

EXERGY ANALYSIS OF GAS-TURBINE COMBINED CYCLE WITH CO₂ CAPTURE USING AUTO-THERMAL REFORMING OF NATURAL GAS

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SUMMARY

A concept for capturing and sequestering CO₂ from a natural-gas fired combined-cycle power plant is presented. Previously, a number of methods for capturing CO₂ from power plants have been suggested, among other including chemical absorption of CO₂ from exhaust gas and stoichiometric combustion with pure oxygen. The present approach is to de-carbonise the fuel prior to combustion by reforming natural gas, producing a hydrogen-rich fuel. The reforming process consists of an air-blown pressurised auto-thermal reformer that produces a gas containing H₂, CO and a small fraction of CH₄ as the combustible components. The gas is then led through a water-shift reactor, where the equilibrium of CO and H₂O is shifted towards CO₂ and H₂. The CO₂ is then captured from the resulting gas by chemical absorption. The gas turbine of this system is then fed with a fuel gas containing approximately 50% H₂. A very important aspect of this type of process is the integration between the combined cycle and the reforming process. The pressurised air for the reforming is taken from a gas turbine compressor bleed, and there is an exchange of MP- and HP-steam between the steam cycle and the reforming process. This integration is necessary in order to achieve acceptable level of fuel-to-electricity conversion efficiency.

The paper presents the process, the chemistry and efficiency considerations. Detailed simulations are made with state-of-the-art computational tools (GTPRO and PRO/II). The exergy concept is reviewed in relation to the present process. A detailed breakdown of exergy losses is presented for variations of the most important process parameters.

INTRODUCTION

In order to reduce the CO₂ emission from natural-gas based power-generation plants, three different main types of concepts have emerged as the most promising.

A) Separation of CO₂ from exhaust gas coming from a standard gas-turbine combined cycle (CC), using chemical absorption by amine solutions. It can either be performed with a direct contact between exhaust gas and absorbent [1-4], or with the use of liquid membranes [5-7].

B) Gas turbine CC with a close-to-stoichiometric combustion with oxygen (97%+ purity) from an air-separation unit as oxidising agent, producing CO₂ and water vapour as the combustion products. In order to keep the combustion-products temperature to a permissible level for the turbine, most of the combustion products are cooled

and recycled, making the gas turbine a semi-closed cycle with mainly CO₂ as working fluid [8-13].

C) Decarbonisation, in which the carbon of the fuel is removed prior to combustion, and the fuel heating value is transferred to hydrogen. This concept can be applied both for natural gas by combining reforming, a water gas shift reaction and CO₂ removal process [14-21], and, in a similar manner, also for coal, where gasification replaces the reforming process [22-24].

Furthermore, several variations of the three main concepts have been proposed. An example is chemical looping or cycling [25-26], which might be regarded as a hybrid version of Concept B as the chemically bound oxygen reacts with natural gas in the gas-turbine combustor.

Concept C has been known for a few years mainly related to studies of CO₂ removal in conjunction with coal gasification integrated with CC. However, the production of electricity from decarbonised hydrogen is unlikely to be competitive with Concept A unless some synergy effect can be achieved by integration between the different process steps, according to [18]. In the present work, focus is put on Concept C; decarbonisation prior to combustion.

Traditional first-law analysis, based upon unit-performance characteristics coupled with energy balances, invariably leads to a correct final answer. However, such an analysis cannot locate and quantify the losses that lead to the obtained result. This is because the first law embodies no distinction between work and heat, no provision for quantifying the quality of energy. These limitations are not a serious drawback when dealing with familiar systems. For these, one can develop an intuitive understanding of the different parametric influences on system performance and a second-law qualitative appreciation of "grade-of-heat" and effect of pressure loss. However, when analysing novel and complex thermal systems, such an understanding should be complemented by a more rigorous quantitative method. Second-law analysis, or exergy analysis, provides such a tool. Second-law analysis is no substitute for first-law analysis, rather a supplement. In the present work, results by using both first- and second-law calculations are presented.

PROCESS DESCRIPTION

Two different cases (1 and 2) were considered as well as a standard combined cycle with no CO₂ capture (Base case). Figure 1 shows the process configurations of Cases 1 and 2. The hydrogen-rich reformed gas is combusted in a gas turbine (GT), which is integrated with the decarbonisation process [14-21]. A model of the gas turbine GE9351FA

from General Electric was used in the simulations, based on GTPRO 10.0 (Thermoflow, Inc.). This gas turbine represents modern technology of today, and it is used in a number of plants built in the last few years. The considered

steam cycle; the heat-recovery steam generator (HRSG), the steam turbine (ST), and the seawater-cooled condenser (COND), is an advanced process with three pressure levels and steam reheat.

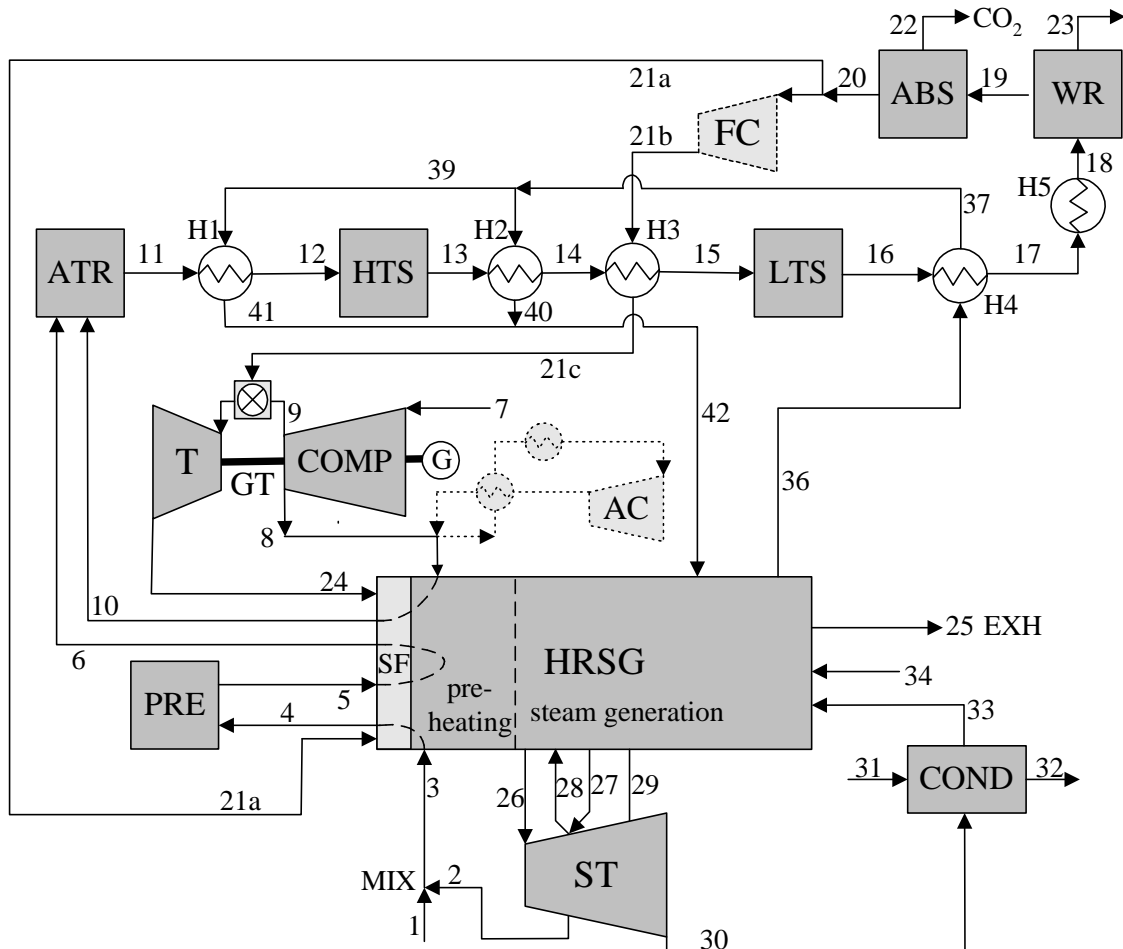


Figure 1 Process flow diagram. Case 1 includes the use of an air compressor (AC), whereas Case 2 includes the use of a fuel compressor (FC).

The reforming process is supplied with high-pressure air (8) and medium-pressure steam (2) from the gas-turbine compressor and the HRSG, respectively. There is integration between the power plant and the reforming process with respect to preheating of feed streams for the reformers (auto-thermal reformer, ATR, and prereformer, PRE). This requires supplementary firing (SF) of the gas-turbine exhaust approximately from 620 °C to 750 °C. The steam production based on exhaust-gas heat, below 600 °C, is very much the same as without any supplementary firing of the exhaust gas. This means that the supplementary firing does not increase steam production, as all the heat from SF is used for preheating of the reformer feed streams.

The pressure of the air extracted from the gas-turbine-compressor exit is typically 25% lower than the required gas-turbine fuel-nozzle pressure. Thus, an extra pressurisation is required. In Case 1, the air for the ATR is pressurised by using an air compressor (AC, see dotted lines in Figure 1). In Case 2, the fuel back to the gas turbine is pressurised by using a fuel compressor (FC). The difference between Cases 1 and 2 is the location of the pressurisation between the air extraction at the compressor

exit (8) and the fuel input to the gas-turbine combustor (21c).

Natural gas (1), mixed with the medium pressure steam (2), is preheated to 500 °C in the HRSG unit prior to the prereformer (PRE). The steam-to-carbon ratio was set to 2 at the prereformer inlet. The air extracted from the gas-turbine compressor (8) and the prereformer products (5) are preheated to 600 °C upstream the ATR unit. Both the prereformer and the main reformer (ATR) are assumed equilibrium reactors. In the prereformer, most of the heavier hydrocarbon components (mainly C₂H₆) are converted to H₂ and CO, whereas the remaining methane is converted in the ATR unit. The ATR outlet temperature was set to 900 °C. The steam cycle takes advantage of the reforming process by utilising the cooling process of the reformer products downstream the ATR to generate additional saturated high-pressure steam (40, 41). The saturated steam (42) is superheated in the HRSG unit, and fed into the steam turbine (26). The produced CO is converted to CO₂ in the high- and low-temperature shift reactors (HTS, LTS). Most of the water (99%+) is removed in the water-removal unit (WR) by condensation at 25 °C. In the simulations, it was assumed that 90% of the CO₂

content is removed (22) in the absorber unit (ABS). The fuel (20) still contains small amounts of CO and hydrocarbons. The removed CO₂ is assumed compressed to 100 bar for storage (not shown in Figure 1). A fraction (8.3-11.4%, see Table 1) of the resulting fuel is used for supplementary firing (21a) in the gas-turbine exhaust at the hot end of the HRSG. The remaining fuel (21b) is compressed (FC) to about 20 bar, heated by the feed stream (14) to the LTS, and then fed to the gas-turbine combustor (21c). By extracting air (8) from the gas turbine, there will be a significant reduction in the gas volume going into the gas turbine expander, and thus a reduction in the gas turbine pressure ratio. However, the fuel volumetric flow rate is such that it more or less replaces the lost volume caused by the air extraction. It is therefore possible to maintain the gas-turbine pressure ratio at about the same level as for a natural-gas-fired gas turbine without any air extraction. It was assumed a pressure drop of 3% in the pre-reformer, heat exchangers, and shift-reactors, whereas 6% pressure-drop was assumed for the ATR.

METHODOLOGY

The combined gas-turbine and steam-turbine cycles were simulated by GTPRO 10.0 (Thermoflow, Inc.), whereas the reforming, separation and supplementary-firing processes were simulated by PRO/II 5.11 (Simsci, Inc.). The two simulation programs were integrated by exchanging mass flows of fuel (21c), steam (2), air (8), exhaust (24/25) and water/steam (36,42), each at their specific states. The balances of mass and energy were solved within each program.

The exergy balance for open, non-transient systems can be written:

$$\sum_{in} \dot{m}_j e_j + \sum_l \dot{Q}_l \left(1 - \frac{T_0}{T_l} \right) = \sum_{out} \dot{m}_k e_k + \dot{W} + \dot{I} \quad (1)$$

Here, \dot{Q}_l is the heat transferred from a reservoir with temperature T_l , \dot{m}_j is the mass flow of inlet j with specific exergy e_j , and correspondingly \dot{m}_k and e_k for outlet k . The first and third terms of the equation are the exergy flowing with mass entering and exiting the system, respectively. The second term is the exergy transferred with heat from the thermal reservoirs. The fourth term, \dot{W} , is the work rate performed by the system, whereas the final term, \dot{I} , is the irreversibility due to the processes within the system. This irreversibility is equal to $T_0 \dot{S}_{tot}$ where \dot{S}_{tot} is the correspondingly generated entropy.

The specific exergy of a mass flow is decomposed into two terms, physical exergy and chemical exergy,

$$e = e_{ph} + e_0. \quad (2)$$

Here, as well as in the energy balance, kinetic and potential energy was neglected. The physical (or thermomechanical) exergy is found from

$$e_{ph} = h - h_0 - T_0(s - s_0), \quad (3)$$

where h and s are the specific enthalpy and entropy, respectively, and subscript 0 indicates that the properties are taken at the temperature and pressure of the environmental state (T_0, p_0). The enthalpies and entropies, *i.e.* the deviations from the environmental state, were calculated by PRO/II.

The molar chemical exergy of a mixture of gases was calculated from

$$\tilde{e}_{0,mix} = \sum_i x_i \tilde{e}_{0,i} + \tilde{R}T_0 \sum_i x_i \ln x_i, \quad (4)$$

where x_i , and $\tilde{e}_{0,i}$ are the molar fraction and the chemical exergy of a chemical species, respectively. The molar values are readily recalculated into specific values. For a two-phase flow (*e.g.* into the WR unit), the contribution from the liquid phase was neglected in the last term of Eq. (4). This can be justified since the liquid phase will be collected into drops and thin layers, and thus, it can be regarded as separated from the gaseous phase.

The chemical exergy of all relevant substances of this study were taken from [27], corrected to the ambient temperature 15 °C according to the procedure given therein. The composition of the dry atmosphere was then defined by the molar fractions (%) N₂: 78.03, O₂: 20.99, Ar: 0.933, CO₂: 0.03, Ne: 0.0018, He: 0.0005, Kr: 0.0001, and Xe: 9·10⁻⁶. For the present simulations, the content of water vapor corresponds to a relative humidity of 52% at 15 °C and 1 atm, which was chosen as the environmental temperature and pressure.

For gases that are present in the atmosphere, the molar chemical exergy is expressed

$$\tilde{e}_{0i} = -\tilde{R}T_0 \ln x_{i0}, \quad (5)$$

where x_{i0} is the atmospheric molar fraction of the species. The chemical exergy of other substances are found as the maximum work from a reversible reaction where the substance reacts with oxygen at atmospheric state (*i.e.* environmental temperature and partial pressure) and releases stable products at their atmospheric state.

RESULTS AND DISCUSSION

A comparison of the different cases shows that both cases with CO₂ capture, as expected, resulted in efficiencies well below that of the conventional combined cycle (Base). Cases 1 and 2 gave LHV-efficiencies around 48%, compared to about 55-56% for the natural-gas-fired combined cycle in the Base case. This was a reduction of 7-8%-points. When including compression of CO₂ to 100 bar for transportation (Andersen *et al.*, 2000), the reduction is 9-10%-points. This is the efficiency penalty for capturing and compressing CO₂ from this type of power cycle.

Case 2 gave slightly higher efficiencies compared to Case 1, which indicates that it is favourable with respect to efficiency to maintain the lowest pressure (approx. 14 bar) through the reforming process, and instead pressurise the reformed fuel before it enters the gas-turbine combustor.

The reason for this is the following: In order to minimise the compressor work, the air stream (8) in Case 1 is cooled before it is compressed to 25 bar. The consequence of this is a lower HRSG preheating inlet temperature and thus more supplementary firing is required. This leads to a lower ratio between the flow of fuel supplied to the gas turbine and the flow of natural gas required as input to the process, resulting in a lower corrected efficiency. Another reason for the better net efficiency of Case 2 compared to Case 1, is related to the pressure of the MP steam extracted from the steam turbine. In Case 2, the pressure of the MP steam is 15 bar compared to 25 bar for Case 1, resulting in a lower efficiency penalty for this extraction.

Table 1 Computational results for Cases 1 and 2 and for Base case.

	Case1	Case2	Base
Natural gas LHV (MW) (1)	879	864	683
Air extracted to ATR (8)	83.2	79.5	
ATR outlet pressure (bar) (11)	22.8	12.8	
ATR inlet (kg/s) (6+10)	141.3	117	
Fuel composition (%) (21c)			
H ₂	55.6	56.3	
N ₂ +Ar	41.2	40.7	2.0
CO	0.3	0.4	
CO ₂	2.0	2.0	1.0
CH ₄	0.5	0.4	93.0
C ₂ H ₆			4.0
H ₂ O	0.3	0.2	
Fuel flow to GT (kg/s) (21c)	67.9	67.4	14.6
Fuel flow to SF (kg/s) (21a)	7.8	5.6	
Power output GT (MW)	253.	256	243.
Power output ST (MW)	179	181	140
Auxiliary power (MW)	5.1	5.1	4.6
Air / fuel compression (MW)	5.5	10.8	
Net power output (MW)	422	421	378
Net efficiency (%) – LHV	47.9	48.6	55.4
Net efficiency (%) -second law-	46.3	47.1	53.7
CO ₂ emissions (g _{CO2} /kWh _{el})	57	56	365
CO ₂ reduc. vs. Base (%/kWh _{el})	84.4	84.7	

An apparent benefit of Case 1 is that the compression of the air upstream the reforming process leads to a lower efficiency penalty than the fuel compression of the other two cases does, due to a lower mass flow. The difference

is, however, not large enough to compensate for the drawbacks of Case 1, mentioned above.

There are, however, other beneficial aspects as the volumetric flow through the pre-reformer and the ATR is considerably lower in Case 1 compared to that of Case 2. This implies lower investment and operating costs for this section.

The degree of CO₂ reduction for the two cases are very much dependent on the assumption of a 90% removal of CO₂ in the absorber unit (ABS, see above), and thus not much focused here. However, the calculated quantities shown in Table 1 gives an indication of what level of total CO₂ emissions that can be expected from such a plant compared to a conventional combined-cycle plant, when the difference in net efficiency is compensated for.

Results of the exergy analysis are shown in Figure 2. The largest exergy-loss contributor was the combustor of the gas turbine. There was a substantially larger loss in a natural-gas-fired gas turbine compared to using a hydrogen-rich fuel. However, the reduced loss is almost counteracted by the conversion losses for the natural gas in the ATR. In an auto-thermal reforming process, natural gas is first transformed into a hydrogen/nitrogen mixture and then into a flue gas by means of combustion. The contributions to the irreversibilities from the units of this conversion process are: PRE (0.4% and 0.3% for cases 1 and 2, respectively), ATR (9.5%, 9.0%), HTS (0.7%, 0.9%), LTS (0.2%, 0.3%) and GT (23.9%, 25.5%). The sum of these terms was close to the value found in the natural-gas-fired gas turbine. The supplementary firing (SF) constituted 3.4%, 2.5% loss. In order of size of the exergy loss, these units follow: HRSG including steam production and preheating of reformer feed streams (3.2%, 3.3%), syngas cooler, H1, (2.8%, 3.3%), steam turbine (1.8%, 1.7%), mixing of medium-pressure steam and natural gas, MIX, (1.6%, 1.3%), and steam condenser, COND, (1.1%). Other losses were less than 1% each.

One should note the difference between Cases 1 and 2 with respect to the requirement to balance the pressure drop in the reforming loop, either by compressing the air (AC) or the fuel (FC). The latter gave a compression loss of 0.2%, whereas use of the air compressor gave a loss of 0.9%.

When comparing Cases 1 and 2 with the Base case, there was, of course, a larger loss for the formers: Supplementary firing (SF) constituted a loss of 2.5-3.4%, cooling of the syngas from about 900°C to 25°C in the heat exchangers H1-H5 gave a loss of about 4.3%, even if additional steam for power generation was produced in H1 and H2.

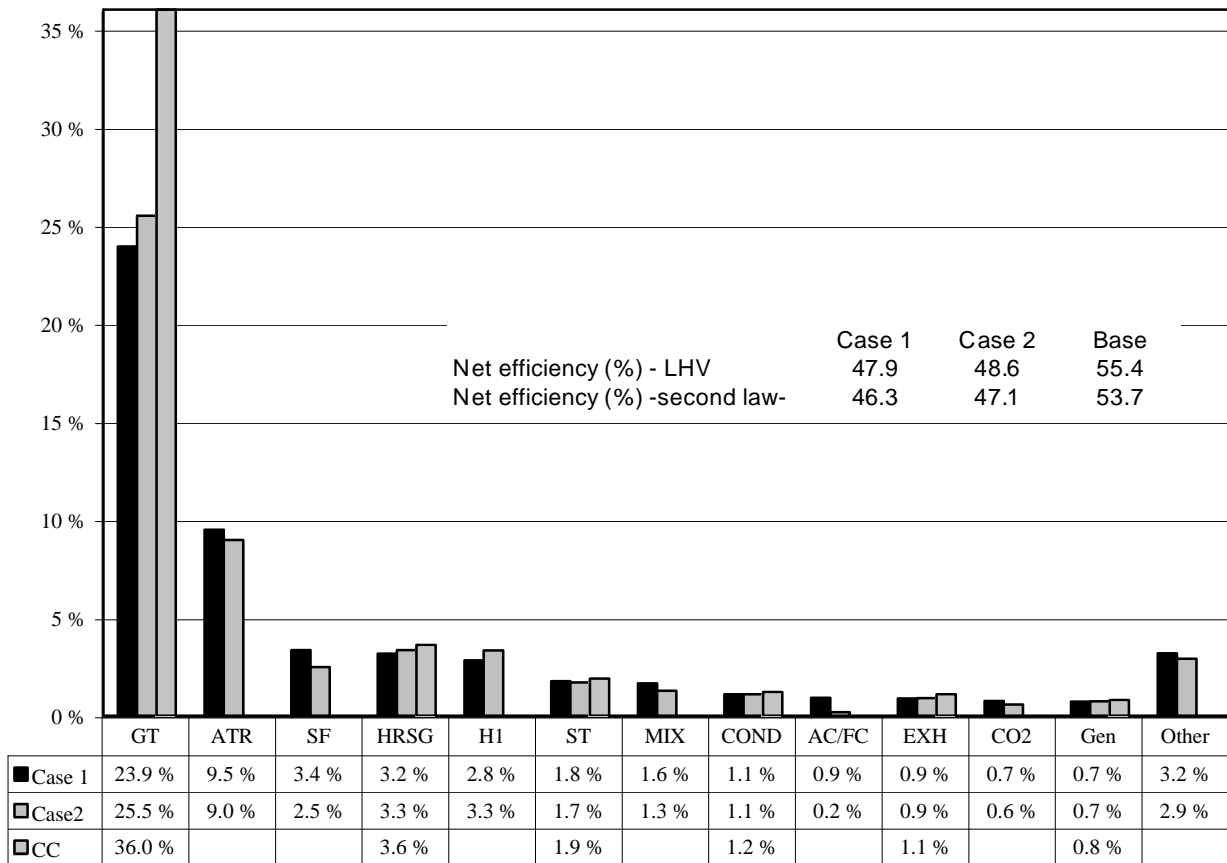


Figure 2 Exergy loss breakdown. In “Other”, the losses of the following units are lumped together: H3, HTS, PRE, ABS, H4, H5, LTS, H2, WR

CONCLUSIONS

Two cases of a gas-turbine combined-cycle power plant with natural-gas reforming, CO₂ capture, and combustion of a hydrogen-rich fuel were simulated. The resulting first-law (LHV) efficiencies were 47.9 and 48.6, respectively. The second-law (exergy) efficiencies were 46.3 and 47.1. A comparable conventional natural-gas fired combined-cycle gave first- and second-law efficiencies of 55.4 and 53.7, respectively.

If it was seen that a lower pressure (approx. 14 bar) in the reforming process and fuel compression was beneficial from a thermodynamic point of view compared to maintaining a high pressure (approx. 25 bar) throughout the process.

The irreversibility (exergy loss) was determined in each unit of the system. The irreversibility of the reactor units, *i.e.* combustor, reformers, shift reactors, was close to that of the conventional natural-gas combustor. The greater loss in the new concept resulted from additional losses in supplementary firing and heat exchange between the reforming and power processes.

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