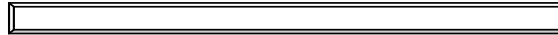


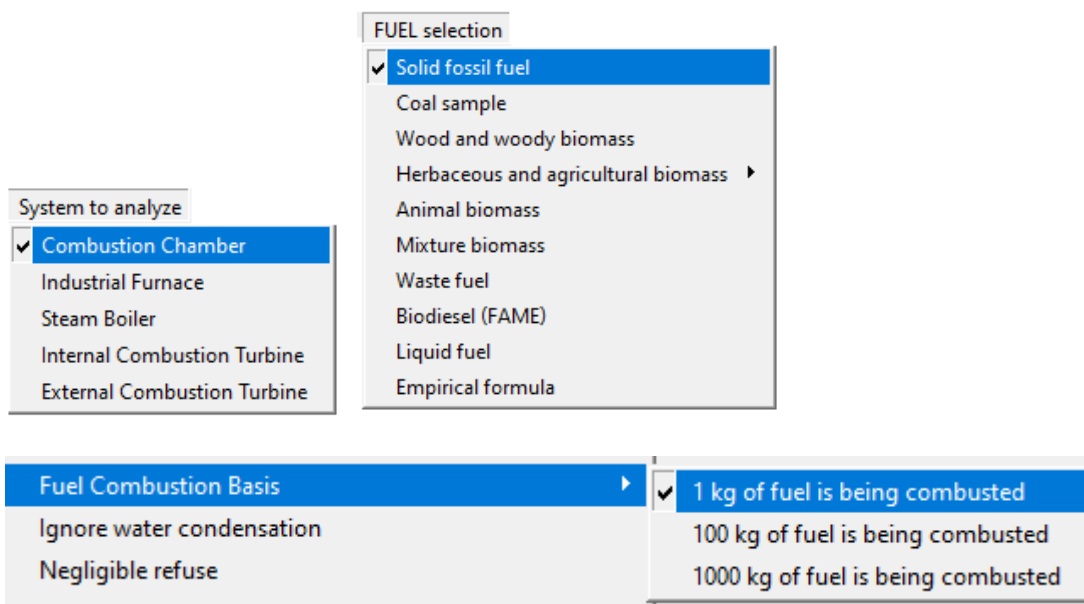
Exercise 1 (solid fossil fuel)

A fuel burns with a fuel defect ($\lambda = 0.9$). Determine the composition of the combustion products by assuming the water-gas reaction for a combustion product temperature of 2000 K. The reagents are at 298K and 1 atm. There is no oxygen present in the combustion products.

Solid fuel: C (60%), H₂ (10%), N₂ (10%), O₂ (15%) and S (5%)



Solution by means THERMOCombustion:



The screenshot shows the following menu selections in the ThermoCombustion software:

- System to analyze:**
 - ✓ Combustion Chamber
 - Industrial Furnace
 - Steam Boiler
 - Internal Combustion Turbine
 - External Combustion Turbine
- FUEL selection:**
 - ✓ Solid fossil fuel
 - Coal sample
 - Wood and woody biomass
 - Herbaceous and agricultural biomass ▶
 - Animal biomass
 - Mixture biomass
 - Waste fuel
 - Biodiesel (FAME)
 - Liquid fuel
 - Empirical formula
- Fuel Combustion Basis:**
 - ✓ 1 kg of fuel is being combusted
 - 100 kg of fuel is being combusted
 - 1000 kg of fuel is being combusted

Combustion, is defined as a chemical reaction during which the fuel combustible elements are rapidly oxidized and a large quantity of energy is released. From a thermodynamic perspective, combustion is analyzed globally in that it focuses neither on the mechanism of combustion, called kinetics of combustion, which is an extremely complex chemical phenomenon, nor on the intermediate products of combustion. Combustion is widely used for energy production both in industry and in household applications.

AIR COMPOSITION ? X

Normal conditions: STP: 0°C, 1atm (DIN 1343)

Molecular Weight (Dry air) kg / kmol

Only two components: N₂, O₂ 28.8507

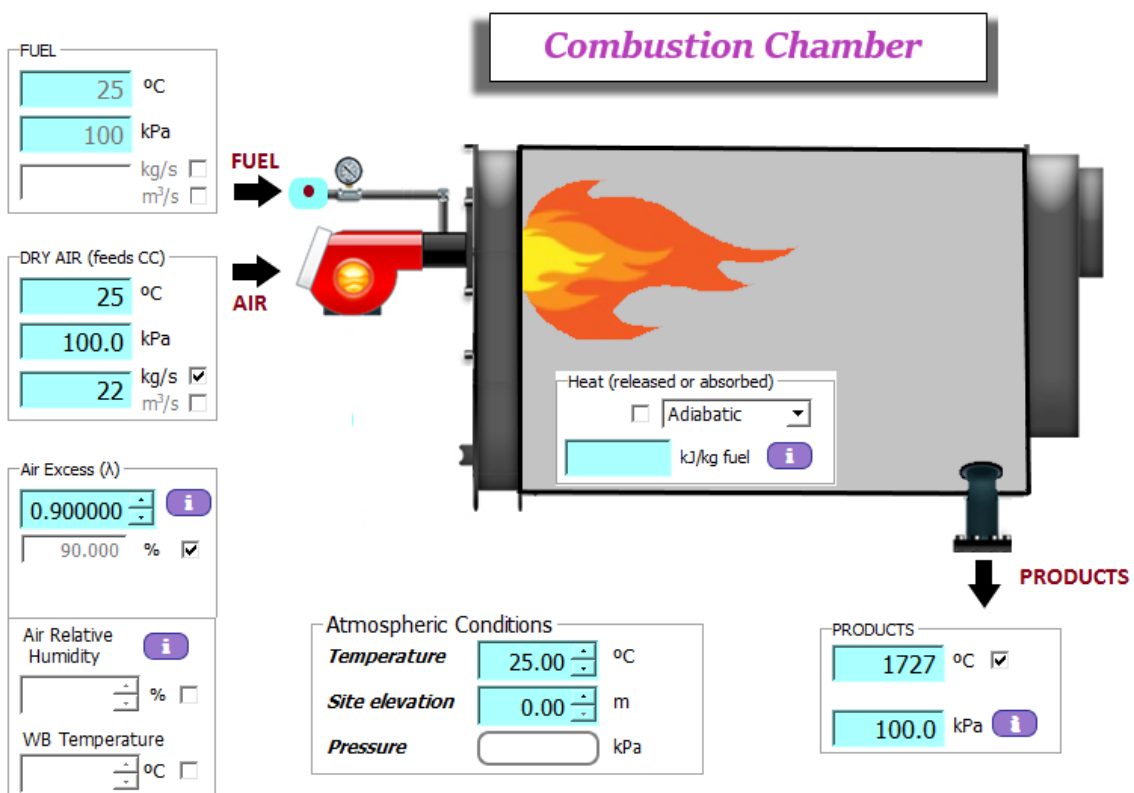
More components: N₂, O₂, Ar, CO₂ 28.9700

DRY AIR Composition

	Weight (%)	Mole (%)
N ₂	76.7075	79.0000
O ₂	23.2923	21.0000
Ar	0.0000	0.0000
CO ₂	0.0000	0.0000
Trace gasses	0.0000	0.0000

Cancel OK

Air is a mixture of about 21% oxygen, 78% nitrogen, and 1% other constituents by volume. For combustion calculations it is usually satisfactory to represent air as a 21% oxygen, 79% nitrogen mixture, by volume. Thus for every 21 moles of oxygen that react when air oxidizes a fuel, there are also 79 moles of nitrogen involved. Therefore, $79/21 = 3.76$ moles of nitrogen are present for every mole of oxygen in the air.



Molar Analysis		Ultimate Analysis		FUEL	
mol/kg fuel	Molar ratio %	Mass ratio %			
49.95422	45.67182	60.0000	<input type="checkbox"/> To estimate	C	CARBON
49.60563	45.35312	10.0000	<input type="checkbox"/> Reset	H ₂	HYDROGEN
3.56971	3.26369	10.0000		N ₂	NITROGEN
4.68750	4.28566	15.0000		O ₂	OXYGEN
1.55939	1.42571	5.0000		S	SULPHUR
				H ₂ O	MOISTURE
9.14274	g/mol (as AF)			ASH	ASH
9.14274	g/mol (as DAF)			Cl	CHLORINE
As received		100.0000	Total (%)		



Hydrogen in the products

There is hydrogen

Water gas shift reaction (Products T^a)

CO + H₂O ⇌ CO₂ + H₂

User Equilibrium temperature °C

K_p =

Molar ratio H₂/CO

Gas compositions are generally reported in terms of mole fractions since the mole fraction does not vary with temperature or pressure as does the concentration (moles/ unit volume). Carbon monoxide (CO) is a byproduct of incomplete combustion and is essentially partially burned fuel. If the air/fuel mixture does not have enough oxygen present during combustion, it will not burn completely.



FLUE GAS (Combustion Products) On wet basis On dry basis

	<input type="checkbox"/> mol/kg fuel	<input type="checkbox"/> kg/kg fuel	Mole %	Mass %
CO ₂	38.64461	1.70074	11.1299	17.2543
CO	11.30961	0.31678	3.2572	3.2138
H ₂ O	46.59503	0.83942	13.4197	8.5161
N ₂	246.09528	6.89399	70.8770	69.9407
O ₂				
SO ₂	1.55939	0.09990	0.4491	1.0135
H ₂	3.01060	0.00607	0.8671	0.0616
Ar				
HCl				
TOTAL	347.2145	9.8569	100.00 %	100.00 %

FLUE GAS (Combustion Products) On wet basis On dry basis

	<input type="checkbox"/> mol/kg fuel	<input type="checkbox"/> kg/kg fuel	Mole %	Mass %
CO ₂	38.64457	1.70074	12.8550	18.8604
CO	11.30949	0.31678	3.7621	3.5129
H ₂ O				
N ₂	246.09527	6.89399	81.8626	76.4512
O ₂				
SO ₂	1.55938	0.09990	0.5187	1.1078
H ₂	3.01106	0.00607	1.0016	0.0673
Ar				
HCl				
TOTAL	300.6198	9.0175	100.00 %	100.00 %

The water dew point is the temperature at which air is saturated with water vapor, which is the gaseous state of water. When air has reached the dew-point temperature at a particular pressure, the water vapor in the

air is in equilibrium with liquid water, meaning water vapor is condensing at the same rate at which liquid water is evaporating.

Water Dew Point T^* (and P_{sat})

H₂O (liquid) mol/mol fuel

% kg/kg fuel

°C kPa

The two fundamental methods of defining the quantities of mixture are by weight (gravimetric) or by volume (molar).

FUEL-AIR gravimetric and volumetric analysis

	<i>Mass (kg)</i>	<i>Mass ratio, mf_i (%)</i>	<i>Molar ratio, x_i (%)</i>	<i>Weight molecular, MW_i</i>	<i>$x_i MW_i$</i>	
A I R	<i>O₂</i>	2.06300	20.67722	20.21233	32.0000	6.46795
	<i>N₂</i>	6.79399	68.09542	76.03695	28.0135	21.30061
	<i>Ar</i>	0.00000	0.00000	0.00000	39.9480	0.00000
	<i>CO₂</i>	0.00000	0.00000	0.00000	44.0098	0.00000
	<i>H₂O (Air HR)</i>	0.00000	0.00000	0.00000	18.0153	0.00000
	<i>Trace gasses</i>	0.00000	0.00000	0.00000	-----	-----
	F U E L	<i>FUEL</i>	1.00000	10.02289	3.75072	9.14274
		9.85699	100.00000	100.00000		28.11148 (kg/kmol)

In this software both ultimate and proximate correlations for the estimation of HHV and LHV can be used. A database of proximate and ultimate analyses data as well as experimental HHV of biomass samples and fossil fuels were obtained from the open literature and presented in this software. In order to enable wide and universal applicability of the proposed correlations, the database included a sets of data from previous studies conducted by researchers from different parts of the world. It is also possible to obtain both calorific powers by means of an energy balance applied to the reactive process.

Energy Balance (25 °C, 1 atm)

Experimental correlations (mass fractions)

Boie: C,H,O,N,S

(Based on the dry and mineral matter free elemental fuel composition)

Boie: C,H,O,N,S

Boie: C,H,O,N,S

Eiserman: C,H,O,S

Channiwala & Parikh: C,H,O,N,S,Ash

Dubbel: C,H,O,S

Dulong: C,H,O

Dulong (exp.): C,H,O,S

Dulong & Petit: C,H,O,S

D'Huart: C,H,O,S

Gumz: C,H,O,N,S

Mahler: C,H,O,N

Burnham: C,H,N,O,S
Burnham: C,H,N,O,S
Loo & Koppejan: C,H,N,S,Ash
Friedl et al.: C,H,N
Lloyd & Davenport: C,H,O,N,S
Sheng & Azevedo: C,H,Ash
Yin: C,H
Wilson (for Waste): C,H,O,N,S
Nhuccen & Afzal (torrified biomass): C,H,N

(for biomass)

	Lower Heating, LHV		Higher Heating, HHV	
		<i>(DAF)</i>		
N	29957.60	kJ/kg fuel	32153.60	G
E	29957.60	kJ/kg fuel	32153.60	R
T	29957.60	kJ/kg fuel	32153.60	O
		<i>(As received)</i>		S
	29957.60	kJ/kg fuel	32153.60	S

i kJ/kg

HEAT OF COMBUSTION ×

i The heat of combustion or net calorific value is the energy released as heat when a compound undergoes complete combustion with oxygen under standard conditions.

The quantity known as higher heating value (HHV) (or gross energy or upper heating value) is determined by bringing all the products of combustion back to the original pre-combustion temperature, and in particular condensing any vapor produced. The higher heating value takes into account the latent heat of vaporization of water in the combustion products.

The quantity known as lower heating value (LHV) (net calorific value (NCV) or lower calorific value (LCV)) is determined by subtracting the heat of vaporization of the water vapor from the higher heating value. This treats any H₂O formed as a vapor. The energy required to vaporize the water therefore is not released as heat.

OK

Enthalpy of formation is the enthalpy change for the formation of 1 mol of a compound from its component elements, such as the formation of carbon dioxide from carbon and oxygen. The formation of any chemical can be as a reaction from the corresponding elements.



Enthalpy of formation Experimental correlations Energy balance

(DAF) kJ/kg fuel (As received)

Absolute entropy Eiserman et al. 1980 (coal, char, ash) (Experimental expression)

(DAF) kJ/kg fuel K

Standard chemical exergy Experimental correlations (Experimental expression) Exergy balance

(DAF) kJ/kg fuel (As received)

Standard Gibbs Free Energy of Formation

(DAF) kJ/kg fuel

H/C molar ratio mol H/mol C

O/C molar ratio mol O/mol C

Carbon content kg C/kg fuel

Hydrogen content kg H/kg fuel

C/H mass ratio kg C/kg H

N/C molar ratio mol N/mol C

Oxygen content kg O/kg fuel

Air/Fuel ratio (dry air)

<i>Theoretical</i>	<i>Actual</i>	
Dry air	Dry air	AIR
<input type="text" value="341.105"/>	<input type="text" value="306.995"/>	<input type="checkbox"/> mol/kg fuel
<input type="text" value="9.84113"/>	<input type="text" value="8.85701"/>	<input type="checkbox"/> kg/kg fuel

Oxygen/Fuel ratio (dry air)

<i>Theoretical</i>	<i>Actual</i>	
Dry air	Dry air	OXYGEN
<input type="text" value="71.632"/>	<input type="text" value="64.469"/>	<input type="checkbox"/> mol/kg fuel
<input type="text" value="2.29222"/>	<input type="text" value="2.06300"/>	<input type="checkbox"/> kg/kg fuel

Nitrogen/Fuel ratio (dry air)

<i>Theoretical</i>	<i>Actual</i>	
Dry air	Dry air	<input type="checkbox"/> mol/kg fuel
269.473	242.526	
7.54888	6.79399	<input type="checkbox"/> kg/kg fuel

NITROGEN ▼

For a combustion process that takes place adiabatically with no shaft work, the temperature of the products is referred to as the adiabatic flame temperature. This is the maximum temperature that can be achieved for given reactants. Heat transfer, incomplete combustion, and dissociation all result in lower temperature.

Products Temperature

1727 °C

Adiabatic Flame Temperature

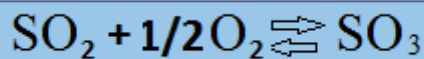
For $\lambda = 0.9000$ **2035.55** °C i

(Actual)

For $\lambda = 1.0$ (max) **2134.95** °C (25°C, 1atm)

(Theoretical)

The acid dew point of flue gas is the temperature at which the acidic elements in your flue gas start to condense. There are multiple formulas available to accurately calculate the Acid Dew Point. Each formula takes the H₂O and SO₃ levels of your flue gas into consideration. Throughout the industry, the Acid Dew Point (ADP) correlations of Okkes and ZareNezhad are mainly used. Verhoff's equation results in a 20 to 40 °C lower Acid Dew Point. The ZareNezhad equation closely follows the Okkes equation at higher SO₃ levels and calculates a slightly lower ADP at lower SO₃ levels. If operation above ADP is desired, it is common to use an additional margin of >10 °C above the ADP. This approach provides an engineering basis for a corrosion free operation.





Experimental correlations:

Verhoff / Banchero (1974)



Sulphuric Acid Dew Temperature

155.23 °C

Requeriment:

Stack Temperature > Dew Temperature

Okkes (1987)

Sulphuric Acid Dew Temperature

150.18 °C

ZareNezhad (2009)

Sulphuric Acid Dew Temperature

153.95 °C

Dew Point for Flue Gas



If the flue gas is cooled sufficiently, condensation will occur and liquid will appear on surfaces At temperatures below the dew point. The liquid phase will contain highly corrosive sulfuric acid. This causes sulfuric acid corrosion, so called low-temperature corrosion.

Low-temperature corrosion needs to be taken into consideration for optimum system design of exhaust gas treatment, oxy-combustion capture of CO₂ and advanced power plants such as IGCC (Integrated Gasification Combined Cycle), IGFC (Integrated Gasification Fuel Cell), etc., which contribute to CO₂ emission reduction.

OK

POLLUTANTS: EMISSION INDEX



The group of gaseous pollutants consists of nitrogen oxides NO_x, carbon monoxide CO and a variety of unburned hydrocarbons UHCs. The amount of gaseous pollutants is usually given by the emission index (EI).

EI = mass of the produced pollutant in g/mass of fuel used in kg

OK



Pollutants: Emission Index

<i>EI (NO, CO)</i>	<input type="text" value="316.8"/>	g/kg fuel	i	<i>EI (SO₂)</i>	<input type="text" value="0"/>	g/kg fuel
<i>EI (NO)</i>	<input type="text" value="0"/>	g/kg fuel		<i>EI (NO₂)</i>	<input type="text" value="0"/>	g/kg fuel
<i>EI (CO)</i>	<input type="text" value="316.8"/>	g/kg fuel		<i>EI (H₂O)</i>	<input type="text" value="0"/>	g/kg fuel

Emission factors (LHV)

Power plant efficiency

%

Gaseous air pollutants

	CO₂ <i>Global Warming</i>	SO₂ <i>Acid Rain</i>
kg/kWh fuel	<input type="text" value="1.869"/>	<input type="text" value="0.109758"/>
kg/GJ fuel	<input type="text" value="519.048"/>	<input type="text" value="30.4884"/>
kg/kWh electricity	<input type="text" value="5.339"/>	<input type="text" value="0.313595"/>
kg/GJ electricity	<input type="text" value="1482.993"/>	<input type="text" value="87.1098"/>
ppm (mass)	<input type="text" value="172543"/>	<input type="text" value="10135"/>

Combustion Efficiency **i**

$$\eta_{\text{comb}} = \frac{Q_f(T_0)}{\text{LHV}}$$

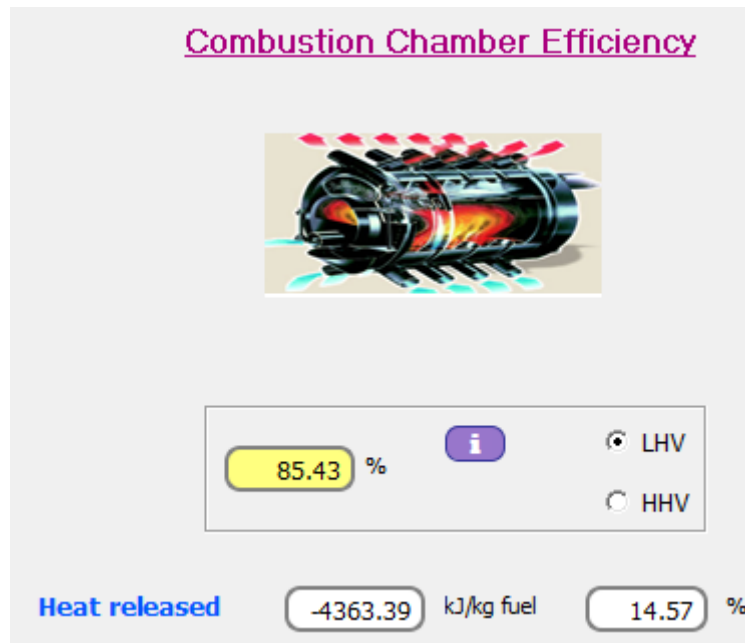
% **(DAF)** **i**

(Incomplete Combustion Loss)

(100% for complete combustion)

Lower Heating, LHV
(energy balance) kJ/kg fuel

Q_f(T₀) kJ/kg fuel



Heat (Released or Absorbed)

4363.390 kJ/kg fuel
 Exothermic
ENERGY

kJ/kg fuel kW

Reactants
 Products

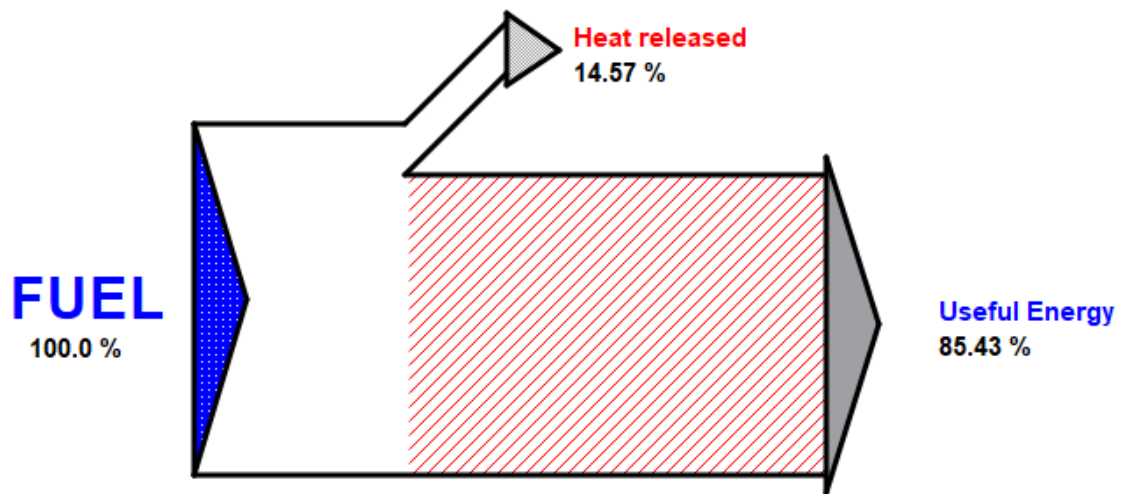
$$Q_f = \sum_{\text{Products}} n_{\text{out}} h_{\text{out}}(T_{\text{out}}) - \sum_{\text{Reactants}} n_{\text{in}} h_{\text{in}}(T_{\text{in}})$$

-6509.68 kJ/kg fuel
 -2146.29

$$Q_f = H_P(T_{\text{out}}, P) - H_R(T_{\text{in}}, P) = H_P(T_{\text{out}}, P) - H_P(T_{\text{adr}}, P)$$

$$H = H_{\text{form}} + H(T, P) - H(25^\circ\text{C}, 1 \text{ atm})$$

The Sankey diagram is very useful tool to represent an entire input and output energy flow in any energy equipment or system such as boiler, fired heaters, furnaces after carrying out energy balance calculation. This diagram represents visually various outputs and losses so that energy managers can focus on finding improvements in a prioritized manner.



Sankey diagram

ENERGY BALANCE: REACTANTS			
	<i>kJ/mol</i>	<i>kJ/kg fuel</i>	
O ₂	0.000	0.000	A I R
N ₂	0.000	0.000	
Ar			
CO ₂			
H ₂ O	0.000	0.000	
TOTAL	0.000	0.000	
Fuel (DAF)	-19.623	-2146.287	F U E L
Ash	0.000	0.000	
TOTAL	-19.623	-2146.287	
TOTAL	-19.623	-2146.287 (AIR+FUEL)	

ENERGY BALANCE: FLUE GAS			
	<i>kJ/mol</i>	<i>kJ/kg fuel</i>	
CO ₂	-302.0800	-11673.7637	
CO	-53.7910	-608.3552	
H ₂ O	-169.1310	-7880.6646	
O ₂	0.0000	0.0000	
N ₂	56.1410	13816.0352	
H ₂	52.9320	159.3571	
SO ₂	-206.6730	-322.2838	
TOTAL	-622.6019	-6509.6748	

From second law evaluations (entropy or exergy evaluations) it is generally known that thermodynamic losses of boilers and furnaces are much higher than the thermal efficiencies do suggest. With thermal losses of around 5 % the thermodynamic losses (exergy losses) of a boiler can be 50 % or more. The combustion process is responsible for a significant part of these losses.

From this point of view, various aspects are important in the design of combustion chambers, boilers and furnaces, for example the atmospheric conditions, fuel and its composition and moisture content, the air factor and the air preheat temperature, etc. Value diagrams can be derived to visualise the exergy loss of combustion and to explain the cause of the irreversibilities in each device of the installation.

Entropy Terms (kJ/kg fuel K) AVAILABILITY

Generated Entropy (S_g) 34.533 ●

$$S_g = -\frac{Q_f}{T_f} + \sum_{\text{Products}} n_{\text{out}} S_{\text{out}} - \sum_{\text{Reactants}} n_{\text{in}} S_{\text{in}}$$

Entropy balance Reactants
 Products

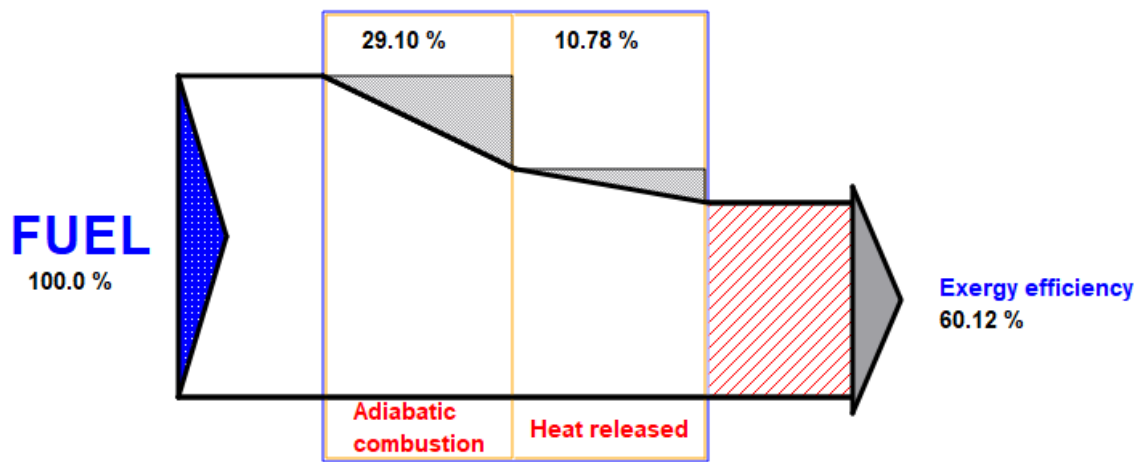
4.3627
30.1700

ENTROPY BALANCE: FLUE GAS ? X

	J/mol K	kJ/kg fuel K	
O ₂	218.009	14.055	A I R
N ₂	193.462	46.919	
Ar			
CO ₂			
H ₂ O	0.000	0.000	
TOTAL	411.471	60.974	
Fuel (DAF)	16.753	1.832	F U E L
Ash	0.000	0.000	
TOTAL	16.753	1.832	
TOTAL	428.224	62.806	(AIR+FUEL)

ENTROPY BALANCE: FLUE GAS ? X

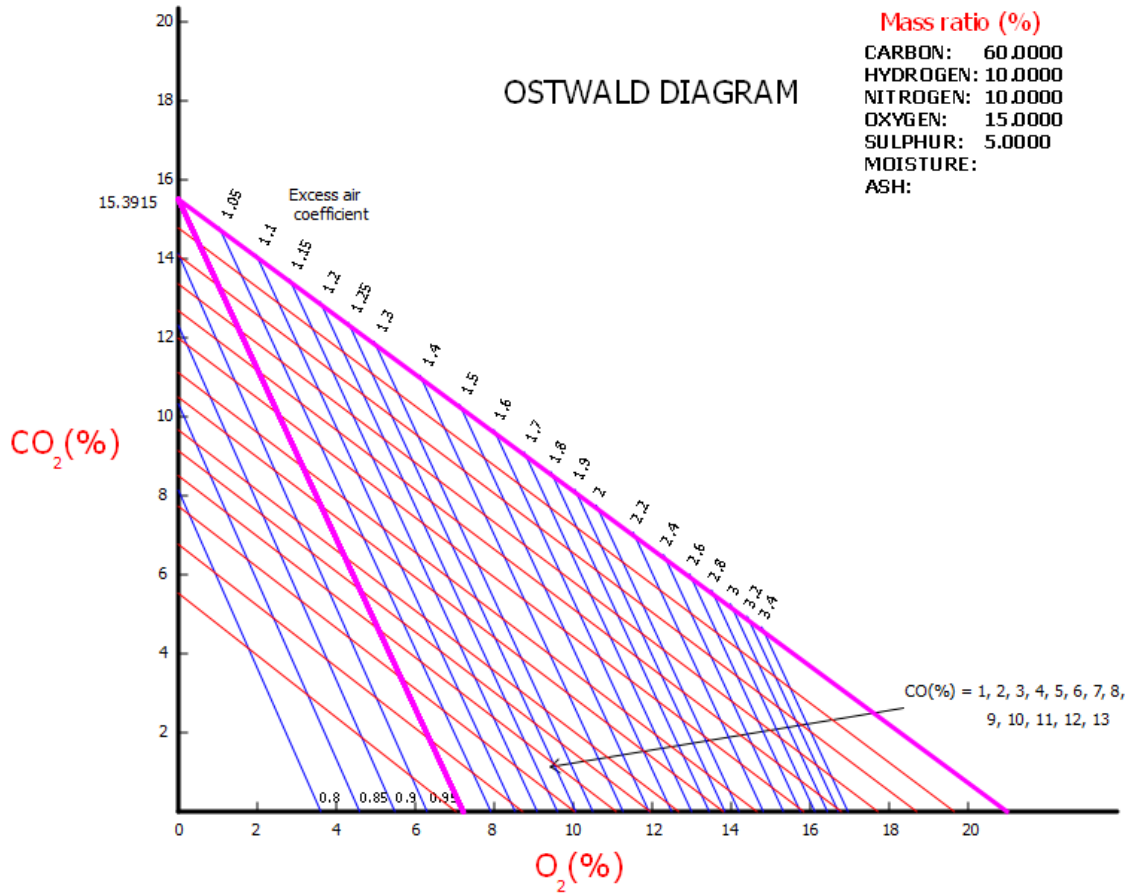
	J/mol K	kJ/kg fuel K
CO ₂	327.4648	12.6547
CO	287.0714	3.2467
H ₂ O	281.2703	13.1058
O ₂	0.0000	0.0000
N ₂	254.8310	62.7127
H ₂	227.7724	0.6857
SO ₂	366.1456	0.5710
TOTAL	1744.5554	92.9766

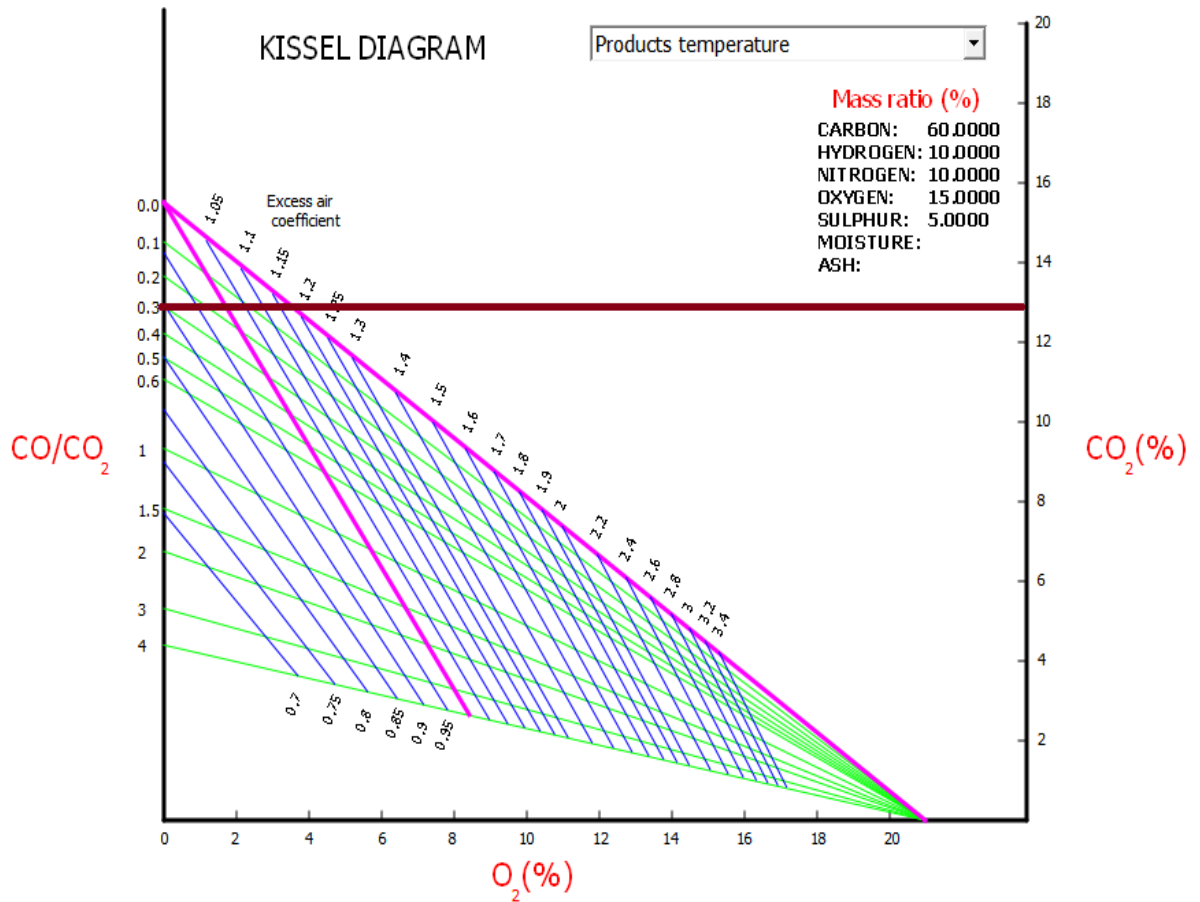


Grassmann diagram



We can verified that $CO/CO_2 = 3.7621/12.8550 = 0.29$

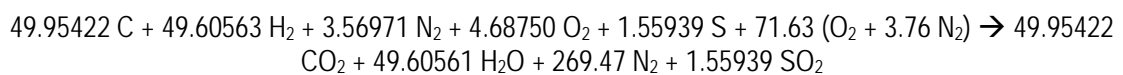




Note (solution without ThermoCombustion):

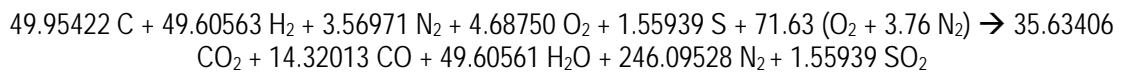
For 1 kg of fuel:

Stoichiometric reaction (mol/kg fuel):



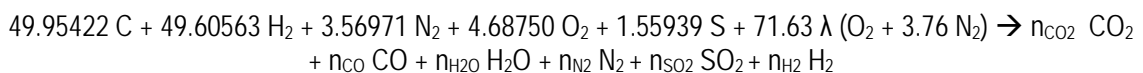
Stoichiometric air: 341.11 mol aire/kg fuel

Actual reaction (withouth H₂):

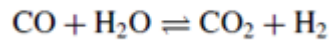


Air real: 306.99 mol aire/kg fuel

Resolution approach:



Reaction water-gas:



Total number of moles:

$$n_{\text{tot}} = n_{\text{CO}_2} + n_{\text{CO}} + n_{\text{H}_2\text{O}} + n_{\text{H}_2} + 1.55939 + 246.095$$

$$n_{\text{tot}} = n_{\text{CO}_2} + n_{\text{CO}} + n_{\text{H}_2\text{O}} + n_{\text{H}_2} + 247.6546$$

Mass balance:

Balance de S: $1.55939 = n_{\text{SO}_2}$

Balance de N: $242.53 + 3.5697 = 246.095 = n_{\text{N}_2}$

Balance de C: $49.95422 = n_{\text{CO}_2} + n_{\text{CO}}$

Balance de H: $49.60563 + n_{\text{water,fuel}} = n_{\text{H}_2\text{O}} + n_{\text{H}_2}$

Balance de O:

$$4.68750 + 64.467 = n_{\text{CO}_2} + 0.5 n_{\text{CO}} + 0.5 n_{\text{H}_2\text{O}} + 1.55939 + 0.5 n_{\text{water,fuel}}$$

$$n_{\text{CO}} = 49.95422 - n_{\text{CO}_2}$$

$$n_{\text{H}_2\text{O}} = 135.190 - 2 n_{\text{CO}_2} - n_{\text{CO}} = 135.190 - 2 n_{\text{CO}_2} - (49.95422 - n_{\text{CO}_2}) - n_{\text{water,fuel}}$$

$$n_{\text{H}_2\text{O}} = 85.236 - n_{\text{water,fuel}} - n_{\text{CO}_2}$$

$$n_{\text{H}_2} = n_{\text{CO}_2} - 35.63037 + n_{\text{water,fuel}}$$

In this case the fuel is dry: $n_{\text{water,fuel}} = 0$

$$n_{\text{tot}} = n_{\text{CO}_2} + n_{\text{CO}} + n_{\text{H}_2\text{O}} + n_{\text{H}_2} + 247.6546 = n_{\text{CO}_2} + 49.95422 - n_{\text{CO}_2} + 85.236 - n_{\text{CO}_2} + n_{\text{CO}_2} - 35.63037 + 247.6546 = 347.214 \text{ moles humos/kg fuel}$$

Mole ratios:

$$X_{\text{CO}_2} = n_{\text{CO}_2}/n_{\text{tot}} = n_{\text{CO}_2}/347.214$$

$$X_{\text{CO}} = n_{\text{CO}}/n_{\text{tot}} = (49.95422 - n_{\text{CO}_2})/347.214$$

$$X_{\text{H}_2\text{O}} = n_{\text{H}_2\text{O}}/n_{\text{tot}} = (85.236 - n_{\text{CO}_2})/347.214$$

$$X_{\text{H}_2} = n_{\text{H}_2}/n_{\text{tot}} = (n_{\text{CO}_2} - 35.63037)/347.214$$

$$K_p = X_{\text{CO}_2} X_{\text{H}_2} / X_{\text{H}_2\text{O}} X_{\text{CO}} =$$

$$= n_{\text{CO}_2} (n_{\text{CO}_2} - 35.63037) / (85.236 - n_{\text{CO}_2}) (49.95422 - n_{\text{CO}_2})$$

Quadratic reaction:

$$(1 - K_p) n_{\text{CO}_2}^2 + (135.190 K_p - 35.63037) n_{\text{CO}_2} - 4257.8978 K_p = 0$$

For $T_{\text{prod}} = 1727 \text{ }^\circ\text{C}$ (2000 K)

$$K_p = 0.220778$$

$$a n_{\text{CO}_2}^2 + b n_{\text{CO}_2} + c = 0$$

$$a = 0.779222$$

$$b = -5.78337$$

$$c = -940.050$$

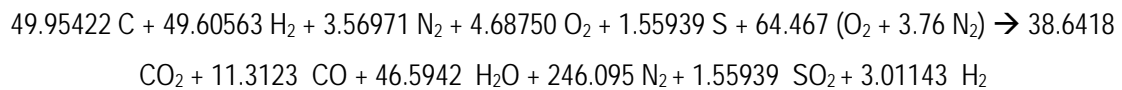
$$n_{\text{CO}_2} = [-b + (b^2 - 4 a c)] / 2a = 38.6418 \text{ moles/kg fuel}$$

$$n_{\text{CO}} = 11.3123 \text{ moles/kg fuel}$$

$$n_{\text{H}_2\text{O}} = 46.5942 \text{ moles/kg fuel}$$

$$n_{\text{H}_2} = 3.01143 \text{ moles/kg fuel}$$

Verification:



$$K_p = 0.220778 = 38.6418 \cdot 3.01143 / (46.5942 \cdot 11.3123)$$