1. Introduction

In recent years the development of stationary gas turbines for power generation resulted in increased turbine inlet temperatures and pressure ratios to fulfill the need for higher thermal efficiencies. This trend is likely to continue, with turbines for stationary power generation with turbine inlet temperatures of 1700°C currently under development (Maekawa, 2011) and military turbojet engines with temperatures close to 2000°C reported (Langston, 2007).

At the same time, the need for reduction of CO₂ emissions to the atmosphere incentivizes the use of carbon-free alternative fuels in gas turbines, such as ammonia and hydrogen at increasingly high pressure ratios and turbine inlet temperatures. This raises concerns whether conventional approaches for estimating the working fluid properties and for heat balance calculations are appropriate under such conditions. Herein, we therefore investigate the effect of several simplifying assumptions for the working fluid and the combustion scheme often made. We find that at high temperatures and equivalence ratios chemical reactions during the expansion of the gas should be considered, in particular at equivalence ratios close to unity. The extent to which chemical reactions occur during expansion in the turbine requires further investigations, as it could have severe consequences for the heat balances and output calculation of the turbine, as well as the concentration of pollutants such as NOₓ in the exhaust gas.

1. Thermodynamic evaluation of open cycle gas turbines with carbon-free fuels H₂ and NH₃ at high temperatures

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Abstract

Due to concerns over CO₂ emissions and higher efficiency requirements future power generation systems with stationary gas turbines are projected to utilize carbon-free fuels such as ammonia and hydrogen at increasingly high pressure ratios and turbine inlet temperatures. This raises concerns whether conventional approaches for estimating the working fluid properties and for heat balance calculations are appropriate under such conditions. Herein, we therefore investigate the effect of several simplifying assumptions for the working fluid and the combustion scheme often made. We find that at high temperatures and equivalence ratios chemical reactions during the expansion of the gas should be considered, in particular at equivalence ratios close to unity. The extent to which chemical reactions occur during expansion in the turbine requires further investigations, as it could have severe consequences for the heat balances and output calculation of the turbine, as well as the concentration of pollutants such as NOₓ in the exhaust gas.

Keywords: Gas turbine, Ammonia combustion, Hydrogen combustion, Brayton cycle, Thermodynamic equilibrium
as enthalpy, specific heat etc., are obtained from tabularized data considering only air, CO₂ and H₂O as constituents (Elmasri, 1988; GasTurb GmbH, 2019). Moreover, it is frequently assumed that the flow in the expansion section of the turbine after the combustor is unreactive. This assumption has been challenged when very high turbine inlet temperature of over 2100 K are attained and it has been suggested that dissociation and recombination reactions may occur at least in the first turbine stage, potentially affecting not only pollutant concentrations but also the overall heat balance and efficiency (Godin et al., 1999, 1997). Therefore, in this work we investigate the effect of several simplifying assumptions for the working fluid and combustion scheme on the heat balance and performance calculation of a simple, open cycle gas turbine fueled with H₂ or NH₃, with the aim of clarifying under which conditions simplifying assumptions are appropriate.

### Nomenclature

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Unit</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>𝐴𝑇文化的, -</td>
<td>ratio of air to fuel at stoichiometric supply of air</td>
<td></td>
</tr>
<tr>
<td>𝑐, 𝑖</td>
<td>kJ kg⁻¹ K⁻¹</td>
<td>specific heat capacity of working fluid at state 𝑖</td>
</tr>
<tr>
<td>𝐶, 𝑖</td>
<td>kJ mol⁻¹ K⁻¹</td>
<td>molar heat capacity of component 𝑗 at temperature 𝑇</td>
</tr>
<tr>
<td>𝐷𝐻, 𝑖</td>
<td>kJ mol⁻¹</td>
<td>standard enthalpy of formation of component 𝑗</td>
</tr>
<tr>
<td>𝐿</td>
<td>kJ kg⁻¹</td>
<td>specific chemical enthalpy at state 𝑖</td>
</tr>
<tr>
<td>𝑥, 𝑖</td>
<td>kJ kg⁻¹</td>
<td>specific enthalpy at state 𝑖</td>
</tr>
<tr>
<td>𝐿𝐻𝑉</td>
<td>kJ kg⁻¹</td>
<td>lower heating value of the fuel used</td>
</tr>
<tr>
<td>𝑚, 𝑖</td>
<td>kg s⁻¹</td>
<td>mass flow of air into the compressor</td>
</tr>
<tr>
<td>𝑚, 𝑓</td>
<td>kg s⁻¹</td>
<td>mass flow of fuel into the combustor</td>
</tr>
<tr>
<td>𝑀𝑊, 𝑖</td>
<td>kg mol⁻¹</td>
<td>molecular weight at state 𝑖</td>
</tr>
<tr>
<td>𝑃𝑅</td>
<td>-</td>
<td>pressure ratio</td>
</tr>
<tr>
<td>𝑠, 𝑖</td>
<td>kJ kg⁻¹ K⁻¹</td>
<td>specific entropy at state 𝑖</td>
</tr>
<tr>
<td>𝑇, 𝑖</td>
<td>K</td>
<td>Turbine Inlet Temperature, temperature of the gas at state 3</td>
</tr>
<tr>
<td>𝑇, 𝑖</td>
<td>K</td>
<td>temperature at state 𝑖</td>
</tr>
<tr>
<td>𝑇, 𝑖</td>
<td>K</td>
<td>temperature after isentropic compression/expansion</td>
</tr>
<tr>
<td>𝑤, 𝑐</td>
<td>kJ kg⁻¹</td>
<td>specific compressor work</td>
</tr>
<tr>
<td>𝑤, 𝑝</td>
<td>kJ kg⁻¹</td>
<td>specific net shaft work</td>
</tr>
<tr>
<td>𝑤, 𝑡</td>
<td>kJ kg⁻¹</td>
<td>specific turbine work</td>
</tr>
<tr>
<td>𝑥, 𝑖</td>
<td>-</td>
<td>molar fraction of component 𝑗 in the working fluid at state 𝑖</td>
</tr>
<tr>
<td>𝑔</td>
<td>-</td>
<td>isentropic coefficient</td>
</tr>
<tr>
<td>𝜙</td>
<td>-</td>
<td>equivalence ratio</td>
</tr>
</tbody>
</table>

### 2. Methods

A simple, open cycle gas turbine engine system is considered as depicted in Fig.1.

![Fig. 1 Illustration of the simple, open cycle gas turbine](image-url)
Dry air is supplied to the compressor at $p_1=1\text{bar}$ and $T_1=298.15\text{ K}$. The fuel is assumed to be provided at $p_2$ and $T_2$. All components of the cycle, i.e. the compressor, the combustion chamber and the turbine, are considered to be adiabatic. The specific net shaft work per mass of working fluid in the turbine is calculated by enthalpy balances around the compressor and the turbine.

$$w_{net} = w_c + w_t = (h_2 - h_3) \frac{m_{\text{air}}}{m_{\text{air}}+m_{\text{fuel}}} + (h_4 - h_3) \tag{1}$$

The ratio of air to fuel ATF at stoichiometric supply of air is defined as:

$$\text{ATF}_{\text{stoich}} = \frac{m_{\text{air,stoich}}}{m_{\text{fuel,stoich}}} \quad \text{ATF}_{\text{stoich},H_2} = 34.08 \quad \text{and} \quad \text{ATF}_{\text{stoich},NH_3} = 6.05. \tag{2}$$

The equivalence ratio $\phi$ is defined as the ratio of the mass of air required for stoichiometric combustion of the fuel and the mass of air actually provided to the turbine.

$$\phi = \frac{m_{\text{air,stoich}}}{m_{\text{air}}} \tag{3}$$

At each state $i$ the total specific enthalpy is comprised of the sensible enthalpy and the chemical enthalpy.

$$h_i = h_{\text{sens},i} + h_{\text{chem},i} = \frac{1}{MW_i} \sum_j x_{i,j} \int_{T_0}^{T_i} C_{p,j}(T) dT + \frac{1}{MW_i} \sum_j x_{i,j} \Delta H_{f,j} \tag{4}$$

Polynomial coefficients for the heat capacity and the standard enthalpy and entropy of formation were obtained from the database provided with the CHEMKIN software (ANSYS, Inc.). The polynomials for the heat capacity are of the following form with a set of coefficients provided for $T<1000\text{ K}$ and for $1000\text{ K}<T<5000\text{ K}$:

$$C_{p,j}(T)/R = a_{1,j} + a_{2,j}T + a_{3,j}T^2 + a_{4,j}T^3 + a_{5,j}T^4 \tag{5}$$

Here, $R$ denotes the universal gas constant. Species considered in the equilibrium calculations are $H_2$, $O_2$, $N_2$, $H$, $O$, $OH$, $HO_2$, $H_2O$, $H_2O_2$, $NH_3$, $NO$, $N_2O$ and $NO_2$. The unused air in the compressor can be considered unreactive and thus the chemical enthalpy before and after compression are identical. Combining equations (1) to (3), the expression for the net shaft work can be simplified.

$$w_{net} = w_c + w_t = (h_{\text{sens},2} - h_{\text{sens},1}) \frac{1}{1+\phi} + (h_4 - h_3) \tag{6}$$

Two different measures are employed to express the cycle efficiency. Efficiency can be expressed based on the heating value of the fuel supplied ($LHV(H_2)=241.8\text{ kJ mol}^{-1}$, $LHV(NH_3)=316.8\text{ kJ mol}^{-1}$).

$$\eta_{LHV} = \frac{-w_{net}(\phi,\text{ATF}_{\text{stoich}}+1)}{LHV} \tag{7}$$

Alternatively, the efficiency can be expressed based on the heat release in the combustor.

$$\eta_{\text{thermal}} = \frac{-w_{net}}{h_{\text{sens},3} - h_{\text{sens},2}} \tag{8}$$

For low equivalence ratios $\phi$ the combustion reactions of the fuel in the combustor are close to complete, and $\eta_{\text{thermal}}$ approaches $\eta_{LHV}$. However, at large $\phi$ these two measures diverge significantly because uncombusted fuel leaving the turbine is not considered as heat input according to the definition of $\eta_{\text{thermal}}$.

The pressure at state 2 and 3 is calculated from the specified pressure ratio, and $p_2=p_1*PR$ and $p_3=p_1$.

$$p_2 = p_1 * PR \tag{9}$$

The temperatures after the compressor and turbine are calculated based on isentropic efficiencies as defined in the following way:

$$\eta_c \equiv \frac{T_2-T_1}{T_3-T_2} = 0.85 \tag{10}$$
\[ \eta_1 \equiv \frac{T_{IT} - T_e}{T_{IT} - T_{a}} = 0.8 \]  

(11)

Here, \( T_{2s} \) and \( T_{4s} \) denote the temperatures after isentropic compression and isentropic expansion, respectively. The temperature after the adiabatic combustor is obtained from an enthalpy balance around the combustor. Three different models are used to calculate the change in chemical enthalpy in the combustor and turbine, and the temperature and properties of the working fluid at states 2, 3 and 4.

**Model 1:** This is the simplest model in which it is assumed that the working fluid at all states is dry air. The compression in the compressor and expansion of the working fluid in the turbine are calculated by assuming an unreactive fluid. The isentropic temperatures \( T_{2s} \) and \( T_{4s} \) are approximated by a 10-stage discretization that assumes constant-pressure heat capacity \( C_{p,k} \) in each stage to avoid any iterative procedure. For the compressor the properties of \( p \) and \( T \) at the \((k+1)\)-th increment are described by that at the \(k\)-th and \((k+1)\)-th values as follows:

\[
p_{k+1} = p_k \cdot PR^{1/10} \tag{12}
\]

\[
T_{k+1} = T_k \cdot \left( \frac{p_k}{p_{k+1}} \right)^{\gamma_k} \quad \text{with} \quad \gamma_k = \frac{C_{p,k}(T_k)}{C_{p,k}(T_k) - R} \tag{13}
\]

The equations for the expansion in the turbine can be written in an analogous way.

The heat release in the combustor is calculated by a simplified scheme. In case of NH\(_3\) as fuel it is first assumed that all NH\(_3\) decomposes according to eq. (14). Then, the released H\(_2\) is combusted according to the availability of O\(_2\) in the gas as described by eq. (15). In case of H\(_2\) as fuel only eq. (15) is considered.

\[
\text{NH}_3 \rightarrow 0.5 \text{N}_2 + 1.5 \text{H}_2 \quad \Delta H^0_{298} = 45.9 \frac{kj}{\text{mol} \text{NH}_3} \tag{14}
\]

\[
1.5 \text{H}_2 + 0.75 \times \frac{1}{\phi} \text{O}_2 \rightarrow \max \left( 0, 1.5 \times \left( 1 - \frac{1}{\phi} \right) \right) \text{H}_2 + \max \left( 0, 0.75 \times \left( \frac{1}{\phi} - 1 \right) \right) \text{O}_2 + \left( 1.5 - \max \left( 0, 1.5 \times \left( 1 - \frac{1}{\phi} \right) \right) \right) \text{H}_2\text{O} \quad \Delta H^0_{298} = -241.8 \frac{kj}{\text{mol} \text{H}_2} \tag{15}
\]

**Model 2:** All the assumptions made in Model 1 are used with the exemption of assuming dry air as the working fluid. Instead, the properties of the working fluid are calculated based on the composition obtained from the simplified combustion scheme, eqs. (14) and (15).

**Model 3:** Full equilibrium calculations are performed for each state of the system, taking into account a range of dissociation and partial oxidation products. Gibbs energy minimization calculations are carried out based on the scheme suggested by Gordon and McBride for chemical systems containing a large number of species (McBride and Gordon, 1996). The flow in the turbine is thus also considered to be reactive and not kinetically constrained. Properties of the working fluid are then calculated based on the so obtained gas compositions according to the scheme outlined in Fig. 2.
3. Results and Discussion

3.1. Heat capacity prediction

In Fig. 3 the heat capacity at constant pressure \( C_p \) of the working fluid at the turbine inlet is shown as a function of Turbine Inlet Temperature (TIT) with different fuels and model assumptions. It can be observed that the deviation between assuming air as a working fluid and considering also the combustion products (Model 1 compared to Models 2 and 3) are largest for NH\(_3\) as a fuel, followed by H\(_2\) and CH\(_4\). This demonstrates that the difference introduced by the assumption of air as working fluid in the turbine calculation is significantly larger for these non-conventional fuels and should be avoided, especially if the turbine is operated at higher \( \phi \) and temperatures. At equivalence ratios approaching one or higher, the difference introduced by considering a simplified combustion product gas composition becomes significant (Model 2 compared to Model 3).

3.2. H\(_2\) as fuel

In Fig. 4 the TIT is shown when H\(_2\) is used as a fuel. At low equivalence ratios the assumption of air as a working fluid already yields a large deviation in TIT prediction. At higher equivalence ratios but still lean mixture of \( \phi=0.6 \) the...
simplified combustion chemistry of Model 2 predicts a substantially higher TIT, which is due to the existence of radicals at such high temperatures.

Fig. 4 Turbine Inlet Temperature TIT with H₂ as fuel

The net shaft work dependence on equivalence ratio is shown in Fig. 5. At PR=5 and low ϕ the net shaft work calculation is rather insensitive to the working fluid modeling assumption. At higher PR a discrepancy in shaft work is noticeable already at low lean mixture of ϕ and becomes more severe at ϕ >1, with Model 3 yielding an increased net shaft work. For Model 1, the net shaft work is highest at an equivalence ratio of one because the turbine inlet temperature is also highest, leading to a higher specific work extractable from the turbine. For Models 2 and 3, at equivalence ratios larger than unity the specific heat capacity of the gas expanding in the turbine is significantly increased (see Figure 3). This is largely an effect of the very high specific heat capacity of unburnt hydrogen. This, in turn, leads to an increase in the net shaft work as more specific work can be extracted even though the turbine inlet temperature decreases.

Fig. 5 Net shaft work with H₂ as fuel

The simple cycle efficiency based on LHV fuel input $\eta_{LHV}$ is shown in Fig. 6. At equivalence ratios larger than unity the LHV-based efficiency drops sharply due to uncombusted fuel leaving the turbine. At low PR Model 2 and Model 3 yield similar tendencies, however at higher PR the LHV-based efficiency is markedly higher when Model 3 is used, due to the larger net shaft work (see Fig. 5).
In Fig. 7 the thermal efficiency and the chemical enthalpy decrease during expansion in the turbine (only Model 3) are shown. When chemical reactions such as radical recombination are considered (Model 3 as compared to Model 2), the projected thermal efficiency increases substantially when the equivalence ratio is in the vicinity of 1. This is due to the large chemical enthalpy decrease under such conditions that in turn increases the sensible enthalpy available for shaft work generation during expansion. This drastic increase in thermal efficiency occurs mainly due to the conventional definition of the thermal efficiency of eq. (8) that only considers the heat released in the combustor as heat input into the system and neglects heat released due to chemical reactions occurring during the expansion of the gas. The definition of the thermal efficiency could thus be revised to also consider the heat released from chemical reactions in the turbine \( h_{\text{chem,3}} - h_{\text{chem,4}} \) as sensible energy input into the gas turbine cycle.

\[
\eta_{\text{thermal, revised}} = \frac{-w_{\text{net}}}{(h_{\text{sens,3}} - h_{\text{sens,4}}) + (h_{\text{chem,3}} - h_{\text{chem,4}})}
\]  

With the definition of eq. (16) the predicted thermal efficiency decreases significantly as indicated in Fig. 7. Under such conditions it may thus be required to change the conventional definition of the thermal efficiency accordingly. However, the extent to which the chemical reactions during the expansion of the gas predicted by the equilibrium calculations actually occur will depend on kinetic limitations, which will be the topic of future work.
3.3. NH₃ as fuel

The TIT as a function of equivalence ratio when NH₃ is used as a fuel is shown in Fig. 8. The TIT with NH₃ is significantly lower than with H₂ as fuel (cf. Fig. 4). The deviation between Model 2 and Model 3 is also smaller when NH₃ is used. This is due to the smaller quantity of radicals with NH₃ as a fuel predicted to be formed with Model 3. Accordingly, a smaller deviation is also observed for the net shaft work, as illustrated in Fig. 9.

![Fig. 8 Turbine Inlet Temperature TIT with NH₃ as fuel (with H₂ in light gray for reference)](image)

Fig. 8 Turbine Inlet Temperature TIT with NH₃ as fuel (with H₂ in light gray for reference)

![Fig. 9 Net shaft work with NH₃ as fuel](image)

Fig. 9 Net shaft work with NH₃ as fuel

In Fig. 10 the LHV-based efficiency is shown, again with noticeable deviations between the models at high pressure ratios.
The thermal efficiency under the different modeling assumptions and the decrease in chemical enthalpy during expansion estimated with Model 3 are displayed in Fig. 11. This specific heat released per mass of working fluid during expansion is substantially smaller than that expected for H$_2$ as a fuel. The exothermicity of the chemical reactions predicted to occur is again most pronounced for equivalence ratios close to 1 and drops sharply at higher equivalence ratios. Analogously to the case when H$_2$ is used as fuel, a large part of the difference in thermal efficiency between Model 2 and Model 3 can be explained by negligence of the heat released during expansion as heat input, cf. eqs. (8) and (16).

3.4. NO emissions

With Model 3 NO concentrations at the combustor outlet / turbine inlet and the turbine outlet can be computed at thermodynamic equilibrium. For both fuels considered this is shown in Figure 12. For H$_2$ fuel the predicted NO concentration at the turbine inlet is very high due to the high combustion temperatures and subsequent thermal NO$_x$ generation. For NH$_3$ fuel the predicted NO concentration at the turbine inlet drops sharply for higher equivalence ratios $\phi>1$, indicating that operation in fuel-rich condition may be feasible without the use of additional NO$_x$ reduction equipment. To illustrate, at $\phi=1.3$ the predicted NO concentration at the turbine inlet corresponds to an emission factor of 0.025 lb/MMBTU fuel input. This is below the 9 ppmv @ 15%O$_2$ limit for conventional gas turbines, which corresponds to an emission factor of 0.036 lb/MMBTU. For both fuels the predicted NO concentrations at the turbine
outlet are orders of magnitude lower than the concentrations at the inlet. While it is unlikely that chemical reactions proceed until chemical equilibrium throughout the expansion process in the turbine due to kinetic limitations imposed by short gas residence times and decreasing gas temperatures, it is likely that some degree of secondary reactions could occur during expansion at very high turbine inlet temperatures. As a consequence, we assume that the predicted equilibrium composition at the turbine inlet and outlet indicate the range of plausible gas compositions that could be attained if measurements or reaction kinetic calculations were to be performed. Thus, the actual NO concentrations at the turbine outlet may be higher than predicted by equilibrium at the turbine outlet, and to which extent is a subject for future work that would include kinetic modeling.

Fig. 12 NO concentration at equilibrium predicted with Model 3 at turbine inlet and outlet for both H₂ and NH₃ as fuel

4. Conclusions

In this work the effect of simplifying assumptions for the working fluid and the combustion scheme for carbon-free fuels H₂ and NH₃ at high temperatures on key output parameters of the turbine were investigated. Expectedly, it was observed that the assumption of air as a working fluid leads to severe deviations in the calculation of the efficiency and output of the turbine. Assuming a simplified combustion scheme yields acceptable results at lower equivalence ratios and temperatures. However, at equivalence ratios close to unity and above the existence of unconverted fuel compounds and dissociated and partially oxidized species should be considered. Also, the possibility of a reactive flow during expansion in the turbine should be taken into account, as heat release and a change in pollutant concentration such as NOₓ could be considerable. This last point warrants further investigation to determine the severity of reactions in the expanding flow under kinetic constraints.

References