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Gas Turbines for Polygeneration? A Thermodynamic Investigation of a Fuel Rich Gas Turbine Cycle

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Abstract

Gas turbines as used nowadays are working far in the fuel lean regime, which is most reasonable for mobile applications, since the formation of pollutants and soot are avoided while the temperatures remain low enough to avoid damage of the turbine. However, from a thermodynamic point of view the exergy utilization is far from optimum at such conditions. For stationary conditions a different approach may be worth a second thought: the use of gas turbines as chemical reactors for hydrogen and carbon monoxide production in combination with power generation and the utilization of the exhaust enthalpy stream. A gas turbine model cycle is analyzed using complex equilibria including radicals and chemical exergies. Chemical exergies were calculated from equilibrating the gas mixtures at different points in each process with a large excess of moist air. Methane was studied as an example fuel. Comparing the exergy losses of the idealized gas turbine process, the losses for fuel rich mixtures are lower than for lean mixtures used in gas turbines nowadays. The exact values of the exergetic efficiency depend on the pressure ratio, which was studied in the range of 10 to 30. The hydrogen to carbon monoxide ratio would be typically near 2.2, while the adiabatic flame temperature would be in a range which either would cause no damage to typical gas turbines or could be handled with carbon fiber reinforced carbon. The composition of the gases is likely to change within the turbine, where temperature and enthalpy drops. This was considered in additional calculations where chemical equilibration of the gas mixture in the turbine is considered. The possibility to combine a partial oxidation with an energy conversion process and thus produce syngas mixtures would add an additional flexibility to the gas turbine process, which is worth consideration.

Keywords: *Polygeneration; turbine; chemical exergy.*

1. Introduction

Most often the conversion of chemically stored energy into electrical or mechanical power is regarded separately from the chemical conversion of natural gas or crude oil to base chemicals. Two quite separated industries arise due to this and also two separated scientific communities exist which do not interact too strongly. However, it is clear that any conversion of some fuel to some more or less oxidized form is accompanied by some energy or temperature change, depending on the process parameters. This raises the question, whether a direct combination of the production of (base) chemicals, heat and power may be advantageous. Generally, the conversion of chemical energy (or better exergy) to mechanical power takes place either in piston/cylinder systems or in gas turbines. The latter shall be addressed in the present contribution.

Gas turbines are important devices used in stationary systems to convert the combustion enthalpy of a fuel into electrical power. In aeroplanes they are used as an engine so the propulsion is the aimed effect. The thermal efficiency of a gas turbine cycle is restricted by the upper temperature limit which can be used at the turbine entrance in order to avoid the degradation of the turbine materials, often steels or super alloys. In order to reduce the combustion temperature and prolong their lifetime, gas turbines are nowadays mainly run in a very lean combustion regime, aiming to hold both the gas phase temperatures and the surface temperatures low. This also has the side effect that the nitric oxide formation, which is strongly coupled to temperature, may be partially avoided. Similarly, soot formation is also of minor importance in the lean regime, while combustion instabilities may become an issue. Generally, the thermal efficiency can be increased significantly if the hot exhaust gases are used in combined gas and steam power plants.

Recently, Yamamoto et al. proposed a combined cycle where one of two gas turbines is run in a fuel rich mode, leading to increased total efficiency (Yamamoto, Lior, Furuhata, & Arai, 2007). One important idea behind this work was that carbon-fibre-reinforced-carbon composites (C/C) may be used as a construction material for turbines in the fuel rich regime, since they survive much higher temperatures in a reducing atmosphere as opposed to an oxidizing atmosphere where carbon would burn. A similar idea using a partial oxidation gas turbine with a subsequent catalytic reactor was discussed earlier by Heyen and Kalitventzeff (Heyen & Kalitventzeff, 1999), while recently Albrecht et al. (Albrecht, Kok, & van der Meer, 2007) proposed a favourable plant that integrates a partial oxidation reactor, a synthesis gas turbine and an air separation unit.

If we now regard the chemical conversion processes as used in the chemical industry, again fossil fuels like natural gas are the starting materials for the production of base

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chemicals like methanol, syngas (H_2/CO) or hydrogen. At the same time, the production processes often consume a considerable amount of exergy even though the reactions for their formation show that theoretically this would not be necessary. Thus, for example Jin et al. studied the possibilities of using several fuels for the simultaneous production of base chemicals and power (Jin, Han, & Gao, 2007; Jin, Sun, Han, & Gao, 2009), combining known processes in a rational but complex way. Polygeneration or multigeneration, as the production of several energetic products is mostly called, often is regarded as a kind of optimization process where existing technologies are combined in a more or less complex way (Chicco & Mancarefla, 2009; Liszka & Ziebik, 2009; Piacentino & Cardona, 2008). However, the possibility of having relatively simple processes capable of providing several useful products, including mechanical power, has to my knowledge not been studied yet. For stationary conditions a different approach may be worth a second thought: the use of gas turbines as chemical reactors for hydrogen and carbon monoxide production in combination with power generation and the utilization of the exhaust enthalpy stream. This would involve combustion processes which are run in an unusual mode. This way, the large knowledge of the scientific combustion community may be used, which includes large reaction mechanisms for combustion which were developed in the last decades, as well as the codes for calculating complex equilibria and complex kinetics.

The present thermodynamic investigation was performed as a starting point in order to see if simple gas turbine processes may be used in principle for the polygeneration of syngas and electrical power or shaft work, generally assuming that the exhaust gases are further used either for heating or for further energy conversion processes like a steam cycle. If a gas turbine cycle is used (also) as a chemical reactor, the properties of the gas mixture expanding in the turbine will be quite different from a typical lean exhaust gas mixture. Larger amounts of hydrogen and carbon monoxide will be present. Also, since the temperatures are generally quite high, chemical reactions may take place in the turbine while the gas mixture expands and due to this the chemical composition may change within the turbine. Due to the high temperatures, the equilibrium concentrations of atoms and radicals in the mixture may be substantial, which in turn influence temperatures and enthalpies. Thus, it appears to be most appropriate to analyze chemical equilibria consisting of the many species that are generally present in such high temperature environments. The equilibrium of a complex mixture can, as is well known, be evaluated by minimizing the free enthalpy. The chemical equilibrium calculation procedures used in the present work are well established and freely available (Goodwin, 2003). These can also be used to calculate chemical exergies according to their definition, as will be described in the modeling section.

In order to analyze a poly-generation gas turbine process, the chemical exergy flows are analyzed together with the energy flows as a function of different parameters. The main parameters were the fuel-to-air ratio, the pressure ratio and also the possibility of chemical equilibration in the turbine, while the temperature is reduced. Also, the possible carbon formation in this process will be discussed.

2. Modeling

2.1. Process description

The modeled process is depicted in Fig. 1. Methane is chosen as the fuel in this work, since it is the main constituent of natural gas and of biogas, thus representing the main features of both. The methane fuel and the air are compressed separately, mixed and burned in the combustor. The combustion products are expanded in the turbine. All steps are modeled as adiabatic processes for different stoichiometries, varying the air mass flow rate $\dot{m}_3$.

With regards to the compressors and the turbine two cases were calculated: First, both were assumed to work reversibly (which is later indicated as *rev*), this case indicates the thermodynamic optimum. As a second irreversible case, typical values for the isentropic efficiencies were assumed for both: 90% for the turbine and 75% for each compressor, this case will be indicated as (*irr*). Pressure losses in the lines or the combustor were neglected throughout.

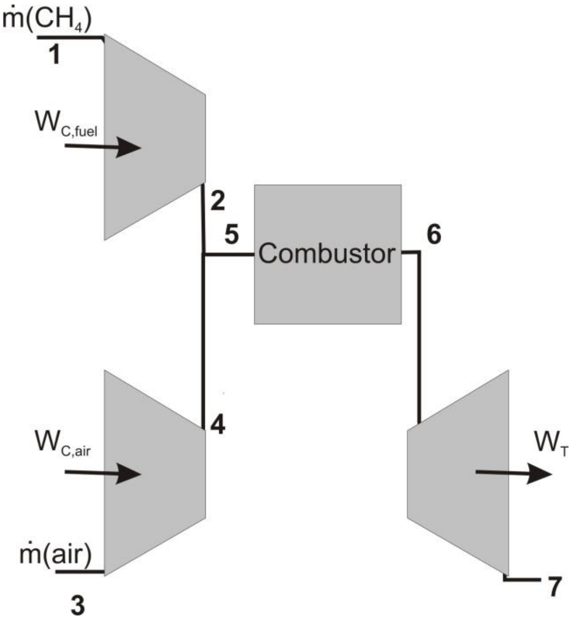

Figure 1. Schematic of the modeled process, all parts are assumed to be adiabatic.

2.2. Calculation of chemical equilibria and chemical exergies

All species and mixture properties were calculated using the Cantera library (Goodwin, 2003) within the Python programming language, which also provides procedures for equilibrating a multi-species gas phase mixture for two constant parameters like temperature and pressure (TP), enthalpy and pressure (HP) or entropy and pressure (SP) by minimizing the free enthalpy at constant elemental composition. In addition, the possibility of carbon (soot) formation was investigated by calculating a two-phase equilibrium, consisting of a complex ideal gas phase and a pure graphite solid phase. The thermodynamic data were taken from the established data base of the GRI 3.0 mechanism (Smith et al., 2000) and the gas phase was assumed to behave as a mixture of ideal gases. Within the GRI mechanism the thermodynamic (and kinetic) data of 53 species are tabulated. No assumptions regarding constant heat capacities were made, instead the NASA polynomials with 5 coefficients are used for a low and a high temperature range each. The program evaluates the enthalpies *h*, entropies *s* and further thermodynamic properties of a given mixture.

However, the calculation of (chemical) exergies had to be implemented. Pure air (mole fractions: O_2: 0.209421, N_2: 0.78084, Ar: 0.00934, CO_2: 0.00038, H_2O: 0.013) was taken as the dead state of the surrounding at 1.013 bar and 300 K, this appeared to be most reasonable for the present purpose. Chemical exergies could have been implemented by including a data base with exergies of the elements to the program and calculating the chemical exergy from the sum of those with the sum of the enthalpies of formation. However, this appeared to be too complicated, in the light of the available computers nowadays. Instead, to calculate exergies, it was deemed most appropriate and easiest to use the definition of exergy, which is just the maximum useful work which can be extracted if a given system is brought reversibly to equilibrium with the surroundings, while the surrounding (nearly) does not change its properties.

Thus, we start with 1 kg of the mixture of interest and a large excess of air (Index: *air*) of r kg. Then for each state the program calculates the initial enthalpy and entropy of the given mixture in a certain thermodynamic state (Index: *i*) and for the r kg of air and then equilibrates the mixture both chemically and reversibly (Index: *eq*). From the differences in enthalpy and entropy (meaning from the application of the first and second law of thermodynamics) the specific exergy *e* per kg of initial mixture is calculated:

$$e_i = \frac{E}{m_i} = \left[(r \cdot h_{air} + h_i) - (r+1) h_{eq} \right] \\ -T_0 \left[(r \cdot s_{air} + s_i) - (r+1) s_{eq} \right] \tag{1}$$

All work terms in the process were taken as pure exergy as usual. The remaining question is which value for *r* is appropriate, how large should the excess of air be chosen? If the value is too low the final composition will deviate substantially from the initial composition of the air, which has to be avoided, whilst if the *r* value is taken too large one can run into trouble with the accuracy of the computer, since tiny differences are calculated from huge numbers. This was studied systematically, and it was found that at values for *r* above 10^4 the calculated exergy per kg of initial mixture was no longer dependent on the exact value of *r*. An excess mass ratio of $r = 10^5$:1 gives excellent results as well as the required accuracy of better than 1:10^4, hence, this value for *r* was used throughout in the following. The procedure was checked for a few species such as methane and produced results very near to the values given in the literature e.g. 836.51 kJ/mol as given in (Kotas, 1995). The initial exergy of methane is evaluated here to be 51.86 MJ/kg (829.75 kJ/mol).

The specific properties as used here are always enthalpy per kg of the given mixture (either air, fuel or fuel/air) or the equilibrated state starting with 1 kg of fuel or fuel/air mixture and 10^5 kg of air.

After the separate adiabatic compression of methane (Figure 1: state 2) and air (state 4), an adiabatic mixing process was regarded (state 5), followed by an adiabatic isobaric chemical equilibration (state 6), which takes place in the combustion chamber. In state (6) the highest temperatures of the cycle are found. This equilibrated gas mixture was then expanded to ambient pressure isentropically in the turbine until state (7) is reached. Here, as said before, two cases were studied, first the chemical composition in the turbine was frozen and the isentropic state at ambient pressure was calculated. However, the temperatures are so high in most calculations that this can only be regarded as one thermodynamic limit with frozen chemistry. Therefore, a second calculation for the turbine was performed with chemical equilibration and constant entropy at ambient pressure, in order to examine the effect of chemical equilibration on the final composition. It was found that in some cases, this leads to considerable changes in the exhaust composition. The real state will be somewhere in between; this can only be evaluated using a kinetic model, some kinetic calculations for simple limiting cases were also performed and will be described later.

In order to evaluate the sensitivity of the investigated processes to irreversibilities in the turbine and the compressors, isentropic efficiencies of 90% and 75%, respectively, were assumed in a further series of calculations, which shall be detailed here. The states behind the compressors and the turbine were calculated the usual way. For the turbine, the exhaust enthalpy was calculated from the initial enthalpy of the entering fluid and the isentropic specific work $w_{t,s=const}$ times the isentropic efficiency:

$$h_7 = h_6 + w_{t,s=const} \eta_{s,T} \tag{2}$$

The isentropic work was calculated from the final enthalpy after equilibration at the given exhaust pressure and initial entropy. The state at this final enthalpy and pressure was recalculated for the non-isentropic case either with frozen composition or with equilibration, as described above. The calculations for the compressors w_c were similar, only the isentropic work was divided by the isentropic efficiency and constant compositions were assumed, because no chemical reactions should take place for the separated fuel or air at these moderate temperatures.

2.3 Efficiencies and yield

Exergetic efficiencies for the state behind the turbine were calculated from the sum of the absolute value of the net work (w_{net}) and the exergy at this state divided by the entering exergy of the fuel:

$$\xi_7 = \frac{|w_{net}| + e_7}{e_{fuel,1}} \tag{3}$$

This assumes that the exergy of state (7), consisting of chemical and thermal exergy, is used in following steps. For the other states, the input of the compressor work is taken as an exergy inflow:

$$\xi_i = \frac{e_i}{w_c + e_{fuel,1}} \tag{4}$$

Thermal efficiencies η were calculated from the absolute value of the net work output related to the specific enthalpy of combustion (lower heating value $\Delta_{r,CH_4} h^0$) of methane:

$$\eta = \frac{|w_{net}|}{\Delta_{r,CH_4} h^0} \tag{5}$$

In the diagrams, the ratio of actual mass flow of air to the mass flow of fuel relative to the stoichiometric value, called theoretical air, are shown as an independent variable:

$$\lambda = \frac{\dot{m}_{air} / \dot{m}_{fuel}}{\left(\dot{m}_{air} / \dot{m}_{fuel}\right)_{stoich}} \qquad (6)$$

For the comparison of the products hydrogen and carbon monoxide, the number of moles at a certain state were normalized by the number of moles of methane in the initial mixture (n(CH_4)$_5$) as present in state 5. This choice may be regarded as a kind of reaction yield and avoids misinterpretations of non-normalized mole fractions. These values were calculated using the mass fraction of methane at state 5 and the mass fraction (*y*) of species *i* at a certain state and converted to mole fractions with the molecular mass (*M*):

$$\frac{n_i}{n_{CH_4,5}} = \frac{y_i / M}{y_{CH_4,5} / M_{CH_4}} \qquad (7)$$

$M=m/n$ is the molecular mass of the mixture.

2.4. Kinetic calculations

From thermodynamics it cannot be decided if a chemical equilibration may take place in the turbine or not. However, the used GRI (3.0) mechanism already includes a validated chemical reaction mechanism for combustion conditions, so that at least some estimation of the extent of reaction was possible. Using the typical length of a gas turbine (L<2 m) and the typical flow velocities of several 100 m/s, the total reaction time within the turbine would be below 20 ms. In order to get an insight into the reaction time scales, a piston cylinder system was modeled in which the gas expands reversibly against a piston (atmospheric pressure on the outside) from the calculated initial state (6) to state (7) at ambient pressure within 20 ms. This expansion ensures a reasonable temporal profile of temperature and pressure in the system. A homogeneous gas was assumed and the temporal change of the gas species was calculated, in addition to the energy balance. The 20 ms can be regarded as an upper limit, if nothing happens after this time, also nothing should happen at shorter reaction times.

3. Results and Discussion

3.1. Overview: A Pressure ratio of 10

First the results for a pressure ratio ($\pi = p_1/p_2$) of 10 leading to a maximum pressure of 1.013 MPa shall be discussed, as shown in Figure 2. The λ values were varied in the range from 0.25 to 4. The adiabatic combustion temperatures (T_6) vary between 1090 and 2400K and are only slightly increased if some irreversibility of the compression process is included. It should be emphasized that these temperatures are resulting from the equilibrium calculation, and give an indication of the parameter range from a rich to a lean mixture, although the higher temperatures around stoichiometric conditions (λ=1) are not useful for practical applications. The difference between a reversible and an irreversible compression gets more pronounced with increasing λ, since more air has to be compressed per kg of methane and thus the efficiency of the process becomes more sensitive to the irreversibility of the compression stage.

The same trend is also seen for the temperature T_7 behind the turbine, which is higher for an irreversible turbine. The difference between both is of the order of 100-200 K. If chemical equilibration in the turbine is included (for the reversible case), the temperatures differ only at small λ values, because the gas mixture forms more CO_2 instead of CO in this regime, leading to a higher temperature at a given enthalpy. It should be remembered that all species mole fractions were related to the initial methane mole fraction in the mixture, state 5, so the given numbers can be understood as a yield per mole of methane.

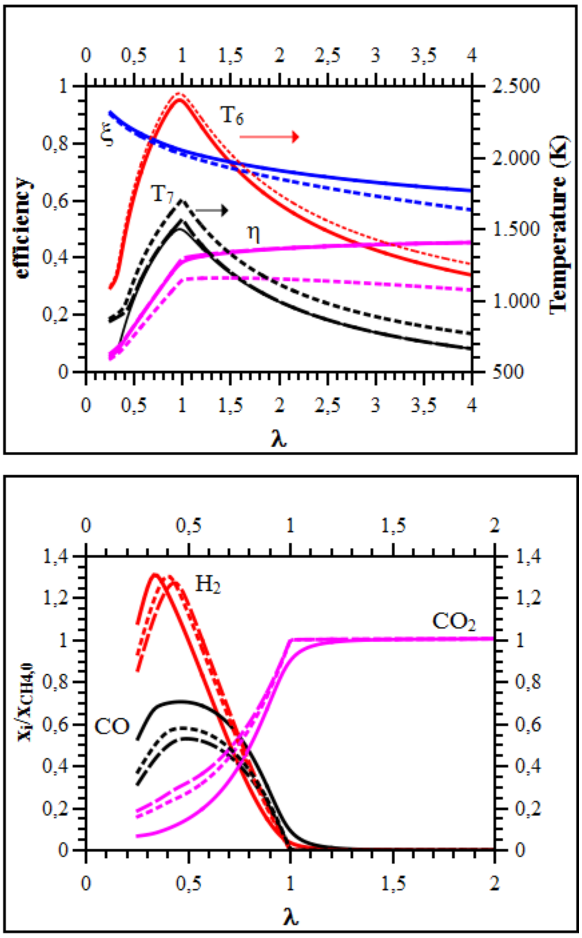

Figure 2. Gas turbine cycle with a compression ratio of 10 calculated for various stoichiometries. Solid lines show the results for the isentropic case, dashed lines for the isentropic case with equilibration in the turbine and the dashed-dotted lines for the non-isentropic case with equilibration.

For clarity, only the target species hydrogen and CO are included in Figure 2 together with the mostly unwanted CO_2, although the complex equilibrium with 53 species was calculated. As can be seen, between 1.54 and 1.71 mole of hydrogen is predicted per mole of initially provided methane and the fuel-to-air ratio range for this is quite narrow around 0.5 ≥ λ ≥ 0.3. Compared to hydrogen, the predicted CO mole fraction peak is relatively flat and per mole methane 0.63 - 0.88 mole CO is formed in equilibrium after combustion. The hydrogen mole fraction is only slightly influenced by chemical equilibration of the mixture in the turbine or by irreversibilities in the compressors and the turbine. In contrast, the CO mole fraction is strongly influenced by chemical equilibration, the relative mole fraction values drops from 0.9 to around 0.63. However, the higher temperatures due to non-reversible compressors and turbine help the formation of larger amounts of CO and after chemical equilibration the value rises to 0.7, depending on the exact fuel-to-air ratio. The temperatures of adiabatic combustion lie between 1485 and 1809 K in the interesting λ range, which is well accessible with the C/C materials and will in part be accessible with conventional gas turbine blades (1723-1773K) (Yamamoto, Kobayashi, Arai, & Tanaka, 1997; Yamamoto et al., 2007).

If gas turbines without blade cooling are used, λ could be further reduced, e.g. to a value of 0.35 leading to a turbine entrance temperature of 1300 K and H_2 and CO values of 1.7 and 0.9 per mole of methane, respectively, in the irreversible case at an exergetic efficiency of 87%. This case will not be discussed in detail further to avoid confusion of the reader due to too many discussed cases, however such conditions seem also to be reasonable and the results are throughout included into the figures.

Table 1 summarizes the main results at two pressure ratios. At each π, the stoichiometry with the maximum hydrogen yield was chosen, as well as a slightly leaner λ for comparison. Exact values can more easily be taken from such a table than out of a graph. We will concentrate on a pressure ratio of 10 first: The thermal efficiencies in the interesting stoichiometry range between λ=0.4 and λ=0.5 seems to be disappointing at first sight with values around 10% (see also Table 1). They were calculated from the relation between the net work output, w_{net}, and the lower heating value of methane. However, this looks much better if the exergetic efficiencies are regarded and the purpose of the process, i.e. producing power and base chemicals, is remembered. One cannot expect to have both at the same time: a high thermal efficiency and an incomplete combustion step, which is not mainly leading to water and carbon dioxide. It should also be stressed, that the exergy of methane is highest without any reaction and the highest exergy losses come from the total conversion to carbon dioxide and water. However, if both, hydrogen and carbon monoxide are needed, such a polygeneration process is quite favorable, regarding the exergetic losses.

Table 1. Properties, work and efficiencies for some states for the process with non-reversible turbine and compressors and chemical equilibration in the turbine.

	π = 10		π = 30	
λ	0.395	0.506	0.427	0.506
p_{max} (MPa)	1.01	1.01	3.04	3.04
$\lvert w_{net}\rvert$(MJ/kg$_{CH4}$)	4.33	6.58	6.44	8.48
w_c (MJ/kg$_{CH4}$)	3.19	3.91	5.90	6.80
$\lvert w_t\rvert$ (J/kg$_{CH4}$)	7.52	10.5	12.3	15.3
$\eta_{thermal}$	0.09	0.13	0.13	0.17
ξ_{2+4}	0.99	0.99	0.99	0.99
ξ_5	0.99	0.98	0.98	0.98
ξ_6	0.87	0.85	0.88	0.87
ξ_7	0.86	0.84	0.86	0.85
T_5 (K)	623	629	836	845
T_6 (K)	1485	1809	1761	1983
T_7 (K)	959	1159	935	1041
$n(H_2)_7/n(CH_4)_1$	1.62	1.30	1.54	1.36
$n(CO)_7/n(CH_4)_1$	0.700	0.676	0.622	0.614

The exergetic efficiencies in this λ range lie between 85-87% and are reduced only very slightly with the introduction of irreversible turbines and compressors. If this value is compared with the exergetic efficiency of 65% for a lean mixture of λ = 3 an important improvement is recognized. This difference is even more pronounced with turbines and compressors having an isentropic efficiency below 1; in the example calculated here, the exergetic efficiency in the lean range is further reduced to values below 61%, which should be an important argument to consider fuel rich mixtures. The main exergy losses take place in the combustion process (between state 5 and state 6) as can be seen from Table 1, while the exergy losses in the other parts are of minor importance. However, the exergy loss in stoichiometric and lean adiabatic combustion is much higher (Caton, 2000; Dunbar & Lior, 1994) than in the investigated rich regime.

In the high temperature regime some radicals like atomic hydrogen and the hydroxyl radical (OH) are present in a considerable amount as seen in Figure 3. The (relative) equilibrium concentrations of these radicals may be in the percent regime at high temperatures, as it is seen for OH, but they only play a minor role after passing the turbine and equilibration takes place at reduced temperatures, thus their curves are hardly recognizable in Figure 3. However, if the chemical equilibration in the turbine is not performed, the concentrations would remain unrealistically high, again being an argument for considering the occurrence of chemical equilibration in the turbine.

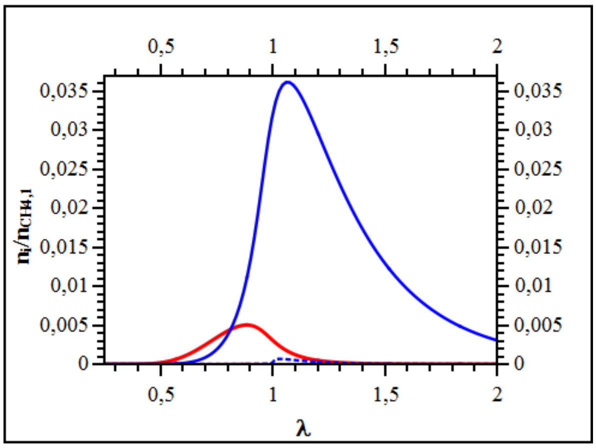

Figure 3. Equilibrium H (red) and OH (blue) mole fractions at the turbine entrance (state: 6) both divided by the initial methane mole fraction, as a function of λ at the turbine entrance (solid lines) and equilibrated behind the turbine (dashed lines) shown for a reversible turbine with an inlet pressure of 1.013MPa.

3.2. Influence of the pressure ratio

The compression ratio is known to be an important parameter for gas turbine cycles. As it is well known, the thermal efficiency of the Brayton cycle increases with the pressure ratio, π. Thus, it was interesting to investigate higher pressure ratios. Since no discontinuities were found, only the highest studied pressure ratio shall be discussed here. Some results for π = 30 are presented; the calculations were performed again for totally reversible compressors and turbine (*rev*) as the limiting case and for the above given isentropic efficiencies (*irr*). Some results from the latter are included in Table 1, while the results at different pressure ratios are also compared Figure 4.

From Figure 4 it is seen that the amount of hydrogen produced in the fuel rich regime is nearly unaffected by the pressure ratio, the hydrogen yield is slightly reduced to 1.54 mole hydrogen per mole methane initially added. Also, the maximum is shifted towards a higher λ value of 0.43, which was therefore included to Table 1. The CO formed per CH_4 is slightly reduced at $\pi = 30$ relative to $\pi = 10$ leading to values of slightly above 0.62. However, for syngas this would be a reasonable mixture composition. The exergetic efficiency at $\lambda = 0.4$ slightly increases to 87-88% for the irreversible case.. Regarding the thermal efficiency, the effect of π is more pronounced: it reaches a value of 13 % for the λ which gives the highest hydrogen yield, compared to 9 % for $\pi = 10$.

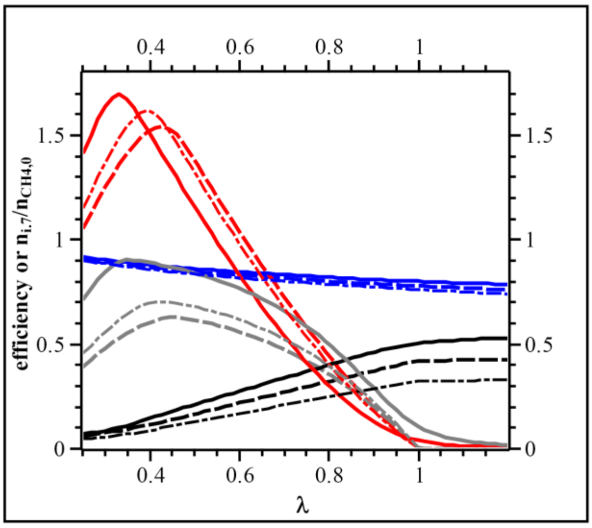

Figure 4. Comparison of the results for $\pi = 30$ with $\pi = 10$. Solid lines: $\pi = 30$, rev, no equilibration in the turbine; dashed lines: $\pi = 30$, irr; dashed-dotted lines: $\pi = 10$, irr. The latter two were both calculated with equilibration in the turbine. Red: H_2, grey: CO, blue: exergetic efficiency, black: thermal efficiency.

If the λ value is increased to 0.51, the thermal efficiency rises to 17%, while the exergetic efficiency is at 87%, meaning that there is some amount of flexibility in the preferred products. However, there is also a drawback: due to the higher pressure ratio, the adiabatic combustion temperatures rise from 1485-1809 K at $\pi = 10$ to 1761-1983 K at $\pi = 30$ for the λ values given in Table 1. Temperatures above 1800 K would be far too high as turbine entrance temperature for conventional turbine blades, thus the pressure ratio may be restricted by the maximum temperature also in the fuel rich regime. However, if C/C turbine blades can be used, the temperature levels would be acceptable since graphite can withstand quite high temperatures in a reducing atmosphere.

3.3. Carbon formation

Another question which arises and may prevent the development of fuel rich gas turbine processes is the possible formation of carbonaceous matter, meaning mainly soot. In order to check this possibility two-phase equilibria, with an ideal gas phase and a solid pure graphite phase, were investigated. Again, the gas phase considered all the species present in the GRI mechanism. The amount of graphite produced per methane input was calculated as a function of temperature and fuel-to-air ratio for initial air-methane mixtures covering the λ range between 0 and 1; at leaner conditions no carbon should be formed in equilibrium.

These calculations were performed for 1, 10 and 30 bar; since the 1 bar case turns out to be most critical, only the results for this pressure are shown Figure 5. At low temperatures and low λ values methane is stable, if λ is near 1 the formation of CO_2 and CO is predominant, while at λ values around 0.4 graphite may be formed at temperatures of around 800 K and ambient pressure. This can be avoided at slightly higher λ values, thus the results for λ=0.51 are also shown in Table 1.

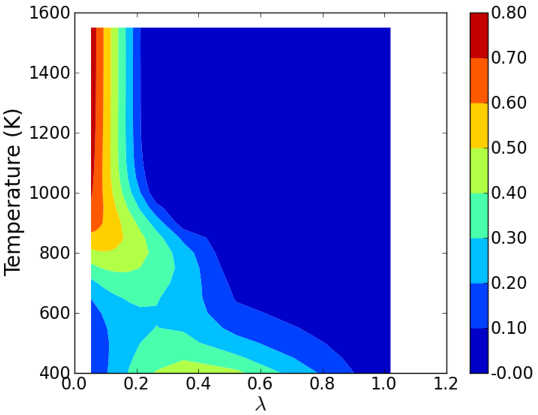

Figure 5. The molar amount of graphite formation in equilibrium per mole of initially present methane calculated at 1 bar (figure is in color in the on-line version of the paper).

Regarding the calculated turbine exit temperatures T_7 (see Figure 2) it is seen that the temperature level is predicted to be above 800 K for the λ range of interest, even at λ values of 0.35. However, the risk of solid carbon or soot formation remains if in a subsequent cooling step, e.g. in a heat exchanger, chemical equilibration is established. Thus, the subsequent cooling should be a fast process, hence introducing further irreversibilities, but this part was not studied here. Investigations of the chemical kinetics of these systems are needed in order to judge the rate of equilibration towards a possible formation of carbonaceous matter while cooling takes place. This is quite a challenging task and was not the aim of the present thermodynamic investigation.

3.4 Kinetic processes in the turbine

As described above, the importance of the equilibration of the gas mixture within the turbine can be estimated using the GRI 3.0 chemical kinetic mechanism. For this the gas is regarded as if it was expanding in an piston/cylinder system, which is just the transformation of the coordinate system from a fixed one to one which is moving with the fluid through the turbine while it is doing some work against the piston or turbine blades, respectively. The initial pressure and temperature as well as the final pressure and temperature are those from the previous equilibrium calculations; both are reduced due to the expansion process where work is transferred from the system. The rate of the "piston" movement was chosen such that the process takes 20 ms. This rate was chosen such that the rate of pressure change was changing in five steps (stages), such that a pressure reduction by a factor of 2 always was performed in the same time interval of 4 ms. Again, choosing a single pressure change rate did not lead to different conclusions. The main result of this calculation was that neither the hydrogen nor the carbon monoxide concentration changed within this time interval. This leads to the conclusion that the regarded homogeneous gas phase reactions of the main compounds are too slow to play an important role in the turbine. However, on a longer time scale, which is needed until the gas mixture is cooled down and separated afterwards, concentrations of hydrogen and carbon monoxide may be changing, but this was not investigated here.

4. Conclusions

A simple fuel-rich gas turbine process running with methane as fuel was investigated and has been shown to be thermodynamically favorable for the polygeneration of base chemicals like hydrogen or syngas together with mechanical power. In the present work, only the basic conversion process was studied without considering the subsequent processes, such as the utilization of the exhaust enthalpy stream as input for a steam power cycle and perhaps also for heating purposes. Also the separation of the product gases was not considered here, which surely will lead to some further exergy losses. But this also holds for any other partial oxidation without power generation. Nevertheless, from this study it is seen that this proposed process may be favorable with quite small exergy losses, if hydrogen or syngas are needed for other industrial processes or as fuel for hydrogen fuelled cars. Predicted thermal efficiencies of 9-17% are clearly small, but this is to be expected if the fuel is not mainly burned to carbon dioxide and water; thus, this is an intrinsic limitation of incomplete conversion. Also, the known possibilities of recuperatively heating the compressed gases (state 5) by the turbine exhaust gases, which generally leads to higher thermal efficiencies, may be worth further investigation.

Regarding the temperature levels at the turbine entrance C/C materials would be most interesting. But also the thermal behavior of nickel based high temperature alloys should be studied under these fuel rich conditions, since the gas mixture is now much less corroding, due to the absence of excess air.

A thermodynamic study can only lead to conclusions whether a process is principally possible and rational. This seems to be the case for the polygeneration of syngas, mechanical or electrical power and possibly also of heat. The possible problems of soot formation and the details of combustion, the rate of equilibration of the product gases in a subsequent cooling process have to be studied in addition to experimental methods and further and more detailed kinetic modeling. Such studies seem to be worth being performed, in order to use gas turbines as chemical reactors. Also, different fuels which may come from regenerative sources like organic alcohols may be interesting in future studies. The advantage could also be a relatively simple but flexible process, avoiding further exergy losses, which arise from coupling numerous flow devices and machines in a complex way.

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Nomenclature

e	specific exergy, kJ/kg
h	enthalpy, kJ/kg
$\dot{m}$	mass flow rate, kg/s
M	molecular mass, kg/mol
n	number of moles, mol
p	pressure, Pa
r	ratio of excess air to fuel for exergy calculation,-
s	specific entropy, kJ/(kg K)
T	temperature, K
T_0	temperature of the surrounding, K
w	work per unit mass of fuel, kJ/kg
y	mass fraction, -

Greek symbols

η	thermal efficiency, -
λ	theoretical air ratio, -
π	pressure ratio
ξ	exergetic efficiency, -

Subscripts

c	compressor
eq	equilibrium state
i	state number i
s=const	isentropic
stoich	stoichiometric
t	turbine
th	thermal

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