A Review on Diesel Fuel Desulfurization by Adsorption Process

Seyed Abolhasan Alavi, and Seyed Reza Hashemi

Abstract—Desulfurization is a process used for the effective removal of sulfur from fuels, diesel deep desulfurization are becoming more serious because the crude oils are getting higher in sulfur content. Several trends are emerging towards achieving the lowering of sulfur content in transportation fuels to below 10 mg/kg, among different type of process ,Adsorption is a physical process that involves the transfer of sulfur compound from the liquid phase to the surface of a solid matrix In adsorption the solute penetrates into the porous structure of the solid matrix variety of adsorbents are commercially used . New synthetic sorbents and catalysts and modified clays are under research to find efficient one in each process

Keywords—Desulfurization, Adsorption, Adsorbent, Diesel desulfurization, Modified Sorbent

I. INTRODUCTION

PETROLEUM has been part of human life since ancient times. It comprises hydrocarbons as the main constituents, in addition to small amounts of sulfur, nitrogen, oxygen, and trace metals. Diesel, among others, is one of the petroleum-derived fuels. Petroleum-derived diesel consists of a mixture of around 75% saturated hydrocarbons and 25% aromatic hydrocarbons. Sulfur is the main contaminant of diesel fuel and is present in a concentration that ranges between 0.1 and 0.5%. It is undesirable for the environment and engines because sulfur increases the polarity of diesel, increasing the stability of emulsions. It also enhances corrosion, poisons catalysts, and confers color and odor to final products. Sulfur oxides formed by diesel combustion can be discharged into the atmosphere as particulates or as gaseous pollutants, such as SO2 and SO3, causing great damage to the environment and to human health. In recent years, many researches for advanced technologies seeking to obtain economically viable and efficient alternatives to remove sulfur from petroleum-derived fuels have been developed [4] The petroleum refining industry, perceived as one of the largest sources of pollution, both direct and indirect via motor exhaust fumes, is on the front line of the battle for achieving environmentally friendly and sustainable operation. The pressure is mounting on the refineries to produce cleaner products while at the same time to minimize or completely eliminate the negative impact on the environment. Several trends are emerging towards achieving these goals and one is the lowering of sulfur content in transportation fuels to below 10 mg/kg. This value is currently maximum allowable sulfur content in diesel fuel in the EU while in the US it is less than 15 mg/kg. Reducing the sulfur level in diesel to less than 50 mg/kg by conventional hydrodesulphurization process is difficult due to the presence of refractory sulfur compounds such as alkyl dibenzothiophenes (DBTs) with one or two alkyl groups at 4 and/or 6-positions [5]. Hydrodesulphurization which is based on the elimination of contaminants by hydrogenation reactions is not an Ideal method. The disadvantages of this process include the need of high investments in facilities, application of extreme temperatures (200 to 425°C) and pressures (150 to 250psi) in the process, and the use of a sophisticated catalysts consisting for example of a basic material impregnated with cobalt and molybdenum [6].

II. ADSORPTION PROCESS

Adsorption is a separation process in which gas or liquid molecules are adsorbed on the surface of an adsorption solid Adsorption is a physical process that involves the transfer of solutes from the liquid phase to the surface of a solid matrix In absorption the solute penetrates into the porous structure of the solid matrix. There is a variety of adsorbents. The most common are activated carbon clay, silica, alumina and zeolite. Activated Carbon as an effective adsorbent has a high surface area, an extensively developed pore structure, a high
crystalline form and mechanical strength [7]. Adsorption processes can also be used to extract sulfur compounds from petroleum-derived fuels. They can be subdivided according to the interaction mechanism between the sulfur compound and the adsorbent. Adsorptive desulfurization is based on the physical adsorption of sulfur compounds on the surface of a solid adsorbent. Desulfurization by reactive adsorption involves the chemical interaction between the adsorbent and the sulfur compounds. Once the phenomenon stops, the adsorbent can be regenerated by eliminating H2S, S, or SOx, depending on the applied process. The efficiency of the method is defined by the adsorbent properties, including: adsorption capacity, selectivity for sulfur compounds, durability, and regeneration of spent adsorbent [8].

Adsorption of a solute molecule from a liquid solution to the surface of a solid matrix depends on the following:

i. The size, shape and molecular weight of solute.
ii. Electrostatic charge on the surface of solute molecule and the size of the solid matrix where adsorption takes place.
iii. Shape of the binding site of the solid matrix.
iv. Polarity of the solute molecule and the binding site of the solid matrix.

A typical adsorption process has four steps:
1. Addition of feed solution and the adsorbent solid particles.
2. Good mixing to enhance the transfer of solutes from the liquid phase to the surface area of the adsorbent solid particles.
3. Separation of the adsorbent plus adsorbate (solute) from the bulk of solution.
4. Removal of adsorbed solute from the surface of the solid adsorbent by using a different solvent. This is called elution of solute and the solvent is called elution solvent.

Note that at steady-state adsorption conditions there is a physical equilibrium between the concentration of solute in the liquid phase and the solid adsorbent phase.

III. ADSORPTION OF LIQUID MIXTURES

Depending on the type of phases in contact, we can consider this process in the following systems: liquid-gas, liquid-liquid, solid-liquid and solid-gas. The major development of adsorption processes on a large industrial scale deals mainly with the solid gas [9] and solid-liquid interfaces [10].

The fundamental concept in adsorption science is that named as the adsorption isotherm. It is the equilibrium relation between the quantity of the adsorbed material and the pressure or concentration in the bulk fluid phase at constant temperature. Adsorption from liquid mixtures is as important as Adsorption from gas mixtures process. The description of multi-solute adsorption is more complex [11]. In terms of this approach some important expressions were developed and used widely for predicting the multi-solute adsorption equilibria by means of single-solute adsorption parameters [12]. Considering adsorption from undiluted solutions and gaseous mixtures under high pressure, the phenomenon of competition among adsorbing molecules towards adsorption centers should be taken into account. In this case, the difference of adsorption potentials of adsorbate molecules plays a significant role and experimental isotherms have the character of excess isotherms [13]. A competitive adsorption process complicates the theoretical description and physical interpretation of adsorption energy distribution function. Moreover, adsorption of more than one type of molecules increases the number of parameters which must be taken into account by theoretical description of the phenomenon. In case of the relatively simple adsorption from a two-component solution over the full range of their concentrations at constant temperature, the process is determined by the following Parameters [14]: (1). Molecular interactions in the bulk phase; (2). Molecular interactions in the surface phase; (3) interactions between the bulk and surface phases; and (4). Molecular interactions at the solid-solution interface. In the case of adsorption from multi-component solutions and adsorption from gas mixtures, the description is largely complicated [15].

IV. DIESEL DESULFURIZATION

The issues of diesel deep desulfurization are becoming more serious because the crude oils are getting higher in sulfur content, while the regulated sulfur limits are becoming lower and lower. Deep reduction of diesel sulfur (from 500 to <15 ppmw sulfur) is dictated largely by 4,6-dimethyl dibenzothiophene, which represents the least reactive sulfur compounds from existing poly aromatics and nitrogen compounds in the feed as well as H2S in the product. New and more effective approaches and continuing catalysis and processing research are needed for producing affordable ultra-clean diesel fuels, because meeting the new government sulfur regulations in 2006–2010 is only a milestone [16].

Among different method for desulfurization of diesel adsorption process is acceptable due to low cost, easy regeneration and operation. Molecular simulation methods are of great importance to computational studies on the design of new synthetic sorbents and catalysts like zeolite, aluminophosphates aluminosilicates, nano- and mesotubes, fullerenes and heterofullerenes, pillared-clays, and other disordered porous solids. The above solid materials are very important in selective adsorption, catalysis and separation technology[22].

V. ADSORPTION ALTERNATIVES FOR DIESEL DESULFURIZATION

Industrial adsorption processes may be classified in three different ways, as regards to (1) sorbate concentrations, (2) Modes of operation and (3) adsorbent regeneration methods. It must be emphasized at this point that these classifications are established only to help the understanding of the several aspects involved in any adsorption process, giving only
Adsorbents are mostly micro porous, high specific surface materials (200 - 2000 m2/g). Most commonly used: Alumina, Silica gel, Zeolite molecular sieves, Active carbon (Ac), Carbon molecular sieves, impregnated carbons (Cu-clorides - CO separation), clays (natural and pillared clays), resins, polymers (biological, ions, large molecules) and Carbon Nanotubes a large specific surface area is preferable for providing large adsorption capacity, but the creation of a large internal surface area in a limited volume inevitably gives rise to large numbers of small sized pores between adsorption surfaces. The size of the microspores determines the accessibility of adsorbate molecules to the internal adsorption surface, so the pore size distribution of microspores is another important property for characterizing adsorptivity of adsorbents. Especially materials such as zeolite and carbon molecular sieves can be specifically engineered with precise pore size distributions and hence tuned for a particular separation.

Representative commercial liquid phase adsorption separations are shown in Table I.

<table>
<thead>
<tr>
<th>Separation (a)</th>
<th>Adsorbent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Normal paraffins / isoparaffins, aromatics</td>
<td>Zeolite</td>
</tr>
<tr>
<td>p-Xylene/o-Xylene, m-xylene</td>
<td>Zeolite</td>
</tr>
<tr>
<td>Detergent-range olefins/paraffin's</td>
<td>Zeolite</td>
</tr>
<tr>
<td>p-Diethyl benzene/isomer mixture</td>
<td>Zeolite</td>
</tr>
<tr>
<td>Fructose /glucose</td>
<td>Zeolite</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Separation (a)</th>
<th>Adsorbent</th>
</tr>
</thead>
<tbody>
<tr>
<td>H2O/organics, oxygenated organics, chlorinated organic, etc.</td>
<td>Silica, alumina, zeolite</td>
</tr>
<tr>
<td>Organics, oxygenated organics, chlorinated organic, etc./H2O</td>
<td>Activated carbon</td>
</tr>
<tr>
<td>Odor, taste bodies/drinking H2O</td>
<td>Activated carbon</td>
</tr>
<tr>
<td>Sulfur compounds/organics</td>
<td>Zeolite, others</td>
</tr>
<tr>
<td>Various fermentation products/fermentor effluent</td>
<td>Activated carbon</td>
</tr>
<tr>
<td>Decolorizing petroleum fractions, sugar syrups, vegetable oils, etc.</td>
<td>Activated carbon</td>
</tr>
</tbody>
</table>

**Table I**

**Representative Commercial Liquid Phase Adsorption Separations**

- Adsorbates listed first
- Adsorbate concentrations of about 10 wt. % or higher in the feed
- Adsorbate concentrations generally less than about 3 wt. % in the feed.

There are many studies to modify the adsorbent for the desulfurization of liquid fuels; these are implemented to achieve more efficiency. Few examples are as follows: Commercial-grade activated carbon was modified by steam activation to improve its surface properties for high temperature desulfurization. The modified sample was also further upgraded by impregnating with KOH and KI to promote the chemisorptions with of H2S. The H2S adsorption performance was tested under the temperature range of 30–550°C using the temperature program adsorption technique to understand the effect of adsorption temperature on the material adsorption characteristic. It was found that at ambient temperature, the impregnation of activated carbon with KOH can promote the H2S adsorption capacity of activated carbon, whereas the impregnation with KI does not provide a significant beneficial effect. At high adsorption temperature (up to 550°C), both KOH and KI impregnation considerably improve the H2S adsorption performance of activated carbon in terms of the adsorption capacity and breakthrough time. It was revealed from N2 adsorption. In the other effort a new type of activated carbon (Bergamot-Based Activated Carbon, BAC) was prepared and oxidized by peracetic acid. The modified BAC was characterized by N2 adsorption, FT-IR, and base titration analyses. The results show that after modification by concentrated per acetic acid for 18 h at 25°C, the obtained materials show increase in pore volume from 0.55 mL/g to 1.73 mL/g, specific surface area from 1,874 m2/g to 2,736 m2/g, and the density of acidic surface oxygen complexes (C=O, C-OH, and COOH) from 0.78 mmol/g to 2.23 mmol/g. IR and base titration results indicated that thiophene reacts with carbonyl groups to form phenols during desulfurization. Batch test results showed that the modified BACs show a good thiophene capture performance at 30°C under the stirring speed of 250 rpm/min, the adsorbents/fuel ratio of 1/20, and reaction time of 30 min. The equilibrium adsorption data were well represented by the Langmuir isotherm equation. The maximum sulfur adsorption capacity of oxidation treated sample is 43.12 mg/g, which is superior to the most carbonaceous materials reported in the literature. The saturated adsorbents can be regenerated with stripping with alcohol solution and nearly 100% of the desulfur capacity was recovered after regeneration [20]. In the other test to find an efficient absorbent for deep desulfurization a simulated diesel fuel by different adsorbents was studied in a fixed-bed adsorption process operated at ambient temperature and pressure. Three different adsorption beds were used, commercial activated carbon, Cu-Y zeolite, and layered bed of 15wt% activated carbon followed by Cu-Y zeolite. Initially Y-zeolite was prepared from Iraqi rice husk and then impregnated with copper, the adsorbents tested for total sulfur adsorption capacity at break through followed the order Ac/Cu-Y zeolite>Cu-Y zeolite>Ac. The best absorbent, Ac/Cu-Y zeolite is capable of producing more than 30 cm3 of simulated diesel fuel per gram of adsorbent with a weighted average content of 5 ppm-S, while Cu-Y zeolite producing of about 20 cm3 of diesel fuel per gram of adsorbent with a weighted average content of 2ppm-S [21]. Working on different types of clay also have been done. Specific sorption characteristics can be achieved in the modified clay.

**References**


