

# Joining semi-closed gas turbine cycle and tri-reforming: SCGT-TRIREF as a proposal for low CO<sub>2</sub> emissions powerplants

Daniele Fiaschi \*, Andrea Baldini

Dipartimento di Energetica "Sergio Stecco", University of Florence, Via C. Lombroso 6/17, 50134 Firenze, Italy

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## ABSTRACT

Methane conversion to a rich H<sub>2</sub> fuel by reforming reactions is a largely applied industrial process. Recently, it has been considered for applications combined to gas turbine powerplants, as a mean for (I) chemical recuperation (i.e. chemical looping CRGT) and (II) decarbonising the primary fuel and make the related power cycle a low CO<sub>2</sub> releaser.

The possibility of enhancing methane conversion by the addition of CO<sub>2</sub> to the steam reactant flow (i.e. tri-reforming) has been assessed and showed interesting results. When dealing with gas turbines, the possibility of applying tri-reforming is related to the availability of some CO<sub>2</sub> into the fluegas going to the reformer. This happens in semi-closed gas turbine cycles (SCGT), where the fluegas has a typical 14–15% CO<sub>2</sub> mass content. The possibility of joining CRGT and SCGT technologies to improve methane reforming and propose an innovative, low CO<sub>2</sub> emissions gas turbine cycle was assessed here. One of the key issues of this joining is also the possibility of greatly reduce the external water consumption due to the reforming, as the SCGT is a water producer cycle.

The SCGT-TRIREF cycle is an SCGT cycle where fuel tri-reforming is applied. The steam due to the reformer is generated by the vaporization of the condensed water coming out from the fluegas condensing heat exchanger, upstream the main compressor, where the exhausts are cooled down and partially recirculated. The heat due to the steam generation is recuperated from the turbine exhausts cooling. The reforming process is partially sustained by the heat recovered from the turbine exhausts (which generates superheated steam) and partially by the auto thermal reactions of methane with fresh air, coming from the compressor (i.e. partial combustion).

The effect of CO<sub>2</sub> on methane reforming (tri-reforming effect) increases with decreasing steam/methane ratio: at very low values, around 30% of methane is converted by reactions with CO<sub>2</sub>. At high values of steam/methane ratio, the steam reforming reactions are dominant and only a marginal fraction of methane is interested to tri-reforming.

Under optimised conditions, which can be reached at relatively high pressure ratios (25–30), the power cycle showed a potential efficiency around 46% and specific work at 550 kJ/kg level. When the amine CO<sub>2</sub> capture is applied, the specific CO<sub>2</sub> emissions range between 45 and 55 g<sub>CO2</sub>/kW h.

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## 1. Introduction

There is an ever increasing consensus, worldwide, that one of the main reasons of earth's climate change is the CO<sub>2</sub> emissions from anthropogenic activities involving the combustion of hydrocarbons (i.e. industry, power generation and utilities) [1]. For this reason, many researchers addressed their efforts to the development of new power cycle concepts, including those with integrated CO<sub>2</sub> capture and subsequent sequestration [2–9]. It seems to be the most promising option to tackle greenhouse issue in the short to midterm [1]. About one third of the anthropogenic carbon dioxide emissions comes from fossil fuelled powerplants [10], thus they

deserve special attention when dealing with CO<sub>2</sub> capture and sequestration. One of the main challenges to succeed in the task of reducing CO<sub>2</sub> emissions from powerplants is closely related to the chance of achieving cost effective ways to capture CO<sub>2</sub> from fluegas [11]. Typically, it is largely diluted with nitrogen when, as in most cases, combustion is done with air. CO<sub>2</sub> concentration in the exhausts ranges from 4% to 6% of gas turbines up to 14–15% of coal fired plants. For this reason, its capture often represents the most energy and costs expensive operation in the overall CO<sub>2</sub> sequestration process and must be carefully integrated and optimised into the whole basic power cycle layout, in order to minimise its impact on performance and costs. Currently, adding CO<sub>2</sub> capture and sequestration to standard GTCCs leads to efficiency drops ranging from 4% to 10% and to an increase in cost of energy from 30% to 60% [11,12].

\* Corresponding author. Tel.: +39 055 4796776; fax: +39 055 4224137.

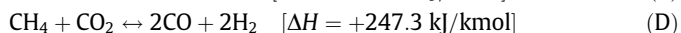
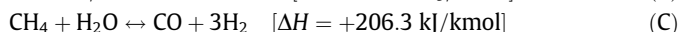
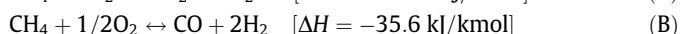
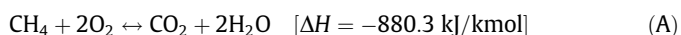
E-mail address: [danif@de.unifi.it](mailto:danif@de.unifi.it) (D. Fiaschi).

Three main ways of CO<sub>2</sub> capture from powerplants were widely investigated [1,10]:

- Post-combustion capture, by removing CO<sub>2</sub> from exhausts. The main advantage is the possibility of applying capture devices as retrofit to existing powerplants, with only modest changes to the cycle layout and to the components design. On the other hand, the main disadvantage is the very low concentration of CO<sub>2</sub> into the atmospheric pressure fluegas, which makes separation and subsequent recompression for storage difficult and high energy demanding [12–14].
- Pre-combustion capture, by fuel decarbonisation, which is a process often integrated into the powerplant layout and shifts the fuel to high hydrogen content while separating and removing a fraction or the whole of carbon content. The main advantage of this technique is the high pressure of fuel, which simplifies CO<sub>2</sub> separation, and the low mass flowrate to be treated. On the other hand, it requires supplemental reactors (for example reforming and shifting [2–5,8]) and relevant modification to the existing cycles layouts.

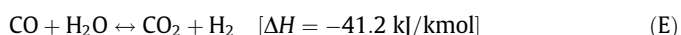
## 2. Basic idea and principles of tri-reforming process

Reuse of carbon dioxide released by human activities (energy production, transports, industry, etc.) could assume a very important role in tackling the worldwide CO<sub>2</sub> emissions issue [15]. Recent studies [15,16] proposed a relatively innovative process for the production of hydrogen rich syngas (with fixed H<sub>2</sub>/CO ratio) from methane reforming. This process, named tri-reforming (TRIREF) joins the reactions of CO<sub>2</sub> reforming, steam reforming, partial oxidation and complete oxidation of methane into the same reactor. The following reactions were considered:



When compared to some more conventional reforming processes (i.e. standard steam reforming, auto thermal reforming, partial oxidation, etc.), the CO<sub>2</sub>-reforming reaction (D) is added by CO<sub>2</sub> enrichment of reactants mixture. The “stand alone” process is well known but, recently, some advantages when combined with standard reforming processes were shown [15,17]. Coupling CO<sub>2</sub> reforming and steam reforming allows the achievement of syngas with the required H<sub>2</sub>/CO ratio, while avoiding the formation of solid carbon coming from the reactions  $\text{CH}_4 \leftrightarrow \text{C} + 2\text{H}_2\text{O}$  and  $2\text{CO} \leftrightarrow \text{C} + \text{CO}_2$ . Some experimental campaigns of Song and Pan showed that the introduction of CO<sub>2</sub>-reforming reaction may also improve the life of eventual catalysts and significantly reduce the temperature range of solid carbon formation [17]. In the same studies, they showed that it is possible to reach up to 95% of primary methane fuel conversion at equilibrium temperature included into the 1073–1123 K range when (I) CO<sub>2</sub>-H<sub>2</sub>O ratio is close to 1, (II) O<sub>2</sub>/CH<sub>4</sub> ratio is 0.1 and (III) (CO<sub>2</sub> + H<sub>2</sub>O + O<sub>2</sub>)/CH<sub>4</sub> ratio is 1.05.

A further important chemical reaction taking place in the TRIREF process is the water gas shift:



which may have an important role in the whole process.

Some interesting studies were carried out when the process is fed with methane and exhausts coming from combustion chambers of powerplants [15,17]. The endothermic reforming reactions are thermally sustained by the heat content of the exhausts and

the partial combustion of primary methane fuel, which is done with the excess oxygen of the exhausts. In this way, the TRIREF becomes specially attractive for gas turbines, where large excess air is present into the exhausts and high methane conversions may be sustained. Often, nickel and magnesium oxide catalysts play an important role in CO<sub>2</sub>-reforming reactions [17].

The interest toward tri-reforming process is connected to its possible integration in gas turbine based power cycles with low CO<sub>2</sub> emissions. The objective is to produce a relatively highly H<sub>2</sub> and CO<sub>2</sub> concentrated fuel, to be decarbonised upstream the combustion chamber.

The methane conversion levels are closely related to the conditions of gas at reformer inlet (specially its CO<sub>2</sub> content, composition and temperature), thus its application to semi-closed gas turbine cycles seems to be attractive [18,19]. Here, the relatively high CO<sub>2</sub> concentration into the fluegas is useful to provide the required amount of carbon dioxide to the TRIREF reactions chain (A)–(E). Moreover, SCGT is a water producer cycle [18,19], which means that the amount of steam required for methane reforming is internally produced, thus the resulting cycle is not water consuming.

## 3. Modelling and parametric analysis of tri-reforming process

The calculations related to tri-reforming reactions were carried out by a dedicated homemade software, developed at the Energy Engineering Dept. of University of Florence by the means of thermodynamic EES software [20]. Once the inlet conditions of reactants into the tri-reforming reactor are known, the Gibbs free energy of each compound in products and reactants is evaluated and the overall difference between Gibbs free energy of products and reactants is minimised through a general procedure providing, as a final result, the equilibrium composition of the syngas fuel. The reactor was considered adiabatic and the kinetics of reactions were neglected.

The thermodynamic model of gas turbine cycle, again developed with EES software at the Energy Engineering Dept. of University of Florence, includes a rather classic and well tested blade cooling procedure, which is able to provide reliable results on current production machines [21–23]. The thermodynamic code of SCGT was developed again within EES environment, starting from the existing one, developed some years ago at the Energy Engineering Dept. of University of Florence in Fortran environment [18,19].

The sensitivity analysis of tri-reforming process to the following four main parameters was carried out:

- Steam flowrate at reformer inlet per unit methane flowrate (H<sub>2</sub>O<sub>ratio</sub>).
- Oxidizer flowrate at reformer inlet per unit methane flowrate (m<sub>ref ratio</sub>).
- Gas turbine pressure ratio (β).
- Inlet turbine temperature (here assumed as the maximum GT cycle temperature T<sub>max</sub>).

This analysis was done to assess (I) the methane conversion potential at different cycle parameters and (II) the contribution of CO<sub>2</sub>-reforming reaction to the overall process. To do this, we referred to a simplified scheme of SCGT-TRIREF (Fig. 1), where no CO<sub>2</sub> sequestration was applied. It allowed a special focus on the TRIREF reactions and the way they are affected by the reformer inlet conditions and main gas turbine parameters. Subsequently, the results and analysis were extended to the complete SCGT-TRIREF with CO<sub>2</sub> removal.

Compared to the standard SCGT configurations (combined cycles SCGT/CC and recuperative–evaporative cycles SCGT/RE [18]), the following main differences in the cycle scheme can be remarked:

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