

## Reforming Natural Gas for CO<sub>2</sub> pre-combustion capture in Combined Cycle power plant

J.-M. Amann<sup>1</sup>, M. Kanniche<sup>2</sup>, C. Bouallou<sup>1</sup>

<sup>1</sup> Centre Énergétique et Procédés (CEP), Ecole Nationale Supérieure des Mines de Paris,  
60 Bd Saint Michel, 75006 Paris, France

<sup>2</sup> EDF, Research and Development Division, Fluid Mechanics, Energies and  
Environment, 6 quai Watier 78401 Chatou cedex, France.

The aim of this study is to assess the conversion of a Natural Gas Combined Cycle power plant (NGCC) using an advanced gas turbine (GE9H) for CO<sub>2</sub> pre-combustion capture. The natural gas is reformed in an auto-thermal reformer (ATR) either with pure oxygen or with air. After CO-conversion shift to CO<sub>2</sub> and physical CO<sub>2</sub> recovery, the synthesis gas contains a high fraction of H<sub>2</sub>. It is diluted with N<sub>2</sub> and steam to lower its low heating value (LHV) for NO<sub>x</sub> emission control. Oxygen purity and reforming pressure have little impact on the performances. High pressure reforming is preferred to reduce the process size. Air reforming results in a slightly higher efficiency but in a bigger process too. The CO<sub>2</sub> recovery rate has a big impact on the power plant efficiency since a lot of steam is required to lower the low heating value (LHV) of the synthesis gas leaving the recovery process. Different values of LHV have been assessed.

### 1. Introduction

CO<sub>2</sub> emissions are become a major concern in our society. Several ways of capturing it for sequestration have been assessed. Chemical absorption is the most common process for recovering CO<sub>2</sub> (Bertucco et al., 2003; Bolland and Undrum, 2003; Alie et al., 2005). But new processes are studied like the O<sub>2</sub>/CO<sub>2</sub> cycle (Bolland and Mathieu, 1998; Anderson and Maksinen, 2002; Singh et al., 2005). Fuel conversion is also assessed: coal gasification (Chiesa and Consonni, 2000) and natural gas reforming (Christensen and Primdahl, 1994; Gambini and Vellini, 2005; Cao and Zheng, 2006). This paper focuses on this latter conversion applied to a Natural Gas Combined Cycle power plant (NGCC). Natural gas is converted into a mixture of H<sub>2</sub> and CO<sub>2</sub> thanks to an auto-thermal reformer and shift conversion reactors. Physical absorption is used to take advantage of the high partial pressure of CO<sub>2</sub>. Particular attention has been paid to the low heating value (LHV) of the synthesis gas before the combustion chamber (CC) to control NO<sub>x</sub> formation. This synthesis gas feeds the combined cycle.

### 2. Integration of the pre-combustion capture

The power plant flowsheet is based on an existing NGCC and has been validated with constructor's data. Its net electrical efficiency reaches 59.4% (LHV) and it emits 339 g/kWh of CO<sub>2</sub>.

### 2.1. Power plant description

The principle of the cycle is the decarbonisation of the natural gas before the combustion in the gas turbine. A sketch of the power plant is given in Figure 1. It shows the two options, oxygen reforming and air reforming.

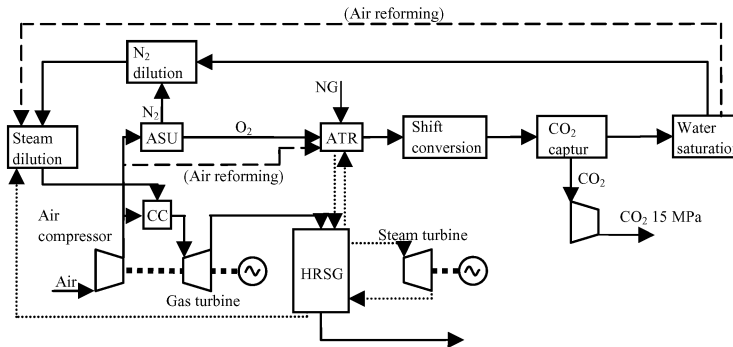


Figure 1. Sketch of the ATR power plant concept

The natural gas (NG) is available at 1.953 MPa and contains approximately 91.2 vol.% of methane. It is converted into a stream mainly composed of  $H_2$  and  $CO_2$  thanks to the auto-thermal reformer (ATR) and the shift conversion reactors (SCR). For air reforming, compressed air is directly sent to the ATR. And for  $O_2$  reforming, compressed air is first sent to an ASU which produces liquid oxygen. After CO-shift conversion into  $CO_2$ , the carbon dioxide is then separated from hydrogen by physical absorption (methanol). The recovered  $CO_2$  is dehydrated and compressed until 15 MPa ready for transportation and sequestration. The synthesis gas, recovered at the  $CO_2$  separation unit, is highly rich in  $H_2$  and its LHV must be reduced to control NOx formation during combustion with air. The synthesis gas is used as a fuel for the combined cycle. The pressure ratio of the air compressor is about 23. The turbine inlet temperature (TIT) has been fixed at 1700 K. In the base case, the steam cycle is optimised for a turbine outlet temperature of 918 K. Since turbine outlet temperature is higher for the retrofitted cases, the extra heat is used to warm up the  $N_2$  before the synthesis gas dilution and the compressed air before entering the CC. The steam cycle has three pressure levels (16.5, 2.4 and 0.32 MPa). The HP and the IP steam are overheated respectively at 835 K and 838 K. The condensation pressure is 3900 Pa. The steam extracted for the reforming and for diluting the synthesis gas is taken into account in the material and heat balance. The Redlich Kwong Soave equation of state has been used in the cycle except where steam is involved, for this latter the STEAMNBS model has been applied.

### 2.2 Natural gas reforming

The reforming process is shown on Figure 2. It requires NG, steam and oxygen. The heat required for steam reforming is supplied by partial oxidation of fuel with oxygen or with air depending on whether technology is chosen, oxygen or air-reforming. Three reforming pressures have been studied: 2 MPa, 4 MPa and 7 MPa. The lower pressure is only devoted to air reforming. For the two higher pressures, NG and air must be

compressed. Air comes from the gas turbine compressor air and is already around 2.3 MPa. For a higher reforming pressure, it is cooled to 303 K and then compressed. When pure oxygen is employed, a pump in the ASU is used to raise the oxygen pressure to the ATR pressure. The steam comes from the high pressure steam turbine and does not require any further compression. Two  $H_2O/C$  molar ratios have been assessed: 1.4 and 1.6. Natural gas and steam are mixed and preheated until 923 K in the heat exchanger HATR (see figure 2). And the oxygen, coming either from the ASU or from the air compressor, is preheated until 873 K. NG is converted into a mixture of CO and  $H_2$  in the ATR. The product stream left the reformer at 1323 K. With this reformer temperature, the conversion rate of methane is higher than 95%. The product stream is used to preheat the incoming streams. This is an advanced option since metal dusting problems may arise in this hot gas-gas exchanger. The product stream is still at high temperature and is used to produce high pressure steam thanks to the heat exchangers HS1 and HS2. The CO is converted into  $CO_2$  with remaining steam in the high temperature shift reactor SCR1 (643 K) and the low temperature shift reactor SCR2 (573 K). More than 93.5% of CO is converted into  $CO_2$  within the two shift reactors.

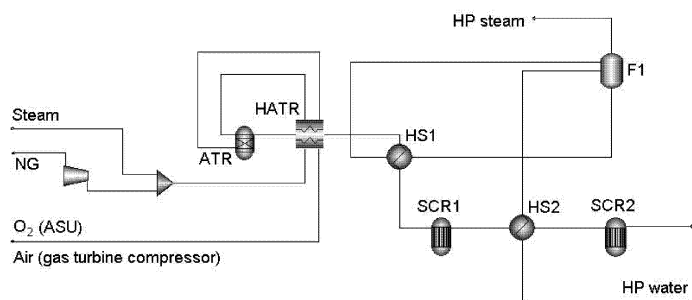


Figure 2. Reforming process

### 2.3 CO<sub>2</sub> recovery process

The CO<sub>2</sub> recovery is based on physical absorption by methanol and is quite conventional (Kohl and Nielsen, 1997). The reformed gas is cooled until 243 K and is sent to the absorber. The rich solvent enters a series of four flash tanks working respectively at 1 MPa, 0.5 MPa, 0.27 MPa and 0.14 MPa. The gas phase of the first flash tank is recycled back to the absorber. The gas phases of the three latter flash tanks, released at different pressures, are compressed, mixed, dehydrated and then compressed until 15 MPa. It is then cooled to maintain the CO<sub>2</sub> flux at supercritical state. The solvent recovered at the bottom of the last flash tank is thermally regenerated in distillation column by using low pressure steam coming from the LP steam drum. Some cooling required in this process is provided by heat exchanging with cooler streams. However, an ammonia compression-expansion system is required to sustain the refrigeration at 243 K.

### 2.4 Low heating value limitation

The synthesis gas recovered from the CO<sub>2</sub> capture process is highly rich in H<sub>2</sub> and must be diluted before to be burnt in the CC. This is required to have a better control on the NO<sub>x</sub> formation. The synthesis gas pressure is set to 2.8 MPa (expansion if the

reforming pressure is above 4 MPa or compression if the reforming pressure is at 2 MPa) and it is heated to 523 K. It is then saturated with water. The different heat duties required in this process are provided by the cooling of gas turbine compressed air before entering the ATR or the ASU and also of the synthesis gas at the SCR2 exit. When an ASU is used, the synthesis gas is then diluted with compressed  $N_2$  recovered at the ASU exit. For air reforming, the synthesis gas is already diluted with air  $N_2$ . IP Steam is finally added to complete the dilution. This steam is extracted from the combined cycle. The  $CO_2$  recovery rate acts upon the steam flow. A conservative value of  $4.8 \text{ MJ.kg}^{-1}$  for the LHV represents the base case. However, the LHV has been increased to  $7.0 \text{ MJ.kg}^{-1}$  to assess the impact on the cycle efficiency.

### 3. Results

For  $O_2$  reforming, high oxygen purity is not required. For a reforming pressure of 4 MPa, several purities have been assessed. Increasing the purity from 85 to 95 mol.% results in a net efficiency decrease of 0.3%-point for a  $CO_2$  recovery rate in the absorber ranging from 75 to 95%. The absorber is not very sensitive to small variations of  $CO_2$  concentration in the reformed stream. In the following, only the cases with a purity of 85 mol.% will be considered. Seven cases have been compared (Table 1, Figure 3): 4 cases with  $O_2$  reforming and 3 cases with air reforming.

Reforming pressure has little influence on the net efficiency according to cases (1), (2), (5), (6) and (7). A reforming pressure of 4 MPa is slightly better (0.1-0.2%-point) but would involve a bigger installation. The steam extracted for NG reforming is at lower pressure increasing the steam cycle output and the different compression works are reduced too. But in the same time, the power recovered from the synthesis gas expansion is lower and the capture process requires a higher solvent flow. Air reforming at 2 MPa (case 7) is the worst case for air reforming. On the one hand, the NG is not compressed and the hydrocarbons conversion rate in the reformer is higher, decreasing the steam flow extracted for lowering the synthesis gas LHV. But, on the other hand, the recovery process is more energy demanding and the synthesis gas has to be compressed before water saturation.

Air reforming seems to be more efficient than  $O_2$  reforming. For a global  $CO_2$  recovery rate of 85 %, the net efficiency increases by 0.6%-point between the cases (1) and (6) and by 0.5%-point between the cases (2) and (7). But the presence of  $N_2$  in the reformed stream increases the size of the reforming process and the  $CO_2$  recovery process. In the other hand,  $O_2$  reforming requires an ASU.

A case where the  $H_2O/C$  molar ratio has been reduced in the reformer has been evaluated (4). Comparing with the case (2), the efficiency increases by 0.5%-point since less amount of steam is extracted from the combined cycle. But this case must be considered with attention as low amount of steam favours carbon deposition on the catalysers of the reformer.

A test with a LHV value of  $7.0 \text{ MJ.kg}^{-1}$ , case (3), shows that the net electrical efficiency increases by 2.3%-points comparing with the case (2). The steam flow extracted from the combined cycle is highly reduced enhancing the efficiency of the steam cycle. While increasing the LHV value, the gas turbine efficiency decreases from 44.7 to 40.3%-points for a 85% global  $CO_2$  recovery since the synthesis gas is not diluted with steam.

When comparing the two higher reforming pressures, it can be noticed that the global CO<sub>2</sub> recovery rate is lower for the highest one for the same recovery rate in the absorber since fewer hydrocarbons are converted in the reformer. The remaining hydrocarbons are burnt in the CC and the associated CO<sub>2</sub> is emitted to the atmosphere.

The efficiency decreases with the recovery rate comes mainly from the steam extraction for the synthesis gas dilution. The steam flow extracted is as high as the CO<sub>2</sub> recovery rate is high since the synthesis gas is less diluted with carbon dioxide.

Table 1. Reforming cases

Case	Oxygen purity (mol.%)	Reforming pressure (MPa)	Molar ratio H <sub>2</sub> O/C	LHV (MJ.kg <sup>-1</sup> )
(1)	85	4	1.6	4.8
(2)	85	7	1.6	4.8
(3)	85	7	1.6	7.0
(4)	85	7	1.4	4.8
(5)	Air	2	1.6	4.8
(6)	Air	4	1.6	4.8
(7)	Air	7	1.6	4.8

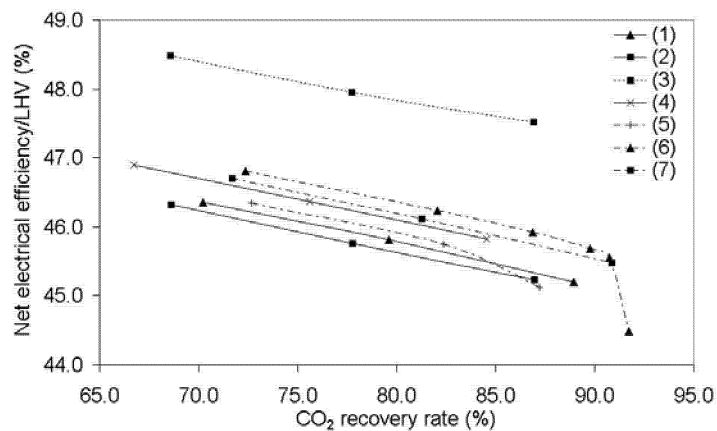


Figure 3. Net electrical efficiency versus CO<sub>2</sub> recovery rate

For a global CO<sub>2</sub> recovery rate of 85 %, the cases (2), (3) and (7) imply respectively an efficiency loss of 14.1, 11.8 and 13.5%-points compared to the base case. This leads to a quantity of avoided CO<sub>2</sub> ranging between 272 and 275 g.kWh<sup>-1</sup>. The efficiency losses found in this study is higher than those of previous works. But those works did not take into account the lowering of the synthesis gas LHV for NO<sub>x</sub> control. Kwamsdal et al. (2007) and Ertesvåg et al. (2005) who considered air-blown ATR and CO<sub>2</sub> chemical absorption, reported respectively an efficiency loss of 9.9 and 9.99%-points comparing with their base case. According to the composition of their synthesis gas, the LHV should be about 9-10 MJ.kg<sup>-1</sup>. Ertesvåg et al. also showed that preheating the streams entering the reformer improves the cycle efficiency. Thus increasing the temperature from 871 to 1073 K increases the efficiency by 1.6 %-points. Bolland and Undrum (2003) assessed a power plant with an air-blown ATR. They used supplementary firing to preheat the streams in the reforming process. Their efficiency loss is about 12.7%-

points mainly due to the change of fuel and the supplementary firing. They report that a H<sub>2</sub> fraction of 50 vol.% is not acceptable for the natural gas low-NO<sub>x</sub> burners but that some preliminary experiments with high H<sub>2</sub> concentration give promising results with IGCC burners. Lozza and Chiesa (2002a, 2002b) studied two type of methane reforming: partial-oxidation and steam reforming. They found that steam reforming leads to a lower efficiency. With partial oxidation, the cycle efficiency reaches 48.5% which represents a loss of 7.6%-points.

#### 4. Conclusion

This study focused on the conversion of a NGCC for CO<sub>2</sub> pre-combustion capture. Oxygen reforming was compared with air reforming. This latter displays a higher efficiency but the reforming process and the recovery process will have bigger scale. However O<sub>2</sub> reforming requires an ASU. Particular attention was paid on the synthesis gas LHV for the CC. Several authors reported an efficiency loss ranging from 7.6 to 10.0%-points but they did not consider the fact that burners are not designed for high H<sub>2</sub> concentration. For a reforming pressure of 7 MPa and a 85% CO<sub>2</sub> recovery, O<sub>2</sub> reforming and air reforming lead respectively to an efficiency loss of 14.1 and 13.5%-points for a LHV value of 4.8 MJ.kg<sup>-1</sup>. For a value of 7.0 MJ.kg<sup>-1</sup>, the efficiency loss is reduced to 11.8%-points for O<sub>2</sub> reforming. Air separation unit, steam extraction for the reformer and the synthesis gas dilution are the main causes of reduction in the cycle efficiency.

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#### References

- Alie C., L. Backham, E. Croiset and P.L. Douglas, 2005, *Energy Convers. Manage.*, 46, 475.
- Andersson K. and P. Maksinen, 2002, master thesis T2002-258.
- Bertucco A., N. Elvassore and A. Monteforte, 2003, *Proceeding - The sixth Italian Conference on Chemical and Process Engineering*, Pisa, Italy.
- Bolland O. and P. Mathieu, 1998, *Energy Convers. Manage.*, 39(16-18), 1653.
- Bolland O. and H. Undrum, 2003, *Advances in Environmental Research* 7, 901.
- Cao W. and D. Zheng, 2006, *Energy Convers. Manage.*, 47, 3019.
- Chiesa P. and S. Consonni, 2000, *J. Eng. Gas Turbines Power*, 122, 429.
- Christensen T. S. and I. I. Primdahl, 1994, *Hydrocarbon Processing*, 73(3), 39.
- Ertesvåg I. S., H. M. Kvamsdal and O. Bolland, 2005, *Energy*, 30, 5.
- Gambini M. and M. Vellini, 2005, *International Journal of Hydrogen Energy*, 30, 593.
- Kohl A. and R. Nielsen, *Gas purification*, 1997, Gulf Publishing Company, Houston.
- Kvamsdal H., K. Jordal and O. Bolland, 2007, *Energy*, 32, 10.
- Lozza G. and P. Chiesa, 2002a, *J. Eng. Gas Turbines Power*, 124(1), 82.
- Lozza G. and P. Chiesa, 2002b, *J. Eng. Gas Turbines Power*, 124(1), 89.
- Singh D., E. Croiset, P.L. Douglas and M.A Douglas, 2003, *Energy Convers. Manage.*, 44, 3073.