

Boosting the IGCLC process efficiency by optimizing the desulfurization step

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1. Introduction

Chemical-looping combustion (CLC) is an emerging technology in which the CO₂ capture is integrated with the power production process. This integration is achieved by combusting the fuel indirectly via an oxygen carrier and therefore a higher electrical efficiency can be obtained than with the conventional CO₂ capture technologies [1,2].

The chemical-looping combustion system can be fueled with coal, natural gas or biomass. Solids can be fed directly to the CLC reactors, but this may imply serious problems to reach full

conversion of the fuel [3]. Alternatively, the solid fuel is first converted to gaseous components by gasification and subsequently the syngas is fed to the CLC reactors. As a solid fuel like coal also contains sulfur, the resulting syngas has a significant content of sulfur compounds (in the order of 0.1–1% by volume). For comparison, the H₂S concentration in natural gas is much lower (<20 ppmv) [4]. Sulfur emissions to atmosphere are regulated at such low levels in most of the countries that sulfur abatement systems are required for industrial use of coal, virtually whatever its sulfur content.

Sulfur can be separated from the fuel by several methods. Sulfur is contained as H₂S and COS in the syngas from coal gasification processes applied in different industrial plants for power generation, production of natural gas, chemicals and liquid fuels from

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Nomenclature

Abbreviations

ASU	air separation unit
BOP	balance of plant
CLC	chemical looping combustion
CGD	cold gas desulfurization
CFB	circulating fluidized bed system
EBTF	European Benchmarking Task Force
GS	gas-steam cycles software
HGD	hot gas desulfurization
HP	high pressure
HRSC	Heat Recovery Steam Cycle
IP	intermediate pressure
LHV	low heating value, J/mol
OC	oxygen carrier
PBR	packed bed reactors

SPECCA specific primary energy consumptions for CO₂ avoided, MJ_{LHV}/kg_{CO₂}

Symbols

E_{CO_2} specific CO₂ emissions, kg/MWh_e

Greek

η net electric efficiency, –

Subscript

e electrical
ref reference plant without CO₂ capture
th thermal

Fischer Tropsch [5]. Well established technologies for removal of gaseous sulfur compounds imply using physical and chemical solvents at ambient (or colder) temperature (CGD, cold gas desulfurization). Amine-based plants (mostly using methyl-diethanolamine, MDEA) are the predominant commercial processes for application carried out at high pressure (depending on the gasification process) and 30–50 °C for selective removal of H₂S (up to 4 ppm). MDEA solvent has a better thermal and chemical stability and the energy requirements for solvent regeneration is lower compared to primary and binary amine solvents (i.e. MEA, DEA).

Physical solvents can also be adopted in coal gasification processes. The most common physical process is the Selexol™ process which is carried out with a mixture of dimethyl ether of polyethylene glycol (DEPG) in order to absorb H₂S (up to 1 ppm). The process works at low temperature (25 °C) and no degradation of the solvent occurs, however high pressures are required to improve the removal at these low temperatures. Similarly, the Rectisol™ process uses chilled methanol to capture H₂S. This process is able to reach a deep removal below 0.1 ppm which is required for chemical processes where the catalyst can be poisoned by the sulfur and it is the predominant process used, if very pure syngas is required (i.e. Fischer Tropsch or ammonia plants). The solvent has good chemical and thermal stability and it works in low temperature range (–30 to –75 °C) and LP steam is required for the solvent regeneration. However, due to the low temperature of the process, high electric consumption is required for the refrigeration which affects the overall plant performance increasing the capital and operational costs. The solubilities of COS, HCN, NH₃ and Ni/Fe carbonyls with chilled methanol are even higher than H₂S and therefore other separation treatments are not required.

Another possibility is to use a mixture of physical and chemical solvents (as for the Sulfinol or Flexsorb processes) which allows for a better solvent loading at high acid gas partial pressure. This process is more suitable in case selective removal of H₂S is not the primary concern as for refineries or a NG plant.

Together with physical and chemical solvents, alkaline salt solutions such as K₂CO₃ (Benfield process) can be considered. H₂S absorption can be achieved in a single step process operated at intermediate temperature (typically 70–120 °C). This process is advantageous for the good stability, low price and minimal degradation of the solvent combined with isothermal absorption-stripping units which reduces the operational costs. However, the solvent is very corrosive and high capital cost is required due to the stainless steel materials. All these processes can be combined with CO₂ absorption as in the case IGCC with pre-combustion capture.

A first alternative to the desulfurization technologies at low temperature (CGD) is to apply hot gas desulfurization (HGD) [6–10] at temperatures above 350 °C: the sulfur removal can occur in-situ during gasification using natural ore as CaCO₃ or downstream with a metal oxide. In this case, the metal oxide is converted to sulfide under reducing hot gas conditions and subsequently regenerated using steam or air. HGD system allows to reach a higher process efficiency because of the absence of the syngas cooling, no sour water treating unit is needed and no black mud is produced in the wet scrubber. Therefore there is a high potential of capital and operating cost savings. Different metal oxides that have been studied [11] and zinc-oxide is currently the leading candidate to commercial application since they can effectively reduce the H₂S to 10 ppm and can be successfully regenerated [12]. However, a significant loss in reactivity is encountered after different cycles. In order to improve the reactivity, it has been investigated to support ZnO on TiO and also in combination with other metal oxide [13]. It has been reported that an efficiency gain of 2.5% points can be obtained if HGD is implemented in an IGCC instead of CGD [14]. Hence, a higher process efficiency can also be expected for the IGCLC process. HGD has been studied in combination with CLC (in combination with H₂ production) by Sorgenfrei and Tsatsaronis [15], but the authors did not compare the performances with cold gas desulfurization.

In case of pulverized coal-fired plant, sulfur is directly oxidized in the boiler and removed downstream in wet flue gas desulfurization (FGD) which provides a high removal efficiency by using limestone as sorbent for the SO₂ to form gypsum [16]. An alternative for combined de-SO_x (up to 99%) and de-NO_x (up to 96%) removal is the SNOX™ process from Haldor Topsoe [17]: sulfur is recovered as commercial grade concentrated sulfuric acid (H₂SO₄), while NO_x is reduced to N₂. This system is characterized by a lower electric auxiliaries consumption for gas cleaning treatment and allows further combustion air pre-heating with a gain in the electrical efficiency of 1–1.5% point compared to conventional flue gas treatment [18].

In the presence of oxy-combustion capture systems, the exhaust gas composition is mostly H₂O and CO₂ (with residual O₂ in order to ensure full combustion). The different gas composition (compared to air-fired system) may affect the plant operation in case of retrofit and in particular in case of higher SO_x concentration [19]. Air Products has studied a system for CO₂-rich stream desulfurization during the compression stage using NO_x as catalyst for the production of H₂SO₄ and the produced HNO₃ is used to remove mercury [20]. An alternative novel method for SO_x removal is the use of activated carbon [21,22]: in this case the SO₂ is adsorbed

in a carbon surface matrix and oxidized to SO_3 which reacts with H_2O to produce H_2SO_4 while NO_x are converted into HNO_3 .

If no acid gas removal unit is employed in an IGCC integrated with chemical looping technology, the syngas stream that is fed to the CLC reactors, contains sulfur, so the oxygen carrier needs to be sulfur tolerant and therefore H_2S is converted to SO_2 or it leaves the reactor as H_2S . Afterwards, the CO_2 stream is desulfurized by FGD (flue gas desulfurization) and compressed.

CLC can be carried out in different reactor types, like circulating fluidized bed systems (CFB) and dynamically operated packed bed reactors (PB). The difference between both reactor type has been quantified in a previous work [23]. It appears that the overall electrical efficiency is scarcely influenced by the selected reactor type, but the operating temperature and the oxygen availability in the fuel reactor is different for the two reaction systems, which is relevant for the formation of metal sulfides or sulfates.

In this paper, the process efficiency of the three desulfurization methods are compared considering both (CFB and PBR) reactor configurations: the first method is based on H_2S separation using the Selexol process (referred to as CGD); the second method adopts HGD using ZnO supported with TiO and in the third case a sulfur tolerant OC is adopted and therefore the sulfur compounds are separated with a FGD system (in the form of SO_2/SO_3). In these IGCLC configurations, hot air is produced in the CLC reactors at 1200°C and 19 bar, which is subsequently fed to the gas turbine and the heat recovery steam generator. First, the IGCLC plant is discussed and in particular the different desulfurization methods. Afterwards, the sulfur tolerance of the oxygen carriers is discussed and then the mass and energy balances of the different processes are compared.

2. Methods and assumptions

2.1. IGCLC power plant description

The IGCLC power plant including the CLC reactors has been evaluated with the GS (Gas Steam cycles) software developed at Politecnico di Milano [24]. In this paper, the IGCLC plant configuration is briefly discussed. The description is mainly focused on the different desulfurization strategies. More detailed information about the IGCLC plant can be found in Spallina et al. [2] and Hamers et al. [23], where the same IGCLC plant configuration is used for the CGD.

The bituminous Douglas coal fuel (with 8 wt% moisture) is dried to a moisture content of 2 wt% with the heat from the combustion of a small amount of downstream syngas. Afterwards, the coal is pressurized by lock hoppers with compressed CO_2 (and a small amount of N_2). The Shell gasifier is operated at 44 bar with oxygen (produced by a stand-alone ASU) and intermediate pressure (IP) steam as oxidants. The produced syngas in the gasifier is first quenched to 900°C with some cold syngas from downstream. After quenching to 900°C , the raw syngas is cooled down in a heat exchanger by producing HP slightly superheated steam at 400°C . In case of CGD the quenching stream is recirculated at 200°C after the water scrubber. In the alternative desulfurization cases, recirculation occurs at 364°C after the high temperature syngas cooling. The recirculated mass flow rate is calculated accordingly. The further treatment of the syngas is dependent on the desulfurization method and is discussed in the next sections after a description of the two reactor types for CLC.

2.1.1. Packed bed CLC (PBR)

The packed bed system consists of at least 5 reactors operated in parallel, as illustrated in the scheme in Fig. 1 a. At least one reactor is in reduction mode, where syngas is converted to CO_2 and H_2O and the OC is reduced. Before the syngas is fed to the CLC reactors, some steam might be mixed to avoid carbon deposition. In case the packed beds are used, it has to be assured that no carbon deposition will occur at 450°C and higher; based on this requirement, the amount of steam was selected [23]. Subsequently, the syngas is heated up to 600°C in a heat exchanger with CO_2 , before it is fed to the reduction reactor. In the reduction reactor, $\text{CO}_2/\text{H}_2\text{O}$ is produced at an average temperature of 832°C . This stream is fed to a heat exchanger, in which HP steam is produced (at 565°C), HP steam from the syngas cooling is heated up from 400 to 565°C and the syngas is preheated to 600°C before it is fed to the CLC reactors. Then the $\text{CO}_2/\text{H}_2\text{O}$ is further cooled and HP water is economized, LP steam is formed and (in case of CGD) the water for the saturator is heated up to 179°C . Afterwards, the water is condensed and the CO_2 is intercooled compressed in three stages and finally pumped to 110 bar.

After the reduction step, the reactor is purged with N_2 produced by the ASU and compressed to 20 bar. Subsequently, the oxygen carrier is oxidized with air, which is compressed adiabatically up to 20 bar and afterwards compressed to 21 bar by a blower to compensate for the pressure drop in the reactor, because the outlet stream is re-used for the heat removal. After the oxidation, the

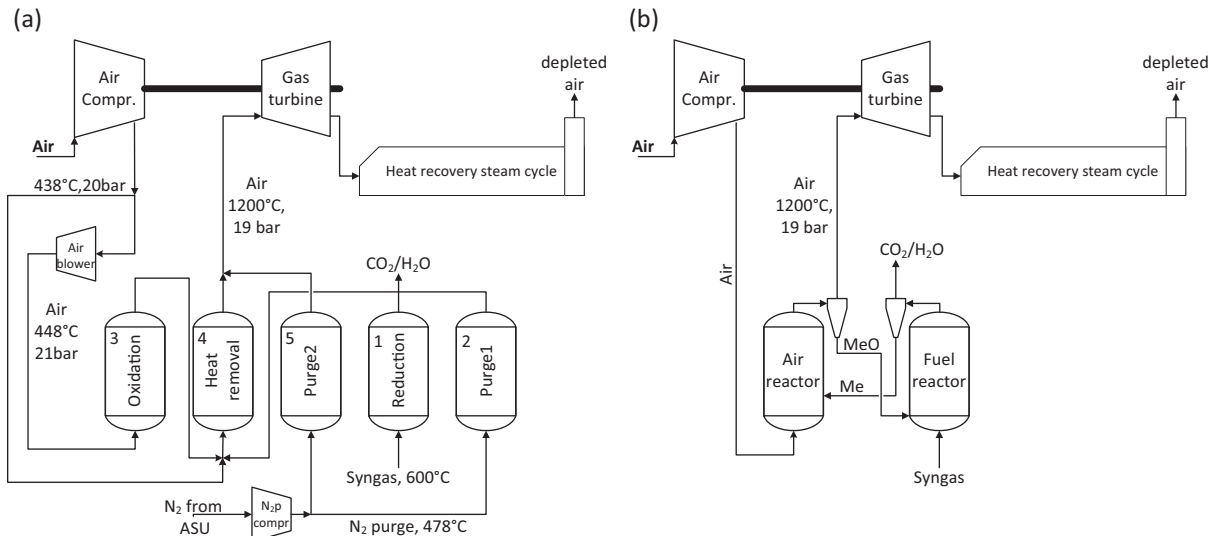


Fig. 1. Schematic of the packed bed configuration (a) and the circulating fluidized bed system (b).

produced heat is blown out of the packed bed during the heat removal step. For this step, air from the GT compressor is used. During the heat removal, the gas (mostly air) is heated up to 1200 °C. This stream (at 19 bar) is first fed to a gas turbine and subsequently to the heat recovery steam generator (HRSG) and then the air is vented. HRSG is designed with three different pressure levels (144, 36 and 4 bar). After the heat removal step, the reactors are purged with N₂ (from ASU) and then the bed is ready to be reduced again.

2.1.2. Circulating fluidized bed CLC system (CFB)

If CLC is carried out in a circulating fluidized bed system, the operation is slightly different. The system mainly consists of an air and a fuel reactor, as shown in Fig. 1b. The gas and solids are separated at the exits of the reactors by a series of cyclones and high pressure filters. This is a critical point of this reactor system, because the gas turbine cannot receive any fines. This separation cannot be effectively and safely carried out with the current technology at 1200 °C and 19 bar. Adopting a configuration with two (or more) cyclones in series may improve the separation efficiency [25], but removal of fines in cyclone systems would hardly be efficient enough to feed a cooled gas turbine. A second challenging issue is related to solid circulation between the high pressure reactors, which has still to be proven. A third critical point is finally related to the stability of the oxygen carrier at such high temperatures. Therefore, here we consider an idealized long-term horizon for the CFB system, assuming the availability of efficient high pressure high temperature filtering technology, a suitable control

system for solids circulation and an oxygen carrier with proper thermal and chemical stability.

In the fuel reactor, the syngas is fed at 300 °C and here CO₂/H₂O is produced at 1200 °C. The syngas inlet temperature has been adjusted, so that the bed temperature does not exceed the limit of 1200 °C. The CO₂ is sent to a heat exchanger and high pressure steam is produced here at 565 °C. In the air reactor, air is sent at 438 °C and 20 bar and O₂-depleted air is produced at 1200 °C and 19 bar, which is sent to the gas turbine and the HRSG (same procedure as the hot gas stream produced in the packed bed reactors).

2.2. Method A: cold gas desulfurization (CGD)

The syngas that has been cooled down to 200 °C (stream #2 in Fig. 2) still contains some H₂S and COS. The separation is carried out with Selexol that is highly selective toward H₂S. Therefore, the COS is first converted to H₂S in a catalytic packed bed that operates at 180 °C. To reach the desulfurization temperature of about 35 °C, the flow is further cooled down. The H₂S is captured with Selexol and then recovered from a stripper, whose reboiler is heated by low pressure steam. Afterwards, elementary sulfur is obtained via the Claus process.

After the Selexol process, the desulfurized syngas is depressurized to 21.6 bar and then sent to the saturator to increase the steam content and to heat up the stream again through low grade heat. Subsequently, it is heated up to 300 °C with high pressure saturated water and in the packed bed case, mixed with steam to avoid carbon deposition and further heated up to 600 °C by the

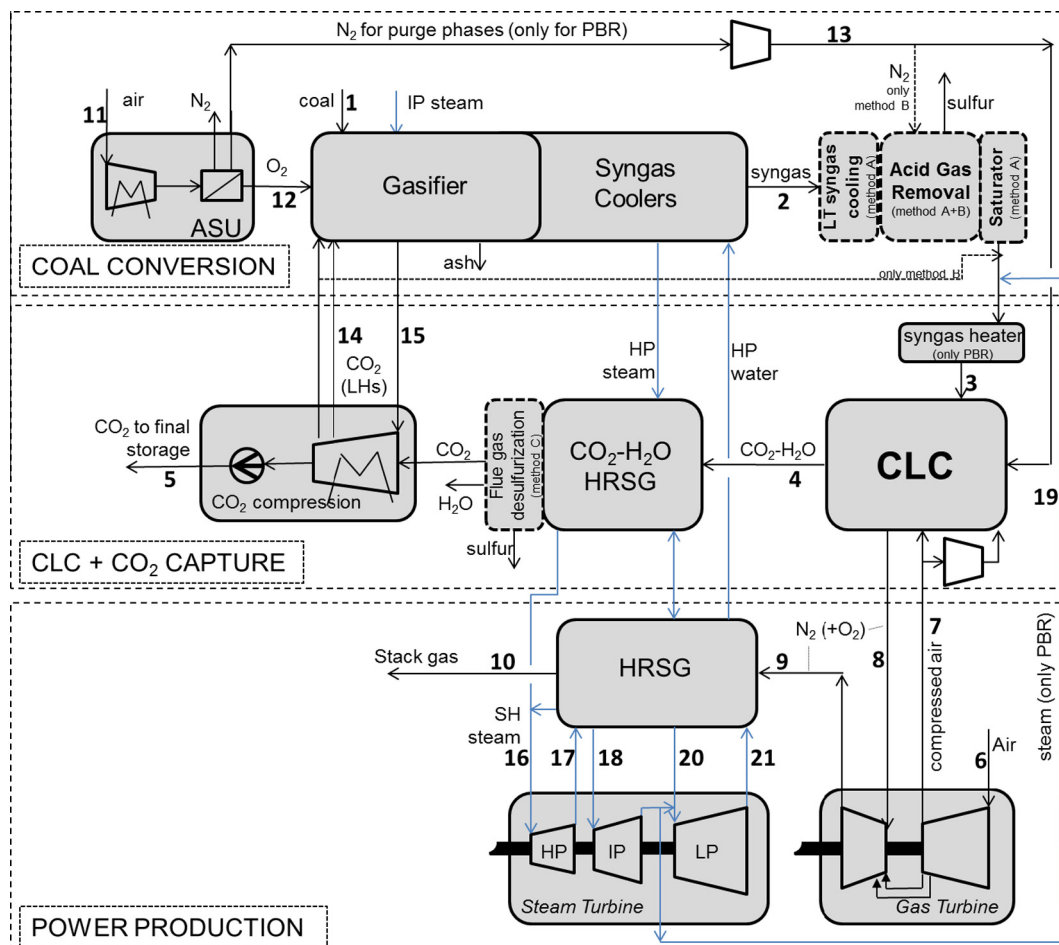
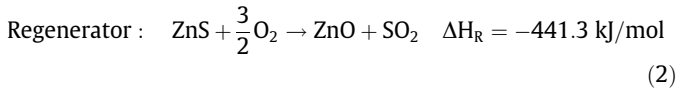
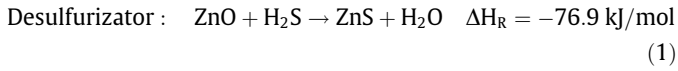


Fig. 2. Simplified IG-CLC power plant scheme (method A: CGD, method B: HGD, method C: post-CLC desulfurization). A more detailed description of the CGD cases can be found in [2,23].

downstream CO₂/H₂O-heat exchanger, which is the same conditions as in other work that discusses the difference between the packed bed and the fluidized bed configuration for CLC [23].

2.3. Method B: Hot gas desulfurization (HGD)

In HGD the H₂S and COS are separated from syngas by reacting it with an oxygen carrier, which is regenerated with O₂. In this case, ZnO/TiO₂ is regarded as oxygen carrier. The following reactions are considered (listed enthalpies at ambient conditions) [14]:



Both reactions are exothermic. The process consists of a circulating fluidized bed system containing a desulfurizer and a regenerator, as illustrated in Fig. 3. In the desulfurizer, the H₂S and COS react with the ZnO forming ZnS, according to Eq. (1). The ZnS is reacted back to ZnO in the regenerator and here SO₂ is formed, according to Eq. (2). The SO₂ is separated afterwards.

The first difference with the CGD case is that the syngas is quenched by a stream with a higher temperature as explained in the beginning of Section 2.1. After the quench and HT cooling, the fines are filtered from the syngas and then it is fed to the HGD-unit, where the H₂S and COS reacts with ZnO. The desulfurizer operates adiabatically at 400 °C and this temperature is controlled by the syngas stream, which has a temperature of 386 °C. After desulfurization, the syngas is sent to a filter again to avoid the entrainment of Zn-sorbent particles. A small amount of CO₂ is therefore also fed to clean the filters. After filtration, a small amount of syngas is combusted to dry the coal to the target moisture content of 2%. Before the syngas is fed to the reduction reactor for CLC, the steam content is increased (in case of the packed bed configuration) to avoid carbon deposition. Differently from the CGD case, syngas saturation (that increases the moisture content by contacting the syngas with a warm liquid water stream) is not featured in this configuration. A higher steam flow rate drawn

from the steam section has to be mixed to achieve the required H₂O content.

The ZnS formed in the desulfurizer is regenerated with air that is diluted with N₂ taken from the ASU. This air is first compressed to 20 bar in the air and N₂ compressors of the CLC system (used during oxidation and heat removal) and then further compressed to 40 bar. This operating condition was selected to be consistent with other works with HGD [8]. However, operation at 20 bar might be possible as well to reduce the number of devices. During the ZnS oxidation ZnSO₄ might be formed, but this reaction is circumvented by keeping the O₂ concentration low (2%) in the regeneration gas stream. While the proper O₂ dilution level to avoid ZnSO₄ is highly uncertain, it was demonstrated that the effect of O₂ concentration on plant efficiency is very low [14]. The temperature of the regenerator is kept at 750 °C. A ZnS/ZnO ratio of 0.1 is assumed for the solids that exit the reactor. After regeneration, the gas is expanded to ambient pressure and then the SO₂ is separated by wet lime-limestone desulfurization process (w-FGD). An electric consumption of 1483 kWh/ton_{SO₂} has been assumed for the FGD process [26]. The assumptions for the HGD process are listed in Table 1.

2.4. Method C: Post CLC desulfurization

If the H₂S and COS are oxidized by the oxygen carrier during the CLC process, SO₂ is formed in the CLC reactors and it can be separated after the CLC process. In that case, the CO₂/H₂O/SO₂-stream is cooled down and subsequently a flue gas desulfurization (FGD) is carried out. In this case, the FGD operates at unusual conditions, featuring high pressure and highly CO₂-concentrated environment. Suitable operating parameters are therefore uncertain. However, the same electric consumption of a conventional w-FGD has been assumed as in the HGD case. Another option, which should be verified according to the CO₂ specifications of the storage site, is SO₂ co-injection or the separation of SO₂ as H₂SO₄ as proposed by Air Products which requires NO_x as catalyst of the sulfuric acid formation [20]. In case this is possible, the electricity consumption for SO₂ absorption from the CO₂-rich stream could be avoided.

When considering post-CLC desulfurization configurations, the interaction between oxygen carriers and sulfur compounds has to be addressed, that is the subject of some experimental studies in literature. Forero et al. [27] discussed the influence of temperature and oxygen carrier circulation rate on sulfur conversion using a Cu-based OC in a 500 W_{th} fluidized bed reactor. They found that the great majority of the sulfur fed to the CLC was converted into

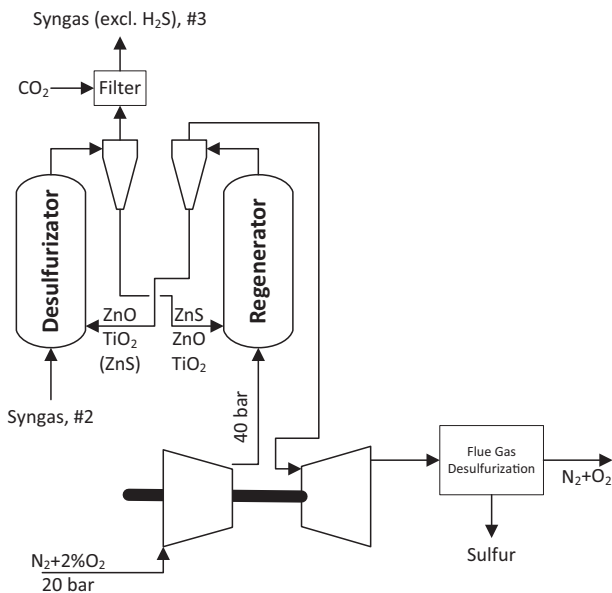


Fig. 3. Schematic overview of the hot gas desulfurization process (method B).

Table 1

List of assumptions regarding the desulfurization methods.

<i>Method A: CGD (Selexol solvent)</i>	
Temperature of absorption tower	35 °C
Syngas pressure loss	1%
Heat of low pressure steam for H ₂ S stripper reboiler	20.95 MJ _{th} /kg _{H₂S}
Sulfur removal and recovery auxiliaries	538.2 kWh _e /ton H ₂ S
<i>Method B: HGD</i>	
ZnS/ZnO-ratio after regenerator	0.1
TiO ₂ (inert) content	50 mol%
Desulfurization temperature	400 °C
100% conversion of H ₂ S	
Regenerator temperature	750 °C
O ₂ content of regeneration stream	2%
Polytropic efficiency of regeneration stream compressor	85%
Polytropic efficiency of regenerator gas expander	92%
Mechanical efficiency of the turbomachines	98.3%
Electricity consumption for SO ₂ separation	1483 kWh/ton SO ₂
<i>Method C: Post-CLC desulfurization</i>	
Electricity consumption for SO ₂ separation	1483 kWh/ton SO ₂

SO₂ in the fuel reactor, while only at low solid circulation rates the Cu₂S was formed with some effect in the OC reactivity. The same reactor has been used to assess the conversion of sulfur-rich sour syngas (with H₂S content up to 15% vol.) using Cu and Fe-based oxygen carriers [28]. The tests showed that Cu is not resistant at high H₂S concentration due to copper sulfide formation, while with Fe-based OC almost 100% of H₂S was converted in the fuel reactor, with no detection of agglomeration or loss of reactivity. The fate of sulfur in a fluidized bed CLOU (chemical looping oxygen uncoupling) process with Cu on MgAl₂O₄ oxygen carrier was also studied in [29] with fuel reactor temperatures of 900–935 °C. In this experimental campaign, about 88% of the sulfur was released from the fuel reactor, while some SO₂ was detected in the air reactor exhausts. As far as OC behavior is concerned, no decay in reactivity, capacity and no agglomeration were experienced. In case of NiO (on alpha-Al₂O₃) a study from Dueso et al. [30] showed the formation of Ni₃S₂ (mainly in the FR) and NiSO₄ (mainly in the AR) when feeding a fluidized bed CLC system operated below 1000 °C with methane enriched with 500 ppmv of H₂S. In the same study, OC regeneration processes were assessed, but complete regeneration was not achieved.

Despite notable studies have been published on the fate of sulfur in fluidized bed CLC systems, none of them has been conducted at pressures and temperatures similar to those considered in this study. Therefore, a discussion on the thermodynamics of sulfur in CLC reactors, also covering conditions relevant for packed beds, has been included in the following section.

3. Thermodynamics of oxygen carriers and sulfur

The post-CLC desulfurization process can only be carried out if no sulfur species are formed on the oxygen carrier, which depends on the oxygen carrier active metal and the process operating conditions. The process conditions depend mainly on the selected CLC reactor configuration: dynamically operated packed beds (PBR) or circulating fluidized beds (CFB).

In the reduction reactor a reaction between the sulfur compounds and the oxygen carrier forming sulfides (MeS_x) or sulfates (Me_xSO₄), like Ni₃S₂ could occur. During oxidation, either SO₂ is formed and then the O₂-depleted air stream needs to be purified as well or the sulfur remains on the oxygen carrier, which might then become deactivated. The oxidation and reduction reaction rates decrease in the presence of H₂S for nickel, copper, iron and manganese oxygen carriers, as it was proven by thermo gravimetric analysis at 800–900 °C [31]. Hence, the MeS_x-formation should be circumvented. Several thermodynamic studies have been carried out on the formation of sulfur compounds on oxygen carriers. It has been demonstrated that this reaction can be suppressed at high temperature, low pressure and high oxygen content (on oxygen carrier or in fuel as CO₂ and H₂O) [32,33].

In the PBRs the reduction reactor temperature is usually low; the temperature at the inlet is equal to the temperature of the fuel (300–600 °C) and the temperature of the rest of the reactor could be 450–1200 °C depending on the heat management strategy [34].

In the CFB-reactors, the temperature in the fuel reactor is close to the temperature of the air reactor due to the external solids circulation [23]. So, the temperature in the fuel reactor is high (around 1200 °C) and in general, the oxygen carrier has a high degree of oxidation. The thermodynamics of reduction with 25% H₂, 35% CO, 10% CO₂, 20% H₂O, 3% H₂S and 7% N₂ have been studied for the most applied oxygen carriers at 1 bar with different oxygen availabilities [32]. In this study, an oxygen excess number was considered between 0.8 and 1.2. For manganese, it is expected that only SO₂ is formed above 800 °C. For nickel, copper and iron this is only the case at high oxygen excess numbers. In case of an

oxygen excess number of 0.8, still some Ni₃S₂, Fe_{0.84}S, FeS and Cu₂S could be formed, also at 1000–1200 °C. It has to be noted that these thermodynamic calculations were carried out with a relatively high H₂S-concentration, 3%, which is one order of magnitude higher than the typical concentration in syngas from coal.

In this section, it is demonstrated to what extent sulfur species can be accepted on nickel, copper, iron and manganese based oxygen carriers in packed bed reactors and in circulating fluidized bed reactors based on thermodynamics. The sulfur components that are included in the calculations are listed in Table 2.

In this study, different oxygen availabilities in the system have been considered. The oxygen availability is defined in Eq. (3). In case the oxygen availability is 1, the stoichiometric amount of oxygen is available for the combustion of the fuel, including the H₂S.

Oxygen availability

$$= \frac{\text{oxygen available on oxygen carrier}}{\text{amount of oxygen required for stoichiometric fuel combustion}} \quad (3)$$

3.1. Thermodynamics in packed bed reactors

The syngas used for the reduction in packed bed reactors is fed at a temperature of 600 °C. The formation of the sulfates and sulfides is thermodynamically favored at lower temperatures. The pressure and the steam content have an influence on the equilibrium, but this effect is negligibly small. At the considered conditions, only metal sulfides are expected.

At the packed bed reactor inlet, the syngas is in contact with a reduced OC, while inside the packed bed, it is in contact with an oxidized OC. After considering different oxygen availabilities it was concluded that for Fe- and Mn-based materials, the highest extent of sulfide formation can be found in a completely reduced bed (with Fe_{0.947}O or MnO). For Ni- and Cu-based materials, the worst case scenario is at a certain oxygen availability (1 for Ni and 0.9 for Cu), because then some oxygen is available to oxidize hydrogen to H₂O, favoring in this way the equilibrium of the sulfide formation reaction.

The maximum H₂S concentration to avoid sulfide formation thermodynamically is shown at different temperatures and oxygen availabilities in Fig. 4. The syngas composition obtained corresponds to a H₂S concentration of 980 ppm. It is shown that for all the oxygen carriers, sulfide formation is expected at that composition at 600 °C. However, the kinetics might be slow and therefore the application for post-CLC desulfurization in packed beds can still be possible (but this should be experimentally demonstrated, which is out of scope of the present study). For the iron and the manganese materials, the sulfide formation could be avoided if the H₂S fraction is reduced. As indicated in Fig. 4, this happens at a H₂S fraction of 139 ppm with a Fe-based or 206 ppm with a Mn-based OC (at 600 °C). So, if the sulfur could be removed to a limited extent prior to the CLC process, post-CLC desulfurization could be carried out with Fe or Mn based OCs.

3.2. Thermodynamics in circulating fluidized bed reactors

In the fluidized bed reactors, the temperature is higher (1200 °C) and oxidized OCs are available all around the fuel reactor thanks to good oxygen carrier mixing. However, despite the

Table 2

The sulfur components that are included in the thermodynamic calculations.

Nickel	H ₂ S, SO ₂ , Ni ₃ S ₂ , NiS, NiS ₂ , Ni ₃ S ₄ , NiSO ₄
Copper	H ₂ S, SO ₂ , Cu ₂ S, CuS, CuSO ₄ , Cu ₂ SO ₄
Iron	H ₂ S, SO ₂ , FeS, Fe _{0.877} S, FeS ₂ , FeSO ₄ , Fe ₂ (SO ₄) ₃
Manganese	H ₂ S, SO ₂ , MnS, MnSO ₄

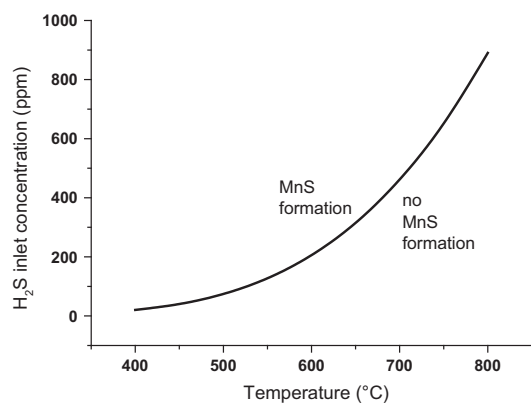
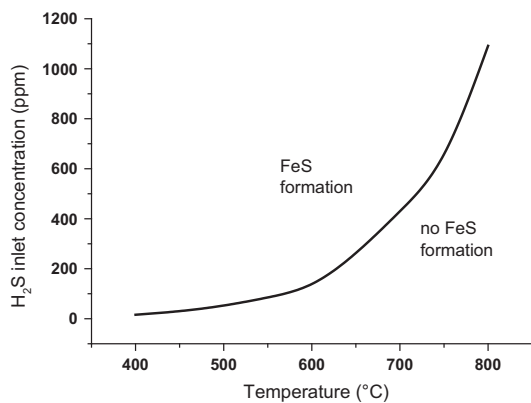
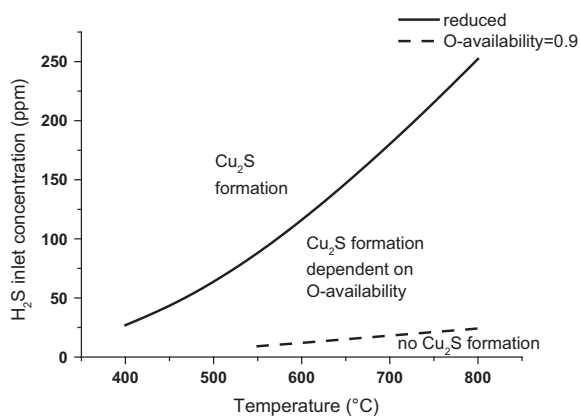
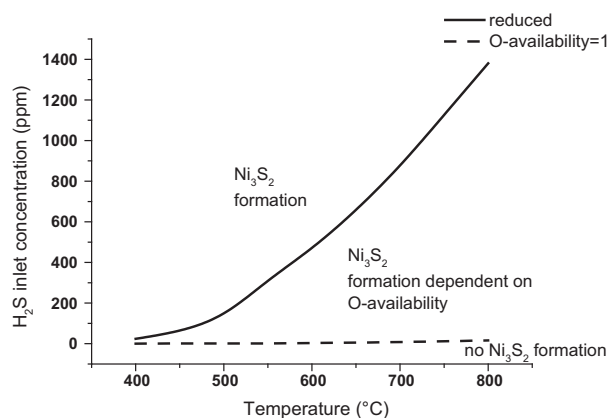


Fig. 4. The formation of sulfides in a packed bed reactor with NiO/Ni, CuO/Cu, Fe_{0.947}O and MnO at 20 bar. The solid lines represent situations with a completely reduced oxygen carrier (expected at the inlet). The dashed lines in the nickel and copper cases show the worst case scenario with the oxygen availability that corresponds to the highest sulfides formation.

oxygen availability is averagely higher than the stoichiometric value, it might be locally lower, which might lead to MeS formation in case of fast kinetics. Therefore, the risk of MeS formation is much lower in the CFB system and might be controlled by adapting the solid circulation rate and by maintaining a good mixing of the solids. Similar thermodynamic calculations have been carried out as for the packed bed case. In the CFB-case, no additional steam needs to be mixed with the fuel to avoid carbon deposition and therefore the H₂S content is higher, 1830 ppm.

Fig. 5 reports the results of the thermodynamics calculation of possible products under these circumstances. Copper is not included in this figure, because the melting point is too low to allow operation at 1200 °C. In case of a nickel-based oxygen carrier, Ni₂S₃ could be formed, even at an oxygen availability of 1. Whether it is formed, depends on the local oxygen availability

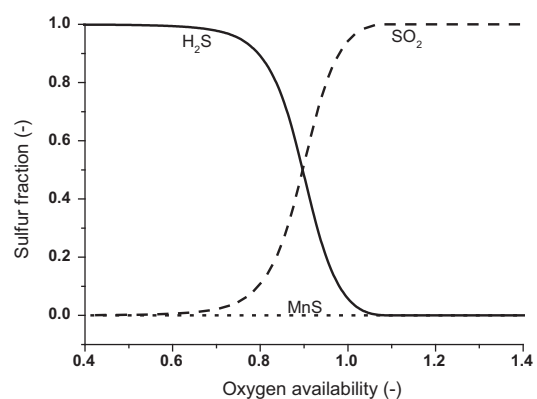
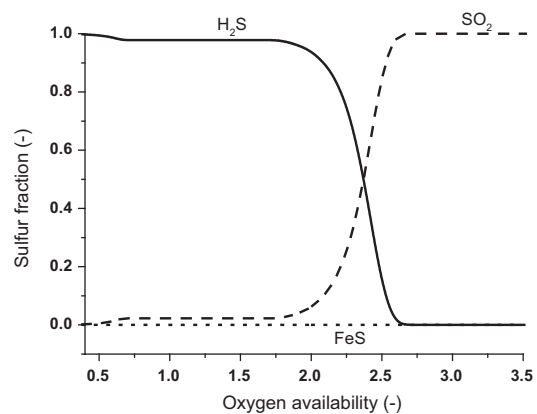
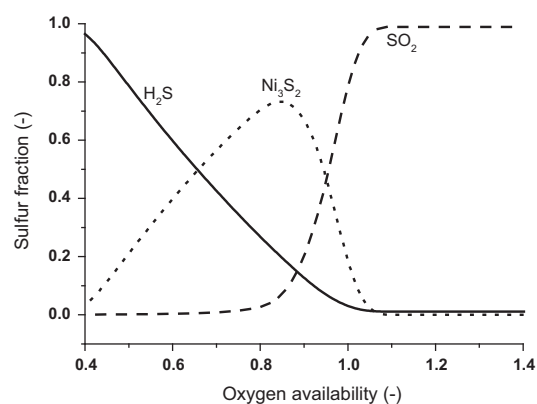


Fig. 5. The thermodynamic equilibriums for nickel, iron and manganese oxygen carriers in circulating fluidized bed reactors at 1200 °C and 20 bar.

Table 3

Comparison streams for the different desulfurization methods for CLC in packed bed reactors.

#	Method A: CGD				Method B: HGD				Method C: Post-CLC desulfurization			
	M, kg/s	T, °C	p, bar	Composition, mol%	M, kg/s	T, °C	p, bar	Composition, mol%	M, kg/s	T, °C	p, bar	Composition, mol%
1	34.1	15	1	Coal	34.1	15	1	Coal	34.1	15	1	Coal
2	78.9	165	42	Ar: 0.89%, CO: 51.57%, CO ₂ : 8.48%, H ₂ : 21.00%, H ₂ O: 16.75%, H ₂ S: 0.16%, N ₂ : 1.16%	69.8	381	43	Ar: 1.04%, CO: 62.74%, CO ₂ : 7.30%, H ₂ : 21.90%, H ₂ O: 5.49%, H ₂ S: 0.18%, N ₂ : 1.35%	69.8	395	43	Ar: 1.04%, CO: 62.74%, CO ₂ : 7.30%, H ₂ : 21.90%, H ₂ O: 5.49%, H ₂ S: 0.18%, N ₂ : 1.35%
3	116.3	600	20	Ar: 0.55%, CO: 32.09%, CO ₂ : 5.28%, H ₂ : 13.07%, H ₂ O: 48.29%, N ₂ : 0.72%	118.9	600	20	Ar: 0.56%, CO: 33.12%, CO ₂ : 4.93%, H ₂ : 11.56%, H ₂ O: 49.09%, N ₂ : 0.74%	116.4	600	20	Ar: 0.56%, CO: 33.45%, CO ₂ : 3.93%, H ₂ : 11.68%, H ₂ O: 49.57%, H ₂ S: 0.10%, N ₂ : 0.72%
4	156.9	832	19	Ar: 0.55%, CO ₂ : 37.37%, H ₂ O: 61.36%, N ₂ : 0.72%	159.5	832	19	Ar: 0.56%, CO ₂ : 38.05%, H ₂ O: 60.65%, N ₂ : 0.74%	157.2	832	19	Ar: 0.56%, CO ₂ : 37.34%, H ₂ O: 61.29%, N ₂ : 0.72%, SO ₂ : 0.10%
5	81.5	28	110	Ar: 1.44%, CO ₂ : 96.70%, N ₂ : 1.76%	81.5	28	110	Ar: 1.44%, CO ₂ : 96.70%, N ₂ : 1.76%	81.5	28	110	Ar: 1.44%, CO ₂ : 96.70%, N ₂ : 1.76%
6	786.2	15	1	Air: Ar: 0.92%, CO ₂ : 0.03%, H ₂ O: 1.03%, N ₂ : 77.28%, O ₂ : 20.73%	789.1	15	1	Air	792.2	15	1	Air
7	729.9	438	20	Air	731.5	438	20	Air	735.5	438	20	Air
8	707.6	1199	19	Ar: 0.94%, CO ₂ : 0.03%, H ₂ O: 1.06%, N ₂ : 81.86%, O ₂ : 16.11%	709.3	1199	19	Ar: 0.94%, CO ₂ : 0.03%, H ₂ O: 1.06%, N ₂ : 81.85%, O ₂ : 16.12%	713.1	1199	19	Ar: 0.94%, CO ₂ : 0.03%, H ₂ O: 1.06%, N ₂ : 81.85%, O ₂ : 16.12%
9	764.0	486	1	Ar: 0.94%, CO ₂ : 0.03%, H ₂ O: 1.06%, N ₂ : 81.52%, O ₂ : 16.45%	765.8	486	1	Ar: 0.94%, CO ₂ : 0.03%, H ₂ O: 1.06%, N ₂ : 81.51%, O ₂ : 16.46%	769.8	486	1	Ar: 0.94%, CO ₂ : 0.03%, H ₂ O: 1.06%, N ₂ : 81.51%, O ₂ : 16.46%
10	764.0	92	1	Same as #9	765.8	95	1	Same as #9	769.8	95	1	Same as #9
11	120.7	15	1	Air	120.7	15	1	Air	120.7	15	1	Air
12	28.9	180	47	Ar: 3.09%, N ₂ : 1.91%, O ₂ : 95.00%	28.9	180	47	Ar: 3.09%, N ₂ : 1.91%, O ₂ : 95.00%	28.9	180	47	Ar: 3.09%, N ₂ : 1.91%, O ₂ : 95.00%
13	18.4	478	20	N ₂	28.9 ^a	478	20	N ₂	18.4	478	20	N ₂
14	23.7	80	56	Same as #5	23.7	80	56	Same as #5	23.7	80	56	Same as #5
15	13.9	80	1	Same as #5	13.9	80	1	Same as #5	13.9	80	1	Same as #5
16	129.5	527	134	Steam	137.8	532	134	Steam	137.4	531	134	Steam
17	129.5	333	36	Steam	137.8	334	36	Steam	137.4	333	36	Steam
18	142.6	458	33	Steam	151.1	458	33	Steam	150.9	458	33	Steam
19	33.4	395	22	Steam	47.1	395	22	Steam	47.1	395	22	Steam
20	37.7	300	4	Steam	47.8	300	4	Steam	48.5	300	4	Steam
21	146.8	32	0	Steam	152.0	32	0	Steam	152.3	32	0	Steam

^a 10.5 kg/s N₂ is included for the regeneration of the ZnS (HGD).

and the kinetics. In case of iron oxide, the analysis has considered the Fe₂O₃/FeO pair, however, full oxidation of the H₂S into SO₂ occurs only when the Fe₂O₃ is converted into Fe₃O₄ and therefore, the oxygen availability leading to complete sulfur oxidation is not 1 but 2.67. In fact the equilibrium composition shows that in presence of FeO as reduced state part of the syngas is not converted [35]. Therefore, iron and manganese based oxygen carriers could be applied in fluidized bed reactors operating at 1200 °C and 20 bar.

4. Results and discussion

4.1. Desulfurization for packed bed CLC with syngas

For the packed bed CLC system a sufficient amount of steam needs to be mixed with the fuel in order to prevent carbon deposition. In the CGD-configuration, there is a saturator that helps to increase the steam content in the syngas. In the two alternative cases, there is no saturator and therefore a larger amount of steam has to be mixed with the syngas (47 instead of 33 kg steam/s). These amounts are listed in #19 of Table 3, which contains the mass balances for the different configurations. If the kinetics of the carbon deposition reactions are slow, the amount of steam could be decreased and a higher overall efficiency can be obtained [23].

The overall results of the mass and energy balances for the different desulfurization technologies are shown in Tables 3 and 4. The power for the compressor and expander for the HGD have been

accounted for in the electrical net output from the gas turbine. The gas turbine output is hardly influenced by the desulfurization technology, because the hot gas flow sent to the turbine does not change much as well, because also the thermal input of the fuel does not depend much on the selected desulfurization method; the H₂S fraction is only 0.2% and therefore its presence during post CLC desulfurization hardly increases the thermal input. In case of HGD and post-CLC desulfurization, 6.2 MW_e are additionally produced by the HRSC, because no steam is consumed for the reboiler and also the syngas stream does not have to be cooled down to 35 °C and heated up again subtracting part of the heat from CO₂ cooling, as in the CGD case. On the other hand, more electricity is consumed by the desulfurization process (1.5 MW_e) and more intermediate pressure steam is mixed with the fuel, which is not used for power production. Also the heat rejection is higher, because the steam cycle condenser produces more heat as well. Because of these effects, the process efficiency is slightly increased in case an alternative desulfurization method is selected (0.5–0.7% point increase).

Some other small differences are shown in the energy balances. In the HGD case, the consumption for the CO₂ compression is somewhat higher, because more CO₂ is mixed with the fuel in the filter downstream of the desulfurization step. This is due to the need of an additional filtration unit downstream of the HGD process to remove the entrained H₂S sorbent particles. The syngas recirculation blower consumes more electricity in the cases B and C, because the temperature of the quenching gas is higher and therefore the mass flow rate is increased to quench the syngas in the gasifier.

Table 4
Energy balances for the CGD, HGD and post-CLC desulfurization in combination with packed bed CLC.

Power	Method A: CGD in PBR	Method B: HGD in PBR	Method C: Post-CLC in PBR
Heat input LHV, MW _{LHV}	853.9	853.9	853.9
Gas turbine, MW _e	225.1 ^a	225.2 ^{a,b}	226.8 ^a
Heat Recovery Steam Cycle, MW _e	183.0	189.3	189.3
Gross power output, MW _e	408.1	414.5	416.1
Syngas blower, MW _e	-0.8	-1.5	-1.5
ASU, MW _e	-33.9	-33.9	-33.9
Lock hoppers CO ₂ compressor, MW _e	-3.1	-3.1	-3.1
Acid gas removal or flue gas desulfurization, MW _e	-0.4	-1.9	-1.9
CO ₂ compressor, MW _e	-11.0	-11.3	-11.0
N ₂ intercooled compressor gasifier, MW _e	-1.3	-1.5	-1.5
Heat of rejection, MW _e	-3.6	-3.7	-3.7
Other auxiliaries, BOP, MW _e	-3.4	-3.4	-3.4
Net power generated, MW _e	350.6	354.3	356.1
LHV efficiency, %	41.05	41.50	41.71
CO ₂ capture efficiency, %	97.1	97.0	97.0
CO ₂ purity, %	96.7	96.7	96.7
CO ₂ emission, kg CO ₂ emitted/MWh _e	24.7	25.5	25.2
CO ₂ avoided, %	96.8	96.7	96.7
SPECCA, MJ LHV/kg CO ₂ , Eq. (4)	1.08	0.96	0.90

^a Gas turbine power includes consumption of air blower and nitrogen compressor for purge.

^b The power of the compressor and the expander of the HGD system are accounted for.

The specific energy cost for CO₂ avoidance is expressed by the SPECCA, which accounts for the efficiency decrease due to CO₂ capture and the CO₂ capture efficiency and can be calculated with Eq. (4). The reference IGCC power plant without CO₂ capture that has been considered in the SPECCA was published by Spallina et al. [2]. In case of CGD, the SPECCA is 1.08, which is much lower than with conventional CO₂ capture with Selexol (3.34, [23]). But the costs of CO₂ capture can even be reduced to 0.9–0.96 by a modification of the desulfurization technology.

The equipment costs for the HGD and post-CLC are expected to be lower than for the CGD technology, because a lower heat exchange surface is needed for the gas–gas heat exchanger for syngas heating. For the post-CLC configuration, the equipment related to syngas cooling is not needed, but it can only be carried out in case no sulfur species are formed on the oxygen carrier.

$$\text{SPECCA} = \frac{\frac{1}{\eta_{\text{el}}} - \frac{1}{\eta_{\text{el,ref}}}}{E_{\text{CO}_2,\text{ref}} - E_{\text{CO}_2}} 3600 \quad (4)$$

4.2. Desulfurization for fluidized beds with syngas

The mass balance for the circulating fluidized bed process is slightly different. In this case, no steam is required to avoid carbon deposition, because the fuel reactor temperature is always higher (1200 °C). The thermodynamic analysis of the plant does not discuss the performance using a specific oxygen carrier and therefore some assumptions have been made such as same outlet temperatures which depends on the heat of reactions and the solid circulation (not considered here) and full gas conversion which could

Table 5
Comparison streams for the different desulfurization methods for CLC in circulating fluidized bed reactors.

#	Method A: CGD				Composition, mol%	Method B: HGD				Composition, mol%	Method C: Post-CLC desulfurization				
	M, kg/s	T, °C	p, bar			M, kg/s	T, °C	p, bar			M, kg/s	T, °C	p, bar		
1	34.1	15	1		Coal	34.1	15	1		Coal	34.1	15	1		Coal
2	78.9	165	42		Ar: 0.89%, CO: 51.57%, CO ₂ : 8.48%, H ₂ : 21.00%, H ₂ O: 16.75%, H ₂ S: 0.16%, N ₂ : 1.16%	69.8	381	43		Ar 1.04%, CO: 62.74%, CO ₂ : 7.30%, H ₂ : 21.90%, H ₂ O: 5.49%, H ₂ S: 0.18%, N ₂ : 1.35%	69.8	395	43		Ar: 1.04%, CO: 62.74%, CO ₂ : 7.30%, H ₂ : 21.90%, H ₂ O: 5.49%, H ₂ S: 0.18%, N ₂ : 1.35%
3	72.7	300	20		Ar: 0.97%, CO: 56.41%, CO ₂ : 9.27%, H ₂ : 22.97%, H ₂ O: 9.11%, N ₂ : 1.27%	71.8	390	20		Ar: 1.05%, CO: 61.41%, CO ₂ : 9.15%, H ₂ : 21.44%, H ₂ O: 5.60%, N ₂ : 1.36%	69.2	395	20		Ar: 1.04%, CO: 62.67%, CO ₂ : 7.36%, H ₂ : 21.87%, H ₂ O: 5.53%, H ₂ S: 0.18%, N ₂ : 1.35%
4	113.3	1200	19		Ar: 0.97%, CO ₂ : 65.68%, H ₂ O: 32.07%, N ₂ : 1.27%	112.4	1200	19		Ar: 1.05%, CO ₂ : 70.55%, H ₂ O: 27.03%, N ₂ : 1.36%	110.1	1200	19		Ar: 1.04%, CO ₂ : 69.89%, H ₂ O: 27.53%, N ₂ : 1.35%, SO ₂ : 0.18%
5	81.5	28	110		Ar: 1.44%, CO ₂ : 96.70%, N ₂ : 1.76%	81.5	28	110		Ar: 1.44%, CO ₂ : 96.70%, N ₂ : 1.76%	81.5	28	110		Ar: 1.44%, CO ₂ : 96.70%, N ₂ : 1.76%
6	716.2	15	1		Air	736.3	15	1		Air	742.2	15	1		Air
7	664.8	438	20		Air	682.5	438	20		Air	689.2	438	20		Air
8	624.2	1200	19		Ar: 0.97%, CO ₂ : 0.03%, H ₂ O: 1.09%, N ₂ : 81.79%, O ₂ : 16.12%	642.0	1200	19		Ar: 0.97%, CO ₂ : 0.03%, H ₂ O: 1.09%, N ₂ : 81.66%, O ₂ : 16.25%	648.4	1200	19		Ar: 0.97%, CO ₂ : 0.03%, H ₂ O: 1.09%, N ₂ : 81.64%, O ₂ : 16.26%
9	675.6	487	1		Ar: 0.97%, CO ₂ : 0.03%, H ₂ O: 1.09%, N ₂ : 81.45%, O ₂ : 16.46%	694.6	484	1		Ar: 0.97%, CO ₂ : 0.03%, H ₂ O: 1.09%, N ₂ : 81.33%, O ₂ : 16.58%	701.4	484	1		Ar: 0.97%, CO ₂ : 0.03%, H ₂ O: 1.09%, N ₂ : 81.32%, O ₂ : 16.60%
10	675.6	89	1		Same as #9	694.6	101	1		Same as #9	701.4	102	1		Same as #9
11	120.7	15	1		Air	120.7	15	1		Air	120.7	15	1		Air
12	28.9	180	47		Ar: 3.09%, N ₂ : 1.91%, O ₂ : 95.00%	28.9	180	47		Ar: 3.09%, N ₂ : 1.91%, O ₂ : 95.00%	28.9	180	47		Ar: 3.09%, N ₂ : 1.91%, O ₂ : 95.00%
13	-	-	-		-	10.5	478	20		N ₂	-	-	-		-
14	23.7	80	56		Same as #5	23.7	80	56		Same as #5	23.7	80	56		Same as #5
15	13.9	80	1		Same as #5	13.9	80	1		Same as #5	13.9	80	1		Same as #5
16	155.3	541	134		Steam	156.0	542	134		Steam	154.7	542	134		Steam
17	155.3	344	36		Steam	156.0	342	36		Steam	154.7	342	36		Steam
18	157.7	458	33		Steam	160.5	458	33		Steam	159.7	458	33		Steam
19	-	-	-		-	-	-	-		-	-	-		-	
20	0.1	300	4		Steam	-20.6	177	4		Steam	-20.0	300	4		Steam
21	157.8	32	0		Steam	161.7	32	0		Steam	161.4	32	0		Steam

Table 6
Energy balances for the CGD, HGD and post-CLC desulfurization in combination with fluidized bed CLC.

Power	Method A: CGD in CFB	Method B: HGD in CFB	Method C: Post- CLC in CFB
Heat input LHV, MW _{LHV}	853.9	853.9	853.9
Gas turbine, MW _e	197.9	206.1 ^a	208.6
Heat Recovery Steam Cycle, MW _e	216.3	217.5	216.5
Gross power output, MW _e	414.2	423.6	425.1
Syngas blower, MW _e	-0.8	-1.5	-1.5
ASU, MW _e	-33.9	-33.9	-33.9
Lock hoppers CO ₂ compressor, MW _e	-3.1	-3.1	-3.1
Acid gas removal or flue gas desulfurization, MW _e	-0.4	-1.9	-1.9
CO ₂ compressor, MW _e	-11.0	-11.3	-11.0
N ₂ intercooled compressor gasifier, MW _e	-1.3	-1.5	-1.5
Heat of rejection, MW _e	-3.6	-3.6	-3.6
Other auxiliaries, BOP, MW _e	-3.4	-3.4	-3.4
Net power generated, MW _e	356.7	363.5	365.3
LHV efficiency, %	41.78	42.57	42.78
CO ₂ capture efficiency, %	97.1	97.0	97.0
CO ₂ purity, %	96.7	96.7	96.7
CO ₂ emission, kg CO ₂ emitted/MWh _e	24.3	24.9	24.6
CO ₂ avoided, %	96.8	96.8	96.8
SPECCA, MJ LHV/kg CO ₂ , Eq. (4)	0.88	0.66	0.61

^a The power of the compressor and the expander of the HGD system are accounted for.

certainly be possible in case a manganese or an iron based oxygen carrier is used. With these oxygen carriers, it is also not expected that sulfur species are formed on the oxygen carrier when operating with a high oxygen availability (Fig. 5). Also for a nickel based oxygen carrier formation of sulfur species might be negligible, but the fuel conversion is lower due to thermodynamic constraints [33].

The mass balances are shown in Table 5. The main difference with respect to the packed bed case is the temperature and the steam content of the syngas fed to the CLC system. In the CGD base case, the syngas inlet temperature is 300 °C. This temperature is somewhat higher in case of the HGD and the post-CLC desulfurization, because the syngas is heated in the hot desulfurization process (method B) or cooled down to a lesser extent in syngas coolers (method C). As far as steam content is concerned, it decreases from 48–50% of the PBR cases to 5–17% of the CFB cases. Among the CFB cases, the maximum steam content is obtained for the CGD case, due to the use of the saturator for low temperature syngas humidification and preheating.

Table 6 contains the efficiencies of the three different configurations. More power is produced by the gas turbine in the cases B and C, because the syngas inlet temperature is higher. Therefore more energy is fed to the CLC system and a larger hot air flow can be generated. The other main differences are similar to the packed bed cases, except that here no steam is mixed with the fuel. Hence, a higher efficiency gain can be achieved than in the packed bed cases (0.8–1.0% point). Because the CO₂ emissions are at the same order of magnitude, the higher efficiency results in a lower SPECCA number.

The efficiency gain of the HGD (method B) compared with CGD (method A) is 0.8% points and this is not as high as in the case of Giuffrida et al. (2.5% points) [14]. The IG-CLC plants have a different power share than a conventional IGCC (where more than 60% of the gross power output comes from the GT) due to the lower turbine inlet temperatures and the higher influence of the steam cycle

integration. Because of the lower efficiency, an increase in sensible heat of the inlet stream has a smaller effect on the net electrical efficiency as well. Additionally in this case, an additional term for the separation of SO₂ has been considered that results in an efficiency decrease of 0.2% points.

5. Conclusions

In this work, the influence of the desulfurization method on the IGCLC process efficiency has been determined. In the conventional desulfurization method, the syngas is cooled down to 35 °C, before it is heated up for the CLC reactors (CGD). Hot gas desulfurization (HGD) and desulfurization after the CLC process (post-CLC) have been studied as alternatives. In the latter case, H₂S is fed to the CLC reactors and then no sulfur species should be formed on the carrier. Otherwise SO₂ could be formed during the subsequent oxidation (and has to be separated from this stream as well) or the oxygen carrier deactivates. The CLC process in packed beds and in a circulating fluidized bed system has been considered.

The efficiency gain of a different desulfurization method is small in case of the packed bed reactors (0.5–0.7% points). In the alternative cases (HGD and post-CLC), there is no saturator and therefore more steam has to be mixed with the fuel. Because of this, the effect of the alternative desulfurization method is small. In these configurations, the syngas is always preheated to 600 °C in a gas–gas heat exchanger and therefore the energy content of the syngas fed to the CLC reactors is almost constant, but a smaller heat exchanger surface is required in case of the alternative desulfurization methods. According to the thermodynamics, some sulfur species may form on the oxygen carrier and therefore this technology can only be applied in case a sufficiently slow kinetics is confirmed by experiments.

In the circulating fluidized bed reactors, a somewhat higher efficiency gain can be achieved by applying a different desulfurization strategy (0.8–1.0% point), because no additional steam dilution is needed for carbon deposition control and the syngas is fed at higher temperature to the CLC reactor in case of the alternative desulfurization technologies. An important condition is that full gas conversion is reached in the reactors. This is not possible with nickel based oxygen carriers due to thermodynamic limitations for the reductions with H₂ and CO, and in case of iron-based the OC should operate from hematite to magnetite. With these materials, it is also not expected that sulfur species are formed at the fuel reactor temperature of 1200 °C.

From this, it can be concluded that the IGCLC process efficiency can be increased in case HGD or post-CLC desulfurization is applied, with a maximum efficiency gain of about 1.0% point. An economic analysis is needed to evaluate the feasibility of these alternative desulfurization processes, considering both the significant savings associated to the lack of equipment for low temperature syngas cooling and reheating and the additional cost for high temperature and post-CLC desulfurization which are currently not mature technologies.

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References

- [1] Erlach B, Schmidt M, Tsatsaronis G. Comparison of carbon capture IGCC with pre-combustion decarbonisation and with chemical-looping combustion. *Energy* 2011;36:3804–15.

- [2] Spallina V, Romano MC, Chiesa P, Gallucci F, Van Sint Annaland M, Lozza G. Integration of coal gasification and packed bed CLC for high efficiency and near-zero emission power generation. *Int J Greenh Gas Control* 2014;27:28–41.
- [3] Lyngfelt A. Chemical-looping combustion of solid fuels – status of development. *Appl Energy* 2013.
- [4] Adanez J, Abad A, Garcia-Labiano F, Gayan P, de Diego LF. Progress in chemical-looping combustion and reforming technologies. *Prog Energy Combust Sci* 2012;38:215–82.
- [5] Korens N, Simbeck DR, Wilhelm DJ. Process screening analysis of alternative gas treating and sulfur removal for gasification. Mountain View California, USA; 2002.
- [6] Park YC, Jo S-H, Ryu H-J, Moon J-H, Yi C-K, Yoon Y, et al. Simultaneous removal of H₂S and COS using Zn-based solid sorbents in the bench-scale continuous hot gas desulfurization system integrated with a coal gasifier. *Korean J Chem Eng* 2012;29:1812–6.
- [7] Meng X, de Jong W, Pal R, Verkooyen AHM. In bed and downstream hot gas desulfurization during solid fuel gasification: a review. *Fuel Process Technol* 2010;91:964–81.
- [8] Giuffrida A, Bonalumi D, Lozza G. Amine-based post-combustion CO₂ capture in air-blown IGCC systems with cold and hot gas clean-up. *Appl Energy* 2013;110:44–54.
- [9] Giuffrida A, Romano MC, Lozza G. Efficiency enhancement in IGCC power plants with air-blown gasification and hot gas clean-up. *Energy* 2013;53:221–9.
- [10] Dou B, Wang C, Chen H, Song Y, Xie B, Xu Y, et al. Research progress of hot gas filtration, desulfurization and HCl removal in coal-derived fuel gas: a review. *Chem Eng Res Des* 2012;90:1901–17.
- [11] Westmoreland PR, Harrison DP. Evaluation of candidate solids for high-temperature desulfurization of low-Btu gases. *Environ Sci Technol* 1976;10:659–61.
- [12] Jothimurugesan K, Adeyiga A. Advanced hot-gas desulfurization sorbents. *Adv Coal-Based* 1997.
- [13] Liang M, Xu H, Xie K. Bench-scale testing of zinc ferrite sorbent for hot gas clean-up. *J Nat Gas Chem* 2007;16:204–9.
- [14] Giuffrida A, Romano MC, Lozza GG. Thermodynamic assessment of IGCC power plants with hot fuel gas desulfurization. *Appl Energy* 2010;87:3374–83.
- [15] Sorgenfrei M, Tsatsaronis G. Design and evaluation of an IGCC power plant using iron-based syngas chemical-looping (SCL) combustion. *Appl Energy* 2013;113:1958–64.
- [16] Nolan PS. Flue gas desulfurization technologies for coal-fired power plants. *Coal-Tech 2000 int conf*; 2000. p. 1–13.
- [17] Schoubye P, Jensen FE. SNOX TM flue gas treatment for boilers burning petcoke. . . makes petcoke more attractive for power and heat generation. *Petcoke conf, Orlando, Florida, USA*; 2007.
- [18] Cau G, Tola V, Bassano C. Performance evaluation of high-sulphur coal-fired USC plant integrated with SNOX and CO₂ capture sections. *Appl Therm Eng* 2014.
- [19] Stanger R, Wall T. Sulphur impacts during pulverised coal combustion in oxy-fuel technology for carbon capture and storage. *Prog Energy Combust Sci* 2011;37:69–88.
- [20] White V, Torrente-Murciano L, Sturgeon D, Chadwick D. Purification of oxyfuel-derived CO₂. *Int J Greenh Gas Control* 2010;4:137–42.
- [21] Mochida I, Korai Y, Shirahama M, Kawano S, Hada T, Seo Y, et al. Removal of SO_x and NO_x over activated carbon fibers. *Carbon N Y* 2000;38:227–39.
- [22] Shah M, Degenstein N, Zafir M, Kumar R, Bugayong J, Burgers K. Near zero emissions oxy-combustion flue gas purification. 2010 NETL CO₂ capture technol., Pittsburgh, PA US; 2010.
- [23] Hamers HP, Romano MC, Spallina V, Chiesa P, Gallucci F, Annaland MvanS. Comparison on process efficiency for CLC of syngas operated in packed bed and fluidized bed reactors. *Int J Greenh Gas Control* 2014;28:65–78.
- [24] GS Software n.d.:<http://www.gecos.polimi.it/software/gc.php>.
- [25] Straub D. Chemical looping combustion – NETL operating experiences n.d.
- [26] EBTF, Anantharaman R, Bolland O, Booth N, van Dorst E, Ekstrom C, et al. European best practice guidelines for assessment of CO₂ capture technologies. <www.gecos.polimi.it/research/EBTF_best_practice_guide.pdf>; 2011.
- [27] Forero CR, Gayán P, García-Labiano F, de Diego LF, Abad a, Adánez J. Effect of gas composition in chemical-looping combustion with copper-based oxygen carriers: fate of sulphur. *Int J Greenh Gas Control* 2010;4:762–70.
- [28] De Diego LF, García-Labiano F, Gayán P, Abad A, Cabello a, Adánez J, et al. Performance of Cu- and Fe-based oxygen carriers in a 500 W_{th} CLC unit for sour gas combustion with high H₂S content. *Int J Greenh Gas Control* 2014;28:168–79.
- [29] Adánez-Rubio I, Abad A, Gayán P, García-Labiano F, De Diego LF, Adánez J. The fate of sulphur in the Cu-based chemical looping with oxygen uncoupling (CLOU) process. *Appl Energy* 2014;113:1855–62.
- [30] Dueso C, Izquierdo MT, García-Labiano F, de Diego LF, Abad A, Gayán P, et al. Effect of H₂S on the behaviour of an impregnated NiO-based oxygen-carrier for chemical-looping combustion (CLC). *Appl Catal B Environ* 2012;126:186–99.
- [31] Tian H, Simonyi T, Poston J, Siriwardane R. Effect of hydrogen sulfide on chemical looping combustion of coal-derived synthesis gas over bentonite-supported metal-oxide oxygen carriers. *Ind Eng Chem Res* 2009;48:8418–30.
- [32] Wang B, Yan R, Lee DH, Liang DT, Zheng Y, Zhao H, et al. Thermodynamic investigation of carbon deposition and sulfur evolution in chemical looping combustion with syngas. *Energy Fuels* 2008;22:1012–20.
- [33] Jerndal E, Mattisson T, Lyngfelt A. Thermal analysis of chemical-looping combustion. *Chem Eng Res Des* 2006;84:795–806.
- [34] Spallina V, Gallucci F, Romano MC, Chiesa P, Lozza G, van Sint Annaland M. Investigation of heat management for CLC of syngas in packed bed reactors. *Chem Eng J* 2013;225:174–91.
- [35] Gupta P, Velazquez-Vargas L, Fan L. Syngas redox (SGR) process to produce hydrogen from coal derived syngas. *Energy Fuels* 2007;2900–8.