Thermodynamic investigation of a new type highly effective gas turbine operating partially at isothermal expansion

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The greatest shortcoming of a gas turbine is that to decrease its inlet temperature, the burning chamber operates with a large excess of air which significantly reduces the efficiency. This work presents the solving of the problem by operating in the burner with lack of air and adding the rest of it, up to the stoichiometric value, thought the internals' cooling channels of the first part of the turbine. This ensures significant increasing of the efficiency and prevention of NO_x emissions.

1. Introduction

The greatest shortcoming of a gas turbine is that to decrease the inlet temperature up to 1200- 1300°C, the burning chamber works with a large excess of air. That is why the compressor which ensures this excess consumes about 2/3 of the energy produced by the turbine. To reduce this shortcoming the overstoichiometric air excess is changed partially (Perkawvec, 1997) or practically fully (Kolev et al. 1997, 2001) with steam. The mechanical efficiency of such a steam injected gas turbine reaches up to 53.5%. (Kolev et al. 2001, 2003). Another possibility to regulate the temperature after the burner is to operate in it at lack of oxygen and to feed the rest of the air, up to the stoichiometric quantity, trough the cooling channels of the turbine internals ensuring a regime close to the isothermal (Kolev and Kolev, 2003), which leads to significant increasing of the turbine efficiency. The aim of this paper is to present some results from the first thermodynamic investigations of a gas turbine able to operate at these conditions. It must be mentioned that half a year after the patent (Kolev and Kolev, 2003) the same idea was presented in a report of US scientists (Bachovchin et al., 2004).

2. Principle of the new cycle

According to Kolev and Kolev (2003) the steam from the boiler after the turbine or a part of it is fed in the burner together with the fuel. The reactions which take place at these conditions are as follows (Guide of nitrogen compounds production, 1986):

$$CH_4 + 2O_2 = CO_2 + 2H_2O + 803712 \text{ kJ/kmol methane}$$
 (1)

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$CH_4 + 1.5O_2 = CO + 2H_2O + 520000 \text{ kJ/kmol methane}$	(2)
$CH_4 + 0.5O_2 = CO + 2H_2 + 35590 \text{ kJ/kmol methane}$	(3)
$CH_4 + H_2O = CO + 3H_2 - 206410 \text{ kJ/kmol methane}$	(4)
$CH_4 + CO_2 = 2CO + 2H_2 - 248280 \text{ kJ/kmol methane}$	(5)
$CH_4 = C + 2H_2 - q$	(6)
CO+H ₂ O=CO ₂ +H ₂ + 41000 kJ/kmol CO	(7)
2CO=C+CO ₂ +172500 kJ/katom carbon	(8)
CO + H ₂ =C+H ₂ O +131300 kJ/kmol CO	(9)
CO=C+O-q	(10)
O_2 =2O -q	(11)

In the above presented reactions the lower calorific effect is given in the Guide of nitrogen compounds production (1986). The higher calorific effects which include the condensation heat of water vapors obtained by burning are necessary for the thermodynamic calculations. The conditions preventing from plugging with soot, that is when no carbon black is generated, are discussed and determined (paragraph 3.2.). The chemical reactions in the isothermal part of the turbine are as follows:

$$2CO + O_2 = CO_2 + 565650 \text{ kJ/kmol } O_2$$
 (12)

$$2H_2 + O_2 = 2H_2O + 574000 \text{ kJ/kmol } O_2.$$
 (13)

The main quantities of CO and H₂ are burning practically isothermally. Their traces left burn adiabatically at a temperature about 900°C after preliminary adiabatic expansion and cooling by feeding steam instead of air in the cooling channels. The purpose is to prevent the synthesis of NO_x, which needs higher temperature and air excess simultaneously. Besides the elimination of the NO_x emissions, the described operation regime has also the following advantages. The strong cooling of the burning chamber because of the endothermic reactions (4) and (5) gives principally the possibility to use pure oxygen instead of air and to obtain pure CO₂ working without recirculation of CO₂ or with quite less recirculation than in the case of Graz cycle (Jericha et al., 1998). When using pure oxygen, the main component of the flue gases is steam. That is why it is possible to cool the gases in a contact economizer operating as vacuum condenser, and thus to operate at lower initial pressure, or at lower temperature of the gas-steam mix. The utilized heat in the contact economizer system can be also used for district heating purpose. The optimal operation conditions of the installation can be found only by thermodynamic investigation. In the present paper only the using of air as oxidant and feeding in the burning chamber of all the steam obtained in the boiler of the installation are investigated. Because the obtaining of carbon black depends on the concentrations of water vapors and CO₂, the possibility to have problems with it can be investigated only after determination of the gas composition.

3. Thermodynamic calculations

The thermodynamic calculations include the following:

- 1. Calculation of the concentrations of the components of the gas leaving the burning chamber as a function of the temperature, pressure, and steam to methane ratio (G_{st}) . The coefficient of air excess λ at these conditions is strongly limited by the heat balance.
- 2. Thermodynamic control of the possibility for building of carbon black.
- 3. Calculation of the thermodynamic efficiency of the installation.

3.1 Calculation of the concentrations of the components of the gases leaving the burning chamber

The problem in calculation of the coefficient of air excess λ in the burning chamber to obtain a given burning temperature is connected with the fact that the thermal effects of the reactions (1-5) and (7) are different and the part of the methane, reacting according to any of these reactions, is not preliminary known. Because the burning temperature is high enough to consider the reaction rates as infinite, the concentrations of the components after the reaction and from here the total thermal effect can be calculated based on the equilibrium of the system. The first reaction is not reversible. The equilibrium coefficients of the other reactions at 1500 K taken from Chemist Guide (1964), p.19-54, are presented in Tab. 1, where P_{CH_4} , P_{H_2O} , P_{CO_2} , P_{CO} , P_{O_2} , P_{H_2} , are the partial pressures of the corresponding components, equal to the product of the absolute pressure P and the corresponding molar concentrations of the components: C_{CH_4} , C_{H_2O} , C_{CO_2} , C_{CO} , C_{O_2} and C_{H_2} . Equations (1-5) and (7) consist of 6 components. The same number of values of partial pressures is included in the respective equations for their equilibrium constants. That means, to determine the necessary concentrations, respectively the necessary partial pressures, two addition equations are necessary. At all initial values of G_{SD} , which are practically important because of the very small values of the equilibrium constants of equations (2-5), the concentration of CH₄ in the gas mix after the reactions can be neglected in the heat and mass balance. On the same base the concentration of the oxygen is also negligible. That is the number of the components which are important for the energy balance of the process is equal to 4. These equations are as follows:

- 1. Equation for K_{p7}
- 2. Balance equation for the carbon containing compounds:

$$G_{0,CH_4} = G_{CO} + G_{CO_2} (14)$$

3. Balance equation for the water vapor:

Table 1

reaction	chemical reaction	equilibrium constant	equilibrium
No			constant at 1500 K
2	$CH_4 + 1.5O_2 = CO + 2H_2O$	$K_{p2} = \frac{P_{CH_4} P_{O_2}^{1.5}}{P_{CO} P_{H_2O}^2}$	
3	$CH_4 + 0.5O_2 = CO + 2H_2$	$K_{p3} = \frac{P_{CH_4} P_{O_2}^{0.5}}{P_{CO} P_{H_2}^2}$	8.15×10^{-12}
4	$CH_4 + H_2O = CO + 3H_2$	$K_{p4} = \frac{P_{CH_4} P_{H_2O}}{P_{CO} P_{H_2}^3}$	4.35x10 ⁻⁶
5	$CH_4 + CO_2 = 2CO + 2H_2$	$K_{p5} = \frac{P_{CH_4} P_{CO_2}}{P_{CO}^2 P_{H_2}^2}$	1.61x10 ⁻⁶
7	$CO+H_2O = CO_2+H_2$	$K_{p7} = \frac{P_{CO}P_{H_2O}}{P_{CO_2}P_{H_2}}$	2.75

$$G_{H,O} = 2G_{0,H,O} + 2(G_{0,O_2} - G_{CO}/2 - G_{CO_2})$$
(15)

4. Balance equation for the hydrogen:

$$G_{H_2} = 2G_{0,CH_4} - 2(G_{0,O_2} - G_{CO} / 2 - G_{CO_2}),$$
(16)

where G_{H_2O} , G_{CO_2} , G_{CO} , G_{O_2} and G_{H_2} are the flowrates of the respective components in kmol/s; G_{0,CH_4} , G_{0,O_2} and G_{0,H_2O} -the respective initial flowrates of the components in the combustor. From the mass balance it follows that

$$G_{0,O_2} = 2\lambda G_{0,CH_4}$$
, (17)

where λ is coefficient of air excess, which in our case is smaller than 1. If G_s is the mol flowrate, equal to the sum of the mol flowrates of the gas components, the partial pressures of the components are as follows:

$$P_{CO} = P \frac{G_{CO}}{G_s}; \quad P_{CO_2} = P \frac{G_{CO_2}}{G_s}; \quad P_{H_2O} = P \frac{G_{H_2O}}{G_s}; \quad P_{H_2} = P \frac{G_{H_2}}{G_s}$$

It is easy to see from these equations and the equation for K_{p7} that

$$K_{p7} = \frac{G_{CO}G_{H_2O}}{G_{CO_2}G_{H_2}}. (18)$$

By substituting the values of G_{CO} , G_{H_2O} and G_{H_2} from equations (14) to (16) in equation (18) it is obtained:

$$K_{p7} = \frac{\left(G_{0,CH_4} - G_{CO_2}\right)\left(2G_{0,H_2O} + 2\left[G_{0,O_2} - \left(G_{0,CH_4} - G_{CO_2}\right)/2 - G_{CO_2}\right]\right)}{G_{CO_2}\left(2G_{0,CH_4} - 2\left[G_{0,O_2} - \left(G_{0,CH_4} - G_{CO_2}\right)/2 - G_{CO_2}\right]\right)},$$
(19)

or
$$AG_{CO_2} + BG_{CO_2}^2 + C = 0$$
, (20)

where
$$A = K_{p7} \left(3G_{0,CH_4} - 2G_{0,O_2} \right) + \left(2G_{0,H_20} + 2G_{0,O_2} - G_{0,CH_4} \right),$$
 (21)

$$B = K_{p7}, (22)$$

$$C = -2G_{0,CH_4} \left(G_{0,CH_2O} + G_{0,O_2} \right) - G_{0,CH_4}^2 . \tag{23}$$

The square equation (20) is easy to solve when the value of K_{p7} is known. The equations are significantly simplified if all flowrates in them are related to 1 mol methane. The value of K_{p7} at different temperatures between 700 and 2000 K can be calculated using the equation:

$$K_{p7} = 0.881 - 0.0049T + 6.073.10^{-6}T^2 - 1.322.10^{-9}T^3$$
(24)

obtained on the basis of the experimental data given in Chemist Guide (1964), p. 42. The maximal difference between the experimental and calculated data is 1.27% and the average one is 0.67%. The values of G_{CO} , G_{H_2O} , and G_{H_2} are easy to determine from equations (14) to (16). For calculation of the sum G_s , the sum G_i of the inert components N_2 and Ar is necessary. It can be obtained by means of the following equation:

$$G_i = G_{0,O_2}(1-0.21)/0.21,$$
 (25)

where 0.21 is the oxygen molar concentration in the air. As it follows from the equations given above, the composition of the mix is a function of the temperature of conversion and the initial flowrates of the methane, steam and air, respectively the

initial values of G_{st} and λ . The temperature on its side depends on the heat obtained and consumed by the reactions. This heat itself is a function of the composition. The complicated problems are solved iteratively.

3.2 Thermodynamic control of the possibility for soot formation

The second step of the thermodynamic calculations is the thermodynamic control of the possibility for formation of carbon black in the gases in the combustor. As already mentioned above, the carbon black can be obtained by the reactions (6), (8) and (9). Based on the second principle of thermodynamics and because of the extremely high temperature in the burning chamber, all reactions can be considered as instantaneous. All of these reactions give the same results about the conditions at which carbon black is formed. Because the necessary equilibrium data for the reaction (8) are easy to find (Guide of nitrogen compounds production, 1986) in the necessary temperature area (1200-1800 K), later the possibility for carbon black formation is determined considering this reaction. The equilibrium constant of the reaction is defined as

$$K_{p8} = \frac{P_{CO}^2}{P_{CO_2}} \,. \tag{26}$$

Using the data presented in Guide of nitrogen compounds production (1986) the following equation is obtained $K_{p8} = 10^{-8.8842 + 0.0121T - 2.7117 \times 10^{-6} T^2}$. (27)

Its average error is 2.54 % and its maximal one- 3 %. The partial pressures of CO and CO_2 at which no carbon black is obtained are determined by the inequality:

$$\frac{P_{CO}^2}{P_{CO_2}} < K_{p8} \,. \tag{28}$$

From expression (28) it can be obtained:

$$Sf = \frac{P_{CO}^2}{K_{p8}P_{CO_2}} < 1. {29}$$

The coefficient *Sf* is called later soot factor. From expressions (28) and (29) it is seen that at all values of this factor smaller than 1 no soot formation is possible. Later on all investigations of the turbine are carried out in the area where no soot is formed.

3.3 Calculation of the mechanical efficiency of the new turbine

The mechanical thermodynamic efficiency η_{GT} is calculated using the energy balance

$$\eta_{GT} = (q_h + Q_{air} + Q_{st} - Q_{fg} - Q_c - Q_p)/q_l, \tag{30}$$

where q_h and q_l are the higher and the lower calorific effects of the fuel; Q_{air} - the energy entering the installation with the inlet air in the compressor; Q_{sr} - the energy entering the engine with the steam from the boiler; Q_{fg} - the energy leaving the turbine with the flue gases; Q_c - the energy given up from the air to the water of the cooled stages of the turbine compressor; Q_p - the energy consumed by the pump for pumping the feed water from the contact economizer to the boiler. For the calculation the efficiency of the pumping installation is assumed 80%. The calculated values of the mechanical efficiency of the new turbine, determined by means of equation (30) at different initial pressures p_l and temperatures tt3, are presented in Fig. 1 (at internal efficiency 0.85). The results show that the reduction of the pressure in the investigated area leads to increasing of the efficiency, which at 30 bar and 1500 K is 75.9%. That is

it is about two times higher than the efficiency of the usual gas turbines, which is about 38.5% (Perkawvec, 1997). At these conditions the end temperature of the flue gases after the turbine is 1264 K, at initial pressure in the adiabatic part of the turbine 2.17 bar. That is why investigations at lower pressures are not carried out. The calculations for estimation of the effects of deviation from isothermality in the isothermal part of the turbine and heat losses show that they reduce the calculated efficiency in Fig.1 with not more than 2%. In the whole investigated area of pressures and temperatures $Sf < 7x10^{-3}$, that is no soot formation is possible.

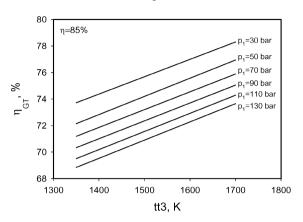


Figure 1. Mechanical efficiency of the new gas turbine at different initial pressures at internal efficiency 85% versus the inlet temperature of the gases.

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