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Investigation of operating and geometric conditions of sweeting process of sour methane gas by zinc oxide nano particles

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ABSTRACT

Nano catalysts are adapted in this paper to vanish H_2S as the toxic, corrosive and pyrophoric contaminant. The important feature which is considered is to improve the adsorption efficiency of hydrogen sulphide from hydrocarbon fuels such as methane gas by applying the zinc oxide as nano catalyst. Totally, the optimum conditions to eliminate the hydrogen sulphide from methane gas are evaluated in this paper, experimentally. In this paper, zinc oxide nano particles are synthesized and are contacted with flow of sour methane. The synthesized nano particles are characterized by SEM and TEM. The process performance of H_2S removal from methane gas on zinc oxide nano particles is illustrated by the ratio of outlet concentration per feed concentration. The effects of operating conditions such as operating temperature and pressure, the amount of H_2S concentration in feed stream, size of nano catalyst and the bed diameter are investigated in this paper. This work studies the adsorption of H_2S from natural gas with an emphasis on the influence of the operating and geometric parameters on process efficiency. Finally, results introduce the amount of pressure 12 atm, temperature 80 $°C$, bed height 70 cm, diameter of catalytic bed 20 cm (for nanocatalysts with 35nm) and 40 cm (for nanocatalysts with 55nm) and 35 nm in diameter nano zinc oxide as the optimum basic properties. Therefore, the amount of C/C_0 is decreased to 0.024 for 35 nm in diameter zinc oxide and 0.033 for 55 nm in diameter zinc oxide, respectively. In addition, this is confirmed that the increase in the feed concentration of H_2S, also the decrease in the diameter of zinc oxide catalyst enhances the process efficiency.

INTRODUCTION

Nanotechnology (sometimes shortened to “nanotech”) is the manipulation of matter on an atomic and molecular scale. The earliest, widespread description of nanotechnology has been referred to the particular technological goal of precisely manipulating atoms and molecules for fabrication of macro scale products, also now is referred to as molecular nanotechnology[1]. A more generalized description of nanotechnology was subsequently established by the National Nanotechnology Initiative, which defines nanotechnology as the study and application of fine particles which are sized from 1 to 100 nanometres in all of the science fields[2].

Sulphur compounds in fuels such as methane gas cause problems on two fronts: they release toxic gases during combustion, and they damage metals and catalysts in engines and fuel cells[3]. They usually are removed using a liquid treatment that adsorbs the sulphur from the methane gas, but the process is cumbersome and requires that the gas be cooled and reheated, making the fuel less energy efficient[4]. To solve these problems, researchers have turned to solid metal oxide adsorbents, but those have their own sets of challenges[5]. While they work at high temperatures, eliminating the need to cool and re-heat the fuel, their performance is limited by stability issues. They lose their activity after only a few cycles of use[6].

Previous studies found that sulphur adsorption works best at the surface of solid metal oxides[7]. So, the authors set out to create a material with maximum surface area. The solution seems to be tiny grains of zinc oxide nano particles, uniting high surface area, high reactivity and structural integrity in a high-performance sulphur adsorbent[8]. Zinc Oxide has been numerously used for removing of hydrogen sulphide from gas streams in processes like reforming[9,10], integrated gasification combined cycle[11] and fuel cell[11,12,13]. Although, ZnO has been well evaluated with hydrogen sulphide feed stocks, the performance of zinc oxide nano structure with different operating conditions and structural characteristics in H_2S removal has not been specially evaluated in details. This work is devoted to using experimental design methodology to identify the optimum conditions for H_2S removal by nano zinc oxide catalysts. Clearly, the nano-sized ZnO is more reactive than the same material in bulk form, enabling complete sulphur removal with less material, allowing for a smaller reactor. The nano particles stay stable and active after several cycles[10].

Thermal Swing Regeneration is a common industry process used for sweetening natural gas. In that process, chemical sponges called sorbents remove toxic and flammable gases, such as rotten-egg smelling hydrogen sulphide from natural gas.

The gas must first be treated with a solution of chemical sorbents that are dissolved in water. That solution must then be heated up and boiled to remove the hydrogen sulphide, in order to prepare the sorbent for future use. Once the hydrogen sulphide is boiled off, the sorbent is then cooled and ready for use again. The repeated heating and cooling requires a lot of energy and markedly reduces the efficiency of the process, scientists say.

In the adsorption process by nano Zinc Oxide, sweetening of natural gas is occurred with minimum heat flux comparing with the other sweetening methods. Also, about 70 to 80 percentage of the initial amount of hydrogen sulphide is removed from the Methane by the proposed adsorption process. Also, Zinc Oxide catalyst is produced due to feasible method and is not expensive comparing with the other catalysts. So, this method is beneficial. Undoubtedly, the zinc oxide nano particles as sorbents have large active surface. So, they can be reused again and again. This method will be developed as soon as possible and will be applied in industrial scale.

In this work, a fixed bed reactor is set up which is equipped by nano zinc oxide catalysts. Some experiments have been held to investigate the effect of different operating pressure, temperature, catalyst diameter, bed height on the performance of H_2S removal. Also, the capability of nano catalysts is surveyed toward changing the amount of H_2S in feed stream and also changing feed superficial velocity. The results are illustrated as the ratio of outlet H_2S concentrationper inlet H_2S concentration. In addition, this work contains the cost estimations for the various operating pressures and temperatures. Consequently the optimum conditions are introduced.

MATERIALS AND METHODS

Zinc oxide nano particle is a common ingredient and has a huge variety of applications. Zinc is an essential mineral and is non-toxic in low concentration[11].

Synthesis method of nano-sized ZnO

Zinc metal is used to make a solution containing one molar Zn^{2+} ion. At first, this solution is purified, and then a type of surface-active reagent (zinc acetate dehydrate) 0.05 M is added. At the next step, approximately, 10% of ethanol is added under the ultrasonic conditions. The produced solution is agitated for 25 to 30 minutes. The obtained solution will be homogenised after this time interval. Same reagents are added to Na_2CO_3, 1M solution under the same conditions. Then another surface active reagent (folic acid) is added. The solution is agitated for 30 min again. In the next step, filtering and washing of the solution is done several times by ethanol and distilled water alternately under the ultrasonic action. The produced substance is prepared to dry for fifty minutes at 80 $°C$. Then it roasted at 450 $°C$ for forty fifty minutes to obtain zinc oxide nano particles. The obtained produced substance has light yellow colour, and can been characterized by SEM and TEM. Produced spherical particles with the average diameter of 35 -55 nm in size are observed approximately and finally the crystal is pure zinc oxide with hexahedral structure. Figure 1 shows TEM and SEM photos of produced nano particles a) in the scale of 5 μm and b) in the scale of 500 nm.

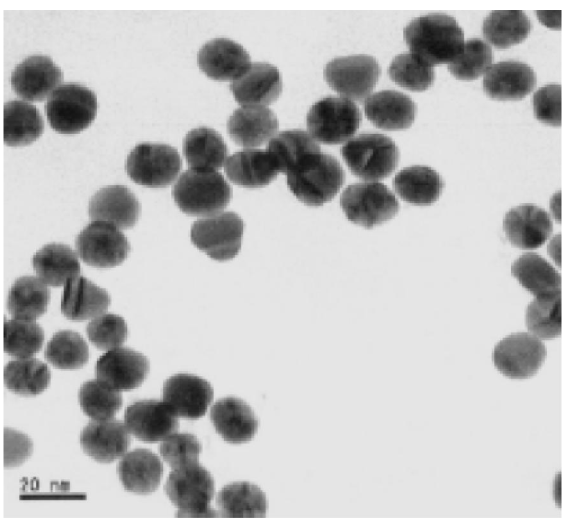

Figure 1-a)

Set up description

One laboratory cylindrical vessel equipped with the nano-sized ZnO catalytic fixed bed is applied for H_2S adsorption process, in this work. The process temperature is adjusted by one steam jacket around the vessel. Methane stream from a tank reservoir is mixed by H_2S and is fed into the bed containing zinc oxide nano particles. The inside diameter is between 15 to 40 cm and the height of the vessel is between 70 to 100 cm, respectively. All the instruments and equipments are made of stainless steel.

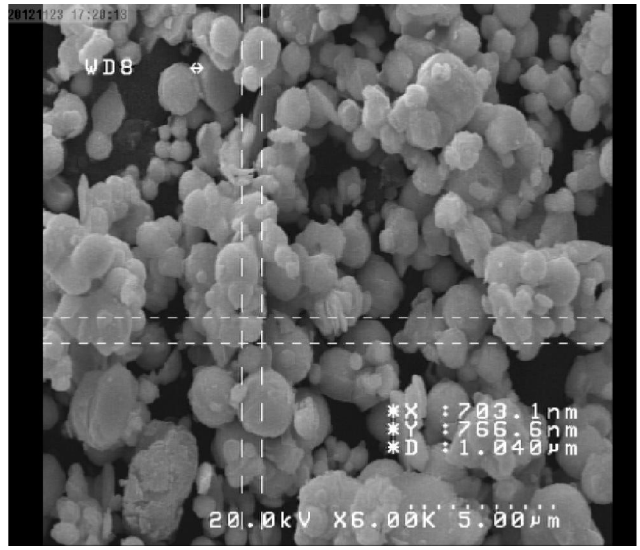

Figure 1-b)

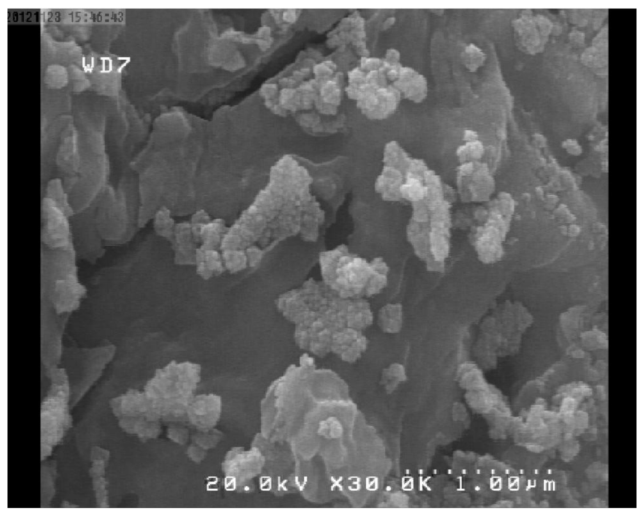

Figure 1-c)

Figure 2 shows briefly the mentioned adsorption experimental setup constructed to remove hydrogen sulphide from methane gas by using zinc oxide nano catalyst.

Methane gas flow rate is controlled by the flow meter and adjusted by valve after passing a filter, then is mixed by the adjusted amount of hydrogen sulphide and compressed to the reactor. The bed height of catalyst can be verified by some separate smaller metallic beds which are located in the vessel. Measuring the hydrogen sulphide concentration in the feed and the discharge flow, defines the performance of the process.

RESULTS AND DISCUSSION

Anyone knows, the hydrogen sulphide is corrosive and toxic, severely. Meanwhile, this component is in several industrial. We know the current technologies use huge resources of energy for removing the hydrogen sulphide component. Therefore, the researchers try to enhance the performance of sweetening process. So, in this paper the zinc oxide are applied as nano catalysts for removal of H_2S . This metal oxide is not expensive comparing with the other metal oxides. So, several experiments are designed to evaluate the performance of sweetening process in this paper, operationally and economically. These experiments were tested to determine operational conditions that would optimize the amount of H2S removed from gas in order to gas sweetening.

Some major parameters are considered experimentally in the gas sweetening process by nano particles. The effects of operating conditions, properties of catalytic bed and zinc oxide catalyst are investigated on the process performance. The ratio of H_2S concentration in the product stream on the initial concentration in the input stream (C/C_0) represents the process performance. The purpose of the experiments is to decrease the amount of hydrogen sulphide below the 4 ppm in the outlet stream. Experimental results are presented in the following Figures.

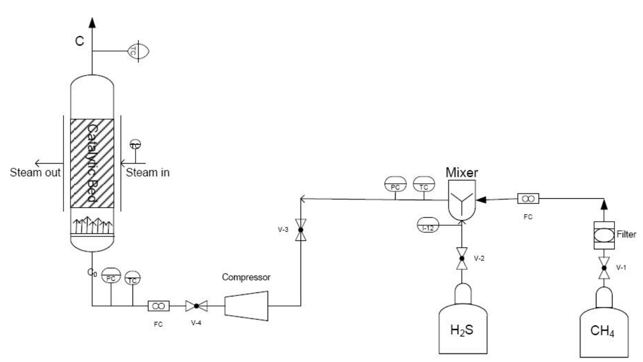

Figure 2

The effect of operating temperature and pressure

Both, temperature and pressure are two important parameters in separation processes. Five $50\,^\circ C$, $70\,^\circ C$, $80\,^\circ C$, $90\,^\circ C$ and $100\,^\circ C$ are examined during different pressures and the amount of C/C_0 is measured. So, to find the best operating temperature, the operating pressure is changed from 5 atm to 15 atm using 35 and 55 nm in diameter catalyst. The feed contains 100 ppm H_2S with 1.67 $\mu m^3/s$ flow rate and the reactor has a bed with 100 cm height. Figure 3 and 4 shows that the 5 atm operating pressure is not effective even at 100 C temperature, since the amounts of C/C_0 are higher than 0.04. Also, the amount of reaches below the 0.04 just when the range of operating temperature is adjusted between $80\,^\circ C$ to 100 and 12 is the operating pressure. The operating pressure 15 atm decreases the amount of near the 0.05 not below the 0.04 just when the range of operating temperature is adjusted between $80\,^\circ C$ to $100\,^\circ C$ and 12 is the operating pressure. The operating pressure 15 atm decreases the amount of C/C_0 near the 0.05 not below the 0.04 at all experimental operating temperatures. So, running the process under 15 atm seems to be more feasible. According to the results in Figure 3 and 4, providing operating temperatures above the 80 $^\circ C$ is just effective on decreasing the amount of hydrogen sulphide at 12 atm. Although the outlet concentration is the same at 80 $^\circ C$ and $100\,^\circ C$, but the consumed energy in steam jacket to provide the operating temperature of 100 $^\circ C$ is higher comparing with 80. So, the temperature of $80\,^\circ C$ and pressure of 12 are preferred as the best operating conditions.

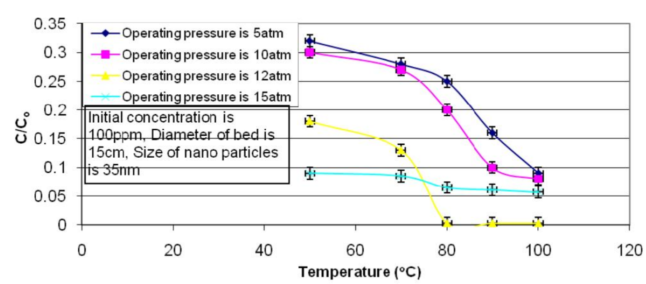

Figure 3

Figure 3 and 4 shows the decrease in the outlet H_2S concentration by the temperature augmentation.

Temperature varies from $50\,^\circ C$ to $100\,^\circ C$. The adsorption progress is obtained by temperature rise. The values of C/C_0 are changed from 0.21 to 0.033 and from 0.18 to 0.0027 when catalyst with 55 *nm* and 35 *nm* in diameter are used at 12 atm, respectively.

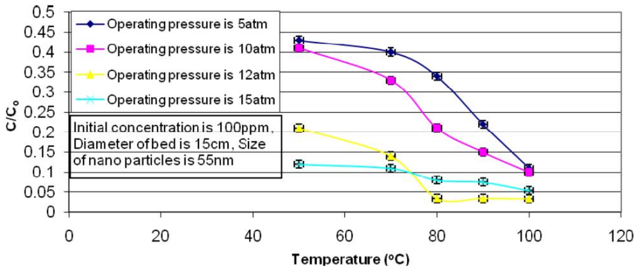

Figure 4

The effect of bed characteristics

The height and diameter of catalytic bed and also catalyst diameter are considered as the shape effects in this section. Bed length is changed from 60 cm to 100 cm and the diameter also is changed from 20 cm to 40 cm. The effect of bed characteristics are investigated on the amount of Hydrogen sulphide removal. The optimum amounts of height and diameter of the nano catalytic bed are studied in this section. Operating temperature and pressure is adjusted at 80 $°C$ and 12 *atm*, respectively.

Effect of bed diameter

The effect of changes in diameter of bed on H2S removal are shown in Figures 5 and 6 for two types of nano particles with 35 nm and 55 nm in diameter, respectively. Figure 5 shows that the increase in the amounts of C/C_0 is considerable when the diameter of the 35 nm catalytic bed changes from 20 *cm* to 40 *cm*. This may relate to the channelling phenomenon and referred to dynamic of passing gas stream in the bed. Although, the curve shows the increase in the amount of outlet H2S due to the increase in the amount of bed diameter, but the results are feasible and all are below the 0.04.

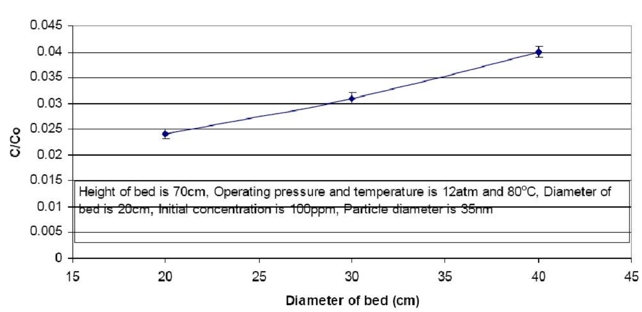

Figure 5

However, the higher bed diameter improves the H2s removal process when the 55 nm of catalytic bed is used. This is concluded the amount of outlet H2S is acceptable at higher bed diameter than 30 cm according to Figure 6.

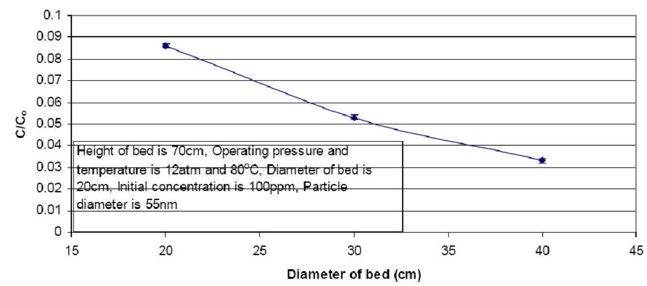

Figure 6

The effect of bed height and particle diameter

Figure 7, 8, 9, 10 and 11 show the effect of bed height in the range of 60 cm to 100 cm at bed diameter of 12 cm, on the efficiency of H2S removal. Also, the effects of different diameters of nanocatalyst are reported in the same figures. The optimum operating temperature 80 C and pressure 12 atm is adjusted for the experiments.

At all heights, Figures indicate on the better adsorption performance of smaller nanocatalyst such as 35 nm in diameter than the larger diameter nanocatalyst such as 55 nm. Figure 7 shows 60 cm height bed doesn't decrease the H2S concentration at the outlet, sufficiently even with 35 nm catalyst in the reactor bed. This may be referred to the insufficient mass transfer area is available at this height.

Nano catalyst with 35 nm and 40 nm in diameter show the acceptable amount of H2S in the outlet at height of 70 cm, according to Figure 7. Changes in di-

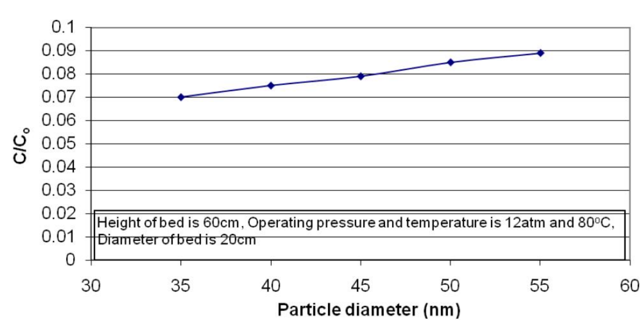

Figure 7

ameter of catalyst in the range of 35 nm to 55 nm reveal different results of C/C0 from 0.025 to 0.087 so, show the effect of diameter of nano catalyst at bed height of 70 cm.

Also, 35 nm catalyst decrease the amount of H2S effectively when the height of bed is adjusted 80 cm, but the other types of catalysts with larger diameter don't show proper performance according to Figure 8.

Figure 9 and Figure 10 obtain the improper performance of all catalyst with different diamteres at height of 90 cm and 100 cm. Although, the bed height is increased but the adsorption process goes worsely. This may refer to the effective mass transfer area of the bed which depends on the diameter of catalyst and also the bed height. Channelling malfunctionality happens on the higher bed length and the undesirable feed distribution is occurred. This is concluded the height of 70 cm is the best height of catalytic bed contains 35 nm and 40 nm of ZnO catalyst and sufficient effective surface area is provided for adsorption processs.

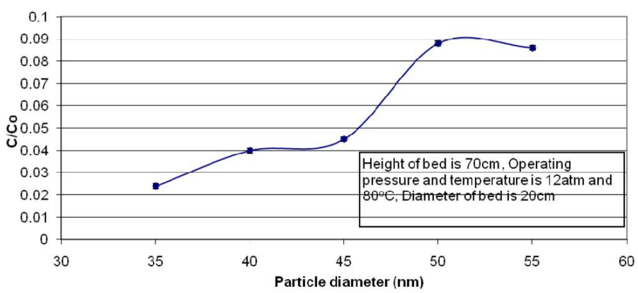

Figure 8

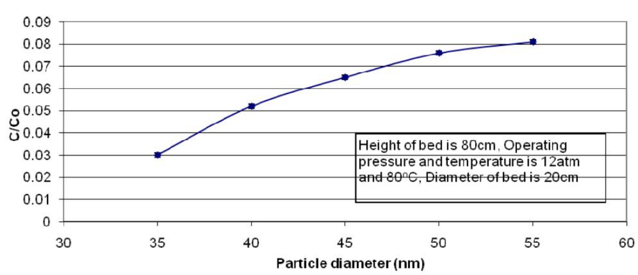

Figure 9

The effect of amount of input hydrogen sulphide

The effect of H_2S content in feed stream on the process performance is studied in Figure 11 for two diameters of catalyst, 35 nm and 55 nm. Each experiment is held at 80 $°C$ and 12 atm in bed with 30 cm and 70 cm in diameter and height, respectively. The increase in the feed concentration causes the increase

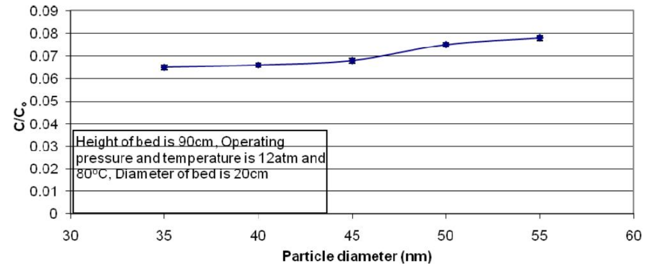

Figure 10

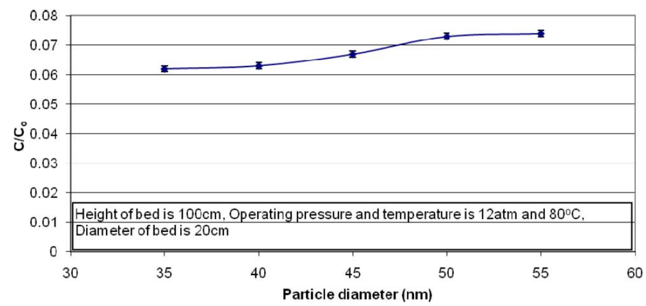

Figure 11

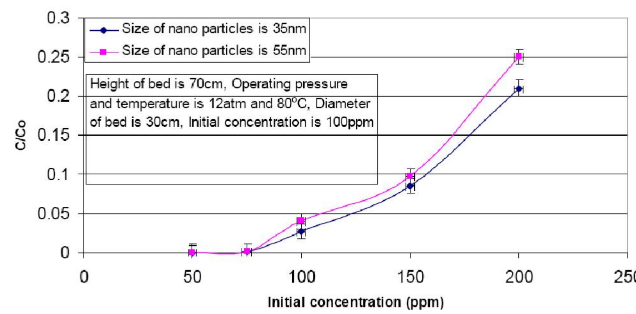

Figure 12

in the amount of H2S in the outlet stream according to Figure 11. This is indicated that the capability of both 3 nm and 55 nm nano catalysts is fixed and the active sites decreased. The proper feed concentration of H2S at the adjusted condition seem to be 50, 75 and 100 ppm, for both 35 nm and 55 nm catalysts and the outlet concentration is below the 0.04.

CONCLUSIONS

Low temperature gas sweetening applying nano catalyst has been investigated and has not commercialized yet. Nano catalyst development in various areas proposes to perform many processes economically and efficiently. The optimum operating conditions and reactor characteristics for hydrogen sulphide removal with ZnO nano catalyst are investigated experimentally in this work. The process performance is considered as the ratio of the outlet concentration of H_2S per the inlet concentration and is presented as value of C/C_0. Experiments are held in the cylindrical reactor in different temperature, pressure, bed height, bed diameter and zinc oxide catalyst diameter to find the best condition to reach the C/C0 value of 0.04 for H2S at the product.

The experimental results indicate that the optimum adsorption performance is obtained at 80 Centigrade degree and 12 atm operating conditions by 35 *nm* zinc oxide catalysts when the bed height is fixed 70 cm and the bed diameter is 30 cm.

Inlet feed which contains 50, 75, 100, 150 and 200 *ppm* H_2S are imposed in the catalytic bed, respectively. The results confirmed that, the capability of nano zinc oxide catalysts decreases by the increase in the initial concentration of and the best inlet concentration is lower than 100 ppm H2S.

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