Simulation of the Effects of Turbine Exhaust Recirculation on the Composition of Flue Gas for A CO₂ Capture Unit

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Abstract

The main objective of this paper is to study the effects of Flue Gas Recirculation (FGR) ratio and Excess Air (EA) in a natural gas-fired turbine for an effective CO₂ absorption by amines. To achieve this goal, the flue gas should contain at least 10% (mol.) of CO₂. Moreover, in order to avoid technical problems related to the oxidative degradation of amines, the flue gas should also contain less than 5% (mol.) of O₂. The simulation results indicate that, for a gas turbine that limits the temperature of the exhaust gas leaving the combustor at 1100°C, an excess air (EA) of 200% and a Flue Gas Recirculation (FGR) ratio of 0.65 are needed to fit the requirements of an effective absorption process by amines. For a turbine that allows temperatures as high as 1500°C, the operating parameters (EA=100% and FGR ratio of 0.4) will be selected.

Keywords: Carbon capture; Flue gas composition; Exhaust gas recirculation ratio; Excess air; Turbine metallurgical limitation

Introduction

One of the largest EOR (Enhanced Oil Recovery) projects worldwide using anthropogenic CO₂ is the Weyburn project in Canada. The CO₂ required for this project is produced at Dakota Gasification Company's synthetic fuel plant in Beulah, North Dakota, USA. The project is expected to produce 122 million bbls of incremental oil, extending the life field by 20-25 years and increasing the oil recovery to 34% of OOIP (Original Oil In Place) [1,2]. In order to provide large volumes of CO₂, to serve EOR projects in the oil fields of the UAE, carbon dioxide need to be captured from industrial facilities such as power and desalination plants, oil refineries, gas processing facilities and/or petrochemical complexes [3]. As shown in Table 1, 76 million tons of CO₂ were emitted in Abu Dhabi and nearby (UAE) during the year 2008.

The valuable fuel gas actually used for EOR techniques in the UAE could be utilized to produce electricity in power generation plants. The captured CO₂ from these plants could be transported and stored in the large oil fields. The use of CO₂-EOR technique will also enhance the production of crude oil in the UAE.

Challenges of the absorption of CO₂ from the exhaust gas of gas turbines

Unlike Pre-combustion and Oxy fuel strategies, Post-combustion CO₂ Capture can be integrated with the existing power generation stations. At the moment, the post-combustion CO₂ capture using amine scrubbing is the most mature technology, and arguably the preferred technology, since the process of absorption has been used for decades in gas treatments [4,5]. The existing size of commercial CO₂ amine scrubbing plants is relatively small (few 100,000 metric tons/year).

However, larger CO₂ capturing plants (>1000,000 metric tons/year) might be required for any future CCS (Carbon Capture and Storage) project [6].

The absorption plants using amine mixtures are most effective at around 10-15 (mol.%) of CO₂ in the flue gas [7]. This percentage depends mainly on the composition of the combustible, the flue gas recirculation (FGR) ratio and the excess air (EA) used in the combustor. Lower CO₂ concentrations in the flue gas require a leaner solvent loading to achieve an adequate “driving force” between the solvent and the flue gas stream for high levels of CO₂ Capture. However, leaner solvent loadings require also a higher CO₂ removal from the solvent, which will increase the amount of energy utilized in the stripper and the cost of the CO₂ Capture plant.

In power-generation plants, natural gas (NG) is preferred to the other heavier fuels because the environmental problems are minimized and the total cost of a CCS plant is reduced by avoiding corrosion and other technical problems due to impurities (H₂S, SOx, NOx, HCl….) in the captured CO₂. In a simplified NGCC (Natural Gas Combined Cycle) power plant configuration (Figure 1), the exhaust gas from the combustor is expanded in a gas turbine (GT) to produce electricity. The flue gas leaving the CTG (Combustion Turbine Generator) at high temperature will generate steam in a heat recovery steam generator (HRSG) before entering the CO₂ capture unit. The steam is utilized to generate electricity from a steam turbine (ST).

In order to keep the temperatures in the gas turbine at permissible levels, the combustor has a typical overall excess air ratio in the range 3-3.5. As a result, flue gas has a percentage of CO₂ in flue gas of about 3-3.5.

<table>
<thead>
<tr>
<th>Industry</th>
<th>Millions Tons of CO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Power generation Plants</td>
<td>33 (43%)</td>
</tr>
<tr>
<td>Gas processing and Refineries</td>
<td>25 (33%)</td>
</tr>
<tr>
<td>Metal Industries</td>
<td>15.8 (21%)</td>
</tr>
<tr>
<td>Petrochemical Plants</td>
<td>2.2 (3%)</td>
</tr>
<tr>
<td>Total</td>
<td>76</td>
</tr>
</tbody>
</table>

Table 1: Estimated amount of CO₂ by industry in Abu Dhabi and nearby for the year 2008 [3].

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Flue gas from natural gas-fired turbines has also relatively high levels of O₂ which can cause corrosion problems and degrade amine solvents. According to Chakravarti et al. [9], oxidative degradation of amines often occurs in CO₂ capture plants when the flue gases contain a high O₂ content such as 5%. To counter the influence of oxygen, the approach currently practiced is the use of chemical inhibitors. For example, the processes licensed by Kerr-McGee/ABB Lummus Global Inc. and by Fluor Daniel [10] use inhibited monoethanolamine solutions. However, corrosion inhibitors could also act as a catalyst towards the solvent degradation. Praxair has been granted two patents for improved oxygen tolerant absorption processes [11,12]. The key aspect of Praxair’s successful approach is handling the dissolved oxygen in amine mixture through process modifications instead of the introduction of additional chemicals.

Flue Gas Recirculation (FGR) in gas turbines for an effective CO₂ absorption by amines

One possible option for increasing the concentration of CO₂ and decreasing the amount of O₂ in the flue gas from power plants using natural gas is recirculation of a part of the flue gas. The effects of Flue Gas Recirculation (FGR) on the concentration of CO₂ and O₂ in the flue gas have been investigated [7,8,13,14]. Akram et al. [7] studied the effects of recirculating part of flue gas in a 100 Kw (plus 150 Kw hot water) CHP gas turbine Turbec T100. Their preliminary results indicate that a recirculation ratio of 0.45 increased the molar percentage of CO₂ from 1.5% to 3.0% and the molar percentage of O₂ decreased from 18.2% to 16.0%. Their results show also that recycling part of the flue gas decreases NOx emissions by decreasing the flame temperature. Using a natural gas-fired power plant of 700 MW, the results presented by Bolland and Saether [8] concluded that the maximum allowable recirculation ratio is about 0.65. Higher values affected significantly the combustion process due to a low percentage of oxygen. Røkke and Hustad [13] used a 65 kW gas turbine combustor to study the effects of FGR on the combustion process. The effects of adding N₂, CO₂ and O₂ in the combustion process were investigated focusing on stability of the flame and emissions of NOx. Their results show that adding N₂ and CO₂ decreases the NOx emissions by decreasing the combustion temperature, whereas O₂ addition increases the NOx emissions. The results show also that a significant decrease of NOx is seen when flue gas is premixed with the fuel, whereas the addition into the air stream has less effect on the NOx emissions. For the stability of the flame in the combustor, the maximum values of the mass ratios O₂/CH₄, CO₂/CH₄ and N₂/CH₄ were respectively 0.79, 1.29 and 1.15. Carbon monoxide (CO) was also detected at high FGR ratios when combustion stoichiometry was approached [15].

The minimum air quantity needed to get a complete oxidation of the fuel gas is known as theoretical air [16]. It is known that the hot temperatures at the gas turbine inlet are a metallurgical limitation for each gas turbine model. These temperatures vary from 800°C to 1700°C depending on turbine blade materials and whether or not they have cooling systems [15]. As a consequence, industrial gas turbines use excess air (EA) values from 100% to 600%. The reason for using high EA in a gas turbine is to keep the turbine inlet temperature at a permissible level. A high turbine inlet gas temperature will then require a lower quantity of secondary and tertiary air to cool down the combustion gas to the specified temperature. The Modelisation results of Martinez et al. [17] show that, at a gas temperature of 1200°C at the inlet of a turbine,
the excess air is 198.79%. If the temperature is 1000°C, the excess air increases to 324.51%. According to the authors, the difference between the calculations of the excess air using dry air and wet air is negligible.

Based on the literature review, the Flue Gas Recirculation (FGR) ratio is optimized in order to minimize the content of fresh secondary and tertiary air used for cooling by recycling part of the flue gas without affecting the amount of oxygen necessary for the stoichiometry of the combustion. The main objective of this study is to determine the operating conditions (flue gas recirculation ratio and amount of excess air) in a gas turbine in order to obtain at least 10% (mol.) of CO2 and no more than 5% of O2 in the flue gas for an effective CO2 capture process. The stoichiometric requirement and is defined as:

$$
CH_4 + (2O_2 + 7.52N_2) \rightarrow CO_2 + 2H_2O + 7.52N_2 \quad (1)
$$

$$
C_2H_6 + (3.5O_2 + 13.17N_2) \rightarrow 2CO_2 + 3H_2O + 3.17N_2 \quad (2)
$$

$$
C_3H_8 + (5O_2 + 18.81N_2) \rightarrow 3CO_2 + 4H_2O + 3.17N_2 \quad (3)
$$

Estimation of the mass flowrate of the natural gas

The composition of the natural gas under consideration is presented in Table 2 [2]. Assuming that the water component of a combustion process is in a vapor state at the end of combustion, the Lower Heating Values (LHV) of the components of the natural gas will be used: LHV (CH$_4$)=50 MJ/kg; LHV (C$_2$H$_6$)=47.8 MJ/kg; LHV (C$_3$H$_8$)=46.35 MJ/kg. For the given composition, the average LHV of the natural gas is equal to 46.7 MJ/kg. Based on Low Heat Value (LHV), the net efficiencies of the NGCC plants with post-combustion capture are around 47.4-49.6% [19]. Therefore, to produce 500 MW with an efficiency of 48.5%, 1030.9 MW is needed from the combustion process. The needed mass flowrate of the methane, ethane and propane is 22.07 kg/s and the corresponding mass flowrate of the natural gas stream is equal to 23.54 kg/s.

Optimum value of mass flowrate of air for combustion

The stoichiometric combustion is a theoretical point in which the optimum amount of oxygen and fuel mix generates the most heat possible and maximum combustion efficiency is achieved. According to the composition of the natural gas, the following reactions are used to calculate the theoretical air for combustion:

$$
CH_4 + (2O_2 + 7.52N_2) \rightarrow CO_2 + 2H_2O + 7.52N_2 \quad (1)
$$

$$
C_2H_6 + (3.5O_2 + 13.17N_2) \rightarrow 2CO_2 + 3H_2O + 3.17N_2 \quad (2)
$$

$$
C_3H_8 + (5O_2 + 18.81N_2) \rightarrow 3CO_2 + 4H_2O + 3.17N_2 \quad (3)
$$

The AFR (Air Fuel Ratio) is calculated from the mass balance of the atoms of Carbon, Oxygen, Hydrogen and Nitrogen in equations (1) to (3). Solving the four atomic material balances, the molar stoichiometric AFR (Air Fuel Ratio) is 9.89 and the corresponding mass AFR is 17.16. As a result, 378.8 kg/s of stoichiometric air need to be added to 23.54 kg/s of natural gas stream for complete combustion. However, for any combustion process there is a balance sought between losing energy from using too much air, and wasting energy from running too rich and producing toxic products like carbon monoxide. The optimum combustion efficiency occurs at the optimum AFR and controlling this provides the best efficiency. This optimum value is often estimated by measuring O2 and CO concentrations in the flue gas [20].

Excess Air (EA) is expressed as a percentage increase over the stoichiometric requirement and is defined as:

$$
EA = \frac{Actual AFR - Stoichiometric AFR}{Stoichiometric AFR} \times 100\% \quad (4)
$$

Methodology

Proposed layout of gas turbine

The Combustion Turbine Generator (CTG) of a NGCC (Natural Gas Combined Cycle) power plant producing 500 MW is under consideration in this study. It is assumed that natural gas (NG) is available in a battery limit of the plant at 3 MPa and 40°C [18]. Air is considered to enter at 101 kPa and 30°C and compress up to 3.1 MPa to mix with natural gas in the burners of the combustor. In order to increase the efficiency of the cycle, the recycled flue gas is cooled at 40°C. In the proposed recycling process, the flue gas is added to the compressed air. The pressure of the recycled gas will increase from 110 kPa to the pressure of the compressed fresh air of 3.1 MPa. The main equipment used in the proposed recycling process (Figure 2) is an air compressor, three flue gas compression stages (compression ratio for each stage=3.1) with intercooling and separators, a combustor and a gas turbine. The proposed recycling process of the flue gas will have the advantage of condensing part of the water in the intermediate separators and decreasing the total energy used for the compression of recycled flue gas and the fresh air.
Flue gas Recirculation (FGR) ratio follow the equation:

\[ FGR_{ratio} = 0.329 + 0.0019(EA) - 2 \times 10^{-6} \times (EA)^2 \]  

The relationship between excess air (EA) and the maximum value of FGR ratio is very close to the value 0.65 given in the literature for an Excess Air (EA) changing from 100% to 600%. The corresponding simulation results are shown in Figure 4.

For this case study, the data indicate that the temperature varied from 1666°C (EA=100% and FGR ratio=0) to 588°C (EA=600% and FGR ratio=0.75). It is shown that both the increase of excess air and flue gas recirculation ratio decrease the temperature of the exhaust gas. However, above an excess air of 400%, the effects of excess air on the temperature of the exhaust gas become less important.

Effects of flue gas recirculation and excess air on the amount of CO\(_2\) in the flue gas

For an effective absorption in a CO\(_2\) capture plant, the molar percentage of CO\(_2\) in the flue gas should be at least equal to 10%. The simulation outputs of the effects of the flue gas recycle ratio (FGR) and the excess air (EA) on the percentage of carbon dioxide in the flue gas entering the absorption unit are shown in Figure 5.

It is clear that increasing the flue gas recirculation (FGR) ratio increases the CO\(_2\) content in the flue gas and increasing the excess air (EA) decreases the amount of CO\(_2\) at the exhaust of the turbine. For example, for an excess air (EA) at 100%, the percentage of CO\(_2\) increased from 5.4% to 11% with the change of FGR from 0% to 50%. On the other hand, for a FGR of 50%, the percentage of CO\(_2\) decreased from 11% to 5% by varying the excess air (EA) from 100% to 300%. It is also shown that for values of EA (Excess Air) ratio higher than 400%, the effects of excess air on the amount of CO\(_2\) become very small.

### Simulation Results

The effects of Flue Gas Recirculation (FGR) ratio and the Excess Air (EA) on the temperature of the exhaust gas leaving the combustor and on the percentage of CO\(_2\) and O\(_2\) in the flue gas stream to the absorption unit have been simulated using Aspen Hysys V 8.0 and the Soave-Redlich-Kwong (SRK) equation of state (Table 3).

### Effects of flue gas recirculation and excess air on the temperature of exhaust gas

In a gas turbine, the blades have a metallurgical limitation and the temperatures could vary from 800°C to 1700°C depending on their materials and whether or not they have cooling systems [15]. Since the amount of excess air depends on the thermal limitation of the turbine, the first part of this investigation is to simulate the effects of excess air and flue gas recirculation ratio on the temperature of the exhaust gas leaving the combustor. The corresponding simulation results are shown in Figure 3.

### Maximum values of FGR ratio

Since gas turbines use different values of EA (excess air), the maximum value of FGR ratio will be estimated in this investigation for excess air varying from 100% to 600%. For example, if a gas turbine use 100% excess air, the corresponding mass AFR is equal to 34.32 kg/s. (416.70 kg/s are used as primary air and 340.92 kg/s are used for cooling). Therefore, the maximum value of the flowrate of primary air for combustion is 416.70 kg/s.

### Maximum values of flue gas Recirculation (FGR) ratio

The maximum FGR ratio of 0.64 for 200% Excess Air (EA) is very close to the value 0.65 given in the literature for an Excess Air Ratio (EAR) of 3-3.5 [10]. The relationship between the maximum FGR ratio and the excess air (EA) values is shown in Figure 3.

According to Figure 3, the effects of EA (Excess Air) on the FGR (Flue gas Recirculation) ratio follow the equation:

\[ (FGR)_{ratio} = 0.329 + 0.0019(EA) - 2 \times 10^{-6} \times (EA)^2 \]
amine in the CO₂ capture plant, the percentage of O₂ in the flue gas should be limited. Moreover, in order to reduce technical problems due to amine oxidative degradation, the molar percentage of O₂ in the flue gas should be lower than 5%. In Figure 6, the effects of excess air (EA) and flue gas recirculation (FGR) ratio on the concentration of O₂ of the flue gas entering the absorption unit are shown.

The flue gas recirculation (FGR) ratio decreased the O₂ content in the flue gas and increasing the excess air (EA) increased the amount of O₂. For an excess air (EA) of 100%, the percentage of O₂ decreased from 11% to 1.1% with the change of FGR from 0% to 50%. On the other hand, for a FGR of 50%, the percentage of O₂ increased from 1.3% to 11% by increasing the excess air (EA) from 100% to 300%. After an excess air of 400%, the effects of excess air on the content of oxygen become insignificant.

Discussion and Conclusion

For an effective carbon capture by an amine mixture, the molar percentage of CO₂ in the flue gas should be at least equal to 10%. Moreover, in order to reduce technical problems due to amine oxidative degradation, the molar percentage of O₂ in the flue gas should be limited to 5%. Because the captured CO₂ will be stored through a CO₂-EOR process, it is also important to limit the content of NOx in the flue gas.

For a NGCC (Natural Gas Combined Cycle) power plant producing 500 MW, Aspen Hysys V 8.0 and the Soave-Redlich-Kwong (SRK) equation of state were utilized in order to simulate the effects of Flue Gas Recirculation (FGR) ratio and excess air (EA) on the temperature of the exhaust gas leaving the combustor and the concentrations of CO₂ and O₂ of the flue gas entering the absorption unit.

For the conditions of an effective absorption process (the molar percentage of CO₂ at least equal to 10%), the simulation results indicate that only a gas turbine with 100% excess air with at least a FGR ratio of 0.45 and a gas turbine with 200% excess air and at least a FGR of 0.65 fit the requirements (Figure 5). The corresponding exhaust gas temperatures are 1450°C and 1035°C respectively. If the metallurgical limitation of the turbine does not allow temperatures higher that 1035°C, the second operating conditions (200% EA and FGR ratio of 0.65) will be the preferred option. For a turbine allowing temperatures as high as 1450°C, the first operating parameters (100% EA and FGR ratio of 0.45) will be selected.

In order to avoid the oxidative degradation of amine solutions, the simulation data show that, only a gas turbine with 100% excess air with at least a FGR ratio of 0.4 or a gas turbine with 200% excess air and at least a FGR ratio of 0.6 are in concordance with the condition (molar percentage of O₂ ≤ 5% in Figure 6). The corresponding exhaust gas temperatures are 1480°C and 1060°C respectively. If the metallurgical limitation of the turbine does not allow temperatures higher that 1060°C, 200% excess air and a FGR ratio of 0.6 should be selected. This option will also decrease the percentage of NOx in the flue gas. For a turbine allowing temperatures as high as 1480°C, the first operating parameters (EA=100% and FGR ratio of 0.4) will be selected.

In conclusion, Flue Gas Recirculation (FGR) ratio increased the content of CO₂ in the flue gas and decreased both the amount of O₂ in the flue gas and the temperature of the exhaust gas. The simulation results indicate also that for excess air values higher than 400%, the effects of excess air on the temperature of the exhaust gas and the amount of carbon dioxide and oxygen in the flue gas become small. Finally, the simulation outputs suggest that, a gas turbine that allows a maximum temperature of 1000°C, an excess air of 200% is needed. For this particular gas turbine, a FGR of 0.65 was required to fit the conditions of an effective absorption process by amines. The molar percentage of CO₂ has increased from 3% to 10 %, while the molar concentration of O₂ decreased from 14% to 2%. Moreover, the combustion temperature has also decreased from 1359°C to 1035°C. These operating conditions (EA=200% and FGR ratio=0.65) are selected because the NOx emissions will eventually be decreased. The corresponding amount of CO₂ produced is 221485 kg/hr. (1.94 Million Tons/year). Therefore, this flowrate is suitable as a feed for a CO₂ Capture unit for a future CCS project.

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