

# Chapter 3

## Emission / Emission Factors and Combustion

- Emission
- Emission factors
- Combustion
  - Combustion Chemistry
  - Calculation of Pollutants in Combustion Chemistry

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### Definition of Emission

- **Emission:**  
Amount of release of a specific pollutant from a specific source into the atmosphere in a unit time/area/source type

Figured as:

mass of pollutant / time

mass of pollutant / time.area

mass of pollutant / time.source

Examples:      kg SO<sub>2</sub>/hr  
                     Mtons CO/year  
                     gr PM/sec  
                     gr CO/vehicle.hr  
                     kg PM/km<sup>2</sup>.day

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# Definition of Emission Inventory

- **Emission Inventory:**

A data base involving

- Pollutant types,
- Pollutant sources

and

-Emission amounts in terms of :

- time

- area

Needed to:

- characterize present air quality in a region,
- monitor trends of change in air quality
- decide for future regulations for better air quality

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# Examples of Emission Inventories

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## ABD'de Endüstriyel Proseslerden Kaynaklanan Partikül Emisyonları (1968)

Endüstri	Emisyon, ton/yıl
Demir-Çelik	1 910 000
Demir döküm	170 000
Demir-dışı metaller	90 000
Çimento	870 000
Fosfat Kayası	205 000
Kireç	450 000
Asfalt	540 000
Petrol Rafinerileri	100 000
Diğer Kimya Sanayi	90 000
Kağıt Sanayi	720 000
Un ve Yem fabrikaları	320 000

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## İstanbul'da 1990 yılındaki kirletici emisyonlarının dağılımı

Kirletici	Toplam Emisyon (%)	Sabit Kaynaklar (%)	Taşıtlar (%)
PM	48.1	47.5	0.65
SO <sub>2</sub>	29.4	29.1	0.26
CO	16.3	9.9	6.64
NO <sub>x</sub>	3.1	1.6	1.44
HC	3.0	1.6	1.40
<b>TOPLAM</b>	100	90	~ 10

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## 3.2. Combustion

- A Chemical oxidation reaction between a type of FUEL and OXIDANT producing combustion products and HEAT

Fuel + Oxidant (O<sub>2</sub>) → Combustion gases  
+ particles  
+ HEAT

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## 3.2. Combustion

- Combustion reactions are involved in
  - thermal power plants
  - residential heating needs
  - motor vehicles
  - hazardous waste incineration plants
  - domestic waste incineration plants.
  - and other systems involving fossil fuel combustion

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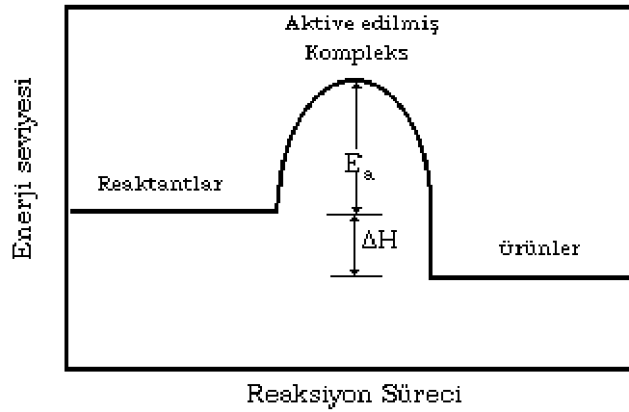
## 3.2. Combustion

- 3 Factors are important for combustion reactions to start:
  - temperature
  - time
  - turbulence

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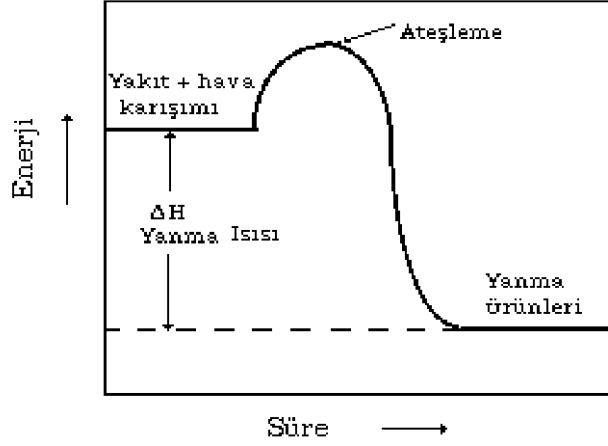
### General change in energy level of exothermic reactions



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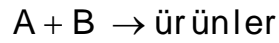
## Change in energy level of combustion reactions



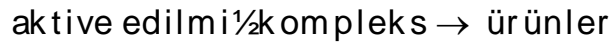
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## Combustion Mechanism



reaksiyonunun mekanizması:



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## 3.2. Combustion

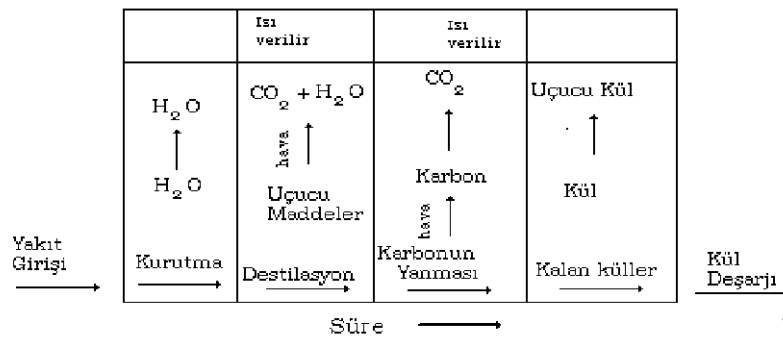
- Combustion mechanism and duration are dependent upon fuel type
- Gaseous fuels:  
Relatively simple reaction between fuel and oxidant
- Liquid Fuels: A simple step for conversion of liquid fuel into gaseous form and combustion reactions

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## 3.2. Combustion

- For Solid fuels: a chain of physical and chemical changes occur before combustion reactions:



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## 3.2. Combustion

- **Fundamental Components of Combustion Reactions**

**Fuel:** All fossil fuels containing C-C and H-C bearing high energy

**Oxidant:** Oxygen for breaking C-C and H-C bonds

**Diluent:** Nitrogen for carrying the oxidant and heat.  
Does not have any role in combustion.

**Also** causes unwanted NO<sub>x</sub> formation reactions due to thermally favoured conditions

**Excess Air:** For better mixing conditions of fuel and oxidant

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## 3.2. Combustion

- **Combustion Products**

- **CO<sub>2</sub>** and **H<sub>2</sub>O** resulting from the breakage of C-C and H-C bonds

- Incomplete combustion products: CO, unburned HCs,

- Impurity reactions: SO<sub>2</sub>, HCl, Dioxins/Furans, PCBs,

- NO<sub>x</sub>'s resulting from thermally favoured conditions

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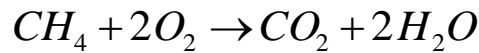
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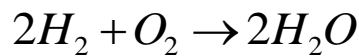
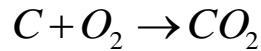
## 3.2. Combustion

- **Ideal Combustion Reactions**

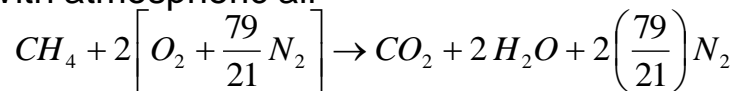
- With pure oxygen



same with the pair of rxns



- With atmospheric air

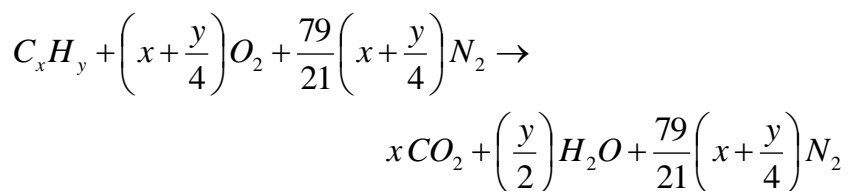


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## 3.2. Combustion

- **Generalized Ideal Hydrocarbon Combustion Reaction**



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## 3.2. Combustion

- **Excess Air Combustion**

- Excess air is introduced in order to guarantee complete combustion

$$\text{Excess air (\%)} = \frac{\text{Excess air}}{\text{Theoretical air}} (100)$$

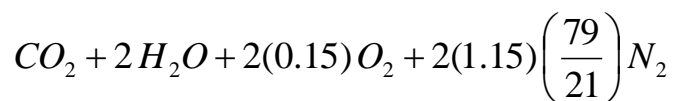
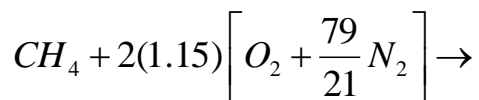
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## 3.2. Combustion

- **Excess Air Combustion**

- **Example:** 15% excess air combustion

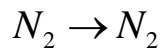
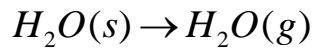
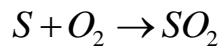
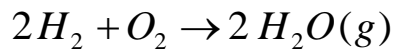
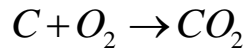


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## 3.2. Combustion

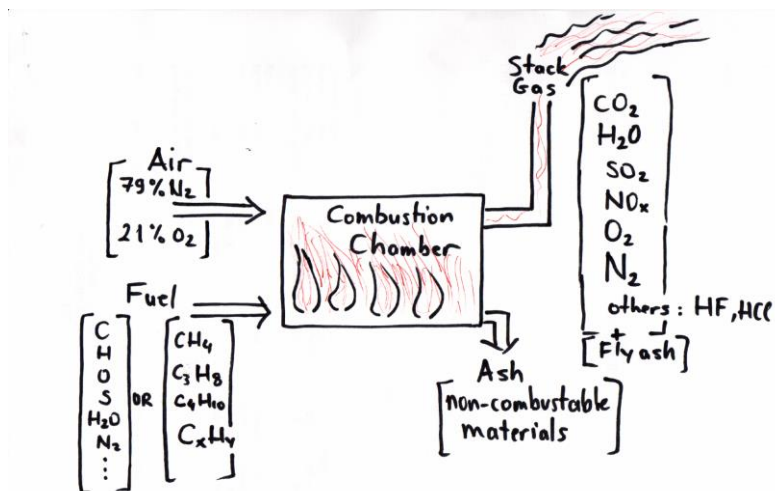
- Fundamental Combustion Reactions



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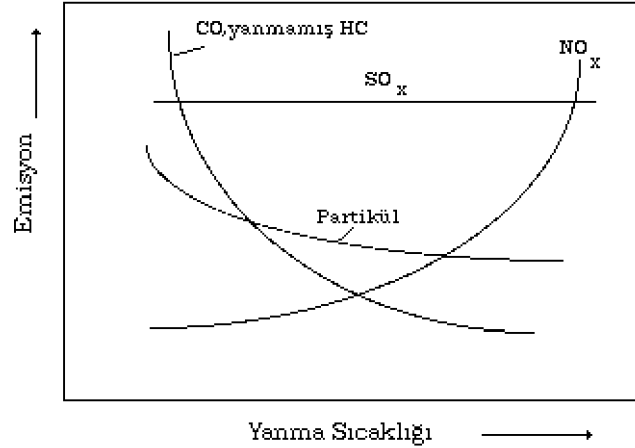
## 3.2. Combustion



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## 3.2. Combustion



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## 3.2. Combustion

- **Aim:** To determine the composition of stack gases (concentrations of pollutants) and mass emission rates of pollutants
  - By combustion rxn calculations
  - or
  - By emission factors calculations
  - or
  - By stack measurements (most reliable way)

### Needed info:

- Analysis of fuel:
  - composition analysis for gaseous fuels
  - elemental analysis for liquid and solid fuels
- Fuel consumption rate in the combustion system
- Emission factors
- Stack gas velocity and stack geometry
- Temp, pressure, humidity etc

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## 3.2. Combustion

- **How to express the amounts of pollutants in stack gas?**
- **Volume concentration**  
valid only for gaseous pollutants

%, ppm, ppb, ppt

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## 3.2. Combustion

- **Mass concentration**  
valid for both gaseous and particulate pollutants

$$\left(\frac{\mu\text{g}}{\text{m}^3}\right) = (\text{ppm}) 10^3 \frac{P M}{R T} \quad \left(\frac{\text{mg}}{\text{m}^3}\right) = (\text{ppm}) \frac{P M}{R T}$$

P: pollutant gas pressure (atm)

M: mol. weight of poll. gas (gr/gmol)

R: ideal gas constant

(0.082 l·atm/gmol·K, or 0.082 m<sup>3</sup>·atm/kmol·K)

T: gas temp. (K)

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## 3.2. Combustion

- **Example 1:**
- A thermal power plant with a rated capacity of 400MW burns pulverized coal. Combustion system has a thermal efficiency of 60% and operates with 30% excess air. The calorific value of coal is 8500 kcal/kg and has an elemental analysis given in the table below.
  - Calculate the total volumetric flowrate of stack gas and its pollutant composition (both as concentrations and mass flow rates)

Element	Mass percent
Carbon (C)	42.0
Hydrogen (H)	2.8
Sulphur (S)	0.7
Oxygen (O)	12.4
Nitrogen (N)	0.7
Ash -----	6.9
Water (H <sub>2</sub> O)	34.8

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## 3.2. Combustion

- **Solution:**
- **Starting point:**
- take 100 unit amount of fuel.
  - Unit amount is
    - mol or volume for gaseous fuels  
(100 mols / kmols or liters / m<sup>3</sup>)
    - mass for liquid or solid fuels  
(100 kg)
- Calculate molar amounts of components in combustion reactions using their molar weights and unit amounts

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## 3.2. Combustion

Taking 100 kg of coal as the basis

Element	Weight percent	Mol weight (kg/kmol)	Mol amounts (kmol)
carbon	42.0	12	3.53 as C
Hydrogen	2.8	2	1.40 as H <sub>2</sub>
Sulphur	0.7	32	0.022 as S
Oxygen	12.4	32	0.39 as O <sub>2</sub>
Nitrogen	0.7	28	0.025 as N <sub>2</sub>
water	34.8	18	1.93 as H <sub>2</sub> O
Ash	6.2	-	- -

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## Combustion Reactions

Combustion Reactions	Reactants	Products
$C + O_2 \rightarrow CO_2$	3.53 kmol C 3.53 kmol O <sub>2</sub>	3.53 kmol CO <sub>2</sub>
$2H_2 + O_2 \rightarrow 2H_2O(g)$	1.4 kmol H <sub>2</sub> 0.7 kmol O <sub>2</sub>	1.4 kmol H <sub>2</sub> O <sup>+</sup>
$H_2O(s) \rightarrow H_2O(g)$	1.93 kmol H <sub>2</sub> O	1.93 kmol H <sub>2</sub> O <sup>+</sup>
$S + O_2 \rightarrow SO_2$	0.022 kmol S 0.022 kmol O <sub>2</sub>	0.022 kmol SO <sub>2</sub>
$N_2 \rightarrow N_2$	0.025 kmol N <sub>2</sub>	0.025 kmol N <sub>2</sub> <sup>*</sup>

†: Havadan gelen nem hariçtir.

\*: sadece yakıttaki azotu ifade etmektedir

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## 3.2. Combustion

- Total stoichiometric amount of oxygen needed for those rxns:  
 $3.53 + 0.7 + 0.022 = 4.25$  kmols (for 100 kg fuel)
- Combustion system operates at 30% excess air. Therefore total amount of oxygen needed for combustion:  
 $4.25 \times 1.30 = 5.53$  kmols oxygen (for 100 kg fuel).
- Amount of oxygen already available in fuel is 0.39 kmol. This will also be used in rxns. Therefore amount of oxygen needed from the atmosphere:  
 $5.53 - 0.39 = 5.14$  kmols (for 100 kg fuel)

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## 3.2. Combustion

- Amount of nitrogen coming together with oxygen:  
 $5.14 \times (79/21) = 19.34$  kmols
- Total amount of air fed to the combustion system:  
 $19.34 + 5.14 = 24.48$  kmols for (100kgs of fuel)
- Excess oxygen leaving the combustion:  
 $5.53 - 4.25 = 1.28$  kmol
- Assume air contains 1.1 % humidity (mol H<sub>2</sub>O/100 mol dry air)  
 $24.48$  kmol dry air  $\times$  (1.1 mol H<sub>2</sub>O/100 mol dry air)  
 $= 0.27$  kmol H<sub>2</sub>O.

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## 3.2. Combustion

Stack gas component	amount (kmol)	Source
CO <sub>2</sub>	3.53	From comb. Rxn.
SO <sub>2</sub>	0.022	From comb. Rxn
N <sub>2</sub>	0.025	From fuel
N <sub>2</sub>	19.34	From air
H <sub>2</sub> O	1.4	From comb. Rxn
H <sub>2</sub> O	1.93	From fuel
H <sub>2</sub> O	0.27	From air
O <sub>2</sub>	1.28	From air (excess oxygen)
Dry base total	24.20	kmols stack gas /100 kg fuel
Wet base total	27.80	kmols stack gas /100 kg fuel

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## 3.2. Combustion

- Legislation for Industrial Pollution Control requires DRY AIR at Standard Conditions:
  - Standard Conditions: 0°C and 1 atm
- Volume of standard air is called Normal volume:
  - Nm<sup>3</sup>

At standard conditions :

1 kmol of gas has 22.4 Nm<sup>3</sup> volume

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## 3.2. Combustion

- **Volume of stack gas (at STP )**

- Dry basis

$$24.20 \text{ kmol} \times (22.4 \text{ m}^3 / 1 \text{ kmol}) = 542 \text{ Nm}^3 / 100 \text{ kg fuel}$$

- Wet basis

$$27.80 \text{ kmol} \times (22.4 \text{ m}^3 / 1 \text{ kmol}) = 623 \text{ Nm}^3 / 100 \text{ kg fuel}$$

Now we have all for concentration calculations

→→→→→

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## 3.2. Combustion

- **Concentration of SO<sub>2</sub> in stack gas:**

- **As % by volume SO<sub>2</sub> :**

$$\begin{aligned} & (0.022 \text{ kmol SO}_2 / 24.20 \text{ kmol dry stack gas}) \times 100 \\ & = \% \mathbf{0.0909 \text{ SO}_2} \end{aligned}$$

**Remember: molar ratios equal volume ratios**

- **As ppm SO<sub>2</sub>:**

$$\frac{0.022 \text{ kmol SO}_2 \times 10^6}{24.20 \text{ kmol kurubaca gazi}} = 909 \text{ ppm SO}_2$$

or

- = % SO<sub>2</sub> × 10 000 = 0.0909 × 10 000 = **909 ppm SO<sub>2</sub>**

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## 3.2. Combustion

- As  $\text{mg}/\text{Nm}^3$   $\text{SO}_2$  concentration:

$$(\text{ppm}) \frac{P M}{R T}$$

$$(909 \text{ ppm}) \frac{(1 \text{ atm}) (64 \text{ kg} / \text{ kmol})}{(0.082 \text{ m}^3 \text{ atm} / \text{ kmol} \cdot \text{K}) (273 \text{ }^\circ \text{K})}$$

$$= 2599 \text{ mg}/\text{Nm}^3$$

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## 3.2. Combustion

- **Correction for reference oxygen level:**

- Oxygen level at stack gas:

$$= (1.28 / 24.20) \times 100 = \% 5.3 \text{ O}_2$$

- Correcting  $\text{SO}_2$  concn wrt 3% ref. oxygen

$$[\text{SO}_2]_{\text{ref}} = \frac{21 - [\text{O}_2]_{\text{ref}}}{21 - [\text{O}_2]_{\text{ölç}}} \cdot [\text{SO}_2]_{\text{ölç}}$$

$$\frac{21 - 3}{21 - 5.3} \cdot (2599)$$

$$= 2980 \text{ mg}/\text{Nm}^3$$

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## 3.2. Combustion

- **Calculation for Volumetric flowrate:**
- Need to know fuel consumption rate:

$$\begin{aligned} \text{Thermal Power: } (400 \text{ MW}) \times \frac{238.8 \text{ kcal/sec}}{1 \text{ MW}} \\ = 95\,520 \text{ kcal/sec} \end{aligned}$$

- Theoretical fuel consumption =  $\frac{95\,520 \text{ kcal/sec}}{8\,500 \text{ kcal/kg}}$   
  
**= 11.24 kg coal/sec**

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## 3.2. Combustion

- **Real fuel consumption rate**  
=  $11.24 / 0.60 = 18.73 \text{ kg coal/sec}$   
= 67.43 tons coal /hour

### **Volumetric flowrate of stack gas:**

For 67.43 tons/hr fuel

$$(67.43 \times 542) / 100 = \mathbf{365\,471 \text{ m}^3/\text{hr dry stack gas}}$$

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## 3.2. Combustion

- **Mass flowrate of pollutants:**
- SO<sub>2</sub> mass flowrate:  
= (2599 mg/Nm<sup>3</sup>) × (365 471 Nm<sup>3</sup>/hr)  
= **950 kg SO<sub>2</sub>/hr.**

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## 3.2. Combustion

- **Example 2:**  
A 300 MW thermal power plant burns natural gas which has 10 000 kcal/kg calorific value. Combustion chamber has 70% thermal efficiency and operates with % 20 excess air.  
Calculate the total volumetric flowrate of stack gas and its pollutants concentrations.

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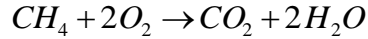
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• **Solution:**

Take 100 m<sup>3</sup> of fuel as the basis.

→ Assume NG is totally composed of methane

So the only combustion reaction is:



$$100 \text{ m}^3 CH_4 + 200 \text{ m}^3 O_2 \rightarrow 100 \text{ m}^3 CO_2 + 200 \text{ m}^3 H_2O$$

Total stoichiometric stack gas:

$$300 \text{ m}^3 (100 \text{ m}^3 CO_2 + 200 \text{ m}^3 H_2O)$$

$$\text{Amount of excess oxygen: } 200 \text{ m}^3 O_2 \times 0.20 = 40 \text{ m}^3 O_2$$

$$\text{Amount of nitrogen: } (200 \text{ m}^3 O_2 \times 1.20) \times (79/21) = 902.8 \text{ m}^3 N_2$$

$$\text{Amount of air feed: } 240 + 902.8 = 1142.8 \text{ m}^3 \text{ (DRY)}$$

→ Assume air contains %1 absolute humidity (0.01 mol H<sub>2</sub>O/mol dry air)

$$\text{Water vapor coming from air} = 0.01 \times 1142.8 = 11.4 \text{ m}^3 H_2O$$

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→ Stack gas constituents =	100 m <sup>3</sup> CO <sub>2</sub>	From combustion rxn
	+ 200 m <sup>3</sup> H <sub>2</sub> O	From combustion rxn
	+ 11.4 m <sup>3</sup> H <sub>2</sub> O	Air humidity
	+ 40 m <sup>3</sup> O <sub>2</sub>	Excess oxygen
	+ 902.8 m <sup>3</sup> N <sub>2</sub>	Total nitrogen from air
TOTAL Volume =	1254.2 m <sup>3</sup>	: wet basis
	= 1042.8 m <sup>3</sup>	: dry basis

All for 100m<sup>3</sup> of fuel

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$$\begin{aligned} \text{Real fuel consumption} &= \frac{(300 \text{ MW}) \cdot \left( 238.8 \frac{\text{kcal/sec}}{\text{MW}} \right)}{\left( 10000 \frac{\text{kcal}}{\text{kg}} \right) \cdot \left( 0.65 \frac{\text{kg}}{\text{m}^3} \right) \cdot (0.7)} = 15.75 \text{ m}^3/\text{sec} \\ &= 56\,682 \text{ m}^3/\text{hr} \end{aligned}$$

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$$\begin{aligned} \text{Real stack gas} \\ \text{volumetric flowrate} &= 1042.8 \frac{\text{m}^3 \text{ stack gas}}{100 \text{ m}^3 \text{ NG}} \times (56\,682 \text{ m}^3/\text{hr}) \\ &= 591\,082 \text{ m}^3/\text{hr} \end{aligned}$$

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- →Is the solution ok?
- Then
- →What pollutants exist in stackgas and in what amounts?
- →No answer via known combustion reactions....
- Then .....
- → what to do to determine pollutants in stack gas?

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### 3.3 Emission factors

- Factors representing the amount of pollutant releases from the combustion of a specific fuel or from a specific activity involving fuel combustion
- mass of pollutant / amount of fuel burned
- mass of pollutant / km travelled

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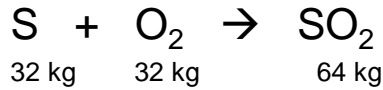
Yakıt Cinsi / Yakma türü	PM	SO <sub>x</sub>	CO	HC	NO <sub>x</sub>
<b>KÖMÜR</b>	<b>kg/ton</b>	<b>kg/ton</b>	<b>kg/ton</b>	<b>kg/ton</b>	<b>kg/ton</b>
<i>Linyit</i>					
Pulverize	3.2 A	13.6 S	0.5	<0.45	6.4
Siklon	2.7 A	13.6 S	0.5	<0.45	7.7
Spreader Stoker	3.2 A	13.6 S	0.5	<0.45	2.7
<i>Bitümlü Kömür</i>					
Pulverize					
- Genel	8 A	19 S	0.5	0.15	9
- Islak	6.5 A	19 S	0.5	0.15	15
- Kuru Taban	8.5 A	19 S	0.5	0.15	9
Siklon	1.0 A	19 S	0.5	0.15	27.5
Spreader Stoker	6.5 A	19 S	1	0.5	7.5
Elle Besleme	10	19 S	45	10	1.5
<b>FUEL-OIL</b>	<b>kg/ton</b>	<b>kg/ton</b>	<b>kg/ton</b>	<b>kg/ton</b>	<b>kg/ton</b>
Termik Santral	1.26	20.5 S	0.005	0.50	13.02
Sanayi Tesisi					
Ağır Fuel-oil	2.9	20.1 S	0.25	0.50	8.96
Hafif Fuel-oil	1.9	20.1 S	0.25	0.50	8.96
Ev ve Ticari İşletmeler	0.1	20.1 S	0.25	0.63	1.46
<b>DOĞALGAZ</b>	<b>g/m<sup>3</sup></b>	<b>g/m<sup>3</sup></b>	<b>g/m<sup>3</sup></b>	<b>g/m<sup>3</sup></b>	<b>g/m<sup>3</sup></b>
Termik Santral	0.24	0.01	0.272	0.016	11.1
Sanayi Tesisi	0.24	0.01	0.272	0.048	3.6
Ev ve Ticari İşletmeler	0.24	0.01	0.272	0.128	1.9
<b>BENZİN (kg/m<sup>3</sup>)</b>	1.4	1.1	275	24	14
<b>DIESEL (kg/m<sup>3</sup>)</b>	13.2	4.8	7.2	16.3	26.6

S: Yakıttaki Kükürt yüzdesi A: Kömürdeki kül yüzdesi

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## Relationship between combustion reactions and emission factors



$$\text{SO}_2 / \text{S} = 64 / 32 = 2$$

→1 kg S causes 2 kg SO<sub>2</sub> formation (if ideal rxn)

→If fuel contains 1% S (i.e. 1 kg S in 100 kg fuel)

→That means 10 kg S in 1000 kg of fuel

→Forming 20 kg SO<sub>2</sub>

→Therefore

**Emission Factor for SO<sub>2</sub> in coal: 20 S kg/ 1 ton fuel**

**S being the sulphur percent in coal**

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- **Emission Factor for SO<sub>x</sub> in coal:**
  - » **20 S kg / 1 ton fuel**
  - » **If less than this amount**
  - » **e.g. 13,6 S or 19 S**
  - » **Easily explicable with our background knowledge:**
  - » **→ Non ideal reaction conditions, therefore not all S reacts**
  
  - » **BUT**
  - » **If more than this amount**
  - » **e.g. 20.1 S or 20.5 S**
  - » **YOU EXPLAIN THIS !!!**

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- **Example 3:**

Calculate the SO<sub>2</sub> concentration in stack gas and its mass emission flowrate in Ex. 2 using emission factors.

Correct the concentration with respect to 3% oxygen level in stack gas if necessary

- **Solution:**

From emission factors table, we have 0.01g/m<sup>3</sup> emission factor for SO<sub>2</sub> in thermal power plants burning natural gas.

$$\text{SO}_2 \text{ mass flowrate} = \left( 56\,682 \frac{\text{m}^3 \text{ NG}}{\text{hr}} \right) \cdot \left( 0.01 \frac{\text{g SO}_2}{\text{m}^3 \text{ NG}} \right) = 566.8 \text{ g SO}_2/\text{saat}$$

$$\text{SO}_2 \text{ concn in dry stack gas} = \frac{566.8 \text{ g SO}_2 / \text{hr}}{591\,082 \text{ m}^3 / \text{hr}} = 0.959 \text{ mg SO}_2 / \text{m}^3$$

→ Do the reference O<sub>2</sub> correction for SO<sub>2</sub> by yourself

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