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Applications of Circulating Fluidized Beds in Energy Production

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Työn tavoitteena on selvittää kiertoleijutekniikan sovelluksia energiatuotannossa. Siinä käsitellään jo olemassa olevia ja mahdollisesti tulevaisuudessa markkinoille tulevia sovelluksia. Myös näiden kannattavuutta on selvitetty lyhyesti.

Työ tehtiin tutustumalla aiheeseen liittyvään kirjallisuuteen ja kokoamalla yhteen tiedot eri sovelluksista. Käytetty kirjallisuus koostui kiertoleijutekniikkaan ja kaasutukseen liittyvistä kirjoista, tieteellisistä artikkeleista ja valmistajien julkaisemista esitteistä.

Kiertoleijutekniikan tärkeimpiä sovelluksia energiantuotannossa ovat kiertoleijukattilat, joita käytetään kiinteiden polttoaineiden poltossa tai kaasutuksessa. Niissä voidaan puhtaasti ja tehokkaasti polttaa kosteita ja epähomogeenisia polttoaineita. Nykyisillä päästörajoituksilla kalliita rikinpoistolaitteita ei kiertoleijukattiloissa tästä syystä tarvita. Kaasutuksessa polttoaine kuumennetaan vähähappisessa tilassa, jolloin vapautuvat palavat kaasut voidaan ottaa talteen ja polttaa muualla. Muita sovelluskohteita ovat happipoltto, kemiallinen kierto ja kalsiumkierto. Happipoltossa polttoaine poltetaan lähes puhtaassa hapessa, jolloin savukaasujen korkea hiilidioksidin konsentraatio helpottaa talteenottoa. Kemiallisessa kierrossa palamishappi toimitetaan hapetetun petimateriaalin kautta, jolloin palamisilmaan ei joudu typpeä. Kalsiumkierrossa kalsiummonoksidia käytetään savukaasujen hiilidioksidin talteenotossa.

Kiertoleijutekniikan suurin haittapuoli ovat sen kalliit rakennuskustannukset. Sopivien päästörajoitusten ja hyvän polttoaineen saatavuuden takia sitä on kannattava käyttää.

ABSTRACT

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This work aims to provide an overview of numerous applications for circulating fluidized beds in energy production. Both existing and potentially upcoming technologies are discussed, along with their economic viability.

The work was done by reading books and scientific papers related to circulating fluidized beds and carbon capture and storage, and presenting the information in the form of a review.

One of the main applications of circulating fluidized beds (CFBs) is in boilers, which can be used to cleanly and efficiently burn or gasify solid fuels, even ones with a high moisture content or that are of nonhomogeneous composition. Costly desulfurization equipment is not needed in CFB boilers, as the required emission levels can be reached by adding limestone to the bed mixture. Another application is gasification, which is the process of partially oxidizing the fuel in sub-stoichiometric conditions, allowing the resultant producer gas to be transported and burnt elsewhere. CFBs can also be used in oxy-firing, i.e. the firing of a fuel in near pure oxygen, chemical looping, in which the required oxygen for combustion is delivered using a solid substance as the oxygen carrier, and calcium looping, in which calcium monoxide is used in the capture of carbon dioxide from flue gases.

The main disadvantage circulating fluidized beds have is their high construction cost. They can be economically viable if low quality fuels are easily available, and if emission restrictions are high enough to require that competing techniques install an external desulfurization system, but low enough that the restrictions can be met by the CFB with the internal use of limestone.

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1 INTRODUCTION

Climate change is one of the biggest challenges faced by the human race this day. The goal set by the Paris Agreement is to limit the increase in average temperature to 2 ºC, but current trends are worrisome. Developing countries seek to increase their energy production, most of which is done by building new coal-fired plants due to the fuel being widely available and the technology being mature and economic. Over two-thirds of the energy produced in Australia, China, India, Poland and South Africa comes from the combustion of coal (IEA 2015a, p. vi). While photovoltaic and aeolic energy systems are commonly seen as the solution to global warming, their implementation at levels above 5–10 % of total electricity generation brings increasingly difficult obstacles to overcome due to their variable nature (IEA 2014, p. 49). In short, the world won't be coal-free by 2020, yet something must be done to reduce carbon dioxide emissions. Because of this, the demand for technologies that enable the clean combustion of coal is high.

Circulating fluidized beds (CFBs) are used in several technologies designed to capture carbon dioxide from flue gases, such as oxy-firing or chemical looping. These are expected to play a vital role in reducing carbon dioxide emissions in the near future, particularly in coal-fired plants. Reducing emissions from coal-fired plants is particularly important given the rate at which countries such as India and China are building new plants, and the overall increase in the use of coal, as can be seen in Figure 1.

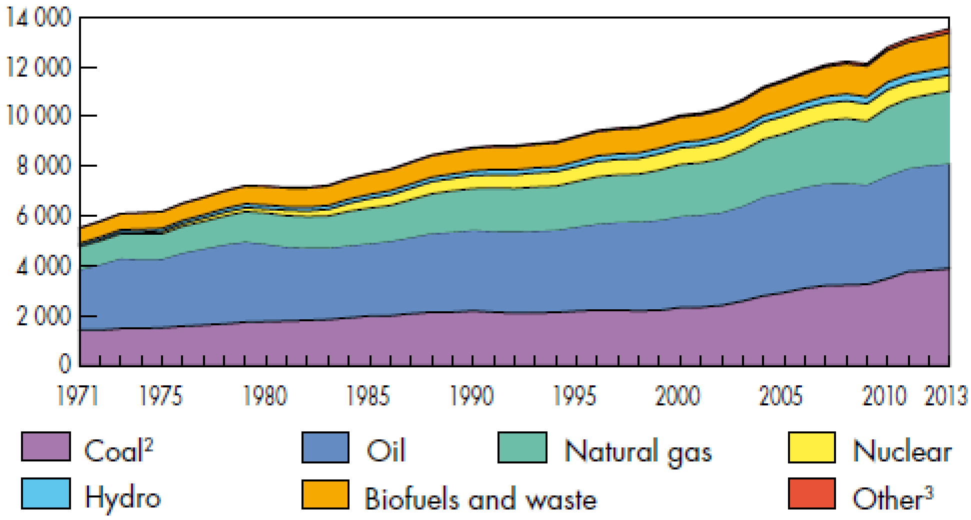

Figure 1. World total primary energy supply by fuel type. (IEA 2015b, p. 6.)

Because of the important role they could play in reducing carbon dioxide emissions in the near future, CFBs have been a popular topic for research around the world, but particularly in China. This work aims to provide the reader with an overview of some of the most promising applications for CFBs. The first chapter describes the fluidization process, while the second chapter focuses on its various applications. The last chapter starts with a short summary of the technologies presented, and concludes with thoughts on the subject.

2 CIRCULATING FLUIDIZED BEDS

Fluidized beds are large reactors in which a mixture of solids is suspended in an upward-blowing flux of air. The force applied by the air current cancels the effect of gravity on the solid particles, and causes them to behave like a fluid, thus the name fluidized bed. A circulating fluidized bed uses air speeds high enough to cause particles to become entrained and be carried with the flow before reaching a recirculation system, typically a cyclone, which prevents the solids from leaving the system and feeds them back into the reactor. Fluidized beds are often used to burn fuels that are inhomogeneous or possess a high moisture content, as the efficient air-solid mixing and long residence times enhance heat transfer and chemical reactions. Figure 2 shows a CFB boiler.

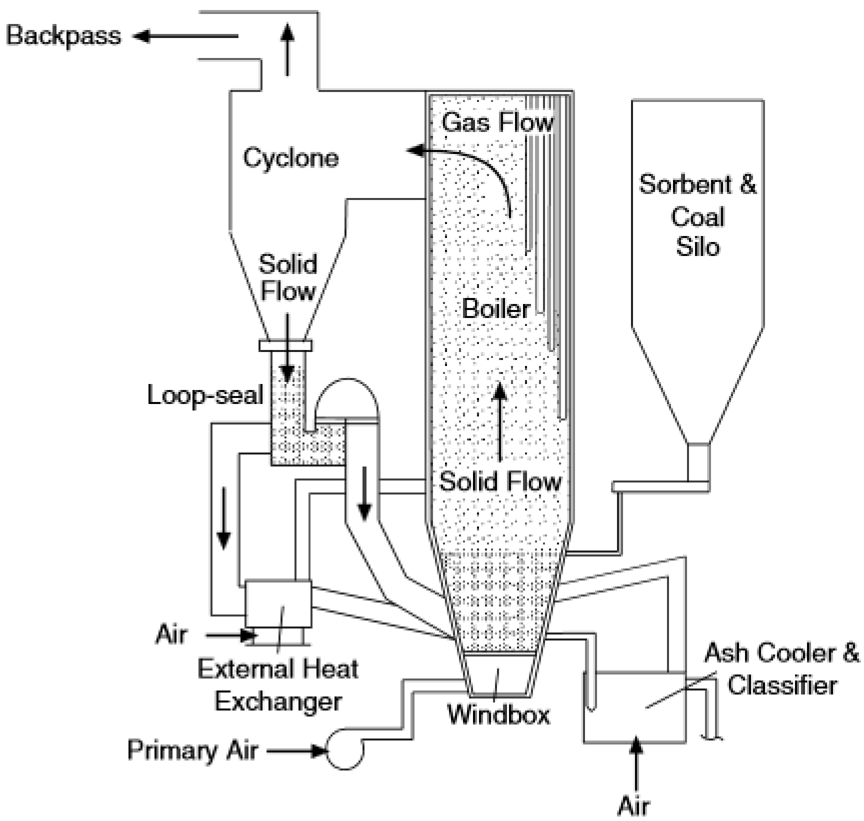

Figure 2. A circulating fluidized bed boiler (Basu 2006, p. 3)

2.1 Development of Fluidized Beds

The first fluidized bed was created by Fritz Winkler in 1921. He blew flue gases through the bottom of a crucible containing coke particles, causing the particles to be suspended and behave like a fluid, thus giving the process the name fluidization. The fluidization process was first used to gasify coal. It was not until the early 1960s that Douglas Elliot had the idea of using fluidized beds to burn coal, starting the development of fluidized bed combustion. (Basu 2006, p.1)

The bubbling fluidized bed boiler is made of a container with the bed material inside, and a grate through which fluidizing air is blown. The container can be made of refractory or heat-absorbing tubes. The space above the bed is called freeboard, and it is enclosed by more heat-absorbing tubes. The remaining heat transfer surfaces are located in the convective section. Fuel can be fed from the top or from the bottom, and ashes are drained from the bottom of the boiler. (Basu 2006, p.7). Figure 3 shows an early BFB boiler.

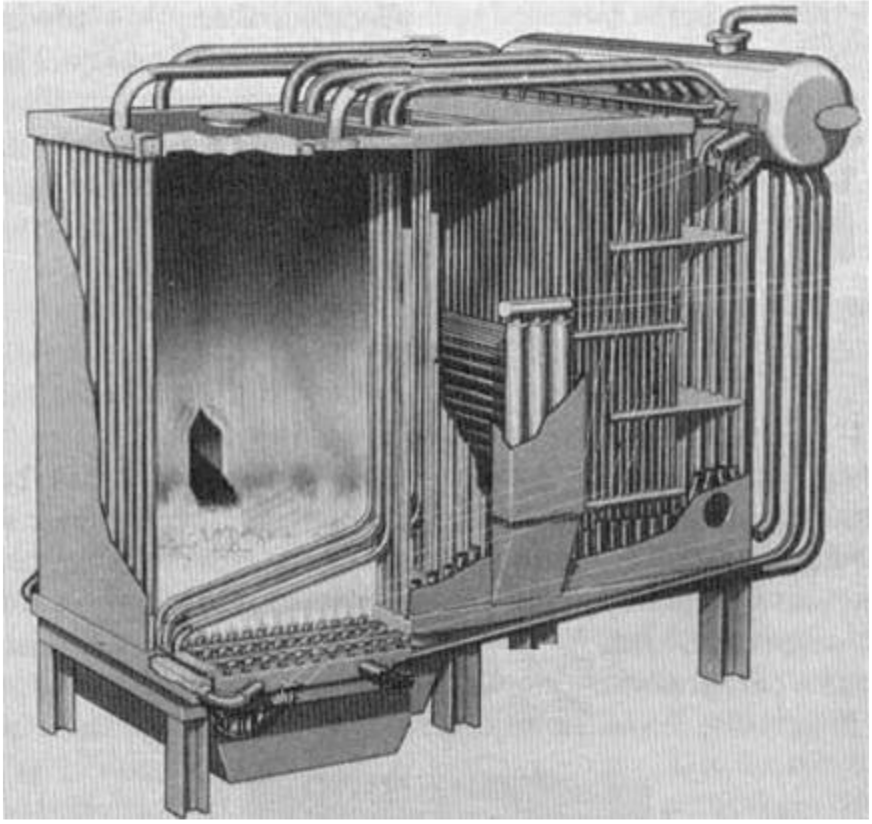

Figure 3. An early bubbling fluidized bed boiler (Basu 2006, p. 2)

In a bubbling fluidized bed, the fluidizing air is blown at the lowest fluidizing speed, around 0.6–4.0 m/s and the bed material is in the size range of 1.0–1.2 mm. The bed consists mainly of sand or gravel, ashes, and may also contain fresh or spent limestone to reduce sulfur emissions when burning high-sulfur fuels. Fuel constitutes only 1–3 % of the total bed material (Basu 2006, p.11). Because of the particles' relatively large size and low air speed, the bed stays at the bottom of the boiler, bubbling, with a well-defined surface, like a boiling liquid. (Roeck 1982, p.1)

Circulating fluidized beds use more advanced fluidization technology. They are defined by higher fluidizing air speeds (3–10 m/s) and smaller bed particles (0.05–0.3 mm). This causes the particles to become entrained and rise with the fluidizing air. There is not a well-defined surface between the bed and freeboard as the solid-gas mixture occupies the entire reactor. (Roeck 1982, p.1). The fluidization velocities of different fluidized reactors are shown in Figure 4.

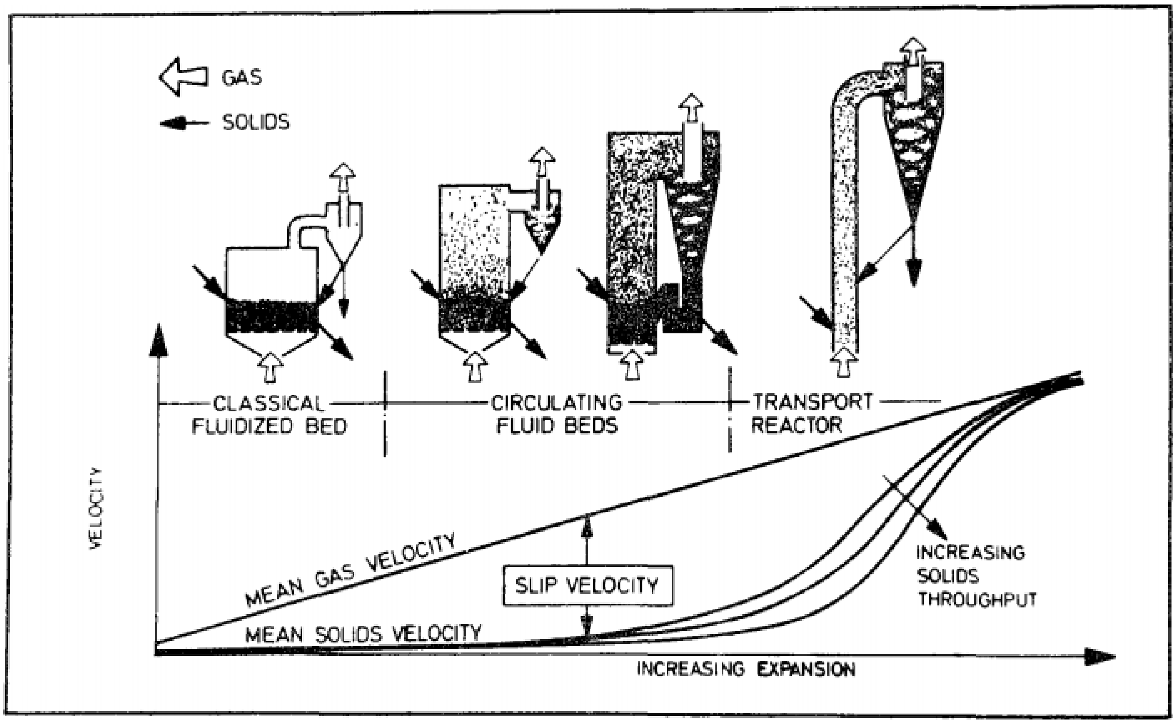

Figure 4. Comparison of fluidization velocities in different reactors (Roeck 1982, p. 2)

The CFB has longer gas-solids contact times compared to a BFB, due to them being in contact over the entire boiler's height. This results in cleaner and more efficient combustion. The CFB is also capable of burning two to three times more fuel than the BFB in a given area because of higher combustion air velocities. Superficial gas velocities in BFBs are limited by bed entrainment. This limits the amount of oxygen available, what in turn limits the heat release rate. (Roeck 1982, p.1)

2.2 Circulating Fluidized Bed Boilers

A circulating fluidized bed boiler is basically a CFB combustor with a heat exchanger to enable the use of the energy produced (Basu, 2006, p.11). Figure 5 shows a coal burning CFB boiler designed by Lurgi.

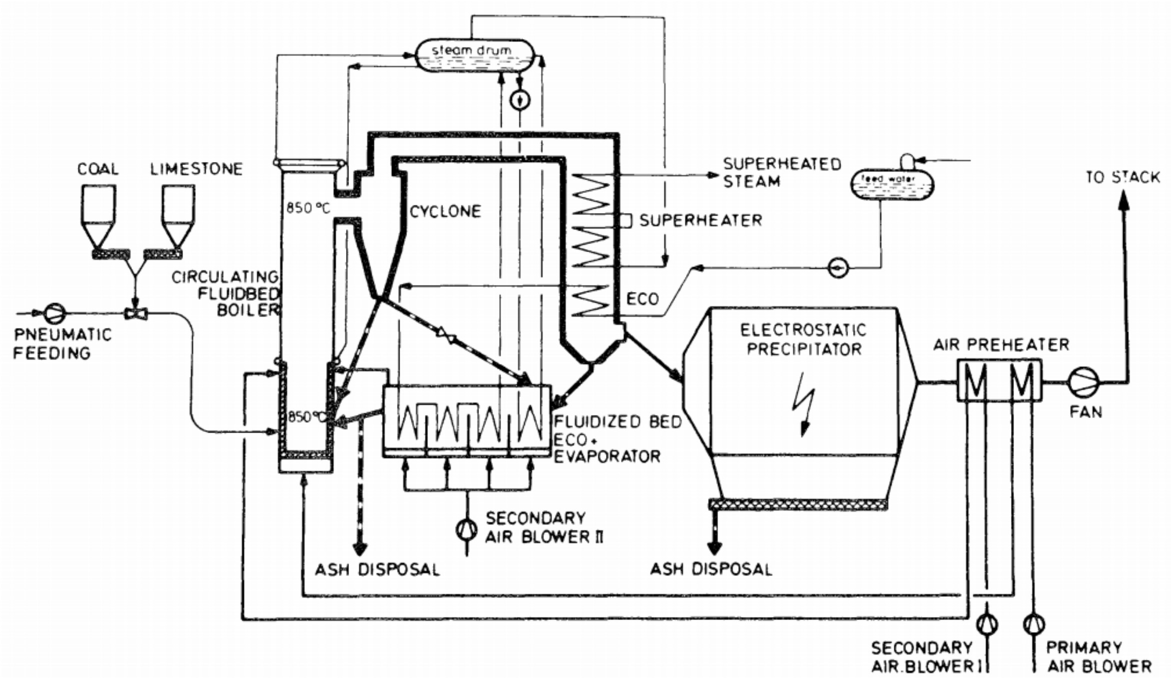

Figure 5. Circulating fluidized bed scheme (Roeck 1982, p. 20)

Fine ground coal (0.2–0.3 mm) and bed material are fluidized at velocities between 6 - 8 m/s at the lower part of the reactor. Due to efficient solids mixing in the CFB, few fuel feed points are needed. Combustion air is fed in two levels. (Roeck 1982, p.21)

The benefits of using staged combustion are reduced NOx emissions: introducing part (70–90 %) of the air as primary air with the fuel results in the combustion happening at a relatively low temperature, with very little oxygen left in the air. The remaining 10–30 % air is fed on a second stage above the combustion zone, where combustion is completed.

The lack of oxygen in the first combustion stage combined with low temperatures limits the formation of nitrogen oxides. Combustion takes place between 800–1000 ºC with 10 % excess air. (IEA Clean Coal Centre 2015)

The combustion chamber is lined with refractory in the lower section for protection and to facilitate start-up. The walls above the secondary air inlets are made of water tubes connected to each other by membranes, this is the boiler's evaporator. (Roeck 1982, p.21)

Circulating fluidized bed boilers require a solids recirculation system, as the entire bed would otherwise be blown away. Most of the solids leaving the furnace are captured by a gas-solid separator, usually a cyclone, and are then recirculated back to the bottom of the furnace through a loop seal. The loop seal is necessary to prevent the high pressure gases in the furnace from escaping to the low pressure cyclone. Modern cyclones are cooled by water or steam for several reasons: cooling reduces maintenance required by the cyclone’s refractory, reduces heat losses, reduces expenses because the cyclone’s surface can be used as a heat exchanger, and improves the boiler’s ramp-up rate. Part of the hot solids at the bottom of the cyclone are guided to an external heat exchanger, where they are cooled in forced convection evaporator and economizer surfaces. (Huhtinen et al. 2013)

Another way to capture solids is with U-beam collectors, which are shown in Figure 6. These steel beams are arrayed in a staggered formation, and are located at the furnace exit. U-beams are able to capture 97 % of the solids passing through. Combined with a secondary multi-cyclone dust collector, the solids separation rate can exceed 99.8 %. (Babcock & Wilcox 2006)

The boiler's convective section is located after the gas-solid separator. That's where the superheaters and the economizer are located. Finer solids may escape the primary separator, but are finally collected by the electrostatic precipitator. (Roeck 1982, p.21)

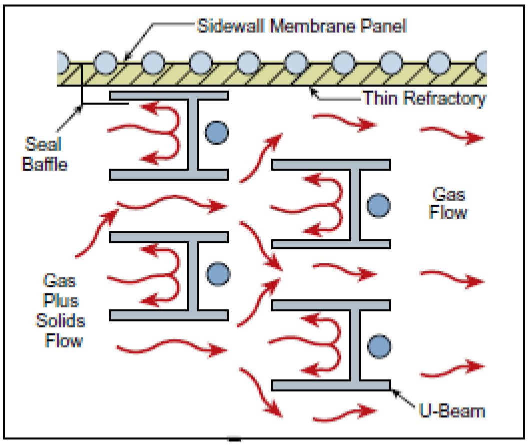

Figure 6. U-beam collector system (Babcock & Wilcox, 2006)

Lurgi's boiler has been tested at their research laboratories. It showed excellent carbon combustion efficiency (99.5 %), a 90 % SO_2 reduction using a Ca/S ratio of 1.5–2, and NOx emissions of 90–100 ppm when using staged air combustion. A bubbling fluidized bed would need twice the amount of calcium to achieve the same SO_2 percentage, and would emit 3–4 times as many nitrogen oxide compounds. (Roeck 1982, p.22)

2.3 Advantages and Weaknesses

Circulating fluidized bed boilers have a few advantages over traditional pulverized coal boilers. Due to the bed's higher heat capacity and long fuel-air contact times, the combustion process isn't as sensitive to changes in fuel quality. For example, a pulverized coal plant requires high-quality coal pulverized to around 75 µm in diameter. Meanwhile, as shown in Figure 7, a CFB can burn a wider variety of fuels, such as low grade coals, biomass, waste, and even old car tires, and there's the possibility to burn multiple different fuels at once. Because of this, several power plants in the USA have started using CFB boilers to co-fire opportunity fuels available in the region, such as pet coke and waste coal, and Chinese facilities consider the technology ideal for burning high-ash anthracite and lignite. Besides being able to burn fuels other plants are unable to, CFB combustors can switch fuels based on changes in fuel price and availability. (IEA Clean Coal Centre 2013)

The efficient mixing of the fuel and bed material means combustion happens in a low, uniform temperature (800–900 ºC), as opposed to the high (up to 1500 ºC) and uneven temperatures of a PC boiler. Because the temperature inside the boiler is so much lower, there are less problems with ash melting and corrosion. (Giglio 2013, p.54)

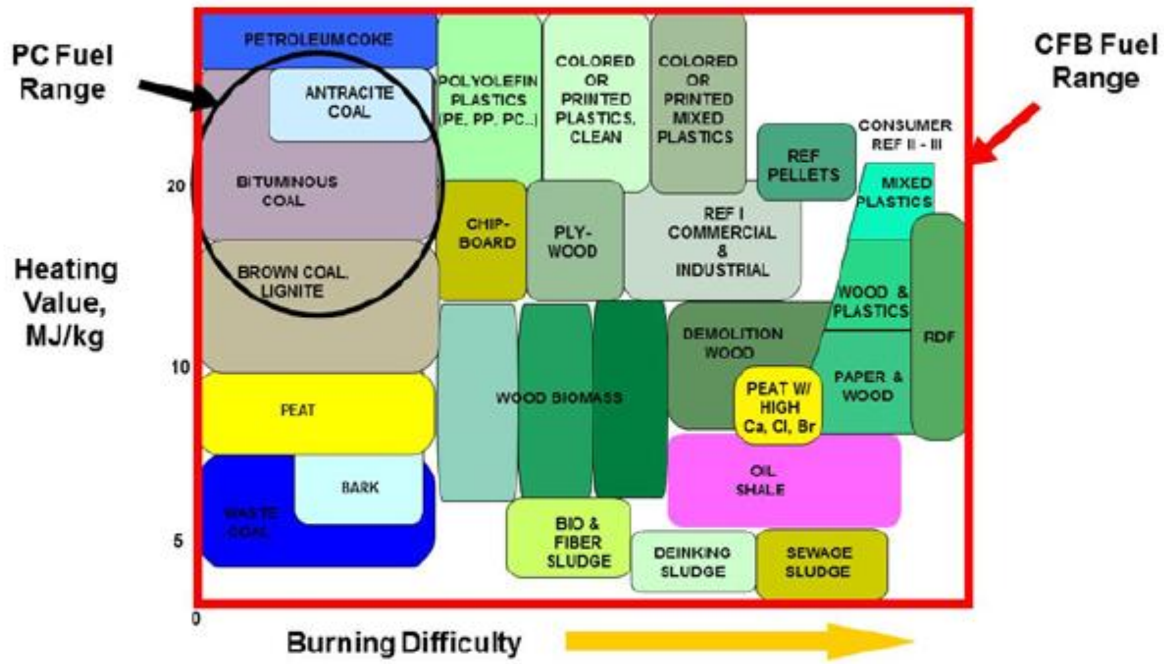

Figure 7. Fuel range of circulating fluidized beds (Kostamo 2012)

Lower temperatures also mean NO_x emissions are greatly reduced, and a Selective Catalytic Reduction (SCR) system is not required. Flue-gas desulfurization (FGD) systems are not needed either, as SO_x emissions can be easily captured by adding limestone to the fuel mixture. The limestone reacts with the SO_2, forming sulfates that become part of the ash. The capital cost of a FGD system for a large, 1,100 MW, plant would be around US$ 93 million. (Giglio 2013, p.59)

Despite the increased efficiency in the newest CFB units and lower prices, PC boilers are still cheaper, and more efficient than subcritical CFBs (IEA Clean Coal Centre, 2013). However, the newest supercritical once-through CFB boilers are on par with similar PC boilers, as can be seen in Table 1.

Table 1. Cost comparison between supercritical PC and CFB power plants (Giglio 2013, p. 58)

Case	1	2
Boiler technology	USC PC	USC CFB
Boiler and steam turbine configuration	1 x 1,100 MWe PC boiler on 1 x 1100 MWe STG	2 x 550 MWe CFB boilers on 1 x 1,100 STG
AQCS equipment configuration	SCR + WFGD	SCR only
Plant fuel	5,500 kcal/kg bituminous coal	4200 kcal/kg indonesian sub-bituminous coal
D&S boiler cost index (Two CFBs burning lower quality fuel are more costly than PC)	1.000	1.106
D&S coal mill cost index (No mills needed for CFB)	Included in boiler price	0.0
D&S FGD cost index (130 $/KWe for WFGD, no FGD for CFB)	0.37	0.0
Total D&S cost index	1.37	1.106
Total boiler + FGD D&S cost (M$) (assuming 350 M$ D&S boiler cost)	**480**	**387**

The economic viability of CFB boilers depends largely on their ability to meet emission requirements without expensive SCR and wet FGD systems. Because of this, possible stricter emission limits in the future, unachievable by the desulphurization methods currently used in CFBs, could have a negative impact on the market share of CFB boilers. (IEA Clean Coal Centre, 2013)

The use of limestone in a CFB as a means to reduce sulfur emissions yields a large quantity of solid waste, which unlike the fly ash and gypsum produced by wet FGD systems in a PC plant, cannot be used as a cement substitute. CFB boiler ashes can instead be used for mine reclamation activity (restoring exhausted mining sites to a natural state). The high auxiliary power demand of fluidization air fans is the most significant factor holding back the efficiency of a CFB plant, but it can be improved by reducing bed material and optimizing fluidization. (IEA Clean Coal Centre, 2013). Figure 8 shows a comparison between conventional and CFB boilers.

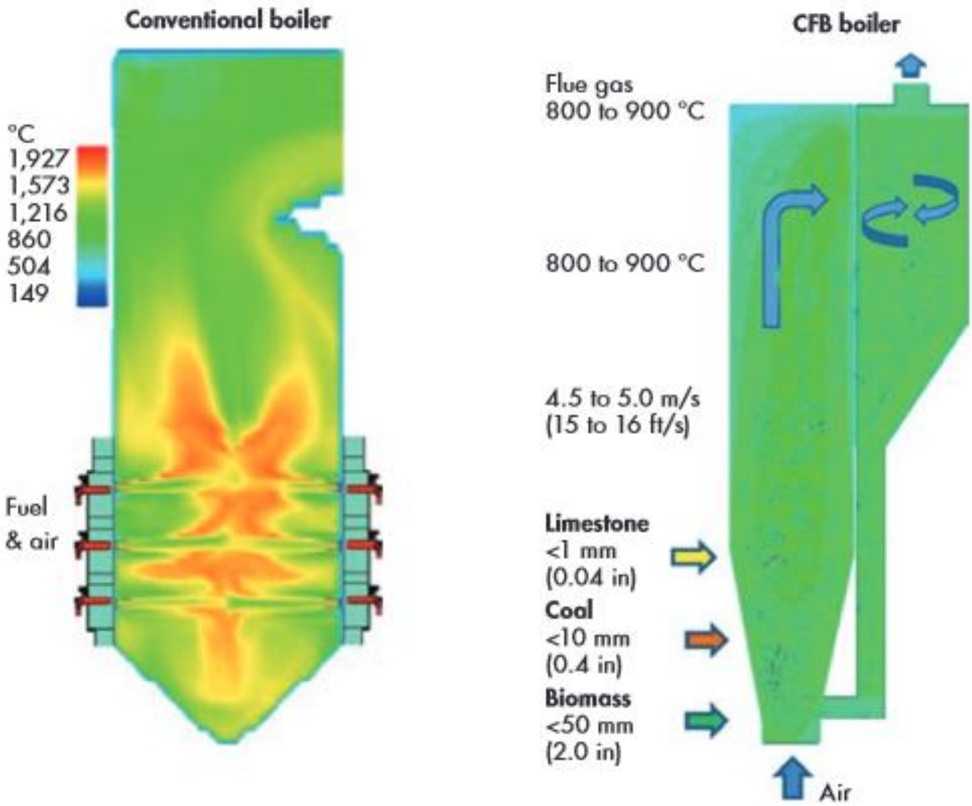

Figure 8. Comparison between a conventional and a CFB boiler (Giglio 2013, p. 54)

2.4 The Łagisza Supercritical CFB

The Łagisza 460 MW supercritical CFB plant, located in Poland, was the first CFB boiler to utilize supercritical steam parameters with once-through steam cycle technology. It is owned by the Polish utility company Południowy Koncern Energetyczny S.A., and was supplied by Foster Wheeler. FW submitted two alternative designs for the unit, one using pulverized combustion, and the other using CFB combustion. In the end the CFB was chosen for the following reasons (Jäntti & Parkkonen, 2010):

- The CFB would be cheaper, because a CFB could meet emission requirements without a wet desulfurization or a SCR system.

- Net plant efficiency using a CFB would be 0.3 %-units better than using pulverized combustion with a similar heat recovery system.

– The CFB solution would enable the use of a wider variety of fuels.

Work on the site started in February 2006, and the plant was handed over to the customer in June 2009. The Łagisza 460 MW unit is part of a project to replace outdated plants with more efficient and environment-friendly ones. (Jäntti & Parkkonen, 2010)

At full load, the station generates 439 MW of net electricity, with a total efficiency of 43.3 %. The use of supercritical steam lowers the fuel usage per energy unit produced by 5 %, which is equivalent to the improvements in efficiency obtained in 10 years of development. Design parameters at full load are (Jäntti & Parkkonen, 2010):

Superheater flow	361 kg/s
Superheater pressure	27.5 MPa
Superheater temperature	560 ºC
Reheater flow	306 kg/s
Reheater pressure	5.48 MPa
Cold reheater temp.	315 ºC
Hot reheater temp.	580 ºC
Feedwater temp.	290 ºC

2.5 Manufacturers

Circulating fluidized bed technology is manufactured by many companies around the world. The largest ones have been listed below.

Alstom S.A. is one of the world's leading energy companies, being present in 100 countries, employing 96,000 people permanently and with sales worth €20.3 billion in 2013/2014. Their headquarters are located in Levallois-Perret, west of Paris, France. (Alstom, 2015)

Amec Foster Wheeler, founded in 1927, offers services in the areas of oil and gas production, chemistry, metals and minerals, pharmaceuticals, as well as in the power sector, employing 40,000 people in over 50 countries. (Amec Foster Wheeler, 2015)

Babcock & Wilcox, founded in 1867, is a global leader in energy and environmental technologies, employing 6,000 people. Their headquarters are located in Charlotte, North Carolina, USA. (Babcock & Wilcox, 2015)

Bharat Heavy Electricals is one of the largest engineering and manufacturing companies of its kind in India, employing 47,525 people. The company offers gas turbines, generators, thermal sets, diesel shunters, turbo sets, hydro sets, power transformers, switch gears, circuit breakers and boilers, as well as valves, compressors and pumps. (Bharat Heavy Electricals Limited, 2015; Bloomberg, 2015a)

Dongfang Electric Corporation Limited, founded in 1993, designs, develops, manufactures, supplies and sells hydro, thermal, nuclear, wind, gas, and solar power generating equipment. Its headquarters are located in Chengdu, China. (Bloomberg, 2015b)

Mitsubishi Heavy Industries Ltd. is a Japanese with over 80,000 consolidated employees. Their major products are in the fields of energy and environment, commercial aviation and transportation, machinery, and integrated defense and space systems. (Mitsubishi Heavy Industries, 2015)

3 APPLICATIONS

Circulating fluidized beds are used in a number of applications related to energy production. Many of the applications presented in the following chapters utilize the CFB's ability to efficiently mix solid particles to ensure fast chemical reactions, for example in different looping processes.

3.1 Gasification

Gasification is the process in which a fuel is subjected to high temperatures in an environment with less oxygen than that required for stoichiometric combustion. This produces a combustible gas, called producer gas or syngas, which consists mainly of carbon monoxide, hydrogen and some methane. Emphasis will be given to solid fuel gasification due to it being the most common fuel type used in CFB gasifiers (Scala 2013, p. 765). In 2015, the world had a combined gasifying power of 71 200 MW_{th}, 51 % of which used coal, 25 % used petroleum, 22 % used natural gas, 1 % used petcoke and 0.5 % used biomass and waste, as shown in Figure 9. (Ahmad *et al.* 2015, p. 1335)

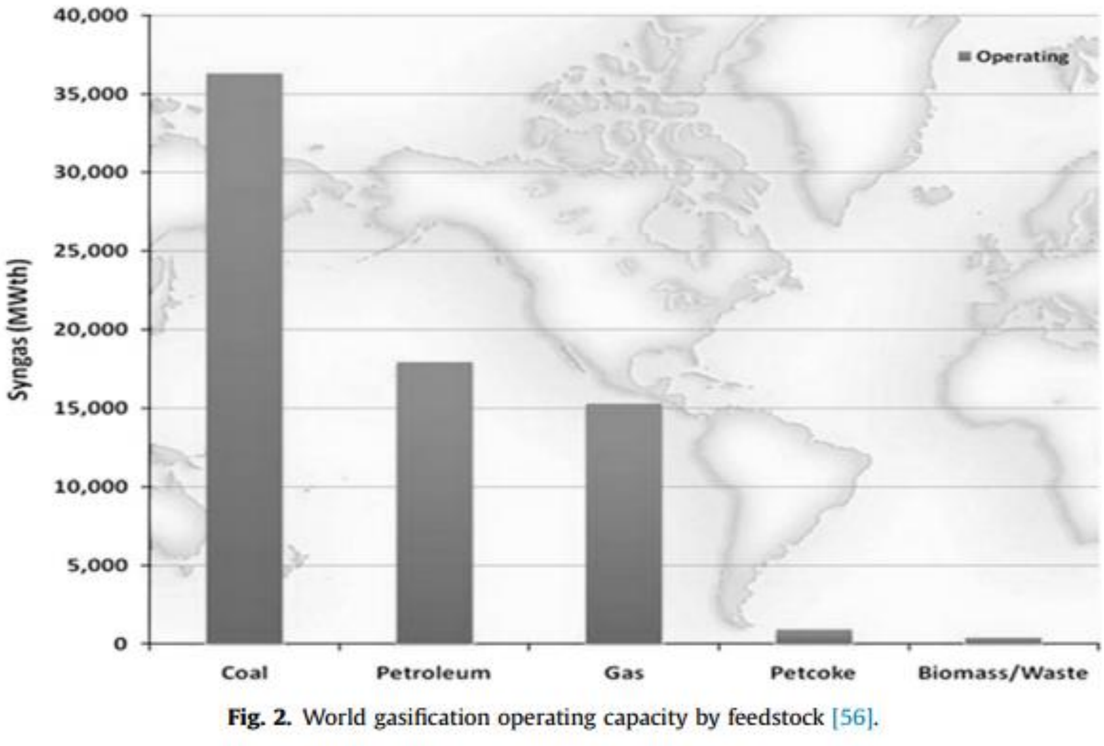

Figure 9. Gasification capacity worldwide by fuel (Ahmad et al 2015, p. 1335)

A simplified gasification process can be broken down to four stages:

- Drying reduces the moisture content of the fuel in temperatures between 100–200 ºC. For biomass, this means a reduction of moisture from 5–35% down to < 5%. (Puig-Arnavat *et al*. 2010, p. 2842)

- Devolatilization (or pyrolysis) happens at temperatures up to 700 ºC. In this stage volatiles are released as permanent gases (H_2, CO, CO_2, CH_4, H_2O and NH_3) and tar, reducing the original fuel to charcoal. (Puig-Arnavat *et al.* 2010, p. 2842; Scala 2013, p. 775)

- During the oxidation and gasification stages hydrogen and carbon present in the char react with oxygen in sub-stoichiometric conditions (air coefficient between 0.25–0.5). This results in less-oxidized gases being produced, such as CO instead of CO_2 and H_2 instead of H_2O. The partial oxidation of carbon into CO produces 72 % less energy than the complete oxidation into CO_2. This energy is stored in the syngas and released when the CO is burned. (Scala 2013, p. 777)

- Tar degradation is the stage in which tar present in the syngas is removed mechanically, thermally or with the aid of catalysts. Tars are gaseous hydrocarbons that may condense if the syngas becomes over saturated with them, leading to fouling in boilers and other surfaces, causing blockages and corrosion, and ruining ceramic filters and Sulphur removal systems. Thermal tar degradation requires temperatures above 1000 ºC, and is thus unsuitable for CFB gasifiers, but tar removal can still be done catalytically (by using mineral- and/or metal-based catalysts) or mechanically (filters, scrubbers, particle separators). (Scala 2013, p. 782)

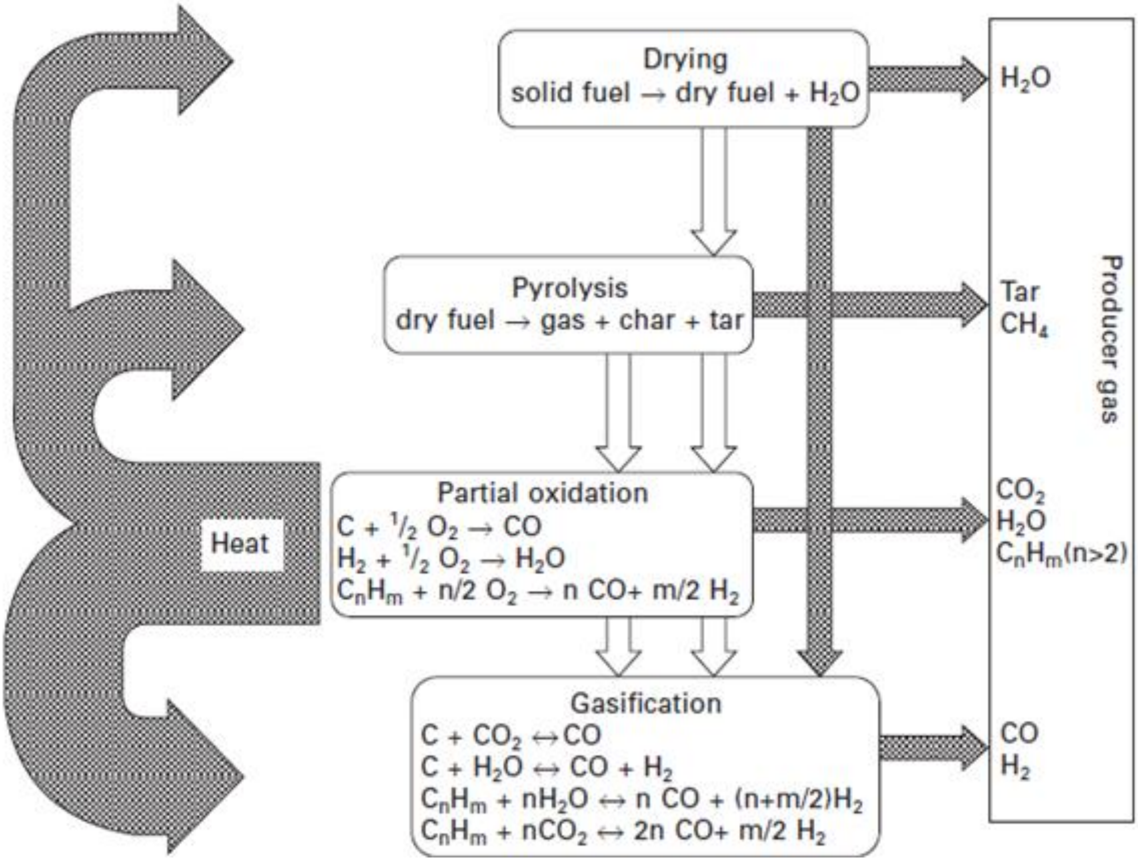

Figure 10. Auto-thermal gasification process (Scala 2013, p. 774)

While burning the original fuel may be a more economical way to produce heat than gasification, the former has a number of advantages when it comes to flexibility. Basu (2010, p. 23) lists a few, including:

- Gasified fuels may be used in processes sensitive to impure flue gases, such as glass blowing and drying.
- Syngas and derived liquid fuels are easier to transport and distribute than solid fuels. For example, syngas produced in a central plant can be distributed to nearby households through pipes.
- Gasification yields a product with a higher concentration of CO_2, which makes carbon capture and sequestration (CCS) easier and cheaper to do.

- Production of mechanical work or electricity in remote locations is easier and cheaper with a gasifier and a gas engine than it is with a combustion system comprising of a boiler, a steam engine and a condenser.

Basu (2010, p. 24) also compares the efficiency of a PC boiler steam plant to an Integrated Gasification Combined Cycle (IGCC) plant. The PC plant had an overall efficiency of 54.4 %, versus 63.8 % for the IGCC plant. Despite the good energy conversion efficiency, two major obstacles for power gasification are calculating the resulting gas and char composition under different conditions, as well as the economic and environmental difficulties faced in search of a reliable cleaning system. (Scala 2013, p. 791.)

Producer gas can be used in the production of energy feedstock (such as methane and carbon monoxide), transportation fuels (diesel and gasoline) and different chemicals, such as methanol (Eq. 3.1) and ammonia (Eq. 3.2), as well as in the production of liquid hydrocarbons through a process known as the Fischer-Tropsch process (Eq. 3.3). (Basu 2010, pp. 385–395.)

$$\mathrm{CO} + 2\mathrm{H_2} \rightarrow \mathrm{CH_3OH} \tag{3.1}$$

$$3\mathrm{H_2} + \mathrm{N_2} \rightarrow 2\mathrm{NH_3} \tag{3.2}$$

$$2n\mathrm{H_2} + n\mathrm{CO} \rightarrow (\mathrm{CH_2})_n + n\mathrm{H_2O} \tag{3.3}$$

Gasifiers can be classified based on many parameters. Gasifiers may operate at atmospheric pressure or they may be pressurized, and they may use air, oxygen, or steam as their gasification agent. Gasifiers can also be divided into directly heated (auto-thermal) and indirectly heated (allo-thermal) gasifiers. Directly heated gasifiers obtain their energy from the partial oxidation of the fuel within the gasifier itself, and use air or oxygen as gasification agent. The use of air in gasification produces syngas with a relatively low LHV (4–7 MJ/Nm^3) due to it being up to 60 % nitrogen. This gas can be burnt in boilers, gas engines or gas turbines. The use of oxygen-enriched air or pure oxygen produces higher quality syngas due to the lower nitrogen content. Syngas produced with pure oxygen can have a LHV of 10–15 MJ/Nm^3, and is suitable for distribution through pipes or for the production of liquid fuels. Indirectly heated gasifiers are oxygen-free and require a heat exchanger or another source of heat to function. Steam is used as the gasifying agent.

This produces a syngas with a high hydrogen concentration and LHV of 15–20 MJ/Nm^3. (Puig-Arnavat *et al.* 2010, p. 2843; Scala 2013, pp. 770–773)

Gasifiers can also be classified based on reactor design. Fixed-bed gasifiers consist of a (non-fluidized) bed of solid fuel, through which air (or any other gasifying agent) is blown from the bottom up, from one side of the reactor to the other or from the top down. These are called updraft, cross-draft and downdraft reactors, respectively, and are the simplest types of gasifiers. Fluidized bed reactors come in three types: bubbling fluidized bed gasifiers (BFBGs), circulating fluidized bed gasifiers (CFBGs) and twin-bed gasifiers. The difference between bubbling and circulating bed reactors is a lower fluidizing speed and lack of a recirculation system for the BFB. Twin-bed reactors have two fluidized bed reactors. One reactor is used to gasify the fuel, while the other is used to burn the char with air. The bed material circulates between the two, transporting char and bed material into the combustor and heated bed material back into the gasifier, as shown in Figure 11. Entrained-flow gasifiers are mostly used in coal gasification. Typical characteristics are high temperatures, high pressures, short residence times and high capacities. (Puig-Arnavat *et al.* 2010, p. 2843)

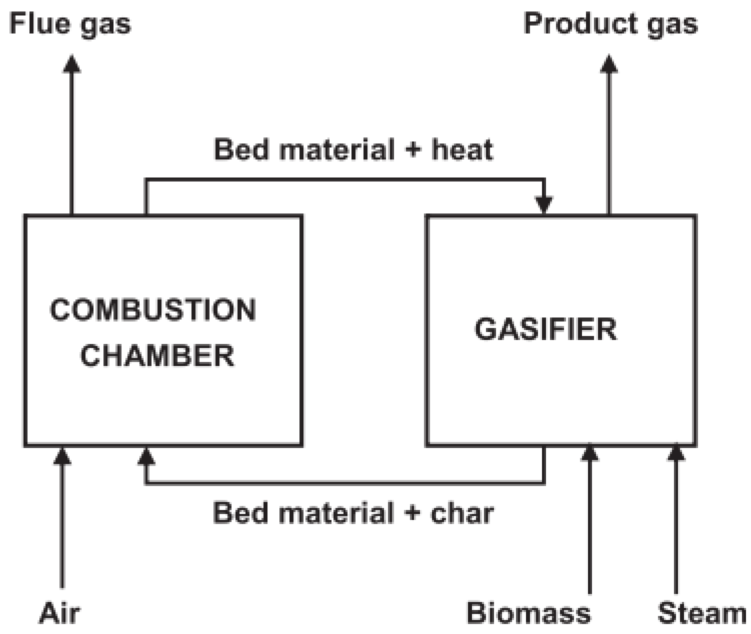

Figure 11. A twin-bed reactor (Puig-Arnavat *et al.* 2010, p. 2843)

CFBGs show great potential, particularly in the gasification of problematic fuels such as biomass and waste. This is mainly due to the fast and efficient mixing of fuel and bed material that results in uniform gaseous products and temperature distribution, and the bed's high heat capacity, which helps stabilize sudden temperature changes caused by variations in fuel size and moisture content. This fuel flexibility enables the use of multiple fuels simultaneously, i.e. co-gasification. The co-gasification of biomass and coal, for example, may serve as a bridge between the use of well-researched fossil fuels and environment-friendly biomass. Co-gasification of coal and biomass has many reported benefits, such as lower pollutant emissions (CO_2, NO_x and SO_x) and elevated gasifier temperatures (and consequently reduced tar formation). (Scala 2013, p. 772.)

Another interesting application for biomass gasifiers is the production of hydrogen to power fuel cells and internal combustion engines. According to Ahmad *et al.* (2015, p. 1345), producing hydrogen in a fluidized bed gasifier would cost around 2 USD/kg, making it an attractive option compared to the 10 USD/kg of electrolyzed hydrogen. However, supercritical water partial oxidation seems to show even greater potential, with an estimated production cost of 0.35 USD/kg_{H2}.

3.2 Oxy-firing

One of the main problems in CO_2 capture is its low concentration in flue gases. Oxy-firing is a combustion method in which the fuel is burned in a mixture of pure oxygen and recycled flue gases in order to facilitate carbon sequestration, as illustrated in Figure 12. Flue gas recirculation is necessary to keep the temperature in the boiler within limits (Ryabov 2010, p. 141). According to Ryabov (2010, p. 141), this produces flue gases with a CO_2 concentration of over 90 %, but other sources, such as Jurado *et al.* (2015, p. 177) mention lower concentrations in the range of 60–70 %. Besides the high concentration of CO_2 in flue gases to facilitate capture, oxy-fired boilers also benefit from reduced NO_x emissions and increased fuel combustion efficiency. However, the high cost of pure oxygen is a major restricting factor in the use of this technology. (Ryabov 2010, p. 141)

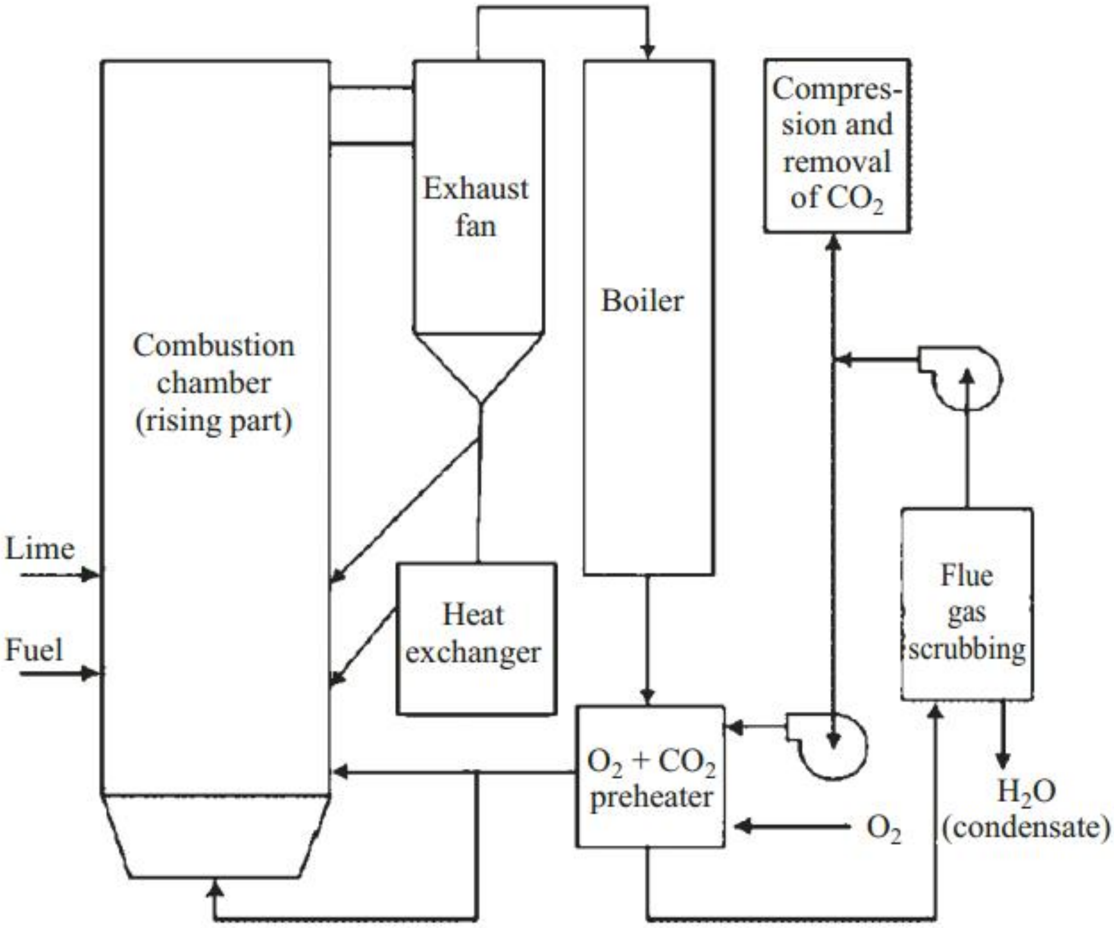

Figure 12. Schematic of an oxy-fired CFB boiler (Ryabov 2010, p. 142)

Oxy-fired CFBs are expected to challenge coal-fired power plants for a number of reasons. For one, the circulating solids facilitate temperature control in the combustor. Other advantages are more efficient mixing, longer residence times of solids and a higher oxygen concentration, that together improve the CFB's efficiency. (Singh 2016, p. 402) Ryabov (2010, p. 142) mentions a comparison between an oxy-fired and an air-fired CFB, both with the same capacity. In his comparison, the oxy-fired unit would only need 51 % of the area and 65 % of the mass of the air-fired unit, resulting in a cost reduction of 32 %, as can be seen in Figure 13.

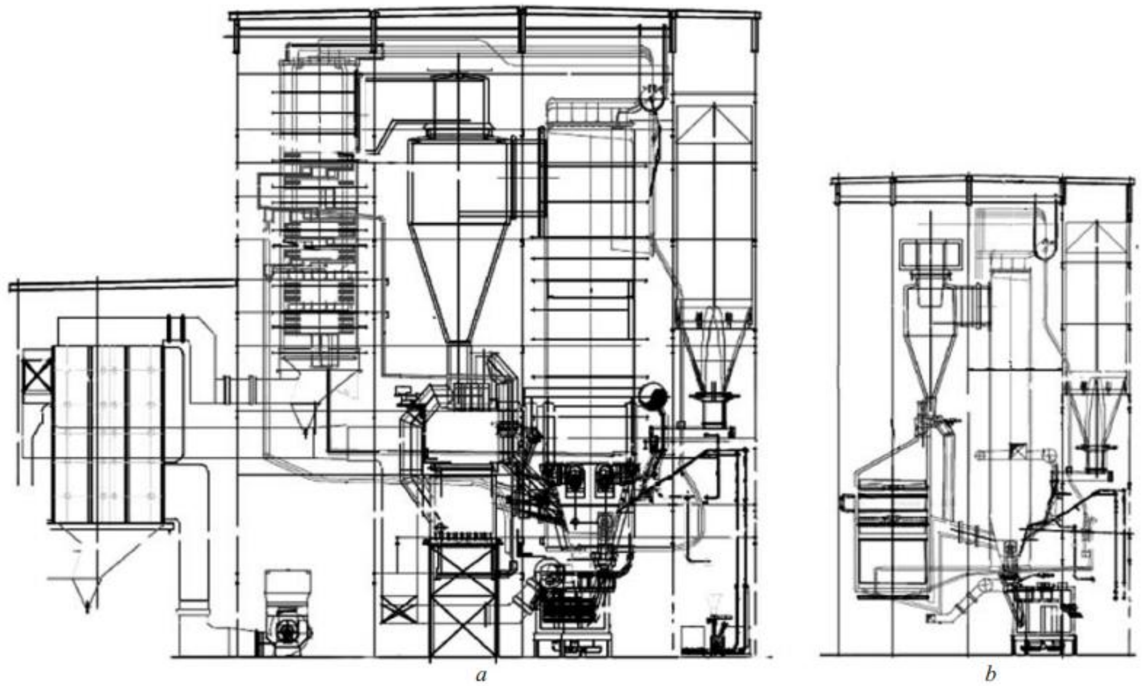

Figure 13. Air fired (*a*) and oxy-fired (*b*) CFB boiler size difference (Ryabov 2010, p. 142)

Oxy-fired CFBs are still relatively new and there is limited information available, but interest in them is growing. Most of the research is done around coal-burning CFBs. CFBs have the advantage of being flexible in regard to the fuel used, and having lower NO_x emissions and a simple in-bed sulphur capture system. The great majority, around 75 %, of the work done on oxy-fired fluidized beds is done on lab-scale (< 10 kW) plants, what hints at the existing gap between theory and actual practical implementation of oxy-firing. All in all, oxy-fired CFBs show potential to fill the demand for carbon dioxide capture technology in commercial power plants in the near future, though it will probably still take a few years before the technology can be used industrially. (Singh 2016, pp. 409-417)

Foster Wheeler is currently working on a 300 MW supercritical oxy-fired CFBC able to capture 90 % of CO_2 emissions. It is expected to be commercially available by 2020. (Scala 2013, p. 885).

3.3 Chemical looping

Another option for producing flue gases with a high concentration of CO_2 for CCS is by Chemical Looping Combustion (CLC). In CLC, a metal oxide, such as CuO or Fe_2O_3, is used to oxidize the fuel, allowing fuels to be burned without direct contact with air. This requires two CFB reactors, one in which the metal is oxidized (Eq. 3.4), and another in which the metal oxide is used to oxidize the fuel (Eq. 3.5). Figure 14 depicts the basic idea behind a chemical looping system. (Anthony 2012, pp.1625–1626).

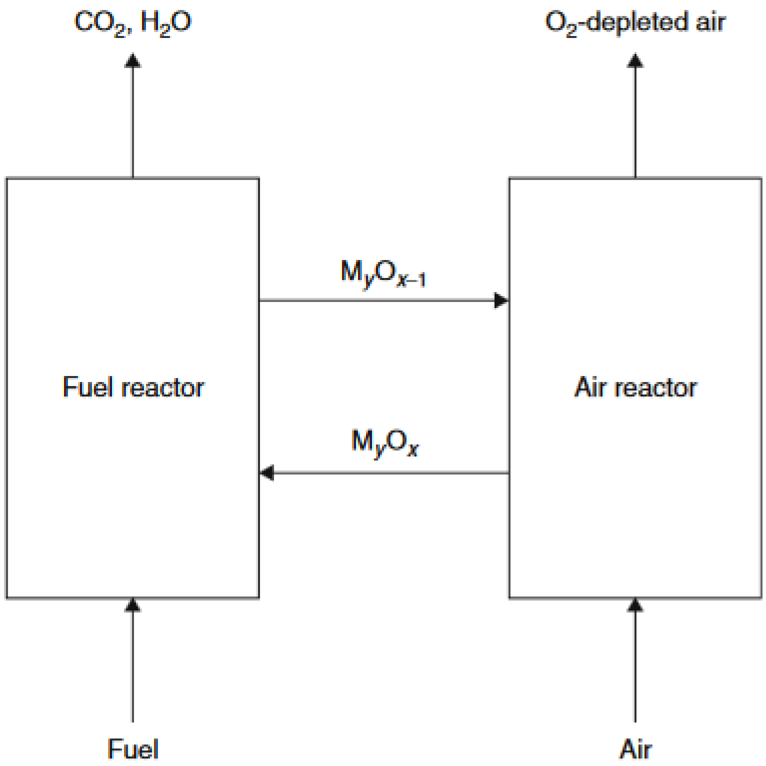

Figure 14. Metal looping cycle (Anthony 2012, p. 1626)

$$\mathrm{M}_y\mathrm{O}_{x-1} + \mathrm{Air} = \mathrm{M}_y\mathrm{O}_x \quad \text{(Eq. 3.4)}$$

$$(2n+m)\mathrm{M}_y\mathrm{O}_x + \mathrm{C}_n\mathrm{H}_{2m} = (2n+m)\mathrm{M}_y\mathrm{O}_{x-1} + m\mathrm{H}_2\mathrm{O} + n\mathrm{CO}_2 \quad \text{(Eq. 3.5)}$$

In most cases, the first reaction is exothermic and the second is endothermic, so that the total energy released is equal to the fuel's heating value. This cycle essentially separates oxygen from air for combustion, in a simple and efficient way. The gases leaving the fuel reactor consist mainly of water vapor and carbon dioxide. The water can be condensed, allowing for easy CCS. (Anthony 2012, p. 1625). Peltola (2014, p. 24) listed the net plant efficiencies of several CLC reactors, with natural gas reactors being in the 52–53 % range. A 300–400 MW atmospheric unit operating in a steam cycle would have a net efficiency of

40.1 %, while a modern steam power plant would have an efficiency close to 41 %, making CLC one of the most efficient CCS technologies.

CLC works best with gaseous fuels, since the metal oxides used are solid and gas-solid reaction times are much shorter than solid-solid reaction times. This poses a problem in coal and biomass gasification, both of which require the fuel to be gasified prior to combustion (Peltola 2014, p. 20). Anthony (2012, p. 1639) states that the use of syngas and natural gas has its challenges, such as minimizing the entry of char carbon into the air reactor. Ash interactions with the oxidizer can also turn out to be a problem, resulting in increased expenses to replace the oxygen carrier. However, the biggest issue with solid fuel gasification is in its reaction speed, as char gasification is a slow process with the large particles and relatively low temperatures typical to fluidized bed systems. (Anthony 2012, 1639).

Another way to deal with solid fuel CLC is by using Chemical Looping with Oxygen Uncoupling (CLOU), in which the carrier releases oxygen in the fuel reactor under the right conditions in a process known as decomposition. Since the oxygen is now in gaseous form in the fuel reactor, solid fuels can be used directly, without the need for a slow gasification process. Suitable oxygen carriers for CLOU are limited, the most interesting one being CuO due to its high reactivity. (Peltola 2014, pp. 20–21).

The most common oxidizing compounds used are Fe- (Fe_2O_3/Fe_3O_4), Ni- (Ni/NiO) and Cu-based (Cu/CuO), see equations 3.6–3.8.

$$3\mathrm{Fe_2O_3} + \mathrm{CO/H_2} = 2\mathrm{Fe_3O_4} + \mathrm{CO_2/H_2O} \tag{3.6}$$

$$\mathrm{CuO} + \mathrm{CO/H_2} = \mathrm{Cu} + \mathrm{CO_2/H_2O} \tag{3.7}$$

$$\mathrm{NiO} + \mathrm{CO/H_2} = \mathrm{Ni} + \mathrm{CO_2/H_2O} \tag{3.8}$$

There are many factors to consider when choosing the oxidizer for a CLC process, reaction speed being an obvious one: studies done show that some of the most reactive compounds are Ni- or Cu-based. A second thing to consider is their resistance to high-temperatures, copper's melting point being 1083 ºC while the typical operating temperature of CLC reactors is in the 700–1000 ºC range. However, tests made have shown that Cu-based oxidizers can be used in temperatures up to 950 ºC without major issues. There are other factors to consider, such as toxicity, availability and thermodynamic conversion rates, but typically the choice of the oxygen carrier is made based on their availability, cost, and reactivity. (Anthony 2012, pp. 1626–1627.)

Chemical looping combustion is a fairly old technology, being first discovered over 60 years ago, but has only recently began to receive more attention. Most of the research has been done around Cu-, Ni-, and Fe-based oxygen carriers, and using natural gas as fuel. The use of solid fuels has received more attention lately, including plans to use it in the production of hydrogen. Overall, it shows potential and is expected to continue developing, considering the high demand for technologies that enable CCS. (Anthony 2012, pp. 1648–1649).

Calcium is another oxygen carrier that can be used in a looping system, but it has two distinctive properties: it is not metallic, unlike all other carriers mentioned, and it has a much higher carrying capacity of 0.47, compared to 0.03 and 0.24 for Fe- and Cu-based carriers. Carrying capacity is defined as

$$\mathrm{Rx} = \frac{m_{\mathrm{ox}} - m_{\mathrm{red}}}{m_{\mathrm{ox}}} \tag{3.9}$$

where m_{ox} and m_{red} are the masses of fully oxidized and reduced samples, respectively.

The two other advantages the calcium cycle has are the good availability and low price of gypsum: it is naturally abundant, and thus relatively cheap (Anthony 2012, p. 1631). Table 2 shows the approximate prices for the oxygen carriers presented so far:

Table 2. Approximate prices for some common oxygen carriers (Alibaba 2016a-d)

Oxygen carrier	Approx. price [USD/metric ton]
CuO	1,000
NiO	10,000
Fe_2O_3	700
$CaSO_4$	300

Anthony (2012, pp. 1631-1632) names two main problems related to the use of calcium as an oxygen carrier. The first problem is the tendency of CaS to react with sulfur to form SO_2, resulting in the loss of sulfur in temperatures typical to chemical looping processes (> 900 ºC), as shown in equations 3.10 and 3.11.

$$2CaS + 3O_2 = 2CaO + 2SO_2 \tag{3.10}$$

$$CaS + 3CaSO_4 = 4CaO + 4SO_2 \tag{3.11}$$

The second problem is sintering, i.e. the agglomeration of materials into larger solid blocks, resulting in a worse surface-area-to-volume ratio, and thus weaker activity. The problems listed make the use of calcium as an oxygen carrier seem less attractive than other options available, despite the advantages listed earlier. However, there have been propositions of using synthetic carriers to reduce sintering and adding a guard bed to capture and return escaping SO_2 back to the system. (Anthony 2012, pp. 1631-1632.)

3.4 Calcium looping

The calcium looping (CaL) uses calcium as a sorbent in a two-part process to capture CO_2 from flue gases. The process consists of the exothermic carbonation reaction, in which CaO reacts with CO_2 to form $CaCO_3$, and the endothermic calcination reaction, in which the $CaCO_3$ decomposes into CaO and CO_2, as in equation 3.12. Unlike pre-combustion capture and oxy-firing, post-combustion carbon capture can be installed in existing power plants without the need to update their combustion system (Chang *et al.* 2013, p. 1525). It is possible to recover a significant part of the heat tied to hot streams leaving the process and of the heat released during the carbonation reaction to be used in the production of electricity, which enables post-combustion CO_2 capture with only a minor loss in net plant efficiency. (Mantripragada 2014, pp. 2199-2205.)

$$CaO + CO_2 = CaCO_3 \tag{3.12}$$

Calcium looping requires two separate fluidized bed reactors: the carbonation reaction takes place in temperatures around 600-700 ºC, and the calcination reaction at around 900 ºC. The heat required in the calcination reaction is obtained by burning coal in the reactor. The coal is oxy-fired, since both calcination and coal combustion take place in the same reactor and this produces a stream of concentrated CO_2 to be captured. The total heat required by the calciner to heat the incoming sorbent and gases is around 40-50 % of the total energy entering the system, but since the outgoing streams leave the reactor at temperatures around 900 ºC, and the carbonation reaction releases energy at a temperature around 650 ºC, their high-quality heat can be used in electricity generation. This is a distinctive feature for the calcium looping system. According to Chang *et al.* (2013, p. 1526), the CaL process can reach a CO_2-capture efficiency of around 90 %. The calcium looping process is shown in Figure 15.

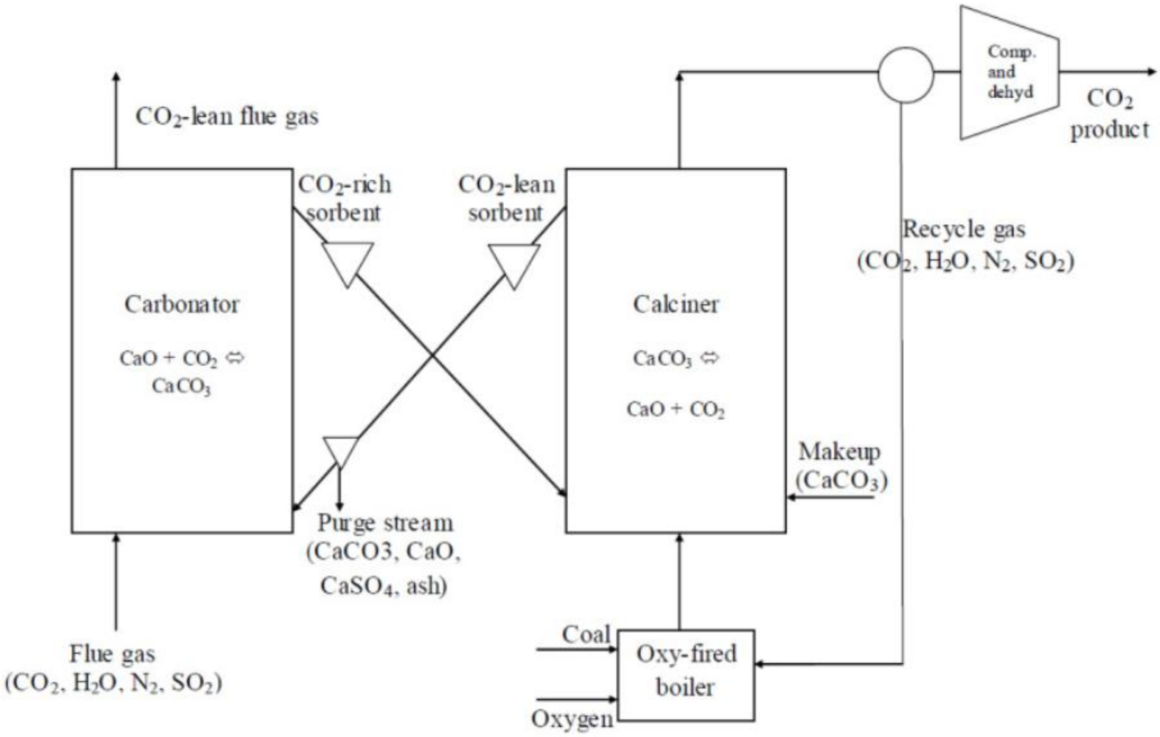

Figure 15. Calcium looping process for post-combustion carbon capture and storage (Mantripragada *et al.* 2014, p. 2200)

An analysis made by Mantripragada *et al.* (2014, pp. 2204-2205) estimates a large coal fired plant's net efficiency (HHV basis) to drop by 3 %-units if a CaL system is installed, from 39 % to 36 %, which is a much smaller drop in efficiency than what is seen with other CO_2 captured processes, where the efficiency loss could be around 11 %-units. According to the study, despite the plant's high efficiency, implementing a calcium looping process in the power plant would more than double its capital costs, from 1,980 USD/kW to 5,375 USD/kW. For comparison, a monoethanolamine-based (MEA-based) CO_2 capture system would bring the plant's capital cost to around 3,050 USD/kW, despite the heavier efficiency loss. Mantripragada attributes the technology's high cost to its early stage of development, stating that if the calculations were done assuming a more mature stage of development, the LCOE of the electricity produced using either a CaL- or a MEA-based CO_2-capture system would be close to one another. He concludes by stating that for the CaL technology to be able to challenge other carbon capture technologies significant improvements would have to be made to the process, such as the implementation of heat integration or the use of an indirect heat supply to the calciner.

3.5 Waste firing

Burning coal slurry in a CFB is the most convenient way of turning slurry into energy. Slurry is a residue obtained from washing coal. It consists of small coal particles (~0.03 mm) and water, resulting in a viscous and moist fuel that is problematic to transport. Coal slurry has a heating value of 14.65~18.32 MJ/kg. Slurry is typically co-fired with coal gangue, which is a low-quality residue separated from mined coal ore during processing. Elemental contents of the coal slurry, gangue and final mixture fired in a 50 MW CFB boiler in Yanzhou, China, are presented in tables 3–5. (Man *et al.* 2009, p. 145.)

Table 3. Slurry ultimate analysis (Man *et al.* 2009, p. 145).

Carbon	Hydrogen	Oxygen	Nitrogen	Sulfur	Ash	Moisture	Volatile	Heat value
Car %	Har %	Oar %	Nar %	Sar %	Aar %	War %	Vdaf %	Qnet. kJ/kg
43.25	2.89	6.59	0.8	0.42	17.05	29	38.07	16309

Table 4. Gangue ultimate analysis (Man *et al.* 2009, p. 145).

Carbon	Hydrogen	Oxygen	Nitrogen	Sulfur	Ash	Moisture	Volatile	Heat value
Car %	Har %	Oar %	Nar %	Sa r%	Aar %	War %	Vdaf %	Qnet. kJ/kg
30.46	2.07	8.2	0.52	0.62	53.83	4.3	43.32	11182

Table 5. Performance coal ultimate analysis, after mixing (Man *et al.* 2009, p. 145).

Carbon	Hydrogen	Oxygen	Nitrogen	Sulfur	Ash	Moisture	Volatile	Heat value
Car %	Har %	Oar %	Nar %	Sar %	Aar %	War %	Vdaf %	Qnet. kJ/kg
39.41	2.64	7.07	0.72	0.48	28.09	21.59	39.65	14771

Overall, coal slurry and gangue firing is a well-tested and reliable way to deal with waste coal. (Man *et al.* 2009, pp. 143–150.)

According to the International Solid Waste Management Association (ISWA, 2013), one billion end-of-life tires were produced globally in 2008. Old tires have traditionally been discarded at tire dumps, but due to the severe environmental risks involved, the Landfill Directive banned the disposal of tires to landfills. Tires have a high heating value, roughly 34 MJ/kg (Wan *et al.* 2007, p. 762), and so most end-of-life tires currently produced in Europe are used in either energy recovery or material recovery (ISWA, 2013).

Wan *et al.* (2007, pp. 761-767) studied the co-firing of coal with a mix of fuel derived from densified refuse (RDF-5), sludge and waste tire in a co-generation CFBB. The composition of the fuels used is presented in Table 6.

Table 6. The proximate and ultimate analyses of the fuels studied by Wan *et al.* (2007, p. 762.).

Property	Coal	Waste tires	Paper sludge	RDF-5
Proximate analysis (wt%)				
Moisture	5.20	4.03	63.47	4.50
Ash	4.18	8.16	10.22	6.37
Volatiles	46.31	63.82	21.88	81.17
Fixed carbon	44.30	23.99	4.43	7.97
LHV(kcal/kg)	4978	8070	607	5703
Ultimate analysis (wt%)				
Carbon	53.31	76.70	8.75	45.98
Hydrogen	5.13	5.76	1.25	6.43
Oxygen	29.96	2.73	15.73	34.55
Nitrogen	1.27	0.36	0.35	0.25
Sulfur	0.90	2.17	0.22	1.08
Chlorine	0.06	0.09	0.02	0.85

The study concluded that densifying municipal, industrial and agricultural waste to RDF-5 is profitable as it reduces treatment costs, increases the utilization of waste energy, and can be co-fired in commercial coal-fired plants, while meeting Taiwanese environmental requirements.

3.6 Biomass co-firing

Co-firing biomass with fossil fuels is the most economic technology available to increase the share of biomass in power generation in the near future. Its main advantage is that biomass can be co-fired in existing power plants without major adaptations, which means co-firing biomass is cheaper than building new biomass power plants. (EPA 2007, p. 30.) Due to the bed's high heat capacity and long combustion time in the boiler, CFBs are particularly well suited to deal with variations in fuel moisture content and size.

The most common boiler types for biomass co-firing are fluidized bed boilers (24 % BFB and 19 % CFB) and pulverized coal boilers (48 %), while grate-fired boilers are less used (9 %). Biomass can be co-fired with coal either directly in the same boiler, in parallel in a separate boiler, or indirectly, where the fuel is gasified beforehand. Direct co-firing is by far the most common method used, accounting for 95.4 % of plants. (Yin 2013, p. 2.)

The co-firing of biomass with coal is used mainly as a means to reduce fuel costs, as it is possible to obtain biomass at zero or negative cost from the wood industry. It is also possible to burn waste such as wood or paper waste that can be obtained at a low cost. Other reasons to adapt existing plants to co-fire biomass are the diversification of fuel sources as well as the need to reduce emissions from coal-fired plants. (EPA 2007, p. 42.)

Co-firing biomass does not result in major losses in boiler efficiency, as long as some adjustments are made, such as changes to design and operation. Without any changes made, co-firing biomass at a share of 10 % of heat input resulted in a loss of 2 % of boiler efficiency. (EPA 2007, p. 43-44)

The greatest challenges associated with biomass firing are slagging and fouling. Slagging, i.e. the partial or complete melting of ashes, happens mainly in the high temperature parts of the boiler. Fouling, on the other hand, is the condensation of alkali compounds on metal surfaces, and happens on the cooler convective surfaces. The formed deposits can cause problems such as corrosion and erosion on the heat transfer surfaces of the boiler. Another issue related to fluidized bed boilers specifically is the agglomeration of bed material due the biomass ash present. This results in less efficient heat transfer in the furnace, as well as increased plant downtime. (Madayanake 2017, pp. 291-292.)

CONCLUSIONS

Circulating fluidized beds (CFBs) have numerous applications in the production of energy. They have applications in boilers for power plants, in gasifiers, and in a number of carbon capture and storage (CCS) technologies.

Two important factors that can make CFB boilers superior compared to pulverized coal plants are fuel availability and the current emission limits: CFBs are generally favored in areas where low quality coals are easily available, and where the use of limestone mixed with the rest of the bed materials is enough to bring sulfur emissions down to acceptable levels, as is the case with the Łagisza unit in Poland (Jäntti & Parkkonen, 2010).

The excellent mixing of solids present in CFBs is the main reason for their popularity in gasifiers and in many CCS technologies, as this results in faster reaction times (Scala 2013, p. 766). Despite the vigorous research done with various CCS methods, they remain a costly alternative, for example a power plant with an installed calcium looping process is estimated to cost more than double the price of a regular power plant. This gap is expected to become smaller as the technology matures. (Mantripragada *et al.* 2014, pp. 2204-2205.)

It is interesting to note how the current emission restrictions would seem to favor CFB units, as more lenient restrictions would mean pulverized coal plants wouldn’t have to install costly wet desulphurization systems. Stricter emission limits, on the other hand, could pose a problem for CFBs in the future, since an external desulphurization system would probably be needed, and this would offset one of the main advantages CFB boilers currently have over the generally cheaper pulverized coal units.

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