixed fuel and air, the flame can *flashback* or enter an area of the burner that cannot tolerate the high temperature, thus destroying the burner. The following section considers combustion with premixed reactants.

4.11 PREMIX AND DIFFUSION FLAMES

In certain industrial settings requiring rapid combustion and short flame lengths, it may be desirable to mix the fuel and air prior to combustion. The device is known as a *premix* burner. [Figure 4.1](#) shows such a burner. It comprises a venturi section, whereby the fuel pressure aspirates combustion air and provides the mixing energy. The fuel is ignited outside the mixing chamber and anchors to the outside of the burner by a mechanism we explain shortly. If the flame were to flashback within the interior of the burner, the burner would be destroyed in short order.

A *diffusion burner* avoids this situation by metering the fuel and air in separate streams ([Figure 4.2](#)). Because neither pure air nor fuel alone is able to sustain combustion, the flame cannot propagate into the fuel line or air inlets. This eliminates the potential for flashback. However, the flame may still lift off or move to an area of insufficient fuel and air. Therefore, in both premixed and diffusion flames, some method is needed to anchor the flame.

4.12 TURBULENT FLAME SPEED AND FLAME HOLDERS

In practice, industrial burners cannot rely on an exact metering of the fuel and air to exactly match the flame speed for several reasons. First, small changes in hydrogen content (usual in refinery applications) would require real-time fuel analysis and some system of precision metering.

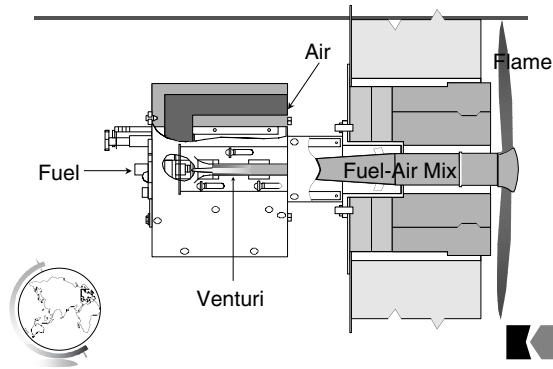


FIGURE 4.1 Premixed burner.

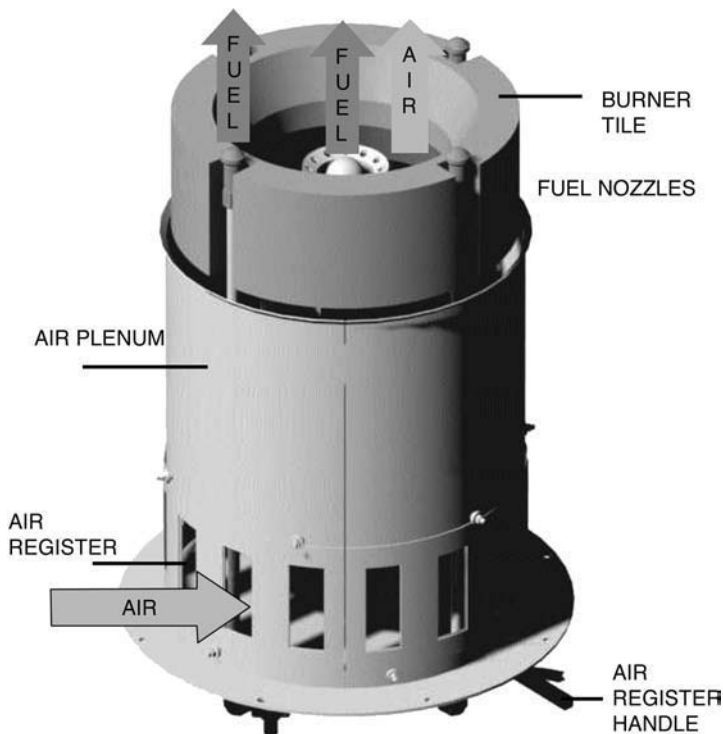


FIGURE 4.2 Staged diffusion burner. Note that fuel and air streams are not mixed prior to combustion.

In practice, neither exists. Second, the laminar flame speed is much too slow to anchor the flame. That is, in most industrial settings, the fuel and air are metered at velocities that well exceed the laminar flame speed. How then can the flame be anchored? One makes use of two phenomena: the turbulent flame speed and flame holders.

Unlike laminar flame speed, *turbulent flame speed* is not properly a function of the fuel alone, but also of the flow conditions. If the velocity is sufficiently high, the flow shifts from laminar flow to turbulent flow. Turbulent flow is characterized by macroscopic recirculation within the flame structure.

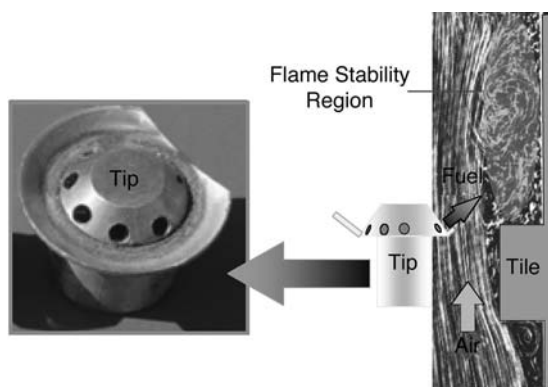


FIGURE 4.3 Burner ignition ledge: tile ledge/fuelport position and angle.

This recirculation mixes hot product gases with the reactants. The result is that the effective flame speed is much higher. It is not uncommon for fuel and air flows to be many times greater than the laminar flame speed in turbulent combustion.

However, because the turbulent flame speed depends on the flow conditions as well as the fuel composition, it is not practical to stabilize the flame front by fuel and air metering. Instead, combustion engineers make use of *flame holders*. As the name implies, a flame holder is a device that anchors the leading edge of the flame. This usually involves providing a region of low velocity in the flame path. For example, [Figure 4.3](#) shows one type of flame holder known as an *ignition ledge*. As the fuel and air flow by the ledge at high velocity, the ledge or step forces some gas to recirculate. Thus, the velocity at the ledge is virtually zero. This allows the flame to burn back to the ignition ledge. The recirculation ensures that the region is recharged with fresh fuel and air. Thus, the flame is anchored or held to the ignition ledge, despite much higher velocities in the adjacent flow field.

The ignition ledge is part of a class of flame holders known as *bluff bodies*. A bluff body is any nonstreamlined shape inserted into the flow field. The trailing edges of the body cause recirculation and anchor the flame. Because the bluff body or ignition ledge must tolerate direct flame impingement, it must be made of high-temperature alloy or refractory. Otherwise, the flame holder will degrade and compromise the flame stability of the burner.

4.13 QUENCHING

In premix burners (see [Figure 4.1](#)), some mechanism must be used to prevent the flame from propagating upstream and causing the premixed fuel and air to ignite inside the burner. There are several methods for doing this. The first is to design the burner so that the fuel/air mixture exceeds the turbulent flame speed. This will cause the flame to move downstream. To keep the flame from lifting off, the burner itself can be designed with slots having square-edged exits. Like the ignition ledge or bluff body, the bluff trailing edge causes recirculation and functions as a flame holder. Because the flame is anchored at this edge, the burner material at this edge must be made of high-temperature alloy.

The flowing fuel and air help cool the burner. However, the hot flame is anchored just outside the burner and just millimeters away from combustible gases. If the only mechanism keeping the flame from flashing back were fuel and air velocity, a momentary fuel reduction would allow the flame to propagate upstream to the interior of the burner. Because the velocity in the interior of the burner is lower than through the passage that the flame has propagated, there is no mechanism

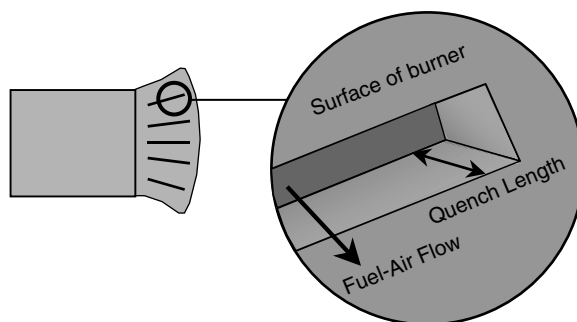


FIGURE 4.4 Detail of premix burner slot.

to force the flame back to the outside when the fuel and air flows resume their design flows. In such a case, the flame will remain internal to the venturi and destroy it in short order. Changes in fuel composition and flow rates occur often enough in refinery environments to mandate additional mechanisms to prevent flashback.

If sufficient enthalpy can be removed from the flame as it begins to flash back, the flame will extinguish. The key is to extinguish or quench only the portion of the flame that is beginning to flash back, while leaving the remainder of the flame to burn as intended. This is done using a *quench distance*. Consider Figure 4.4, an enlarged section of the premix burner exit. The gas flows through long metal passageways before being ignited. The sidewalls of this passageway are relatively cool because of the flowing but unignited gases. Should the flame begin to flash back, the cool metal will extract heat and quench the flame, preventing it from entering the interior of the burner. However, the method is not foolproof. If the flow is reduced beyond the design limit for extended periods, the entire burner may reach a temperature insufficient to quench flame propagation. In short, burner design requires a thorough knowledge of fluid mechanics, heat transfer, combustion, and prior art.

4.14 NATURAL- AND FORCED-DRAFT BURNERS

Burners can receive their airflow in two ways. If the flame must be short and compact, one can provide air to the burner using a fan or blower. The resulting system is known as a *forced-draft* system, and the burners are forced-draft burners. Forced draft provides additional mixing that helps increase flame turbulence and shorten the flame. It also allows for smaller furnace volumes. Thus, it decreases the capital cost of the boiler or process heater. However, the capital cost is reduced at the expense of operating cost for the blower or fan. One way of compensating for this cost is to allow the air to be preheated by the exiting flue gases in a device known as an air preheater. The recovery of heat allows the process to operate more efficiently. Cooler flue gases exit the stack.

Natural-draft burners rely on the natural tendency of cold air to displace hot gases in the furnace, forcing them out the exit stack. Resorting to the ideal gas law and conservation of energy, we can model this phenomenon. The difference in weight between a hot and cool volume of gas (Δmgh) can be harnessed to perform work (pV). Normalizing the quantities by the mass (m) gives Equation 4.6:

$$\Delta p = \Delta \rho gh \quad (4.6)$$

where Δp is the stack draft, $\Delta \rho$ is the density difference between the cool and hot flue gases, g is the acceleration due to gravity (32.174 ft/s^2), and h is the height of the furnace. Making use of the

ideal gas law and the definition of molecular weight, we can recast the equation in terms of temperature difference:

$$\Delta p = \frac{PM}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) h \quad (4.7)$$

Example 4.8

Calculate the draft at the floor given by a 40-ft furnace with an average temperature of 1600°F. Assume a molecular weight of the flue gas of 28 lb_m/lbmol, and an outside temperature of 60°F. Further, assume that the exit of the furnace is at -0.1 inches of WC due to the influence of a warm stack.

Solution:

From Equation 4.7,

$$\Delta p = \frac{14.7[\text{psia}] 28 \left[\frac{\text{lb}_m}{\text{lbmol}} \right]}{10.73 \left[\frac{\text{psia ft}^3}{\text{lbmol}^\circ\text{R}} \right]} \left(\frac{1}{1600 + 460} - \frac{1}{60 + 460} \right) \left[\frac{1}{^\circ\text{R}} \right] 32.2 \left[\frac{\text{ft}}{\text{s}^2} \right] 40[\text{ft}] = -71.03 \left[\frac{\text{lb}_m}{\text{ft s}^2} \right]$$

This is not a very useful unit of pressure. In general, draft is measured in inches of water column (in. WC). As the name denotes, in. WC represents the pressure necessary to raise a column of water 1 inch in elevation. For example, the pressure in one's mouth must be a few inches of WC below atmospheric to drink water through a straw. To convert lb_m/ft s² to in. WC, one divides by 167.6. Therefore, the resulting pressure is -0.42 in. WC. The negative sign means that the pressure in the furnace is lower than atmospheric. A general rule of thumb is that a furnace generates ~0.1 in. WC for each 10 ft in height. Adding back the -0.1 in. WC from the stack contribution, the draft available at the burner is -0.52 in. WC.

To convert inches of WC to psi, divide by 27.67.

Although this force appears to be quite feeble, it is capable of drafting an enormous amount of air in through the burner opening; 1 in. WC is capable of drafting air at velocities up to 66 ft/s at 60°F! Under these conditions, a single burner with a throat opening of 1 ft² (~8 in. diam.) can support up to 7 MMBtu/hr HHV of CH₄ combustion. Typical natural-draft burners for the petrochemical industry operate on ~0.5 in. WC draft and deliver 8 MMBtuh with 2 to 3 ft² of throat area. Some additional area is required to account for air friction through the throat and burner internals.

4.15 NO_x AND CO

An *emission* is any unwanted egress of a substance or quantity. CO, and NO_x are byproducts of the combustion process. With proper design, they can be reduced to acceptable levels, but never eliminated. CO emissions are generally an indicator of too little air, poor mixing, or insufficient furnace temperature. With proper burner design, excess oxygen concentrations of 2 to 5%, and greater than 1100°F furnace temperatures, CO is not typically a problem.

The combustion process also produces CO₂ and H₂O, which cannot be considered byproducts because proper combustion results in complete conversion of hydrocarbon fuels to CO₂ and H₂O. Both H₂O and CO₂ are chemical products of aerobic respiration and produced by plants, animals, and humans. However, CO₂ is coming under scrutiny as a so-called greenhouse gas — an active

infrared absorber and emitter that can potentially elevate terrestrial temperatures. Actually, H_2O is more active in this regard, but CO_2 is a greater political concern.

If and to what extent CO_2 is considered an emission will dictate some combustion practices in the future. There are only two ways to control CO_2 emissions: reduction of carbon in the fuel or post-combustion treatment; that is, capturing CO_2 after it is produced. Hydrogen combustion produces no CO_2 (see Equation 4.2). However, many are surprised to learn that hydrogen combustion with air produces more NO_x than hydrocarbon fuels such as natural gas and gasoline. This is due to hydrogen's very high flame temperature and the thermal-bound NO_x mechanism. We consider NO_x next.

4.15.1 NO_x EMISSIONS

NO_x is formed in very low quantities (parts per million on a volume basis) as a byproduct of combustion in several ways. NO_x contributes to ground-level ozone via a complex reaction with hydrocarbons and other reactive compounds. Ground-level ozone can be a severe problem for a certain distressed portion of the population (e.g., asthmatics and those with diminished lung capacity). For these and other reasons, NO_x emissions are regulated to very low levels (e.g., <30 ppm). Typical industrial combustion produces 100 to 200 ppm NO_x . However, low- NO_x burners can achieve remarkably low levels of NO_x emissions, on the order of 10 ppm (Figure 4.5).

4.15.2 THERMAL NO_x

The *thermal NO_x* mechanism comprises several steps, but can be reduced for discussion purposes, to two main ones:



Equations 4.8 and 4.9 give *elemental* steps and are shown by an equals sign (=). An elemental step represents the exact atomic and molecular entities involved in an actual product-forming collision. Therefore, according to Equation 4.8, in a favorable collision, a nitrogen atom collides with an oxygen molecule to form a nitric oxide molecule and an oxygen atom. In Equation 4.9, the oxygen atom collides with a nitrogen molecule to produce another molecule of nitric oxide

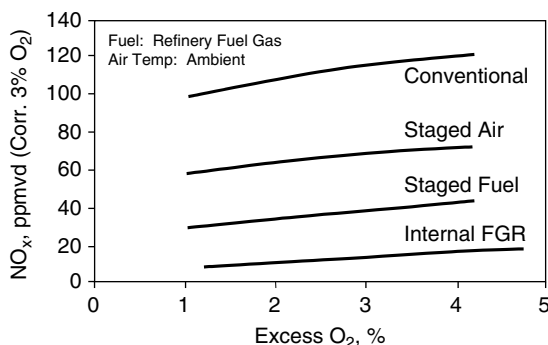


FIGURE 4.5 Effect of burner model on NO_x .

and a nitrogen atom, continuing the chain represented in Equation 4.8. The net result (Equation 4.10) is that nitrogen and oxygen generate nitric oxide (NO).

NOx in combustion generally refers to NO or NO₂ (nitrogen dioxide), although nitrogen can form other molecular species (e.g., N₂O, N₂O₃). However, only NO and NO₂ are regulated or formed in any quantities of concern.

High temperatures are required to generate the atomic species in Equations 4.8 and 4.9. Industrial flames can achieve such temperatures. Oxygen molecules comprise a double bond (O=O) and molecular nitrogen comprises a triple bond (N≡N). Therefore, the oxygen double bond is the easiest to rupture (Equation 4.8). Owing to the difficulty of rupturing the N≡N triple bond, Equation 4.9 is the *rate-limiting step* and paces the reaction. If we presume that atomic oxygen is in equilibrium with its molecular counterpart, we can write a rate law governing nitric oxygen production. Details of the derivation are given in other texts.¹

$$[\text{NO}] = A[\text{N}_2] \int e^{\frac{b}{T}} \sqrt{[\text{O}_2]} d\theta \quad (4.11)$$

where the square brackets [] denote volume concentrations of the enclosed species, A and b are constants, T is the absolute temperature, and θ is the time under those conditions.

Unfortunately, one cannot integrate Equation 4.11 because one does not have sufficient information regarding the oxygen-temperature history within the flame. However, Equation 4.11 is useful as a heuristic for pointing out the main features of thermal NOx formation.

First, temperature is an exponent indicating that NOx formation is very sensitive to temperature. Hot spots in the flame contribute significantly to NOx formation. Second, high oxygen concentration inflates NOx. The relation is square root proportional within the integral. However, upon integration, NOx would be related to oxygen concentration raised to a higher power. Studies² show that NOx is approximately proportional to oxygen concentration. Nitrogen varies little over the course of combustion and there is no convenient way to reduce nitrogen concentration. Therefore, it can be regarded as approximately constant. Hence, it is shown outside the integral.

Equation 4.11 suggests the following NOx reduction strategies:

1. Reduce peak flame temperatures.
2. Reduce oxygen concentration.
3. Reduce the time of high-temperature combustion in the vicinity of oxygen.

4.15.3 FUEL-BOUND NOx

When nitrogen is a part of the fuel molecule, it can form NOx. It is important to emphasize that the nitrogen must be part of the fuel molecule. Diluting natural or refinery gas with molecular nitrogen cannot contribute to the fuel-bound mechanism. Indeed, the addition of diluents such as nitrogen to the fuel stream will reduce NOx from both the thermal and fuel-bound mechanisms as it reduces the concentrations of the active species and the flame temperature.

The first step in forming NOx from the fuel-bound mechanism is a rapid pyrolysis of the parent molecule into cyano intermediates:



These intermediates are oxidized with oxygen to form nitric oxide:



We can write a rate law with the following assumptions:

1. The oxidation of the cyano intermediates is the rate-limiting step, involving, as it does, the rupture of a C≡N triple bond,
2. Cyano intermediates are proportional to the nitrogen concentration in the parent [N].

$$[\text{NO}] = k \int [\text{N}]^\alpha [\text{O}_2]^\beta d\theta \quad (4.14)$$

where k , α , and β are experimentally determined constants.

Equation 4.14 suggests that minimizing the oxygen concentration and reducing the nitrogen concentration in the fuel will reduce NOx from the fuel-bound mechanism. In localities having strict NOx limits, nitrogen is eliminated from the fuel supply, thereby eliminating all possibility of fuel-bound NOx. Low-NOx burners greatly reduce NOx from the thermal mechanism. However, another mechanism contributes to NOx production — the *prompt NOx* mechanism.

4.15.4 PROMPT NOx

Prompt NOx is similar to fuel-bound NOx, with the important exception that the nitrogen comes from the molecular nitrogen in the combustion air. Notwithstanding, cyano intermediates are still formed per Equation 4.15:



However, the cyano intermediates involve the rupture of a N≡N triple bond, as opposed to simple pyrolysis in the fuel-bound case. Therefore, the mechanism is not facile and is responsible for less than 20 ppm of NOx in most cases. The cyano intermediates are oxidized per Equation 4.13.

Presuming that Equation 4.15 represents a rate-limiting sequence, a possible rate law is:

$$[\text{NO}] = k[\text{N}_2] \int [\text{CH}_x] d\theta \quad (4.16)$$

It is not practical to limit nitrogen concentration in combustion air for most applications. Glass melting furnaces are an exception. In some cases, it can be economically feasible to justify combustion with pure oxygen. However, this is not the general case for boilers or process heaters. Therefore, the only strategy for reducing prompt NOx is to dilute the fuel species before combustion. This can be done in the burner itself by allowing the fuel jet to entrain combustion products in the furnace before reaching an ignition zone.

REFERENCE

1. I. Glassman, *Combustion*, Third Edition, Academic Press, 1996.