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Parametric Study of Major Items in Desulphurization of Petroleum Gas

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Abstract

In this paper, aluminum oxide nano particles are synthesized and are contacted with a flow of sour LPG. The synthesized nano particles are characterized by SEM and TEM. The process performance of mercaptan removal from LPG 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 mercaptan concentration in feed stream, size of nano catalyst, the bed diameter and also, height of the bed are investigated in this paper. This work studies the adsorption of mercaptan from liquefied petroleum gas with an emphasis on the influence of the operating and geometric parameters on process efficiency. The experimental results show the changes of height from 6 cm to 7 cm decrease the amount of quality index from 0.032 to 0.027. But the variation from 7 to 9 doesn't show any changes in the amount of C/C0 as quality index.

Keywords

Diameter, Catalytic, Pressure, Temperature, Efficiencey, Optimization

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1. Introduction

Today, in the young field of nanotechnology (sometimes shortened to "Nanotech"), scientists and engineers are taking control of atoms and molecules individually, manipulating them and putting them to use with an extraordinary degree of precision. Word of the promise of nanotechnology is spreading rapidly, and the air is thick with news of Nanotech breakthroughs. Governments and businesses are investing billions of dollars in nanotechnology R&D, and political alliances and battle lines are starting to form. Nanotechnology 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 nanometers in all of the science fields [2]. Sulfur compounds in fuels such as liquefied petroleum gas cause problems on two fronts: they release toxic gases during combustion process, and they damage metals and catalysts in engines and fuel cells [3]. They usually are removed using a liquid treatment that adsorbs the sulfur compounds from the liquefied petroleum gas, but the process is cumbersome and requires that the hydrocarbon 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 higher 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].

Sulfur compounds and mercaptans in hydrocarbon and

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petroleum cuts lead to environmental pollution and corrosion problems in pipelines and storage tanks. So it is necessary to decrease sugar and mercaptans concentrations in hydrocarbon cuts to international standard levels in petroleum industries. For this purpose, DMD process has been developed as a demercaptanization process, providing the possibility of demercaptanization of different hydrocarbon cuts even crude oil as a feed.

Previous studies found that sulfur compound adsorption works best on 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 super adsorbent [8]. Zinc Oxide has been numerously used for removing of sulfide compounds from liquefied petroleum 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 sulfide compounds feedstocks, the performance of the zinc oxide nano structure with different operating conditions and structural characteristics in mercaptan removal has not been specially evaluated in details. This work is devoted to using an experimental design methodology to identify the optimum conditions for mercaptan removal by nano zinc oxide catalysts. Clearly, the nano-sized ZnO is more reactive than the same material in bulk form, enabling complete sulfur 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 industrial process used for desulphurization process. In that process, chemical sponges called Sorbents remove toxic and flammable gases, such as rotten-egg smelling hydrogen sulfide from natural gas.

The liquefied petroleum gas must first be treated with a solution of chemical solvents that are dissolved in water. That solution must then be heated up and boiled to remove the sulfide compounds, in order to prepare the Sorbent for future use. Once the sulfide compounds are boiled off, the solvent 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 liquefied petroleum gas is occurring with minimum heat flux comparison with the other sweetening methods. Also, approximately, 70 to 80 percentage of the initial amount of mercaptan is removed from the liquefied petroleum gas 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 a 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 mercaptan removal. Also, the capability of nano catalysts is surveyed toward changing the amount of mercaptan in feed stream and also changing feed superficial velocity. The results are illustrated as the ratio of outlet mercaptan concentration per inlet mercaptan concentration. In addition, this work contains the cost estimations for the various operating pressures and temperatures. Consequently the optimum conditions are introduced.

2. Materials and Methods

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

2.1. Synthesis of Aluminum Oxide Nano Particles

The two precursors used in the synthesis of Al_2O_3 by the sol - gel method were of different chemical nature: inorganic – aluminium chloride ($AlCl_3$) and organic–aluminium triisopropylate $(C_3H_7O)_3Al$. a). In the case of $AlCl_3$ (p.a., Fluka) as a precursor, the sol-gel synthesis consisted in the preparation of a 0.1 M $AlCl_3$ ethanolic solution (p.a., Chemical Company). By adding a 28% NH_3 solution (p.a. Fluke) a gel was formed. The gel was let to maturate for 30 hours at room temperature and then dried at 100 ^oC for 24 hours. b). For $C_9H_{21}AlO_3$ (p.a., Fluka) used as a precursor, the sol-gel synthesis consisted in the preparation of a 0.1 M $(C_3H_7O)_3Al$ ethanolic solution (p.a., Chemical Company). A 28% NH_3 solution (p.a., Fluka) was added in order to form a gel. Mild shaking at 90 ^oC for10 hours was utilized. The gel was let to maturate at room temperature for 24 hours, and then dried at 100 ^oC for 24 hours. The resulting gels were calcined in a furnace for 2 hours (heating rate 20 ^oC /min.), at temperature values of 1000 ^oC and 1200 ^oC [2].

Figures 1, 2 and 3 show the SEM and TEM of producing nano particles. The parts of a and b is taken by scanning electron microscopy and the third section is taken by transmission electron microscopy.

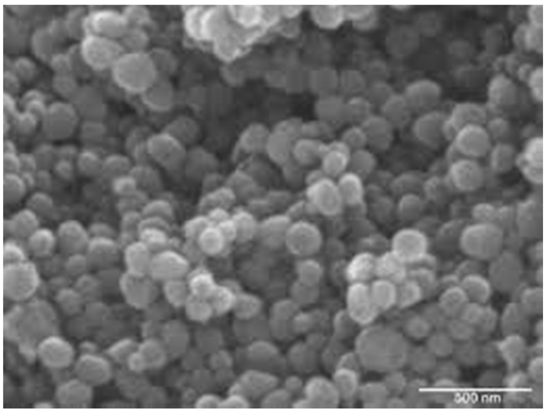

Figure 1. The SEM picture.

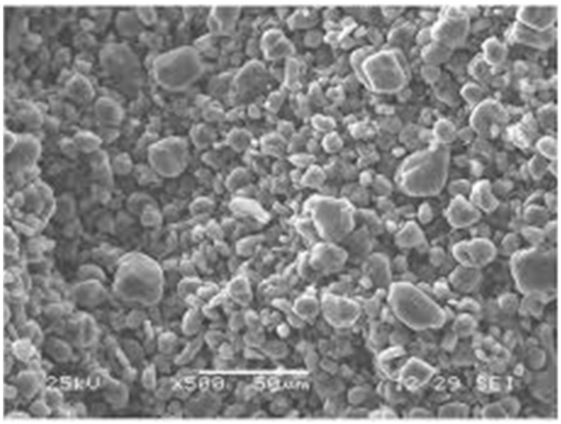

Figure 2. The SEM picture.

Figure 3. The TEM picture.

2.2. Set up Description

One laboratory cylindrical vessel equipped with the nano-sized Al2O3 catalytic fixed bed is applied for mercaptan adsorption process, in this work. The process temperature is adjusted by an electrical coil around the inlet pipe. Liquefied petroleum gas stream from a tank reservoir is mixed by mercaptan and is fed into the bed containing aluminium oxide nano particles. The inside diameter of bed is designed 3 cm and the height of the vessel is 12 cm, respectively. All the instruments and equipments are made of stainless steel.

3. Results and Discussion

Demercaptanization process from LPG using aluminium oxide catalytic bed is considered in this section. The effect of some major operating parameters, particle and bend characteristics on the removal of the mercaptan with nano aluminium oxide are investigated. Experimental results of the setup are shown in this section. Temperature, pressure, initial concentration of feed, catalytic bed height, catalytic bed diameter, particle diameter and shape of nano catalyst are changed and the optimum amounts of each specification are surveyed. A factor which is selected to evaluate the performance of mercaptan removal from LPG is the fraction of outlet concentration per inlet concentration C/C0. Experimental parameters have been considered here since of their effects on the coefficients related to mass transfer and heat transfer such as mass transfer area, Reynolds number, Prandtl number, diffusion coefficient, convective and conductive heat transfer coefficient in the adsorption process. The results can help to predict the optimum overall operation conditions and optimum design of the reactor.

3.1. The Effect of Shape of Temperature

The increase of operating pressure and temperature, predict the decreasing trend of C/C0. The Figure 4 shows the effect of pressure and temperature for a catalytic bed with 2.5 cm diameter, 7 cm height, and mercaptan initial concentration of 58 ppm contains spherical nano aluminum oxide. The increase in temperature from 82 C to 90 C decreases the factor of C/C0 from 0.42 to 0.12, 0.4 to 0.1, 0.22 to 0.05, 0.14 to 0.06 for 6, 9, 12 and 15 atm, respectively. Figure 5 also shows the effect of temperature and pressure on the amount of C/C0 for cylindrical catalyst.

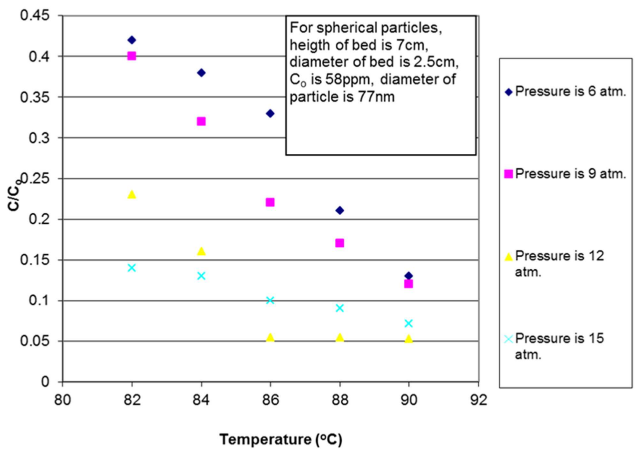

Figure 4. The effect of temperature and pressure on C/C0 for spherical catalyst.

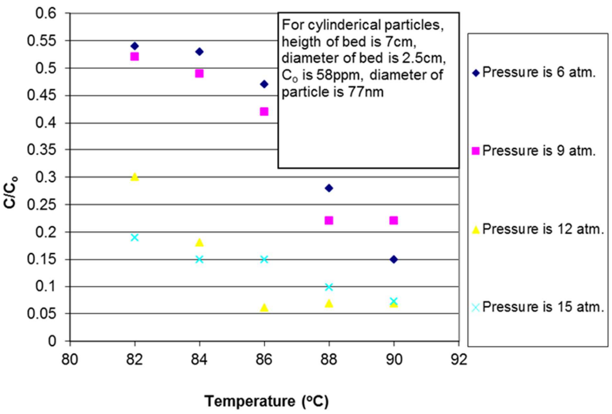

Figure 5. The effect of temperature and pressure on C/C0 for cylindrical catalyst.

Comparing the Figure 4 and and also, the Figure 5 obtain the higher mercaptane removal from the LPG using spherical nano aluminum oxide. The increase in temperature showthe decrease in the amount of C/C0 from 0.55 to 0.15, 0.52 to 0.22, 0.3 to 0.051, 0.19 to 0.06 for pressure 6, 9, 12 and 15 atm, respectively.

Both Figure 4 and also, the Figure 5 shows the irregular changes in the decrease trend of C/C0 at 12 atm and 15 atm from 86 C to 90 C. The amounts of C/C0 at 12 atm are lower than that are obtained at 15 atm. Usually, the incraese in pressure with temperature increases the adsorption mechanism however observations for 86 C to 90 C are the other behavior. This may since the nonproper collision between gas and catalyst at these conditions. For both cylindrical and spherical types of catalysts the optimum temperature and pressure seems to be 86 C and 12 atm. The minimum amount of C/C0 factor is obtained 0.5 and 0.51 for both types of catalysts.

3.2. The Effect of Height of Bed

The effect of height of cylindrical type of catalytic bed on the amount of mercaptan in the outlet stream is shown in the Figure 5. At the optimum temperature and pressure, different heights of bed (6 cm, 7 cm and 9 cm) show the 0.04, 0.032 and 0.031 of C/C0. The increase in the amount of height decreases the amount of C/C0. The increase in height of bed increases the mass transfer surface area for the process. However at 7 cm and 9 cm there is not much difference in the amount of C/C0. This may relate to the channelling of the LPG stream in bed. Also, the high portion of mercaptan is removed at height of 7 cm. So, this high can be as the optimum height of bed for cylindrical particles.

Figure 6 shows the effect of bed height of spherical nanoparticles on the amounts of C/C0. Changes of height from 6 cm to 7 cm decrease the amount of C/C0 from 0.032 to 0.027. But variation from 7 to 9 doesn't show any changes in the amount of C/C0.

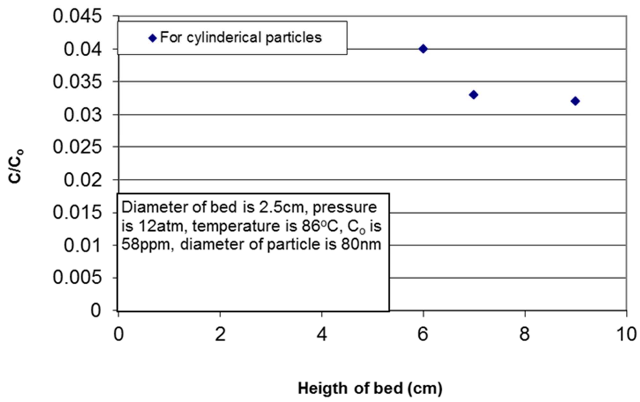

Figure 6. The effect of bed height of cylindrical catalyst on C/C0.

4. Conclusions

Performance of one nano aluminium oxide, packed bed in the demercaptanization process of liquefied natural gas is considered here. So, different parameters which are necessary to predict mass transfer coefficient or heat transfer coefficient like, temperature (82 C, 84 C, 86 C, 88 C and 90 C), pressure (6 atm, 9 atm, 12 atm, 15 atm), height of bed (6 cm, 7 cm, 9 cm), diameter of bed (1.25 cm, 1.75 cm, 2.5 cm), particle diameter (60 nm, 70 nm, 80 nm, 90 nm) and type of particle(cylindrical and spherical) are considered here. The experimental results show the changes of height from 6 cm to 7 cm decrease the amount of C/C0 from 0.032 to 0.027. But the variation from 7 to 9 doesn't show any changes in the amount of C/C0.

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