

Dipl.-Ing. Christian Hermsdorf
Prof. Dr.-Ing. Alfons Kather
Dipl.-Ing. Mathias Klostermann, Dipl.-Ing. Karl Mieske

Hamburg University of Technology

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Oxyfuel Process for Hard Coal with CO₂ Capture: First results

Introduction

The oxyfuel process is one of the most frequently discussed options for a so called “Zero-Emission-Power-Plant” based on fossil fuels. Although state-of-the-art power plants already meet strict emission regulations thanks to advanced flue gas cleaning technologies, the emission of carbon dioxide is still unavoidable. Therefore, the idea of the oxyfuel process is to capture the carbon dioxide from the flue gas and to store it into geographical deposits. The main component of flue gases from fossil fuel combustion is, however, nitrogen, which does not make an efficient CO₂ separation feasible. Thus, eliminating the nitrogen from the air with an air separation unit would allow burning the fuel with almost pure oxygen. This would produce a flue gas with a very high CO₂ concentration which could be separated far more efficiently.

It can easily be noticed, that separating the air before, as well as capturing the CO₂ after the combustion, would reduce the power plant’s net efficiency. On the other hand, producing electricity with almost no CO₂-emissions could be worth while. Although the oxyfuel process is known since many years, there is still great uncertainty regarding the exact net plant efficiencies that can be obtained, especially when operating under realistic conditions.

The objective of the research project at the Hamburg University of Technology (TUHH) is therefore to identify all factors that are decisive for both the feasibility and economic efficiency of an oxyfuel power plant with all its components. In order to do this, the analysis of the overall process is divided into four subprojects currently progressing at the TUHH.

The first subproject is focused on the CO₂ separation technology including the drying of the flue gas. In order to be able to draw reliable conclusions about the feasibility and the efficiency of a CO₂ separation unit it is of major importance to develop the basics of the phase equilibria of carbon dioxide and oxygen in the presence of nitrogen, argon, and the pollutants NO_x and SO₂. This will be accomplished experimentally. Based on the findings, a rough design layout of a CO₂ separation unit will be developed.

The second subproject is devoted to the combustion of hard coal in different atmospheres. This is investigated by experiments in an entrained flow reactor in order to study the burnout and emission control by means of a systematic variation of factors such as excess oxygen, oxygen content, O₂/CO₂-ratio, and temperature.

The design of the boiler for an oxyfuel process is objective of the third subproject. One of the prominent characteristics of an oxyfuel power plant is the fact that a conventional rotary air

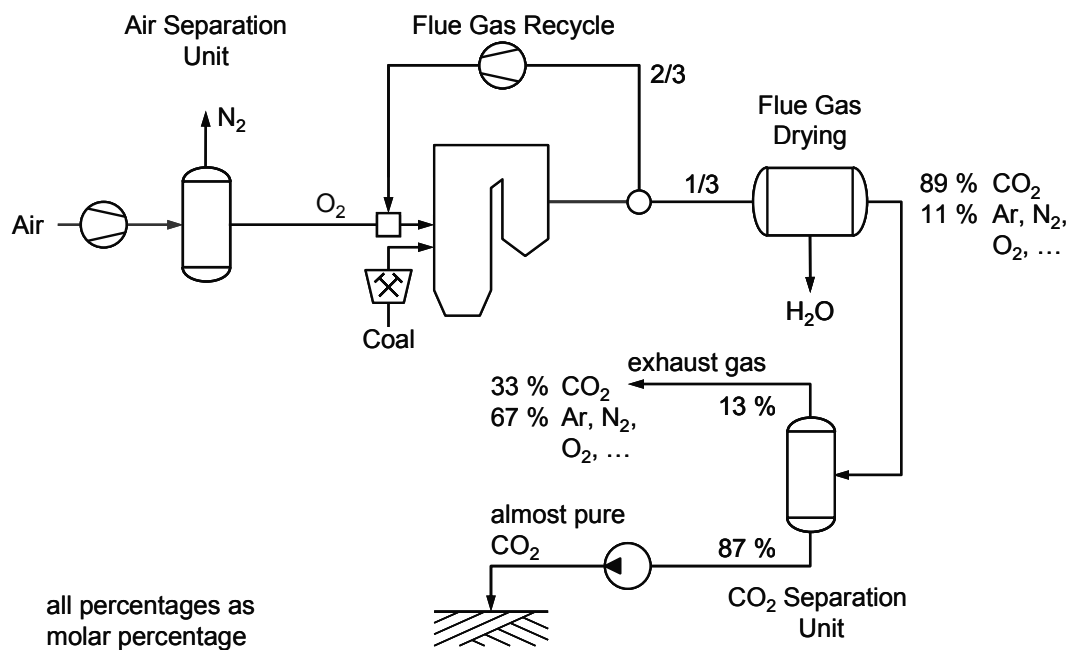


Figure 1: Simplified scheme of the oxyfuel process.

preheater cannot be employed as it causes oxygen to infiltrate into the flue gas. Therefore, alternative possibilities in using the low calorific heat have to be developed. A further aspect is the fact that the combustion with oxygen instead of air requires cold flue gas to be recycled back into the furnace, in order to limit the combustion temperature. This requires precise analysis of all boiler components such as the dust precipitator, the recycle fan, the duct system design and the coal mills. Only then, a reasonable assessment of the feasibility of the oxyfuel process for power generation can be obtained.

The objective of the fourth and last subproject is to analyze and optimize the overall process by integrating the findings of the other subprojects.

Feasibility of the Flue Gas Recycle

A current research topic is the feasibility of an oxyfuel boiler. Due to the lack of nitrogen, which usually serves as a heat sink and thus limits the adiabatic combustion temperature to about 2000 °C (under stoichiometric conditions), it is necessary to recycle flue gas from the boiler's cold end back into the furnace, see Figure 1. First estimations revealed that approximately two thirds of the cooled-down flue gas have to be recycled to limit the adiabatic combustion temperature to a level corresponding to combustion with air.

Regarding flue gas recirculation design, various aspects concerning corrosion, erosion as well as investment costs have to be taken into account. Basically, flue gas recirculation can be accomplished either as a low-dust or a high-dust recycle, see Figure 2. The benefit of a low-dust concept is that the maximum dust load would be limited to about 26 g/m³ in the boiler (at standard temperature and pressure, subsequently referred to as @STP). This concept is realized using an electrostatic precipitator (ESP) before the branching-out of the flue gas recycle, which reduces dust concentration in the recycle duct system to less than 300 mg/m³ (@STP), which facilitates using a highly efficient axial-flow fan. However, this

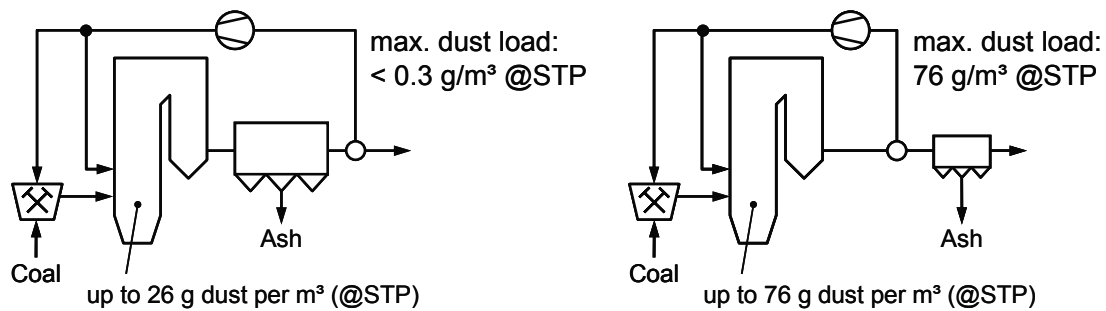


Figure 2: Low-dust (left) and high-dust (right) flue gas recycle configurations. The coal mill, the boiler, the dust precipitator and the flue gas recycle fan are shown.

configuration means that the ESP would have to handle the total flue gas volume and would be larger, accordingly, which in consequence would result in very long recycle ducts.

A high-dust recycle on the other hand allows for short ducts in the very proximity of the boiler. Moreover, the ESP would now have to handle only about one third of the flue gas volume. The drawback of this configuration is, however, that the dust concentration in the boiler and the recycle ducting would be as high as $76 \text{ g/m}^3 \text{ (@STP)}$. As a consequence, less efficient radial-flow fans have to be employed, in order to reliably handle the dust-laden flue gas.

Apart from the above mentioned design considerations, the temperature at which the flue gas is recycled has to meet certain requirements as well. Besides the fact that axial flow fans do not allow temperatures exceeding $190 \text{ }^\circ\text{C}$ (or possibly $270 \text{ }^\circ\text{C}$ when blade cooling is employed), low temperatures are also desirable to reduce the recycled gas mass flow and its specific volume, thus reducing the fan's power demand. On the other hand, the drying of hard coal in the mills is usually performed at elevated temperatures of the order of $300 \text{ }^\circ\text{C}$. Whether or not increasing mill gas flow can compensate for a lower recycle temperature is currently being investigated.

The influence of the recycle gas temperature on the recycle requirement, for different coals, is depicted in Figure 3. The basic condition of the underlying calculation thereby is the assumption that the adiabatic temperature of the oxyfuel combustion has to equal that of a normal combustion with air, under otherwise identical conditions for each coal considered. The only difference, however, is that the oxygen is assumed not to be preheated.

The results show that the required recycle gas flow increases from 65.17% to 68.06% when the recycle temperature varies between 100 and $400 \text{ }^\circ\text{C}$ using South African coal. Thus, increasing flue gas cooling does not lower the recycle requirement significantly, which is decisive with regard to the ducts' dimensions and the power consumption of the fan. A more significant reduction in recycle requirement, however, can be observed if the permitted adiabatic combustion temperature is raised by about 300 K , which could be achieved by means of a slag tap firing for instance. This would lower the required recycle by approximately 9 to 10% (rel.), which alone would reduce the fan's power demand by 9 to 10% as well.

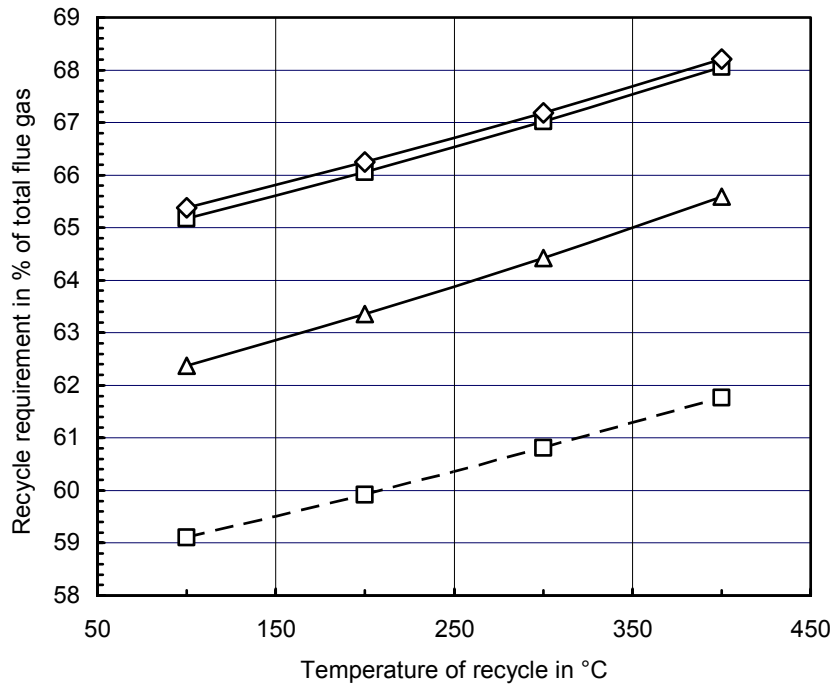


Figure 3: Recycle demand as a function of recycle temperature, coal type and permitted adiabatic temperature. Solid lines represent the recycle demand for different coals for a permitted adiabatic combustion temperature that is corresponding to their combustion with air. The dashed line represents the recycle demand for South African coal, if the permitted adiabatic combustion temperature is 300 K higher (i.e. by slag tap firing). □ – South African coal, ◇ – Russian coal, Δ – Indonesian coal.

The influence of a different coal quality can also be seen in Figure 3, where the recycle requirement for an Indonesian coal is significantly lower, mainly caused by its high water content (see Table 1). This behavior is of great significance regarding the recycle control when changing coals during operation.

Combustion Experiments

In an oxyfuel power plant the almost pure oxygen has to be mixed with recycled flue gas. The technically simplest way is to mix both components completely prior to the combustion. Accordingly, first combustion experiments will be based on this assumption. In order to

Table 1: Composition of selected coals. The adiabatic temperatures (t_{ad}) are calculated for combustion with preheated air (320 °C) and an air excess of 15 %.

Coal	Composition (in wt%)							NCV MJ/kg	t_{ad} °C
	C	H	O	S	N	Ash	H ₂ O		
South Africa	65.93	3.63	7.25	0.61	1.58	13.60	7.40	25.40	2126
Indonesia	58.70	4.43	8.82	1.00	1.05	5.00	21.0	22.69	2008
Russia	70.09	3.70	7.37	0.30	1.23	9.81	7.50	27.20	2160

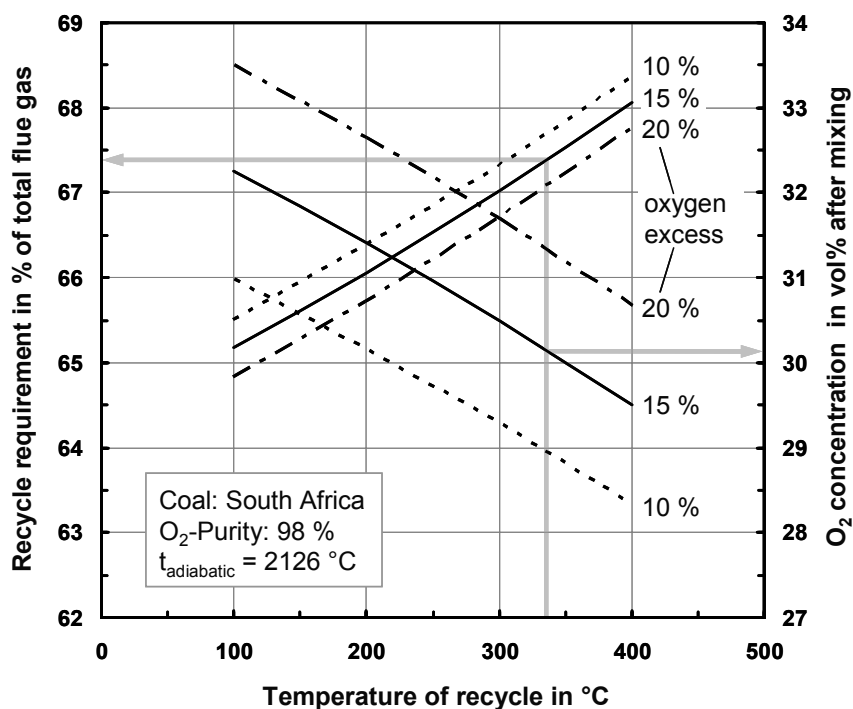


Figure 4: Oxygen concentration in the combustion atmosphere when mixing recycled flue gas and oxygen completely prior to the combustions.

facilitate a systematic analysis, calculations were conducted for all coal types in Table 1. The resulting oxygen concentrations in the combustion atmosphere as a function of the oxygen excess and the recycle temperature, and thus the recycle requirement, are shown in Figure 4. A significant consequence of this calculation is the fact that the oxygen content in the combustion atmosphere is always above 21 vol% and increases with reducing recycle requirement, the latter caused by reducing the recycle's temperature. Preliminary results from the first experiments prove the expectation that the increased oxygen concentration improves fuel burnout.

Further experiments will be conducted to analyze the benefits of different oxygen concentrations at different stages of the combustion, particularly with regard to burnout and emission control. The complexity that would be required in order to perform corresponding measures will then be evaluated with respect to the economic efficiency.

CO₂ Separation

The technique to separate carbon dioxide in the oxyfuel process is based on the physics of condensation. Ideally, the flue gas from an oxyfuel process would consist of nothing but carbon dioxide and water, which would allow a simple separation of the CO₂ by liquefaction once the water has been removed. Although it seems trivial at first sight, the removal of water needs to be studied in detail as a complete removal of water by mere condensing is not possible. This is crucial for CO₂ separation insofar as freezing of residual water during the CO₂ liquefaction would impair the process significantly. The only possibility known for removing the water completely is the usage of molecular sieves. Their installed volume, however, will be considerable and they will have to be regenerated repeatedly by means of

water-free gases. Whether or not flue gas drying in this manner is feasible in practice, is currently being studied. Moreover, the solubility of pollutants such as SO₂ and NO_x in the water will also be investigated, in order to be able to define the flue gas cleaning requirements more precisely.

The separation of carbon dioxide is also accomplished through condensation, by either increasing the pressure, decreasing the temperature or doing both. As soon as the proper combination of temperature and pressure is achieved, a steady liquefaction begins, provided that the gas consists of pure carbon dioxide. In the presence of non-condensables, however, the partial pressure of carbon dioxide in the gaseous phase is lowered once the condensation is in progress, thus bringing condensation to an end quickly. It is therefore necessary to further lower the temperature or raise the pressure, both of which increase the power consumption of liquefaction.

But even if a steady liquefaction can be sustained, non-condensable impurities impair CO₂ separation by limiting its efficiency. Figure 5 shows a simplified model of a CO₂ separation unit which uses two temperature stages at the same pressure. The numbers shown are results from a simulation using Aspen® Plus®. Although more sophisticated designs are possible, this simple model readily demonstrates the negative influence of non-condensables on CO₂ separation efficiency. The dried flue gas, which in the present case has an assumed CO₂ concentration of 89 mol%, is at first compressed to a pressure of 25 bar. The complete condensation of pure CO₂ would then require a temperature of -13.15 °C. In the presence of impurities, however, the simulation reveals that a separation of 76 % of the CO₂ (including residues of dissolved non-condensables) requires a temperature of -30 °C. Although exact coefficients for the solubility of the non-condensables in liquid CO₂ are not available yet, it is reasonable to assume that only a very small amount will be dissolved. As a consequence,

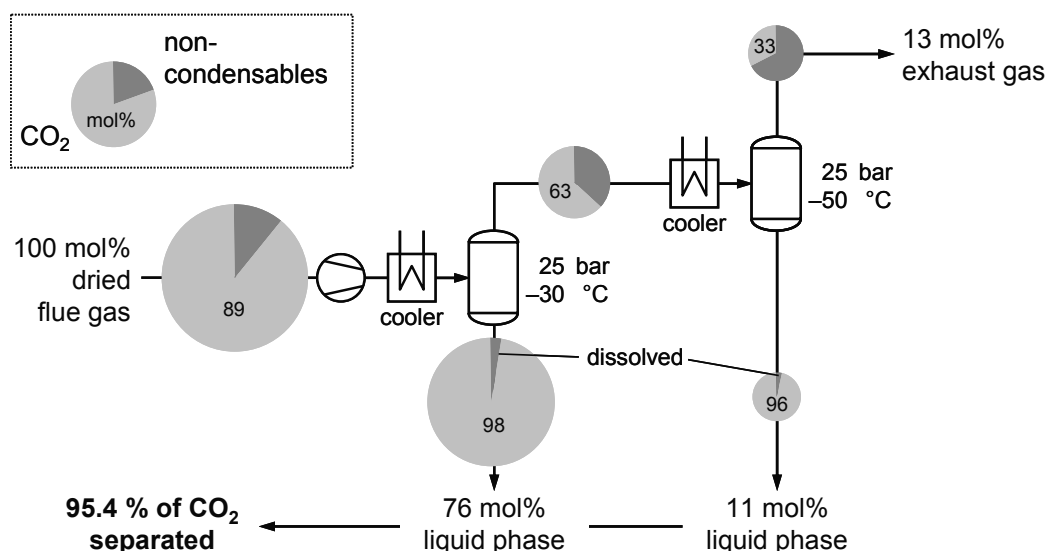


Figure 5: Simplified model of a CO₂ liquefaction unit with two temperature stages. The dry flue gas composition corresponds to an oxygen excess of 15 %, an oxygen purity of 98 %, and 0.8 % leakage air.

almost all non-condensables remain in the gas phase, thus lowering CO₂ concentration to 63 mol%, which corresponds to a significant reduction in the carbon dioxide's partial pressure. In order to be able to further separate carbon dioxide from the exhaust gas, the temperature has to be lowered further (and/or the pressure has to be increased), yielding approximately 46 % separation when cooling down to -50 °C at constant pressure. Again, very little of the non-condensables is assumed to be dissolved in the liquid phase. As a consequence, their concentration in the exhaust gas increases again, which finally leads to the fact that a complete separation of the carbon dioxide by means of condensation is not possible and a small amount of the carbon dioxide is being released along with the exhaust gas. This, according to the example above, amounts to roughly 5 % of the total carbon dioxide.

It has to be noted, however, that these calculations are based on phase equilibria which are supplied by Aspen® Plus® and which need to be validated as soon as our experimental data become available. This will reveal if the separation efficiencies calculated above are reasonable and will allow for configuring the model power plant parameters with realistic phase equilibria.

The significant impact of non-condensables on CO₂ separation efficiency calls for a close identification of their sources. A major and inevitable source, particularly when burning solid fuels, is the remaining oxygen in the flue gas due to the required oxygen excess, which is at least as low as 15 % for current state-of-the-art pulverized coal firing systems. It will be studied, however, if lower oxygen excess ratios may be possible, even though this does not seem to be possible for conventional air-operated coal power plants. Other impurities are gases associated with the imperfect air separation (mainly Argon). Additionally, the fuel's nitrogen is also contributing to these impurities. All these sources of non-condensables form 6 to 8 wt% of the flue gas (on a dry basis), which means that the carbon dioxide concentration cannot exceed 94 wt%.

Besides the sources of impurities mentioned above there is an additional significant source of impurities, namely leakage air, whose major component is nitrogen. Given that, for safety reasons, all conventional atmospheric power plants are operated below atmospheric pressure, any gap in the flue gas system results in ambient air being sucked into the flue gas. Based on estimations from current practice, the amount of leakage in conventional state-of-the-art coal power plants is about 3 % of the total flue gas flow and usually increases over the years to an estimated 10 %.

It is shown in Figure 6 that the strongest impact on the attainable carbon dioxide concentration in the dry flue gas is to be attributed to leakage air. According to the diagram, an oxyfuel combustion plant with an oxygen excess of 15 %, an oxygen purity of 99.5 vol%, and 3 % of leakage air would produce flue gas with a carbon dioxide concentration not exceeding 83 vol% (on a dry basis). The same process, however, would produce a flue gas with carbon dioxide concentration of more than 90 vol% (on a dry basis) if the leakage can be limited to values below 1 %. Considering the fact that the CO₂ separation efficiency is dominated by the CO₂ concentration it is evident that leakage air has to be minimized as much as practicable.

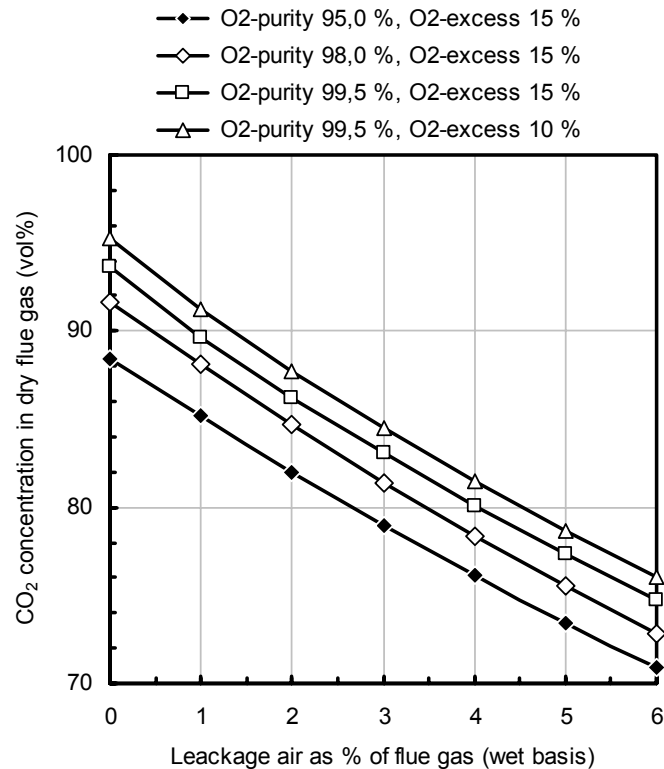


Figure 6: Attainable concentration of CO₂ in dry flue gas as a function of oxygen purity, oxygen excess, and leakage air.

Flue Gas Desulfurization and Denitrification

Basically the oxyfuel process offers the advantage that desulfurization and denitrification could be limited to the treatment of the exhaust gas. Referring to Figure 5, the volume flow of the exhaust gas is approximately only 13 vol% of the total dry flue gas volume, which corresponds to 10 vol% of the wet flue gas volume. The volume of the flue gas cleaning facilities could thus be reduced significantly. However, the critical issue is the solubility of sulfur and nitrogen oxides in liquid carbon dioxide, as there is great uncertainty about how these compounds impair the CO₂ storage under ground. Current experiments at the Hamburg University of Technology are therefore conducted in order to determine the solubility of the above mentioned compounds in liquid CO₂. Provided that the solubility is sufficiently low so that no problems would occur under ground, desulfurization and denitrification of the exhaust gas could be a feasible alternative.

Regarding the flue gas desulfurization (FGD) facility it has to be considered that today's FGD plants use ambient air blown into the FGD unit, to form gypsum through oxidation. As in an oxyfuel plant, however, the infiltration of air is to be avoided at all costs, other solutions have to be developed like using a separate oxidizer.

Efficiency of an Oxyfuel Power Plant

The key power consumers of an oxyfuel power plant are with no doubt the air separation and the CO₂ separation unit. Based on an air operated hard coal power plant with a net electric power output of 556 MW (corresponds to the latest power plant concept developed in

Germany, referred to as Reference Power Plant North-Rhine Westphalia) the air separation unit alone would consume about 110 MW when using a standard two-column process. Additionally, a simple CO₂ separation unit would consume about 50 MW. These parasitic loads would result in a net efficiency loss of about 13 percentage points (absolute). It seems possible, however, to reduce these losses significantly. One promising way is to use an alternative air separation unit concept, based on the so-called three column process. This could reduce power consumption by approximately 40 MW or 36 %, at the expense of less oxygen purity. In turn, the latter would directly impair the CO₂ separation efficiency. Regarding CO₂ liquefaction, using absorption refrigeration seems to be a promising way to reduce the power consumption significantly.

Another significant issue to be considered is the actually required CO₂ separation efficiency with respect to emission trading. Whilst the power consumption can be reduced by lowering the separation efficiency, the number of CO₂ allowances that can be sold within the scope of emission trading is reduced, as well. The determination of the economic ideal separation efficiency is thus a matter of the current price for emission allowances. This aspect will be part of the overall process optimization.