Turkish Journal of Engineering

DESULPHURIZATION OF SYNGAS PRODUCED FROM BIOMASS USING DOLOMITE AS ADSORBENT

Ademola Stanford Olufemi *[1], Olusegun Samson Osundare [2], Isaiah Oluwadamilare Odeyemi [3] and Mirwais Kakar [4]

[1] Osmangazi University, Department of Chemical Engineering, Eskişehir, Turkey
ORCID ID: 0000-0003-4523-1454
e-mail: 503520181006@ogrenci.ogu.edu.tr

[2] University of Glasgow, School of Engineering, Glasgow, UK
ORCID ID: 0000-0001-9668-9030
e-mail: sammie1308@gmail.com

[3] Istanbul University, Department of Chemistry, Istanbul, Turkey
ORCID ID: 0000-0002-8369-9130
e-mail: i.odeyemi@ogr.iu.edu.tr

[4] Osmangazi University, Department of Chemistry, Eskişehir, Turkey
ORCID ID: 0000-0002-4215-9795
e-mail: 501520181002@ogrenci.ogu.edu.tr

ABSTRACT

This article deals with the cleaning of generated gas for energy use in high-temperature fuel cells by the method of high-temperature adsorption in the potential utilization according to Industry 4.0. The study presents the methods of preparation of a wide range of sorbents, test equipment, used analytical methods and overview of achieved results. This project focused on high-temperature removal of acidic components such as hydrogen sulfide, Carbonyl sulfide, hydrogen chloride and hydrogen floride (H_2S, COS, HCl and HF), using laboratory-made or commercial sorbents, from the gas resulting from the gasification of biomass. In the theoretical part of the biomass and its gasification, cleaning possibilities of the raw gas and, above all, of selecting a suitable adsorbent for high-temperature removal of unwanted components was the major focus. The possibilities of using purified gas in fuel were also mentioned in the article and the properties and structure of the fuel cell. The experimental part of the project addressed the testing of specific adsorbents at different temperatures. The task was to find a sorbent that would clean the raw gas at the specified temperature to the desired concentrations of undesirable components in order to enter as fuel into a high-temperature fuel cell. Commercial and naturally obtained dolomite were modified and tested. The effective time range of sorbents at atmospheric pressure (101.325 kPa) and at different temperatures ranging from 300 to 600 °C were also measured. From the results obtained, modified dolomite was established to be more effective adsorbent for the removal of hydrogen sulphide gas from syngas produced from biomass.

Keywords: Industry 4.0, High-Temperature Adsorption, Hydrogen Sulfide, Dolomite, Syngas

1. INTRODUCTION

The expectation from Industry 4.0 is high, and one of the major demands is energy as its utilization plays an indispensable role. One of the possibilities for energy generation or recovery is the gasification of solid waste or biomass. Fossil fuels, as the main sources of the world energy, do not only pose a threat in term of their reserve limits but also their environmental emissions. The emissions of greenhouse gases and other combustion-related pollutants have caused non-negligible consequences such as global warming and air pollution, which are seriously threatening the biosphere (Yin & Yip, 2017). Therefore, it is imperative to explore alternative sources of energy, which are sustainable by nature and pose less or no environmental concerns.

Biomass is one of the potential resources, which is renewable/sustainable, abundant, and carbon neutral. Utilization of energy from biomass will reduce dependence on fossil resources and the environmental hazards associated with the use of fossil resources. Gasification of biomass with steam is more beneficial than with air or oxygen as higher hydrogen concentration and yield is obtained (Chutichai *et al.,* 2015; Kalinci *et al.,* 2009; Li *et al.,* 2018; Parthasarathy & Narayanan, 2014). Therefore, product gas with a higher heating value can be obtained (Kalinci *et al.*, 2009; Li *et al.,* 2018; Mahishi & Goswami, 2007).

During biomass gasification, a gas blend containing mainly hydrogen, carbon monoxide, carbon dioxide, water-vapour and methane (H_2, CO, CO_2, H_2O and CH_4) is generated together with certain unwanted byproducts, in which their concentrations depend on the feedstock, gasifier design, and process conditions (Cheah *et al.,* 2009). The undesired byproducts include organic tars, sulfur and nitrogen heteroatom species such as (thiophene, pyridine), and inorganic substances such as sulfur (H_2S, COS) chlorine (HCl) Nitrogen (NH_3, HCN), and alkali metals (Cheah *et al.,* 2009; Leppdahti & Koljonen, 1995).

The usage of dolomite sorbent is a promising way for the removal of acidic gases from biomass gasification products. Dolomite ($CaMg(CO_3)_2$) has abundant reserves and it is comparatively inexpensive. Upon calcination of dolomites, decomposes to form a highly porous CaO/MgO compound (Su *et al.,* 2019; Valverde *et al.,* 2015). Exposure of dolomite to the high temperature of gasification conditions makes the minerals undergo calcination reaction as stated below:

$$CaCO_3 + MgCO_3 \leftrightarrow CaCO_3 + MgO + CO_2 \leftrightarrow CaO + MgO + 2CO_2$$
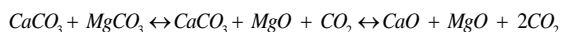
The CaO is the active component, while MgO is inert (Abbasian *et al.*, 1990; Husmann *et al.,* 2016).The desulfurization step is as follows:

$$CaO + H_2S \leftrightarrow CaS + H_2O$$
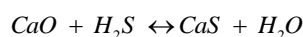
The equilibrium of the desulfurization reaction depends majorly on the temperature of the reaction environment and the steam content (Bakker *et al.,* 2003; Husmann *et al.,* 2016). The high content of steam in the syngas (as water is formed during desulfurization step) is disadvantageous for the residual H_2S content in the gas downstream of a desulfurization unit.

In addition, the use of zinc and copper oxides on alumina-shaped cylinders as commercial sorbents for removal of acidic gas in biomass gasification product. The zinc-based sorbents are currently the leading sorbent contenders (Gupta & Brien, 2000). Zinc oxide has a high sulfur adsorption capacity (Wu *et al.,* 2018). On fractional desulfurization basis, zinc can be accepted up to 1,149.85 °C with ZnS as the sulfide form while the stable form is ZnO with excess. However, zinc-based sorbents do suffer from metal volatility (ZnO reduces to Zn above 499.85 °C and volatilizes at 699.85 °C) (Lee & Feng, 2012). Whereas copper-based sorbents do not suffer from metal volatility problems, they were determined serviceable at the temperature of 799.85 °C and above (Lee & Feng, 2012). By reducing atmospheres, copper oxides are reduced to Cu or CuO at a temperature above 199.85 °C. The equilibrium of Cu-based sorbents with H_2S concentrations are very low, about 1-5 ppm at 726.85 °C. However, Cu in a mixed oxide state can reduce the sulfur level to below 1 ppm (Lee & Feng, 2012).

The objective of this study is to perform a suitability test on a naturally sourced limestone (dolomite) for removal of acid gas components from syngas produced during the gasification of biomass.

2. EXPERIMENTAL

2.1. Material and Sample Preparation

Two types of sorbents were used. The first was a metamorphic limestone, classified as dolomite natural material harvested from Ikpeshi, Akoko-Edo Area of Edo State, Nigeria (Latitude 070 11' mN and Longitude 060 15' mE). These dolomite- sorbent materials were calcinated by annealing in an oven (PRECISION, Model 6525) at 700 °C for about 1 hour and at 850 °C and 950 °C for approximately 30 minutes to a constant weight. The sample was thoroughly washed in distilled water to remove the sludge off the surfaces so that the dolomite is cleaned.

It was subsequently cooked for about 7 minutes, filtered, dried for 1 hour at 110 °C, and finally, after drying, the sample was annealed for one hour in an oven at 700 °C.

The exact elemental composition of the dolomite limestone was determined using a Rigaku MiniFlex300 X-Ray Diffractometer with Cu-K α radiation ($\lambda \approx 0.154$ nm) which shows that the dolomite contains $CaCO_3$ 61.59 %, $MgCO_3$ 33 %, SiO_2 2.99 %, Al_2O_3 1.57 % and Fe_2O_3 0.297 %.

The second sorbent was a commercial dolomite of a given composition in the shape of small cylinders of 5.2 x 3.2 mm. These dolomites have been tested for natural and readily available sources with the composition of ZnO 46 %, CuO 33 % and Al_2O_3 21 %.

Other reagents and chemicals were obtained from two different manufacturers they include hydrofluoric acid (38 – 40 %), hydrochloric acid (36 %) and sodium hydroxide, potassium nitrate, lead acetate from Spolana and potassium nitrate from Erba Lachema.

The microstructure of the natural, calcined and sulphated dolomite was visualized in a scanning electron microscope (Hitachi TM3000) with a magnification capacity of up to 30,000 times, with 5 kV and 15 kV beams. The samples were placed on an aluminium stand when viewed. A JEOL JSM 6060 scanning electron microscope with an accelerating voltage of 0.3 to 30 kV

and a magnification capacity of up to 300,000 times was also used. In this microscope the visualization was made after metallization of the dolomite limestone particles with gold.

Specific area and pore volume were determined by BET method in specific area analyser (Quantachrome Nova 1000), with nitrogen as adsorption gas. Samples were pre-treated in vacuum for 3 hours at 300 °C. In the particle size analysis, a laser granulometer (Cilas 1180) was used. Sample density was determined on a Quantachrome MVP-1 multi-helium gas pycnometer.

2.2 GC-MS Analysis of the Produced Bio-Gas

The chemical composition of the gaseous mixture (representing the gas produced by biomass gasification) produced gas was determined using PerkinElmer Clarus 500 GC Gas chromatograph which is equipped with a flame ionization detector (FID) and a capillary column (Elite– 5), 60 m x 0.32 mm x 0.25 mm with a packing of 5 % phenyl/95 % dimethylpolysiloxane. The analysis was done using the method reported by Wauton and Ogbeide (Wauton & Ogbeide, 2019).

2.3 Experimental Set-up

Tests for the absorptive efficiency of the syngas produced from biomass has been carried out through the bench-scale experimental rig illustrated schematically in Fig. 1. The materials used to test the properties of selected sorbents include: For the measurements, two types of reactor, double-walled, were used (small) with the dolomite test frit and single-shell (large) reactor for commercial measurement sorbent and also a dolomite based material from Ikpeshi, Akoko-Edo, Nigeria.
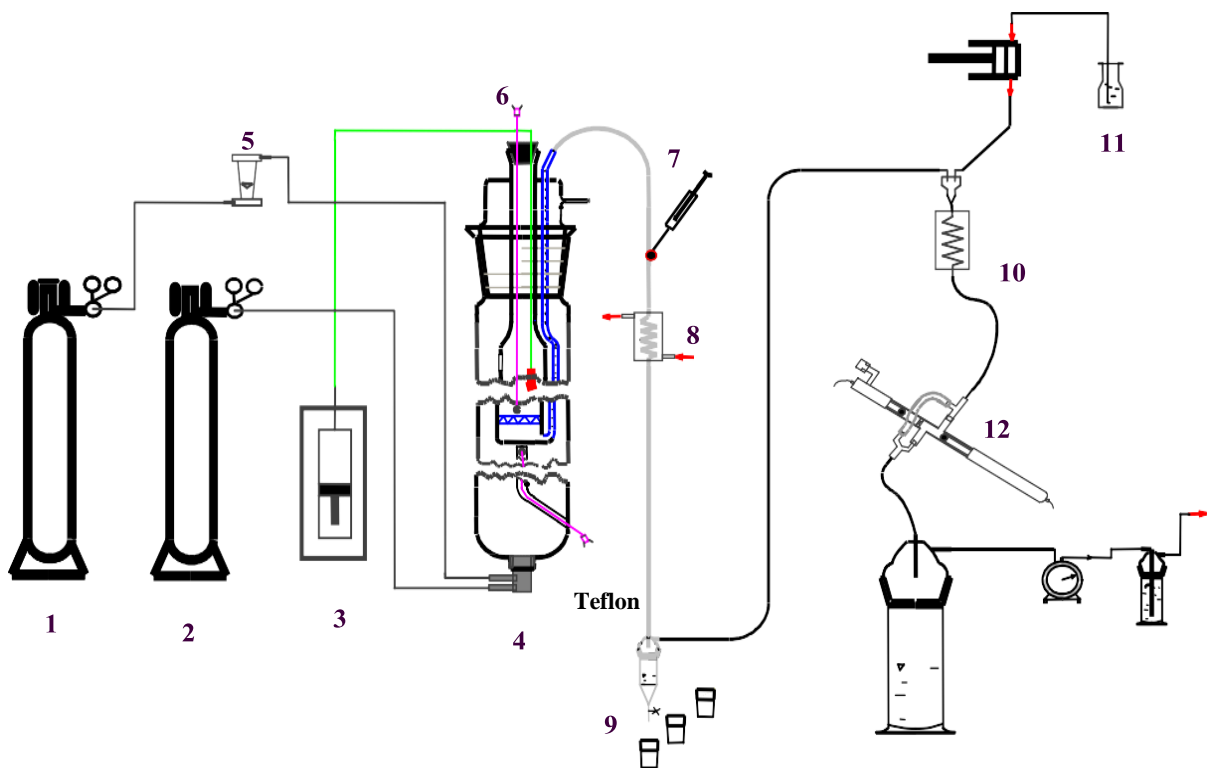

Fig. 1. The Schematic Diagram of the Experimental Set-up

Legend to Fig. 1:
1. gas mixture
2. nitrogen
3. linear pump
4. furnace with the reactor (inside)
5. rotameter
6. thermocouple
7. syringe for dispensing distilled water
8. cooler
9. sampling for liquid chromatography
10. absorber
11. NaOH solution tank
12. a sulfide electrode filled with KNO_3 solution

2.4. Experimental Procedure

The gas mixture produced after the biomass gasification (100 ppm sulphate content), passes from the cylinder (1) through the flowmeter (5) to the lower part of the reactor (4). The volumetric flow of the gas mixture is set to 85 L/h. Nitrogen (2) is also injected into the bottom of the reactor, which is used to flush the apparatus before and after the measurement. Flushing is important for two reasons. First, leakage of the whole unit is checked and secondly, the air (oxygen) that could form an explosive mixture with the hydrogen contained in the gaseous mixture (limits of explosive hydrogen are in the range of 4–75 %). The reactor head comes with an aqueous solution of acids (HCl and HF), which evaporates in the gas mixture. Acids are delivered to the device by a linear metering pump (3). The dosage is set at a flow rate of 9.026 mL/hr, resulting in a water concentration (13 %), HCl (150 ppm) and HF (20 ppm) after evaporation of the mixture.

In this study, two reactors (small and large), were made of quartz glass. The gas mixture enriched with the evaporated aqueous acid solution passes through the bed of the reactor containing the sorbent to be tested. The reactor was placed in an oval heating chamber (oven) which was heated to attain the coveted measuring temperature.

The gaseous mixture passed through the adsorbent bed emerges from the reactor head and continues into the condenser (8) where it is cooled to the condensation temperature of the acids and the sulphate remains in the gas phase. To improve the condensate drain, a syringe filled with distilled water (7) is injected into the liquid chromatography sampling device (9) and is injected at the site between the reactor and the condenser. A temperature measuring device is located at the outlet of the heat sink, where it is used to check that the temperature does not fall below the value at which the sulphate may be accidentally condensed.

The hydrogen gas mixture containing hydrogen sulfide continues into the absorber (10), where it is also supplied from the reservoir (11) by the sodium hydroxide solution. There is a dissociation of NaOH and H_2S and the increase of the S^{2-} ion potential is recorded by the sulfide electrode (12) on the potentiometer display (in mV). The electrode is filled with KNO_3 solution, which has the salt bridge function. The gas further passes through a container in which papers soaked in lead acetate are placed. If the sulfate concentration in the gas exceeds 1 ppm, the paper begins to blackout. After leaving this vessel the gas goes into the fume cupboard.

The weighed test material was poured into the reactor bed located in the furnace. In the case of a double-jacketed reactor, weighing was approximately 2 g of sample with a particle size range between 50 - 500 μm, and in a single-shell reactor, different heights of a 2 to 10 cm measured sorbent layer were tested with a particle size of 4 mm, corresponding to about 18 - 90 g of the sample. A potassium nitrate solution was added to the sulfide electrode and sodium hydroxide solution was added to the reservoir. The rectangular shaped paper was soaked in lead acetate and placed in a vessel that is connected to the electrode and serves to visualize the hydrogen sulfide penetration.

The temperature at which the oven was to be heated was set on the furnace display. Our temperature ranges from 300 to 600 °C. Prior to the measurement, it was necessary to flush the entire apparatus with nitrogen. Thereafter, the nitrogen inlet was closed, a gas cylinder containing a gaseous mixture (simulating the composition of the gas from the biomass gasification) was opened, and it was also possible to start an aqueous solution of HCl and HF by means of a linear pump. Both streams were mixed and penetrated through a test sorbent located on the reactor bed, where sulfate, HCl and HF were captured. Exhaust gas emerges from the reactor head. Subsequently, it is cooled in the cooler to a temperature at which acid condensation occurs and the sulphate is still in the gaseous state. Every 10 minutes the pH of the condensate is checked using litmus paper. If the paper begins to turn red, it means that the pH of the condensate is in the acidic area and the measured sorbent is no longer picking up the acid. The acid-containing condensate is withdrawn every 30 minutes for liquid chromatography. Hydrogen sulphide remains in the gaseous state and passes through a sorbent filled with sodium hydroxide where dissociation occurs. The increase in the potential of S^{2-} ions is recorded on the potentiometer using a sulfide electrode filled with KNO_3 solution. The gas further passes through a container in which papers soaked in lead acetate are placed. If the sulfate concentration in the gas exceeds 1 ppm, the paper begins to black out. After the measurement was completed, the apparatus was also purged with nitrogen again.

2.5. Analytical Methods

Determination of outlet concentrations of undesirable acidic components of the gas after purification (H_2S, HCl and HF) was performed by two analytical methods.

The first was the hydrogen sulphide content determination, which was done potentiometrically using a sulfide electrode filled with KNO_3 solution. An indication of the penetration point of H_2S (above 1 ppm) by lead acetate.

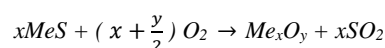The second is the concentration of HCl and HF in the condensate resulting from the cooling of the gas exiting the reactor was determined by ion chromatography.
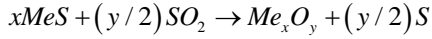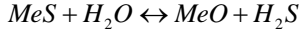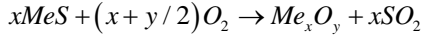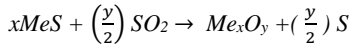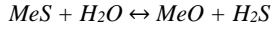
2.6. Chemistry of Adsorbent Reaction

The performance of the solid sorbent depends on its affinity for hydrogen sulfide, porosity, mechanical resistance, and resistance to high operating temperatures ranging from 500-800 °C. Emphasis is also placed on the possibilities of regeneration, the durability of consumed sorbent and the cost of the sorbent.

The high-temperature removal of sulfur components by means of a solid sorbent is based on the following reactions:

$$Me_xO_y + xH_2S + (y-x)H_2 \leftrightarrow xMeS + zH_2O$$

$$Me_xO_y + + xCOS + (y-x)CO \leftrightarrow xMeS + zCO_2$$
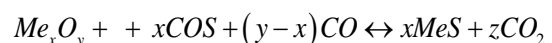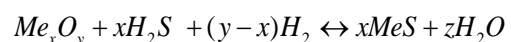
Regeneration of the sorbent used takes place according to these reactions and depends on whether unwanted side reactions occur:

$$xMeS + (x + \frac{y}{2})O_2 \rightarrow Me_xO_y + xSO_2$$

$MeS + H_2O \leftrightarrow MeO + H_2S$

$xMeS + \left(\frac{y}{2}\right) SO_2 \rightarrow Me_xO_y + (\frac{y}{2}) S$

$xMeS + \left(x + y/2\right)O_2 \rightarrow Me_xO_y + xSO_2$

$MeS + H_2O \leftrightarrow MeO + H_2S$

$xMeS + \left(y/2\right)SO_2 \rightarrow Me_xO_y + \left(y/2\right)S$

Westmoreland *et. al.,* (1977) analyzed the gas desulphurization of 28 metal oxides at high temperature by minimizing free energy in the C-H-N-O-S system, which was in contact with the excess of the tested oxide at a constant pressure of 2 MPa and temperature in the range of 360 to 1560 °C. From their experiment, only the following 11 metal oxides - Fe, Zn, Mo, Mn, V, Ca, Sr, Ba, Co, Cu and W - appeared to be suitable.

3. RESULTS AND DISCUSSION

From the experimental setup shown in Fig. 1, for the determination of the adsorption capacity, the adsorbed gas quantity was determined in four (4) steps at different values of temperature between 300 to 600 °C. A digital technical balance with an accuracy of 10-12 g was employed to determine the quantity of adsorbate adsorbed in the fixed bed, by subtracting the mass of packed bed after the adsorption from its initial mass.

3.1. Dolomity

Dolomite-based sorbents from Ikpeshi, Akoko, Edo State, Nigeria were measured into both small and large reactors. The dolomite material was tested, which was used directly without further processing and was calcined at various temperatures (700 °C, 850 °C and 950 °C) subsequently flushed with distilled water. The modifications made were believed to improve the efficiency of the sorbent.

Measurement on a double-jacketed reactor was carried out at a temperature of 600 °C with an average particle size of 50-500 μm, measured by laser particle size and the results are summarized in Tables A1 and A2, which shows that neither different dolomite treatments had a great effect on the capture of hydrogen sulphide. The penetration occurred at the beginning of the measurement, but even after the sorption broke, a certain amount of sulfate was retained. In the case of acid seizure, the dolomite exhibited good results, especially in crude dolomite No. 2 and in the calcined sorbent. Even after the penetration of the dolomite, there was still another seizure of acids.

When measuring a single-shell reactor, the same height of the sorbent layer was 2 cm, the sample having a grain size of 4 mm (gravel). The difference between the dolomite samples was at different calcination temperatures and also at the various temperatures at which the measurements were made. Even in large reactor testing, sulphide sorption was not sufficient. The acid uptake improved with the decreasing measurement temperature and the best results were achieved at 300 °C. The better adsorption mechanism of dolomites can be attributed to the fact that after calcination and emission of CO_2, what is left of dolomite is the mixture of CaO and MgO. Since MgO does not react with H_2S, this leaves a higher porosity for H_2S to fill in the core of the grains according to Puigjaner (2011).

3.2. Commercial Sorbent

In addition, commercial sorbents - zinc and copper oxides on alumina-shaped cylinders measuring 5.2 x 3.2 mm were tested. Their effectiveness was measured at different temperatures (500 °C, 400 °C and 300 °C) and different layer heights (10 cm, 4 cm and 2 cm). When measured at a temperature of 500 °C, the elemental zinc was reduced to block the apparatus, therefore the temperature and the height of the layer decreased due to shorter testing time. At a temperature of 400 °C and a layer height of 4 cm, the acid did not penetrate and the hydrogen sulfide seizure was at a good level, therefore, in this case, the height of the layer was reduced. In spite of this reduction of the layer, good results were obtained during testing as well as at 300 °C.

By testing, it was found that the commercial sorbent is particularly suitable for capturing sulfate, whereby the desired concentration can be below 1 ppm. Mineral acid sorption is also advantageous.

Based on this, the adsorbed mass of the sample (Mads) and adsorption capacity denoted as q (mg/g), can be unveiled. The adsorbed gas quantity, the initial and final conditions which were considered as vital parts were calculated with the relationship:

$$\frac{dq}{dt} = k_f \left(C - C^* \right) \tag{1}$$

$$M_{ads} = QC_0 \int_0^t \left(1 - \frac{C}{C_0} \right) dt \tag{2}$$

$$q = \frac{C_0 - C}{M} V \tag{3}$$

Where C_0 represents the initial concentration (mg/L), C stands for the outlet concentration (mg/L); the adsorbent dosage is denoted by M and measured in (g); Q connotes the flow rate and V as the volume of the reactor. This reaction is used during adsorption and desorption (purge) stage.

Next, the pressurized–depressurized stages need to obey the ideal gas law (PV= nRT).

The percentage deviation is given by:

$$Percentage\ Deviation = \sum \left(\frac{C_{pred} - C_{obs}}{C_{obs}} \right) \frac{100}{n} \tag{4}$$

3.3. Characterization of Natural Dolomite

Dolomitic limestone is characterized by its compact structure when observed under a scanning electron microscope, as it is a metamorphic limestone (Fig. 2). However some pores and uneven surface formed by steps were also observed. It has been shown that a dolomitic limestone has a less compact structure than a calcitic limestone (Mazlumoğlu and Gülaboğlu, 2017).
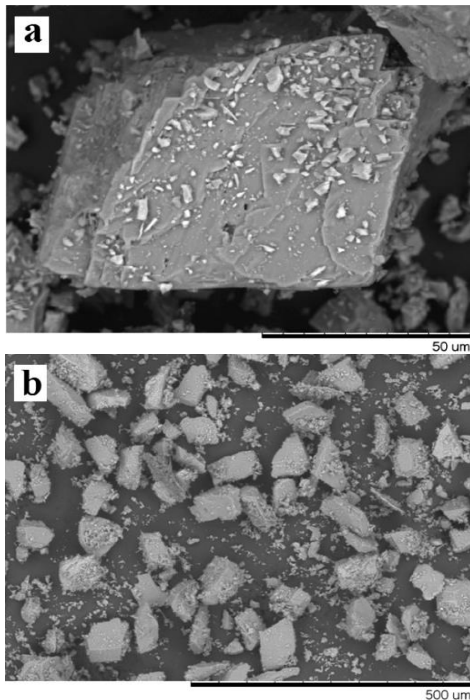
Fig. 2. SEM micrographs of in natural dolomite limestone. a) compact surface, b) particle size distribution

Due to the structure and origin, the specific area measured and the pore volume were low, and are presented in Table A3, along with the particle size distribution as measured by laser particle size. As a rule, dolomite limestone rocks have low initial porosity (Rubiera *et. al.,* 1991). The particle size range used had an average diameter of ~ 50 μm, but with some particles >100 μm. $D_{10\%}$ was represented by very fine particles smaller than 3.81 μm.

3.4. Characterization of Calcined Dolomite

The calcination of dolomitic limestone in the furnace was performed to analyze the texture and microstructure developed at 850 °C in air at atmospheric pressure. Calcination caused a reduction in the average and relative diameter of the particles according to surface fractures, and this reduction was similar for calcination by gradual heating and thermal shock. In Fig. 3d we can observe the greater amount of fines due to fracture, when compared to limestone in natura (Fig. 2b). According to the particle size distribution data presented in Table A4, it can be seen that in the granulometry used for dolomitic limestone, the reduction of mean and relative diameter during calcination at 850 °C in the furnace is not so expressive, being the main one is gas-solid contact, decreasing the resistance to intraparticle diffusion (Fuertes *et. al*., 1995).

During the calcination, high temperatures and CO_2 diffusion change the texture and microstructure of the dolomite, being marked by the opening of porosity and micro and macrofractures that eventually favor the complete rupture of larger particles and therefore the increase in fine particles; this is important in order to increase the reactive surface area of the particle. Fig. 3 shows the microstructure of the calcareous particle after calcination. The microstructure did not vary with regard to gradual heating or thermal shock calcination, and was

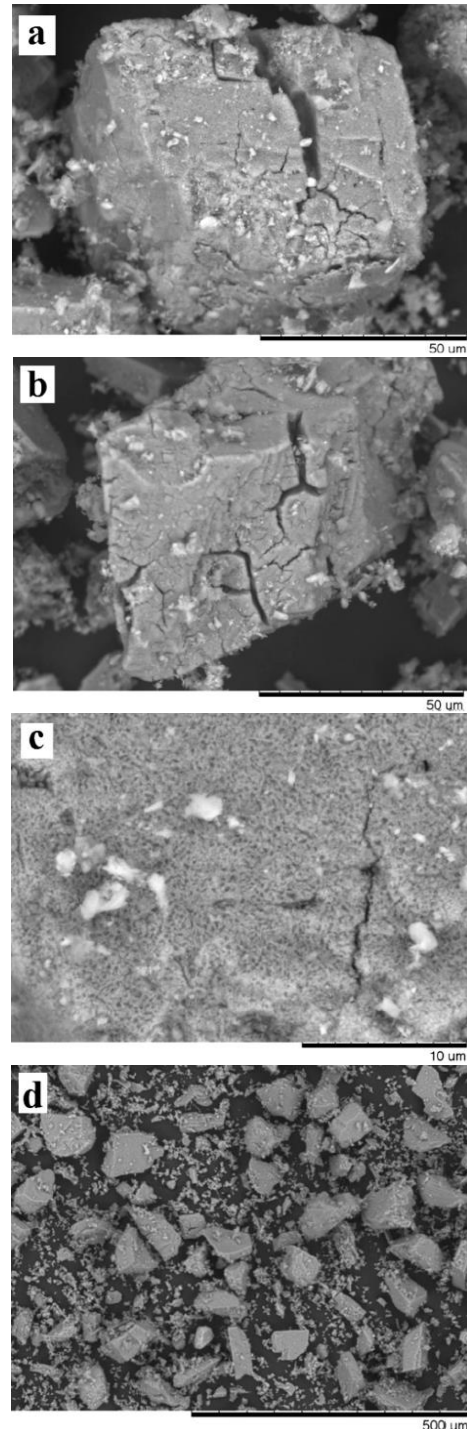marked by some fractures and small pores on the surface (Fig. 3).

Fig. 3. SEM micrographs of calcined dolomite; a, c) gradual heating and b) thermal shock d) particle size after calcination on furnace.

3.5. Effect of the Inlet Concentration

As the affinity of adsorbate for a given adsorbent is dependent on its size, shape, polarity of the fluid and the system temperature, the importance of the partial pressure as in gases, or concentration in fluid cannot be over

emphasized. The optimization data were investigated using the commercial sorbent and the locally sourced dolomite material. Breakthrough curves were drawn to determine the adsorption capacity or efficiency for different concentrations of fluorine and chlorine and the quantity of H_2S adsorbed at different temperatures and masses. Here, the results obtained for the gas flow rate at 0.2 L/min and the adsorbed H_2S were analyzed and at different inlet concentrations are as shown in Figs. 4-6 below.
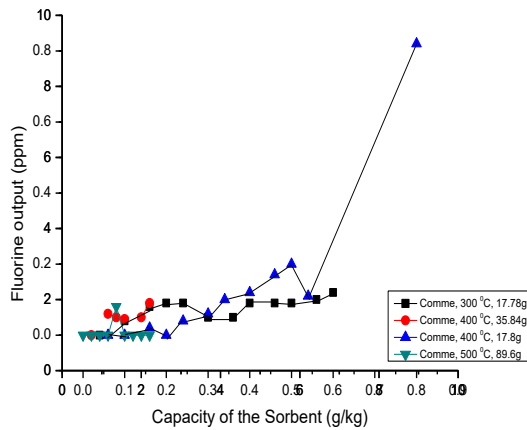

Fig. 4. Breakthrough curves of commercial sorbent for different fluoride temperatures
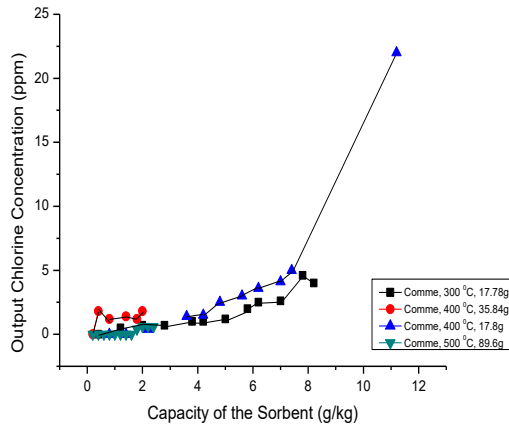

Fig. 5. Breakthrough curves for commercial sorbent for different chloride temperatures

As shown in Figs. 4 and 5, the commercial sorbent was optimized at 400 °C and 17.8 g appear to possess a higher absorption capacity.
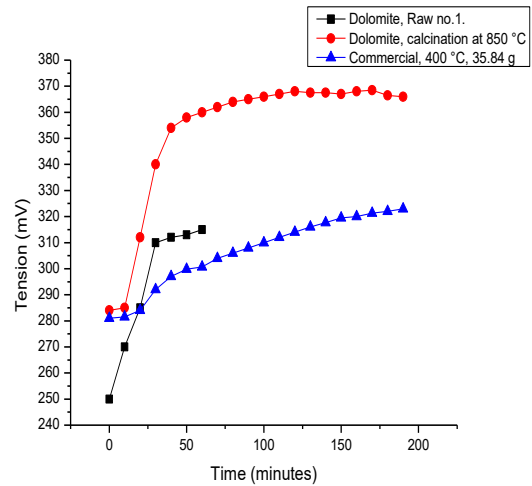

Fig. 6. Breakthrough representatives of the penetration curves for all H_2S graphs.

As it can be seen in Fig. 6, the potential difference, which corresponds to the amount of sulphide deposited from the effluent gas, is proportional to the equilibration time; it can be observed that the raw natural dolomite has a short equilibration time which shows its weakness sorption capacity but when modified at a temperature of 850 °C, its efficiency increased.

It can also be seen that as the sorption capacity increases, the breakthrough curve is shifted to the right, which is of longer breakthrough times because more molecules of the adsorbate are held by the adsorbent. Fig. 6 shows that at increased temperature of calcination of the locally sourced adsorbent, the percentage removal of adsorbed H_2S increases as well as the rate of adsorption.

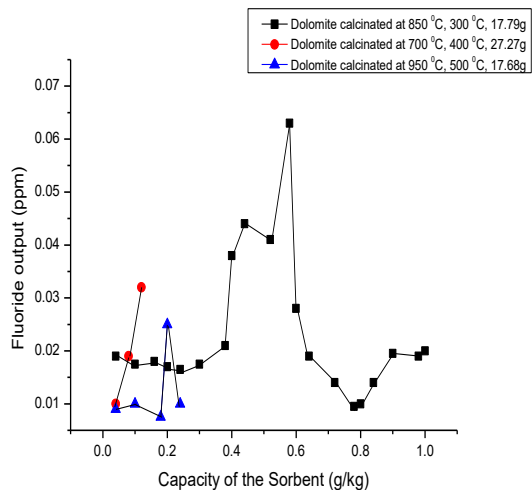### 3.6. Effect of Temperature on Modified Adsorbent

Fig. 7. Fluoride adsorbed in the dolomite for different degrees of temperature modification.
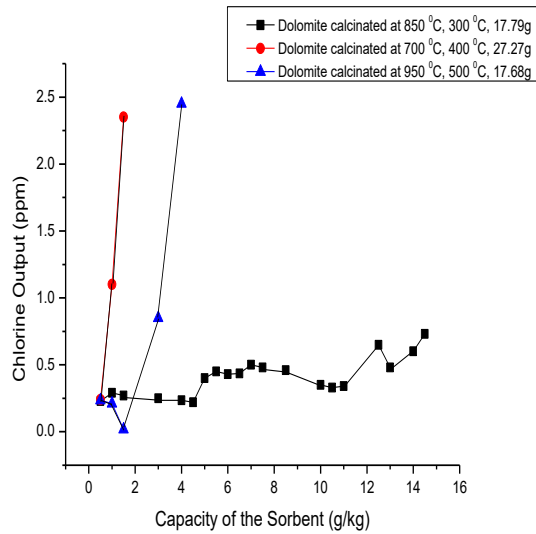
Fig. 8. Chloride adsorbed in the dolomite for different degrees of temperature modification.

In Fig. 7 and 8, it is presented that the dolomite modified at 850 °C and 17.68 g has a more sorption capacity for fluoride than the other ones modified at 700 °C and 950 °C. Its weakness was obvious in Fig. 6 against chlorine even when the sorption capacity was increased. But the modified dolomite at 950 °C, 17.68 g has a faster output which shows that at high temperature of modification, dolomites can give a large quantity of chorine.
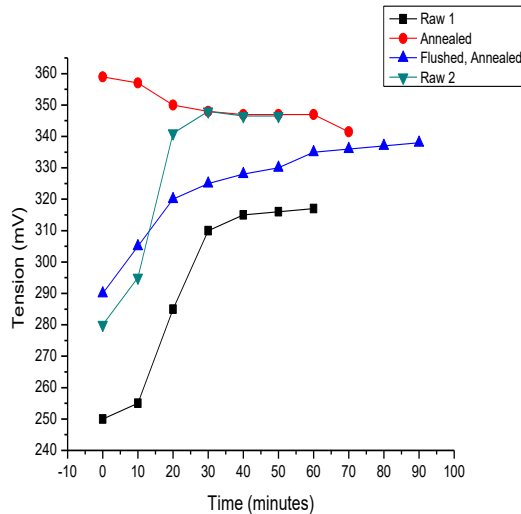

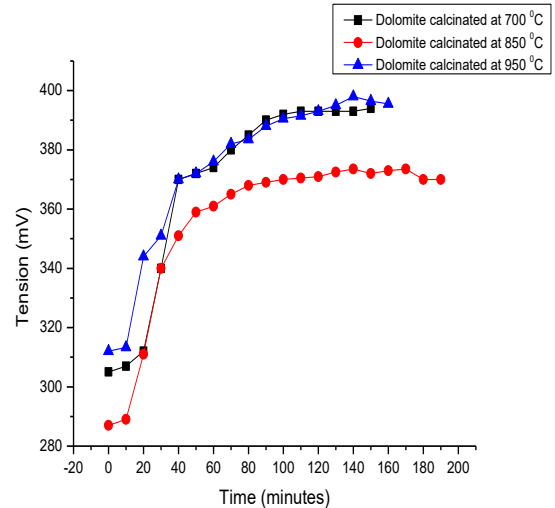Fig. 9. Small reactor dolomite penetration curves at 600 °C for H_2S

Fig. 10. Small reactor slot curves of dolomite sorbent for H_2S sorption at different temperatures of treatment

According to the results presented in Fig. 9, it can be seen that the amount of sulphide left in effluent increases with temperature. An equal weight of calcinated dolomite was used to adsorb the components of a fixed concentration of biogas mixtures. Fig. 10 shows that Dolomite calcined at 850 °C shows the most effective optimization. Calcinated dolomite at 850 °C possess the lowest amount of Sulphide deposit after adsorption which shows that more sulphate had been adsorbed by the adsorbent. The 850 °C calcined dolomite also shows an extended equilibration time, which affirms its higher adsorption capacity, according to the work of Delgado & Aznar (1997).

The percentage removal of adsorbed H_2S increases as well as the rate of adsorption.
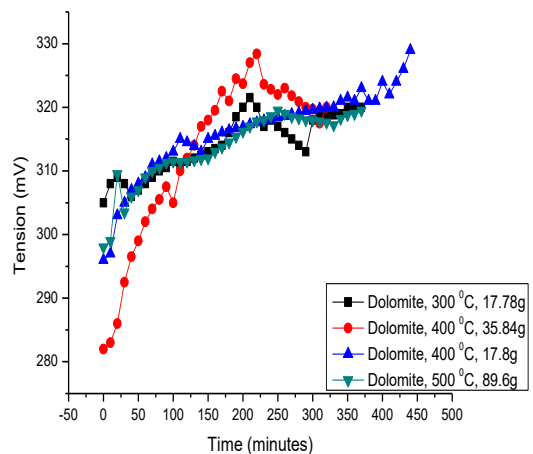
Fig. 11. Large reactor slot curves of dolomite sorbent for H_2S sorption at different temperatures of treatment

The amount of sulphide removed according to Fig. 11 shows that the dolomite material modified at 400 °C and at a capacity of 17.8 g was more effective than others. This is in line with the work of Delgado & Aznar (1997). The constant parameters (a, b, c, d, k_1 and k_2) presented in the kinetic equations were calculated by linear

regression analysis. Table A5 presents the R-squared, percentage deviation, estimated value of all statistical parameters; a, b, c, d, k_1 and k_2 included. The R^2 values and % deviations can be seen in table A5 shows there is correlation between the three kinetic equations. The power function shows the least correlation with an R^2 value ranging between 64 and 80 %, while the proffered equation demonstrates an optimum correlation with an R^2 value ranges between 97 and 99 %.

According to the R^2 value and the percentage deviation obtained, the 950 °C modified dolomite's kinetic was observed to have the least correlation as possesses an R^2 value of 90 % and a lower percentage deviation when compared to other dolomites calcined at different temperatures.

The dolomite calcined at 400 °C have the highest value of R^2 and lowest percentage deviation values. This colludes with the results obtained by other researchers which claims the ability of the simple Elovich equation to satisfactorily explain the kinetics of adsorption on lignite and cashew nut shell (Gu & Ding, 1996; Senthilkumar *et al.,* 2011). The order of adequate correlations for all modified dolomites and the predicted percentage deviation with Power Function (PF), Simple Elovich (SE) and the Proposed Equation (PE) also affirms the order;

$$PE > SE > PF$$

It can therefore be concluded that the proffered equation can adequately describe the kinetics of the modified dolomites.

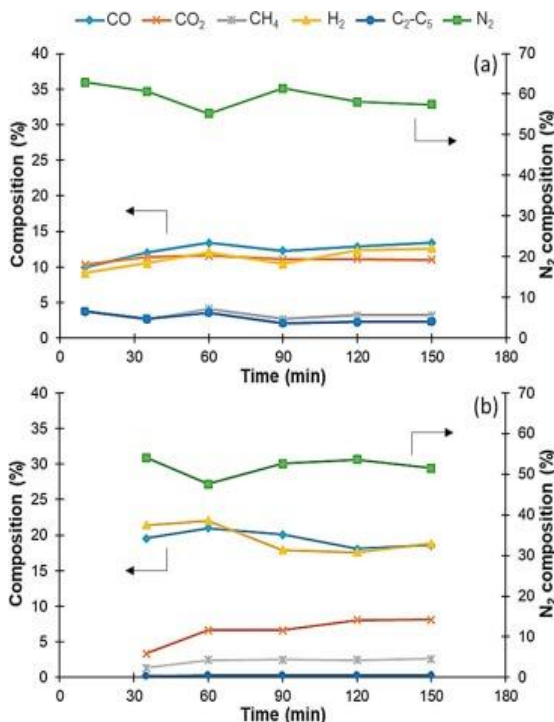### 3.7. GC-MS Analysis of The Purified Syngas

Fig. 12. GC-MS Analysis of the purified gas mixture

The chromatogram in Fig. 12 above is the actual response of the gas mix on the parallel configuration. The neat thing about the first cluster is the gas peak from the GC followed by the separation of the other components (less the H_2S) on the mol-sieve. It was found to contain CO 20 %, H_2 17.5 %, CO_2 8.6 %, H_2S 100 ppm and N_2 residue.

4. CONCLUSION

Considering the environmental and efficiency standpoint, gasification technologies have proven to be among the prime auspicious means of generating electrical power as they allow thorough and nondetrimental use of coal and other carbonaceous materials assorted with coal with high Sulphur byproducts included.

The goal of this study was to improve the removal of these by-products from the produced syngases. Considering its low cost in reducing H_2S in biomass gasification and its properties, natural dolomite which has affinity of reaction with H_2S so as to form calcium sulphate was selected among several earth-alkaline compounds for this study. Tests were carried out using dolomite obtained from Ikpeshi, Edo State, Nigeria. This dolomite sorbent was modified by calcination at different temperatures without chemical blending before being used. The dolomite was sulphurized in a pressurized fixed bed using a mixture of gases that acts as the gasification gas. The factors that affect sulphurization conditions such as gas velocity, bed length, the effect of temperature on the modified dolomite, effect of gas concentration, and gas composition were investigated.

This study established that dolomites can be used as effective adsorbents for the removal of hydrogen sulphide gas from syngas produced from biomass.

REFERENCES

Abbasian, J., Rehmat, A., Leppin, D., & Banerjee, D. D. (1990). Desulfurization of Fuels with Calcium-based Sorbents. *Fuel Processing Technology*, *25*, 1–15.

Bakker, W. J. W., Kapteijn, F., & Moulijn, J. A. (2003). A high capacity manganese-based sorbent for regenerative high temperature desulfurization with direct sulfur production Conceptual process application to coal gas cleaning. *Chemical Engineering Journal*, *96*, 223–235. https://doi.org/10.1016/j.cej.2003.08.022

Cheah, S., Carpenter, D. L., & Magrini-bair, K. A. (2009). Review of Mid- to High-Temperature Sulfur Sorbents for Desulfurization of. *Energy & Fuels*, *23*, 5291–5307. https://doi.org/10.1021/ef900714q

Chutichai, B., Patcharavorachot, Y., & Assabumrungrat, S. (2015). Parametric analysis of a circulating fluidized bed biomass gasifier for hydrogen production. *Energy*, *82*, 406–413. https://doi.org/10.1016/j.energy.2015.01.051

Delgado, J., & Aznar, P. M. (1997). Biomass Gasification with Steam in Fluidized Bed : Effectiveness of CaO , MgO , and CaO - MgO for Hot Raw Gas Cleaning. *Ind. Eng. Chem. Res.*, *35*, 1535–1543. https://doi.org/10.1021/ie960273w

Fuertes, A.B., Velasco, G., Alvarez, T., Fernandez, M.J. (1995). Sulfation of dolomite particles at high CO_2 partial pressures, *Termochim. Acta*, 254, 63.

Gu, J. M., & Ding, D. R. (1996). A study on the characteristics of adsorption for Zn2+, Cu2+, Pb2+ ions onto peat and lignite. *Environmental Chemistry*, *15*, 343–346.

Gupta, R. P., & Brien, W. S. O. (2000). Desulfurization of Hot Syngas Containing Hydrogen Chloride Vapors Using Zinc Titanate Sorbents. *Industrial & Engineering Chemistry Research*, *39*, 610–619. https://doi.org/10.1021/ie990533k

Husmann, M., Zuber, C., Maitz, V., Kienberger, T., & Hochenauer, C. (2016). Comparison of dolomite and lime as sorbents for in-situ H_2S removal with respect to gasification parameters in biomass gasification. *Fuel*, *181*, 131–138. https://doi.org/10.1016/j.fuel.2016.04.124

Kalinci, Y., Hepbasli, A., & Dincer, I. (2009). Biomass-based hydrogen production : A review and analysis. *International Journal of Hydrogen Energy*, *34*(21), 8799–8817. https://doi.org/10.1016/j.ijhydene.2009.08.078

Lee, J., & Feng, B. (2012). A thermodynamic study of the removal of HCl and H_2S from syngas. *Chemical Engineering Science*, *6*(1), 67–83. https://doi.org/10.1007/s11705-011-1162-4

Leppdahti, J., & Koljonen, T. (1995). Review Nitrogen evolution from coal , peat and wood during gasification : Literature review. *Fuel Processing Technology*, *43*, 1–45.

Li, Q., Song, G., Xiao, J., Sun, T., & Yang, K. (2018). Exergy analysis of biomass staged-gasification for hydrogen-rich syngas. *International Journal of Hydrogen Energy*, *44*(5), 2569–2579. https://doi.org/10.1016/j.ijhydene.2018.11.227.

Puigjaner, L. (2011). Syngas from Waste: Emerging Technologies *Green Energy and Technology.* Springer Science & Business Media, 127.

Mahishi, M. R., & Goswami, D. Y. (2007). Thermodynamic optimization of biomass gasifier for hydrogen production. *International Journal of Hydrogen Energy*, *32*, 3831–3840. https://doi.org/10.1016/j.ijhydene.2007.05.018

Mazlumoğlu, H., & Gülaboğlu, M. (2017). Effect of Temperature on SO_2 Absorption. *Journal of the Turkish Chemical Society B*, 1(1), 135–48.

Parthasarathy, P., & Narayanan, K. S. (2014). Hydrogen production from steam gasification of biomass: Influence of process parameters on hydrogen yield - A review. *Renewable Energy*, *66*, 570–579. https://doi.org/10.1016/j.renene.2013.12.025.

Rubiera, F., Fuertes, A.B., Pis, J.J., Artos, V., & Marbàn, G. (1991). Changes in textural properties of limestone and dolomite during calcinations, *Termochim. Acta*, 179, 125.

Senthilkumar, P., Ramalingam, S., Sathyaselvabala, V., Kirupha, S. D., & Sivanesan, S. (2011). Removal of copper (II) ions from aqueous solution by adsorption using cashew nut shell. *Desalination*, *266*(1–3), 63–71. https://doi.org/10.1016/j.desal.2010.08.003

Su, Y., Han, R., Gao, J., Wei, S., Sun, F., & Zhao, G. (2019). Novel method for regeneration/reactivation of spent dolomite-based sorbents from calcium looping cycles. *Chemical Engineering Journal*, *360*(August 2018), 148–156. https://doi.org/10.1016/j.cej.2018.11.095

Valverde, J. M., Perejon, A., Medina, S., & Perez-maqueda, L. A. (2015). Thermal decomposition of dolomite under CO2: insights from TGA and in situ XRD analysis. *Physical Chemistry Chemical Physics*, *17*, 30162–30176. https://doi.org/10.1039/c5cp05596b

Wauton, I., & Ogbeide, S. E. (2019). Characterization of pyrolytic bio-oil from water hyacinth (Eichhornia crassipes) pyrolysis in a fixed bed reactor. *Biofuels*, *0*(0), 1–6. https://doi.org/10.1080/17597269.2018.1558838.

Westmoreland, P.R., Gibson, J.B. & Harrison, D.P. (1977). Comparative kinetics of high-temperature reaction between hydrogen sulfide and selected metal oxides. *Environmental Science & Technology*. 11(5), 488-491.

Wu, J., Liu, D., Zhou, W., Liu, Q., & Huang, Y. (2018). Status of Coal Gas H_2S Removal. In *High-Temperature H_2S Removal from IGCC Coarse Gas* (pp. 21–55). Springer Singapore.

Yin, H., & Yip, A. C. K. (2017). A Review on the Production and Purification of Biomass-Derived Hydrogen Using Emerging Membrane Technologies. *Journal of Catalysts and Catalyzed Reactions*, *7*(297), 1–31. https://doi.org/10.3390/catal7100297

Appendix

Table A 1: Dolomite measurement results on a small reactor

	Sample	Weighing	$T_{calcination}$ °C	T_{try} °C	Capacity of H_2S-dolomite penetration (g/kg)	Capacity of H_2S-dolomite adsorbed at max. (g/kg)	Capacity of dolomite penetration (g/kg)	Capacity of dolomite end (g/kg)
Small reactor	Dolomite No.1.	2g	Not executed	600	0.00	5.98	0.00	5.44
	Dolomite No.2.	2 g	Not executed	600	1.00	2,99	4.46	7.12
	Dolomite	2 g	700	600	0.00	0.00	3.96	11.50
	Dolomite	2 g	700+hydr.	600	0.00	8.95	0.51	4.72

Table A 2: Dolomite measurement results on a big reactor

	Sample	Weighing	$T_{calcination}$ °C	T_{try} °C	Capacity of H_2S-dolomite penetration (g/kg)	Capacity of H_2S-dolomite adsorbed at max. (g/kg)	Capacity of dolomite penetration (g/kg)	Capacity of dolomite end (g/kg)
Big reactor	Dolomite	27.3 g, 2 cm	700	400	0.15	1.10	1.60	1.60
	Dolomite	17.7 g, 2 cm	950	500	0.11	1.71	3.74	3.74
	Dolomite	17.8 g, 2 cm	850	300	0.11	1.92	Not reached	15.15

Table A 3: Particle size distribution and texture data for natural dolomite

	Sample size (µm)
$D_{10\%} <$	3.81
$D_{50\%} <$	54.07
$D_{90\%} <$	83.42
D_{medium}	48.48
Surface density (m²/g)	4.9
Pore volume (cm³/g)	0.0064
Density (g/cm³)	2.86

Table A 4: Particle size distribution, texture and weight loss for calcined dolomite

Sample size (µm)	Gradual heating	Thermal shock
$D_{10\%} <$	5.54	5.92
$D_{50\%} <$	31.14	31.6
$D_{90\%} <$	60.80	59.53
D_{medium}	32.80	32.84
Surface density (m²/g)	14.5	12.1
Pore volume (cm³/g)	0.022	-
Density (g/cm³)	2.69	-
Weight loss (%)	32.3	28.4

Table A 5: Parameters from six different kinetic equations

Absorbate (Calinated at ^0C)	Power Function $C_{ads} = at^b$				Simple Elovich $C_{ads} = C + d\ln t$				Proposed Equation $C_{ads} = \dfrac{k_1 t}{1 + k_2 t^2}$			
	$a \times 10^{-4}$	b	R^2	% Dev.	$C \times 10^4$	$d \times 10^4$	R^2	% Dev.	$k_1 \times 10^6$	$k_2 \times 10^2$	R^2	% Dev.
Dolomite at 300 ^0C	1.90	0.459	0.748	0.801	4.12	1.15	0.847	0.528	1.87	2.24	0.996	3.43
Dolomite at 400 ^0C	6.94	1.251	0.540	8.88	9.35	7.16	0.966	0.210	8.32	2.60	0.998	1.28
Dolomite at 500 ^0C	2.00	0.273	0.733	0.747	1.78	1.28	0.891	2.332	1.14	0.430	0.992	3.28
Dolomite at 700 ^0C	1.52	0.202	0.643	0.634	5.79	1.63	0.899	0.520	0.430	1.41	0.991	2.10
Dolomite at 850 ^0C	2.86	1.224	0.740	0.759	7.09	7.00	0.909	6.591	5.29	1.23	0.997	3.81
Dolomite at 950 ^0C	1.80	0.305	0.759	0.740	2.85	2.82	0.892	1.238	2.61	1.439	0.990	1.73