Presentation of novel basic conditions for sweetening of crude oil

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ABSTRACT

The important feature which is considered is to improve the adsorption efficiency of hydrogen sulphide from hydrocarbon fuels such as petroleum oil by applying the zinc oxide as nano catalyst. Totally, the optimum conditions to eliminate the hydrogen sulphide from petroleum oil are evaluated in this paper, experimentally. In this paper, zinc oxide nano particles are synthesized and are contacted with flow of sour petroleum. A method of removing sulphur from sour oil by nano catalyst is a novel method. ZnO nano catalyst of 35 nm in diameter is used to treat the sour oil. The useful correlations are presented to predict the optimum conditions for sweetening of crude oil by ZnO as nano catalyst.
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INTRODUCTION

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[1].

Sulphur compounds in fuels such as petroleum oil cause problems on two fronts: they release toxic oiles during combustion, and they damage metals and catalysts in engines and fuel cells. They usually are removed using a liquid treatment that adsorbs the sulphur from the petroleum oil, but the process is cumbersome and requires that the oil be cooled and reheated, making the fuel less energy efficient[2]. To solve these problems, researchers have turned to solid metal oxide adsorbents, but those have their own sets of challenges. 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[3].

Previous studies found that sulphur adsorption works best at the surface of solid metal oxides. 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. Zinc Oxide has been numerously used for removing of hydrogen sulphide from oil streams in processes like reforming[4], integrated oilification combined cycle and fuel cell[5,6]. 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.

MATERIALS AND METHOD

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Figure 1 shows the oil sweetening experimental set up. All equipments are made up of glass since it is non corrosive material and makes the oil tracking in catalytic bed possible.

Storage tank is equipped with a hot water jacket and a stirrer to increase the oil temperature uniformly, moving easily through the set up. Surely, temperature and pressure is controlled in feed tank, necessarily. The oil is pumped upward and passes through a filter and then is fed into the reactor with an adjusted flow rate. Feed oil is distributed on the catalytic bed by a glass distributor.

The reactor is a vessel with 14 cm diameter and 14 cm height. Changing the height of the catalytic bed, there are some catalytic sections with 2 cm height which can be located into the reactor vessel. A hot water jacket keeps the reactor temperature at the adjusted experimental temperature. TABLE 1 shows the API density

TABLE 1 : Charactristics of oil samples used in this work

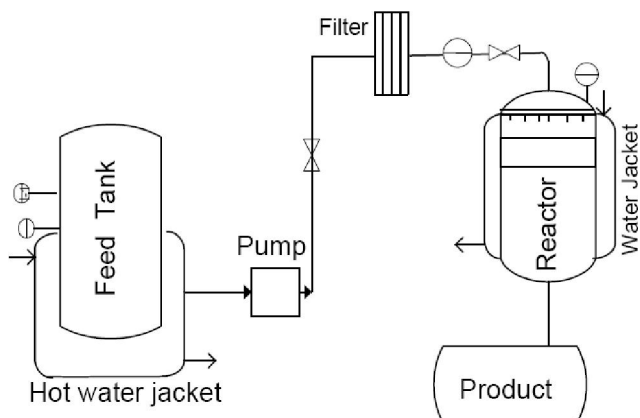| Type of crude oil	API	Amount of sulphur (wt%)
Heavy Iranian crude	29.6	2
Light Iranian crude	33.4	1.37

Figure 1 : Schematic of proposed sweetening process

and amount of H_2S in four types of sour oil.

Preparing nano-sized ZnO

To prepare nano ZnO, one molar Zn^{2+} ion solution is purified, then a type of surface-active reagent (zinc acetate dehydrate) 0.05 M is added. Uunder the ultrasonic conditions 10% of ethanol is added. The produced solution is agitated and homogenized for 25 to 30 minutes. Same reagents are added to Na_2CO_3, 1 M solution under the same conditions. Then another surface active reagent (folic acid) is added. The solution is

agitated for 30 min again. After filtering and washing of the solution several times by ethanol and distilled water alternately under the ultrasonic action the produced substance is heated to dry for fifty minutes at $80 \, ^\circ C$. Then it roasted at $450 \, ^\circ C$ for forty fifty minutes to obtain zinc oxide nano particles. The obtained produced substance has light yellow colour, and can been characterized by SEM. 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 a and b shows SEM photos of produced nano particles.

RESULTS AND DISCUSSION

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 hydrogen sulphide removal. 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 oil in order to oil sweetening.

Some major parameters are considered experimentally in the oil 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.

The effect of temperature

As obtained experimental results, the correlation numbers 1 and 2 are represented. The regression of this correlation is calculated, also. This correlation shows the effect of variations in moderate temperatures from $50 \, ^\circ C$ to $80 \, ^\circ C$ on the value of C/C_0.
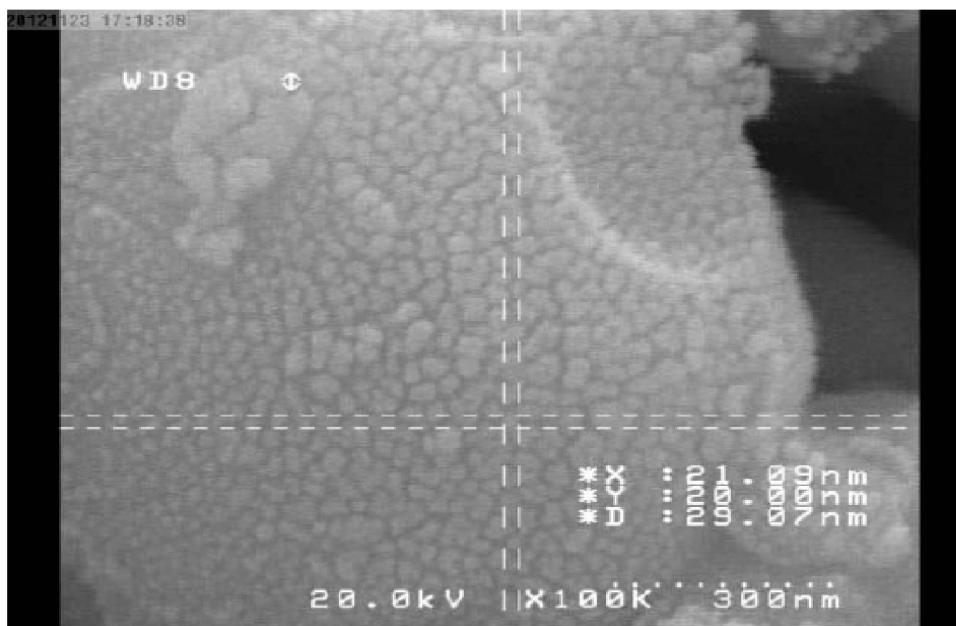
Figure 1a : SEM photo of produced zinc oxide nano particles

Figure 1b : SEM photo of produced zinc oxide nano particles

$$\left(C/C_0\right)_{lightoil} = 0.0003T^2 - 0.0405T + 1.3709 \quad (1)$$

$$R^2 = 0.9878 \quad (2)$$

$$\left(C/C_0\right)_{heavyoil} = 0.0005T^2 - 0.0657T + 2.3946 \quad (3)$$

$$R^2 = 0.9781 \quad (4)$$

$$\left(C/C_0\right)_{lightoil} = 0.0188H^2 - 0.2709H + 0.9123 \quad (5)$$

$$R^2 = 0.937 \quad (6)$$

$$\left(C/C_0\right)_{heavyoil} = 0.0168H^2 - 0.2612H + 0.9956 \quad (7)$$

$$R^2 = 0.9975 \quad (8)$$

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This correlation state the effective temperature for reaching to the minimum amount of C/C_0 is $70 \, °C$.

The effect of bed height

After finding the optimum temperature correlation in hydrogen sulphide removal process, the second parameter which is considered in this section is bed height. The height of catalytic bed is changed from 2cm to 10cm.

CONCLUSION

Oil sweetening by nanocatalyst has been not developed industrially, yet. So, finding the optimum conditions of this operation is interesting. Oil catalytic sweetening is investigated experimentally using 35 nm ZnO catalyst. Respectively, four types of heavy and light oil with density of 29.6 and $33.4 \, °API$ are sweetened catalytically. The initial amount of sulphur in the light and heavy crude oils are 1.37 wt% and 2 wt%, respectively. Experiments are conducted to survey the effect of operating temperature and pressure of sour oil, bed diameter and bed height on the amount of outlet H_2S concentration. The quality of the sweetening process is shown by the fraction of outlet concentration of H_2S on the amount of inlet H_2S. The optimum conditions obtained are $70 \, °C$ as operating temperature and 6cm as height of bed. According to the mentioned optimum conditions, the amount of C/C_0 decreases in 0.0067 and 0.0036 for heavy and light oil, respectively.

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