Experimental Evaluation of Dimensionless Groups for Scale Up of Sulfur Removal Process

Atefeh Hakimi1, 2, Farshad Farahbod3, *

1Department of Chemical Engineering, Science and Research Branch, Islamic Azad University, Sirjan, Iran
2Department of Chemical Engineering, Sirjan Branch, Islamic Azad University, Sirjan, Iran
3Department of Chemical Engineering, Firoozabad Branch, Islamic Azad University, Firoozabad, Iran

Abstract
The effect of low range temperature and pressure, initial concentration, interfacial velocity, the ratio of height to diameter of the bed and particle diameter on the outlet sulfur is investigated. Also, cost estimation due to pressure and temperature is presented. Results indicate on achieving the proper result of sulfur content in outlet to the initial sulfur lower than 0.012 at 1.7 atm, 35 C and ratio of height to diameter of packed bed is 3 which contains 50 nm nano carbon tubes.

Keywords
Operating and Geometric Condition, Desulphurization, Efficiency, Novel Method

1. 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 are 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.

1.1. Desulfurization Processes
In the past two decades petroleum refining has changed extensively and the fortunes of hydro treating, in particular, have witnessed a sea change [5]. Hydro-treaters 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 pre-treatment purposes [6 and 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 automotive emission control and FCC. Commercial hydro treating catalysts are, typically, Zn, Co or Mo. For example, 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 such as metal oxides can promote the heating and cooling process [8 and 9]. For example, the nano substances like; metal oxides can enhanced the thermal
1.2. Processes Efficiency

Today, about 90 percent of vehicular fuel needs are met by oil. Petroleum also makes up 40 percent of total energy consumption in the United States, but is responsible for only 1 percent of electricity generation. Petroleum's worth as a portable, dense energy source powering the vast majority of vehicles and as the base of many industrial chemicals makes it one of the world's most important commodities. Viability of the oil commodity is controlled by several key parameters, number of vehicles in the world competing for fuel, quantity of oil exported to the world market (Export Land Model), Net Energy Gain (economically useful energy provided minus energy consumed), political stability of oil exporting nations and ability to defend oil supply lines.

The top three oil producing countries are Russia, Saudi Arabia and the United States. About 80 percent of the world's readily accessible reserves are located in the Middle East, with 62.5 percent coming from the Arab 5: Saudi Arabia, UAE, Iraq, Qatar and Kuwait. A large portion of the world's total oil exists as unconventional sources, such as bitumen in Canada and extra heavy oil in Venezuela. While significant volumes of oil are extracted from oil sands, particularly in Canada, logistical and technical hurdles remain, as oil extraction requires large amounts of heat and water, making its net energy content quite low relative to conventional crude oil. Thus, Canada's oil sands are not expected to provide more than a few million barrels per day in the foreseeable future.

In its strictest sense, petroleum includes only crude oil, but in common usage it includes all liquid, gaseous, and solid hydrocarbons. Under surface pressure and temperature conditions, lighter hydrocarbons methane, ethane, propane and butane occur as gases, while pentane and heavier ones are in the form of liquids or solids. However, in an underground oil reservoir the proportions of gas, liquid, and solid depend on subsurface conditions and on the phase diagram of the petroleum mixture.

An oil well produces predominantly crude oil, with some natural gas dissolved in it. Because the pressure is lower at the surface than underground, some of the gas will come out of solution and be recovered (or burned) as associated gas or solution gas. A gas well produces predominantly natural gas. However, because the underground temperature and pressure are higher than at the surface, the gas may contain heavier hydrocarbons such as pentane, hexane, and heptane in the gaseous state. At surface conditions these will condense out of the gas to form natural gas condensate, often shortened to condensate. Condensate resembles petrol in appearance and is similar in composition to some volatile light crude oils.

The proportion of light hydrocarbons in the petroleum mixture varies greatly among different oil fields, ranging from as much as 97 percent by weight in the lighter oils to as little as 50 percent in the heavier oils and bitumens. The hydrocarbons in crude oil are mostly alkanes, cycloalkanes and various aromatic hydrocarbons while the other organic compounds contain nitrogen, oxygen and sulfur, and trace amounts of metals such as iron, nickel, copper and vanadium. The exact molecular composition varies widely from formation to formation but the proportion of chemical elements varies over fairly narrow limits as follows. Distillation, the process by which oil is heated and separated in different components, is the first stage in refining. Crude oil is any naturally-occurring flammable mixture of hydrocarbons found in geologic formations, such as rock strata. Most petroleum is a fossil fuel, formed from the action of intense pressure and heat on buried dead zooplankton and algae. Technically, the term petroleum only refers to crude oil, but sometimes it is applied to describe any solid, liquid or gaseous hydrocarbons. Petroleum consists primarily of paraffins and naphthenes, with a smaller amount of aromatics and asphalts. The exact chemical composition is a sort of fingerprint for the source of the petroleum.

In this work, Carbon nano catalyst is applied for sweetening process of two samples of oil which contain H2S contaminant. So, the operating and geometrical parameters are evaluated in this paper. In addition, economic investigation is discussed in this study to clear more uncertain aspects. Therefore, the gained results can be interesting for related industries and can be applicable in process optimization.

2. Materials and Methods

![Figure 1. A schematic of layered packed bed.](image-url)

He oil flow rate is adjusted by a valve and flow meter in the line of oil movement. After passing the filter the oil flows through a pump to reach the required pressure of the feed.
The oil flows from the top of vessel to down through the distributor on the catalytic packed bed contains nano carbon tubes. Packed bed contains layers equipped with nano carbon particles on their surfaces. Figure 1 shows a schematic of this layered packed bed. Temperature in bed is provided by an electrical heater which is around the vessel and process pressure by pump. A digital recorder saves temperature trough the bed and pressure difference of top and bottom of the bed. Product sample is analyzed to obtain the amount of sulfur.

3. Results and Discussions

To evaluate the effect of important operating and manufacturing parameters on the performance of the sweetening process, experiments are held. The quality performance of the process is reported as the ratio of outlet sulfur concentration to the inlet sulfur concentration, $C/C_0$. The amount of 0.6 ppm sulfur in outlet petroleum is desirable according to the standards.

3.1. Pressure and Temperature

Sulfure removal from petroleum by nano catalyst is categorized as an adsorption process which needs low temperature and high pressure according to the literature. The experimental conditions are adjusted in the range of 30, 35, 40, 45 and 50 °C as temperatures and 1, 1.5, 1.7 and 2 atm as operation pressures. The initial catalytic bed which is selected for evaluation experiments is 0.05 m in height and 0.02 m in diameter, nano carbon with 50 nm in diameter and 50 ppm initial concentration.

Figure 2 shows the changes in the amount of $C/C_0$ versus temperature at different pressures.

At 1 atm, the decreasing trend in the amount of $C/C_0$ is observed by the increase in the amounts of pressure. This trend obeys the usual predicted trend for the adsorption processes. However, the increase in temperature evaporates some light compounds in petroleum which have high heating value. So, the component loss is not profitable somewhat the sulfur concentration is low.

The increase in the amount of pressure to 1.5 atm and higher, the sulfur concentration decrease considerably from 0.03 to 0.0069 and lower as the amount of $C/C_0$. The decrease trend in value of $C/C_0$ is continued at 1.5 atm, to 40 °C ($C/C_0=0.0061$) and then a slight increase in trend is obtained using temperatures higher than 40 °C. The increase trend may since of bubbles got out of petroleum at that temperature and pressure. Although all the values of $C/C_0$ are in the acceptable range of sulfur content at the temperatures higher than 40 °C.

At higher temperatures than 40 °C and the higher pressure values (1.7 atm and 2 atm) the decreasing trend in the amount of $C/C_0$ is shown. At 1.7 atm the all values of $C/C_0$ are acceptable (below 0.6 ppm sulfur content equals to $C/C_0=0.012$) using the values of temperature. However, using 2 atm as pressure and operation temperatures higher than 35 °C leads in values of $C/C_0$ lower than 0.012.

Also, the lower amounts of high heating value compounds are lost. Because performing high pressure, high temperature process is not cost efficient, so considering the acceptable amount of $C/C_0$, the value of 1.7 atm and 35 °C is selected as the best conditions of the adsorption process.

3.2. Diameter of Nano Catalyst

The effect of diameter of nano carbon catalyst used in the adsorption vessel on the performance of sweetening process is reported in Figure 3. The particle diameter changes in values of 40, 50, 60 and 80 nm. The operating condition of the vessel is set at 35 °C and 1.7 atm. The amount of $C/C_0=0.009$ (sulfur content of 0.6 ppm) is shown at 50 nm in particle diameter. The initial concentration of sulfur and geometrical configuration of catalytic bed is also set as before, 50 ppm, 0.05 m in diameter and 50 ppm initial concentration.

Figure 2. The effect of temperature and pressure on $C/C_0$.

Figure 3. The effect of particle diameter on the value of $C/C_0$. The effect of diameter of nano carbon catalyst used in the adsorption vessel on the performance of sweetening process is reported in Figure 3. The particle diameter changes in values of 40, 50, 60 and 80 nm. The operating condition of the vessel is set at 35 °C and 1.7 atm. The amount of $C/C_0=0.009$ (sulfur content of 0.6 ppm) is shown at 50 nm in particle diameter. The initial concentration of sulfur and geometrical configuration of catalytic bed is also set as before, 50 ppm, 0.05 m in diameter and 0.02 m in diameter. The ratio of $C/C_0$ is increased using the larger particle than 50 nm in diameter to 0.021. The amount of $C/C_0$ is 0.01 at the value of 40 nm and 0.009 using 50 nm particle diameters. This may be related to the proper mass transfer area which is provided using 50 nm in diameter catalyst at that determined geometry of the bed.
4. Conclusions

Nano carbon tubes are proposed in the adsorption sweetening process of oil in this work. Sulfur removal from sour oil by nano particles is studied as a viewpoint of characterization of the reactor and finding the best operation conditions and manufacturing properties.

Experiments are held to evaluate the effect of low temperature (30, 35, 40, 45 and 50 °C) and pressure (1, 1.5, 1.7 and 2 atm) on the sulfur amount of the outlet stream of oil. The ratio of outlet sulfur on the input sulfur is selected as the criteria of the process performance. The proper conditions are such which lead to the outlet sulfur concentration below 0.6 ppm. According to the results, findings can be revealed as below: At 1 atm operation pressure, none values of the proposed temperatures lead to the values of C/C0 below 0.012. At a pressure of 1.5 atm and temperatures higher than 35 °C the result is obtained. Using 1.7 and 2 atm with all proposed temperatures leads to the proper C/C0 below than 0.012. However, The increase in temperature at 1 atm and 1.5 atm may evaporate some high heating value components. Results somewhat obey the trend of adsorption process. So, 1.7 atm and 35 °C is suggested as the best operating conditions. After finding proper operation conditions the other parameters are investigated. Different nano particle diameter 40, 50, 60 and 80 nm is examined in a fixed packed bed of 0.02 m in diameter and 0.05 m in height. 50 nm diameter shows the value of C/C0 equals to 0.009. This may relate to the proper mass transfer area provided by 50 nm particles.

Nomenclature

<table>
<thead>
<tr>
<th>Abbreviations</th>
<th>Parametric</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>T</td>
<td>Temperature</td>
<td>°C</td>
</tr>
<tr>
<td>P</td>
<td>Pressure</td>
<td>bar</td>
</tr>
<tr>
<td>D</td>
<td>Diameter of catalytic bed</td>
<td>cm</td>
</tr>
<tr>
<td>d_p</td>
<td>Diameter of nano catalyst</td>
<td>nm</td>
</tr>
<tr>
<td>C_o</td>
<td>Initial concentration</td>
<td>ppm</td>
</tr>
<tr>
<td>H</td>
<td>Height of catalytic bed</td>
<td>cm</td>
</tr>
<tr>
<td>C</td>
<td>concentration of outlet stream</td>
<td>ppm</td>
</tr>
<tr>
<td>c_p</td>
<td>Heat capacity</td>
<td>kJ/kg.K</td>
</tr>
</tbody>
</table>

References


