The Evaluation of the Oxycombustion for Power Cycles

GHEORGHE DUMITRASCU

Engineering Thermodynamics, Thermal Machines, and Refrigeration Department
"Gh. Asachi" Technical University of Iasi,
Blvd. D. Mangeron, 59–61, 700050-Iasi,
ROMANIA

Abstract: The sustainable energy systems require zero emissions into environment. The main emission's component is CO2 that contributes mainly to the global warming. The goal of zero emissions follows two ways: reduction of carbon intensity factor, e.g. Clear Sky initiative in USA, and the capture of CO2, respectively the European move towards. On a global scale, the growth of population will lead to expansion of needs that will cause an increasing impact on environment by exhausting consume of resources, and raw materials, accompanied by a much more use of energy and these will ruin intensively the environment by harmful emissions. The CO2 capture from fossil fuelled power plants is technically feasible, but it nevertheless remains to find viable solutions for actual retrofitted or new large-scale power generation systems, workable economically and environmentally. The paper seeks to evaluate the cycles based on atmospheric/pressurised oxy-combustion in recycled/rich CO2 medium, that have the benefit to use the high efficient combined cycle technology. The oxy-combustion has the advantage to supply a very rich in CO2 exhaust flue gases stream, allowing consequently a more effectual CO2 capture&sequestration. Power plant processes based on pressurised oxy-combustion, producing enriched CO_2 flue gas ready for disposal, are neither demonstrated on a pilot scale nor have the necessary components tested out in semi-technical or pilot plants. Investigations by the IEA GHG programme have estimated cost, efficiency and emission data for various types of power stations, including both current and future technology providing representative base cases for studies of CO_2 capture and storage. According to this study, power plant process options with CO_2 capture are: -conventional power plants with chemical CO_2 scrubbing of the atmospheric flue gas; -integrated oxygen/steam-blown gasification of fossil fuel and combined cycle (IGCC) plants with CO shift and separation of CO_2 and H_2 before combustion; -combustion/gasification of fossil fuel (especially coal) in an atmosphere of pure oxygen and recycled CO_2. The probability of further technical research and developments in each of the main types of plant has also been examined. This paper evaluates the oxy-combustion processes in recycled/rich CO2 medium.

Keywords: oxy-combustion based power cycle evaluation, first laws efficiencies

1 Introduction

In the field of the design of new co–generation energy plants and of optimization of existing ones, there has been a substantial effort dedicated to the repowering techniques, new fuels, renewable and recovered energy, new suitable working fluids, second law optimization, modelling, and simulation, study of technical solutions to diminish the non – desired operating influences. The co–generation systems that combine a gas turbine engine to a steam engine are very sensitive to the intake state parameters of the ambient air. The convenient operation mode must assure a constant power output at constant rpm. This paper performs an evaluation of the oxy-combustion process in recycled/rich CO2 streams.

At present, it is almost impossible to decide which technologies of CO_2 capture & sequestration are applicable to large power plants for the future. Taking all known facts into account, it appears to be a promising solution to use pure oxygen instead of air, either to produce H_2 by gasification or for a direct combustion

process. The arrangement of power generation systems might be foreseeable for the next future, and it is obvious that there still stay behind a larger contribution of fossil fuels. Noticeably, to meet the demands for a cut in CO_2 emissions, on one hand it becomes necessary to raise the overall efficiency of power generation processes and on the other hand to settle proper procedures for CO_2 capture. Besides coal and natural gas, oil plays a minor role for power generation in the countries of the EU, therefore in diminishing the CO_2 the researches should focus on coal and natural gas. Table 1 shows an overview of process principles for fossil fuelled power generation with low CO_2 emissions. The table includes combustion (1a) as well as gasification processes (1b) at atmospheric or higher pressure, subject of CASTOR and *ENCAP EC-Projects.*

The targets are: -to identify the "best scheme" for high efficiency oxycombustion-based power plants for CO_2 capture; -to develop and pre-design prototypes of critical components and to test them; -to analyse the feasibility

of the concepts at large scale; to develop advanced engineered CO_2 capture options

Table 1: Overview of process principles for CO_2-reduced power generation from fossil fuels

a: Processes based on Combustion

with air		with O₂ and recycled CO₂
atmospheric	pressurised	*atmospheric*
		Air separation
CO₂	*CO₂*	*(O₂ separation*
Flue gas scrubbing	Flue gas scrubbing	*by membranes)*

b: Processes based on Gasification

with air		with pure O₂		with O₂ and recycled CO₂	
atmospheric	pressurised	atmospheric	*pressurised*	atmospheric	pressurised
		CO-shift	*CO-shift*	Air separation	Air separation
CO₂ flue gas scrubbing	CO₂ flue gas scrubbing	CO₂/H₂ separation	*CO₂/H₂ separation*	(O₂ separation by membranes)	(O₂ separation by membranes)
		utilizable with fuel cells	*utilizable with fuel cells*	utilizable with fuel cells	utilizable with fuel cells

2 Thermodynamic Processes

The studied scheme of the air/oxygen – flue gases paths is represented in Figure 1. The thermodynamic processes considered are: 0→1 oxygen–air mixing, 1→2 flue gases (air–oxygen) mixing, 2→3 adiabatic compression, 3→4 combustion, 4→5 adiabatic expansion, 5→6 exhaust heat use.
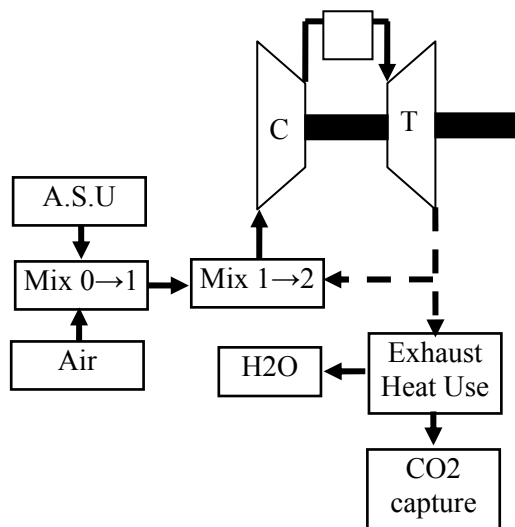

Fig. 1. The path flow scheme

The employed restrictive conditions are:
- compression ratio 10 to 30;
- environmental parameters $p_0 \approx 1$ bar, $T_0 = 288$ K
- combustion temperature 1200^0C
- isentropic efficiencies, 0.88/compression and 0.94/expansion
- combustion efficiency 0.97
- combustion pressure drop coefficient 0.98

- mechanical efficiency 0.98
- fuel composition, 15% H_2 and 85%C

The numerical code, OXYCOM-TUI, was computed in MATHLAB and consists of modules:
- MC – compute the mixing process,
- COMP – compute the adiabatic compression considering variable heat capacities and adiabatic exponents as ratio of enthalpy to internal energy variations,
- COMB+ – compute the combustion process in a sequential logical scheme, respectively a combustion without dissociation followed by a dissociation of resulting flue gases,
- TURB – compute the adiabatic expansion considering both the variable heat capacities and adiabatic exponents as ratio of enthalpy to internal energy variations, and the dependence of the dissociation degree function of the temperature and pressure,
- BOIL – compute the exhaust heat use considering both the variable heat capacities, and the condensation of water vapor below dew point, and the dissociation degree function of the temperature and pressure
- PERFOPT – compute the performance criteria (e.g.: first and second law efficiencies, entropy generation by irreversibility) and builds the numerical results matrices used in optimization.

The dissociation process was analyzed by the intermediary of chemical equilibrium constants of selected primary and secondary dissociation reactions.

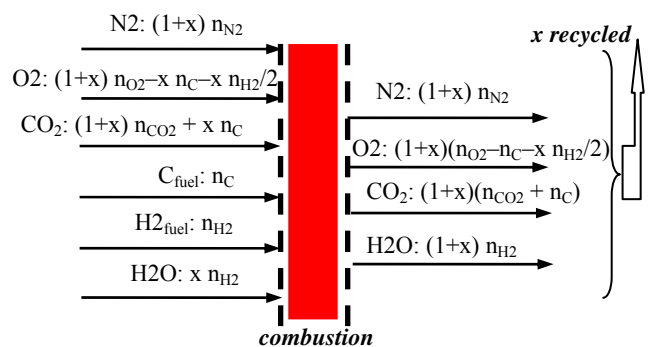The combustion mass flow balance scheme is showed in Figure 2.

Fig. 2. The combustion mass flow balance
n – kmol's number; x the recycled flue gases fraction

2.1 Main Basic Equations
- **saturation pressure of the water vapor:**

$$\log p_{VS}(T) = -\frac{1}{T}A_1 + A_2 + TA_3 + T^2A_4 + T^3A_5 \quad (1)$$

The coefficients A_i, for the fixed range of temperatures, were found by Gauss technique.

- **composition of humid gases:**

$$xv = \frac{H_2O \; kmoles}{dry \; gases \; kmole} = \frac{\phi p_{VS}(T)}{p - \phi p_{VS}(T)} = \frac{r_V p}{p - r_V p} \quad (2)$$

- **enthalpy of humid gases:**

for processes without dissociation

$$h_n = \left(\sum_i r_i \int_{T_0}^{T} c_{p,i} dT \right)_{\substack{dry \\ gases}} + xv \left(L_0 + \int_{T_0}^{T} c_{p,V} dT \right) \quad (3)$$

4th order polynomials were used for c_p

for processes with dissociation

$$h_n^d = \sum_j \left[n_j \left(h_{f,j}^0 + \int_{T_0}^{T} c_{p,j} dT \right) \right]_{gas}^d \quad (4)$$

The N_2 mole fraction made the equivalence of units.

- **entropy of humid gases at equilibrium:**

$$s = \sum_i \left(r_i \int_{T_0}^{T} c_{p,i} \frac{dT}{T} \right)_{\substack{dry \\ gases}} - R \log \frac{p(1 - r_V)}{p_0(T_0)} + $$
$$+ xv \left(\frac{L_0}{T_0} + \int_{T_0}^{T} c_{p,V} \frac{dT}{T} - R \log \frac{r_V p}{p_{VS}(T_0)} \right) \quad (5)$$

The "0" state $(s = 0)$ is defined by:
$p_0 = 1 bar$, $T_0 = 273.15K$ for dry gases,
$p_{VS}(T_0) = 610.8 \; Pa$ and $T_0 = 273.15K$ for H_2O vapor.

- **density of humid air or gases at equilibrium**

$$\rho = M \frac{p}{RT} \quad (6)$$

2.2. Calculation of processes without dissociation

Mixing of humid gases and oxygen, (supposed to be isobaric and isothermal):

$$\left(0.21 + n_{O_2}^{inj} \right) M_{O_2} + 0.79 M_{N_2} = $$
$$= r_{O_2}^{dry \; gases} M_{O_2} + \left(1 - r_{O_2}^{dry \; gases} \right) M_{N_2} \quad (7)$$

where $n_{O_2}^{inj}$ is the number of kmoles of oxygen injected into 1 kmole of dry air. Equation (7) reflects the mass conservation law and allows the calculation of $n_{O_2}^{inj}$.

Remember that ϕ and x remain constant since the absolute pressure and temperature of the gaseous mixture remain unchanged. By knowing the composition, the pressure, and the temperature in state 1, we use Eqs. (2)–(6).

Adiabatic processes

reversible adiabatic process:

$$\left[s_n(T, r_i, xv) \right]_{in} = \left[s_n(T, r_i, xv) \right]_{out} \quad (8)$$

The unknown temperature T_{out} is calculated by using the Newton-Raphson technique. Constant humidity and dry gas composition are assumed. The theoretical output parameters are obtained on the basis of the final composition, pressure and temperature.

irreversible adiabatic process:

The final state of the irreversible adiabatic compression results as:

$$\eta_s = \frac{\left(h_n^{out} - h_n^{in} \right)_{rev}}{\left(h_n^{out} - h_n^{in} \right)_{irrev}} \Rightarrow$$
$$\Rightarrow \left(h_n^{out} \right)_{irrev} = \left(h_n^{in} \right)_{irrev} + \frac{\left(h_n^{out} - h_n^{in} \right)_{rev}}{\eta_s} \quad (9)$$

The temperature of the final state is calculated using the Newton-Raphson technique. Assuming once again the constant humidity and constant composition of the dry gases and knowing the enthalpy of the final state, the other parameters can be calculated. In addition, the mean adiabatic exponent is calculated on the basis of the reversible adiabatic equation of the ideal gas (knowing the initial and final pressures and temperatures) as the ratio of enthalpy to internal energy variations.

Heating / Cooling

The calculation implies firstly the determination of final enthalpy and subsequently, by a trial and error method the finding of final dew point and the final humidity, knowing that (r_i) of dry gases remain constant. In this calculus, we get final temperature and composition.

3 Combustion Calculus

Characteristics of the liquid fuel:

$n_C = 0.85 \; kg \; C/kg \; fuel$,
$n_H = 0.15 \; kg \; H_2/kg \; fuel$,
higher heating value $H_s = 46000 \; kJ/kg$

3.1 Classical Combustion Calculus

The classical combustion equations are employed, yielding the products as

$$n_{CO_2}^{fg} = n_{CO_2}^{combustion} \quad [kmole \; CO_2/kg \; fuel] \quad (10)$$

$$n_{H_2O}^{fg} = n_{H_2O}^{combustion} + n_{H_2O}^{recycled}$$
$$[kmole \; H_2O/kg \; fuel] \quad (11)$$

3.2 The Adiabatic Flame Temperature

In order to calculate the adiabatic flame temperature, a heat balance equation that describes the energy transfer within the ideal combustion chamber. The compressed

combustion humid gaseous mixture, and the liquid fuel, enter the fictitious combustor, where takes place the combustion without dissociation. After this combustion, the flue gases dissociate within a fictitious dissociation cell and leave it with the adiabatic temperature. The heat balance is:

$$H_s + \sum_i \left(n_i \int_{T_0}^{T_2} c_{p,i} dT \right)_{dry} = \sum_j \left(n_j \int_{T_0}^{T_{fg}} c_{p,j} dT \right)_{fg} + xL_0 \quad (12)$$

where $\sum_i \left(n_i \int_{T_0}^{T_2} c_{p,i} dT \right)_{dry}$ and $\sum_j \left(n_j \int_{T_0}^{T_{fg}} c_{p,j} dT \right)_{fg}$

are the sensible enthalpies of the dry mixture entering and of the flue gases that exit the ideal combustor respectively. Thus, since Eq. (12) is function of the unknown temperature T_{fg}, the solutions of this equation has been determined by the Newton-Raphson technique, the imposed error for the difference between two successive values of the iteration being 0.1 K.

3.3. Combustion Calculation with Dissociation

The products of the ideal combustion reactions can dissociate due to the high combustion temperatures. The products of the dissociation reactions dissociate themselves, leading to a chain of dissociation reactions. Only the most important reactions were considered, divided into primary reactions and secondary reactions (in which some products of the primary reactions participate among the reactants).
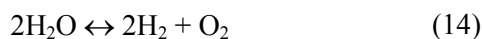
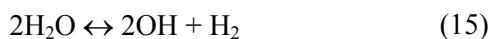### Primary Dissociation Reactions

Dissociation of CO_2

$$2CO_2 \leftrightarrow 2CO + O_2 \quad (13)$$
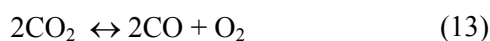
Dissociation of H_2O
Dissociation in hydrogen and oxygen:

$$2H_2O \leftrightarrow 2H_2 + O_2 \quad (14)$$

Dissociation in hydroxyl and hydrogen:

$$2H_2O \leftrightarrow 2OH + H_2 \quad (15)$$

Dissociation of N_2

$$2N_2 \leftrightarrow 2N \quad (16)$$

Secondary Dissociation Reactions

Dissociation of O_2

$$2O_2 \leftrightarrow 2O \quad (17)$$

Combination of N_2 and O_2

$$O2 + N2 \leftrightarrow 2NO \quad (18)$$
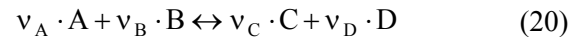
Dissociation of H_2

$$2H_2 \leftrightarrow 2H \quad (19)$$

The fraction of the reactants converted into dissociated products can be calculated from the relations of the kinetic constants of the reactions, which are determined from tables as a function of the temperature.

Calculation of the Dissociated Fractions

The general expression of a chemical reaction is:

$$\nu_A \cdot A + \nu_B \cdot B \leftrightarrow \nu_C \cdot C + \nu_D \cdot D \quad (20)$$

The reaction take place in both directions and the "control" of its direction and "intensity" is exerted by the temperature-dependent equilibrium constant K, whose expression is:

$$K = K_0 \left(\frac{p}{p_0} \right)^{\nu_C + \nu_D - \nu_A - \nu_B} = \frac{z_C^{\nu_C} \cdot z_D^{\nu_D}}{z_A^{\nu_A} \cdot z_B^{\nu_B}} \left(\frac{p}{p_0} \right)^{\nu_C + \nu_D - \nu_A - \nu_B} \quad (21)$$

The procedure used in the calculation of the dissociation fractions for the considered reactions consists of the derivation of the general expressions of the equilibrium constants for each equation in simplified expressions. These simplified expressions are necessary since the dissociation reactions take place simultaneously, and the solution of the resulting non-linear system of equations is very difficult to obtain. Consequently a trial-and-error iterative method is employed. The first step uses the simplified expressions to calculate the initial dissociation fractions, which are utilized as start values for the iterative technique that provides the final values by means of the general expressions. The calculation process implies information over the temperature-dependence of the equilibrium constants. The tabulated values of K_0 were interpolated by polynomials.

3.4. Calculation of the Flue Gases Temperature after Dissociation

The heat capacities in the heat balance equation used to determine the flue gases temperature after dissociation are temperature-dependent, thus leading to a composite equation in terms of temperature (for the heat capacities of O, H, and N, the constant value 20.7845 [kJ/kmole K] is assumed). In such cases, one has to follow one of the two paths:

- a trial-and-error technique is used,
- a numerical method for the transcendental equations roots has to be applied.

The second way is employed here, by using the Newton-Raphson technique. The outcome of the procedure described above is the flue gases temperature of the flue gases after dissociation and the flue gases composition $(n_k)_{fg}$, which depends on final temperature.

4 Numerical Results

Figures 3 and 4 show the first law efficiencies for the path flows without recycled flue gases.
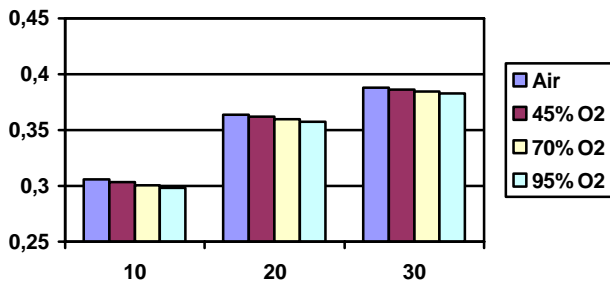

Fig. 3. The first law efficiency of the gas turbine engine function of the compression ratio
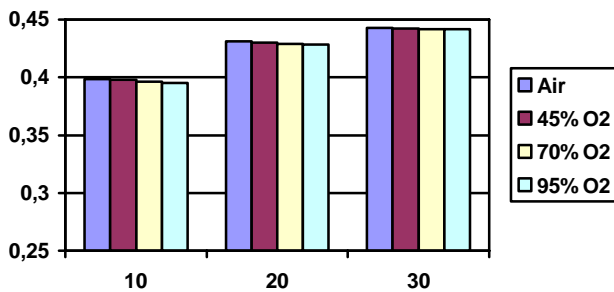

Fig. 4. The first law efficiency of the combined cycle, function of the compression ratio, supposing that the exhaust heat is used in a Rankine cycle having a second law efficiency of about 50%

5 Conclusions

The use of the oxy-combustion in a contemporary gas turbine cycle does provide a first law efficiency higher than those obtained currently for air-based combustion. The paper concisely presents a numerical code useful in evaluation of simple or combined cycle based on oxy-combustion. The numerical results are arguable because this work is a first step in analyzing and optimizing such cycles. This step took into account only the complete development of the numerical code in order to apply it to advanced energy systems using oxy-combustion. Similar calculations made for the so called humid gas turbine engines (using the cooling by adiabatic humidification between compression stages and the injection of water during or after the combustion process) can achieve larger first law efficiencies.

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Nomenclature

c_p mole heat capacity (kJ/kmole K)
h_f^0 enthalpy of formation (kJ/kmole)
h mole enthalpy (kJ/kmole)
H_s higher heating value (kJ/kg fuel)
K equilibrium constant of chemical reaction
L_0 water mole latent heat at 0^oC (kJ/kmole)
M Mass per mole (kg/kmole)
n number of kmoles
p pressure
p_0 standard state pressure (N/m^2)
r mole fraction
R universal constant of ideal gases
s_n mole entropy (kJ/kmole K)
T temperature (K)
T_0 standard state temperature (K)
xv mole humidity (kmole/kmole dry gases)

Greek symbols
η isentropic efficiency
ν stoichiometric coefficient
ρ density (kg/m^3)
ϕ relative humidity

Subscripts
fg   flue gases
V   water vapor in air

Superscripts
d   dissociated
fg   flue gases

Abbreviations
C   compression stage
T   turbine