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DESULFURIZATION OF CRUDE OIL

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ABSTRACT

The poor quality of crude oil obviously leads to high sulfur contents of oil products, and the technology for desulfurization of crude oil is urgently needed so that the sulfur contents in petroleum product could be reduced from the root. The desulfurization methods including variations thereon that are discussed include hydro desulfurization, extractive desulfurization, oxidative desulfurization, bio desulfurization and desulfurization through alkylation, chlorinolysis , and by using supercritical water. Catalytic desulfurization of residual oil has been carried out through partial oxidation in supercritical water and thus 60% of the sulfur was removed.

I.INTRODUCTION

Desulfurization is the process of removing sulfur from crude oil (or its fractions).It prevents contamination and also improves the efficiency of petroleum. Desulfurization removes elemental sulfur and its compounds from solids, liquids and gases. These processes are of great industrial and environment importance as they provide the bulk of sulfur used in industry, sulfur-free compound that could otherwise not be used in a great number of catalytic processes and also reduce the release of harmful sulfur compounds into the environment, particularly sulfur dioxide which leads to acid rain.

Effect of Sulfur in Industries: -

- Sulfur present in chemicals can harm the catalyst that are used in the refining of that particular chemical into the many useful products obtained from crude oil.
- If sulfur remains in chemical may sometimes leads to the formation of corrosion which in result decreasing the quality of the chemical and sometime it may react and changes the properties of chemical.

Effect of Sulfur on Humans: -

The SO_2 is hygroscopic, when it is in the atmosphere it reacts with humidity and forms sulfuric and sulfurous aerosol acid that is later part of the so-called acid rain. The air pollution by SO_2 has the following effects on human beings:

- Corneal haze
- Breathing difficulty
- Airways inflammation
- Eye irritation
- Psychic alterations.
- Heart failure.
- Circulatory collapse.

Sulfur dioxide is also associated with asthma, chronic bronchitis, morbidity and mortality increase in old people and infants.

Effect on sulfur on Environment: -

When Sulphur dioxide combines with water and air, it forms sulphuric acid, which is the main component of acid rain. Acid rain can:

- Cause deforestation
- Acidify waterways to the detriment of aquatic life
- Corrode building materials and paints

METHOD OF DESULPHURIZATION: -

- Caustic Washing Method for Oil Desulfurization
- Dry Gas Desulfurization Method
- Hydro-Desulfurization (HDS)
- Oxidative Desulfurization
- Hydrogenation-Bacterial Catalytic Desulfurization
- Microwave- Catalytic Hydrogenation Process for Desulfurization
- Adsorption Process

LOW COST ADSORBENTS PROCESS FOR DESULPHURIZATION: -

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Desulphurization prior to combustion has been viewed in recent years with the objective of ensuring clean fuel combustion and hence to avoid environmental degradation. There are three major approaches recognized for controlling sulphur oxides pollution[1].

a) The first is to use fuels of naturally low sulphur content.

b) The second approach is the desulphurization of the fuel, which in the case of oil is usually accomplished by hydrogen processing.

c) The third method is the removal of sulphur compounds from stack gases primarily from large combustion operation such as power generator.

Neem leaves powder: -

Sulphur content was measured using UV visible Spectrometer according to ASTM standard method. Also it was found that sulphur content was reduced from 410 ppm to 251 ppm using 5% adsorbent material and further reduction and up to184.6 ppm using 10% sorbent material.

One of the easy and fast method to remove sulphur from diesel oil is adsorption desulphurization process. Adsorption desulphurization process of diesel fuel was proposed and examined. Local diesel fuel was treated by using natural adsorbents like Neem leaves powder by using batch process. The Experiments for Effect of adsorbent dose, Effect of initial concentration and time, Effect of initial concentration and temperatures .Also observed that nature of graph between sulphur content vs. time is decreasing[2]. They were carried out number of experimental runs for determination of residual sulphur concentration in the solution with time (t) during the initial sorption period.

The flyash:-

The fly ash mixed with flyash can be used as the absorbent for desulfurization of power plants burning low-sulphur coals. Fly ash is sphere or aggregation of the microsphere, with a particle diameter of 1– 100 μm and density of 2.02–2.56 g/cm3. The particle size of the absorbent is one of the important factors that influence the reaction rate. The desulfurization rate is improved when the particle size is reduced, because, at the same conditions, smaller particles will provide more contact area for gas-solid reaction.

The utilization of fly ash depends mainly on the content and reaction activity of the oxides.Fly ash is mainly composed of SiO_2, Al_2O_3, Fe_2O_3, and CaO Contained with a significant content of porous amorphous SiO_2 and Al_2O_3, fly ash thus could play a role in absorbing acid gas SO_2. The ash samples were separated by sieving. Particles with average sizes from 100 to 40μm were used in the study. The purpose of analysing the particle size of flyash is to confirm the influence of fly ash particle size on the pH value of the hydration solution. Through the particle size analysis of fly ash, the study provides the basis for taking fly ash as absorbent[3].The key components in fly ash for desulphurization are 'active' CaO and MgO. 'Active' refers to the fact that these oxides can be dissolved in the aqueous solution with low pH value, and generated in dissolvable calcium and magnesium salt with the absorbed SO_2.

II.DESULPHURIZATION BY ADSORPTION:

Desulfurization is a chemical process for the removal of sulfur from a material. 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.

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 H_2S, S, or SOx, depending on the applied process.

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 site 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.

MATERIALS AND METHODS

REQUIREMENTS: -

Materials Used: -

(a) Model Diesel oil: -

A model diesel oil was prepared by doping of DBT into cyclohexane at different amount for different concentration. A model oil is a generally an oil that has same property to the diesel oil.**(b) Neem leaves: -**

Neem laves were collected from nearby sources (trees).It is a cheap source, easily available, and use for burning.

(c) Fly ash: -

The fly ash is a waste product of coal combustion process composed of fine particles that are driven out of the boiler with the flue gases. Depending upon the sources and makeup of the coal being burned, it is bought from Jhalawar thermal power plant (Rajasthan).

Chemical Used: -

- Di-benzothiophene (DBT)
- Cyclohexane
- Deionized water

Equipment Used: -

- Electronic balance
- Grinder
- Mash (BS-85)
- Shaker

UV/visible spectrophotometer:

Ultraviolet–visible spectroscopy or ultraviolet-visible spectrophotometry (UV-Vis or UV/Vis) refers to absorption spectroscopy or reflectance spectroscopy in the ultraviolet-visible spectral region. This means it uses light in the visible and adjacent ranges.

Comparison between Two Adsorbent for Effective Sulphur Content Removal: -

For fly ash: -

Take 50ml solution of model oil having 500ppm Sulphur content and add 2.25gm of fly ash in it. Shake well for 2.5 hours to get adsorb the adsorbent properly in the solution. Put this sample in the cuvette as an unknown sample and put this in the spectrophotometer taking cyclohexane as reference[7]. Calibration will be done and 2% Sulphur content removal is observed when fly is taken as an adsorbent.

For Neem leaves: -

Take 50ml solution of model oil having 500ppm Sulphur content and add 2.25 gm of neem leaves in it. Shake well for 2.5 hours to get adsorb the adsorbent properly in the solution. By taking the neem leaves as an adsorbent in the model oil and calibrating it by the spectrophotometer the Sulphur content removal is observed to be around 20%.

Therefore, further calibration at 500,400 and 300ppm is done by taking neem leaves as an adsorbent by taking three different variables i.e., by dosing (taking different amounts of adsorbent), time and temperature[8].

Amount of Desulphurization Adsorbent: -

- Take 10ml solution of different concentration i.e. at 500,400and 300 ppm.
- Add 1, 2, 3 and 5gm of adsorbent in the 10ml sample.
- Shake the sample for 3 hours in the shaker.
- Now, after shaking calibrate the above sample in the UV/VIS spectrophotometer.
- Note the reading for different concentrations for different-different adsorbent dosing.
- Hence, we observe that for 2gm of adsorbent the percentage of Sulphur removal is most effective

Time: -

As we observed that 2gm of dosing is most effective. Therefore, we will check the percentage of Sulphur removal at different time intervals for same dosing.

- Take three 10ml samples and add 2gm of an adsorbent individually.
- Shake all the three samples for 1, 2 and 3 hours[9].
- Now after shaking, calibrate all the three samples in the UV/vis spectrophotometer.
- Note the readings at different time intervals.

Temperature: -

- Take three 10ml samples and add 2gm of an adsorbent in it.
- Three samples taken should be treated at different temperatures i.e.at room temperature (38°C), at hot temperature(48°C) and at cold temperature(14°C)[9].
- Shake all the three samples for 3 hours.
- Now after shaking, calibrate all the three samples in the UV/vis spectrophotometer.
- Note the readings at different temperature.

III.RESULT AND DISCUSSION

EFFECT OF DOSING: -

An adsorbent dosage is an important parameter, because this factor determines the capacity of an adsorbed for a given initial concentration of the adsorbent10 ml model oil sample of differentconcentrations (500ppm, 400ppm and 300 ppm) were treated with different adsorbent dosages (1g, 2g, 3g and 5g) for time of 3 hours[10]. From the graph 4.1 The Sulphur removal is observed to increase rapidly with an increase in mass of adsorbent up to about 2gms per 10 ml of model oil

Table-Effect of Adsorbent Dose

Adsorbent	**% Sulfur Removal**		
Concentration(in gm)	**500 ppm**	**400 ppm**	**300 ppm**
1	13.52	7.2	6.17
2	18.42	12.93	9.9
3	20.23	13.3	10.53
5	20.47	13.59	10.98

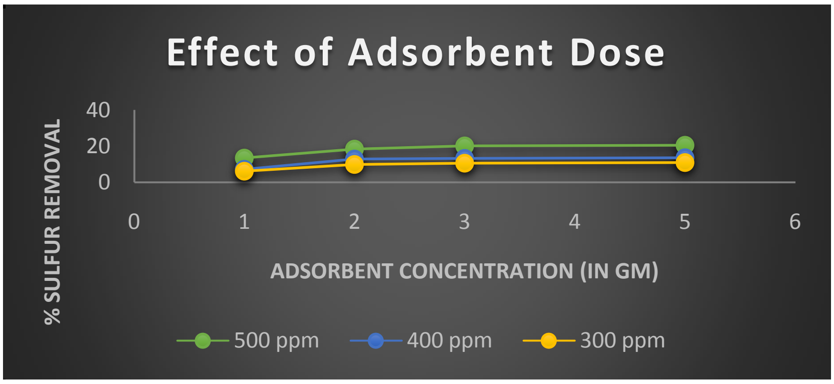

Fig:Effect of Adsorbent Dose

EFFECT OF TIME

The effect of time on amount of Sulphur removed is studied. The model oil sample of concentration 10 ml was treated with adsorbent dose of 2g.The sample was constantly stirred for different time interval of 1, 2, 3 and 4 hours were studied and graph of Sulphur content vs. time is plotted. The nature of graph is decreasing. The removal of Sulphur content is approximately constant after 3 hour[11]. The nature of percentage Sulphur removal with respect to time is observed. It is observed the percentage Sulphur removal is constant after 3 hour.

Table: Effect of Time on sulfur content

Time (in hr)	**Sulfur Content (in ppm)**

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1	442.32
2	415.75
3	410
4	408.35

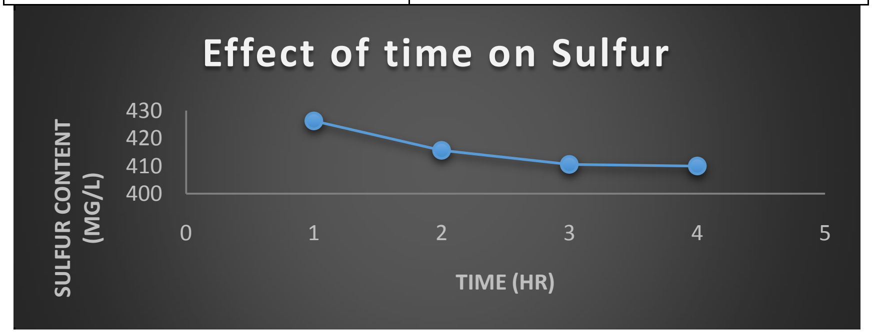

Fig: Effect of Time on Sulfur Content

Table - Effect of Time on % Sulfur Removal

Time (in hr)	**% Sulfur Removal**
1	11.53
2	16.85
3	18
4	18.33

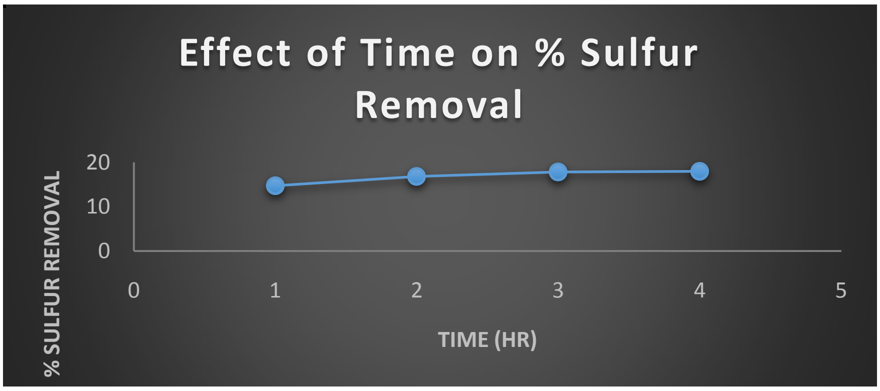

Fig - Effect of Time on % Sulfur Removal

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Table : - Effect of Temperature

EFFECT OF TEMPERATURE: -

The effect of temperature on amount of Sulphur removed is studied. The model oil sample of concentration 10 ml was treated with adsorbent dose of 2gms.The sample was constantly stirred for 3 hours was studied and graph of Sulphur content vs. temperature is plotted. The nature of graph is decreasing. The nature of percentage Sulphur removal with respect to temperature is observed[12].

Table-Effect of temperature

Temperature (in K)	**% Sulfur Removal**
287.15	20.40
311.15	18.42
321.15	15.34

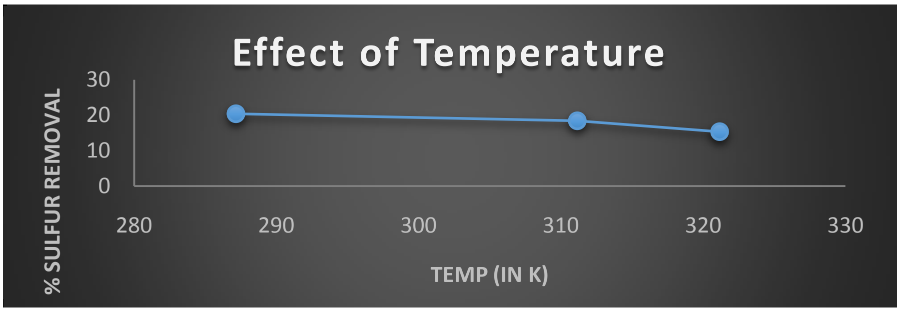

Fig.: - Effect of Temperature

IV.CONCLUSION

- The removal of Sulphur is occur effectively on using neem leaves powder and more than the fly ash.
- The desulphurization of model oil by adsorption process using neem leaves powder shows a reduction in the amount of sulfur by 20% from the original amount of Sulphur.
- In the desulphurization process the removal of Sulphur from model oil is affected by the time, and percentage Sulphur removal is increases with timeup to 3hr effectively, after 3hr the variation in percent removal is not occur in significantly.
- The optimum conditions were recognized as contact time of 3 hrs. and dose of neem leaves powder of 2gm in 10ml of model oil and temperature of 14^{0}C was obtained.

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- The effect of different temperatures on adsorption process has been observed which shows that temperature does not favor the percentage removal of Sulphur in model oil which represents the nature of process as an exothermic process, since with the increase in temperature, concentration of Sulphur removal decreases & removal of Sulphur is occur 20% at 14^0C.

- The Sulphur removal from model oil can be done with neem leaves at low temperature. This process is effective for higher concentration of Sulphur in model oils or diesel oil.

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