Air Independent Propulsion

For non-nuclear submarines, submersibles and unmanned vehicles; AUV, UUV, torpedoes Torpedo propulsion was originally stored high pressure air.** It evolved to heated air at the turn of the century using kerosene, alcohol or Otto fuel. Current torpedoes employ electrical storage or lithium sulphur hexafluoride systems. (Sulphur hexafloridegas is sprayed over a block of lithium which generates heat.

As is well known typical submarine propulsion uses a storage battery with engine recharging. In all the stored systems, the challenge is storage of the oxygen component,

** The initiative behind the self-propelled torpedo was provided by an Austrian frigate captain Giovanni Luppi. After some unsuccesful attempts to propel a charge laden boat with a springdriven clockwork. In 1864 he turned to Robert Whitehead (1823-1905), then technical manager in an Italian factory to design an improved version. The result was a torpedo in October 1886: length 3.35 m, diameter 25.5 cm, weight 136 kg. Propulsion was provided by 20 to 25 kg of compressed air, driving a reciprocating engine with a high and low pressure cylinder. Taken from "Swedish Torpedo 100 Years; 1876 - 1976.

Secondary Batteries Lead acid-

	solid solid liquid => so $Pb + Pb \cdot O_2 + 2 \cdot H_2 \cdot S \cdot O_4 = 2 \cdot H_2 \cdot G \cdot G \cdot G \cdot G \cdot G = 2 \cdot H_2 \cdot G \cdot G \cdot G \cdot G \cdot G = 2 \cdot H_2 \cdot G \cdot G \cdot G \cdot G \cdot G = 2 \cdot H_2 \cdot G \cdot G \cdot G \cap G$	•	O	charges 2.1 - 2.6 V per cell electrolyte H_2SO_4 energy density 67 lb/kW*hr
	$2 \cdot Pb$ (2 + 8)·O	2·Pb 2·S	check	$67 \frac{\text{lbf}}{\text{lsW}} = 30.391 \frac{\text{kgf}}{\text{lsW}}$
	4·H =	$(8+2) \cdot O$		kW·hr kW·hr
Silver - Zinc	2·S	4∙H		$\frac{1}{67 \cdot \frac{\text{lbf}}{\text{kW} \cdot \text{hr}}} = 14.925 \frac{\text{W} \cdot \text{hr}}{\text{lbf}}$
Silver - Zilic	discharges 1.1 - 0.8 V per c charges 1.6 - 2.0 V per cell electrolyte KOH energy density 20 lb/kW*hr		$20 \frac{\text{lbf}}{\text{kW} \cdot \text{hr}} = \frac{1}{20 \cdot \frac{\text{lbf}}{\text{kW} \cdot \text{hr}}}$	

problem (both cells): hydrogen release in charging. New developments: NiCd, Li rechargeable

Fuel Cell

originally developed by Roger Bacon. H_2 and O_2 are supplied to special electrodes with various electrolytes. KOH in the alkaline cells, proton exchange membranes (PEM) and high temperature carbonate in the molten carbonate cells, solid oxides in other cells. Energy conversion is relatively high ~ 60%

figure later overall reaction $H_2 + \frac{1}{2} \cdot O_2 = H_2 \cdot O$ complete $H_2 + 2 \cdot O \cdot H = 2 \cdot H_2 \cdot O + 2 \text{ electons}$ theoretical voltage: 1.23 V, practical voltage ~ 0.8 V $\frac{1}{2} \cdot O_2 + H_2 \cdot O = 2 \text{ electrons} + 2 \cdot O \cdot H$

This is an ever moving technology. These notes represent an overview but may not represent the latest parameters.

discharges 2 - 1.8 V per cell

maximum power at constant T_1 $\frac{w_dot_{max}}{m_dot} = h_1 - T_1 \cdot s_1 - (h_2 - T_1 \cdot s_2) = G_1 - G_2 = \Delta G$ $G = Gibbs_function$

 $h_1 - h_2$ = heating_value_of_fuel

. ~

$$\frac{\Delta G}{hhv} = 0.825 to_{.0.95}$$
 depending on T₁ and state of H₂O liquid or vapor with internal losses (~ 60% conversion)

H2 consumption:
$$0.111 \frac{lbf}{kW \cdot hr} = 0.05 \frac{kgf}{kW \cdot hr}$$
O2 consumption: $0.889 \frac{lbf}{kW \cdot hr} = 0.403 \frac{kgf}{kW \cdot hr}$ reactants $1.0 \frac{lbf}{kW \cdot hr} = 0.454 \frac{kgf}{kW \cdot hr}$

the volume is important and depends on the storage method: as cryogenic liquids:

O₂ sp_gr = 1.14
$$71 \frac{lbf}{ft^3} = 1.137 \times 10^3 \frac{kgf}{m^3}$$

H₂ sp_gr = 0.064 $4.0 \frac{lbf}{ft^3} = 64.074 \frac{kgf}{m^3}$

Other methods of storage include: high pressure gas, hydrides (driven out by heat and pressure reduction) or as liquid fuel which has to be reformed. A summary of ypes of fuel cells from

Fuel Cell Handbook (Sixth Edition) DOE/NETL-2002/1179 By EG&G Technical Services, Inc. Science Applications International Corporation Under Contract No. DE-AM26-99FT40575 U.S. Department of Energy Office of Fossil Energy National Energy Technology Laboratory P.O. Box 880 Morgantown, West Virginia 26507-0880 November 2002 A brief description of various electrolyte cells of interest follows. A detailed description of these fuel cells may be found in Sections 3 through 7.

Polymer Electrolyte Fuel Cell (PEFC): The electrolyte in this fuel cell is an ion exchange membrane (fluorinated sulfonic acid polymer or other similar polymer) that is an excellent proton conductor. The only liquid in this fuel cell is water; thus, corrosion problems are minimal. Water management in the membrane is critical for efficient performance; the fuel cell must operate under conditions where the byproduct water does not evaporate faster than it is produced because the membrane must be hydrated. Because of the limitation on the operating temperature imposed by the polymer, usually less than 120°C, and because of problems with water balance, a H2-rich fuel is used. Higher catalyst loading (Pt in most cases) than that used in PAFCs is required for both the anode and cathode. Because CO "poisons" the catalyst, the fuel may contain no CO.

Alkaline Fuel Cell (AFC): The electrolyte in this fuel cell is concentrated (85 wt%) KOH in fuel cells operated at high temperature (~250°C), or less concentrated (35-50 wt%) KOH for lower temperature (<120°C) operation. The electrolyte is retained in a matrix (usually asbestos), and a wide range of electrocatalysts can be used (e.g., Ni, Ag, metal oxides, spinels, and noble metals). The fuel supply is limited to non-reactive constituents except for hydrogen. CO is a poison, and CO2 will react with the KOH to form K2CO3, thus altering the electrolyte. Even the small amount of CO2 in air is detrimental to the alkaline cell.

Phosphoric Acid Fuel Cell (PAFC): Phosphoric acid concentrated to 100% is used for the electrolyte in this fuel cell, which operates at 150 to 220°C. At lower temperatures, phosphoric acid is a poor ionic conductor, and CO poisoning of the Pt electrocatalyst in the anode becomes severe. The relative stability of concentrated phosphoric acid is high compared to other common acids; consequently the PAFC is capable of operating at the high end of the acid temperature range (100 to 220°C). In addition, the use of concentrated acid (100%) minimizes the water vapor pressure so water management in the cell is not difficult. The matrix universally used to retain the acid is silicon carbide (1), and the electrocatalyst in both the anode and cathode is Pt.

Molten Carbonate Fuel Cell (MCFC): The electrolyte in this fuel cell is usually a combination of alkali carbonates, which is retained in a ceramic matrix of LiAIO2. The fuel cell operates at 600 to 700°C where the alkali carbonates form a highly conductive molten salt, with carbonate ions providing ionic conduction. At the high operating temperatures in MCFCs, Ni (anode) and nickel oxide (cathode) are adequate to promote reaction. Noble metals are not required.

Solid Oxide Fuel Cell (SOFC): The electrolyte in this fuel cell is a solid, nonporous metal oxide, usually Y2O3-stabilized ZrO2. The cell operates at 600-1000°C where ionic conduction by oxygen ions takes place. Typically, the anode is Co-ZrO2 or Ni-ZrO2 cermet, and the cathode is Sr-doped LaMnO3.

Electrolyte	PEFC Ion Exchange Membranes	AFC Mobilized or Immobilized Potassium Hydroxide	PAFC Immobilized Liquid Phosphoric Acid	MCFC Immobilized Liquid Molten Carbonate	SOFC Ceramic
Operating Temperature	80°C	65°C - 220°C	205°C	650° C	600-1000°C
Charge Carrier	H∙	OH-	H⁺	CO ₃ -	O⁼
External Reformer for CH₄ (below)	Yes	Yes	Yes	No	No
Prime Cell Components	Carbon-based	Carbon-based	Graphite-based	Stainless based	Ceramic
Catalyst	Platinum	Platinum	Platinum	Nickel	Perovskites
Product Water Management	Evaporative	Evaporative	Evaporative	Gaseous Product	Gaseous Product
Product Heat Management	Process Gas + Independent Cooling Medium	Process Gas + Electrolyte Circulation	Process Gas + Independent Cooling Medium	Internal Reforming + Process Gas	Internal Reforming + Process Gas

Table 1-1 Summary of Major Differences of the Fuel Cell Types

Aluminum - Oxygen semi-cell Solid Oxide Cell

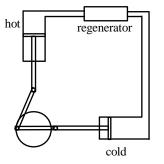
$4 \cdot \mathrm{Al} + 6 \cdot \mathrm{H}_2 \cdot \mathrm{O} + 3 \cdot \mathrm{O}_2 > 4 \cdot \mathrm{Al} \cdot (\mathrm{OH})$	termed gibbsite or h	ydragillate figure later
Fuel Cell Technologies, Ltd formerly Alupower	AI consumption:	$0.62 \frac{\text{lbf}}{\text{kW} \cdot \text{hr}} = 0.281 \frac{\text{kgf}}{\text{kW} \cdot \text{hr}}$
(http://www.fct.ca)	O ₂ consumption: H2O + KOH	$0.58 \frac{\text{lbf}}{\text{l}.98 \frac{\text{lbf}}{\text{kW} \cdot \text{hr}}} = 0.263 \frac{\text{kgf}}{\text{kgf}}$ $1.98 \frac{\text{lbf}}{\text{kW} \cdot \text{hr}} = 0.898 \frac{\text{kgf}}{\text{kW} \cdot \text{hr}}$

voltage: 1.4 - 1.5 V per cell

simplified model of Stirling cycle

closed; constant mass, states at end points shown; drive rotates $\pi/2$ clockwise between each state compare with continuous plot below volumes are designated 0, 0.5 and 1.0 to go with min, midway and max in each cylinder.

state 1:



 $vol_{hot} = 0.5$ $vol_{cold} = 1.0$ $vol_{total} = 1.5$

state 2: $vol_{hot} = 0.0$ $vol_{cold} = 0.5$ $vol_{total} = 0.5$

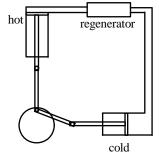
action 2 - 3: \sim constant volume, heat added to system from regenerator, note that end state volume is the same but what was in cold cylinder (2) goes to the hot (3)

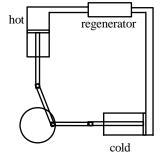
state 3: $vol_{hot} = 0.5$ $vol_{cold} = 0.0$ $vol_{total} = 0.5$

action 3 - 4: working fluid is expanded with T = constant, positive work done and heat is added

state 4: $vol_{hot} = 1.0$ $vol_{cold} = 0.5$ $vol_{total} = 1.5$

action 4 - 1: ~ constant volume, heat removed from system to regenerator, note that end state volume is the same but is in hot cylinder vs. cold





regenerator

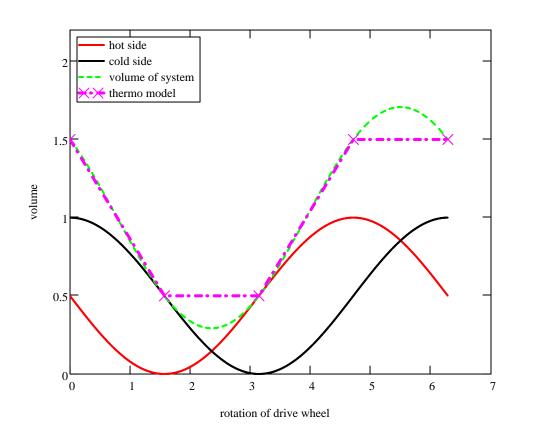
cold



hot

▶ volume plot data

plot shows volume in cylinders and thermodynamic model with rotation



define some units

$$kJ := 10^3 \cdot J$$

Stirling Cycle thermodynamic analysis

kmol := 10^3 mole

* The ideal Stirling cycle is made up of four totally reversible processes:

1-2 Constant temperature compression (heat rejection to external sink)

2-3 Constant volume regeneration (internal heat transfer from regenerator back to the working fluid).

- 3-4 Constant temperature expansion (heat addition from external source)
- 4-1 Constant volume regeneration (internal heat transfer from the working fluid to regenerator)

from gas relationships

$$\underline{p \cdot v = R \cdot T} \quad (3.2) \qquad \boxed{\frac{p_1 \cdot v_1}{T_1} = \frac{p_2 \cdot v_2}{T_2}}_{V_2} \quad (3.5)$$

$$W_{1_2} = \int_{V_1}^{V_2} p \, dV = p_1 \cdot V_1 \cdot \int_{V_1}^{V_2} \frac{1}{v} \, dV = p_1 \cdot V_1 \cdot \ln\left(\frac{V_2}{v_1}\right) \quad (4.5)$$

$$\underline{s_2 - s_1 = c_{vo} \cdot \ln\left(\frac{T_2}{T_1}\right) + R \cdot \ln\left(\frac{v_2}{v_1}\right)}_{V_1} \quad (7.24)$$

$$\underline{du = c_{vo} \cdot dT} \quad vo \quad \stackrel{=> \text{ constant volume}}{\text{ ideal gas}} \quad (5.20)$$

data for example:

again, parameterize in terms of p p1 c_{vo} = constant $c_{po} = constant$ $mw_N2 := 28 \frac{kg}{kmol}$

$$\begin{split} T_{H} &\coloneqq 1000 K \qquad p_{1} \coloneqq 1 \text{ bar } N_{2} \qquad c_{p} \coloneqq 1.042 \cdot \frac{kJ}{kg \cdot K} \qquad R_{-}m \coloneqq 8.3144 \cdot \frac{kJ}{kmol \cdot K} \qquad R_{w} \coloneqq \frac{R_{-}m}{mw_{-}N2} \qquad R = 0.297 \frac{kJ}{kg \cdot K} \\ T_{L} &\coloneqq 300 K \qquad v_{1} \coloneqq \frac{R \cdot T_{L}}{p_{1}} \qquad v_{1} = 0.891 \frac{m^{3}}{kg} \qquad \gamma \coloneqq 1.4 \qquad c_{v} \coloneqq \frac{c_{p}}{\gamma} \qquad c_{v} = 0.744 \frac{kJ}{kg \cdot K} \\ T_{1} &\coloneqq T_{L} \qquad P \cdot V = R \cdot T \\ s_{1} &\coloneqq 1 \frac{kJ}{kg \cdot K} \qquad r \coloneqq 3 \qquad \text{compression ratio} \qquad \text{ten increments} \qquad NN \coloneqq 10 \quad i \coloneqq 0 \dots NN \end{split}$$

<u>1 - 2 compression, constant internal energy, heat rejection at constant temperature (negative)</u> work done

$$p \cdot v = R \cdot T$$
 $p_1 $p_2 := r \cdot p_1$ $p_2 = 3 \text{ bar}$$

incremental for plots

$$p_{1_{2}i} \coloneqq \frac{p_{2} - p_{1}}{NN} \cdot i + p_{1} \quad v_{1_{2}i} \coloneqq \frac{R \cdot T_{1}}{p_{1_{2}i}} \qquad \frac{v_{1_{2}0}}{v_{1_{2}10}} = 3 \quad T_{2} \coloneqq T_{1} \qquad v_{2} \coloneqq v_{1_{2}NN} \quad v_{2} = 0.297 \frac{m^{3}}{kg}$$

$$w_{1_{2}} = \int_{1}^{2} p \, dv = R \cdot Th \cdot \int_{1}^{2} \frac{1}{v} \, dv = R \cdot T_{1} \cdot \ln\left(\frac{v_{2}}{v_{1}}\right) \qquad w_{1_{2}} \coloneqq R \cdot T_{1} \cdot \ln\left(\frac{v_{2}}{v_{1}}\right) \qquad w_{1_{2}} = -97.868 \frac{kJ}{kg}$$
first law, mass constant c_{v} , T constant $\Delta H = 1 - 2 = 0$

$$q_{1_{2}} = w_{1_{2}} = R \cdot T_{1} \cdot \ln\left(\frac{v_{2}}{v_{1}}\right) = T_{1} \cdot (s_{2} - s_{1})q_{1_{2}} \coloneqq w_{1_{2}} = q_{1_{2}} = -98 \frac{kJ}{kg} \qquad s_{2} \coloneqq \frac{q_{1_{2}}}{T_{1}} + s_{1} \qquad s_{2} = 0.674 \frac{kJ}{kg}$$

plot 1 - 2

2 - 3 constant volume heat addition (from regenerator)

$$q_{2_{3}} \coloneqq c_{v} \cdot (T_{H} - T_{L}) \qquad q_{2_{3}} \equiv 521 \frac{kJ}{kg} \qquad p \cdot v \equiv R \cdot T$$

$$v_{3} \coloneqq v_{2} \quad T_{3} \coloneqq T_{H} \qquad s_{2_{3}} = 521 \frac{kJ}{kg} \qquad s_{2_{3}} = c_{vo} \cdot \ln\left(\frac{T_{2}}{T_{1}}\right) + R \cdot \ln\left(\frac{v_{2}}{v_{1}}\right) \qquad (7.24)$$

$$p_{3} \coloneqq \frac{R \cdot T_{3}}{v_{3}} \quad p_{3} \equiv 10 \text{ bar} \qquad T_{2_{3}}(p_{2_{3}}) \equiv \frac{p_{2_{3}} \cdot v_{2}}{R} \qquad s_{2_{3}}(p_{2_{3}}) \equiv s_{2} + c_{v} \cdot \ln\left(\frac{T_{2_{3}}(p_{2_{3}})}{T_{2}}\right) \qquad \text{functionally}$$

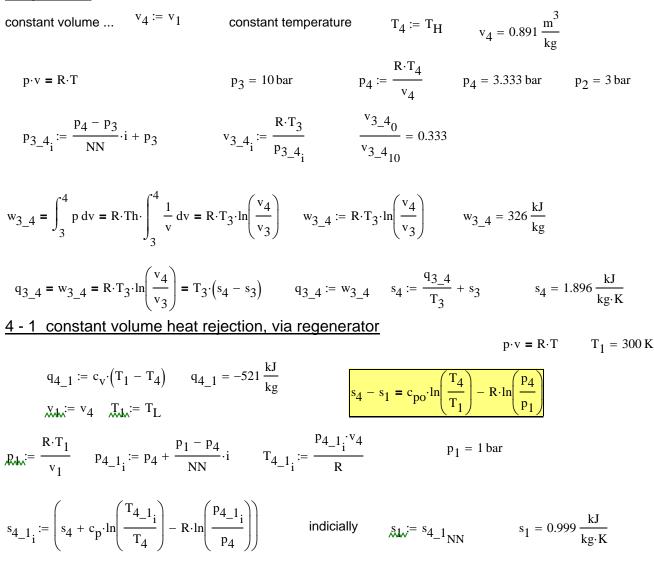
incremental for plots

$$p_{2_{3_{i}}} \coloneqq p_{2} + \frac{p_{3} - p_{2}}{NN} \cdot i \quad T_{2_{3_{i}}} \coloneqq \frac{p_{2_{3_{i}} \cdot v_{2}}}{R} s_{2_{3_{i}}} \coloneqq \left(s_{2} + c_{v} \cdot \ln\left(\frac{T_{2_{3_{i}}}}{T_{2}}\right)\right) \text{ indicially } s_{3} \coloneqq s_{2_{3_{NN}}} s_{3} = 1.57 \frac{kJ}{kg \cdot K}$$

$$\textcircled{Point 2 - 3}$$

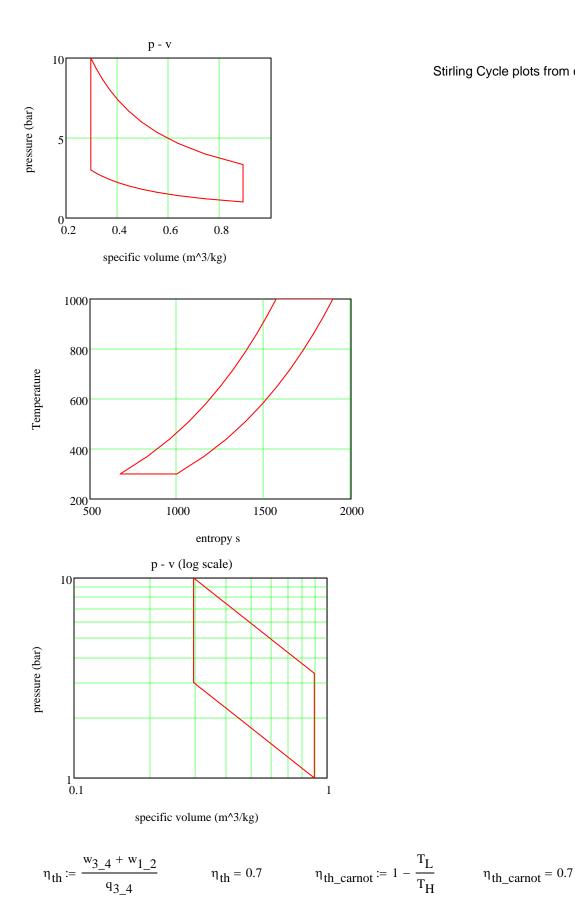
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3 - 4 (+) work done by fluid; expansion at constant internal energy, heat addition; at constant temperature



here could have used cv relationship as well. both are consistent as the area will show

set up plot



Stirling Cycle plots from calculations

from combustion.mcd

this is on a stochiometric basis (mole basis- i.e. 1 mole of $C_{12}H_{26}$ combines with 18.5 moles of O_2 etc.) or volume basis to convert to weight use molecular weights

$$C_{12} \cdot H_{26} + 18.5 \cdot O_2 + 69.6 \cdot N_2 = 13 \cdot H_2 \cdot O + 12 \cdot C \cdot O_2 + 69.6 \cdot N_2 + heat$$

$$mw_O2 := 32 \frac{kg}{kmol} \qquad mw_C12_H26 := (144 + 26) \cdot \frac{kg}{kmol} \frac{mw_N2}{kmol} := 28 \frac{kg}{kmol}$$

 $mw_H2_O := (2 + 16) \cdot \frac{kg}{kmol} \quad mw_C_O2 := (12 + 32) \cdot \frac{kg}{kmol}$

 $1 \text{ kmol } \text{C}_{12} \cdot \text{H}_{26} + 18.5 \cdot \text{ kmol } \cdot \text{O}_2 + 69.6 \cdot \text{ kmol } \cdot \text{N}_2 = 13 \cdot \text{ kmol } \cdot \text{H}_2 \cdot \text{O} + 12 \text{ kmol } \cdot \text{C} \cdot \text{O}_2 + 69.6 \text{ kmol } \cdot \text{N}_2 + \text{LHV}$

$$\left(\frac{1 \text{kmol} \cdot \text{mw}_{\text{C}12} \text{H26}}{170} \text{C}_{12} \cdot \text{H}_{26} \dots \right) = \left(\frac{13 \cdot \text{mw}_{\text{H}2} \text{O}}{170} \cdot \text{kmol} \cdot \text{H}_{2} \cdot \text{O} \dots \right) + \text{LHV}$$
 this is divided by 170 - the molecular weight of C₁₂H₂₆ to express on a per 1 kg fuel basis $\left(\frac{12 \text{kmol} \cdot \text{mw}_{\text{C}} \text{O}_{2}}{170} \cdot \text{C} \cdot \text{O}_{2} \dots \right) + \frac{69.6 \cdot \text{kmol} \cdot \text{mw}_{\text{N}2}}{170} \cdot \text{N}_{2}$ (1kmol) $\cdot \text{mw}_{\text{C}} \text{C}_{12} \text{H26} = 170 \text{ kg}$

▶ for symbolic calculation

result is ... combustion of $C_{12}H_{26}$ by weight ...

 $1 \text{kg} \cdot \text{C}_{12} \cdot \text{H}_{26} + 3.48 \cdot \text{kg} \cdot \text{O}_2 + 11.46 \cdot \text{kg} \cdot \text{N}_2 = 1.38 \cdot \text{kg} \cdot \text{H}_2 \cdot \text{O} + 3.11 \cdot \text{kg} \cdot \text{C} \cdot \text{O}_2 + 11.46 \cdot \text{kg} \cdot \text{N}_2 + \text{heat} \cdot \text{Kg} \cdot \text{H}_2 \cdot \text{O} + 3.11 \cdot \text{kg} \cdot \text{C} \cdot \text{O}_2 + 11.46 \cdot \text{kg} \cdot \text{N}_2 + \text{heat} \cdot \text{Kg} \cdot \text{Kg}$

weight of air : weight of fuel = air-fuel ratio

power := 10000kW

$$\eta = \frac{kW}{m_{f_dot} \cdot LHV} \qquad \text{sfc} = \frac{m_{f_dot}}{kW}$$
$$LHV := 43000 \frac{kJ}{kg} \qquad m_{f_dot} := 1 \frac{kg}{s}$$

$$\eta := \frac{\text{power}}{\text{m}_{f_dot} \cdot \text{LHV}} \qquad \qquad \eta = 0.233 \qquad \text{sfc} := \frac{\text{m}_{f_dot}}{\text{kW}} \qquad \text{sfc} = 3.6 \times 10^3 \frac{\text{kg}}{\text{kW} \cdot \text{hr}}$$