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# Development of a small-scale biogas purification process

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## 1. Introduction

The work was focused on the development of an effective and economical hydrogen sulphide ($H_2S$) removal system for biogas refining, primarily tailored to meet the needs of small agro-food companies that want to have their own biogas generation system.

Biogas typically consists of methane, carbon dioxide and very small quantities of hydrogen sulphide. $H_2S$ is extremely reactive with most metals, so it has to be removed very early in the process of biogas purification to avoid corrosion in compressors, gas storage tanks and engines. Moreover, if biogas has to be upgraded to biomethane ($CH_4$ percentage > 95% vol), $H_2S$ content must decrease drastically (< 5 ppm for admission in gas distribution grids). [1]

Very effective $H_2S$ separation technologies are necessary, and the most appropriate choice is physical or chemical adsorption. [2] In this work, chemisorption on a packed bed was adopted and the adsorbent was hematite, a special iron oxide selected according to the following criteria: removal capacity, availability, regeneration potential, economic and environmental issues. The fundamental reaction between hematite and $H_2S$ can be represented as: [3]

$$Fe_2O_3 + 3\,H_2S \leftrightarrows Fe_2S_3 + 3\,H_2O$$

Hematite was directly synthesized in order to obtain a solid with suitable characteristics, chiefly a high porosity and therefore a high specific surface area. A final reproducible preparation procedure was optimized leading to a hematite powder with the desired properties and satisfactory performance.

A method for economic pelletisation that does not affect the performance of the adsorbent was developed. Moving from powder to pellets is an essential step for the industrial (scaled) use of the product. Different possibilities were investigated: physical compaction, coating of inert supports, and blending of the powder with a binder. This last option proved to be the better choice, allowing to prepare suitable pellets of desired dimensions (mean size about 3 mm). The performance of the produced hematite-based pellets was assessed in a lab plant exploring the influence of operating conditions such gas flow rate, $H_2S$ concentration, bed length, temperature. The performance was compared with that of other common commercial pelletised adsorbents and was found noticeably better.

## 2. Methods

The hematite preparation procedure consisted in a forced hydrolysis of a Fe(III) aqueous salt solution through addition of NaOH, followed by a drying phase for the removal of adsorbed water and a calcination phase for the final transformation of the product into hematite. Pellets were prepared mixing the hematite powder with poly(vinyl alcohol). Each adsorbent sample was characterized using different instrumental techniques: field emission scanning electron microscopy, X-ray diffraction, thermogravimetric analysis, and volumetric system porosimeter for the study of surface area and porosity. A dedicated lab plant was designed and realized to carry out the chemisorption performance study. A special reactor allowing also temperature control was used to hold the packed bed (see Figure 1).

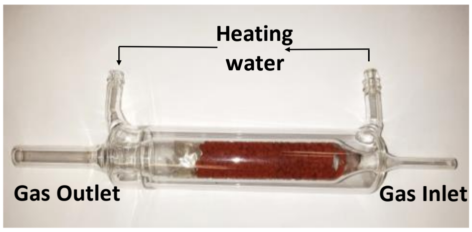


**Figure 1**.The reactor housing the packed bed of hematite-based pellets.

## 3. Results and discussion

The critical parameters investigated in the different step of this work are summarized here.

- Synthesis: pH of hydrolysis, type of basic reagent.
- Calcination: temperature, time.
- Bed packing: particle size, bed length.
- Reactor operation: $H_2S$ concentration in the feed gas, gas velocity, temperature.

The specific surface area of a solid is usually expressed in $m^2/g$, and a high value is a fundamental requirement for an efficient adsorbent system. The results obtained during the development of the preparation procedure revealed that the calcination temperature is the key variable which determines the final surface area of the produced hematite powder (Table 1).

**Table 1**. Porosimeter measurement on for hematite samples calcined at four different temperatures.

| Sample | Calcination temperature (°C) | Specific Surface Area ($m^2/g$) |
|---|---|---|
| $\alpha$-$Fe_2O_3$ | 300 | 105 |
| | 400 | 51 |
| | 500 | 31 |
| | 600 | 6 |

During the adsorption process, the reaction temperature was found to have a great effect on the efficiency of the adsorbing bed. The performance of the produced hematite-based pellets was compared with that of two common commercial products, zinc oxide and SulfaTreat® 410 HP, as summarized in Table 2. Here $q$ is the quantity of $H_2S$ adsorbed on the bed at the break point time, the time span at which in the effluent gas an $H_2S$ concentration ($C$) is detected which is one-hundredths of the initial one ($C_0$).

**Table 2**. Adsorption performance of different pelletised products.

| Sample | Temperature (°C) | t break point (min) | $q$ adsorbed (mg/g) at $C/Co$ =0.01 |
|---|---|---|---|
| $\alpha$-$Fe_2O_3$ | 25 | 225 | 3.9 |
| $\alpha$-$Fe_2O_3$ | 50 | 610 | 9.1 |
| ZnO | 25 | 237 | 2.4 |
| ZnO | 50 | 304 | 3.2 |
| SulfaTreat® | 25 | 150 | 2.5 |

The hematite-based pellets have in any case the best adsorbent capacity, and this finding is more striking at the higher temperature.

## 4. Conclusions

An effective and economical hydrogen sulphide removal system for biogas refining was manufactured. The results were very satisfying and proved that the work brought to the development of an economic, environmentally friendly, well-performing adsorption process.

## References

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