METHODS FOR DESULFURIZATION OF CRUDE OIL- A REVIEW

[1]Solat Ullah Siddiqui, [1]Kashif Ahmed*
[1]Department of Chemistry, Ned University of Engineering and technology, Karachi, Pakistan
soulat87@gmail.com, kashif25473@yahoo.com

***ABSTRACT**: The survey of literature, consisting the estimation approaches for crude oil desulfurization has been reviwed. These desulfurization approaches include oxidative desulfurization, adsorptive desulfurization, and desulfurization by photo oxidation, hydro desulfurization, desulfurization by extraction, c-alkylation, s-alkylation, microbe desulfurization, and desulfurization by ultrasound oxidation, aerobic microbedesulfurizatio, anaerobic microbe desulfurization and supercritical water desulfurization. Desulfurization proceeds due to crude oil properties mainly high boiling range, high fluidity, high sulfur content and nature of sulfur content.*

Keywords: Desulfurization-crude oil-Hydrodesulphurization (HDS)-Microbe desulfurization-Oxidative desulfurization (ODS)

1. INTRODUCTION

Crude oil is a complex mixture consists of hydrocarbons as well as containing various contaminant compounds, such as sulfur containing compounds and suspended particles. The nature of the crude oil varies with respect to geological position; the composition of the crude oil taken from the same well is differing with respect to the exploration time. But the basic physical and chemical trend is same for every type of crude oil [1]. It is notice that the crude oil is a raw material for the downstream sector of petroleum. Crude oil typically contains hydrocarbons and non-hydrocarbons, but during an exploration and shipping of crude oil also contains some contaminants such as moisture content, sludge content and salt content [2]. Crude oil typically contains paraffinic, naphthenic and aromatic compound [3]. Crude oil also contains olefins which are ranges from carbon (1-120).from carbon (1-4) generally are in gaseous form, carbon ranging from (5-15) mainly are straight chain alkanes and alkanes above to carbon (17) are paraffinic waxy material [4]. These paraffinic waxes are responsible to increase the cloud and pour point. Crude oil also contains some aromatic compounds, in which toluene and xylene which are alkyl derivative of benzenes are the most common, other aromatic compounds like naphthalene and phenentherene are also recognize in the crude oils. In petroleum after carbon and hydrogen sulfur is most common constituent. Crude oil contains both organic and inorganic sulfur compounds, organic sulfur compounds which are in crude oil mainly thiophene, thiols and sulfides. Pyrite and hydrogen sulfide are present in crude oil in the suspension form as an account of in organic sulfur compound [5].

Refine products from a crude oil requires desulfurization [6]. Sulfur content is very important during transportation of fuel and in refineries processing cost. Crude oil containing high sulfur content increases the boiling range and also pollutes the environment, so before refining the crude oil sulfur must be removed by different desulfurization methods [7]. Desulfurization of aromatic sulfur compounds much complicated as compare with desulfurization of aliphatic sulfur compounds [8].high viscosities and high API gravities crude oil contains high amount of sulfur content and also a complex sulfur compounds, acyclic aliphatic sulfides such as thioethers and cyclic thiolane can be removed easily by a process of thermal treatment or commonly known as HDS [9]. On the other hand aromatic rings sulfur such as thiophene and derived its benzologs can be removed easily by HDS [10].table1shows some well locations in sindh,Pakistan and table2 shows specifications of table1 crude oil wells.

Table: 1. Oil fields well situated in sindh,Pakistan [11]

Crude oil	*Well situation*
1	Tando Adam Oil Field Well No 3,Sindh,Pakistan
2	Tando Adam Oil Field Well No 7, Sindh,Pakistan
3	Kunnar Oil Field Well No 10, Sindh, Pakistan

Table: 2. Physical specification of crude oils in Sindh, Pakistan [11]

Characteristics	*ASTM Methods*	*Crude Oils*		
		1	*2*	*3*
Sulfur content (wt %)	D-4294	0.018	0.276	0.2360
API Gravity@60/60°F	D-1298	38.77	37.75	37.96
SP.Gravity@60/60°F	D-1298	0.8310	0.8360	0.8350
Water content (vol %)	D-95	0.05	0.05	0.05
Pour point (°C)	D-97	+18	+18	+21
Kin. viscosity@40°C(cSt)	D-445	1.99	2.00	1.95
Carbon Residue (wt %)	D-189	0.64	0.55	0.62
Calorific value (Btu/lb)	D-240	18955	18960	18950

Table: 3. Illustrate the distillation range of sulfur compound in crude oil with total sulfur content of 1.2% [12]

Distillation range(°C)	*Sulfur content (%)*	*(%) distribution of sulfur compounds*		
		Sulfides	*Thiols*	*Thiophene*
70-180(naphtha)	0.02	50	50	Trace
160-40(kerosene oil)	0.2	25	25	35
230-350 (distillate)	0.9	15	15	35

2. METHODS

2.1. Oxidative Desulfurization (ODS)

oxidative desulfurization is a method in which chemical reacion

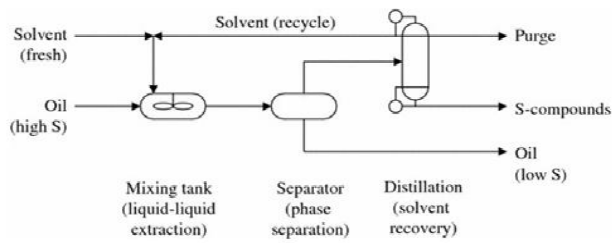

Fig. 1 The ODS treatment

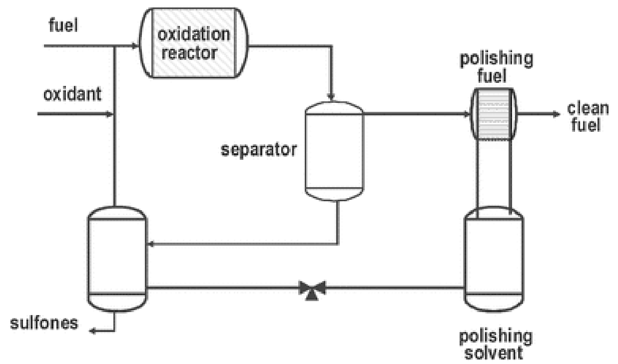

Fig. 2 The ADS treatment

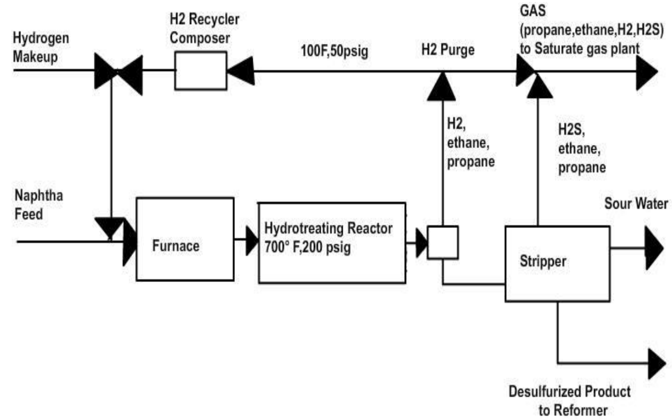

Fig. 3 The HDS treatment

on proceed between an oxidant and sulfur containing compou nds [13].ODS looks like a single process methods but chemic ally involves two phases. In the first phase oxidation of sulfur takes place then in second phase sulfur removed from the star ting material [14].sweetening is the most common and readily used method in the industrial process for the desulfurization o f hydrocarbon. In sweetening process the sulfur compound sp ecifically thiols is converted into disulfides [12]. For industria l aspect the conversion of thiols into disulfide required basic media which increase the reactivity of thiols to oxygen. In co mmercial scale aqueous sodium hydroxide is used as a base. Sweetening process is only feasible for thiols not implies for other sulfur compound. Sweetening process implies only for l ight hydrocarbons [15]. The process of ODS can be illustrate in Fig 1.

2.2. Adsorptive Desulfurization (ADS)

Removal of sulfur by adsorption method is very prominent industrial method. In this method sulfur compounds from hydrocarbon adsorb on the solid adsorbent surface. The method productivity is related to the selectivity of adsorbent material [16].adsorptive desulfurization further proceed into two major pathways which are follows:

1. **Physisorptions**, in this method the sulfur compounds removed by physical phenomena and in this method no chemical procedure taken.
2. **Chemisorptions**, in this method the sulfur compound removed from hydrocarbons by involving a chemical treatment, sulfur in hydrocarbons flowed on the adsorbent surface as a result of adsorption sulfur adsorbed on the adsorbent in the form of sulfide. Normally zeolite, activated carbon, silica-aluminas and metal organic framework are used in account of adsorbent material [17,18]. Fig 2 illustrates the ADS treatment

Desulfurization by Photo oxidation

Removal of sulfur content from hydrocarbon through photo oxidation is very coherence process. This method is favorable in very lenient reaction condition [19]. This method followed by two pathways: initial in the polar solvent sulfur content are accumulate from the hydrocarbon stream then the photo oxidation process takes place flooded by UV radiation [20].

2.3. Hydro-desulfurization (HDS)

In petroleum sector the most common method used for the removal of sulfur content in crude oil is hydrodesulfurization.HDS is execute when oil feed stock is with hydrogen in the presence of standard HDS catalyst. The standard catalyst used for this method are $NiMo/Al_2O_3$ and $CoMo/Al_2O_3$ [21].In this method the sulfur containing compound in crude oil is transformed in to hydrogen sulfide.HDS is fissile when conditions typically range from with respect to temperature 200-425 degree centigrade and with respect to pressure 1-18MPa [22].These conditions are depending on the nature of the sulfur compound which is in feed stock.HDS treatment is much favorable with a feed containing aliphatic sulfur compounds, because through HDS treatment sulfur completely removed from feed [23].Fig 3 shows the HDS treatment in a more summarize way.

2.4. Desulfurization by extraction

Extractive desulfurization is another very common and useful method for the removal of sulfur content from the feed stock. The solubility of the sulfur content depends on the particular solvents which are used in this process. It is a homophase extraction process, in the feed stock mixing tank the solvent and the sulfur compounds mixed together and due to high solubility sulfur compounds extracted in the solvent. Separation of hydrocarbon takes place from the solvent in the separator [24].

2.5. Desulfurization by alkylation

1. C-alkylation

Desulfurization on the basis of alkylation is very useful method for the removal of specific sulfur compounds called it thiophenes.In commercial scale this method is useful for light hydrocarbons. In this method thiophenic sulfur compound alkylated with olefins in the presence of acidic catalyst as a result molar mass and boiling point of thiophenic sulfur compound becomes increase which is easily disparate from the hydrocarbon stream in the distillating chamber [22].

2. S-alkylation

This method also applies for the desulfurization of thiophenic sulfur compounds. In this method sulfur compounds specifically thiophenes react with methyl iodate under silver tetrafluroborate presence to formed sufonium salts of s-methyl. This alkylated sulfonium salts form precipitates in hydrocarbon which is easily separate without followed any distillation process [25].

2.7. Microbe desulfurization (MDS)

Desulfurization followed by specific microorganism and reaction proceed at mild condition i-e at low temperature and pressure is commonly known as MDS. In this method the sulfur compounds in feed stock are metabolized by specific microbes. This method is cost effective over other desulfurization method [26].MDS method is an edge on the HDS method, in that way the operation cost of HDS is 15% less as compare with the HDS method [27,28,29]. Recently the BDS method not commercially used for desulfurization of crude oil, the reason behind this are handling, transportation, storage and microorganisms which is used in the refinery production.

2.8. Supercritical water Desulfurization (SCW)

Supercritical water method is a useful method for the removal of sulfur compounds from the hydrocarbon. In this method experimentally found that at a temperature of 400 degree centigrade and at pressure of 25 MPa [30] the bonds between carbon and sulfur becomes disintegrate.SCW do not support the sulfur compound which are aromatic in nature, but through SCW we can achieve the aliphatic sulfur compounds from the aromatic sulfur compounds [31].Fig 4 illustrates the SCW treatment for diesel [32].

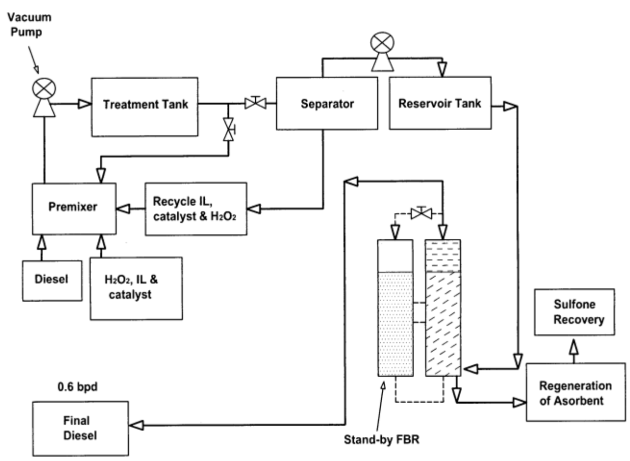

Fig. 4 The SCW treatment

2.9. Desulfurization by ultrasound oxidation

Removal of sulfur compound from hydrocarbons by a method of oxidation followed by ultrasound is a useful method. This method required an energy which acquired from ultrasound. In this method the feed stock and oxidant are mixed in the presence of surfactants and water in the reactor. In the reactor two phases generated i-e polar and non polar phases [33]. During a process a free radical is formed, sulfur compounds in the mixture are readily oxidized with free radical to form sulfones, sulfoxide and sulfates; these compounds are accumulating in the polar phase. Sulfur compound are separated from the mixture by solvent extraction [34].

2.10. Aerobic microbe desulfurization

Aerobic MDS is another method and it is an alternate to HDS method of crude oil. It was noted that 91% of sulfur content removed from the crude oil by the help of combining two methods i-e oxidative desulfurization and microbe desulfurization [35]. from this method the microorganisms which is effectively used is Alcaligenes xylosoxidans, this microorganism effectively work at a temperature of range 30-50 °C. The microorganism breaks the carbon sulfur bond in the hydrocarbon and as a result we accumulate inorganic sulfur compound from the organic sulfur, inorganic sulfur is soluble in water so it is easily separate from the non-polar phase [36].

2.11. Anaerobic microbe desulfurization

Anaerobic microbe desulfurization is more convenient method than aerobic MDS.Anaerobic MDS method edge on the aerobic MDS method in that way upon hydrocarbon oxidation anaerobic MDS produced negligible amount of colored and sticky material as compare to aerobic MDS [37].In this method the bacterium which is used for the removal of sulfur content from the hydrocarbon is called desulfovibrio desulfuricans or more commonly known as M6 [38,39].Desulfovibrio desulfuricans bacteria notably effective for the removal aromatic as compare to aliphatic sulfur compound. For thiophenic sulfur class compound this desulfovibrio desulfuricans M6 converted the benzothiophene as 96% and the dibenzothiophene as 42 % [40].

3. CONCLUSION

In the upstream and downstream sector of petroleum numerous methods were recommended for the desulfurization of crude oil. These approaches comprise oxidative desulfurization, Adsorptive desulfurization, Desulfurization by photo oxidation, Hydro desulfurization, Desulfurization by extraction, C-alkylation, S-alkylation, Microbe desulfurization and supercritical desulfurization. Desulfurization proceed due to crude oil properties which are high boiling range, high fludity,high sulfur content and nature of sulfur content. After review literature of desulfurization following findings to be notice

1. Every desulfurization method has its own limitations, beyond its limit it does not work.
2. Desulfurization methods applies for specific sulfur compounds, not for general sulfur compounds
3. Supercritical water method does not precede desulfurization process, but this method fulfils the requirement of starting material which is used in another method.
4. Due to high boiling, high viscous, high sulfur content and complex nature of a crude oil, the separation is difficult to proceed so make it easy the sulfur compounds goes through first alkylation and oxidation method
5. Removal of sulfur compounds from the hydrocarbon by BDS not effectively suitable for desulfurization due to high boiling point, high viscosity and high complex nature of the sulfur compounds.

REFERENCE

[1] Roussel, J. & Boulet, R.," Composition of crude oils and petroleum products", *Characterization of crude oils and petroleum fractions: Petroleum Refinig*, **1**: 1-84(1995).

[2] Bawazeer, K. & Zilouchian, A., in *Neural Networks, International Conference on.* 157-162 (1997).
[3] Wang, Z., Fingas, M. & Li, K.," Fractionation of a light crude oil and identification and quantitation of aliphatic, aromatic, and biomarker compounds by GC-FID and GC-MS, part II", *Journal of chromatographic science,* **32**: 367-382 (1994).
[4] Maldonado, A. G., Doucet, J., Petitjean, M. & Fan, B.-T.," Molecular similarity and diversity in chemoinformatics: from theory to applications", *Molecular diversity* ,**10**:39-79 (2006).
[5] Gray, M. R., Ayasse, A. R., Chan, E. W. & Veljkovic, M.," Kinetics of hydrodesulfurization of thiophenic and sulfide sulfur in Athabasca bitumen", *Energy & Fuels,* **9**: 500-506 (1995).
[6] Anisimov, A. & Tarakanova, A.," Oxidative desulfurization of hydrocarbon raw materials", *Russian Journal of General Chemistry,* **79**: 1264-1273 (2009).
[7] Ito, E. & Van Veen, J. R.," On novel processes for removing sulphur from refinery streams", *Catalysis Today,* **116**: 446-460 (2006).
[8] Zheng, X.-d., Dong, H.-j., Wang, X. & Shi, L.," Study on olefin alkylation of thiophenic sulfur in FCC gasoline using La2O3-modified HY zeolite", *Catalysis letters,* **127**: 70-74 (2009).
[9] Eßer, J., Wasserscheid, P. & Jess, A.," Deep desulfurization of oil refinery streams by extraction with ionic liquids", *Green chemistry,* **6**: 316-322 (2004).
[10] Agarwal, P. & Sharma, D.," Comparative studies on the bio-desulfurization of crude oil with other desulfurization techniques and deep desulfurization through integrated processes". *Energy & Fuels,***24**: 518-524 (2009).
[11] Yasin, G. *et al.,"* Quality and chemistry of crude oils", *Journal of Petroleum Technology and Alternative Fuels,* **4**: 53-63 (2013).
[12] Javadli, R. & de Klerk, A.," Desulfurization of heavy oil", *Applied Petrochemical Research,* **1**: 3-19 (2012).
[13] Murata, S., Murata, K., Kidena, K. & Nomura, M.," A novel oxidative desulfurization system for diesel fuels with molecular oxygen in the presence of cobalt catalysts and aldehydes", *Energy & Fuels,* **18**: 116-121 (2004).
[14] Moschopedis, S. & Speight, J.," Oxidative degradation of Athabasca asphaltenes", *Fuel,* **50**: 211-217 (1971).
[15] Babu, D. R. & Cormack, D. E.," Low temperature oxidation of Athabasca bitumen", *The Canadian Journal of Chemical Engineering* ,**61**: 575-580 (1983).
[16] Blanco-Brieva, G., Campos-Martin, J., Al-Zahrani, S. & Fierro, J," Removal of refractory organic sulfur compounds in fossil fuels using MOF sorbents", *Global Nest J,* **12**: 296-304 (2010).
[17] Irvine, R., Benson, B. & Varravsto, D.," in *NPRA", Annual Meeting* (1999).
[18] Salem, A. B. S.," Naphtha desulfurization by adsorption", *Industrial & Engineering Chemistry Research* ,**33**:336-340 (1994).
[19] Ancheyta, J., Rana, M. S. & Furimsky, E.,"Hydroprocessing of heavy petroleum feeds: Tutorial",*Catalysis Today,* **109**: 3-15 (2005).
[20] Purcell, J. M. *et al.,"* Sulfur speciation in petroleum: Atmospheric pressure photoionization or chemical derivatization and electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry", *Energy & Fuels,* **21**: 2869-2874 (2007).
[21] Lecrenay, E., Sakanishi, K. & Mochida, I.," Catalytic hydrodesulfurization of gas oil and model sulfur compounds over commercial and laboratory-made CoMo and NiMo catalysts: Activity and reaction scheme", *Catalysis Today,* **39**: 13-20 (1997).
[22] Rana, M. S., Samano, V., Ancheyta, J. & Diaz, J.," A review of recent advances on process technologies for upgrading of heavy oils and residua", *Fuel* ,**86**:1216-1231(2007).
[23] Bataille, F. *et al,"* Alkyldibenzothiophenes hydrodesulfurization-promoter effect, reactivity, and reaction mechanism", *Journal of Catalysis,* **191**: 409-422 (2000).
[24] Zhao, D., Liu, R., Wang, J. & Liu, B.," Photochemical Oxidation− Ionic Liquid Extraction Coupling Technique in Deep Desulphurization of Light Oil", *Energy & Fuels,***22**: 1100-1103 (2008).
[25] Zhang, H., Gao, J., Meng, H. & Li, C.-X.," Removal of thiophenic sulfurs using an extractive oxidative desulfurization process with three new phosphotungstate catalysts", *Industrial & Engineering Chemistry Research,* **51**:6658-6665 (2012).
[26] Soleimani, M., Bassi, A. & Margaritis, A.," Biodesulfurization of refractory organic sulfur compounds in fossil fuels", *Biotechnology advances,* **25**: 570-596 (2007).
[27] Kaufman, E. N., Harkins, J. B. & Borole, A. P.," Comparison of batchstirred and electrospray reactors for biodesulfurization of dibenzothiophene in crude oil and hydrocarbon feedstocks", *Applied biochemistry and biotechnology*,**73**:127-144 (1998).
[28] Linguist, L. & Pacheco, M.," Enzyme-based diesel desulfurization process offers energy, CO2 advantages", *Oil and Gas Journal,* **97**: 45-50 (1999).
[29] Pacheco, M. A. *et al.,"* Recent advances in biodesulfurization of diesel fuel", *NATIONAL PETROCHEMICAL AND REFINERS ASSOCIATION-PUBLICATIONS-ALL SERIES* (1999).
[30] Paspek Jr, S. C.," Google Patents" (1984).
[31] Forte, P.,"process for the removal of sulfur from petroleum faractions", Google Patents (1996).
[32] Cheng, S.-S. Google Patents (2010).

[33] Sun, M., Zhao, D., Sun, W. & SONG, G.-l., "Study on the oxidative desulfurization of diesel fuel with power ultrasound", *Chem Adh* ,**30**: 65-68(2008).

[34] Mei, H., Mei, B. & Yen, T. F., "A new method for obtaining ultra-low sulfur diesel fuel via ultrasound assisted oxidative desulfurization", *Fuel* ,**82**: 405-414 (2003).

[35] Adschiri, T., Shibata, R., Sato, T., Watanabe, M. & Arai, K.," Catalytic hydrodesulfurization of dibenzothiophene through partial oxidation and a water-gas shift reaction in supercritical water",*Industrial & Engineering Chemistry Research*, **37**: 2634-2638 (1998).

[36] Attar, A. & Corcoran, W. H., "Desulfurization of organic sulfur compounds by selective oxidation. 1. Regenerable and nonregenerable oxygen carriers", *Industrial & Engineering Chemistry*

[37] McFarland, B. L.," Biodesulf urization", *Current opinion in microbiology*, **2**: 257-264 (1999).

[38] Bahrami, A., Shojaosadati, S. & Mohebali, G., "Biodegradation of dibenzothiophene by thermophilic bacteria," *Biotechnology letters* ,**23**: 899-901 (2001).

[39] Lizama, H. M., Wilkins, L. A. & Scott, T. C.," Dibenzothiophene sulfur can serve as the sole electron acceptor during growth by sulfate-reducing bacteria", *Biotechnology letters* ,**17**:113-116 (1995).

[40] Armstrong, S. M., Sankey, B. M. & Voordouw, G., "Evaluation of sulfate-reducing bacteria for desulfurizing bitumen or its fractions", *Fuel,* **76**: 223-227 (1997).