Kinetics of H$_2$S removal using alkaline residue as in-bed sorbent in fluidized bed gasification of biomass and wastes

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ARTICLE INFO

ABSTRACT

The use of alkaline residue from the acetylene industry (carbide slag, CS) as in-bed sorbent to remove H$_2$S from syngas from biomass/waste fluidized bed (FB) gasification was investigated. Measurements were conducted in a laboratory FB applying differential conversion technique, tracking the reaction using both gas measurements and solid analysis. Apparent reaction kinetics was obtained, without external mass transfer limitations, for different gas mixtures containing CO$_2$, H$_2$O, CO, H$_2$ and CH$_4$, having relatively low H$_2$S concentration (500–1000 ppm). The addition of CO$_2$ and H$_2$O to an N$_2$-H$_2$-H$_2$S mixture showed that the reaction rate was reduced in the presence of these species. Varying the H$_2$ concentration between 7 and 14% in simple (N$_2$-H$_2$-H$_2$S) reactive gas mixtures did not affect the results, while both CO and H$_2$ potentially affected the reaction rate if also CO$_2$ was present in the gas. Other operating parameters, such as sorbent particle size, sulfidation- and calcination temperature also affected the CaO sulfidation rate, which increased with temperature between 800 and 900 °C and was enhanced by higher calcination temperature. Specific surface area and pore size distribution of the calcined CS was measured before and after the sulfidation reaction, showing that CS maintained a large fraction of its original pore volume even after most of the CaO had been converted into CaS. The sulfidation rate of calcined limestone was also measured for comparison showing that the reaction rate using CS was slightly lower, but similar to that using limestone, showing that CS is a promising alternative to conventional calcium-based sorbents for high temperature H$_2$S removal, contributing to promote the circular economy, while avoiding the current stacking of CS at the acetylene production sites.

1. Introduction

The air-gasification of urban wastes has shown numerous potential benefits compared to the incineration of these residues [1,2], but it presents some challenges, such as the presence of inorganic contaminants in the gas produced. H$_2$S content in gasification gas in processes treating raw fuels containing significant amounts of sulfur, such as waste fuels and coal can be high (typically well above 1000 ppm) [3]. Removal of H$_2$S is required to avoid corrosion or catalyst poisoning in downstream equipment, damage to turbines and gas engines during power generation, to reduce the SO$_2$ emissions in the final exhaust gas or sulfur content in generated products. H$_2$S removal is also necessary for the gasification gas obtained from the processing of fuels with relatively low sulfur content, such as biomass. For these processes, H$_2$S contents in the gas typically below 1000 ppm are reported [4], but values measured in

pilot/bench scale plants might be affected by measurement difficulties and interactions of H$_2$S with pipes and equipment walls [5]. Both supported and unsupported metal oxides have been tested for H$_2$S removal at low to medium temperature [6], but high temperature gas cleaning presents various advantages compared to cold applications. On the one hand, if the desulfurization is carried out at high temperature it can be conducted separately from the removal of other contaminants such as HCl, HN$_3$, heavy metals and tars which is an advantage from a process design perspective and, on the other hand, performing gas cleaning at high temperature helps improving the overall efficiency of the gasification process. Different metal oxides have been tested as medium to high-temperature desulfurization sorbents, such as zinc, manganese, copper, iron, and calcium oxides [4,7]. Among these materials those presenting the lowest cost and highest possible operation temperature are calcium-based sorbents. These solids can operate at high

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temperature, having the potential to be employed as in bed sorbents [8,9]. Other materials tested for high temperature H_2S removal, such as char from biomass and waste, have shown to be less effective compared to Ca-based sorbents [10]. For typical conditions in atmospheric gasification processes (temperature above 800 °C and CO_2 concentration below 25 %v) the $CaCO_3$ contained in Ca-based sorbents such as limestone and dolomite will decompose generating calcium oxide. Calcined limestone has shown to be more efficient for H_2S removal compared to the un-calcined solid [11,12]. This has been related to the porous solid structure that is generated when the calcium carbonate decomposes liberating CO_2. The reaction occurring when H_2S is removed using calcium oxide is:

$$CaO + H_2S \leftrightarrow CaS + H_2O \qquad (1)$$

Due to equilibrium limitations, in practical applications, the minimum H_2S concentration that can be achieved using calcium sorbents is in the order of 100 ppm [4]. This is not low enough for catalytic downstream applications but is useful as bulk H_2S removal method as well as for gasification applications with electricity production by burning the gas in an internal combustion engine. In these processes, if the moisture content and temperature of the gas are low enough, sufficient H_2S removal could theoretically be achieved from calcium sorbents alone.

Calcium sulfide is not a stable chemical suitable for disposal. Its stabilization is conducted through oxidation to generate $CaSO_4$, but this is not a straightforward operation. The process is highly exothermic and has several undesirable side-routes that yield SO_2 [13,14]. The difficulties of CaS stabilization are also present during the reduction of $CaSO_4$ occurring in in-situ sulfur capture in FB combustion. The (re) oxidation of CaS to $CaSO_4$ is a complicating factor in these processes, since CaS is rather stable under the reactor conditions. The thermodynamics of CaS stabilization depends on the partial pressures of O_2 and SO_2, as well as temperature. The best results are obtained around 800–900 °C, since higher temperatures give significant SO_2 release. Several industrial solutions have been implemented. A first example is the U-GAS process [15], a gasifier with an integrated zone for the conversion of calcium sulfide to stable calcium sulfate environmentally acceptable for disposal that could be discharged from the gasifier along with the agglomerated ash. Another process option for CaS stabilization is based on two fluidized bed reactors operating at 1150 °C and 850 °C, respectively. SO_2 that is released during the first stage is recaptured in the second reactor [16].

Apart from the stabilization of CaS, its application to produce elemental sulfur has also been investigated [17,18].

The use of dolomite and limestone as H_2S sorbents has been extensively studied [11,19–23], however, many of these works have focused on conditions representative of coal gasification applications, employing high H_2S concentration in the gas (typically above 5000 ppm) and sometimes also high total pressures. Many studies have quantified the sulfidation rate using gravimetric analysis, without measuring the outlet gas composition. Depending on the operating conditions, sorbent properties, particle size and degree of conversion, the rate of reaction (1) may be influenced by pore diffusion, chemical kinetics as well as product layer diffusion [11,20].

In gasification applications, the gas cleaning systems comprise a large portion of the operation costs and, to reduce these expenses, it is necessary to find new sorbents that are cheaper compared to conventional calcium sorbents. This is especially important since the regeneration of Ca-based sorbents is not practically achievable, limiting them to one use [24]. A very cheap alternative calcium sorbent that has gained increasing interest in recent years is carbide slag (CS), which is an alkaline residue generated in the acetylene production process, using calcium carbide as raw material. The acetylene is consumed mainly for PVC production, which has increased in recent years. CS takes the form of a slurry with a high moisture content, typically between 60 and 80%, whose solid fraction is composed of mainly $Ca(OH)_2$, smaller amounts of

$CaCO_3$ and other minor species. CS cannot be disposed of without serious harm to the environment, mainly due to its high alkalinity and this has led to stacking of CS at the acetylene production sites. Therefore, it is urgent to find a suitable application for this residue and to achieve its transformation into a safe and stable product. The $Ca(OH)_2$ contained in CS dehydrates into CaO if heated to temperatures above approximately 350 °C and could then be used as a substitute for calcined limestone or dolomite in medium to high temperature gas cleaning processes. The application of CS for this purpose would contribute to the creation of a circular economy, but it is still in the research phase and only a small number of studies have been conducted. The application of CS for CO_2 capture [25,26], SO_2 removal by both dry and wet methods [27,28] and as HCl sorbent [29] have been investigated. Its use as H_2S sorbent has been tested with the aim of assessing the effect of using sorbent subjected to different numbers of calcium looping cycles [30], but there is a need for studies measuring the kinetics of the reaction to enable comparison with conventional Ca-sorbents and assessing the influence of different operating parameters, as for example, gas composition, temperature, and sorbent particle size.

In this work, the use of a CS from an acetylene production plant located in Spain for high temperature H_2S removal is investigated. The reaction rates under different conditions have been determined measuring both the outlet gas composition and analyzing the solid product. The experimental method has been designed to allow for determination of apparent kinetics in the absence of external mass transfer limitations, that can be useful for the design of continuous gas cleaning systems using CS as H_2S sorbent. Gas conditions applicable to gasification applications have been applied i.e. relatively low H_2S concentration (500–1000 ppm) and complex gas mixtures containing H_2, CO_2, H_2O, CO and CH_4. The influence of the concentration of different gas species on the reaction rate has been assessed, as well as the influence of reaction temperature, calcination temperature and sorbent particle size. The results obtained using CS have been compared to those measured using limestone of the same size to assess the applicability of CS as an alternative to conventional calcium sorbents.

2. Material and methods

2.1. Material

In this work, two calcium sorbents were tested. The primary aim was to test the use of the carbide slag (CS) (also called acetylene sludge) coming from an acetylene production plant in Spain, but also a limestone material was tested for comparison. For both solids, different particle sizes were studied, CS and limestone particles of sizes < 35 μm and 44–74 μm were tested and additional experiments were conducted using 160–200 μm CS particles.

The carbide slag was received in the form of a sludge made up of approximately 70% water. The solid employed in the desulfurization experiments (in the following referred to as CS), was obtained by eliminating the water from the sludge in a two-step process: 1) decantation during 24 h, where 10% of supernatant water was removed, 2) air drying at 45 °C for 30 h, obtaining a 26.74% of solid fraction (on a weight basis). A semi-quantitative X-ray diffraction analysis of this material resulted in the following composition: 85% $Ca(OH)_2$ (portlandite) and 15% $CaCO_3$ (calcite), the XRD patterns are included as supplementary material.

XRF analysis was employed to measure the composition of major elemental constituents of both CS and limestone and the data are given in Table 1. The loss on ignition of the limestone, given in Table 1, is in accordance with the mass of CO_2 contained in the sample assuming that all the calcium is in the form of carbonate and for CS it agrees well with the distribution of the calcium between $Ca(OH)_2$ and $CaCO_3$ given by the XRD analysis. Apart from the differences in the nature of the calcium compounds, other major differences between the two samples are observed to be that the CS has a significantly higher sulfur content, while

Table 1

Content of major components in the CS and limestone employed in this study expressed in % weight of the solid sample (data obtained using PANanalytical ZETIUM Minerals analyzer).

Component	Carbide slag (CS)	Limestone
CaO	67.84	52.93
SiO_2	2.27	2.73
SO_3	0.82	0.03
Al_2O_3	0.94	0.55
Fe_2O_3	0.24	0.47
MgO	0.10	0.33
Na_2O	0.06	0.01
TiO_2	0.03	0.03
SrO	0.02	0.02
Mn_3O_4	0	0.01
K_2O	0	0.10
P_2O_5	0.02	0.02
V_2O_5	0.01	0
SrO	0.02	0.02
CuO	0.01	0
HfO	0.01	0
LOI*	27.68	42.79

*Loss on ignition.

the limestone contains comparably more Fe and Mg.

Due to the cohesive nature of CS particles, dry powder laser diffraction method was selected for particle size distribution measurement. The result from this analysis is shown in Fig. 1.

Fig. 2 shows the results of a DSC-TGA analysis of the carbide slag sample carried out under air flow and with a heating rate of 15 °C/min.

It can be observed that the main mass loss occurs between approximately 400 and 450 °C, caused by the decomposition of $Ca(OH)_2$ to give CaO. The figure also shows a smaller mass loss occurring at approximately 600–700 °C, related to the decomposition of $CaCO_3$. No significant variation in sample mass occurs above 850 °C. The DSC curve has two negative peaks representing the endothermic decomposition processes of $Ca(OH)_2$ and $CaCO_3$. The heat flow curve also shows an exothermic process occurring without any detectable mass loss at temperatures between approximately 850 and 1000 °C that could be related to a rearrangement of the crystalline structure of CaO.

2.2. Experimental setup

Fig. 3 is a schematic representation of the experimental setup employed. The test rig consists of a vertical cylindrical quartz reactor with an inner diameter of 32 mm, surrounded by an electrical oven. The reactor is equipped with a porous plate that supports the solids inside the vessel and serves as a gas distributor. A thermocouple is situated inside
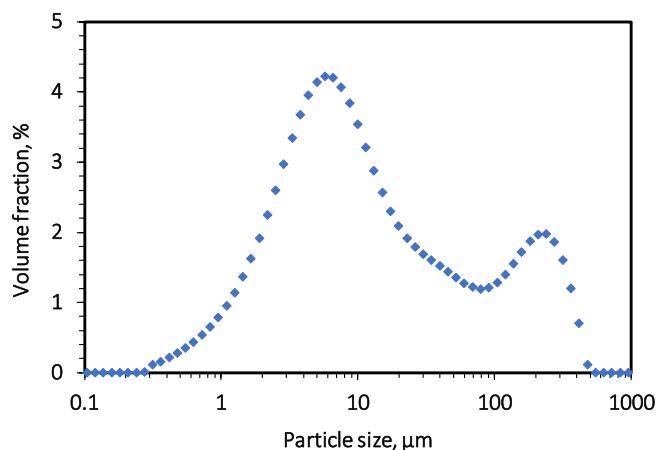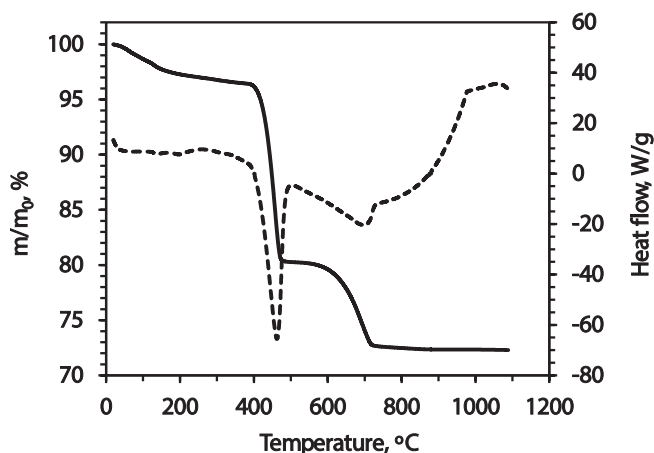
Fig. 2. Results of a TGA-DSC analysis of the CS sample tested, TGA results, relative mass (g/g of initial sample) (—) and DSC results, heat flow (– – –) (data obtained using TA Instruments SDT Q600II).

the reactor at approximately 4 cm above the static bed height of the solids and is employed to control the reaction temperature. The part of the thermocouple that is located inside the reactor is protected by a protecting sheath made of quartz, to avoid direct contact between the gas flow and the thermocouple. Different gas bottles and mass flow controllers were employed to generate the gas mixtures fed to the reactor. The gas bottles available contained: (i) mixture of 3000 ppm of H_2S in N_2), (ii) mixture of 20% H_2 in N_2, (iii) pure CO_2, (iv) pure N_2, and (v) mixture of 25% CO_2, 25% CO and 5 % CH_4 in N_2. Some experiments were also carried out to study the effect of adding steam to the feed gas. The steam was generated by feeding a controlled flow of water into the heated part of the reactor a few centimeters below the distributor plate, using a syringe pump. The composition of the exit gas was measured online using an UV apparatus ABB Limas11 for H_2S measurements, IR methods for measuring CO, CO_2 and CH_4 and thermal conductivity for H_2 concentration.

2.3. Experimental conditions

The reactor operated at atmospheric pressure and the sulfidation kinetics experiments were conducted varying temperature applied during both sorbent calcination and subsequent CaO sulfidation, gas composition, nature of sorbent, sorbent particle size and gas velocity in the reactor.

The different experimental conditions employed are summarized in Table 2, where the concentrations of different gas species are expressed on a volume basis.

The CaO samples employed in the sulfidation measurements were generated in-situ, by heating the solid sorbent under air flow up to a selected preheating temperature (referred to as calcination temperature). The duration of the desulfurization measurements varied between 30 and 90 min. Some of the experimental conditions were tested more than once to check the repeatability of the results and, additionally, some conditions were repeated, but with a different test duration. In total more than 25 desulfurization experiments were conducted.

To enable proper tracking of the reaction progress through measurement of the outlet H_2S concentration but still guaranteeing quasi-differential tests, small batch size of sorbent was used, approximately 30 mg. To ensure even distribution of the material in the reaction zone and to facilitate the loading of material into the reactor, the sorbent was mixed with an inert solid, during kinetics measurements. Finely crushed and sieved quartz particles were employed as bed material to avoid any possible interactions with H_2S, being this a very reactive gas, especially at high temperature. Two different sizes of quartz particles were used, one which was a fine powder of similar size as that of the sorbent and
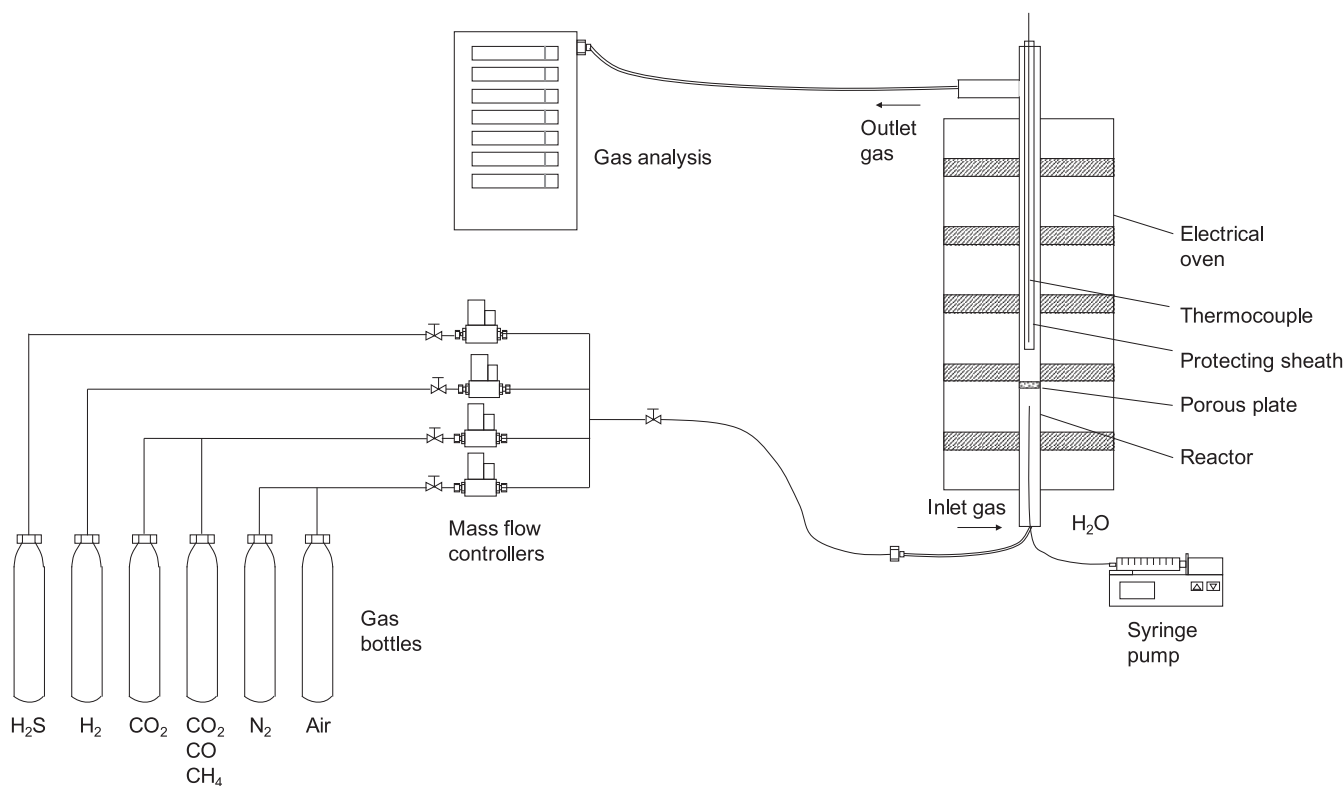
Fig. 1. Particle size distribution of CS measured by dry powder laser diffraction method (analytical equipment employed: Mastersizer 2000).

Fig. 3. Experimental setup.

Table 2
Summary of experimental conditions tested during CaO sulfidation measurements. For each parameter, the most frequently applied condition is underlined.

Parameter	Values tested
Sorbent	Carbide slag (CS), limestone
Sorbent particle size, μm	As received, <32, 44–74, 160–200
Sulfidation temperature, °C	800, 850, 900
Calcination temperature, °C	800, 900
Gas superficial velocity, m/s	0.12, 0.18, 0.24
H_2S inlet concentration, ppm	500, 1000
H_2 concentration, %	7.7, 10.6, 14.2
CO_2 concentration, %	0, 11.2, 11.8, 16.2
CO concentration, %	0, 11.2
H_2O concentration, %	0, 15

one comprised of larger particles of 1–2 mm. The mass of inert material used in the experiments was approximately 5 g for the fine quartz particles and 10 g for the larger particles, giving a total static bed height of approximately 25 mm.

2.4. Experimental procedure

Before each experiment the reactor was cleaned thoroughly with water to eliminate any residue from the previous test run. The clean reaction vessel was placed inside the oven and dried under air flow at approximately 150 °C. The material was then loaded into the reactor. First, a fraction of large particles was added to protect the distributor plate from being clogged by fine powder at the beginning of the experiment. The sorbent was weighed into the same glass as the fine quartz particles and the whole content of this glass was poured into the reactor, to make sure that the whole batch of sorbent fell into the reaction vessel. The rest of the large quartz particles were then added, and the reactor exit was connected to the sampling line. At this point the unit was heated at a rate of approximately 20 °C/min up to the selected calcination temperature (800 °C for most experiments, see Table 2),

which was maintained for 15 min and then, if necessary, heated (or cooled by turning off the oven) to reach the designated sulfidation temperature. The feed gas was then switched to N_2 to purge all the O_2 from the reactor and the flows of the different gases (except H_2S) to be employed (N_2, N_2-H_2 mixture, CO_2, CO_2-CO-CH_4-N_2 mixture, steam, etc.) were adjusted. The experiment started when H_2S was introduced with the feed stream and the feeding of H_2S was maintained for the set test duration and was then interrupted. Afterwards the oven was switched off and the reactor was cooled down under N_2 flow. The cool reactor was opened, the content was carefully collected in a glass and the vessel was rinsed with distilled water to make sure that virtually all the solids were recovered. The collected material was then analyzed using iodometry to determine the total amount of calcium sulfide formed. This was done to enable comparison with the results from the online H_2S concentration measurements. To measure the amount of sulfide, the solids were dissolved in acid and then 10 ml of a 0.1 N standardized iodine solution was added. The excess iodine was then quantified using titration with a 0.05 N sodium thiosulfate solution that was prepared using analytical grade solid and checked against the iodine solution, before each analysis. The general accuracy of the iodometric CaS analysis method was tested by analyzing samples of pure analytical grade CaS pre-weighed using a precision balance. A dedicated experiment was also carried out to confirm that the use of the inert bed material in the reactor did not affect the result of the sulfide analysis.

2.5. Data treatment

The extent of the reaction of H_2S with the two calcium sorbents is determined from the time dependent consumption of H_2S inside the reactor. For each test run a blank experiment was conducted using the same feeding gas and reactor temperature, as well as the same amount of inert material, but without any Ca-sorbent in the reactor. At any time, the amount of H_2S reacted is quantified from the difference between the H_2S concentration measured in the blank experiment and in the one with Ca-sorbent in the reactor. The use of blank experiments allowed to

determine the solid conversion rate without possible effects of dispersion in the gas exit line or gas phase reactions taking place in the reactor. Prior to the kinetic measurements, cold experiments were conducted to characterize the movement of solids in the bed, and it was observed that, at the gas velocities employed, the bed was fully fluidized with continuous movement of the solids and after each experiment uniform distribution of sorbent and quartz particles of different size was observed throughout the bed. Based on these observations and given the small sample size, uniform conversion of the sorbent particles along the reactor was assumed during the kinetics measurements. The results of blank experiments with and without bypassing the reactor, showed that the gas flow could be approximated by plug flow and this assumption was employed to determine kinetic parameters from the quasi-differential sulfidation tests.

Fig. 4 shows a comparison between the final CaO conversion obtained using the two measurement methods described above: i) from the time dependent H_2S exit concentration and ii) from the iodometric titration analysis of the final solid sample (see Section 2.4).

The data represented in Fig. 4 show reasonable agreement between the two measurement methods and indicates that the experimental method applied here is valid. The results presented in the following section are those obtained from the H_2S exit concentrations, which enables to study the evolution of the reaction through different degrees of solid conversion. The abnormally large deviation between the final conversion measured using the two methods, observed for one of the experiments (see Fig. 4), will also be discussed in the following section.

3. Results and discussion

3.1. Preliminary studies

3.1.1. Gas phase reactions

A preliminary study was conducted to assess the extent of gas phase reactions inside the reactor for the experimental conditions studied. It was observed that if a gas containing only H_2S and N_2 was fed to the reactor there was an observable difference between the outlet and inlet concentrations of H_2S, but that if H_2 was added to the gas, this effect could be avoided almost completely. It is well known that H_2S can decompose giving sulfur and H_2 at high temperature, but that the addition of a low concentration of H_2 can significantly reduce this reaction, due to the approach to equilibrium [31]. Also, the influence of adding CO_2 and CO to the gas was studied and the results show that a CO_2 concentration of 10–15% can lead to significant reduction of H_2S,

especially above 800 °C, but the addition of equal concentration of CO upon that had no observable influence. It was also observed that the influence of CO_2 was much less pronounced when also H_2 was present in the gas. The outlet gas was scanned using a mass spectrometer to identify possible products of the reaction between CO_2 and H_2S and a clear peak at a molecular mass of 60 was observed, caused by COS and in addition some smaller peaks at 76 and 78 were detected, possibly indicating some CS_2 formation. The formation of COS when adding CO_2 to the gas has been observed in previous works [32–35]. The addition of different concentrations of H_2O or CH_4 did not have any effect on the outlet H_2S concentration. No influence of gas phase reactions on the concentrations of gas species other than H_2S was detected, but if a significant amount of sorbent was present in the reactor, a catalytic effect on the water gas shift reaction (WGSR) was observed. For example, when feeding a gas mixture with 11–12% of both CO_2 and H_2 with 1.5–2 g of calcined CS inside the reactor, 25–30% of the inlet CO_2 reacted with H_2 to give CO. No such effect was observed during the kinetics measurements, since the mass of sorbent employed was very small, only≈30 mg. The catalytic effect of calcium sorbents on the WGSR has been observed previously [32]. Given the observations described above, it was decided to add a certain concentration of H_2 to the feed gas during all the experiments, to minimize the extent of gas phase reactions. In this way, the effects of gas phase interactions could be avoided, when no CO_2 was fed in the gas, but when CO_2 was present, the difference between inlet and outlet concentrations of H_2S, due to gas phase reactions, was about 5–6%. This was considered in the data treatment method applied, as has been discussed in section 2.5.

3.1.2. Physical properties of the sorbents

Dedicated experiments were conducted to generate samples for analysis of specific surface area and pore size distribution of the calcined sorbents, both before and after reaction with H_2S. During these tests 1.5–2 g of sorbent was added to the reactor, without any inert bed material, and the calcination was carried out under air flow using the same method as for the desulfurization kinetics measurements. For CS two different calcination temperatures were employed, while limestone was calcined only at 800 °C. To obtain a sample of CaS generated from CS, the sorbent was first calcined at 800 °C and then sulfided in an H_2-H_2S-N_2 mixture up to a conversion of 75%. Table 3 shows the results of N_2 physisorption analysis of the different samples. For the analysis of calcined CS and limestone results measured for two samples generated under identical conditions are shown, indicating reasonable repeatability.

The samples shown in Table 3 were also analyzed using mercury intrusion porosimetry. The pore size distributions of the different samples are shown in Fig. 5. Good repeatability was obtained for samples generated from the same material and under the same conditions, so for better visualization of the results, only one sample is shown for each condition.
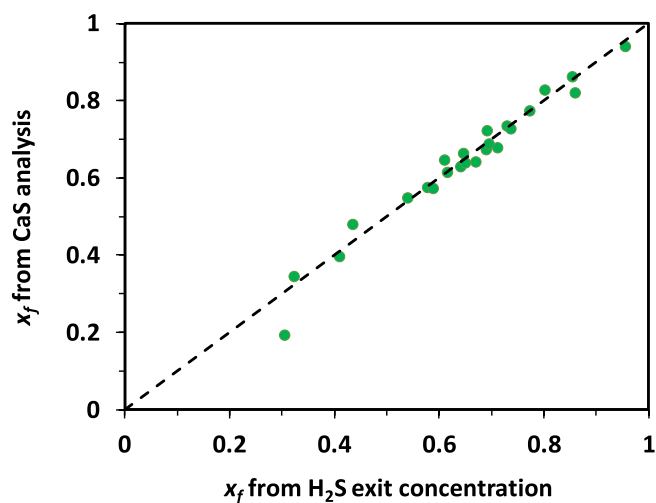

Fig. 4. Comparison between final CaO conversion (x_f) of different experiments measured using: i) the time dependent H_2S exit concentration and ii) iodometric analysis of the solid.

Table 3
Results of the nitrogen physisorption analysis (data obtained using Micromeritics ASAP 2420).

| Initial material	Sample generation method	BET surface area, m²/g	Pore volume, cm³/g	Average pore size, nm
Carbide slag	Calcination at 800 °C	23.68; 21.33	0.169; 0.167	33.08; 29.77
Carbide slag	Calcination at 900 °C	13.98; 16.37	0.0543; 0.0556	18.61; 15.66
Limestone, 44–74 μm	Calcination at 800 °C	8.08; 10.82	0.070; 0.0869	35.86; 32.10
Carbide slag	Calcination at 800 °C and sulfidation until ≈ 75% conversion	19.14	0.113	26.38
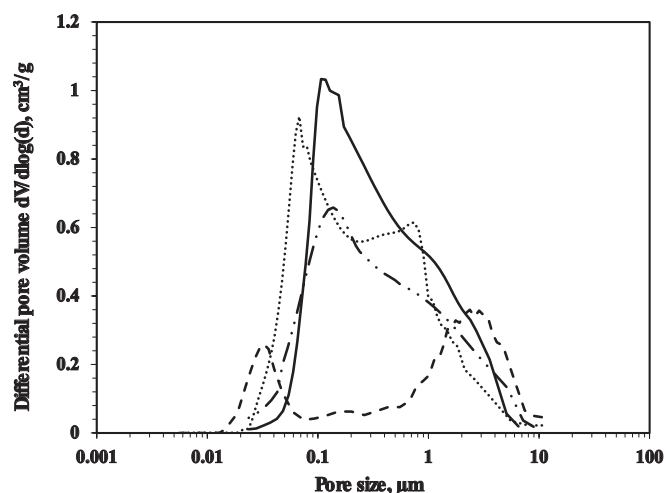
Fig. 5. Pore size distribution measured by mercury penetration porosimetry, CS calcined at 800 °C (—), and at 900 °C (●●●●), limestone calcined at 800 °C (– – –), CS calcined at 800 °C and then partially sulfided to a conversion of 75% (–●●–) (analytical equipment employed: Quantachrome 3G).

The calcined CS shows a widespread and continuous pore size distribution between 7 nm and 7 μm. For calcined limestone a bimodal distribution was obtained, similar to that of calcines studied in previous works, but under different operating conditions [20,36]. It can be observed that the total pore volume is larger for the sample obtained from CS compared to limestone, as was also shown from the results of the N₂ adsorption.

The results from the N₂-adsorption indicate a substantial reduction in pore volume with increasing calcination temperature, but this large difference is not evident from the pore size distributions shown in Fig. 5 and the Hg porosimetry analysis gave very similar results of intruded volume for both samples. The data represented in Fig. 5 show that the distribution of pores is displaced toward smaller sizes as the calcination temperature increases. The peak pore size for the sample generated at 800 °C was approximately 0.11 μm and the peak size for CS calcined at 900 °C was around 0.06 μm.

The results of the partially sulfided sample show that the total pore volume decreases to some extent due to the sulfidation reaction, but that the sample still maintains a substantial fraction of its original pore volume and specific surface area after 75 % of the original CaO has reacted. The reduction of pore volume occurs almost evenly along the range of pore sizes between 90 and 2000 nm. It is also seen that the fraction of pores smaller than 50 nm (mesopores) increases due to the reaction, which can be expected as the size of larger pores is reduced. The pore structure of the spent H₂S-sorbent is an important aspect since the CaS formed needs to be stabilized before its final disposal, as has been discussed in the introduction.

3.2. Results of CaO sulfidation experiments and discussion

3.2.1. Influence of H₂S concentration

To study the influence of H₂S concentration, experiments were conducted at 800 °C using CS without particle size separation and N₂-H₂-H₂S mixtures as feed gas. The H₂ concentration was kept stable at 7.7%, while two different H₂S inlet concentrations were tested: 500 ppm and 1000 ppm. Fig. 6 shows the conversion versus time curves measured for the two H₂S concentrations studied. It was observed that the experimental results agreed well with first order kinetics with respect to H₂S concentration and a simple expression for the apparent reaction kinetics was proposed:
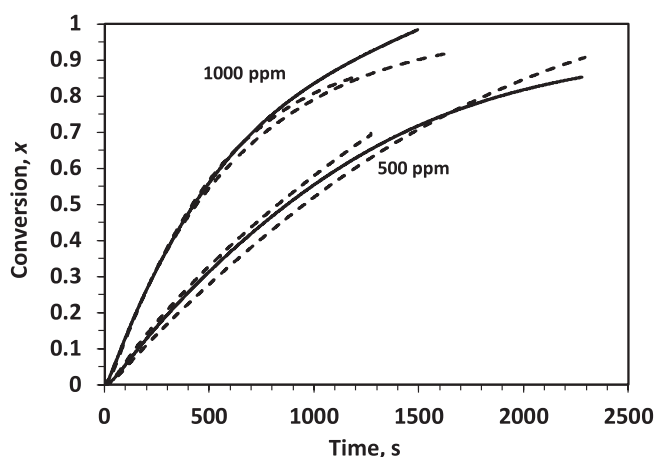
$$R(x) = k_{app}(x)P_{H_2S,\infty} \tag{2}$$

Fig. 6. CaO conversion as a function of time for CaS (without particle size separation) sulfidation measurements carried out at 800 °C in N₂-H₂-H₂S mixtures with H₂ concentration of 7.7% volume and two different H₂S inlet concentrations, 500 and 1000 ppm, measured experimentally (– – –) (two experiments are shown for each H₂S concentration) and calculated using an average value of $k_{app}(x)$(—).

Being x the degree of conversion of the solid calculated as the mol of Ca reacted/total mol of Ca in the sample and $R(x)$ the observed reaction rate expressed in $mol/(s\ kg_{CaO})$, k_{app}, the apparent kinetic constant, expressed in $mol/(s\ kg_{CaO}\ atm)$ and $P_{H_2S,\ \infty}$ the partial pressure of H₂S, expressed in atm. The subindex *app* is employed to point out that it is an apparent kinetic constant. The values of $k_{app}(x)$ at different degrees of conversion are not dependent on the H₂S concentration but will change if other experimental parameters such as temperature, sorbent nature, particle size and concentrations of other gas species such as H₂, CO₂, H₂O and CO are modified. As will be discussed in following sections, the sulfidation rate (and thus also $k_{app}(x)$) is usually affected by intraparticle mass transfer limitations even for small particle sizes. The use of $k_{app}(x)$ is a useful approach for assessing the influence of different parameters, since the H₂S concentration in the reactor might vary in different experiments with equal H₂S inlet concentration (as has been discussed in previous sections), due to the existence of gas phase reactions or small differences in the inlet H₂S volume fraction occurring in some cases due to the different gas mixtures produced using mass flow controllers.
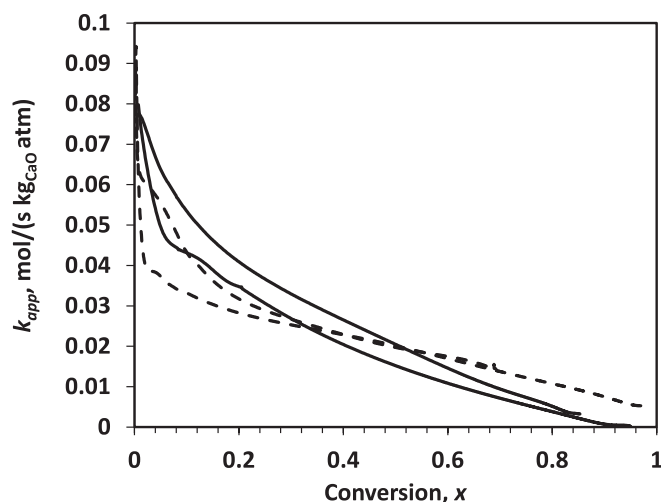

Fig. 7. Apparent kinetic parameter, $k_{app}(x)$, $mol/(s\ kg_{CaO}\ atm)$ (see equation (2)) obtained from measurements carried out at 800 °C, using CS without particle size separation in N₂-H₂-H₂S mixtures with H₂ concentration of 7.7% volume and H₂S inlet concentrations of 500 ppm (– – –) and 1000 ppm (—).

Fig. 7 shows the $k_{app}(x)$ as a function of the degree of conversion, x, measured during experiments using N_2-H_2-H_2S mixtures with H_2S inlet concentrations of 500 ppm and 1000 ppm.

The results show that similar values of k_{app} are obtained for the two H_2S concentrations studied, showing that the assumption of first order kinetics is acceptable, within this range of H_2S concentration, in agreement with previous works [20–22]. Based on these results, an average k_{app} (x) function for experiments using N_2-H_2-H_2S mixtures, was calculated, and will be employed in the following to compare with results obtained using complex gas mixtures. It can be observed that the kinetic constant decreases rapidly with increasing CaO conversion at the beginning of the reaction, up to about 10% conversion, and then the decrease becomes significantly slower for higher x values. For conversion degrees of 10% and higher, k_{app} (x) values measured in N_2-H_2-H_2S mixtures agree well with the simple empirical equation: k_{app} $(x) = 0.0437(1-x)^{1.164}$, showing that during most of the reaction the rate is approximately first order with respect to the solid conversion. The conversion versus time curves calculated for 500 and 1000 ppm of H_2S using the average k_{app} (x) function are included in Fig. 6 and it can be observed that they show good agreement with experimental curves, at least for conversion degrees of up to 0.8–0.9.

3.2.2. Influence of temperature

For assessing the effects of changing temperature experiments were conducted varying the sulfidation temperature, but for fixed calcination conditions set at 800 °C. Another experiment was carried out to assess the influence of the calcination temperature, by conducting the calcination at 900 °C and then performing the kinetics measurement at 800 °C. All these experiments employed CS of size <32 μm and N_2-H_2-H_2S mixture with H_2S inlet concentration of 500 ppm and H_2 concentration of 7.7%. Fig. 8 represents the apparent kinetic constant obtained during the experiments carried out at different sulfidation and calcination temperatures. The results show higher reaction rate with increasing sulfidation temperature and a certain influence of calcination temperature, with a slight increase in reaction rate as this temperature is raised, (at least in the initial stages of reaction, for CaO conversion of up to 0.45–0.50). The solids calcined at 800 °C and 900 °C have different specific surface are and pore size distributions (see section 3.1.2), so they could be expected to present different reactivities. The results presented here show that the sample with the highest reactivity is the one generated at 900 °C, even though it has lower porosity and specific surface area, according to N_2-adsorption analysis.
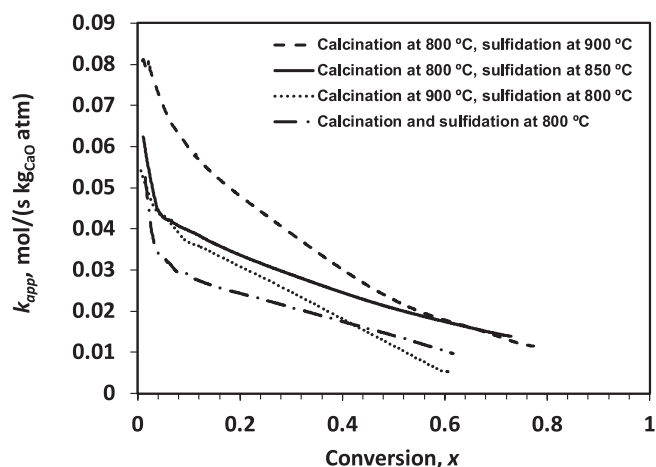
It is not likely that the differences between the two samples are related to a pure sintering process, since the TGA-DSC curves indicate that the alterations occurring in this temperature range are exothermic. The influence of calcination temperature has been studied before using limestone as sorbent by Efthimiadis et al. [21], who preheated the sample under CO_2 flow before calcination, to control the temperature at which the decomposition of the $CaCO_3$ occurred. They observed increased sulfidation reactivity with increasing calcination temperature and it was argued that a porous structure with higher degree of connectivity between pores was formed when calcination occurred at higher temperature.

3.2.3. Influence of gas velocity and particle size

To assess the influence of mass transfer limitations on the reaction rate, experiments were carried out varying the fluidizing gas velocity and the solid particle size (maintaining all the other operating conditions constant). It was found that the gas velocity had no observable influence on the measured reaction rates, indicating that external mass transfer limitations are not significant, for the gas velocities tested (see Table 2). The initial solid particle size, on the other hand, was observed to influence the rate of CaO sulfidation significantly. Fig. 9 shows the CaO conversion versus time for experiments measured using CS of different initial size and using a H_2S feed concentration of 500 ppm.

The results in Fig. 9 clearly show that the reaction rate is influenced by the initial sorbent particle size, indication that the extent of intraparticle mass transfer limitations is significant, within the particle size range studied. The influence of interparticle diffusion on the reaction rate has been observed in previous works [20,21].

On the other hand, comparing the results obtained using particles of size below 32 μm and without particle size separation, they were observed to be very similar. This can be explained by looking at the particle size distribution of the CS (see Fig. 1), which shows that the fraction of particles of size larger than 32 μm is rather small, so it seems that removing these particles has small influence on the reaction rate. Thus, for simplicity, for most experiments, when studying the influence of gas composition, CS without particle separation has been employed. The results in Fig. 9 show that the reaction rates measured here (even for the largest particles studied) are more than ten times higher than those reported by Hu et al. [30] using a carbide slag of similar chemical composition and the same H_2S inlet concentration (500 ppm). These differences may be related to differences in physical properties of the CS samples tested or in the experimental method employed.
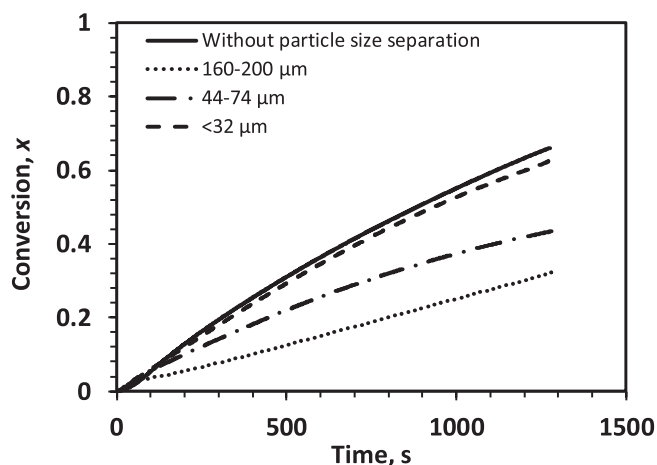

Fig. 8. Apparent kinetic parameter, $k_{app}(x)$, $mol/(s\ kg_{CaO}\ atm)$ (see equation (2)) in, N_2-H_2-H_2S mixture with H_2S inlet concentration of 500 ppm and H_2 concentration of 7.7% at different reactor temperature: calcination temperature of 800 °C and three different sulfidation temperatures, 900 °C, 850 °C and 800 °C; calcination temperature of 900 °C and sulfidation temperature of 800 °C. The solid employed was CS of size <32 μm.

Fig. 9. CaO conversion as a function of time for sulfidation measurements carried out at 800 °C in N_2-H_2-H_2S mixtures with H_2 concentration of 7.7% volume and H_2S inlet concentration of 500 ppm, for different initial particle sizes of CS: <32 μm, 44–74 μm, 160–200 μm and without particle size separation.

3.2.4. Influence of sorbent nature

Fig. 10 shows a comparison of the results obtained for experiments conducted with limestone and CS of two different particle sizes.

It can be observed that also for the sulfidation of calcined limestone the reaction rate varies with sorbent particle size. A comparison of the results obtained using the same particle size, but sorbents of different nature show that although the reaction rates of the two sorbents (CS and limestone) are comparable, the fastest rates are obtained using limestone, even though the calcined CS has both larger specific surface area and total pore volume compared to calcined limestone (see Section 3.1.2). The calcined limestone, on the other hand, contains a more significant fraction of large mesopores that might favor the intraparticle diffusion of reactants. Wu et al. [37] tested three CaO samples of similar BET surface area, but different pore size distribution and found that the samples with a significant fraction of large micropores gave a substantially higher reaction rate. Nimmo et al. [38] also observed higher reaction rate of CaO samples with larger pore size compared to other samples that had higher specific surface area. Nevertheless, this aspect is not expected to explain solely the difference between the two sorbents as also differences in chemical composition and CaO crystalline structure may affect the results. Hartman et al. [36] found large differences in reactivity between calcines prepared from different limestones but with similar porosities and chemical composition. They correlated the variations in reactivity with the crystallite grain size of the original limestones, being the samples with the smallest grain size the most reactive. Similar observations were made by Eftimiadis et at., [21].

3.2.5. Influence of H_2 concentration

Although most of the tests conducted here used H_2 concentration of 7.7%, the actual concentration of this species in gasification processes might vary depending on the operation conditions and therefore a higher H_2 concentration in the inlet gas of 14.2%, was also tested to check the influence of this parameter. For this purpose, in Fig. 11 the results of experiments conducted with 14.2 % H_2 are compared with those using 7.7% (other conditions equal: 800 °C and 500 ppm of H_2S, being the rest N_2) showing very similar kinetics, which is qualitatively in agreement with previous works, although direct comparison is not possible: Lin et al. [12], found a small reduction of the reaction rate when varying the H_2 concentration in the range of 0–2.6% in a gas containing only N_2, H_2S and H_2; Heesink and Swaaij [39] observed a slight inhibition effect in the temperature range of 500–600 °C, but for an H_2S partial pressure 40 times higher than that studied here; Chauk
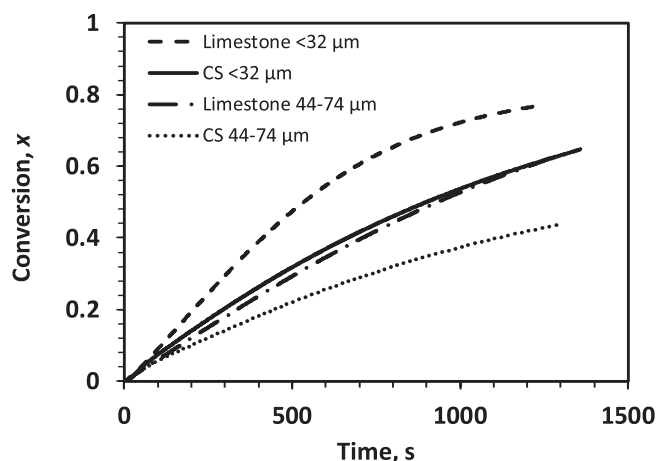

Fig. 11. Apparent kinetic parameter, $k_{app}(x)$, $mol/(s\ kg_{CaO}\ atm)$ (see equation (2)) obtained from measurements carried out at 800 °C in N_2-H_2-H_2S mixtures with H_2S inlet concentrations of 500 ppm and H_2 concentration of 7.7% volume (– – –) and 14.2% volume ppm (—).

et al., [22] also studied the sulfidation of CaO at high pressure and found that the increase in H_2 concentration at H_2/H_2S molar ratios above 15 (which is well below the values employed here), did not have a significant influence.

3.2.6. Influence of CO_2, CO and H_2O concentration in the bulk gas

The influence of adding CO_2, CO and H_2O was investigated since, in addition to H_2, these are the main gas species present in gasification gas. Firstly, experiments were carried out using 500 ppm H_2S inlet concentration and 7.7 % vol H_2, 11.3 % vol of both CO and CO_2 and 2.3 % CH_4, being the rest N_2. Additionally, two experiments were conducted adding only CO_2 (apart from N_2, H_2 and H_2S), to assess the influence of the addition CO_2 alone. In these two experiments two different CO_2 concentrations were investigated, 11.8% and 16.2%. The values of $k_{app}(x)$ obtained using the different gas mixtures containing CO_2 are represented in Fig. 12, that also includes the results from tests using N_2-H_2-H_2S mixture for comparison.

The results from Fig. 12 clearly indicate that the rate of the CaO

Fig. 10. CaO conversion as a function of time obtained at 800 °C in N_2-H_2-H_2S mixture with H_2S inlet concentration of 500 ppm and H_2 concentration of 7.7% and using two different sorbents and two different initial sorbent particle sizes: limestone of sizes <32 μm and 44–74 μm and CS of sizes <32 μm and 44–74 μm .
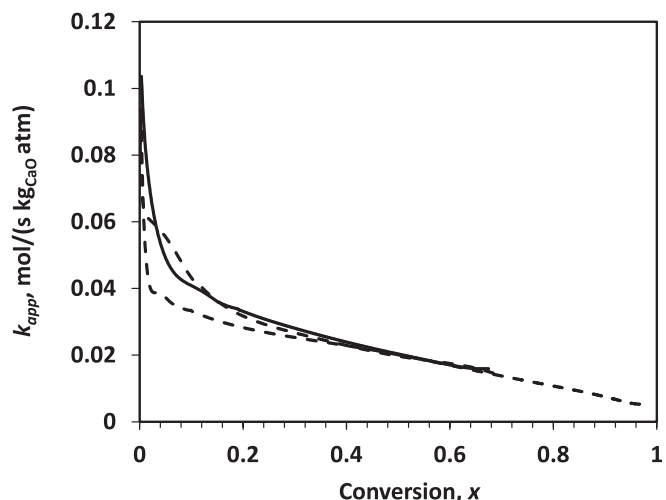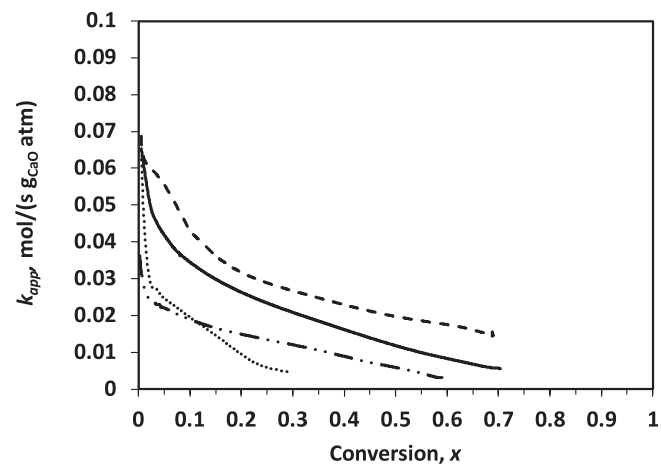

Fig. 12. Apparent kinetic parameter, $k_{app}(x)$, $mol/(s\ g_{CaO}\ atm)$ (see equation (2)) obtained from measurements carried out at 800 °C in different mixtures having H_2S inlet concentration of 500 ppm, N_2-H_2-H_2S (7.7% H_2) mixture (– – –), N_2-H_2-H_2S-CO-CO_2-CH_4 mixture (7.7% H_2, 11.3% CO, 11.3% CO_2, 2.3% CH_4) (—) and two N_2-H_2-H_2S-CO_2 mixtures: i) (11.8% CO_2, 12.1 % H_2) (–••–); ii) (16.2% CO_2, 10.5% H_2)(••••).

sulfidation reaction decrease with the presence of CO_2 in an N_2-H_2-H_2S gas mixture. It was also observed that the experiment with 16.2% of CO_2 in the feed gas, the final CaO conversion measured using iodometric analysis of the solids is significantly lower than the result obtained from the H_2S exit concentration, showing this test a much greater deviation compared to the other experiments conducted in this study (see Fig. 4). Some further investigation was conducted to elucidate if this observation was due to an isolated experimental error or the possible formation of some other solid species different than CaS. Authors of previous works have suggested that the CaS formed could be oxidized by CO_2 present in the gas to form $CaSO_4$ and CO is often added to the gas together with the CO_2 to suppress this reaction [22,23,36,40]. To investigate the possibility of a reaction occurring between CaS and CO_2 under the experimental conditions tested here, two different CaS samples were subjected to a gas stream of 12.6% of CO_2 in N_2 at 800 °C for 1 h and 10 min. The two samples tested were a commercial CaS sample and a carbide slag sample that had been previously calcined at 800 °C and then sulfided up to a CaO conversion of 75% (sample 4 in Table 3). The two samples were analyzed before and after the experiment, but no difference in CaS content due to contact with CO_2 at 800 °C was observed. These observations are in qualitative agreement with some previous studies [41,42]. The possibility that the carbonation of the CaO may occur under these conditions can also be ruled out, since the equilibrium partial pressure of CO_2 at 800 °C is above 0.25 atm. In any case, it was checked experimentally that no carbonation of calcined CS occurred at 800 °C in an atmosphere containing 25% of CO_2 in N_2.

Previous studies have found that the presence of CO_2 can significantly enhance the sintering of CaO [43] and CaS [40], leading to decreased specific surface area and porosity of the solid. This effect could partly explain the influence of the CO_2 concentration on the CaO suldfidation rate observed here.

Additional tests were conducted to investigate if the results were affected by addition of 15% H_2O to the feed gas and to measure the sulfidation rate in a gas stream containing all the main gas components present an air-gasification gas (N_2, CO_2, CO, H_2, CH_4 and H_2O). Fig. 13 shows the conversion versus time curves for experiments carried out with 500 ppm of H_2S and different mixtures containing CO_2, CO and H_2O.

Comparison between the results from the experiment using N_2-H_2-H_2S-CO-CO_2-CH_4 mixture and the one using the same mixture but with

15% H_2O, indicates that the addition of H_2O reduces the sulfidation rate. The influence of adding CO_2 and H_2O has been studied before, using conventional Ca-sorbents. Álvarez-Rodríguez and Jul [32] observed a significant reduction in the sulfidation rate of dolomite when adding 10% of H_2O to the feed gas, while the addition of 6% of CO_2 upon that did not have much influence. The negative effect of H_2O on the rate of CaO sulfidation is not unexpected since its concentration affects the equilibrium of reaction (1). In addition, the presence of H_2O at the same concentration and temperature employed here has also shown to enhance the sintering of CaO formed from the thermal decomposition of $Ca(OH)_2$ [43]. The oxidation of CaS with H_2O to generate CaO, with the subsequent emission of SO_2 and H_2 has also been observed experimentally [37], but the measured reaction rate was very low at 800 °C.

To understand the effect that the addition of CO, might have on the CaO sulfidation rate, the results obtained using the N_2-H_2-H_2S-CO-CO_2-CH_4 mixture (7.7% H_2, 11.3% CO, 11.3% CO_2, 2.3% CH_4) and the N_2-H_2-H_2S-CO-CO_2 mixture (11.8% CO_2, 12.1% H_2). Both mixtures contain similar concentrations of CO_2, but only the former contains CO. The results indicate that the sulfidation was faster for the mixture containing CO, although it was not entirely possible to confirm that this effect is due to the presence of CO, since the H_2 concentration was decreased simultaneously. Due to the limitations of the mass flow controllers employed to feed the gas mixtures it was not possible to maintain the same H_2 concentration in the mixtures with and without CO. Some previous works have studied the effect of CO, but in mixtures without CO_2 and H_2O and at high partial pressure of H_2S. Heesink and van Swaaij [39] found a slight inhibitory effect of increasing CO concentration at low temperature (600 °C), while Chauk et al. [22], observed no effect at 800 °C.

Although the results from Section 3.5 indicate no influence of varying the H_2 concentration in an N_2-H_2-H_2S mixture, this does not mean that when the gas contains also other gases, such as CO_2, the H_2 concentration does not have an effect. Lin et al. [12] found that the increase in CO_2 concentration from 0 to 18 % in a gas containing just N_2 and 10000 ppm of H_2S (apart from the CO_2) led to a mild decrease in sulfidation rate, but that when CO_2 was fed together with H_2, the effect was much more significant. They also observed that increasing the H_2 concentration in a mixture containing a fixed concentration of CO_2 lead to a decrease in the sulfidation rate. This observed synergetic inhibition effect of CO_2 and H_2 was attributed to the reverse WGSR. This explanation also adds-up for the results obtained in this work, since the addition of H_2O has shown to slow down the sulfidation process and, on the other hand, the CaO formed from the thermal decomposition of CS has a catalytic effect on the WGSR. The addition of CO_2 together with H_2 could lead to the formation of H_2O at the solid surface through the reverse WGSR, thus reducing the sulfidation rate, as observed in this work, while the addition of CO upon the CO_2 and H_2 already present, together with a decrease in H_2 concentration, would reduce the formation of H_2O and thus lead to an increase in the sulfidation rate, also observed in this work.

4. Conclusions

The use of an industrial residue carbide slag (CS) and calcined limestone (for comparison) as in-bed sorbent to remove H_2S in fluidized bed biomass gasification has been studied. Experiments were conducted in a laboratory-scale fluidized bed at temperatures between 800 and 900 °C using different gas mixtures containing H_2, CO_2, CO, H_2O and CH_4 and relatively low H_2S concentration (500–1000 ppm). Apparent reaction kinetics was obtained without external mass transfer limitations. The reaction rates measured were influenced by particle size above 32 μm showing that intraparticle mass transfer limitations influence the CaO sulfidation rate. Hg porosimetry measurements showed that the calcined CS sample maintained a significant part of its pore volume even after 75% of the CaO had been converted into CaS.

It was also found that increasing the calcination temperature resulted
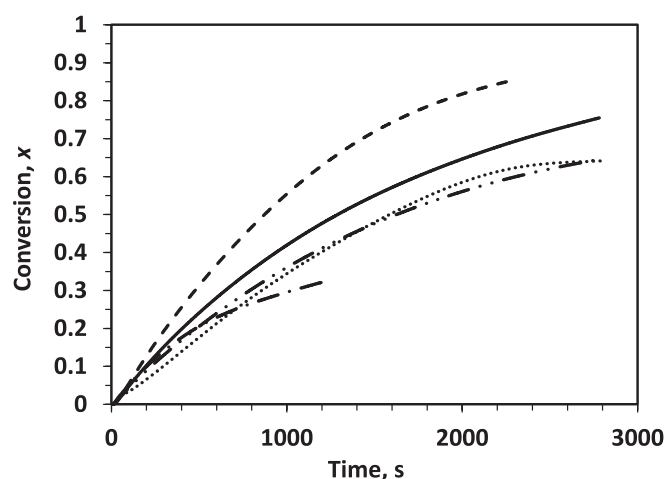
Fig. 13. CaO conversion as a function of time for sulfidation measurements carried out at 800 °C in different mixtures having H_2S inlet concentration of 500 ppm, N_2-H_2-H_2S mixture (7.7% H_2) (– – –), N_2-H_2-H_2S-CO-CO_2-CH_4 mixture (7.7% H_2, 11.3% CO, 11.3% CO_2, 2.3% CH_4) (——), N_2-H_2-H_2S-CO-CO_2-CH_4-H_2O mixture (7.7% H_2, 11.3% CO, 11.3% CO_2, 2.3% CH_4, 15% H_2O) (••••)and two N_2-H_2-H_2S-CO_2 mixtures: i) (11.8% CO_2, 12.1% H_2) (–••–); ii) (16.2% CO_2, 10.5% H_2)(–•–).

in higher reactivity, although the original CaO sample had lower porosity and surface area.

The increase in CO_2 concentration in a mixture containing N_2, H_2 and H_2S led to lower reaction rates and it was confirmed experimentally that no reaction occurred between CaS and CO_2. The addition of H_2O to a complex gas mixture led to slower reaction, while the addition of CO together with a slight reduction of H_2 concentration enhanced the reaction rate.

Overall, significant sulfidation rate was obtained using CS, that was comparable to that obtained using calcined limestone, showing that this residue is a promising alternative to conventional Ca-sorbents.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgements

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.cej.2023.142460.

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