CUSTOMER REPORT



Optimisation of Partial Oxygen Combustion

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Summary This report presents the results of the study concerning partial oxy-combustion. In partial oxy- combustion air is enriched with oxygen. Partial oxy-combustion power plant would require both oxygen plant and CO_2 removal unit, leading to more but smaller units than required in either air-blown combustion power plant or oxy-combustion power plant. When comparing oxy-combustion to air-blown combustion, the volumetric flow rate of the flue gas decreases and CO_2 concentration increases with increasing oxygen content in enriched air. The most significant effect to operational cost was the decrease in energy consumption of the flue gas blower and the stripper. The investment costs of the main equipment in CO_2 absorption process were decreased due to the smaller size of the equipment. The investment and operational costs of oxygen plant were not taken into account.							
The advantages of other CO_2 re process in partial oxy-combustion flue gas to attain economically fer was too high to be beneficial con- technology and vacuum pressur CO_2 concentration increased in the level of removal efficiency and CO_2 limits (adsorbent efficiency, men	moval technologies compared to n were also studied. Power cons easible CO_2 partial pressure (10 npared to amine absorption. Bot e swing adsorption (VPSA) techn flue gas. However, neither techn CO_2 purity as the absorption tech nbrane selectivity).	amine-based absorption sumed for compressing the bar) for physical absorption th membrane separation nology would benefit if the ology can reach the same nology today due to material					
Special attention was paid to CC absorption technology mostly re CO_2 removal from partial oxy-co designed and simulated using A be a possible alternative to amin environmentally friendly and tech consumption of water wash proc	D_2 removal by water wash absorp placed by more efficient CO ₂ ren mbustion flue gas by water wash spen Plus simulation software. V the absorption. Water wash absorp nnically a less complicated process was estimated to be higher	otion which is an old physical noval methods. A concept for absorption process was Vater wash absorption could ption is more ess but the power than of amine absorption.					
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1. Description and objectives

Oxy-fuel combustion is one of the most promising CO_2 capture technologies that are about to be demonstrated in this decade. Similarly to the competing CO_2 capture technologies oxy-fuel combustion requires additional investments and relatively high energy requirements, which makes CO_2 capture very costly. In oxy-fuel combustion most of the investment costs and energy requirements are related to the air separation unit, which supplies oxygen to the burner. But since the flue gas consists mainly of CO_2 and water, the actual capture unit is relatively simple.

In partial oxy-fuel combustion, the combustion air would not be replaced completely with oxygen. Instead, the combustion air would be enriched with oxygen. Although nitrogen from air will be present in the flue gas stream, the CO_2 concentration of the flue gas stream would be significantly higher than in conventional air combustion. Although CO_2 capture from the flue gas stream would be more demanding than in full oxy-fuel combustion, it would still be less demanding than in air combustion.



2. Literature background

In coal combustion the concentration of CO_2 in flue gas is typically below 15 % (wet), leading to a complicated and expensive CO_2 separation process. At the moment technically and economically most feasible CO_2 capture process is evaluated to be some variation of amine based chemical absorption. However, the amine solvent regeneration consumes significant amount of energy. The estimation of energy consumption varies depending on the source, published values include for example 4-6 GJ/tonne of CO_2 recovered (Bounaceur 2006) or 2-4 GJ/tonne of CO_2 recovered (Favre 2009).

Compared to air blown combustion, partial oxy-combustion results in decreased total volume of the flue gas and thus in decreased dimensional size of equipment and decreased investment costs. In addition, other CO_2 removal technologies like physical absorption, pressure swing adsorption (PSA) or membrane separation may become feasible if the concentration of CO_2 in flue gas increases due to use of enriched air. In the following chapters the benefits and disadvantages of the above-mentioned CO_2 removal technologies are discussed.

2.1 Physical absorption

According to Rackley (2010) the typical feed gas of the physical absorption process is at 20 - 50 bar pressure and contains between 5-60 % (volume) acid gas with partial pressure ranging in between 7 - 30 bar. Kanniche (2010) states that physical absorption is feasible for CO_2 partial pressure greater than 8 bar and chemical absorption below that.

Commercial acid gas removal processes such as Selexol and Rectisol are examples of state-of-the-art physical absorption processes. In the Selexol process dimethyl ether of polyethylene glycol (DEPG) is used as solvent and in the Rectisol process the solvent is methanol. A comparison of the most common physical absorption processes for CO_2 removal has been carried out for example by Burr (2008). According to Burr all common physical absorption technologies are effective and the choice of the most suitable physical absorption technology for CO_2 removal is carried out taking into account specific requirements and restrictions of the specified process.

2.2 Water wash

Water wash of CO_2 is considered a physical absorption process. However, water wash has not been included in potential CO_2 removal methods from power plant flue gases in literature.

Capturing CO_2 by water wash is an old physical absorption technology. It is mostly been replaced by more efficient physical solvents like methanol of the Rectisol process or dimethyl ether of polyethylene glycol (DEPG) of Selexol process. The advantages when using water as an absorbent are relatively simple plant design and inexpensive solvent, which is not reactive with O_2 and other possible trace constituents. The principal disadvantage of the water wash absorption process is very poor CO_2 removal efficiency leading to high pumping load and relatively impure CO_2 stream. (Kohl 1997)

The solubility of CO_2 to water is significantly lower compared for example to methanol (Rectisol) or DEPG (Selexol). The solubility of CO_2 to water, DEPG and methanol are presented in Table 1.



	Temperature °C	Solubility dm³/dm³
Methanol	-25	13.4 ¹
DEPG	25	3.63 ¹
Water	20	0.88 ²

Table 1. Comparison of solubility of CO_2 to some physical solvents.

1 Burr (2008)

2 Seppänen (1991)

The solubility of CO_2 to water defines the theoretical maximum for the removal process. The detailed solubility data of gaseous CO_2 in water is presented in Figure 1. As seen from the solubility data, lower temperature and higher pressure increase the solubility leading to lower solvent circulation rate. For example, solubility of CO_2 at the pressure of 1 bar and 20 °C is 0.2 kg/ 100 kg H₂O, whereas solubility at the pressure of 10 bar and 10 °C is around 2 kg $CO_2/100$ kg H₂O. According to Kohl (1997), economically considered the process is generally limited to CO_2 partial pressure of 3.5 bar or higher.

Industrially water wash is used today for biogas upgrading around Europe. For example, in Sweden there are 11 plants using water wash for CO_2 removal in biogas upgrading (Tynell 2007). Biogas is produced from anaerobic digestion process of biodegradable material like sewage sludge. In biogas upgrading the methane content of the biogas is upgraded to the level of natural gas by removing CO_2 . The composition of typical biogas is presented in Table 2. The content of CO_2 in biogas (25-55 %) is in the same range as could be obtained in the partial oxy-combustion.

According to Bauer (2013) water wash is considered mature technology in biogas upgrading since many years. The schematic figure of the process is presented in Figure 2. The water flow rate in biogas upgrading by water wash varies in between 120-220 I_n (H₂O)/m³_n raw biogas (Bauer 2013, Haagen 2001) depending on the process conditions. Typically used operation pressure is 6-10 bar and operation temperature 10-20 °C. The pressure at the first flash is 2.5-3.5 bar and gas from flash is recycled to the absorber. Carbon dioxide is desorbed from water by a stripper using air at atmospheric pressure. Typical operating conditions of water wash are presented in Table 3.

In biogas upgrading typical water wash absorption column diameter is 0.5 m and height 10 m. Water velocity in absorber varies in between 0.02 m/s - 0.33 m/s. Foaming is problem in some plants, solved by using antifoaming agent (Tynell 2007). According to Kohl (1997), typical gas velocity in water wash absorption process varies in between 1.5-3.0 m/s in a counter current packed absorber and the pressure drop varies in between 2 - 7 Pa. To prevent corrosion due to acid water when absorbing CO_2 some corrosion inhibitor need to be used (Kohl 1997).





Figure 1. Solubility of carbon dioxide in water at pressures of 1 atm and greater (Kohl 1997).

Table 2. The main components of typical biogas (Hagen 2001).

Component		Content % (vol)
CH ₄	%	45 - 75
CO ₂	%	25 - 55
N ₂	%	<1





Figure 2. A simplified water wash process schema for biogas upgrading (Bauer 2013).

Parameter	Unit	Process		
Capacity range	m ³ biogas/h	10 - 1000		
Input				
CH ₄	%	45 - 75		
CO ₂	%	25 - 55		
N ₂	%	< 1		
Output				
CH ₄	%	> 98		
CO ₂	%	< 2		
Process conditions				
Absorption pressure	bar	6-12		
Absorption temperature	°C	10 – 25		
Pressure in flash tank	bar	2-5		
Desorption pressure	bar	atmospheric		
Water flow ¹	m ³ /h	12-20 ¹		

Table 3. Typical water wash operating conditions (Hagen 2001).

¹ Depending on the absorption pressure and degree of regeneration, for every 100 m³/h processed biogas.

Manufacturers of water scrubbing units and their homepages are listed in Table 4. Swedish manufacturers of the water scrubbing units are Econet Vatten & Miljöteknik AB, Greenlane Biogas AB and Malmberg Water AB.



 Table 4. Manufacturers of water scrubbing units. (Bauer 2013)

Company	Homepage
Econet Vatten & Miljöteknik AB	www.econetgroup.se
Greenlane Biogas AB	www.greenlanebiogas.com
Malmberg Water AB	www.malmberg.se
RosRoca	www.rosroca.com
DMT	www.dmt-et.nl

The energy consumption in water wash process has three main sources: a biogas compressor, a water pump and a cooling machine. Energy consumption estimates are presented in Table 5. The temperature of the refrigerant in cooling machine is typically 5-15 °C. The machine normally operates with coefficient of performance (COP) between 2 and 5, corresponding to 20-50 kW_e to cool 100 kW heat. (Bauer 2013)

Table 5. Energy consumption for water wash process (6-8 bar). (Bauer 2013)

	Energy consumption kWh/m ³ _n raw biogas
Compression	0.10-0.15
Water pump	0.05-0.10
Cooling system	0.01-0.05

Regeneration by using air in the stripper is not possible when the aim is to capture and storage CO_2 . Thus the options to remove absorbed CO_2 from water are either a stripper with a reboiler or a partial vacuum flash of the rich solvent. Rasi (2009) used a low pressure flash for desorption when demonstrating water wash absorption process for landfill gas in Jyväskylä. The pressure of the flash was either 1 bar (atmospheric) or 0.7 bar(a).

2.3 Pressure swing adsorption (PSA)

Pressure swing adsorption (PSA) is used for separation of different molecules, in this case N_2 and CO_2 , by adsorbing CO_2 onto the surface of adsorbent. In a PSA process flue gas is fed into a reactor containing adsorbent material. CO_2 molecules adhere on the surface of the adsorbent material while nitrogen remains unaltered in gas stream. After the removal of the gas stream containing mostly nitrogen molecules from the reactor, adsorbed CO_2 molecules are removed from the surface of adsorbent by lowering pressure in the reactor. The PSA process is dynamic, and requires several parallel reactors which are constantly at different phases of the process cycle. A schematic picture of a simple two-stage adsorption process is presented in Figure 3.





Figure 3. Simplified scheme of a two-stage VPSA process using AC beads as adsorbent material (Shen 2012).

For CO₂ removal from flue gas at atmospheric pressure, a more economic option than PSA is vacuum pressure swing adsorber (VPSA). In VPSA process the whole feed gas stream (flue gas) does not need to be pressurised. Power consumption in VPSA process consists mainly of flue gas blower before VPSA unit and a vacuum pump to remove CO₂ from the surface of adsorbent. Typical adsorption and desorption pressures are presented in Table 6. Flue gas drying is necessary before PSA/VPSA. The limiting factor in both PSA and VPSA processes is the adsorption efficiency of the adsorbent material.

Method	Adsorption pressure, bar	Desorption pressure, bar
Pressure swing adsorber (PSA)	6	1.0
Vacuum pressure swing adsorber (VPSA)	1.5	0.05-0.1

Table 6. Typical adsorption and desorption pressures.

A comparison of different modelling results of PSA/VPSA process performance to an amine absorption process is presented by Shen (2012). At the moment 2-stage processes are required to reach even a lower removal efficiency and lower purity level. For example a two-stage VPSA for CO₂ capture from flue gases using activated carbon as adsorbent would attain 95% purity of CO₂ with 74.4% removal efficiency of CO₂ from flue gases and the estimated total power consumption is 724 kJ/kg CO₂ (Shen 2012). Higher CO₂ concentration improves the result of VPSA process. When the CO₂ concentration is over 25%, one-stage VPSA using Zeolite 13 may produce CO₂ stream with high purity of CO₂ (99%) at the removal efficiency of 70 % (Shen 2012). Investment costs were not considered in the article.

The modelling of dynamic PSA process using steady state simulation program like Aspen plus is complicated. The models for PSA systems are usually made by other programs, for example Matlab. Estimation of the efficiency and investment costs of VPSA process with varying CO_2 content in flue gas was too complicated for this work.



2.4 Membrane separation process

Membrane separation is a technology which selectively separates materials via pores in membrane material. Membrane separation processes are used industrially for example in air separation, hydrogen recovery and CO_2 removal from natural gas. Membrane separation process of CO_2 from nitrogen by membrane technology is presented in Figure 4. Separation can be performed either by compressing the feed gas or vacuum pumping in permeate site. Vacuum pumping is energetically more effective in this case but after separation CO_2 gas stream requires compressing for transportation.



Figure 4. Membrane separation process.

At the moment the efficiency of membrane separation technology is not comparable with absorption technology for CO₂ removal from flue gases. The selectivity of present membrane materials for N₂/CO₂ (α =50) is too low for an effective separation. However, if a new membrane material with higher selectivity would be developed, membrane separation technology would be a potential option for CO₂ removal, especially in partial oxy-combustion because higher CO₂ content in flue gas improves the separation efficiency. Thus, although the membrane separation is not feasible technology for CO₂ removal from flue gases today, the development of membrane material may change the situation. (Favre 2009, Bounaceur 2006)



3. Concept evaluation

3.1 Combustion process and flue gas

The combustion process was modelled using Aspen Plus software. The simplified flow sheet of the process is presented in Figure 5.



Figure 5. Simplified process flow sheet.

Fuel used in modelling was a mixture of coal, biomass and peat (thermal energy input 442 MW). Fuel consisted of 55 % of biomass, 33 % of coal and 12 % of peat. Moisture content of peat and biomass was 50%. The detailed composition and mass flow rate of the fuel mixture are presented in Table 7.

	Table 7.	The fuel	composition	for the	model.
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Model input		Fuel mixture	Coal	Biomass	Peat	Enriched air (O ₂ 21-95%)
Mass flow rate	kg/s	28.6	9.4	15.8	3.5	O ₂ : 38 N ₂ : 14-124
Mass percent of fuel mixture	%	100	33	55	12	
LHV	MJ/kg (dry)		28.9	19.7	20.3	
Thermal energy input	MW	442	252	155	35	
Elemental composition						
Moisture	%	36	7.0	50	50	
Carbon	% (dry)	58	76	49	53	
Hydrogen	% (dry)	5.6	4.7	6.0	6.0	
Nitrogen	% (dry)	1.2	1.3	1.0	2.0	
Sulphur	% (dry)	0.3	0.7	0.05	0.1	
Oxygen	% (dry)	31.3	9.5	43.5	33.4	
Ash	% (dry)	3.7	8.3	0.5	5.5	



Fuel mass flow rate was fixed to 29 kg/s (442 MW_{th}) in the model. The required oxygen for combustion was calculated to attain residual oxygen content of 2.1 % (wet) in flue gas when using air. The air was assumed to be dry. Argon accumulation in recycling stream was not considered.

Part of flue gas was recycled, if oxygen content of the enriched air was over 30 %, to ensure that oxygen content in combustion chamber would be below 30 %. The recycling ratio of flue gas varied in between 0 - 0.61.

A sensitivity analysis was carried out varying the oxygen content of enriched air and comparing the results to a case using air (O_2 21 %) and to an oxy-combustion case (O_2 98 %). The sensitivity analysis resulted in varying flue gas flow rates at 80 °C (above the dew point of the gas in all cases) as well as varying flue gas compositions depending on the oxygen content in the enriched air. The flue gas composition is presented in Table 8.

Table 8.	The effect	of oxygen	content in	n enriched	air to	the flue	gas	composition,	compared
to basic	air and oxy	-combustie	on cases.						

O ₂ content in	Recycling ratio of	O_2 in combusting	Volumetric flow rate	Flue gas composition (wet)			
enriched air	flue gases	gas	of flue gas (wet)	CO ₂	N_2	H ₂ O	02
% (vol)	-	% (vol)	m³/s	% (vol)	% (vol)	% (vol)	% (vol)
21	0.00	21	193	14	67	16	2.1
23	0.00	23	179	16	65	17	2.2
25	0.00	25	165	17	62	19	2.4
28	0.00	28	150	18	58	21	2.6
32	0.06	30	136	20	54	23	2.9
37	0.17	30	121	23	48	26	3.3
44	0.28	30	107	26	41	29	3.7
54	0.39	30	93	30	32	34	4.3
69	0.50	30	78	36	19	40	5.1
98	0.61	30	57	44	2	49	5.9

The variation of volumetric flow rate of both wet and dry gas is presented in Figure 6. For example if the oxygen content in enriched air was 32 %, the volumetric flow rate decreased 30 % (from 193 m³/s to 136 m³/s). In Figure 7 the flue gas composition is presented for dry gas.



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Figure 6. Volumetric flue gas flow rates depending on the oxygen content in enriched air at the temperature of 80 $^{\circ}$ C.



Figure 7. Variation of dry flue gas composition depending on oxygen content in enriched air.



3.2 Carbon dioxide capture

The effects of partial oxy-combustion to CO_2 capture process were estimated compared to combustion process using air. In addition to the base case, CO_2 removal by amine absorption, also physical absorption for CO_2 removal was considered. As a special case a water wash process based on the operating conditions used in biogas upgrading was considered.

Fuel input and thus the mass flow rate of the CO_2 to be removed were constant (CO_2 42 kg/s) in all cases, regardless of the oxygen content in enriched air. Only the total volumetric flow rate and concentration of CO_2 in flue gas varied, depending on the amount of diluting nitrogen. The flue gas was assumed to be at temperature of 80 °C (above the dew point of the gas) before the capture process. Pressure drop in the process was mainly not taken into account. The compression and liquefaction of CO_2 stream was not included.

3.2.1 Amine absorption

The influence of partial oxy-combustion to CO_2 removal by amine absorption process was estimated. The base case was air-blown combustion process (Table 8, oxygen in enriched air 21%). In addition, the flue gas compositions deriving from the oxygen content in enriched air of 25, 32 and 44% were simulated.

The estimation was based on a simplified amine process (Figure 8) modelled using Aspen Plus. The modelling was adjusted to attain 90 % capture ratio of CO_2 . Murphree efficiency used for CO_2 removal by amine absorption varies relatively much in literature (Mofarahi 2008, Huseby 2012, Øi 2012, Schach 2010). In this study Murphree efficiency of 75% was used.



Figure 8. Simplified schematic amine scrubber process.

With the increasing oxygen content in enriched air the flue gas flow rate decreased leading to decreased dimensional size of equipment. The decreased flue gas flow had the same mass flow rate of CO_2 but higher concentration (Table 8), which intensified the absorption process. This led to higher CO_2 content in the rich absorption solution and thus smaller solution circulation rate.



The investment costs decreased because of the smaller dimensional size of equipment. The reduction in the investment cost was estimated roughly using the following equation.

$$C_i = C_{i,ref} \left(\frac{X_i}{X_{i,ref}}\right)^{\alpha} \tag{1}$$

where

Ci	= cost of the component
C _{i,ref}	= known cost of the reference component
Xi	= scaling factor of the component
X _{i,ref}	= scaling factor of the known component (base case)
α	= cost regression index

The cost of the reference component was given a value of 100 in this evaluation, to define the percentage decrease in the investment cost. The scaling factors and the cost regression indexes of the main components are presented in Table 9.

Component	Quantity	Scaling factor	Cost regression index
Absorber	1	volume (m ³)	0.90 ²
Stripper	1	volume (m ³)	1.00 ¹
Blower	1	power (MW)	0.60 ¹
Flue gas DCC	1	volume (m ³)	0.90 ²
1			

Table 9. Equipment details of the amine absoprtion.

Holland (1997)

² Remer (1980)

The scaling factors of main equipment were determined based on the data in Table 9 and the data from the simulation model. A coarse investment cost reduction estimate was calculated using the equation (1). The investment cost reductions depending on the oxygen content in enriched air are presented in Figure 9.

The operational costs of CO₂ removal process were also affected by the increasing oxygen content in the enriched air. The main part of the operational costs consists of energy consumption. The reboiler of the stripper is the main energy consumer, using a high amount of steam for the stripping of CO₂. If CO₂ concentration in the flue gas increases, the required solvent circulation decreases leading to decreased steam consumption in the stripper. However, the decrease in steam consumption was not very large, because the total mass flow rate of CO₂ did not decrease. The other main energy consumer is the blower of the flue gas. The power demand of the blower decreased significantly, when the total volumetric flow rate of the flue gas decreased. Also the energy consumption of solvent pumps decreased due to the decreased solvent flow rate. The decrease in make-up solution does not have a remarkable effect on the operational costs. Energy consumption in the CO₂ removal process depending on the oxygen content in enriched air is presented in Figure 10.

Also the production of oxygen has relatively high investment and operational costs. The benefit of partial oxy-combustion process depends on the investment and operational costs of the whole power plant.





Figure 9. Percentage variation in the investment cost of an equipment depending on the oxygen content in the enriched air.



Figure 10. Percentage variation in energy consumption depending on the oxygen content in enriched air.



3.2.2 Physical absorption

Economically feasible CO_2 capture by physical absorption process like Selexol or Rectisol requires partial pressure of CO_2 in flue gas stream to be at least 7-8 bar (Rackley 2010, Kanniche 2010). Required pressure level and thus required power for compression of the flue gas depend on the concentration of CO_2 in the flue gas and the total pressure.

The suitability of physical absorption process in partial oxy-combustion concept was estimated. The first step was to determine power required for compressing flue gas to attain CO_2 partial pressure of 10 bar. Compression was performed using four staged compressor with intermediate cooling to 35 °C. The isentropic efficiency of the compressor was fixed to 0.85. The results are presented in Table 10.

For comparison, the power required for cryogenic production of oxygen was also calculated. According to Favre (2009) the power consumption per tonne of relatively pure O_2 at atmospheric pressure and temperature is 250 kWh/t O_2 . An estimate based on data from Smith (2001) results in power consumption of 260 kWh/t O_2 . However, according to Darde (2009) Air Liquide has managed to produce low pressurised oxygen with oxygen purity of 95% requiring 200 kWh/t O_2 , and designed new units which would require only 160 kWh/t O_2 .

Because of the variation in the data concerning energy consumption in O_2 production, the power required to produce oxygen enrichment was calculated using both the value for relatively pure O_2 at atmospheric pressure and temperature (260 kWh/t O_2) and the value for oxygen purity of 95% (200 kWh/t O_2). The results are presented in Table 10. For comparison, the production of relatively pure oxygen for oxy-combustion process would require 79 MW power (if the consumption is 260 kWh/t O_2). The results indicate that due to the huge power demand of the compression, the physical absorption does not seem to be a feasible solution for CO_2 removal.

O2 in enriched air	CO₂ in flue gas	Total pressure of compressed flue gas	Power required for compression	Required power to produce O ₂ enrichment ¹	Required power to produce O ₂ enrichment ²
% (vol)	% (vol dry)	bar	MW	MW	MW
1	21	70	88	0	0
2	23	65	78	9	7
3	25	59	69	17	13
4	28	54	60	26	20
5	32	49	51	35	27
6	37	44	42	44	34
7	44	39	34	53	41
8	54	33	26	62	47
9	69	28	19	70	54

Table 10. Estimated power consumption required for compression of flue gas to reach CO₂ partial pressure of 10 bar.

 $\frac{1}{2}$ Based on the power consumption of 260 kWh/t O₂.

 $^{\rm 2}$ Based on the power consumption of 200 kWh/t $O_{\rm 2}.$



3.2.3 Water wash

The process conditions for water wash must be modified from the reported process conditions of upgrading biogas water wash plants in Sweden (Bauer 2013). The main difference is that air cannot be used for the stripping agent for CO_2 in this case. Stripping of CO_2 from water using low pressure seems to be the best option. This method has been tested by Rasi (2009). One option of the process is presented in Figure 11.



Figure 11. A water wash process for CO_2 removal from flue gas.

A suitable property method (PSRK) in Aspen was found by comparing the equilibrium solubility value of Aspen to the value reported by Kohl (1997). Both values are presented in Table 11.The solubility of CO_2 at equilibrium calculated in Aspen (property method PSRK) is at the same level as the solubility of CO_2 reported by Kohl (1997).

Table 11. Comparison of the equilibrium solubility data of CO_2 in water at total pressure of 10 bar.

	Temperature	Partial pressure of CO ₂	CO2 content (volume)	Solubility
	О°	bar	%	kg CO ₂ /kg H ₂ O
Solubility data at equilibrium ¹	15	10	100	0.015 ¹
Aspen (PSRK) at equilibrium	16	10	100	0.018
Aspen (PSRK) at equilibrium	14	3.6	36	0.0039

Reference Kohl 1997



A partial oxy-combustion case of 44 % O_2 in enriched air was chosen so that dried flue gas had a CO_2 partial pressure over 3 bar. The operating conditions in the absorber were chosen to be 10 bar and 14 °C. Two flash columns were used to strip absorbed CO_2 from water. Aspen calculations of CO_2 solubility into water at varying flash pressures are presented in Table 12. The lower flash pressure was chosen to be 0.7 bar, optimising between the power required for pumping the water back to 10 bar and the CO_2 concentration left in lean water. The removal efficiency of 86 % was obtained with lean water flow rate of 11400 kg/s.

Table 12.	The equ	ilibrium s	olubility o	of CO ₂ in	water	at diffe	rent flash	pressures	(Aspen
calculatio	ons).								

Pressure	Solubility		
Bar	kg CO ₂ /kg H ₂ O		
0.5	0.0008		
0.55	0.0009		
0.6	0.0010		
0.65	0.0011		
0.7	0.0012		
0.75	0.0013		
0.8	0.0014		
0.85	0.0014		
0.9	0.0015		
0.95	0.0016		
1.00	0.0017		

The main process parameters and results are presented in Table 13. The results are compared to the results of amine absorption process in a partial oxy-combustion case of 44 % O₂ in enriched air. The removal efficiency was 86 % for water wash and 90 % for amine absorption. The pressure of the captured CO₂ stream in both processes was 1 bar. Compression and liquefaction of the captured CO₂ was not included in power consumption either in amine absorption or in water wash.

Table 13. Comparison of some main values of water wash and amine absorption process (Aspen simulation).

	O ₂ in enriched air	CO ₂ in flue gas	Dried flue gas flow rate into absorption tower		Solvent circulation rate	CO ₂ removal efficiency	Power consumption	Steam consumption
	% (vol)	% (vol dry)	kg/s	m³/s	kg/s	%	MW	MW
Water wash	44	37	89	6.0	11400	86	31 ¹	-
Amine absorption	44	37	90	63	1032	90	1.2	120

¹ This value does not include power required for cooling flue gas and water.

The detailed power consumption and production in water wash absorption process is presented in Figure 12. However, this does not include the power required for cooling flue gas and water. The main power consumer is the flue gas compressor which uses 59 % of the required power.





Figure 12. Power consumption and production in water wash absorption.

The CO_2 removal efficiency of the water wash absorption process may be further improved by changing the operating conditions, for example by lowering the flash pressure, lowering the absorption temperature or increasing the absorption pressure. All of these modifications on the other hand consume more power. A comprehensive optimisation is required to find the best operating conditions for the CO_2 removal unit.

The modelling was based on the absorption equilibrium. Absorption equilibrium defines the theoretical maximum of the absorption. In reality, the required water flow rate to remove CO_2 is higher than theoretical optimum. However, the water wash in biogas upgrading seem to operate at the same level of water flow rate as this simulation case and to obtain higher removal efficiency. This results most likely from the lower CO_2 content in lean water due to stripping with air.



4. Conclusions and summary

This study focused on partial oxy-combustion of coal. Partial oxy-combustion power plant requires both oxygen plant and CO_2 removal unit, resulting in more but smaller units than in either air-blown combustion power plant or in oxy-combustion power plant.

The consequence of using enriched air in coal combustion was studied and compared to airblown combustion. The mass flow rate of CO_2 was constant because of the constant fuel input but the total flue gas flow rate varied depending on the rate of nitrogen. The volumetric flow rate of the flue gas decreased and CO_2 concentration increased with increasing oxygen content in enriched air. For example if the oxygen content was changed from normal 21 % to 32 % the volumetric flow rate of flue gas decreased 30 % and volumetric CO_2 content in dry flue gas increased from 17 % to 26 %. This change in flue gas led to decrease in both operational costs and investment costs of the amine absorption process. The most significant effect to operational cost was the decrease in energy consumption of the flue gas blower and the stripper. The most significant effect to investment costs was the decreased size of main equipment. However, the investment and operational costs of oxygen plant were not taken into account.

The advantages of other CO_2 removal technologies were also studied in case of partial oxycombustion. Other CO_2 removal technologies included industrially widely used physical absorption processes, membrane separation technology and vacuum pressure swing adsorption (VPSA) technology. In this case considered industrial physical absorption processes were Selexol and Rectisol. However, power required for compressing the flue gas to attain economically feasible CO_2 partial pressure (10 bar) is too high to be beneficial compared to amine absorption. Both membrane separation technology and vacuum pressure swing adsorption (VPSA) technology would benefit from increased CO_2 concentration in flue gas. Both technologies require two-stage process with dilute flue gas containing 15 % CO_2 but one-stage process may be enough if the CO_2 concentration reaches the limit of 25-30 %. In addition the removal efficiency and purity of CO_2 stream increases. However, neither technology today due to material limits (adsorbent efficiency and CO_2 purity as the absorption technology today due to material limits (adsorbent efficiency, membrane selectivity). If more efficient materials will be developed these technologies would be interesting options to absorption technology.

Special attention was focused to CO_2 removal by water wash absorption. Although mostly replaced by more efficient CO_2 removal methods, water wash was found to be in use in a special brand, biogas upgrading. CO_2 concentration level of biogas, 30-40%, could be obtained using partial oxy-combustion. A process concept for CO_2 removal from flue gas by water wash absorption was designed based on the biogas upgrading process and a simulation model of the concept was realised. A case of partial oxy-combustion with oxygen content of 44 % in enriched air was executed using the simulation model. The main results from simulation model were compared to the simulation results of the same case using amine absorption for CO_2 removal. The results showed that water wash could be an alternative to amine absorption. Water wash absorption is more environmentally friendly and technically a less complicated process. However, the power consumption was not carried out. The investment costs were not considered.



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