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Desulphurization of Paraffinic Stream by a Fixed Bed of Zinc Oxide

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ABSTRACT: *Almost all crude oils are known to contain sulphure in varying amount. The amount of sulphure can vary from 0.04 % to nearly 10 %. The sulphure in petroleum has been defined as consisting of hydrogen sulphide , free sulphure and organic sulphure compound viz mrercaptans , organic sulphide R-S-R , disulphide's R-S-S-R , carbon disulphide , thiophene and its homologues. The presence of these compound in petroleum fraction is not desirable due to their foul odour , corrosiveness , interferences with combtion characteristics of fuels, aggravation of atm. pollution byproduct of combtion etc.*

The process used to reduce sulphure content of petroleum fraction may broadly classified as sweeterning process and catalytic desulphurization.

Catalytic desulphurization process are those which destroy and remove all sulphure compound, hydrogen sulphide, mercaptance.Although the use of zinc oxide as a part of sandwich catalyst in the catalytic HDS is beneficial,.; Also no hydrogen is required for desulphurization by zinc oxide and this is attractive point in the view of what have been said above concerning modern researcher in catalytic HDS(hydrodesulphurization).

I. INTRODUCTION

Petroleum fraction used as final product for chemical processing have to meet stringent specification regarding their sulphure content.Even at the level of crude oil, crude is devided into sour and sweet on the basis of sulphure content. Sour crude are define as those contain sulphure more than 0.5 wt %. It has been estimated that large proportions of crude reserves contain more than 1 wt % sulphur. Even accordingly to recent estimate of crude oil availability in our country , considerable amount of crude oils will continue to be imported in the future and all these would have to come from West Asian sour crude containing 1 to 2.6 % sulphure.Hydrodesulphurization process are now a day's used not only to pretreat the charge stock to catalytic reformer(hydrodesulphurization of low boiling distillate is almost always carried out for this purpose) but also as finishing process in case of middle distillate(200-410 ^{o}c) and even high boiling feed stock which may have sulphure content up to 5 wt %. Considerable research has been and being carried out in the field of composition of hydrodesulphurization catalysts, improving the selectivity of hydrodesulphurization and reducing the amount of hydrogen consumed by hydrogenation reaction.

II. MATERIAL AND METHODS

The reactor was packed with materials given below in a ascending order.
a)Initial 12 cm pyrex tubing.(2.5 x 0.4 x 0.1 cm)
b) 3 m thick layer of silica chip to make surface of lower packing horizontal.
c) Nearly 36.8 gm ZnO Catalyst pellets.
The pellets were arranged at random but the top surface was made as horizontal as possible.
d) 3-5 mm thick layer of silica chips.
e) 15-17 cms glass tubing (2.5 x 0.4 x 0.1)
The catalyst is the constant temp region. Reactor was heated nearly for 2-3 hr to bring it to the required (350^{o}c) temperature and held at this temp for 30 min. Two 5 x 1.5 cm strips of whatman 40 filter paper were soaked in freshly preperaed (10 %) solution of lead acetate in water and placed in the tube. The first drop collected in 45 sec after it separated from tip. Liquid product were drawn out every 15 min, each portion was collected graduated tube, volume noted and then transfed to stoppred conical flask. In this way four samples for flowrate 30 ml/hr was transferred to separate conical flask. Gas flow rate was also read every 20 min interval. . Runs were carried out in most cases for 210- 300 min. Balandine burette was disconnected , reactor was flushed with nitrogen to displace hydrocarbon vapours(for 20 min at rate of 1 lit/10 min) and allowed to cool to room temp in the current of nitrogen.If necessary run was recommended in this manner as described above , runs were carried out for further 210-240 min. Long runs with interruption were carried out in this manner.
Identification of serial No. in the following Tables:
1. Room temp oc
2. Feed:Conc of mercaptan(gm mole/lit) x 10^3
3. Refractive Index
4. Density
5. Catalyzate-inportions: Period of collection, min.
6. ml collected

7. Density
8. Wt % of feed.
9. mercaptan conc(gm mole) x 10^4
10. H2S from exit gases(gm mole) x 10^4
11. CM= Mercaptan conc(gm atom of S /100 gm of catalyzate) x 10^4
12. Start of H2S Evolution in exit gases, min .

Table No.1: Desulphurization by ZnO Run No.1:

Initial wt of catalyst=35.0171 gm, Reaction Temp=350^{o}c , Feed=N-amyll mercaptan in n hexane,
Flow rate=30 ml/hr , Bed length=3.0 cm , CoM-(g.atom of s/100 g of feed10^4)=369.231

1	25^0 c	--	--	--	--	--	--	--
2	240	----	---	----	----	----	---	----
3	1.372	---	---	----	---	---	--	---
4	0.650	----	----	----	-----	-----	----	---
5	0-60	60-120	120-180	180-240	240-300	300-360	360-420	420-480
6	26.5	29.0	29.8	29.9	29.7	29.8	29.6	29.7
7	--	0.648	--	0.648	--	0.648	---	---
8	95	99.33	99.33	99.66	99	99.33	98.66	99
9	0	0	0	0	0.9	1.8	4.3	4.9
10	0	0	0	0	0	0	0	Traces
11	0	0	0	0	1.30	2.75	6.52	7.8
12	456 min	---	---	---	----	---	---	---

Table No.2: Desulphurization by ZnO Run No.2

Initial wt of catalyst=36.8753gm , Reaction Temp=350^{o}c , Feed=N-amyll mercaptan in n hexane,
Flow rate=30 ml/hr , Bed length=3.0 cm , CoM-(g.atom of s/100 g of feed10^4)=359.05

1	25 o c	---	---	----	---	---	---	---
2	242	----	---	---	---	--	---	----
3	1.385	----	---	---	----	----	---	----
4	0.674	----	----	----	----	----	----	---
5	0-60	60-120	120-180	180-240	240-300	300-360	360-420	420-480
6	26.5	29.3	29.6	29.7	29.9	29.9	29.8	29.7
7	--	--	0.673	--	0.673	--	0.673	--
8	94	94	97.66	98.66	99	99.66	99.66	99.33
9	0	0	0	0	0.87	2.0	4.5	4.9
10	0	0	0	0	0	0	0	Traces
11	0	0	0	0	1.2927	2.971	6.686	7.28
12	455 min	---	----	----	---	----	---	---

Table No.3: Desulphurization by ZnO Run No.3

Initial wt of catalyst=36.8500 gm , Reaction Temp=350^o c , Feed=N-amyll mercaptan +Heptane+N-Compounds(pyridine),
Flow rate=30 ml/hr , Bed length=3.0 cm , CoM-(g.atom of s/100 g of feed10^4)=361.06

1	25 oc	---	---	---	---	---	---	--
2	244	---	---	---	---	---	----	---
3	1.387	----	----	---	----	----	---	---
4	0.678	----	---	---	---	---	---	--
5	0-60	60-120	120-180	180-240	240-300	300-360	360-420	420-480
6	27	29.5	29.7	29.8	29.9	29.9	29.8	29.7
7	--	--	0.676	--	0.676	--	0.676	--
8	89.73	98.04	98.71	99.04	99.37	99.37	99.04	98.71
9	0	0	0	0	0.85	1.8	4.6	4.9
10	0	0	0	0	0	0	0	Traces

11	0	0	0	0	1.257	2.662	6.80	7.248
12	455 min	---	---	---	----	----	---	--

Pyridine and N-amyl mercaptan are taken in 1:1 ratio.

Table No.4: Desulphurization by ZnO Run No.4

Initial wt of catalyst=36.7822 gm , Reaction Temp=350^o c , Feed=N-amyll mercaptan +Heptane+N-Compounds(pyridine), Flow rate=30 ml/hr , Bed length=3.0 cm , CoM-(g.atom of s/100 g of feed10^4)=357.25

1	25 oc	---	---	---	----	---	-----	----
2	244	---	---	---	---	---	----	----
3	1.387	---	----	----	-----	----	----	---
4	0.678	---	----	---	---	-----	-----	----
5	0-60	60-120	120-180	180-240	240-300	300-360	360-420	420-480
6	27	29.8	30	30	30	30	29.7	29.8
7	--	0.681	--	0.681	--	0.682	--	0.683
8	89.73	99.04	99.70	99.85	99.70	99.85	99.70	99.99
9	0	0	0	0	1.2	2.6	8.0	13.2
10	0	0	0	0	0	0	0	Traces
11	0	0	0	0	1.76	3.812	11.615	19.198
12	---	---	-----	----	----	----	----	---

Pyridine and N-amyl mercaptan are taken in 2:1 ratio

Table No.5: Effect of H20 ON DESULPHURIZATION OF H.C by ZnO Run No.5

Initial wt of catalyst=36.806 gm , Reaction Temp=350^{o}c , Feed=N-amyll mercaptan +Heptane+H2O(distilled), Flow rate=30 ml/hr , Bed length=3.0 cm , CoM-(g.atom of s/100 g of feed10^4)=373

1	25 oc	---	---	---	---	---	----	--
2	254	---	----	----	----	----	----	----
3	1.387	----	----	----	----	----	----	---
4	0.678	---	----	---	---	-----	----	---
5	0-60	60-120	120-180	180-240	240-300	300-360	360-420	420-480
6	26.5	29.2	29.8	29.9	30	29.9	30	30
7	--	0.674	--	0.674	--	0.674	--	0.674
8	87.42	96.33	98.31	98.64	98.97	98.64	98.97	98.97
9	0	0	0	0	0.8	2.4	4.4	5.6
10	0	0	0	0	0	0	0	Traces
11	0	0	0	0	1.186	3.55	6.53	8.31
12	460 min	---	---	----	-----	---	-----	_____

III. RESULT AND DISSCUSSION

The aim is to investigate the effect of following factor on desulphurization of hydrocarbon stream by a fixed bed of Zinc oxide.1)Efeect of presence of nonsulphure non hydrocarbon compound in feed.With n-heptane as feed and n-amyl mercaptan as sulphure compound the effect of presence of following compound was investigated.

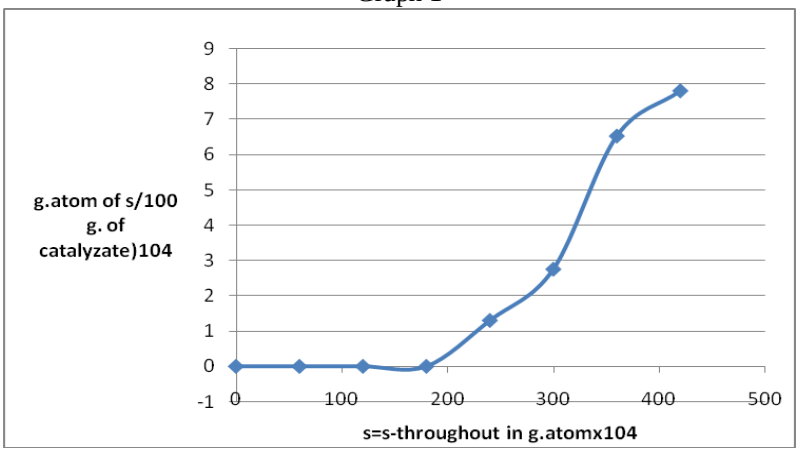
a) Distilled water b) Sodium chloride c) carbon dioxide d) Nitrogen compound

2) Effect of hydrocarbon feed were tried.

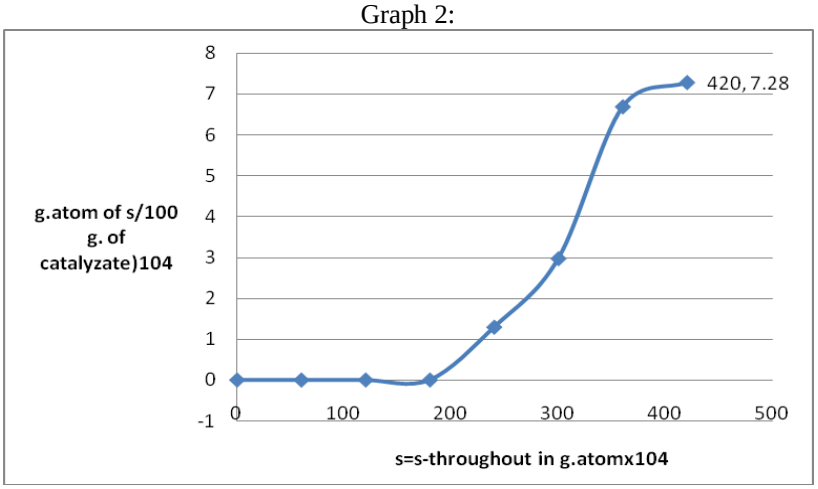
a) n heptanes alone b)Hexane(Petroleum fraction) c)Benzene + Heptane d)Toluene + heptanes.

The result of experiment carried out to investigate these aspect are given below on which breakthrough curves are drawn .All the following graph are plotted **(gm.atom of S/100 gm of catalyzate)10^4 against (S-throughout in gm. Atom x 10^4**

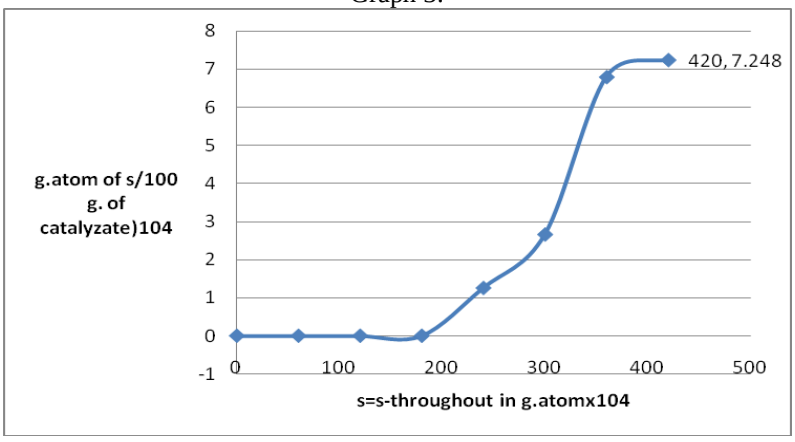
Graph 1



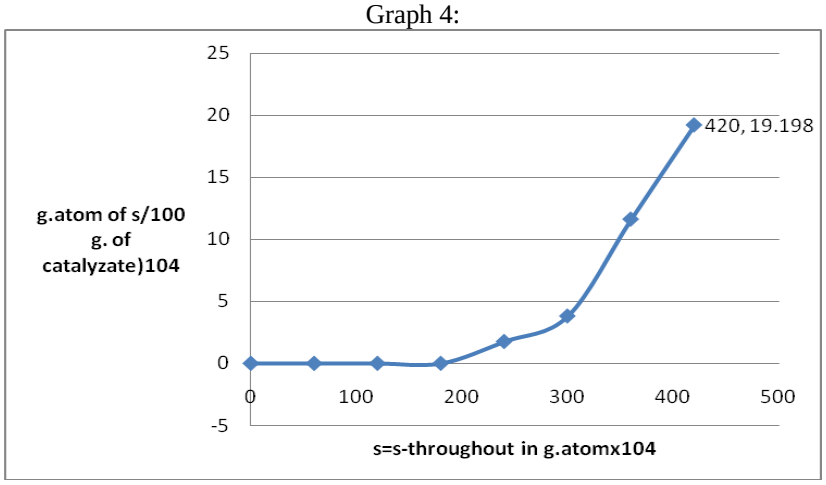
Graph 2:



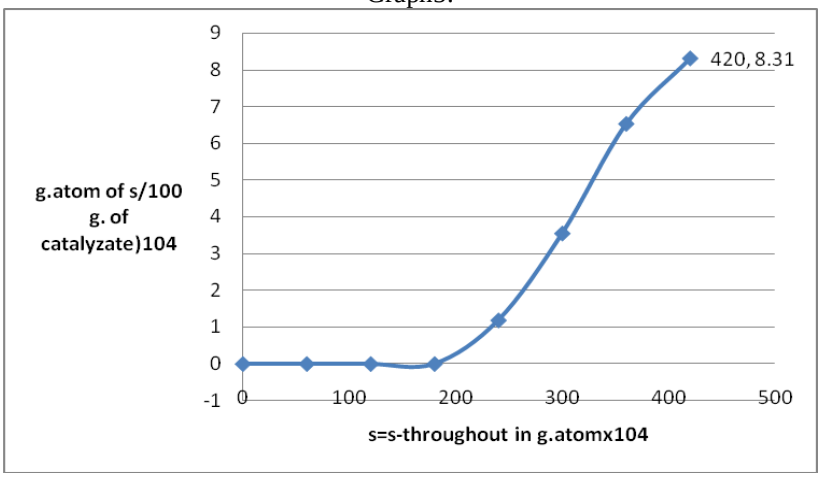
Graph 3:



Graph 4:



Graph5:



IV. CONCLUSION:

The objective of these studies is to make possible prediction of sulphure breakthrough curve in the desulphurization of hydrocarbon stream by fixed bed of zinc oxide and thus aid in the design of industrial units meants for desulphurization.

The theoretical basis of breakthrough curve for a system in flow of these type studied here ie with fixed bed catalyst is well developed in chemical engineering literature with regards to sorption.

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