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Experimental Investigation of Sulphur Removal from LPG: New Aspect

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ABSTRACT

Nano catalytic sulphur removal process is surveyed in this research, experimentally. Qualification of sulphur removal from liquefied natural gas process is investigated due to catalytic bed geometries which contains nano ferrite oxide and operation conditions. The purpose of experiments is finding the conditions which lead to the lowest amount of sulphur content in the out stream. Fraction of sulphur content in the outlet to the amount of sulphur in the inlet is considered as the operation criteria in this work. The effects of operating conditions such as operating temperature and pressure, the amount of sulphur concentration in feed stream, size of nano catalyst, the bed diameter and bed height are investigated. The different correlations with high confidence factor are introduced in this paper. Results show the diameter changes from 1-2 cm and the ratio of C/C_0 changes from 0.05-0.03.

Key words: Sulphur, optimization, concentration, different conditions

INTRODUCTION

Sulphur 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 (Zhang *et al*., 2013; Hosseinkhani *et al*., 2012; Christoforidis *et al*., 2012). They usually are removed using a liquid treatment that adsorbs the sulphur compounds from the liquefied petroleum gas but the process is cumber some and requires that the hydrocarbon be cooled and reheated making the fuel less energy efficient (Balouria *et al*., 2013). To solve these problems, researchers have turned to solid metal oxide adsorbents but those have their own sets of challenges (Eow, 2002). 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 (Habibi *et al*., 2010). Sulphur compounds and sulphurs in hydrocarbon and petroleum cuts lead to environmental pollution and corrosion problems in pipelines and storage tanks. So, it is necessary to decrease sulphur and sulphurs concentrations in hydrocarbon cuts to international standard levels in petroleum industries. For this purpose, DMD process has been developed as a desulphurization process providing the possibility of desulphurization of different hydrocarbon cuts even crude oil as a feed. Previous studies found that sulphur compounds adsorption works best at the surface of solid metal oxides (Novochinskii *et al*., 2004a). So, the authors set out to create a material with maximum surface area. The solution seems to be tiny grains of ferrite oxide nano

particles, uniting high surface area, high reactivity and structural integrity in a high-performance sulphur adsorbent (Novochinskii *et al*., 2004b). Ferrite oxide has been numerously used for removing of sulphide compounds from liquefied petroleum gas streams in processes like reforming (Arthur and Nielsen, 1997; Habibi *et al*., 2009) integrated gasification combined cycle and fuel cell (Fotoohi and Farahbod, 2015). Although, Fe_2O_3 has been well evaluated with sulphide compounds feed stocks, the performance of ferrite oxide nano structure with different operating conditions and structural characteristics in sulphur removal has not been specially evaluated in details. This work is devoted to using experimental design methodology to identify the optimum conditions for sulphur removal by nano ferrite oxide catalysts. Clearly, the nano-sized Fe_2O_3 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 (Habibi *et al*., 2009). Thermal swing regeneration is a common industry process used for desulphurization process. In that process, chemical sponges called sorbents remove toxic and flammable gases, such as rotten-egg smelling hydrogen sulphide from natural gas. The liquefied petroleum 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 sulphide compounds, in order to prepare the sorbent for future use (Arthur and Nielsen, 1997). Once the sulphide compounds are 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 (Novochinskii *et al*., 2004b; Arthur and Nielsen, 1997). In the adsorption process by nano ferrite oxide, sweetening of liquefied petroleum gas is occurred with minimum heat flux comparing with the other sweetening methods. Also, approximately, 70-80% of the initial amount of sulphur is removed from the liquefied petroleum gas by the proposed adsorption process (Arthur and Nielsen, 1997; Habibi *et al*., 2009). Also, ferrite oxide catalyst is produced due to feasible method and is not expensive comparing with the other catalysts. So, this method is beneficial. Undoubtedly, the ferrite 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 (Habibi *et al*., 2009).

In this work, a fixed bed reactor is set up which is equipped by nano ferrite oxide catalysts. Some experiments have been held to investigate the effect of different operating pressure, temperature, catalyst diameter, bed height on the performance of sulphur removal. The results are illustrated as the ratio of outlet sulphur concentration per inlet sulphur concentration.

MATERIALS AND METHODS

Synthesis method of nano-sized Fe_2O_3: Using 0.01 M ferric nitrate which is prepared by dissolving $Fe(NO_3)_3 \cdot 9H_2O$ in distilled water. After 15 min duration of ultrasonic the solution is rest for about 15 min. Then, hydrazine monohydrate with concentration of 0.5 M is added dropwise to the solution under sonication (600 W, 20 kHz) for about 2 h and the pH value of reaches about pH = 5. Black particles are precipitate after cooling the solution. Then the solution is centrifuged and washed using distilled water and acetone, respectively. Nano powder is reached after 5 h drying time at 70°C in air.

Set up description: One laboratory cylindrical vessel equipped with the nano-sized Fe_2O_3 catalytic fixed bed is applied for sulphur adsorption process in this work. The process temperature is adjusted by one steam jacket around the vessel. Liquefied petroleum gas stream from a tank reservoir is mixed by sulphur and is fed into the bed containing ferrite oxide nano particles.

RESULTS AND DISCUSSION

Regarding the studies, few experimental, bench or pilot surveys have been done on mercaptan removal on nano catalyst. There are not any reports and study in this special field. So, detailed discussion or comparison study is not possible here.

Clearly, utilization of nano particles specially nano metal particles provides large mass transfer surface area and also heat transfer area, introducing low energy consumed, cost benefit and efficient separation processes, according to the investigations about the nano particles. However, operational conditions affect the process performance in each case. So, finding proper ranges of temperature and pressure using nano particle are considered in mercaptan removal from LPG to enhance the product quality and reduce operational cost. Also, the optimized amount of required nano particle should be considered as finding the proper geometrical properties of bed such as diameter and depth.

The authors try to enhance the performance of sweetening process. So, in this paper the ferrite oxide are applied as nano catalysts for sulphur removal. This metal oxide is not expensive comparing with the other metal oxides. Several experiments were held to determine operational conditions that would optimize the amount of sulphur removed from LPG in order to LPG sweetening. Some major parameters are considered experimentally in the liquefied petroleum gas desulphurization process by nano particles. The effects of operating conditions, properties of catalytic bed and ferrite oxide catalyst are investigated on the process performance. The ratio of sulphur concentration in the product stream on the initial concentration in the input stream (C/C_0) represents the process performance. Experiments are conducted to show the effect of operating temperature, pressure and also bed height and bed diameter on the quality of liquified petroleum gas sweetening by ferrite oxide as nano catalyst. Below correlations can introduce the results. The quality of sweetening process is determined by the fraction of outlet mercaptan concentration, C on the inlet concentration of mercaptan C_0.

Capability of three zeolites (13X, NaY and 5A) in sulfur removal from mixture of butane and propane as a part of their purposes. The break through curves were showed that only one type of zeolite could decrease the sulfur concentration to 2 ppm and kept this concentration till 35 min duration of process. In this study, nano ferric oxide is used to remove sulfur from LPG and different parameters are surveyed (Xiang *et al*., 2016). Sulfur removal by liquid absorption on fiber film providing larger-mass transfer area than conventional absorption columns (Zhang *et al*., 2015). In this study the adsorption on nano catalyst is applied considering to provide large mass transfer area.

Effect of operating temperature and pressure: The correlations 1, 2, 3 and 4 state the process quality of desulphurization process from LPG. The confidence factors of introduced correlations are very high (Table 1).

The increase in the amount of operation pressure from 5.5-8.5 atm at temperatures of 82-88°C decreases the amount of C/C_0. For higher amounts of pressure from 11.5-14.5 atm the increase in

Table 1: Correlation between temperature and pressure with quality of desulphurization process from LPG

Operation pressure	C/C_0 ratio	Uncertainly (%)
1<P<5.5 (atm)	$-0.0066T^2+1.085T-43.991$	0.0500
5.5<P8.5 (atm)	$-0.0013T^2+0.1715T-5.12$	0.0530
8.5<P<11.5 (atm)	$-0.0066T^2-1.15T+51.154$	0.0506
115<P<14.5 (atm)	$-0.0004T^2+0.0533T-1.5404$	0.0503

LGP: Liquified petroleum gas

the amount of temperature from 86-90°C decreases the amount of C/C_0. The strange behavior in the decreasing trend of C/C_0 is obtained at temperature of 90°C which the higher amount of C/C_0 is obtained at 8.5 atm comparing with 5.5 atm. Also, the equal amounts of C/C_0 are obtained at 11.5 and 14.5 atm and at 90°C. The amounts of concentrations which are obtained at 15 atm are higher than those are obtained at pressure of 11.5 atm in ranges of temperatures from 86-90°C. Results shows the changes in the amount of C/C_0 due to the changes in temperatures and pressures. Results indicate the optimum amount of pressure and temperature is 11.5 atm and 66°C which leads to the amount of 0.05 ppm.

Lv *et al*. (2014) indicated that the advantages of adsorption process in sulfur removal comparing with the usual absorption processes. Also, they showed that the increase of temperature from 25-60°C decreased the performance of desulphurization over AgO/NaY and the increase from 60-90°C improves the desulphurization performance. Although nano Fe_2O_3 particle is used in this study but the positive effect of temperature increase on the sulfur removal (Fotoohi and Farahbod, 2015). Farahbod *et al*. (2013) also obtained the positive effect of increase in values of temperature and pressure on decreasing the amount of sulfur compounds over ZnO nano particle (Lv *et al*., 2014).

Effect of geometrical characteristics: Al-Zuhair *et al*. (2015) investigated the performance of ZnO in sulfur adsorption from LPG on 2015. Two aspect ratios of packed bed as diameter to height of adsorption bed were used by applying two experimental column with different diameters. Although one column was made from stainless steel and the other was made from glass but they neglected the possible effect of material on the performance of adsorption. They revealed that the effect of aspect ratio on sulfur removal was small and was further decraesed by increasing the amount of adsorbant. Also, the increase in the amount of adsorbent decreased the first order kinetic constant (Al-Zuhair *et al*., 2015). In this study, the effect of height and diameter is investigated over nano ferric oxide, separately.

The height and diameter of catalytic bed and also catalyst diameter are considered as the shape effects in this section. Bed length is changed in the range of 4.5, 6.5 and 8.5 cm. Also the bed diameter changes are in range of 1, 2 and 3 cm. The effect of bed characteristics are investigated on the amount of sulphur removal. The optimum amounts of height and diameter of the nano catalytic bed are studied in this section.

Effect of bed diameter: The effect of changes in diameter of bed on sulphur removal is shown in formula. The increase in value of bed diameter provides higher mass transfer area and also leads higher rate of mass transfer. So, the decrease trend is obtained with higher values of bed diameter. The diameter changes from 1-2 cm and the ratio of C/C_0 changes from 0.05-0.03. For the optimum condition:

$$C/C_0 = -0.0063d_b+0.054$$

So, the increase of 63% in the amount of bed diameter improves the amount of C/C_0 about 0.197. Bed height values are 4.5, 6.5 and 8.5 cm.

Effect of bed height: Bed height is the other dimensional parameter of bed which affects the amounts of C/C_0. The increase in the amount of bed height decreases the amounts of C/C_0 from 0.05 to 0.012. Changes in values of C/C_0 at the optimum pressure, temperature and bed diameter values

which are obtained before due to the changes in bed height are state in the below correlation. The higher value of bed height provides higher mass transfer area using catalyst, so decreases the amount of C/C_0. The optimum condition for bad height:

$$C/C_0 = -0.0022h^2_b-0.0352\ h_b+0.173$$

The increase in the amount of bed height for about 50% decreases the amount of C/C_0 for about 33%.

Also, the previous study from the author over zinc oxide nano catalyst showed the same resulte with which are obtained in this survey over ferric oxide nano particle (Lv *et al*., 2014).

CONCLUSION

Nano catalyst development in various areas proposes to perform many processes economically and efficiently. The optimum operating conditions and reactor characteristics for sulphur removal with Fe_2O_3 nano catalyst are investigated experimentally in this work. The process performance is introduced as the ratio of the outlet concentration of sulphur per the inlet concentration and is presented as value of. Results show the diameter changes from 1 cm and the ratio of C/C_0 changes from 0.05-0.03. Results show the increase of 63% in the amount of bed diameter improves the amount of C/C_0 about 0.197. The increase in the amount of bed height for about 50% decreases the amount of C/C_0 for about 33%.

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