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Integrated carbon capture and storage for an oxyfuel combustion process by using carbonation of $Mg(OH)_2$ produced from serpentinite rock

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Abstract

The increasing atmospheric carbon dioxide concentration has lead to concerns about global warming. One of the options that can contribute to the reduction of carbon dioxide emissions is CO_2 sequestration by mineral carbonation. In this paper we will present a model of an oxyfuel combustion process integrated into a carbonation process using $Mg(OH)_2$ produced from magnesium silicate mineral. Therefore, the objective of this work is to develop integrated carbon dioxide capture and storage methods for an oxyfuel combustion process where CO_2 will be captured directly from the flue gas in a carbonation reactor. There it reacts with injected magnesium hydroxide $Mg(OH)_2$ solid, with thermodynamically stable $MgCO_3$ as the final product. In this paper we will present a process model that illustrates how the carbonation process integrated into oxyfuel combustion could be an alternative process for oxyfuel combustion followed by geological storage of CO_2. We will also present a simulation model for this process by using Aspen Plus® simulation software.

Keywords: Oxyfuel, Mineral carbonation, Process simulation, Aspen Aspen Plus®

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1. Introduction

Oxyfuel combustion technology offers an alternative integration with CCS, besides more conventional CCS chains used in post-combustion process arrangements. Although less conventional and currently in a demonstration-scale (Vattenfall's unit operating in Germany since 2008 [1]) it offers the benefit of replacing the separation of CO_2 from a flue gas as in post-combustion set-up. The combustion takes place in a mixture of oxygen, steam and CO_2 besides minor amount of other species (oxides of nitrogen and sulphur, and trace elements). The high concentration

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of CO_2 makes its separation from the flue gas relatively easy, although there is still a need for removal of minor pollutants, moisture and, more importantly oxygen, before transport and storage. For more detail on oxyfuel technology, see for example IPCC (2005) [2], and the more recent reporting from, for example, the demonstration unit in Germany.

Although oxyfuel combustion technology is an advanced technology that is somewhat less suitable for retrofit and is also less attractive for natural gas firing, it can offer great opportunities for solid fuels and solid fuel mixtures, including mixtures of fossil fuel (coal, lignite, peat), biomass, and eventually also solid waste-derived fuel. While for fossil fuels it may be more attractive to apply gasification integrated with a combined cycle turbine heat and power generation arrangement (which may be operated as a polygenerator for heat, power, syn-gas and/or methanol) the oxyfuel principle offers opportunities for combustion in fluidized bed boilers. This is of great interest to Finland, one of the main actors in the development and global sale of fluidized bed combustion equipment and technology, with special expertise on firing mixtures that contain large fractions of biomass.

At the same time, lacking opportunities for geological sequestration of CO_2 (if not CO_2 is separated and transported over considerable distances to, for example, the North Sea) a decade of R&D efforts has resulted in considerable progress of CO_2 mineralisation technology in Finland. While initial work focused on the vast resources of serpentinite rock in Central Finland, current work covers also resources available in Southern Finland besides a range of rock types from abroad, as a result of cooperation in several international project consortia. (Countries like Portugal, Australia, Canada, Singapore but also large international companies are more and more embracing CO_2 mineralisation, while the technology that is under development however, it offers an alternative for the “state-of-the-art” method developed in the US.)

Thus, a logical combination from a technology development and Finland’s export point of view is to merge the oxyfuel combustion - preferably in fluidized beds - with the staged process for CO_2 mineral sequestration that is being developed in Finland. This paper gives a first analysis of combining these two technologies, one aim being to show that on-site integration of the technologies gives a better energy efficiency than the conventional oxyfuel process.

2. Oxyfuel combustion

For oxyfuel processes, the combustion process takes place in an oxygen-rich environment which results in low emissions fossil fuel combustion. The basic principle for an oxyfuel combustion process is illustrated in Figure 1. Oxygen is fed to the boiler via a cryogenic air separation unit where oxygen is separated from the nitrogen. Removing nitrogen from the air, and then combusting the input fuel in an oxygen-rich environment, results in a highly concentrated CO_2 flue gas stream. The composition of the flue gas from the boiler may vary depending on the type of combusted fuel, but, typical flue gas composition can be the following: 65-% CO_2, 33-% H_2O, the rest being nitrogen, oxygen and argon [3]. The fly ash particles are then removed from the flue gas by particle removal. Firing with pure oxygen results in a very high flame temperature, thus 70-% of the flue gas is recycled back to the boiler for controlling the boiler temperature.

After the particle removal stage, SO_x, NO_x and H_2O could be removed from the flue gas via flue gas treatment process. During this stage, the water vapour and other condensable species that exist within the flue gas are removed via cooling and condensation. The process is followed by the removal of other non-condensable gases, such us N_2, Ar, and some surplus of O_2 and this will take place as an integrated part of the CO_2 separation stage. A phase transfer of CO_2 to the liquid state may be performed and thereafter the non-condensable gases are flashed from the CO_2 liquid. Depending on the end use for the CO_2 (storage or enhanced oil recovery) pure or relatively pure carbon dioxide is then transported to the final storage site. On the other hand, if oxyfuel is combined with mineral carbonation the requirements on gas purity are less strict as it will tolerate the presence of oxygen, water, SO_x and NO_x.

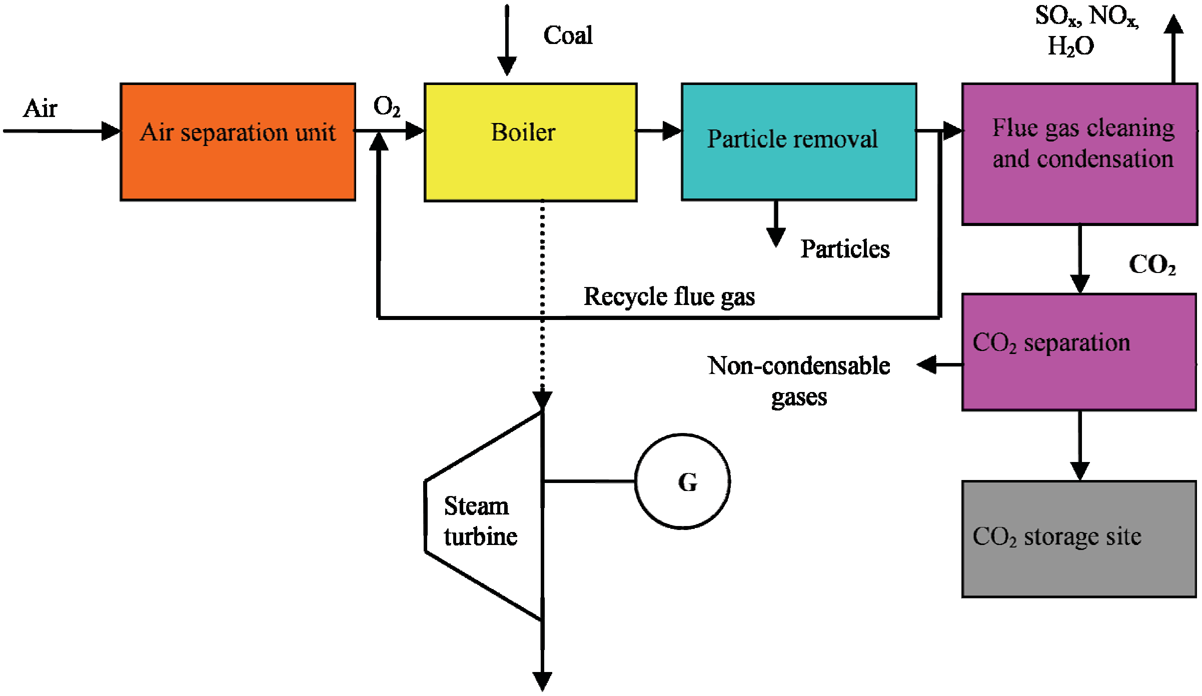

Figure 1 Basic principle for an oxyfuel combustion process

3. Process integration-oxyfuel combustion with carbonation of $Mg(OH)_2$

3.1. Production of magnesium hydroxide from magnesium silicate minerals

This section gives more detail on the method for producing magnesium hydroxide, $Mg(OH)_2$ from magnesium silicate minerals (mainly serpentinite rock containing serpentine mineral, $Mg_3Si_2O_5(OH)_4$ as the active compound) for the purpose of large-scale carbon capture and storage (CCS). Serpentinites and olivines of different chemical compositions and from different locations (see Table 1) have been tested using this method.

Table 1 The elemental composition (%-wt) and Mg to Fe ratio of the different rock types used for $Mg(OH)_2$ production at ÅAU (taken from [4]).

	Elemental composition (%-wt)										
Rock type	Mg	Fe	Si	Ca	Mn	Ti	Cu	Ni	S	Al	Mg/Fe (kg/kg)
Åheim olivine (Nor)	29.60	5.03	19.50	0.14	0.07	-	-	0.24	-	2.79	5.90
N.S. Wales serp.(Aus)	23.00	4.80	19.5	0.04	0.07	0.01	-	-	-	0.47	4.80
Finnish serp. (Fin)	21.80	10.10	11.6	0.34	0.08	0.02	0.01	0.02	0.48	0.02	2.20
Lithuania serp. (Lit)	18.90	12.30	15.9	0.86	0.04	-	0.01	0.01	-	0.12	1.50

The process route of producing magnesium hydroxide involves a staged process of Mg extraction using a moderately high temperature (400- 500 °C) solid state reaction of Mg-silicate rocks and ammonium sulfate (AS) salt followed by precipitation of magnesium hydroxide in aqueous ammonia. The reactions of olivines and serpentinites with ammonium sulphate are endothermic, and produce recoverable ammonia (NH_3), water vapour, magnesium sulphate ($MgSO_4$) and silicon dioxide (SiO_2). These reactions can be represented in (R1) and (R2) respectively for olivines and serpentinites.

$$Mg_2SiO_4(s) + 2(NH_4)_2SO_4(s) \rightarrow 2MgSO_4(s) + SiO_2(s)+4NH_3(g)+2H_2O(g) \quad \text{(R1)}$$

$$Mg3Si_2O_5(OH)_4(s)+ 3(NH_4)_2SO_4(s) \rightarrow 3MgSO_4(s) + 2SiO_2(s)+6NH_3(g)+5H_2O(g) \quad \text{(R2)}$$

Magnesium sulphate as described above is soluble in water at 260 g/l (at 0°C) to 740 g/l (at 100°C). Increasing the pH of $MgSO_4$-rich solution (using recovered ammonia from reactions (R1) & (R2)) results in the precipitation of magnesium hydroxide and the formation of aqueous ammonium sulphate. Ammonium sulphate can be crystallized from the solution, recovered and re-used in the first step.

$$MgSO_4 (s) + 2NH_4OH (aq) \leftrightarrow (NH_4)_2SO_4 (aq) + Mg(OH)_2 (s) \quad \text{(R3)}$$

Reaction (R3) happens at pH 10-12, and up to 64 - 66 % Mg-extraction (%.-wt of magnesium extracted from the mineral) has been reported for the following reaction conditions; reactants' (serpentinites./AS) mass ratio, 0.5 - 0.7; reaction temperature, 400 - 440 °C and reaction time, 30 - 60 minutes. Under the same conditions 0.33 – 0.34 g of valuable solid products (> 70 wt.% $Mg(OH)_2$ and < 30 wt.% FeOOH) were produced per gram of mineral. FeOOH (also occurs naturally as goethite) is a by-product of the process, which is produced from the significant fraction of iron in typical Mg-silicate minerals (see Table 1). This product is considered a useful raw material in the iron- and steelmaking industry [5]. Details of the results including effects of reaction parameters, physical and chemical composition of minerals, particle size and reaction kinetics are given elsewhere [2, 4, 6].

3.2. Integration of oxyfuel combustion with carbonation of $Mg(OH)_2$

Figure 2 illustrates the concept of integrated carbon capture and storage for oxyfuel combustion process by using carbonation of magnesium hydroxide, $Mg(OH)_2$. Serpentinite is the source of magnesium (being readily available in Finland and other countries) and it is crushed and grinded into the size fraction required in the first step of the process, which is the $Mg(OH)_2$ production step. Then the produced $Mg(OH)_2$ will react with the carbon dioxide in the flue gas stream from the oxyfuel combustion and produces thermodynamically stable $MgCO_3$. In this integration model, the carbonation unit replaces the CO_2 separation unit and the CO_2 storage unit in the oxyfuel combustion process and this could decrease the investment and production cost for the conventional oxyfuel technology.

Carbonation of $Mg(OH)_2$ is exothermic and can be described by the reaction below:

$$Mg(OH)_2 (s) + CO_2 (g) \leftrightarrow MgCO_3 (s) + H_2O (g) \quad \text{(R4)}$$

The reason for not directly carbonating serpentinite is that the reaction between CO_2 and serpentinite is not fast enough [7,8]. However, producing a more reactive form of magnesium, such as magnesium hydroxide, should allow for the utilization of the heat of reaction between $Mg(OH)_2$ and gaseous CO_2 [11-19].

At ambient conditions this reaction is slow, but in accordance to kinetic theory, the reaction rate can be accelerated by increasing the temperature, thereby in this integration model the carbonation process will occur at ~500° C and 20 bar [8]

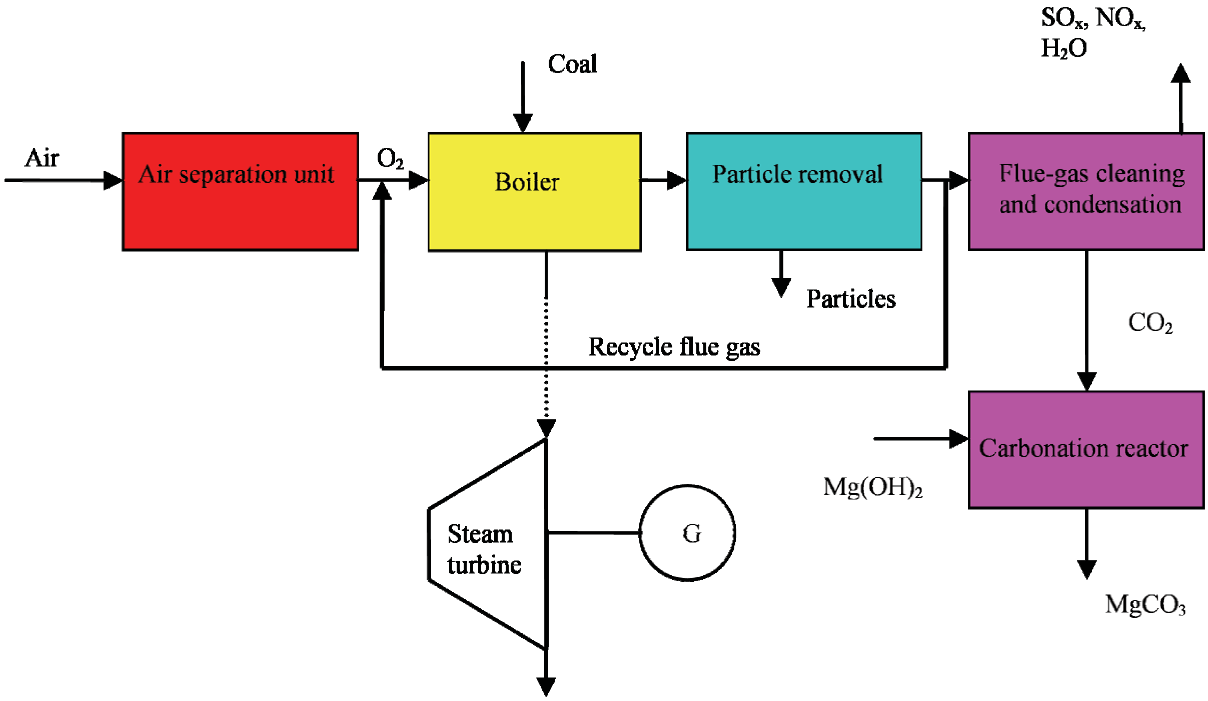

Figure 2 Integrated oxyfuel combustion with carbonation of $Mg(OH)_2$

4. Aspen Model

The integration process of carbon capture and storage for the oxyfuel combustion process (electrical output 79.65 MWe) is modeled by using Aspen Plus® simulation software (Figure 3). The model consists of five major process units: 1) combustion unit; 2) power generation unit; 3) flue gas treatment unit; 4) carbonation unit; and 5) product treatment unit. However, the air separation unit is excluded form this model. The combustion unit consists of two reactors (DECOM and BURNER) and one separator (Sep-1). The DECOM reactor is used to decompose the coal into its constituent elements before the combustion. This is done in a so called RYield module in Aspen Plus®, and the heat of reaction associated with the decomposition of coal has been considered in the coal combustion (HEAT, in Figure 3). RYield is useful when the reaction stoichiometry is unknown, but the yield distribution is known. Here the RYield module can convert its feed into a stream made up by the equivalent elemental components of the feed at the same enthalpy level. After decomposing the coal, it is combusted in a combustion reactor (BURNER) with pre-heated oxygen (O2-out) at 180°C. The combustion process is modeled with RGibbs reactor. The RGibbs reactor calculates the chemical equilibrium by minimizing Gibbs free energy of the process step. Ash is removed from the flue gas in the separator (Sep-1), and flue gas is used to heat-up feed water to the boiler (BOILER) from 200°C to 600°C. The steam generated as a result of heated water is then used in a steam turbine to generate 83.25MW electricity from the power generation unit. The flue gas from the boiler is then used to pre-heat the combusting medium, oxygen in the heat exchanger (HEX-1), 70% of the flue gas is then recycled back to the combustion reactor (BURNER) while the remaining flue gas is cooled down in another heat exchanger (HEX-2). Water content of the remaining flue gas is flashed out in a flasher (FLASH-1) in the flue gas treatment unit prior the carbonation unit. Finally $Mg(OH)_2$ injected into the carbonation reactor (CARBONAT) captures the CO_2 from the flue gas.

The carbonation reactor (RGibbs) operates at 500°C and 20 bar; hence, the flue gas is compressed in two steps (COMPRE-1 and COMPRE-2) before injecting it into the carbonation reactor. Final products from the reactor are separated in (Sep-4) into solid-$MgCO_3$ and flue gas at 500°C and 20 bar. The remaining flue gas is then introduced into an expansion turbine (GT) for generating “extra” electricity, and after the turbine the flue gas is used to pre-heat the feed water to the boiler in a heat exchanger (HEX-5).

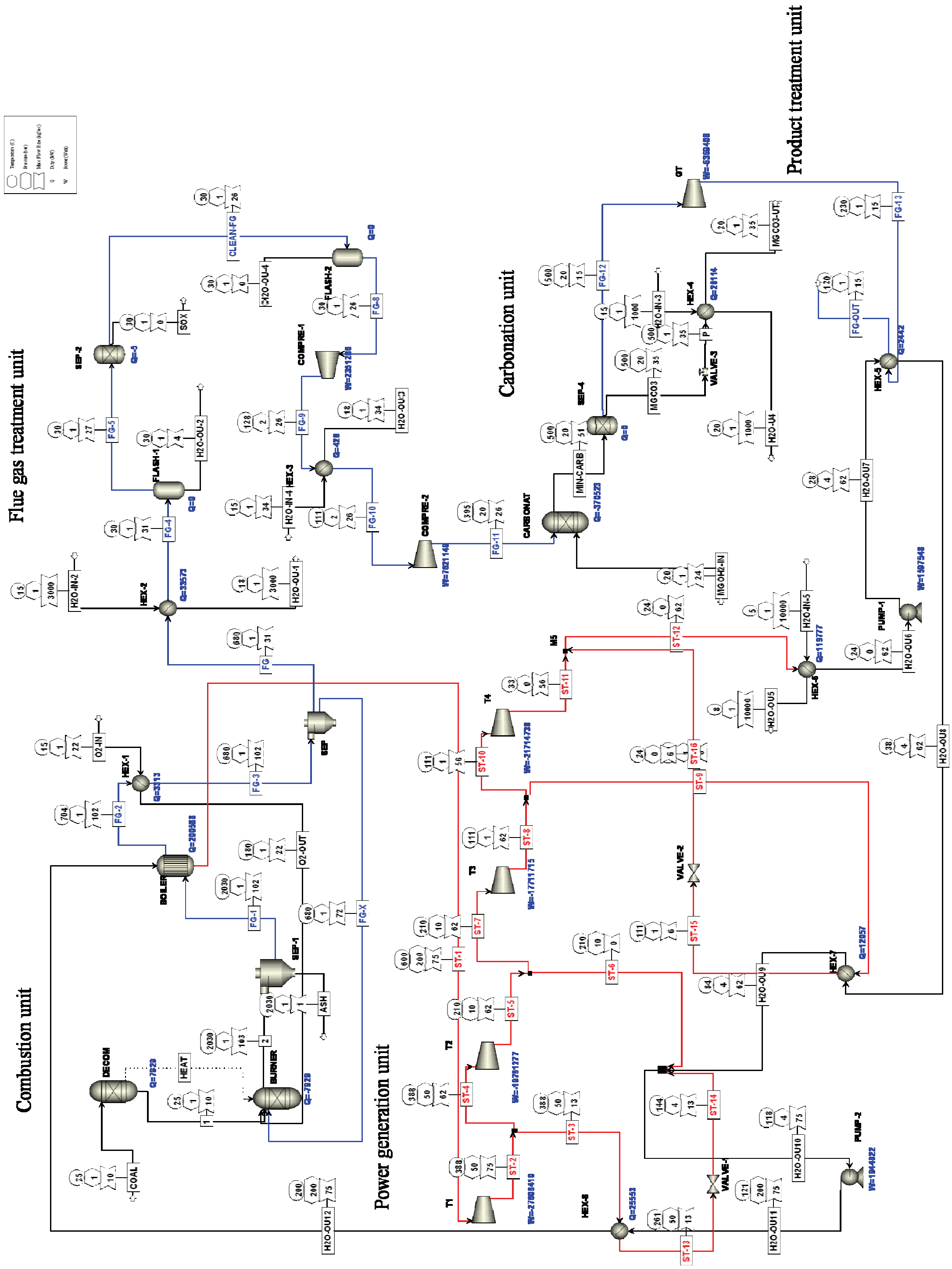

Figure 3 Aspen model oxyfuel combustion integrated with carbonation of $Mg(OH)_2$

5. Results and Discussion

In the Aspen model the carbonation reactor receives input stream of 24 kg/s of $Mg(OH)_2$ and 20.27 kg/s of CO_2 and it produces 35 kg/s of $MgCO_3$ (see Table 2). The carbonation process is extremely exothermic with the net heat duty of -370.52 MW. In other words the process produces a significant surplus of heat which minimizes its dependence of an external heat utility. During the carbonation process 90-% of the CO_2 emissions from the oxyfuel process is captured via carbonation of $Mg(OH)_2$ into $MgCO_3$ which is a stable white-solid environment friendly mineral. $MgCO_3$ has a variety of applications from simple landfill to fine chemicals.

Table 2 Aspen model's in/out streams for a 79. 65 MWe unit

Streams	**In (kg/s)**	**Out (kg/s)**
Flue gas	26.29	15.00
CO_2 - in the flue gas	20.27	2.63
$Mg(OH)_2$	24.00	-
$MgCO_3$	-	35.00

Also, we made a comparative analysis between two process cases, namely, the conventional oxyfuel combustion process without integration of carbonation process and an oxyfuel combustion process with integrated carbonation processes. Both process cases are modeled with Aspen Plus® for the same process conditions, and Table 1 summarizes the results from the two process cases.

The integration process enables both capturing and storing the CO_2 while producing more electricity (79.65) than the conventional oxyfuel process (74.22), as can be seen from Table 3. Additionally it has zero transportation and monitoring cost compared to the conventional oxyfuel combustion process. This is because the CO_2 separation process is an extremely energy intensive process, and in addition to that it requires CO_2 logistical and storage side monitoring costs. On the other hand, due to the high temperature and pressure for the exhausted flue gas (500°C and 20 bar) from the integrated process, it enables almost 7-% extra electricity to the net power production. However, more detailed process optimization could improve the efficiency even further.

Table 3 A comparative analyses between the conventional oxyfuel combustion without integration of carbonation process and an oxyfuel combustion process with integrated carbonation

Process Type	**Net Power (MWe)**	**Electricity efficiency (-%)**	**CO_2 Separation required**	**CO_2 Transportati on required**	**CO_2 Storage and monitoring required**
Oxyfuel combustion without carbonation process	74.22	26.04	Yes	Yes	Yes
Oxyfuel combustion with integrated carbonation process	79.65	27.95	No	No	No

6. Conclusions

Integration of oxyfuel combustion with carbonation of $Mg(OH)_2$ into $MgCO_3$ enables simultaneous capture and storage of CO_2 with less production and investment cost than in the case of the conventional oxyfuel combustion process. Hence, this process route will enhance the economical feasibility for the oxyfuel technology; therefore we recommend more research and development to this process route.

One future research task will be to investigate the possibility of co-capturing SO_2 and CO_2 via carbonation process so that the expensive desulphurization process could be omitted. We will also model integration process of carbon capture and storage for post and pre-combustion processes by using carbonation of $Mg(OH)_2$.

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