Chapter 14:

CHEMICAL REACTIONS

1

INTRODUCTION

In the preceding chapters we limited our consideration to non-reacting systems (systems whose chemical composition remains unchanged during a process).

This was the case even with mixing processes during which a homogeneous mixture is formed from two or more fluids without the occurrence of any chemical reactions.

In this chapter, we specifically deal with systems whose chemical composition changes during a process, that is, systems that involve *chemical reactions.*

When dealing with non-reacting systems, we need to consider only the *sensible internal energy* (associated with temperature and pressure changes) and the *latent internal energy* (associated with phase changes).

When dealing with reacting systems, however, we also need to consider the *chemical internal energy,* which is the energy associated with the destruction and formation of chemical bonds between the atoms.

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INTRODUCTION

In this chapter we focus on a particular type of chemical reaction, known as *combustion,* because of its importance in engineering.

But the reader should keep in mind, however, that the principles developed are equally applicable to other chemical reactions.

We start this chapter with a general discussion of fuels and combustion.

Then we apply the mass and energy balances to reacting systems.

In this regard we discuss the adiabatic flame temperature, which is the highest temperature a reacting mixture can attain.

Finally, we examine the second-law aspects of chemical reactions.

FUELS AND COMBUSTION

Any material that can be burned to release thermal energy is called a **fuel.**

Most familiar fuels consist primarily of hydrogen and carbon.

They are called **hydrocarbon fuels** and are denoted by the general formula C_nH_m.

Hydrocarbon fuels exist in all phases, some examples being coal, gasoline, and natural gas.

The main constituent of coal is carbon.

Coal also contains varying amounts of oxygen, hydrogen, nitrogen, sulfur, moisture, and ash.

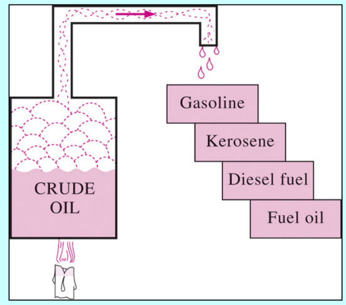
It is difficult to give an exact mass analysis for coal since its composition varies considerably from one geographical area to the next and even within the same geographical location.

FUELS AND COMBUSTION

Most liquid hydrocarbon fuels are a mixture of numerous hydrocarbons and are obtained from crude oil by distillation (see Figure).

The most volatile (unstable) hydrocarbons vaporize first, forming what we know as gasoline.

The less volatile fuels obtained during distillation are kerosene, diesel fuel, and fuel oil.



The composition of a particular fuel depends on the source of the crude oil as well as on the refinery.

Although liquid hydrocarbon fuels are mixtures of many different hydrocarbons, they are usually considered to be a single hydrocarbon for convenience.

For example, gasoline is treated as **octane,** C_8H_{18}, and the diesel fuel as **dodecane,** $C_{12}H_{26}$. Another common liquid hydrocarbon fuel is **methyl alcohol,** CH_3OH, which is also called *methanol* and is used in some gasoline blends. 5

FUELS AND COMBUSTION

The gaseous hydrocarbon fuel natural gas, which is a mixture of methane and smaller amounts of other gases, is often treated as **methane,** CH_4, for simplicity.

Natural gas is produced from gas wells or oil wells rich in natural gas.

It is composed mainly of methane, but it also contains small amounts of ethane, propane, hydrogen, helium, carbon dioxide, nitrogen, hydrogen sulfate, and water vapor.

Ethanol is obtained from corn, grains, and organic waste.

Methonal is produced mostly from natural gas, but it can also be obtained from coal and biomass.

Both alcohols are commonly used as additives in oxygenated gasoline and reformulated fuels to reduce air pollution.

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FUELS AND COMBUSTION

A chemical reaction during which a fuel is oxidized and a large quantity of energy is released is called **combustion**.

The oxidizer most often used in combustion processes is air, for obvious reasons—it is free and readily available.

Pure oxygen O_2 is used as an oxidizer only in some specialized applications, such as cutting and welding, where air cannot be used.

On a mole or a volume basis, dry air is composed of 20.9 percent oxygen, 78.1 percent nitrogen, 0.9 percent argon, and small amounts of carbon dioxide, helium, neon, and hydrogen.

In the analysis of combustion processes, the argon in the air is treated as nitrogen, and the gases that exist in trace (small) amounts are disregarded.

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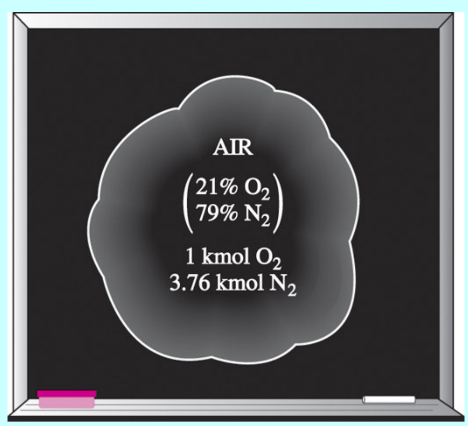
FUELS AND COMBUSTION

Then dry air can be approximated as 21 percent oxygen and 79 percent nitrogen by mole numbers.

Therefore, each mole of oxygen entering a combustion chamber is accompanied by 0.79/0.21 = 3.76 mol of nitrogen (see Figure).



$$1 \text{ kmol } O_2 + 3.76 \text{ kmol } N_2 = 4.76 \text{ kmol air}$$

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FUELS AND COMBUSTION

During combustion, nitrogen behaves as an inert gas and does not react with other elements, other than forming a very small amount of nitric oxides.

However, even then the presence of nitrogen greatly affects the outcome of a combustion process since nitrogen usually enters a combustion chamber in large quantities at low temperatures and exits at considerably higher temperatures, absorbing a large proportion of the chemical energy released during combustion.

Throughout this chapter, nitrogen is assumed to remain perfectly inert.

Keep in mind, however, that at very high temperatures, such as those encountered in internal combustion engines, a small fraction of nitrogen reacts with oxygen, forming hazardous gases such as nitric oxide.

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FUELS AND COMBUSTION

Air that enters a combustion chamber normally contains some water vapor (or moisture), which also deserves consideration.

For most combustion processes, the moisture in the air and the H_2O that forms during combustion can also be treated as an inert gas, like nitrogen.

At very high temperatures, however, some water vapor dissociates (separate) into H_2 and O_2 as well as into H, O, and OH.

When the combustion gases are cooled below the dew-point temperature of the water vapor, some moisture condenses.

It is important to be able to predict the dew-point temperature since the water droplets often combine with the sulfur dioxide that may be present in the combustion gases, forming sulfuric acid, which is highly corrosive.

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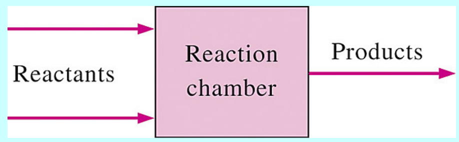
FUELS AND COMBUSTION

During a combustion process, the components that exist before the reaction are called **reactants** and the components that exist after the reaction are called **products** (see Figure).

Consider, for example, the combustion of 1 kmol of carbon with 1 kmol of pure oxygen, forming carbon dioxide,

$$C + O_2 \rightarrow CO_2$$



Here C and O_2 are the reactants since they exist before combustion, and CO_2 is the product since it exists after combustion.

Note that a reactant does not have to react chemically in the combustion chamber.

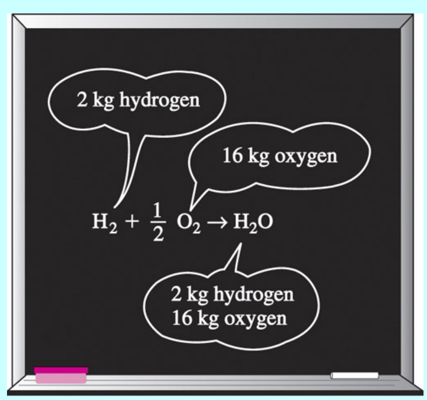
For example, if carbon is burned with air instead of pure oxygen, both sides of the combustion equation will include N_2.
That is, the N_2 will appear both as a reactant and as a product.

FUELS AND COMBUSTION

As you may recall from your chemistry courses, chemical equations are balanced on the basis of the **conservation of mass principle** (or the **mass balance**), which can be stated as follows:

The total mass of each element is conserved during a chemical reaction

That is, the total mass of each element on the right-hand side of the reaction equation (the products) must be equal to the total mass of that element on the left-hand side (the reactants) even though the elements exist in different chemical compounds in the reactants and products.



Also, the total number of atoms of each element is conserved during a chemical reaction since the total number of atoms is equal to the total mass of the element divided by its atomic mass.

FUELS AND COMBUSTION

For example, both sides of this Equation contain 12 kg of carbon and 32 kg of oxygen, even though the carbon and the oxygen exist as elements in the reactants and as a compound in the product.

$$C + O_2 \rightarrow CO_2$$

Also, the total mass of reactants is equal to the total mass of products, each being 44 kg.

However, notice that the total mole number of the reactants (2 kmol) is not equal to the total mole number of the products (1 kmol).

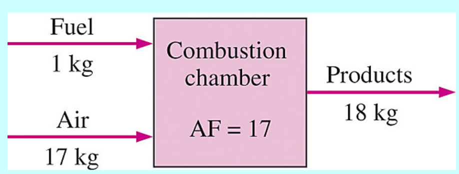
That is, *the total number of moles is not conserved during a chemical reaction.*

FUELS AND COMBUSTION

A frequently used quantity in the analysis of combustion processes to quantify the amounts of fuel and air is the **air–fuel ratio** AF.

It is usually expressed on a mass basis and is defined as *the ratio of the mass of air to the mass of fuel* for a combustion process (see Figure). That is,

$$AF = \frac{m_{air}}{m_{fuel}}$$



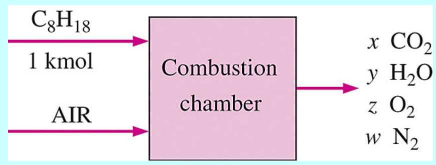
The mass m of a substance is related to the number of moles N through the relation $m = NM$, where M is the molar mass.

The air–fuel ratio can also be expressed on a mole basis as the ratio of the mole numbers of air to the mole numbers of fuel. But we will use the former definition.

The reciprocal of air–fuel ratio is called the **fuel–air ratio.**

EXAMPLE 14–1
Balancing the Combustion Equation

- One kmol of octane (C_8H_{18}) is burned with air that contains 20 kmol of O_2, s shown. Assuming the products contain only CO_2, H_2O, O_2, and N_2, determine the mole number of each gas in the products and the air–fuel ratio for this combustion process.



$$C_8H_{18} + 20(O_2 + 3.76N_2) \rightarrow xCO_2 + yH_2O + zO_2 + wN_2$$

C: $8 = x \rightarrow x = \mathbf{8}$

H: $18 = 2y \rightarrow y = \mathbf{9}$

O: $20 \times 2 = 2x + y + 2z \rightarrow z = \mathbf{7.5}$

N_2: $(20)(3.76) = w \rightarrow w = \mathbf{75.2}$

$$AF = \frac{m_{air}}{m_{fuel}} = \frac{(NM)_{air}}{(NM)_C + (NM)_{H_2}}$$

$$= \frac{(20 \times 4.76 \text{ kmol})(29 \text{ kg/kmol})}{(8 \text{ kmol})(12 \text{ kg/kmol}) + (9 \text{ kmol})(2 \text{ kg/kmol})}$$

$$= \mathbf{24.2 \text{ kg air/kg fuel}}$$

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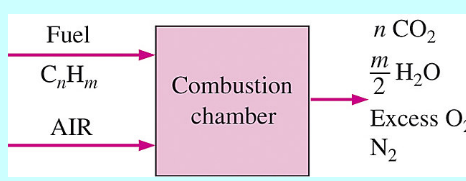
THEORETICAL AND ACTUAL COMBUSTION PROCESSES

It is often instructive (useful) to study the combustion of a fuel by assuming that the combustion is complete.

A combustion process is **complete** if all the carbon in the fuel burns to CO_2, all the hydrogen burns to H_2O, and all the sulfur (if any) burns to SO_2.

That is, all the combustible components of a fuel are burned to completion during a complete combustion process (see Figure).

Conversely, the combustion process is **incomplete** if the combustion products contain any unburned fuel or components such as C, H_2, CO, or OH.



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THEORETICAL AND ACTUAL COMBUSTION PROCESSES

Insufficient oxygen is an obvious reason for incomplete combustion, but it is not the only one.

Incomplete combustion occurs even when more oxygen is present in the combustion chamber than is needed for complete combustion.

This may be attributed to insufficient mixing in the combustion chamber during the limited time that the fuel and the oxygen are in contact.

Another cause of incomplete combustion is *dissociation,* which becomes important at high temperatures.

Oxygen has a much greater tendency to combine with hydrogen than it does with carbon. Therefore, the hydrogen in the fuel normally burns to completion, forming H_2O.

Some of the carbon, however, ends up as CO or just as plain C particles (dirt) in the products.

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THEORETICAL AND ACTUAL COMBUSTION PROCESSES

The minimum amount of air needed for the complete combustion of a fuel is called the **stoichiometric** or **theoretical air.**
The theoretical air is also referred to as the *chemically correct amount of air,* or *100 percent theoretical air.*

Thus, when a fuel is completely burned with theoretical air, no uncombined oxygen is present in the product gases.

A combustion process with less than the theoretical air is clear to be incomplete. The ideal combustion process during which a fuel is burned completely with theoretical air is called the **stoichiometric** or **theoretical combustion** of that fuel.

For example, the theoretical combustion of methane is:

$$CH_4 + 2(O_2 + 3.76N_2) \rightarrow CO_2 + 2H_2O + 7.52N_2$$

Notice that the products of the theoretical combustion contain no unburned methane and no C, H2, CO, OH, or free O2.

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THEORETICAL AND ACTUAL COMBUSTION PROCESSES

In actual combustion processes, it is common practice to use more air than the stoichiometric amount to increase the chances of complete combustion .

The amount of air in excess of the stoichiometric amount is called **excess air.** The amount of excess air is usually expressed in terms of the theoretical air as **percent excess air** or **percent theoretical air.**

For example, 50 percent excess air is equivalent to 150 percent theoretical air, and 200 percent excess air is equivalent to 300 percent stoichiometric air.

Of course, the theoretical air can be expressed as 0 percent excess air or 100 percent theoretical air.

Amounts of air less than the stoichiometric amount are called **deficiency of air** and are often expressed as **percent deficiency of air.**

For example, 90 percent theoretical air is equivalent to 10 percent deficiency of air.

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THEORETICAL AND ACTUAL COMBUSTION PROCESSES

The amount of air used in combustion processes is also expressed in terms of the **equivalence ratio,** which is the ratio of the actual fuel–air ratio to the theoretical fuel–air ratio.

$$EQ_r = (FA)_a / (FA)_{th} = (AF)_{th} / (AF)_a$$

Predicting the composition of the products is relatively easy when the combustion process is assumed to be complete and the exact amounts of the fuel and air used are known.

All one needs to do in this case is simply apply the mass balance to each element that appears in the combustion equation, without needing to take any measurements.

Things are not so simple, however, when one is dealing with actual combustion processes.

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THEORETICAL AND ACTUAL COMBUSTION PROCESSES

For one thing, actual combustion processes are hardly ever complete, even in the presence of excess air.

Therefore, it is impossible to predict the composition of the products on the basis of the mass balance alone.

Then the only alternative we have is to measure the amount of each component in the products directly.

A commonly used device to analyze the composition of combustion gases is the **Orsat gas analyzer.**

In this device, a sample of the combustion gases is collected and cooled to room temperature and pressure, at which point its volume is measured.

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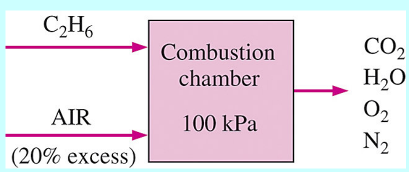
EXAMPLE 14–2
Dew-Point Temperature of Combustion Products

- Ethane (C_2H_6) is burned with 20 percent excess air during a combustion process, as shown. Assuming complete combustion and a total pressure of 100 kPa, determine:
- (*a*) the air–fuel ratio and
- (*b*) the dew-point temperature of the products.



$$C_2H_6 + 1.2a_{th}(O_2 + 3.76N_2) \rightarrow 2CO_2 + 3H_2O + 0.2a_{th}O_2 + (1.2 \times 3.76)a_{th}N_2$$

$$O_2: \quad 1.2a_{th} = 2 + 1.5 + 0.2a_{th} \rightarrow a_{th} = 3.5$$

$$C_2H_6 + 4.2(O_2 + 3.76N_2) \rightarrow 2CO_2 + 3H_2O + 0.7O_2 + 15.79N_2$$

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EXAMPLE 14–2
Dew-Point Temperature of Combustion Products

- Ethane (C_2H_6) is burned with 20 percent excess air during a combustion process, as shown. Assuming complete combustion and a total pressure of 100 kPa, determine:
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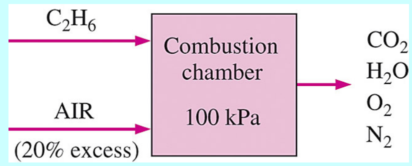


$$\mathrm{AF} = \frac{m_{\text{air}}}{m_{\text{fuel}}} = \frac{(4.2 \times 4.76\ \text{kmol})(29\ \text{kg/kmol})}{(2\ \text{kmol})(12\ \text{kg/kmol}) + (3\ \text{kmol})(2\ \text{kg/kmol})}$$

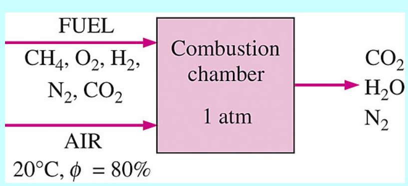
$$= \mathbf{19.3\ kg\ air/kg\ fuel}$$

$$P_v = \left(\frac{N_v}{N_{\text{prod}}}\right)(P_{\text{prod}}) = \left(\frac{3\ \text{kmol}}{21.49\ \text{kmol}}\right)(100\ \text{kPa}) = 13.96\ \text{kPa}$$

$$T_{\text{dp}} = T_{\text{sat @ 13.96 kPa}} = \mathbf{52.3°C} \qquad \text{(Table A–5)}$$

EXAMPLE 14–3
Combustion of a Gaseous Fuel with Moist Air

- A certain natural gas has the following volumetric analysis: 72 percent CH_4, 9 percent H_2, 14 percent N_2, 2 percent O_2, and 3 percent CO_2. This gas is now burned with the stoichiometric amount of air that enters the combustion chamber at 20°C, 1 atm, and 80 percent relative humidity, as shown in Figure. Assuming complete combustion and a total pressure of 1 atm, determine the dew-point temperature of the products.



$$\begin{aligned}
&\text{C:} && 0.72 + 0.03 = x && \rightarrow && x = 0.75\\
&\text{H:} && 0.72 \times 4 + 0.09 \times 2 = 2y && \rightarrow && y = 1.53\\
&\text{O}_2\text{:} && 0.02 + 0.03 + a_{\text{th}} = x + \frac{y}{2} && \rightarrow && a_{\text{th}} = 1.465\\
&\text{N}_2\text{:} && 0.14 + 3.76a_{\text{th}} = z && \rightarrow && z = 5.648
\end{aligned}$$

$$\overbrace{(0.72CH_4 + 0.09H_2 + 0.14N_2 + 0.02O_2 + 0.03CO_2)}^{\text{fuel}} + \overbrace{a_{\text{th}}(O_2 + 3.76N_2)}^{\text{dry air}} \rightarrow xCO_2 + yH_2O + zN_2$$

EXAMPLE 14–3
Combustion of a Gaseous Fuel with Moist Air

- determine the dew-point temperature of the products.

$$P_{v,\text{air}} = \phi_{\text{air}} P_{\text{sat @ 20°C}} = (0.80)(2.3392 \text{ kPa}) = 1.871 \text{ kPa}$$

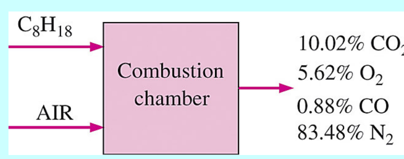
$$N_{v,\text{air}} = \left(\frac{P_{v,\text{air}}}{P_{\text{total}}}\right) N_{\text{total}} = \left(\frac{1.871 \text{ kPa}}{101.325 \text{ kPa}}\right)(6.97 + N_{v,\text{air}}) \qquad N_{v,\text{air}} = 0.131 \text{ kmol}$$

$$\overbrace{(0.72CH_4 + 0.09H_2 + 0.14N_2 + 0.02O_2 + 0.03CO_2)}^{\text{fuel}} + \overbrace{1.465(O_2 + 3.76N_2)}^{\text{dry air}}$$
$$+ \overbrace{0.131H_2O}^{\text{moisture}} \rightarrow 0.75CO_2 + \overbrace{1.661H_2O}^{\text{includes moisture}} + 5.648N_2$$

$$P_{v,\text{prod}} = \left(\frac{N_{v,\text{prod}}}{N_{\text{prod}}}\right) P_{\text{prod}} = \left(\frac{1.661 \text{ kmol}}{8.059 \text{ kmol}}\right)(101.325 \text{ kPa}) = 20.88 \text{ kPa}$$

EXAMPLE 14–4
Reverse Combustion Analysis

- Octane (C_8H_{18}) is burned with dry air. The volumetric analysis of the products on a dry basis is CO_2: 10.02 percent O_2: 5.62 percent CO: 0.88 percent N_2: 83.48 percent Determine:
- (*a*) the air–fuel ratio,
- (*b*) the percentage of theoretical air used, and
- (*c*) the amount of H_2O that condenses as the products are cooled to 25°C at 100 kPa.



N_2:	$3.76a = 83.48$	→	$a = 22.20$
C:	$8x = 10.02 + 0.88$	→	$x = 1.36$
H:	$18x = 2b$	→	$b = 12.24$
O_2:	$a = 10.02 + 0.44 + 5.62 + \frac{b}{2}$	→	$22.20 = 22.20$

$$xC_8H_{18} + a(O_2 + 3.76N_2) \rightarrow 10.02CO_2 + 0.88CO + 5.62O_2 + 83.48N_2 + bH_2O$$

EXAMPLE 14–4
Reverse Combustion Analysis

- Determine:
- (*a*) the air–fuel ratio,
- (*b*) the percentage of theoretical air used, and
- (*c*) the amount of H_2O that condenses as the products are cooled to 25°C at 100 kPa.

$$1.36C_8H_{18} + 22.2(O_2 + 3.76N_2) \rightarrow 10.02CO_2 + 0.88CO + 5.62O_2 + 83.48N_2 + 12.24H_2O$$

$$C_8H_{18} + 16.32(O_2 + 3.76N_2) \rightarrow 7.37CO_2 + 0.65CO + 4.13O_2 + 61.38N_2 + 9H_2O$$

$$AF = \frac{m_{air}}{m_{fuel}} = \frac{(16.32 \times 4.76 \text{ kmol})(29 \text{ kg/kmol})}{(8 \text{ kmol})(12 \text{ kg/kmol}) + (9 \text{ kmol})(2 \text{ kg/kmol})}$$

$$= \mathbf{19.76 \text{ kg air/kg fuel}}$$

EXAMPLE 14–4
Reverse Combustion Analysis

- Determine:
- (*a*) the air–fuel ratio,
- (*b*) the percentage of theoretical air used, and
- (*c*) the amount of H_2O that condenses as the products are cooled to 25°C at 100 kPa.

$$C_8H_{18} + a_{th}(O_2 + 3.76N_2) \rightarrow 8CO_2 + 9H_2O + 3.76a_{th}N_2$$

$$O_2: \quad a_{th} = 8 + 4.5 \rightarrow a_{th} = 12.5$$

$$\text{Percentage of theoretical air} = \frac{m_{air,act}}{m_{air,th}} = \frac{N_{air,act}}{N_{air,th}} = \frac{(16.32)(4.76) \text{ kmol}}{(12.50)(4.76) \text{ kmol}} = \mathbf{131\%}$$

$$\frac{N_v}{N_{prod,gas}} = \frac{P_v}{P_{prod}}$$

$$\frac{9 - N_w}{82.53 - N_w} = \frac{3.1698 \text{ kPa}}{100 \text{ kPa}}$$

$$N_w = \mathbf{6.59 \text{ kmol}}$$