



TAMPEREEN TEKNILLINEN YLIOPISTO
TAMPERE UNIVERSITY OF TECHNOLOGY

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RAIKO:**

**COMPARISON BETWEEN TWO OXYGEN PRODUCTION
METHODS FOR POWER PLANTS CAPTURING CARBON
DIOXIDE**

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ABSTRACT

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Comparison between two oxygen production methods for power plants capturing carbon dioxide

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In this report possible carbon capture process concepts are evaluated in order to find the most techno-economically viable method for a carbon capture process in a PC power plant.

Oxyfuel combustion and partial oxyfuel combustion technologies need high concentrate oxygen. Oxygen production processes are highly energy intensive, which leads to low efficiencies in power plant processes. Partial oxyfuel process needs lower concentrations of oxygen and it means that oxygen could be produced with smaller energy penalties. Linde and Nurmia oxygen production processes are compared in this report.

Recent studies show that the partial oxyfuel process offers the best solution for carbon capture especially in retro-fit cases where carbon capture is applied to an existing PC power plant. The only commercially available system for carbon capture is an amine scrubber, which also benefits from partial oxyfuel combustion.

TIIVISTELMÄ

TAMPEREEN TEKNILLINEN YLIOPISTO

RIKU MERIKOSKI, AKI LINJAMAA, MIKKO PAAVOLA, RISTO RAIKO:

Kahden hapenvalmistusmenetelmän vertailu hiilidioksidin talteenotolla varuste-
tuissa voimalaitoksissa

Tutkimusraportti, 25 sivua

Lokakuu 2012

Avainsanat: hapen valmistus, happipoltto, hiilidioksidin talteenotto ja varastointi
(CCS), savukaasun käsittely

Tässä raportissa esitetty hanke on osa CLEEN Ltd -yritysklusterin Hiilidioksidin talteenotto ja varastointi -ohjelmaa (CCSP). Tämän tutkimushankkeen on rahoittanut Fortum Heat and Power Oy osana CCSP-ohjelmaa.

Selvityksen lähtökohtana oli tutkia erilaisia prosessikonsepteja, jotka sopivat hiilidioksidin talteenottoon hiilivoimalaitoksissa ja niiden toteutuskelpoisuutta. Tutkimuksessa käytettiin uusinta ja parasta tutkimustietoa, jota aiheesta oli saatavilla. Tärkeänä lähtökohtana oli myös Matti Nurmian kehittämän hapenvalmistusprosessikonseptin taloudellisuuden ja hyödyllisyyden selvittäminen happipoltossa. Tutkimuksessa kävikin ilmi, että juuri Nurmian prosessille sopivia osittaishappipolttokonsepteja on viime aikoina alettu kehittää.

Happipoltoa käytetään hiilidioksidin talteenotossa, sillä poistamalla tyypeä poltto-prosessista saadaan hiilidioksidin osapaine suuremmaksi savukaasuvirrassa, josta hiilidioksidia otetaan talteen. Korkea hiilidioksidin osapaine parantaa talteenoton hyötysuhdetta. Hiilidioksidia voidaan ottaa talteen kaupallisilla amiinipesureilla tai savukaasun nesteytyksellä kryogeenisissä olosuhteissa. Tässä tutkimuksessa esitellään myös hiilidioksidin talteenottokonsepti, jossa yhdistetään nesteytystä ja pesuri-prosessia.

Nurmian hapenvalmistusprosessissa tuotteena saadaan 50 % happea sisältävää happi-tyyppi-seosta, jota ei voida käyttää perinteisessä happipoltossa. Nurmian prosessin happea voidaan kuitenkin käyttää osittaisessa happipoltossa. Nurmian metodin 50 % happiseosta on kuitenkin energiatehokkaampaa valmistaa kuin kaupallista Linde-prosessin happikaasua, joka on eroteltu kryogeenisissä olosuhteissa ilmasta.

Kappaleessa 3 tutkimme puhtaan happipolton tuottamien savukaasujen ja osittaisen happipolton savukaasujen eroja tekemällä laskennallisen savukaasuanalyysin. Täydellisessä happipolttoprosessissa hiilidioksidin osuus savukaasuissa oli noin 60 % ja Nurmia-prosessin tuottamassa 50 %:n osittaishappipoltossa se oli noin 36 %. Osittaishappipolton savukaasuissa hiilidioksidin osapaine on niin alhainen, että kryogeenisestä talteenottoprosessista tulisi merkittävästi energiaa kuluttava, mikä tekisi talteenoton taloudellisesti mahdottomaksi. Kuitenkin uudet hybriditalteenottokonseptit ja amiinipesurit ovat mahdollisia vaihtoehtoja kun käytetään osittaista happipoltoa.

Savukaasun suurempi massavirta osittaisessa happipoltossa tuo myös etuja suhteessa täydelliseen happipolttoon. Savukaasun uudelleenkierrätystä ei tarvita niin paljon, koska osittaisessa happipoltossa polton savukaasut pysyvät happipoltoa kylmempinä. Tämä

mahdollistaa myös vanhan hiilivoimalaitoksen muokkaamisen osittaihappipolttoon sopivaksi ilman merkittäviä muutoksia lämpöpintoihin. Täydellisessä happipoltossa ongelmaksi saattaa muodostua myös rikkidioksidin suuri osapaine savukaasuissa. Varsinkin paljon rikkiä sisältävää hiiltä poltettaessa saattaa tulla vastaan tilanne, jossa savukaasun kierrätyspiiriin joudutaan asentamaan rikin talteenottojärjestelmä korroosion estämiseksi. Osittaisella happipoltolla ongelma on pienempi, sillä savukaasuissa lisääntyneen typen ansiosta rikkidioksidin osapaine pienenee ja savukaasun kierrätystarve on vähäisempää.

Vertailtuamme eri hiilidioksidin talteenottomenetelmien vaikutusta voimalaitoksessa tuotetun sähkön hintaan päädyimme siihen lopputulokseen että tavanomainen kaupallinen amiinipesuri on kallein vaihtoehto niin jälkiasennuksena vanhaan voimalaitokseen, kuin myös vaihtoehtona uuden laitoksen talteenottomenetelmäksi. Tämän vaihtoehdon hyvänä puolena on kuitenkin sopivuus kaikkiin olemassa oleviin laitoksiin ilman muutoksia kattilaan. Osittaisen ja täydellisen happipolton välillä emme havainneet suurta eroa kaupallisessa mielessä, kun käytössä oli Linde-prosessilla tuotettu happi. Mikäli Nurmian menetelmällä saadaan aikaan toimiva happitehdas laitospaavassa ja sillä tuotettu happi osoittautuu yhtä edulliseksi kuin mitä alustavat tutkimustulokset näyttävät, on se erittäin varteenotettava vaihtoehto osittaisen happipolton yhteyteen. Tällöin hapenvalmistuskustannukset olisivat vain neljänneksen verrattuna Linde-prosessiin ja osittainen happipoltto selvästi kilpailukykyisin vaihtoehto.

Koska kaikki vaihtoehdot ovat selvästi kalliimpia kuin referenssinä käytetty normaali ilmapoltto, on koko talteenottokonseptin kannattavuutta arvioitava päästökaupan tuomien kustannusten valossa. On myös todennäköistä että laitos, johon järjestelmä asennetaan, toimii hyvin suuren osan vuodesta tuottaen perusvoimaa. Investointikustannukset nousevat kuitenkin niin suuriksi, että laitoksen käyttäminen säätövoiman tuotannossa vain ajoittain vuoden aikana vaikuttaa mahdottomalta.

Eräs tärkeä kaupallinen näkökulma on tutkia talteenottojärjestelmän soveltumista asennettavaksi vanhaan voimalaitokseen. Täydellinen happipoltto tuottaa ongelmia hyvin erilaisen savukaasuvirtansa osalta. Savukaasun määrä ja ominaislämpökapasiteetti muuttuvat hyvin oleellisesti, eikä ole taattua, että ilmapoltolle suunnitellut lämmönvaihtimet toimivat kunnolla tässä ympäristössä. Kattilan lämpöpintojen muokkaaminen taas on erittäin kallista ja siitä saattaa olla seurauksena ongelmia lentotuhkan kanssa. Yhteenvetona voidaan todeta, että savukaasuiltaan huomattavasti ilmapoltoa lähempänä oleva osittainen happipoltto on paljon mielenkiintoisempi vaihtoehto vanhan laitoksen modernisointiin. Lisäksi kyky käyttää Nurmian menetelmällä tuotettua happea on talteenottomenetelmälle merkittävä etu. Havaitsimme että hapen määrä osittaisessa happipoltossa ei ole kovin merkittävä tekijä hyötysuhteen kannalta vaan säästöt happitehtaan kustannuksissa johtavat hyvin samassa suhteessa lisäkuluihin hiilidioksidin talteenotossa.

Osittaisen happipolton savukaasuille voidaan miettiä erilaisia talteenottokonsepteja, sillä hiilidioksidin osapaine savukaasuissa on melko suuri. Tässä työssä esiteltävä hybridimenetelmä on mielenkiintoinen, mutta yksi vaihtoehto voisi olla esimerkiksi

alimitoitettu amiinipesuri, jolloin suurin osa hiilidioksidista saataisiin talteen ja vain pienestä osasta jouduttaisiin maksamaan päästöoikeudet.

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TERMS AND DEFINITIONS

ASU	Air separation unit
CO ₂ capture efficiency	Quantity of CO ₂ captured divided by the quantity of CO ₂ produced
FGD	Flue gas desulphurisation
Joule-Thomson effect	The effect which occurs when a gas or liquid is forced through a valve while it is kept insulated. As a result, the gas cools.
SCR	Selective catalytic reduction, a method to control NO _x emissions
MEA	Monoethanolamine, an organic chemical compound that is both a primary amine and a primary alcohol. It is used as a scrubbing liquid in amine scrubbers.
ASPC	Air-fired supercritical pulverized coal - plant
BESP	Break even selling price

1 INTRODUCTION

The report is a part of the Carbon Capture and Storage Program (CCSP) of the CLEEN Ltd., the Cluster and Strategic Centre for Science, Technology and Innovation (CSTI, in Finnish SHOK) for energy and environment, and it is funded by Fortum Power and Heat Oy, a consortium member of the CCSP. In this research report the aim is to compare two different methods to produce oxygen and then use the oxygen in a power plant using the oxyfuel combustion method to capture carbon dioxide. The first method is cryogenic air separation which is the standard method for oxygen production (Cooke 2007). The second is a new method invented by Matti Nurmi, whose method has been researched earlier at Tampere University of Technology (Suhonen 2011). Cryogenic air separation is able to produce fairly pure oxygen unlike Nurmi's method, but on the other hand it consumes much more energy. Actually, the first target of this report is to evaluate how large the difference in energy use is.

After this estimate, the oxygen is used to combust pulverised coal in a quite conventional power plant. However, pure oxygen cannot be used in normal combustion chambers as the adiabatic flame temperatures would be too high for the surrounding materials (Buhre et al. 2005). Therefore, a part of the flue gas must be recycled in order to keep the temperature at a reasonable level (Buhre et al. 2005). The flue gas flowing out of the system is then a mixture of recycled and newly formed flue gas. The composition of this gas is calculated in this report as the knowledge is important for the carbon capture process.

As Buhre et al. (2005) show, the flue gas which is not recycled is then taken to various gas cleanup systems. Even though the combustion process is somewhat different than normally, the flue gas still probably contains SO_x and particulates, which are detrimental to many carbon dioxide capture systems and harmful to the environment. Consequently, they must be removed from the flue gas before the carbon capture unit.

One of the main ideas of oxyfuel combustion is to increase the partial pressure of carbon dioxide in the flue gas, as it allows using simpler and less expensive carbon capture systems. As the preceding parts of the report reveal the composition of the flue gas in oxyfuel combustion systems, the task of the next part is to assess which systems could be used for this purpose. The performance of such capture systems is also studied, as the later transport and storage of the carbon dioxide set important requirements for the CO_2 purity.

2 COMPARISON OF TWO OXYGEN PRODUCTION METHODS

Although several oxygen production methods exist, cryogenic air separation is currently the most important production method (Cooke 2007). It can be used to produce large amounts of oxygen, as needed in many industrial applications, which makes it a primary candidate for oxyfuel power plants, too. However, big power plants would actually require several times more oxygen than current industrial users. (Rubin et al. 2007a.)

Cryogenic air separation can be used to produce very pure oxygen, but maximum purity does not seem to be essential for oxyfuel combustion purposes, as it is reasonable to assume that some air leaks will anyway exist in real power plants. Furthermore, cryogenic air separation has a very large energy requirement and capital costs, which poses problems for the whole oxyfuel combustion technology. (Rubin et al. 2007a.)

As a result, alternative oxygen production methods have been developed. Cooke (2007) mentions membrane separation, pressure swing adsorption (PSA) and vacuum swing adsorption (VSA) as newer options. Ion transport membranes (ITM) for oxygen production are even developed partly with United States Department of Energy funding to create a new method for providing oxygen to power plants (Air Products 2011). Another method has been suggested by a Finnish inventor, Matti Nurmia, and this technology is compared to cryogenic air separation in this report (Nurmia 2002).

The first and second subchapters briefly introduce the two technologies, while the third subchapter focuses on the comparison between the two. The energy requirements of the systems are the main focus of this part of the report, as other aspects are dealt with in later chapters.

2.1 Cryogenic air separation

In the cryogenic air separation process, the air is liquefied and separated into its constituents by cryogenic technology. As Smith & Klosek (2001) clearly show, it is a leading solution for large-scale oxygen production. Additionally, it has an excellent by-product capability, which further enhances its competitiveness in many cases (Smith & Klosek 2001). Nitrogen is the most common by-product, but also noble gases, such as argon, neon, krypton and xenon can be separated from air in the process. To give a crude overview of the possible production volumes, the composition of normal dry air is given in Table 2.1.

Table 2.1. The composition of dry air. The amount of water in air is highly variable, but it is typically about 1 %. All other gases combined compose less than neon alone. (NASA 2010.)

Gas	
Nitrogen (N ₂)	78.08 %
Oxygen (O ₂)	20.95 %
Argon (Ar)	0.934 %
Carbon dioxide (CO ₂)	0.038 %
Neon (Ne)	0.0018 %

In practice, this means that cryogenic air separation can produce much nitrogen and oxygen, but smaller amounts of other gases. But because these other gases are rarer, they are also more valuable (Cooke 2007). On the other hand, the oxygen demand would multiply if hundreds of oxyfuel power plants were built. It can be considered unlikely that the demand for nitrogen and the other by-products would increase as much, which would have negative consequences for the overall economics of the air separation units. This view is also supported by the production statistics shown in McKetta (1990). However, the magnitude of this effect is hard to evaluate and it is thus not discussed further.

The history of cryogenic air separation goes back to the beginning of the 20th century, when Carl von Linde invented a method to liquefy air. This requires very cold temperatures, about -150 °C in high pressures and about -200 °C in atmospheric pressure, which partly explains the large energy use of the process. The principles of the separation remain the same as in the first air separation units, although several improvements to the process have been developed. (Linde 2009.) A simplified version of the main process is shown in Figure 2.1.

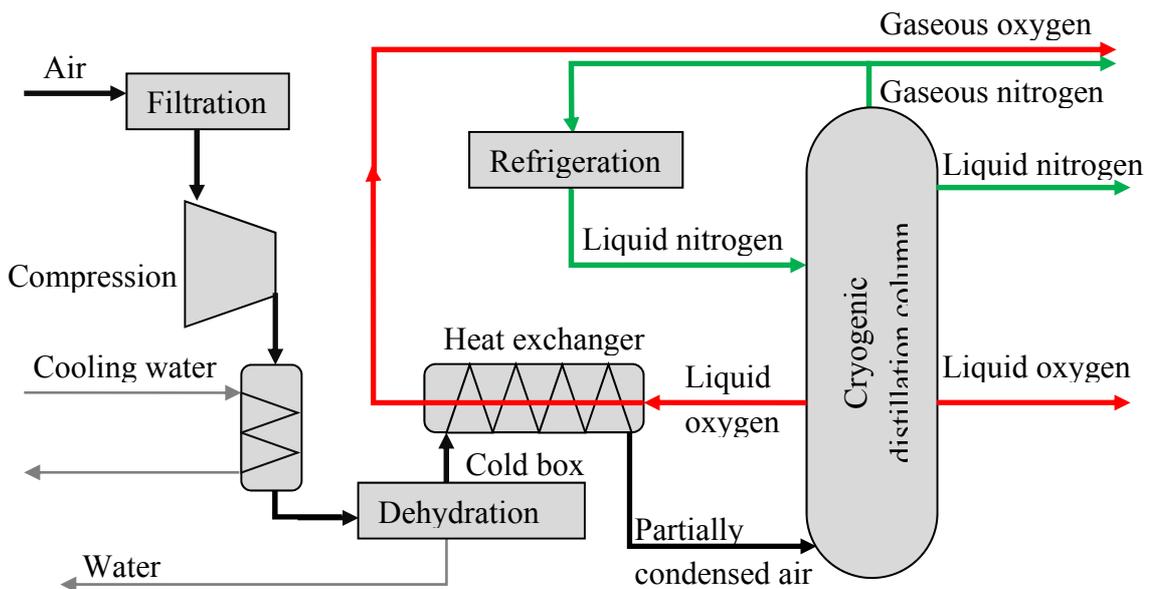


Figure 2.1. Cryogenic air separation process (after Rackley 2010).

As can be seen in the figure, the incoming air is first filtered and then compressed. As the compression warms it up, it is then cooled to ambient temperature with water. After drying, the air is taken to another heat exchanger, where a part of the produced liquid oxygen cools the air. After the cooling, the air is expanded through a valve and cooled to liquefaction temperature by the resulting Joule-Thomson effect. The liquefied air continues into a tray or a packed distillation column. Because nitrogen has a lower boiling point (-196 °C at normal pressure), it vaporises easier than oxygen (-183 °C). This leads to a gaseous nitrogen stream going out from the top of the tower and a liquid oxygen stream which can be taken out at a lower part of the tower. Such a simple single-tower process yields a fairly pure liquid oxygen stream and a gaseous nitrogen stream containing 5 - 10 % of oxygen. (Rackley 2010.)

Further modifications are possible to increase the purity of the nitrogen stream and to produce argon and other noble gases. Linde (2009) presents some common examples of such modifications. Argon has its boiling point just below that of oxygen, so if high-purity oxygen (> 95 %) is needed, argon needs to be removed from the oxygen. (Rackley 2010.) However, argon is extremely inert, so it is unlikely to have any significant effects in the later combustion process (Cooke 2007). As Rubin et al. (2007a, p.4) show, many previous studies have assumed that 95 % oxygen purity is enough for oxyfuel combustion purposes. Consequently, this work also uses the same figure. Naturally, this saves investment costs and is consistent with the earlier considerations about the difficulty of finding buyers for the large volumes of by-products.

Castle (2002) and Kruger (2003) clearly state that it is the air compressor which consumes a major part of the power in the process. Kruger (2003) also shows that other power users are motors of blowers and pumps. Rubin et al. (2007b) state that the three main factors affecting the required power input to an air separation unit are the amount of oxygen to be produced, the purity of the product and the delivery pressure of the product. The amount of oxygen needed naturally depends on the size of the power plant. As the combustion process for which the oxygen is intended occurs at atmospheric pressure in this report, oxygen needs to be delivered at only atmospheric pressure.

Based on McKetta (1990), Rubin et al. (2007b) have developed a model of the power consumption of an air separation unit (ASU). As power consumption increases more sharply after oxygen purity of 97.5 %, the model consists of two parts, shown in equations 1 and 2.

$$ASU \text{ Power} = (0.00488 * \varphi + 0.4238) * 264.13 \quad , \text{ if } \varphi \leq 97.5 \% \quad (1)$$

$$ASU \text{ Power} = \left(\frac{0.0736}{(100-\varphi)^{1.3163}} + 0.8773 \right) * 264.13 \quad , \text{ if } 97.5 \% < \varphi < 99,5 \% \quad (2)$$

where ASU Power is in kWh/t O₂ product and φ = O₂ product purity in mol-%. A tonne of oxygen is equivalent to 264.13 cubic feet at normal temperature and pressure. With 95 % oxygen purity, the model gives about 234 kWh/tO₂.

However, Castle (2002) mentions several recent technical developments and forecasts about 220 kWh / tO₂ for a tone of gaseous oxygen in 2010. Cormos (2011; 2012)

uses 225 kWh per tonne of 95 % pure oxygen at 2.4 bar in his estimates, so 225 kWh/tO₂ can be considered a conservative estimate at atmospheric pressure. In some oxyfuel combustion concepts the oxygen may be needed at higher pressures, which naturally increases the power consumption. The model of Rubin et al. (2007b) includes another equation, which can be used in such cases. Because pressurisation is not needed in the concept studied in this report, this effect is not discussed further.

2.2 Nurmia oxygen enrichment method

As the energy consumption of cryogenic air separation is fairly high, new methods are actively researched. Membranes and different adsorption systems are commonly known alternative technologies, as stated earlier. Professor Matti Nurmia from University of Jyväskylä has invented his own patented method. The Nurmia process also uses very cold temperatures like the cryogenic method, but only the oxygen concentrate is liquefied. Also the pressures used are low, which decreases energy costs. (Nurmia 2002.)

The process principles are shown in Figure 2.2. The incoming air is blown in through a drier, a CO₂ removal system and a particle filter. The air at atmospheric pressure is then cooled by the outgoing gas streams to about 81.5 K, which is the condensation temperature of air. As this temperature is very low, the area inside the dashed line must be well insulated. Vacuum insulation is one possibility for this, as shown in Figure 2.2. After the heat exchangers the air flows to the separation vessel. (Nurmia 2002.)

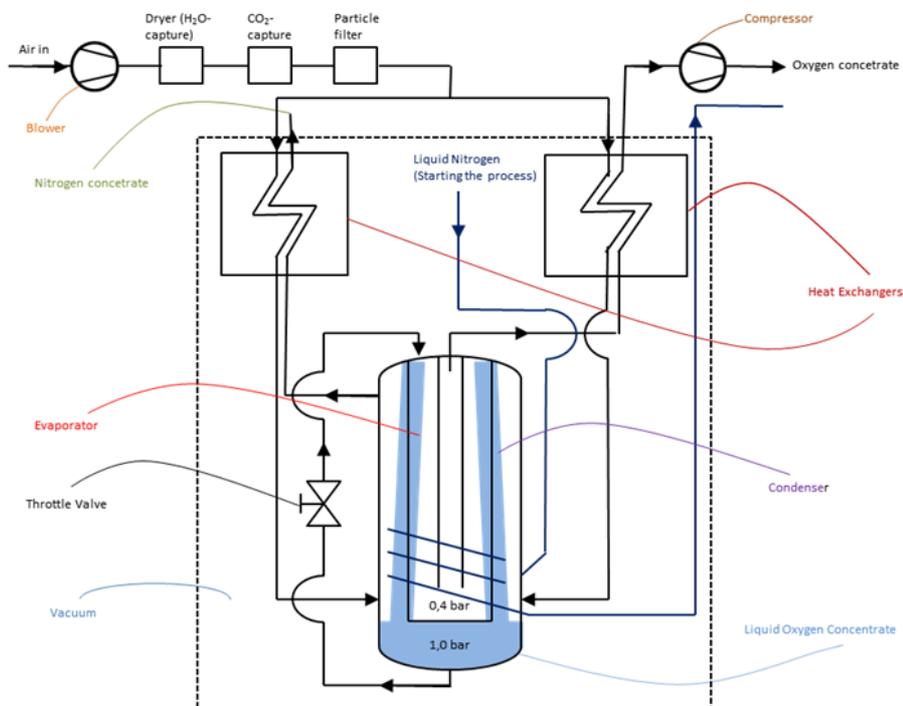


Figure 2.2. The Nurmia process (Nurmia 2002; Suhonen 2011).

The separation vessel is a double column consisting of two thermally connected parts. The incoming air enters the outer column and flows at first upwards, but it is cooled by the cooler gas in the inner column. Therefore, the oxygen, which has a higher boiling point than oxygen, starts to liquefy and flows to the bottom of the column. This

means that the liquid becomes rich in oxygen and the gas rich in nitrogen. The liquid is then taken from the bottom of the column to the inner column through a valve, which throttles it to about 0.4 bar causing a temperature drop of 3-4 K. (Nurmia 2002.)

The oxygen-rich liquid is sprayed into the inner column, but because the outer column is warmer, it vaporises. On the other hand, this consumes heat which in turn causes condensation on the other side of the column wall. The gaseous oxygen-rich stream (about 50 % O₂) is then taken out of the column to the heat exchangers pre-cooling the air. As the oxygen concentrate is still in low pressure, it is finally compressed to atmospheric pressure for later use. (Nurmia 2002.) As shown in the original patent (Nurmia 2002) and in the report of Suhonen (2011), Nurmia has also invented a method to further enrich the oxygen with a two-staged inner column, which can yield oxygen with 80 % purity. However, in this report the focus is on the 50 % oxygen concentrate, as it is simpler to produce.

With good enough insulation, the process should not need external cooling. However, some liquid nitrogen is needed to provide cooling as the process is started, as shown also in Figure 2.2. This means that the only significant users of power in the process are the air blower and the oxygen compressor. According to Suhonen (2011), the energy consumption of the process is 42 - 60 kWh per tonne of concentrate. The actual consumption depends mainly on the pressure loss of the air blower. Nurmia (2002) estimates it to be 0.1 - 0.3 bar, so in this report a pressure loss of 0.2 bar is assumed. With this pressure loss, the Nurmia method consumes 51 kWh per tonne of 50 % oxygen concentrate, which equals 102 kWh / tO₂. (Suhonen 2011.) This is much less than with cryogenic air separation, which explains the interest to the method.

3 COAL COMBUSTION WITH THE OXYFUEL METHOD

In the previous chapter, two methods of producing oxygen are introduced. This chapter focuses on the combustion of coal with the oxygen produced by those methods. Coal is used as the example fuel as it is a very common fuel, but it has high CO₂ emissions. As combustion with pure oxygen would lead to excessively high flame temperatures, amount of oxygen in the combustion chamber must be limited to about 30 %. Because the goal of oxyfuel concepts is to reduce the amount of nitrogen in the flue gas, a part of the flue gas is recycled in the process. Altogether, such a modification also reduces gas flows in the process, which naturally means also smaller volumes of gaseous emissions. (Buhre et al. 2005.)

Consequently, the primary task of this chapter is to calculate the gas flows in the process and especially the outgoing flue gas, which continues further to the CO₂ removal process. To make the differences of the two oxygen production methods clear, the calculations are performed for the same fuel with both methods. As in normal combustion, the amount of oxygen has to be a little over the stoichiometric amount needed for combustion to ensure complete combustion. However, as the partial pressure of oxygen is higher in oxyfuel concepts, 5 % excess oxygen is assumed to be sufficient (Buhre et al. 2005).

Table 3.1 shows the composition of the gases which are used as oxidants for the combustion. As both oxygen production methods use liquefaction as the separation technology and the boiling of argon is very near that of oxygen, the argon content is likely to increase from its content in air. Because argon is nonreactive and its market volumes small (McKetta 1990), it can be considered unlikely that it would be separated from the oxidant gas at oxyfuel power plants. Rubin et al. (2007a) also note that in real power plants air leaks will occur, although this should naturally be avoided. However, their calculations show that even a small leak, providing just 1 % more oxygen to the process has a significant effect on the amount of nitrogen in the process.

Table 3.1. *The composition of the oxidant gases by oxygen production method. The values for cryogenic air separation are based on Rubin et al. (2007a) and the values for the Nurmia method are a crude estimate of the authors.*

Species	Oxygen production method	
	Cryogenic air separation	Nurmia method
O ₂	95 %	50 %
N ₂	0.8 %	48 %
Ar	4.2 %	2 %

When the practically inevitable leaks are taken into account, the composition of the actual combustion gases changes somewhat. Table 3.2 shows the resulting compositions, which are naturally based on the values in Tables 2.1 and 3.1. The air leakage is approximated to provide 1 % extra oxygen to the process, which is less than Rubin et al. (2007a) suggest but in line with some other studies they mention. These values are used throughout this report. As can be seen, the oxygen concentrate can then be assumed to be just a mixture of oxygen and nitrogen, because the amount of argon is negligible compared to either gas. For the cryogenically separated air the change is that there is now less oxygen and more nitrogen.

Table 3.2. *The estimated compositions of the actual gases used in combustion by oxygen production method.*

Species	Oxygen production method	
	Cryogenic air separation	Nurmia method
O ₂	92 %	50 %
N ₂	4 %	50 %
Ar	4 %	0 %

Before the combustion products can be calculated, the composition of the fuel is also needed. As already noted, the fuel used in this report is coal, but there are various types of coal. Their properties vary significantly depending on the production site, the mining practices, the length of storage and various other factors (Alakangas 2000). Most of the coal used in Finland comes from Russia, more specifically from Kuznetsk Basin in Siberia (Finnwatch 2010). The sulphur content in this coal is generally low (Miller 2005), which is beneficial in the European market because of the comparatively strict environmental regulation of sulphur dioxide emissions (European Parliament and Council Directive 2001/80/EC).

Naturally, the exact composition of the coal is never the same, but Table 3.3 contains average composition of Russian coal imported to Finland. Naturally, no coal shipment can be expected to have exactly this composition, but this approximation is good enough for the purposes of this work. This coal can be classified as high-volatile bituminous coal according to Miller & Tillman (2008). This type of coal is often used in power plants and the majority of the coal used in Finland is such coal (Kivihiilitoimikunta 2004; Taipale 1996), so it is relevant for this report. The lower heating value of such coal can be estimated to be about 25 MJ/kg (as received), which is very near the long-term average of coal imported to Finland (Alakangas 2000; Kivihiilitoimikunta 2004).

Table 3.3. *The average composition of Russian coal imported to Finland. Data from Taipale (1996) according to Alakangas (2000). The values of the analyses have been slightly modified, as the sum of averages is not 100 %, but they are within the minimum and maximum values shown in Alakangas (2000).*

Proximate analysis	Percentage (wt-%)
Moisture (as received)	10.4 %
Ash (on dry basis)	15 %
Volatile matter (on dry basis)	33 %
Fixed carbon (on dry basis)	52 %
Ultimate analysis (on dry basis)	
Carbon (C)	72.3 %
Hydrogen (H)	4.6 %
Oxygen (O)	5.6 %
Nitrogen (N)	2.0 %
Sulphur (S)	0.5 %

After the compositions of the fuel and the gas which is used to provide oxygen are known, this report can move on the actual combustion. This is done by stoichiometric calculations as usual. Subchapter 3.1 includes the calculations for cryogenically separated oxygen and Subchapter 3.2 those for oxygen concentrate produced by the Nurmia method. As noted above, 5 % excess oxygen is considered sufficient for oxyfuel purposes and this value is used also by Rubin et al. (2007a), so it is used in these calculations. Data from Tables 3.2 and 3.3 are used throughout this part of the report.

In both subchapters, the values are at first calculated for 1 kg/s of coal in order to facilitate calculation for differently-sized power plants. It should be noted that the calculations here are intended mainly to compare the compositions and the volumes of the flue gases resulting from the two different oxygen production technologies. Much more detailed calculations of the different mass flows in oxyfuel systems can be found in DOE/NETL (2008, p. 155-168).

3.1 Coal combustion in cryogenically separated oxygen

There have been numerous studies, in which people have studied the composition of flue gas resulting from the combustion of coal with oxygen of high purity, both theoretically and empirically. This report is not claiming to provide new information about the subject, but this part is mainly intended to provide a comparable flue gas for the flue gas which results from the combustion in the oxygen concentrate of the Nurmia method. For a more complete description of various challenges and assumptions behind the calculations and oxyfuel systems in general, the reader is advised to sources such as Rubin et al. (2007a), Mathieu (2010) and Habib et al. (2011).

In Table 3.4, the combustion products are calculated. As can be seen, the composition of the flue gas is about 60 % CO₂, 30 % water and 10 % other gases, which is well in line with the values given in Mathieu (2010, p. 290). A major part of this flue gas is later recycled to the boiler to keep the oxygen levels at about 30 %. This recycle rate varies, but a common assumption is that about 70 % of the flue gas would be recycled and the rest would continue to CO₂ separation. The flue gas can be recycled as wet or dry, but wet flue gas recycling seems to be the more studied option. (Rubin et al. 2007.) Wall et al. (2011) also state that partial drying of the flue gas can be used in order to reach the desired water content. This report does not focus on this question, so Table 3.4 includes the compositions of both wet and dry flue gas. However, the composition of the dry flue gas is important in any case, as the water is condensed from the non-recycled flue gas flow prior to compression and CO₂ purification, which can easily be noticed in DOE/NETL (2008, p. 159-168).

Table 3.4. The combustion products of Russian high-volatile bituminous coal 1 kg/s in cryogenically separated oxygen. 5 % excess oxygen is present and air leakage is taken into account in the composition of the oxidant gas.

Substance	M (g/mol)	m (g/s)	N (mol/s)	O2 need (mol/s)	CO2 (mol/s)	H2O (mol/s)	N2 (mol/s)	O2 (mol/s)	SO2 (mol/s)	Ar (mol/s)
C	12,01	647,8	53,94	53,94	53,94					
H2	2,016	41,2	20,44	10,22		20,44				
O2	32	50,2	1,57	-1,57						
N2	28	17,9	0,64	-			0,64			
S	32,1	4,5	0,14	0,14					0,14	
H2O	18,02	104	5,77	-		5,77				
Ash		134,4								
Total		1000	82,49	62,73						
5 % extra O2			3,14					3,14		
Real O2 need				65,86						
Other gases in the oxidant										
N2 (4 %)			2,86				2,86			
Ar (4 %)			2,86							2,86
Total in flue gas					53,94	26,21	3,50	3,14	0,14	2,86
Flue gas flow			89,79							
Flue gas composition (mol-%)					60,07 %	29,19 %	3,90 %	3,49 %	0,16 %	3,19 %
Dry flue gas composition (mol-%)					84,83 %		5,51 %	4,93 %	0,22 %	4,50 %

Naturally, recyclable flue gas is not available during start-up of the plant, so the oxyfuel plants are likely to be started with air firing and then gradually switched to oxyfuel mode (Wall et al. 2011). Because of this, the flue gas composition of Table 3.4 would only be reached after the power plant has been in operation for some time.

It should be noted that the ash from the fuel should be collected before recycling to avoid operational problems (DOE/NETL 2008).

With NO_x and SO_x the situation is not so clear. The NO_x formation is, of course, significantly reduced compared to the air firing case because of the small amount of nitrogen present in the boiler, so selective catalytic reduction (SCR) systems for NO_x control are usually not considered necessary (Rubin et al. 2007). On the other hand, because of the relative lack of nitrogen in the flue gas and the recycling of the flue gas, the SO_x concentration in the flue gas can be even threefold compared to air firing (Wall et al. 2009). This means that the flue gas becomes more corrosive, especially with high sulphur coals. According to Wall et al. (2009) this means that either oxyfueling must be limited to only low sulphur coals or a flue gas desulphurization unit must be installed in the recycling cycle.

Because of this problem, the oxyfuel concepts in DOE/NETL (2008) include a FGD system. However, White et al. (2010) argue that in some cases SO_x and NO_x components can be removed during compression of raw oxyfuel-derived CO_2 without traditional SO_x and NO_x removal systems, which would result in significant cost savings.

Actually, this kind of consideration leads to the most important advantage of oxyfuel systems, which is the lack of a complicated CO_2 separation system. As the dry flue gas is very rich in carbon dioxide, it can be purified to transportable purity (> 95.5 % CO_2 for pipelines) with just a series of refrigerated flash steps. (DOE/NETL 2008, p.169; Aspelund 2010.) CO_2 capture efficiency can still be well over 90 % with such a system. It should be noted that if lower CO_2 purities are accepted, even higher CO_2 capture efficiency can be achieved without extra costs at the power plant (DOE/NETL 2008). However, as Finland lacks CO_2 storage capacity (Teir et al. 2010), CO_2 purification to transportable purity seems to be a necessity for any Finnish power plants capturing carbon dioxide.

3.2 Coal combustion in oxygen produced by the Nurmia method

There haven't been many studies from the combustion of coal with oxygen produced by Nurmia method or indeed any method which provides partially enriched oxygen. Since the Nurmia method produces about 50 % oxygen, some flue gas recycling is still needed in order to keep the oxygen concentration at 30 % in the combustion chamber. Another possibility is to use air to reduce the oxygen content. The advantage in this is that it requires considerably less changes to the boiler in retrofit case. This however is not studied in this report because the resulting flue gas would be almost identical compared to normal air firing and thus it is unlikely that there would be any significant advantages in CO_2 recovery. Also with current interest rates and fuel prices operating costs play a much bigger role than capital costs, so it is considered profitable to make a small modification investment even in retrofit case (Doukelis et al. 2009). In Table 3.5, the combustion products are calculated. Based on the flue gas components and the oxygen

concentration in the oxidant it can be estimated that the suitable flue gas recycle rate is about 40% for this method. For this method also the more studied option is wet flue gas recycling (Doukelis et al. 2009).

Table 3.5. The combustion products of Russian high-volatile bituminous coal 1 kg/s in oxygen produced by Nurmia method. 5 % excess oxygen is present and air leakage is taken into account in the composition of the oxidant gas.

Substance	M (g/mol)	m (g/s)	N (mol/s)	O2 need (mol/s)	CO2 (mol/s)	H2O (mol/s)	N2 (mol/s)	O2 (mol/s)	SO2 (mol/s)	Ar (mol/s)
C	12,01	647,8	53,94	53,94	53,94					
H2	2,016	41,2	20,44	10,22		20,44				
O2	32	50,2	1,57	-1,57						
N2	28	17,9	0,64	-			0,64			
S	32,1	4,5	0,14	0,14					0,14	
H2O	18,02	104	5,77	-		5,77				
Ash		134,4								
Total		1000	82,49	62,73						
5 % extra O2			3,14					3,14		
Real O2 need				65,86						
Other gases in the oxidant										
N2 (50 %)			65,86				65,86			
Ar (0%)			0,00							0,00
Total in flue gas					53,94	26,21	66,50	3,14	0,14	0,00
Flue gas flow			149,93							
Flue gas composition (mol-%)					35,98 %	17,48 %	44,36 %	2,09 %	0,09 %	0,00 %
Dry flue gas composition (mol-%)					43,60 %		53,75 %	2,54 %	0,11 %	0,00 %

The main disadvantage of partial O₂ fired method compared to cryogenically separated oxygen method is immediately apparent. The CO₂ concentration in the flue gas is so low that a series of refrigerated flash steps is not a feasible option for CO₂ recovery. Alternative methods compared in this report are a conventional amine scrubber (Doukelis et al. 2009) and a hybrid scrubber (Huang et al. 2012) which integrates an amine scrubber to a series of refrigerated flash steps.

Another thing worth noticing is that now the SO₂ concentration is significantly lower and therefore the flue gas is less corrosive and better suited for recycling. Still if the coal used has high sulphur content it might be necessary to have a flue gas desulphurization unit in the recycling cycle in order to prevent corrosion (Wall et al. 2009).

In conclusion flue gas resulting from partial oxyfuel firing is not as well suited to CO₂ capture as the pure oxyfuel flue gas, but since it is much richer in CO₂ than the flue gas from normal air firing, it is possible to use smaller solvent flow rates in amine

scrubbers or the hybrid system introduced in the next part of this report. One possibility is to consider an undersized amine scrubber, which can recover most of the CO_2 . This would be cheaper than demanding full recovery of CO_2 . Of course it would result to some extra costs in CO_2 emission rights, but since the partial pressure of CO_2 is fairly high even this undersized scrubber could achieve good results.

Considering the retrofit case partial oxyfuel firing becomes even more interesting since the combustion and resulting gas flows and gas compositions are much closer to air firing than in the full oxyfuel case. This means that in most retrofitting cases no or only small modifications are needed to the existing boiler. In full oxyfuel case problems start to occur in convectional heat exchangers because flue gas is so rich in CO_2 and H_2O and the flue gas flow is so small. In the full oxyfuel case the heat capacity of flue gas is almost double to that of air firing, and since the heat exchangers, of course, have been designed to work with air firing, this might be a major problem. Modification of existing thermal surfaces of the boiler is really complicated and expensive. On top of that, it is not guaranteed how, for example, the fly ash behaves if some modifications are attempted. In conclusion, it can be said that full oxyfueling might only be a sensible option for a brand new plant, where everything can be designed in a way, which takes into account the massive flue gas recirculation rate with SO_2 rich gas, the smaller flow rates in other places and the different heat capacity of the gas.

4 POSSIBLE CONCEPTS FOR CO₂ CAPTURE

There are two familiar options for carbon capture. There is the so called oxyfuel method, where pure oxygen is used instead of air. Since there is no nitrogen in the process, CO₂ can be liquefied with few cryogenic flash steps. Other established method for carbon capture is post-combustion capture where amines are used as solvents to capture CO₂.

At the moment, a couple of new concepts have surfaced that use the partial oxyfuel methods. A concept introduced by Zanganeh et al. (2007) mixes pure oxygen with air to lower the energy penalty of the ASU plant. Another concept introduced by Doukelis et al. (2009) studies how mixing oxygen to combustion process affects post-combustion carbon capture methods. The idea is that the increased partial pressure of CO₂ in flue gases makes the amine process more efficient. Both of these new conceptual carbon capture methods can be applied to an existing power plant since the amount of flue gases stays approximately the same as in normal air combustion. These concepts are studied in large PC power plants.

In this chapter, these partial oxyfuel processes are presented, as they can be retrofitted to the existing PC plant. Nurmia oxygen production method can be applied to these hybrid processes where pure oxygen is not needed. Also smaller ASU plant can be used in order to produce oxygen to these processes. Economic aspects of these processes are evaluated in Chapter 5.

4.1 Hybrid process for CO₂ capture

Hybrid process for CO₂ capture was first introduced by Zanganeh et al. (2007). This process combines partial oxyfuel combustion with hybrid post-combustion methods for CO₂ capture. This method is designed specifically to reduce the cost and energy consumption of the ASU plan. This process uses air with O₂ enrichment and would require CO₂ purification and compression units.

The ASU plant would be smaller than in conventional oxyfuel combustion process and the CO₂ purification and compression systems would be smaller than in air-firing. This system has significant potential to reduce energy consumption and costs.

In a hybrid process ambient air is used as primary air to carry coal to the burners. Secondary air is a combination of the recycled flue gas and pure (95%) oxygen from the ASU plant as shown in Figure 4.1.

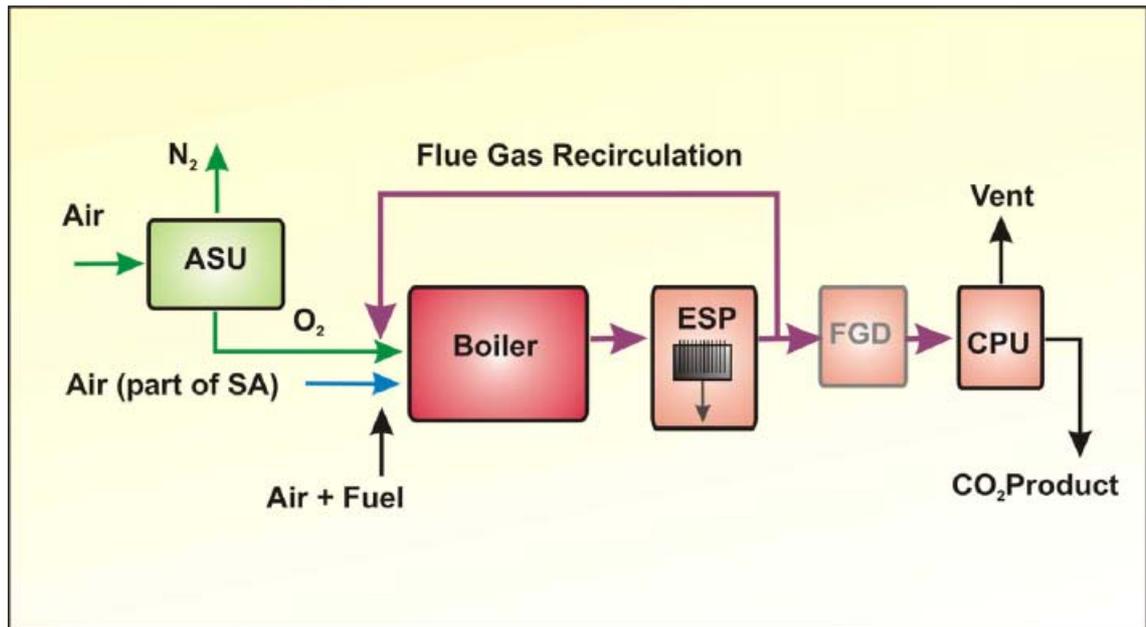


Figure 4.1 Hybrid process introduced by Huang et al. (2010)

The carbon dioxide separation and cryogenic liquation unit is formed as shown in Figure 4.2. The first step is drying the flue gas with simple condensation where the water, ash and dissolved gases are removed from the stream. After that the flue gas is compressed in a dual-bed desiccant dryer to reduce the moisture content. The dry gas is then passed to a cryogenic distillation unit where most inert gases are removed using CO₂ refrigeration. The separated inert gases can be heated and expanded through the turbine to produce additional power as shown in Figure 4.2.

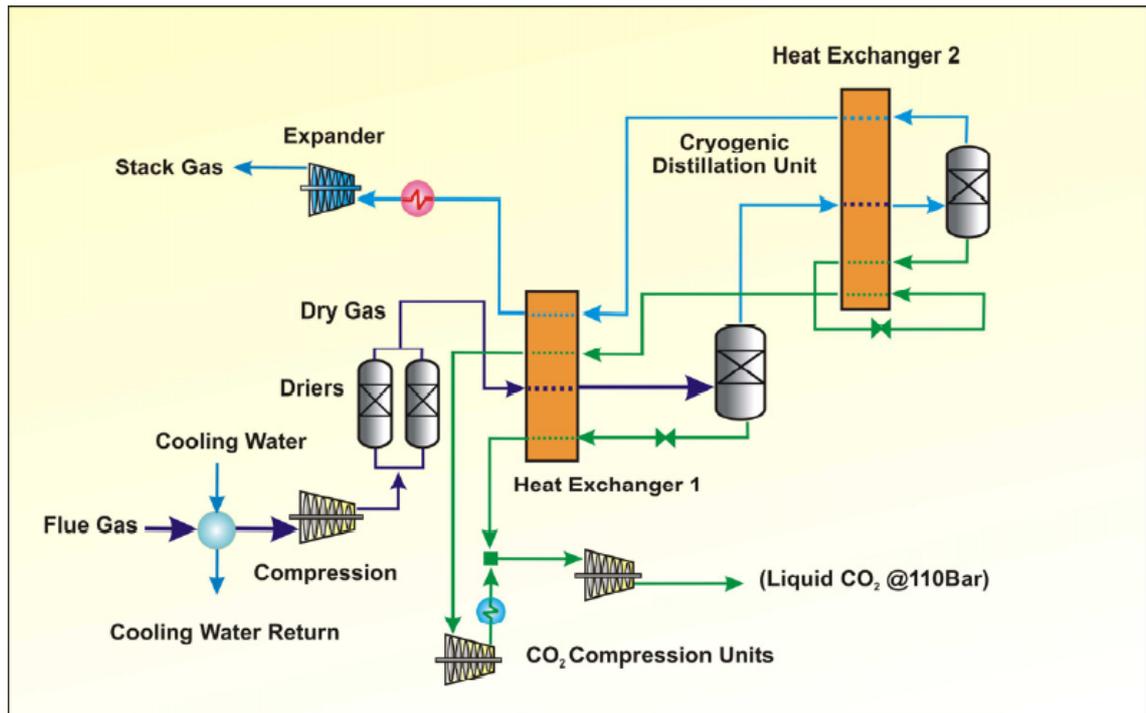


Figure 4.2 Cryogenic CO₂ capture unit in hybrid process introduced by Huang et al. (2010)

Optimum air addition to hybrid oxyfuel process according to Huang et al. (2010) is 30 % air addition. Considering that, Nurmia (basic) process would offer too low oxygen concentration to pursue this method.

4.2 Solvent scrubber process for CO₂ capture

The post-combustion method with partial oxyfueling introduced by Doukelis et al. (2009) differs from the hybrid process due to a distinct carbon capture process. In post-combustion processes CO₂ is not captured cryogenically, but it is captured using solvent scrubbing as seen in figure 4.3.

In this process regular air carries the coal to the boiler whereas oxygen is added to the process as secondary air. Some parts of the flue gas is circulated back to the boiler after electrostatic precipitator (ESP). After that flue gas goes the air and water preheaters. Then flue gas is cleaned from NO_x and SO_x compounds before CO₂ is separated in CO₂ capturing plant (PCC).

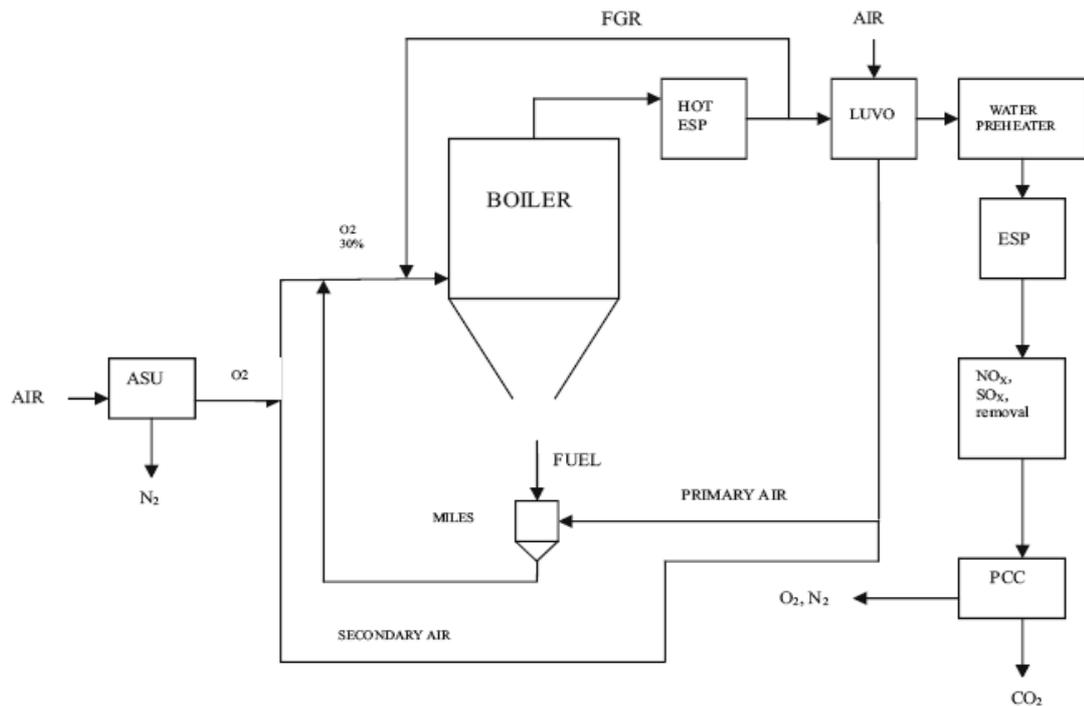


Figure 4.3 Partial oxyfueling with post-combustion CO₂ capture studied by Doukelis et al. (2009)

Partial oxyfuel combustion makes solvent processes more efficient than they are in regular air combustion. This so called ECO-Scrub system is designed to capture CO₂ from old PC plants with smaller capital cost and with smaller energy penalties. The basic idea in this system is to increase the partial pressure of the CO₂ in flue gases in order to make the amine solvent reaction more efficient and the solvent plant smaller.

5 ECONOMICAL EVALUATION OF DIFFERENT OXYFUEL CO₂ CAPTURE SYSTEMS

The main purpose of this economical evaluation is to provide some kind of idea which CO₂ recovery solution is economically the most sensible one. Since there is no operating oxygen factory based on the Nurmia method, we can only assume that the cost of oxygen produced by Nurmia method is pretty similar to that of traditional Linde process. This is a conservative estimation, because as seen in Chapter 2 of this study, based on Nurmias theory and patent application (Nurmia 2002), this should be a cheaper way of producing oxygen. This means that especially processes like Eco-Scrub could benefit from this cheaper oxygen significantly, since the flue gas treatment and CO₂ separation in this kind of process can handle nitrogen in the flue gas. In this study this option, however, is not considered and all the economical evaluations made are based on oxygen produced by commercially available Linde method.

In the two studies conducted by Doukelis et al. (2009) and Huang et al. (2012) it can be seen that all applications of CO₂ capture technologies lead to massive increase in energy generation costs, even up to 60 – 70 %. This is mostly due to the increased operating and maintenance costs of the plant. Increase in investment costs is about 20 – 25 % depending on the technology used. Increase in investment cost, however, is noticeable especially if the plants' full-load time is short. Economic analysis on the study (Doukelis et al. 2009) is based on 7500 annual operating hours. It is likely that if this kind of an investment is made to a plant, it needs to be operating almost all the time thus providing base load power. Whether this is economically viable or not depends largely on the local electricity market conditions and the cost of CO₂ emission rights compared to the extra cost of energy generation with CO₂ capture.

According to Huang et. al. (2012) the optimum amount of air addition into pure oxygen is around 20 – 30 %, which results to extra costs due to CO₂ capture in the order of 24 €/MWh. The interesting part is that even with 50 % air addition the difference in CO₂ capture costs is quite small. Therefore it can be assumed that 50 % oxygen concentration produced by Nurmia method could be financially interesting provided that the price of Nurmia's oxygen is considerably lower. We have collected the most important economic figures of different capture methods into Tables 5.1 and 5.2 from studies conducted by Doukelis et al. (2009) and Huang et al. (2012).

Table 5.1 Economic key figures of 330MW_{el} lignite-fired plant (Doukelis et al. 2009).

	Reference	Oxyfuel	Post combustion	Partial oxyfuel
Increase in investment costs %	-	24.81	21.80	22.74
Increase in costs due to CO ₂ capture %	-	40.30	36.03	37.12
Increase in electricity generation cost per gross electric production %	-	29.69	50.13	42.75
Total electricity generation costs €/MWh net	24.6	40.7	41.9	40.4
Increase in electricity generation costs %	-	65.32	70.18	64.12

Table 5.2 Economic key figures of 826MW_{el} ASPC plant (Huang et al. 2012).

	Reference	Oxyfuel	Post combustion	Partial oxyfuel (Air addition 10-50%)
Total capital investment M€	1232.2	1642.8	1491.3	1576-1631
Specific investment €/kW _e	1372.6	2254.9	2439.6	2234.4-2248.4
BESP (€/MWh)	46.9	71.7	79.3	71.3-72.5
Increase in cost due to CO ₂ capture (€/MWh)	-	24.3	32.4	24.4-25.6
Increase in electricity generation costs %	-	52.8	69.08	52.03-54.58

In Table 5.2 the partial oxyfuel price fluctuation is always from minimum value to the maximum regardless which specific air addition it resulted from. Thus it can be said that the amount of air addition to the pure oxygen in the partial oxyfuel method does not have a big impact on anything. It looks like any advantage gained in smaller oxygen factory is fairly equally cancelled in CO₂ capture system. In fact, the partial oxyfuel method seems to be pretty similar in economic performance compared to full oxyfuel firing as can be seen in break-even selling price of electricity (BESP).

The price difference of the oxyfuel methods compared in these two studies can be explained by the retrofitting option which was taken into account in the Doukelis et. al. (2009) study. Another factor is the hydrid recovery system used in Huang et. al. (2012) study. Post-combustion systems of course do not require big changes to the existing boiler and therefore the price of this capture method is really similar in these studies.

The main interest of this study was to find out how partial oxyfuel firing compares to the known carbon capture methods and based on these studies it seems that both in retrofit case and in a brand new plant the operational performance is better than in amine based post-combustion methods and fairly similar to that of full oxyfuel combustion. Based on the simulations of Huang et al. (2012), it seems that 20 % air addition to cryogenically separated oxygen leads to optimal performance of the plant. The interesting bit is that even with 50 % air addition, the performance is still really close to that of the full oxyfuel method. This means that if it is possible to build and operate a full scale oxygen factory, which operates on the Nurmia principle, and if the oxygen produced by this plant is considerably cheaper than by current methods it is possible to achieve notable cost savings using Nurmia oxygen in partial oxyfuel systems. As noted earlier, partial oxyfuel systems are also considerably better suited for retrofit cases as well.

6 CONCLUSIONS

In this report, our goal was to study new possible carbon capture technologies for PC power plants. An important part of most carbon capture systems is an oxygen production unit which is considered to be necessary for many carbon capture processes. Oxygen is produced in an ASU, which consumes considerable amounts of energy leading to economically significant energy penalties. Considering this problem, research and new process solutions are needed to lower the energy penalties of the carbon capture processes.

A possible solution for the high operational cost of the ASU plant could be partial oxyfuel combustion. Oxygen for this partial oxyfuel process can be produced with conventional Linde process or with the new Nurmia process concept. Two different carbon capture concepts were also presented and they fit into the partial oxyfuel combustion process.

According to Huang et al. (2012) and Doukelis et al. (2009), the most efficient process concept for carbon capture is partial oxyfuel combustion. As mentioned by Huang et al. (2012), the amount of air addition does not affect the process considerably, which means that the Nurmia oxygen production method could benefit the partial oxyfuel combustion even more.

The partial oxyfuel method also makes it easier to retro-fit a carbon capture process to an existing plant since the volume of the flue gas flow is almost the same as in air firing. This means that convectional heat transfer surfaces work just like in conventional air firing according to the calculations in Chapter 3.

Making comparisons between post-combustion technologies is hard because the only commercially available system is the amine scrubber with a MEA solvent. In this report, a hybrid concept for carbon capture was presented. This process seems to be technologically and economically viable, but is still very much in concept state.

In conclusion, it can be said that the partial oxyfuel method concept is techno-economically the most promising option for carbon capture in a PC plant especially in a retro-fit case. For a brand new plant, where the different flue gas composition of full oxyfuel firing can be taken into account in the design process, there is very little difference between partial and full oxyfuel firing economically. However, it seems that conventional post combustion capture with amine scrubber leads to the highest price of CO₂ capture in any case. The only advantage of this method is that it can be easily retrofitted to any boiler requiring no major changes to the existing systems. Increase in electricity generation costs using post combustion methods is around 70 % compared to that of oxyfuel firing of 52 – 65 % depending on the amount of oxygen used and whether it is a retrofit case.

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