ISSN: 0974 - 7516 Volume 10 Issue 8

Organic CHEMISTRY
An Indian Journal
Full Paper

OCAIJ, 10(8), 2014 [332-336]

Parametric study of sweetening process of sour oil by nano catalyst

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ABSTRACT

A method of removing sulphur from sour oil by nano catalyst is a novel method. ZnO nano catalyst of 45 nm in diameter is used to treat the sour oil. Two types of heavy oil with density of 29.6 and 29.7 API are sweetened catalytically. So, the different operating conditions which effect on the sweetening process of crude oil is investigated in this paper. Results show 70 C and 1.2 atm are the optimum temperature and pressure respectively when ZnO is applied as nano catalyst. Also, the optimum designed parameters for diameter and height of bed are 6 cm and 10 cm respectively. Investigations show the efficiency of proposed process is very high. So, tests approve the sweetening process of sour oil which can be replaced conventional process.

INTRODUCTION

Desulfurization of crude oil is an important process used in a petroleum refinery to reduce the sulfur concentration and production of fuel products such as gasoline, jet fuel, kerosene, diesel and heating oil[1]. So, the resulting fuels meet environmental protection standards[2].

The challenge of fulfilling the world's growing transportation energy needs is no longer a simple issue of producing enough liquid hydrocarbon fuels[3]. This challenge is instead accentuated by a complex interplay of environmental and operational issues. Environmental issues include societal demands that liquid hydrocarbon fuels be clean and less polluting[4]. The emergence of new refining processes and the increasing use of new forms of energy production, e.g., fuel cells, exemplify operational issues. Together, these trends are driving the need for deep desulfurization of diesel and jet fuels.

Desulphurization processes

In the past two decades petroleum refining has changed extensively and the fortunes of hydrotreating, in particular, have witnessed a sea change[5]. Hydrotreaters now occupy a central role in modern refineries and more than 50% of all refinery streams now pass through hydro-treaters for conversion, finishing, and pretreatment purposes[6,7]. Hydro-desulfurization is the largest application of catalytic technology in terms of the volume of material processed. On the basis of usage volume, HDS catalysts are ranked third behind catalysts used for automobile emission control and FCC. Commercial hydrotreating catalysts are, typically, Mo or Zn. Mo, known for its high hydrogenation activities, is preferred as a promoter when feed stocks containing high amounts of nitrogen and aromatics need to be processed.

It seems, nano particles sucha as metal oxides can promote the heating and cooling process[8,9]. For example, the nano substances like; metal oxides can enhanced the thermal stability of some of materials[10].

In this work, ZnO nano catalyst is applied for sweetening process of sour oil. So, the operating and geometrical parameters are evaluated in this paper.

Therefore, the gained results can be interesting for related industries and can be applicable in process optimization.

MATERIALS AND METHOD

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 and amount of H_2S in two types of sour oil.

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
Foroozan crude	29.7	2.2

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. Under 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 shows SEM photo of produced nano particles in the scale of 5 μm.

RESULTS AND DISCUSSION

Experiments are conducted to show the effect of operating temperature, pressure and also bed height and bed diameter on the quality of oil sweetening by catalyst. Below curves can introduce the results. The quality of process is determined by the fraction of out-

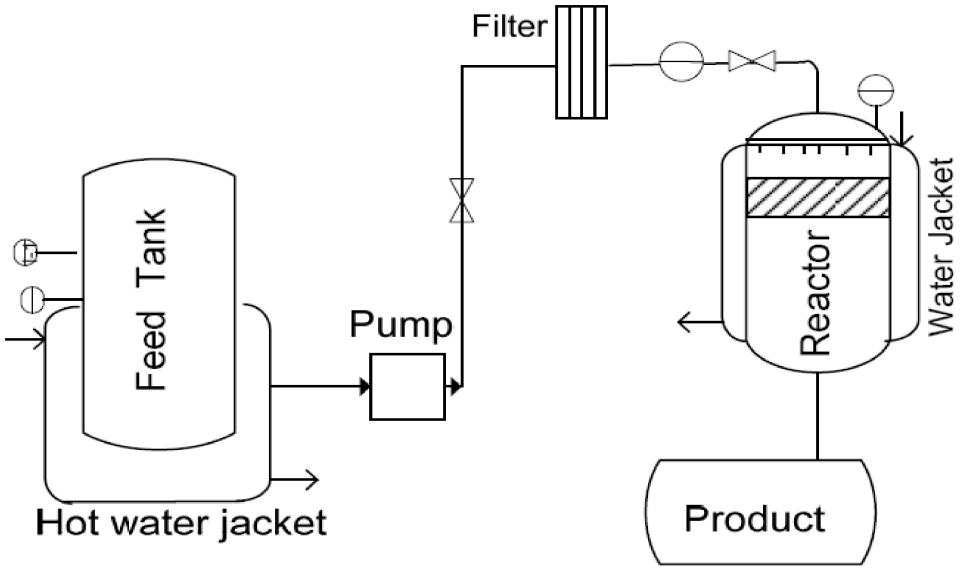

Figure 1

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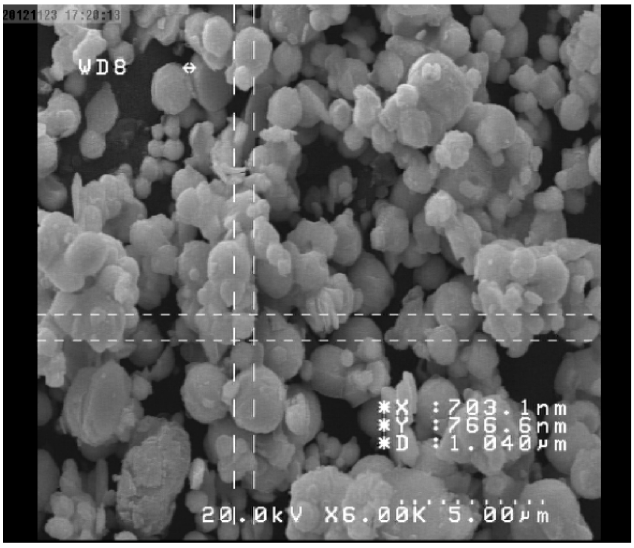

Figure 2

let H_2S concentration C on the inlet concentration of H_2S, C_0.

The effect of temperature

Figure 2 shows the effect of moderate temperature variations from 50 °C to 80 °C on the value of C/C_0.

The amount of C/C_0 increases with temperature elevation, higher than 60 °C for all samples however it never becomes higher than 0.1.

According to Figure 2, it seems the effective temperature in which the minimum amount of C/C_0 is reached is 70 °C for two samples.

Also, the effect of initial amount of H_2S on the quality of adsorption process is shown in Figure 2.

The effect of bed height

After finding the optimum temperature in H_2S elimination, the second parameter considered in this section is bed height. The height of catalytic bed is changed from 2 cm to 10 cm. Although, the amount of C/C_0 increases with the increase in bed height, but all results for light oil treatment, lead to the sweet oil specification. Also, oil characteristic affect the distribution of liquid in the catalytic packed bed, so channelling is obtained after 8cm. So, the amount of H_2S adsorption increases in the outlet for higher length of bed.

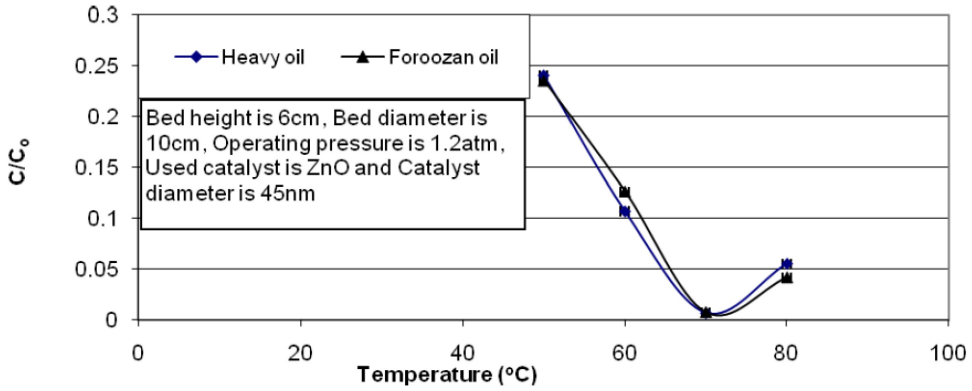

Figure 3 : The effect of temperature on the quality of oil sweetening

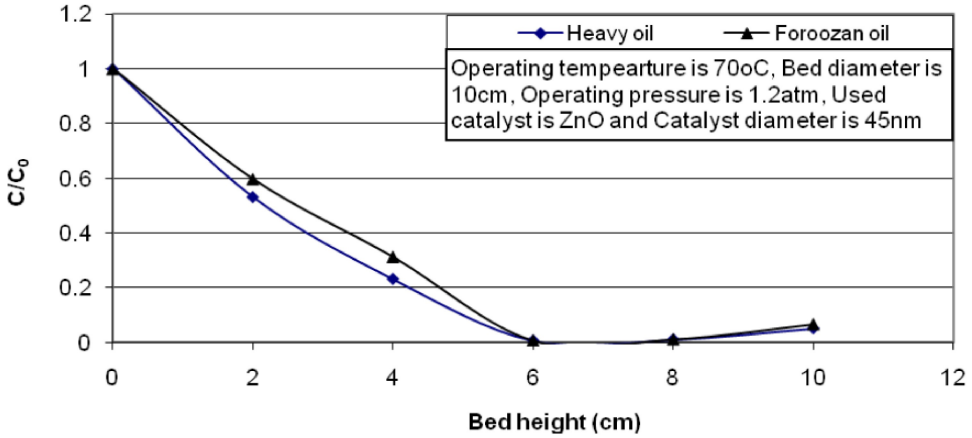

Figure 4 : The effect of bed height on the quality of oil sweetening

Clearly, lower API leads higher oil density and this increases the channelling probability in higher length of bed. On the other hand, samples have higher initial amount of H_2S and this parameter also causes the higher amount of H_2S in the outlet.

Figure 3 shows the effect of bed height on oil sweetening quality when ZnO is used in the bed. The approprate bed height for Soroosh oil sweetening is in range of 6cm to 8 cm.

The effect of operating pressure

The peroformance of catalyst at 70 C and in bed with 10 cm diameter is surveyed in Figure 4. The optimum 6 cm height is considered for using ZnO catalytic bed. The appropraite operating pressure for sweetening of heavy oil and foroozan oil is in range of 1.2 atm to 1.25 atm. Decreasing- increasing trend in the amount of C/C_0 versus operating pressure is obtained for all samples.

Bed diameter

In this section, considering the optimum conditions which are obtained in previous experiments, the effect of bed diameter and bed surface toward the oil stream is investigated on the amount of C/C0. The increase in bed diameter from 5 cm to 12 cm decreases the amount of C/C0, with 45 nm ZnO at 70 C, 1.2 atm and through

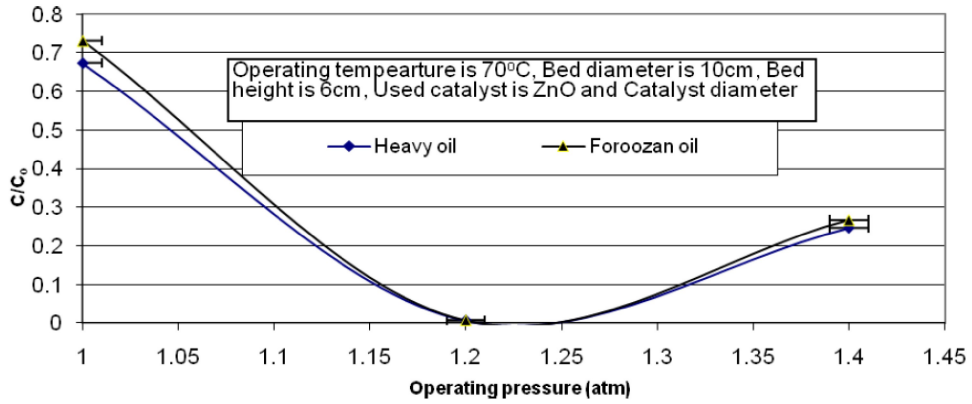

Figure 5 : The effect of operating pressure on the quality of oil sweetening

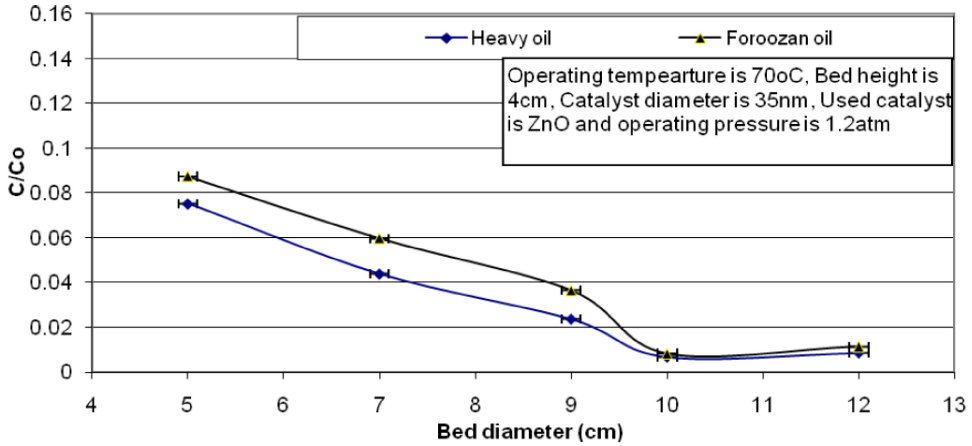

Figure 6 : The effect of bed diameter on the quality of oil sweetening

4 cm bed height. The best diameter is 10 cm according to Figure 5.

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 45 nm ZnO catalyst. Two types of dense sour oil with 29.6 and 29.7 API are sweetened. The initial amount of sulphur in the crudes are 2 wt% and 2.2 wt%, respectively. Experiments are conducted to survey the effect of operating temperature and pressure, bed diameter and bed height on the amount of outlet H_2S concentration. The quality of the sweetening process is shown by the frac-

tion of outlet concentration of H_2S on the amount of inlet H_2S. The optimum conditions obtained are 70 C, 1.2 atm, 6 cm height and 10 cm diameter of bed. According to the mentioned optimum conditions, the amount of C/C_0 decreases in 0.0067 and 0.0082 for heavy oil and Foroozan oil, respectively.

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