

Simulation of the Effects of Turbine Exhaust Recirculation on the Composition of Flue Gas for a $\rm CO_2$ Capture Unit

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Abstract

For an effective CO_2 absorption by amines, the flue gas should contain at least 10% (mol.) of CO_2 . 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 O_2 . This paper presents preliminary calculations and simulation of the effects of Flue gas recirculation (FGR) ratios and excess air (EA) on the temperature and the concentration of CO_2 and O_2 in the exhaust gas of a natural-gas fired turbine. The results of the methodology utilized (preliminary calculations and simulation) indicate that, for a gas turbine that limits the temperature of the exhaust gas leaving the combustor at 1035°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 1480°C, the operating parameters (EA=100% and FGR ratio of 0.4) will be selected.

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

Introduction

One of the largest EOR (Enhanced Oil Recovery) projects worldwide using anthropogenic CO_2 is the Weyburn project in Canada. The CO_2 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 field life 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 CO_2 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. As shown in Table 1 [3], 76 million tons of CO_2 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 CO_2 from these plants could be transported and stored in the large oil fields. The use of CO_2 -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 CO_2 Capture can be integrated with the existing power generation stations. At the moment, the post-combustion CO_2 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 CO_2 amine

Industry	Millions Tons of CO ₂	
Power generation Plants	33 (43%)	
Gas processing & Refineries	25 (33%)	
Metal Industries	15.8 (21%)	
Petrochemical Plants	2.2 (3%)	
Total	76	

Table 1: Estimated amount of \rm{CO}_2 by industry in Abu Dhabi and nearby for the year 2008 [3].

scrubbing plants is relatively small (few 100,000 metric tons/year). However, larger CO_2 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 CO_2 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 CO_2 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 CO_2 Capture. However, leaner solvent loadings require also a higher CO_2 removal from the solvent, which will increase the amount of energy utilized in the stripper and the cost of the CO_2 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 (H_2S , 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

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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% [8]. 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 CO, 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 Saether8 show that, using a recirculation ratio of 0.4, the molar percentage of CO₂ increased from 3.3% to 5.5% and the molar

percentage of O_2 decreased from 13.8% to 9.8%. To maintain high cycle efficiency, flue gas was cooled before reinjection in the combustor.

Abu Zahra [14] used Aspen plus and the Peng-Robinson equation of state, to simulate the effect of flue gas recirculation in an IGCC power plant using a low-pressure gasifier. With all the other parameters of the gas turbine constant, the results indicated that the concentration of CO_2 increased from 7.3 (% mol.) to 14.0 (% mol.) with the increase of the flue gas recirculation ratio from 0% to 45%. Moreover, the concentration of O_2 decreased from 14.2 (% mol.) to 8.0 (% mol.) with the same increase of flue gas recirculation.

Maximum value of Flue gas recirculation (FGR) ratio in gas turbines

To reduce the cost of a CCS project, high Flue Gas Recirculation (FGR) ratios are desirable to achieve the maximum CO₂ concentration in the flue gas to be treated in the absorption unit. However the combustion process sets a limit due to the corresponding reduction in O2 concentration. Due to the importance of the recirculation rate on the overall performance of the CO, removal process, combustion studies are required to define the maximum achievable recirculation rate. The maximum FGR ratio value will depend mainly on the combustible, the amount of excess air used and the turbine mechanical limitations. Using natural gas in a turbine of 700 MW, Bolland and Saether8 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 $\mathrm{N_2}$ and $\mathrm{CO_2}$ 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

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Components	Mole % 1.0	
CO ₂		
CH ₄	93.0	
C ₂ H ₆	3.0	
C ₃ H ₈	1.0	
0 ₂	2.0	
Total	100	

Table 2: Natural gas composition.

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 systems15. 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 is198.79%. 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 CO_2 and no more than 5% of O_2 in the flue gas for an effective CO_2 capture process with minimum technical problems related to the oxidative degradation of the amine mixture.

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 3MPa and 40°C [18]. Air is considered to enter at 101 kPa and 30°C and compress up to 3.1MPa

to mix with natural gas in the burners of the combustor. The flue gas is assumed to be recycled after the HRSG (Heat Recovery Steam Generator). 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.

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_2H_6)=47.8 MJ/kg; LHV (C_3H_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:

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

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

$$C_{3}H_{8} + (5O_{2} + 18.81 N_{2}) \rightarrow 3CO_{2} + 4H_{2}O + 18.81 N_{2}$$
 (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

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EA (%)	Mass AFR	Total air (kg/s)	(Air + NG) (kg/s)	Maximum Flue gas recycled (kg/s)	Maximum FGR ratio
100	34.32	757.62	781.16	340.92	0.436
200	51.49	1136.43	1159.97	743.27	0.640
300	68.65	1515.23	1538.77	1122.07	0.729
400	85.82	1894.04	1917.58	1500.88	0.782
500	102.98	2272.85	2296.39	1879.69	0.818
600	120.15	2411.41	2434.95	2018.25	0.828

Table 3: Maximum values of Flue gas Recirculation (FGR) Ratio for different values of EA (Excess Air).



Figure 3: Relationship between excess air (EA) and the maximum value of FGR ratio.



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 O_2 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

$$EA = \frac{Actual \ AFR - Stoichiometric \ AFR}{Stoichiometric \ AFR} x100\% \tag{4}$$

It is sometimes convenient to use the Excess Air Ratio (EAR) defined as:

$$EAR = \frac{Actual AFR}{Stoichiometric AFR}$$
(5)

For a turbine using natural gas, no more than 10% excess air is normally added to the stoichiometric air for combustion [21]. Using equation (4) and for 10% excess air, the optimum value of the molar and the mass AFR are 10.88 and 18.88 respectively. The corresponding optimum flowrate of primary air for combustion is 416.70 kg/s.

Maximum values of flue gas recirculation (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 Therefore, the needed amount of air for combustion and cooling is equal to 757.62 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 the recycled flue gas is equal to the amount of air (340.92 kg/s) used for cooling the turbine. This value corresponds to a maximum value of FGR ratio of 0.436. Table 2 shows the corresponding values of the maximum FGR for EA (Excess Air) changing from 100 % to 600%.

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 (Excess Air = 200%-250%)10. The relationship between the maximum FGR ratio and the excess air (EA) values is shown in Table 3.

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

$$(FGR)_{Ratio} = 0.329 + 0.0019(EA) - 2x10^{-6}x(EA)^2$$
 (6)

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.

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 4.

For this case study, the data indicate that the temperature varied from 16660C (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 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.



Figure 5: Effects of Flue Gas Recirculation Ratio and Excess Air on the content of CO_2 in the flue gas.



Figure 6: Effects of Flue Gas Recirculation Ration and Excess Air on the content of O_2 in the flue gas.

Effects of flue gas recirculation and excess air on the amount of CO₂ 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.

Effects of flue gas recirculation and excess air on the amount of O, in the flue gas

To reduce technical problems linked to oxidative degradation of amine in the CO_2 capture plant, the percentage of O_2 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 O_2 content in the flue gas and increasing the excess air (EA) increased the amount of

 O_2 . For an excess air (EA) of 100%, the percentage of O_2 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 O_2 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 CO_2 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 O_2 in the flue gas should be limited to 5%. Because the captured CO_2 will be stored through a CO_2 -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 CO_2 and O_2 of the flue gas entering the absorption unit.

The first advantage of the Flue Gas Recirculation (FGR) is the decrease of the temperature of the exhaust gas (Figure 4) which will eventually lead to a decrease in NOx emissions. For example, for an excess air of 100%, the temperature decreased from 1666°C to 1478°C by changing the FGR from 0 to 0.4.

For the conditions of an effective absorption process (the molar percentage of CO_2 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 $O_2 \leq 5\%$ 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, preliminary calculations and simulation of the effects of Flue gas recirculation (FGR) ratios and excess air (EA) for an effective CO_2 absorption by amines have been presented in this paper. Simulation results show that the increase of Flue Gas Recirculation (FGR) ratio has increased the content of CO_2 in the flue gas and decreased both the amount of O_2 in the flue gas and the temperature of the exhaust gas. The simulation results indicate also that, for values higher of EA 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 1035°C, an excess air

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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 CO_2 has increased from 3% to 10%, while the molar concentration of O_2 decreased from 14% to 2%. These operating conditions (EA=200% and FGR ratio =0.65) are selected because the NOx emissions will eventually be decreased.

Based on the methodology utilized and the simulation results, future study will include experimental analysis on flue gas recirculation with a detailed effect on the temperature, concentration of CO_2 and O_2 at the exit of the gas turbine.

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