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Evaluation of methods to eliminate sulfur from crude oil among “Esfandiyar” oil reservoirs

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Abstract:

According to problems of environmental pollution problems due to burning fuels having high Sulfur as furnace oil and because of related limitations, Sulfur removal methods have been emphasised to heavy crude oil patches. If Sulfur removal is necessary to furnace oil, and parts of crude oil would be processed but it should be pointed that this process include of operational problems as furnace oil Sulfur removal because of asphaltic components and metal contaminations developed chemical methods to mercaptan may not be used to crude oil and heavy parts. Therefore, it is attempted to provide new method to remove Sulfur composition from crude oil. in this paper all related methods to remove Sulfur compositions have been evaluated and operational problems have been assessed. Then, the best possible method has been introduced and supplementary discussion and economic evaluation have been provided.

Introduction:

According to environmental pollution problems of burning fuels having high Sulfur as furnace oil and due to related limitations, the methods to remove Sulfur have been emphasised to crude oil patches. If Sulfur removing is necessary to furnace oil, all crude oil parts should be processed to remove Sulfur. Therefore, the idea to remove Sulfur from crude oil would be drawn. There is operational problems due to having asphalt composition and metal contaminations related chemical methods to mercaptan may not be used to crude oil and heavy parts. By this extensive efforts have been allocated to provide new methods to remove Sulfur from crude oil. In this paper related methods have been evaluated to remove Sulfur from crude oil and operational problems have been discussed (Borgne, 2015).

Crude oil is complex mixture of hydrocarbons by extensive range of boiling point.

Hydrocarbons include of various molecules as methane as simplest and lightest and bitumen as heaviest sample. Therefore, 50 to 98% of crude oil include of hydrocarbons. Crude oil hydrocarbons include of below items:

- Paraffin or alkanes (saturated chain compositions)

- Oleffin or alkens (non-saturated chain compositions)

- Naphten (saturation circular chain)

- Aromatic (non-saturated circular chain) (Nelson, 2015)

Process to remove Sulfur from oil products:

Defination of Sulfur:

Sulfur is one of the elements of periodic table and it is nonmetal. It is located in third row and sixth group having atomic number of 16 and mass number of 32.

Sulfur is one of the non-hydrocarbonic derivatives include of compositions having Sulfur, oxygen and azot. The percentage of these compositions is not high in oil. Oxygenated and Sulfur compositions include of 2% of crude oil that may be changed.

These compositions are found among heavy patches amount of Sulfur of residential consumption gas is 4-6 ppm and in LPG 30 ppm (sherman, 2015). All known oil types include of Sulfur. Discovered oils from south America, middle east and near east include of more Sulfur. Amount of Sulfur in Iran is 1.22% in crude oil of haftgol and 2.46% in Khark crude oil. Eastern European, India, Pakistan and Barme crude oil include of lower Sulfur amount of Sulfur and API cover two properties having highest effect on valuating crude oil. Amount of Sulfur is defined as %W of Sulfur as 0.1 to 5% (crude oil). The oils include of more than 0.5 % Sulfur require extensive process and Sulfur removal (Kertezes, 2016).

Sulfur components of crude oil include of below parts:

Generally, Sulfur is harmful material that should be eliminated. At the other hand, it may be used to produce fertilizer as useful.

Fertilizer having Sulfur coverage that maybe synthesized slowly. By this output and advantages would be high to sail and herbs this types of fertilizer show high applications in agricultural industries. Recently, due to low output of area chemical fertilizers, it's loss, high contamination of salts and under earth water by nitrate and nitride, low absorption of clements due to high PH of soil, using this types of fertilizer is recomended to lands that are soaked under water. Beside to above advantages, Sulfur is vital elements of proteins due to decrease of soil PH, therefore, it is used to

absorb materials as iron and zinc. It is necessary to say that low level of iron and zinc is manifested among our people (Borgne, 2015).

Sulfur disadvantages and the reasons to eliminate it:

Organic Sulfur compositions are significant part of crude oil Sulfur components that is estimated as 0.25 to 3.23 % in Iran crude oil. Therefore in Iran oil reservoirs, highest amount is predicted combustion of crude oil derivatives as gas oil and petroleum would lead to produce Sulfur oxides. By this contamination and acidic rain would be non-activited. Due to acidic rain, constructional materials would be damaged, rivers toxicity would be accured and forests would be destructed. High percentage of Sulfur in oil products is harmful and their elimination by one of important affairs in refinery having Sulfur in petroleum is harmful due to corrosion of molar parts specially during winter by gathering SO2 in water. Also corrosion of shaft should be emphasised. At the other hand, solved mercaptan in oil derivatives would lead to corrosion of copper and brass in relation to air. Also mercaptan include of non-desirable effects on lead sensivity and product color stability if there is free Sulfur it is corrosive. Petroleum Sulfur and other fuels release SO2 based on combustion Sulfurs, di-sulfur and thiofens have lower corrosive properties but octane number would be decrease due to lead tetraethyl. Significant part of H2S would be released from oil under temperature of 400, 330 F (Shennan, 2015).

Sulfur is found in furnace oil, some critical properties include of gravity and amount of Sulfur. Due to prevention of air pollution at 2018, amount of Sulfur of furnace oil would be decreased and low level Sulfur oil would be used in some points (Kertesz, 2015).

Heavy furnace oil include of lower Sulfur and it is more desirable. Therefore, it's price is near to primary crude oil, Sulfur effect on lead and quality of oil product is confirmed as negative Sulfur of mazot would lead to corrosion and would lead to decrease of resistance against oxidizing, By this hardness of sediments would be increased (Nelson, 2015).

The effects of Sulfur in lubrication:

Due to decrease of Sulfur diesel fuels at 1990, lubricative properties have been emphasised by producers of motor and fuel injection systems. This is result of decreasing lubricative properties of fuels due to Sulfur limitations based on pollution control regulations. Infact, by decrease of Sulfur, corrosion of fuel injection system parts and injectors have been increased significantly. Therefore, most of organizations and producers acted to determine lubricative properties among diesel fuels. It is hope to provide compiled scales to world. The effects of decreasing Sulfur od diesel fuels have been manifested from first of 1990 by low Sulfur gas oil in seweden as corrosion of pumps and parts of fuel supply system. By this additives and increase of lubricative properties have been emphasised (Borgne 2015).

To determine amount of corrosion and friction due to low Sulfur fuels, field tests are the best but it's duration is long and would not be possible. Using lab pumps is not economic despite lower cost and time. The most accessible method is high frequency reciprocahion Rig (HFRR) that it's result would be achived during several hours (schennan, 2015).

By this most of manufactures and producers of diesel fuels have been confirmed based on lubricative properties. For example European association defined min properties of diesel fuel due to lubrication based on En 950 (Nelson, 2015).

The similarities between elimination of nitrogen and Sulfur:

Invented catalyst to process with hydrogen from oxides of cobalt, molibden, aluminum and nickel, molibdat oxide, tangestan, nickel and vanadium oxid sulphid and catalyst of cobalt oxid and molibden aluminum are the best options. These materials may be retested and recovered beside to resistance against toxins. They should be transformed from oxide to sulfide through processed metals with hydrogen. Therefore, of nitrogen elimination is important, catalyst should be from compositions of nickel, cobalt, molibden or alumin molibden-nickel usually elimination of nitrogen from hydrocarbon is more difficult that Sulfur elimination. Before achievement to reaction temperature, catalyst

having nickel would be activated. By this pre-sulphid process would be formed by carbon disulphid mercaptan or dimethyl sulfide. Some of refineries perform this work through sulphidizing chemical materials injection in oil feed during performance. Sulphidizing produce high temperature but high temperature is not proper during activation (Morcelis, 2016).

Evaluation of role of thermal and catalystic reactions during Sulfur elimination process:

Today hydrotreating process is important process in crude oil refinery. Infact, this is most applicable catalyst process in refinery unit. After output gas refinement catalyst and cracking catalyst, this is most expensive item of consume catalyst. The basic goal of said processes is elimination of heteroation (Sulfur, nitrogen, oxygen, metals) with pressure of hydrogen and from processed oil. Depending on regions, oil include of percentage of heteroatoms to define this process, the formula would be defined. Therefore, depending on type of eliminated heteroatoms, the process would be categorized to 4 groups (Marcelis, 2016).

1. HDS (hydro de sulfurization)

2. HDO (hydro de oxidation)

3. HDN (hydro de hydrogenation)

4. HDM (hydro de metallization)

Percentage of oil nitrogen is 5 to 20 times lower than Sulfur during industrial hydrogen refinement thermal and catalyst reactions are parallel and depending on eliminated hetro atoms, role of thermal and catalyst directions would be changed. During HDS process, two directions include of direct effect in elimination if Sulfur and some compositions would be transformed having Sulfur. During HDN process, just catalyst direction include of direct effect of elimination of nitrogen. Now, we want to evaluate the effects of thermal and catalyst reactions on Sulfur elimination from heavy oil patch. The catalyst include of nickel-molibden on alumina. The feed include of heavy Canadian oil patch (Borgne, 2015).

Due to high viscosity of feed, cylinder and piston system is used to feed reactor. Heavy feed is injected to above of cylinder and piston and the system would be maintained with 150 C temperature. Lighter oil would be injected to below of cylinder and piston. By this, heavy feed would be moved among reactor. Cylinder hydrogen would be mixed with feed under pressure and 4.8 litre/sec debi and entered to reactor.

The mixer act with 800 round/min. Reactor pressure would be controlled by control value in reactor exit direction.

The pressure is 13.9 MPa. The temperature of reaction is 400 to 450 C as isothermal liquid and gas products would be separate by parallel seperators. Liquid products would be gathered in two reservoirs gas products would be discharged passing absorption column and contour (to eliminate H2S, NH3). During test, gas products would be injected to gas chromatography device to determine light hydrocarbon. Liquid products would be analyzed to determine %w of distillation patches and Sulfur of any patch. To analyze lab data, residence time would be defined as feed debi proportion to liquid volume of reactor finally reactor liquid volume would be measured after isolation of reactor and discharge of conten (Nelson, 2015).

Amount of Sulfur in gas oil fuels:

Evaluation of 33 countries show Sulfur of fuel have been decreased compared to previous years during 1995, Sulfur of diesel fuels was 1000 to 2000 mg/kg in most of countries but during 1998, this amount is decreased as 50 to 500 mg/kg . This decrease should be continued. According to Sulfur contamination on gas oil fuels among European association countries, this amount was 50 mg/kg at 2005 in U.S.A and Canada and 15 mg/kg at 2006 (Shennan, 2015).

The plan of decreasing amount from 500 to 50 mg/kg was performed in some points of Japan at 2003. In countries as Belgium, Denmark, Finland, Norway, Netherlands and England, gas oil 500 mg/kg have been produced. Also Sulfur content of gas oil in Germany, Sweden and Italy is 10 mg/kg.

According to statistics, max authorized amount of Sulfur to diesel fuels in some of countries are as below:

European, U.S.A, Canada, Japan, Thailand and Singapore 500 ppm, Hong Kong 350 ppm and Australia as 500 ppm (Nelson, 2015).

Sulfur elimination methods:

There are various methods to extract simple Sulfur compositions from light oil patches by chemical materials and solvents but some of them may be used to heavy patches as remained black oil or crude oil having thiofen. Developed chemical methods to mercaptan may not be used to thiofen sulfur removal. In fact, more expensive chemical materials would be required (Kertesz, 2016).

Various processes to remove sulfur include of below items:

1. Bacteriaoligical sulfur elimination

2. Sulfur elimination with metals and metal composition

3. Sulfur elimination with chemical methods

4. Sulfur elimination with oxidation

5. Bio sulfur elimination

6. Hydrogen sulfur elimination

7. Softening method (Borgne, 2015).

1. Bacteriaological method:

Sulfur bacteria include of heterogeneous group of microbes with non-organic sulfur composition that act in metabolism as basic part. At the other hand, there is limited relation although they have contact in sulfur based ecosystems naturally, for example, contaminated pool would lead to decrease of sulfate in deep water based on practical applications, sulfur bacteriaes are categorized to 4 groups:

1. Oxidized bacteriaes as thiobacillus

2. Sulfate reduction bacteriaes as desulfovibio

3. Non-colored sulfur bacteriaes as beggiatoa

4. Colered sulfur bacteriaes as chromatium and chlobium (Shennan, 2015).

2. Sulfur elimination by metals and metal composition:

Metals and it's compositions specially oxides would react to sulfur compositions to produce stable sulfide. This method may be used to refinery. Comparing to hydrogenated method, this method is not economic. The basic problem is related to metal compositions that is very expensive (Marcelis, 2016).

3. Elimination of sulfur using chemical methods (di sulfurization):

During recent years various innovations have been done to di sulfurization of heavy elements and crude oil using chemical methods. Some of used materials include of maleic acid, saccinic acid, potassium hydroxide 7 to 25 % w of water, potassium hydroxide 10 to 15% w of water with presence of oxygen, cesium hydroxide with 10 to 20 % w of water and mixture of lime and lime stone and soil, during said processes, di sulfurization is accounted as 60%.

4. Di sulfurization using oxidation method:

Based on related innovative method to British petroleum heavy elements would be desulfurized using oxidation by various factors of oxidation and placing in exposure to thermal synthesis or rapid thermal process (SO2). Various factors of oxidation as peroxides, hydroperoxide, peracid chlorine, nitrogen oxide, ozone and oxygen oxidation is done at 130-180 C during 30 min to 20 hr. The process would be continued at 300 - 400 C (Kertesz, 2016).

5. Bio di sulfurization:

BDS include elimination of sulfur composition of oil using anzyme catalyst reactions under limited temperature and pressure. During process air circulated bio reactors would be used due to simplicity, air circulation and lower cutting street compared to stirred reactors (Marcelis, 2016).

To decrease limitations as low volumetric ratio of water to oil, limitation of bio catalyst circulation to reactor and high prices of sample bio catalyst, BDS is performed. Oxygen transfer is one of the important factors to bio reactor design. Based on bio di sulfurization, we are faced to water emulsion in oil patches (Borgne, 2015).

6. Hydrogen di sulfurization:

One of the basic reasons to lack of commercial method of di sulfurization is technical problems, lack of economic motives and weak rules to prevent of burning oil with high amounts of sulfur technical problems, high amounts of asphalten and metals as nickel and vanadium would result in quick cock production and non-active catalyst.

To perform hydrogen di sulfurization and using crude oil with high amounts of sulfur, half of sulfur would be eliminated because during intensive process, high amount of asphaltic elements would lead to quick production of cock on catalyst. By this catalyst would became passive during short time. Using intensive process would be impossible because life of catalyst is short and slow process of di sulfurization would not lead to desirable result with low sulfur technical di sulfurization is very hard because of asphaltic compositions and metal contaminations that would result on passive catalyst asphaltic compositions would not be distilled non solved cock in oil may be combined to sulfur, nitrogen, oxygen and various metals asphaltic materials would be dispersed as colloidal materials. By warming, polymerization and coagulation would be done. Therefore, in atmospheric remained or vacuum, polymerized asphalten would be seen as semi-solid materials at ambient temperature (Nelson, 2015).

Metal contamination as nickel and vanadium are common but there is other metals as iron, copper, lead and zinc. Metal contaminations may not be seen as metal oxides or sulfide, particles or solved salts in oil. Usually these metals maybe seen as organic-metal composition with high molecular mass as metallic probhyrin and its derivatives.

By using hydrogen to hydrocarbon including organic-metal compositions, metals would be sedimented on catalyst and with progress of process, viscosity would be increased. Therefore, during hydrogen di sulfurization, short life or passive catalyst would be result of below items:

1. Extensive sediment of cock on catalyst

2. Gathering metal sedimens on catalyst

During commercial hydrogen di sulfurization, the process would be successful as 75 to 80% (Shennan, 2015).

7. Softening method:

During this process di sulfurization from sulfur, mercaptan and sulfur compositions would be based on elements.

The most important methods include of below items:

7.1. Cellutizer method:

This method is related to extraction of all minerals from oil patches (resulted from distillation, cracking or reforming)

Advantages include of increase of petroleum capability to accept lead because of di sulfurization of sulfur compositions.

7.2. Doctor method:

Using this method, various types of petroleums and more heavier compositions and crozone would be treated. In this methods sodium plombit alkaline solution would be used to treatment (Borgne, 2013).

7.3. Hypochlorit:

Hypochlorit is oxidizing factor to decrease odor to perform process, mercaptan may be used in oil patches. This method is supplementary to treatment using soda (Marcelis, 2016).

7.4. Cholor quiverick (perco method):

Using these methods, copper choloror would be added and mercaptan would be transformed to disulfur.

7.5. Catalyc treatment method:

In this method, instead of previous compositions, catalyzor would be used. Merax method is catalytic treatment method that catalyzer is fixed bed of lead oxides with life cycle more than 3 years (Borgne, 2015).

Di sulfurization by bio surfactants:

Bio surfactants are organic compositions that are produce by oil eating bacteriaes.

There’s 3 groups to them as below

1. Cationic

2. Anionic

3. Neutral (Kertesz, 2016).

All of them mould of specified properties.

Beside to decrease of surface tension, bio surfactant break uniform oil layer would be emulsified and solved in water. Also the ratio of surface to volume of oil stain would be increased and oil eating bacteria gather around oil particles and synthese them (Borgne, 2013).

Applications of bio surfactants is very extensive for example these compositions may be used in pharmaceutical industries to decrease surface tension of pharmaceutical competition in body and better absorption , also it may be used to washing materials to increase product quality. At the other hand, food industries use them. But the most important application is oil extraction. Today they may be used to produce third oil from extracted wells having high economic value (Nelson, 2015).

Biologic di sulfurization using RIPI-S81 battery:

Today BDS is performed using microorganisms on sulfur aromatic composition. Now, we evaluate performance of new bacteria of RIPI-S81 that is extracted from oil field by oil industry researching center, microbiology unit using them, di-benzo thiofen would be processed and transformed to 2-hydroxy diphenel based on 45 direction.

According to research findings, bacteria has special capability to eliminate sulfur from 4-methyl di-benzo thiofen and 4,6 - dimethyl di-benzo thiofen during growth phase actived is of daily bacteria (without growth) performe di sulfurization to di-benzo thiofen and alkali derivatives resulted metabolite molecular structure of said process would be identified using GC-MS device analysis. All refiners use HDS method to perform di sulfurization from fossil fuels. This method is very expensive and require high energy. Also this method is proper to aromatic sulfur heterocyclic compositions as benzo thiofen , di benzo thiofen and alkali derivatives among them, di-benzo thiofen include of sulfur near to positions of 4 or 6.

The highest resistance against di sulfurization is related to HDS method. Basic specification of resistance is related to special obstacles during breaking carbon-sulfur bond. In fact, placing in positions of 4 and 6 would lead to prevention of beta elimination during hydrogen di sulfurization. Therefore, direct di sulfurization direction would be corred in alkali derivatives of di-benzo thiofen.

Today microorganisms are new methods to eliminate sulfur from hydrocarbon elements by this carbon Skelton would not be changed.

Biologic di sulfurization is supplementary method to HDS without need to high temperature and pressure. By this sulfur aromatic hetrocyclic compositions would be covered. This method is in conformity to environment. Today extensive researches have been performed to aerobic microbial di sulfurization and di-benzo thiofen is used as model. During research carbon atom is separate from di-benzo thiofen and 2-hydroxy bi phenol would be produced.

During said specialized metabolic process, 4 enzymic phases are defined. Therefore, it is named as 4S. The process is shown at below (Borgne, 2015)

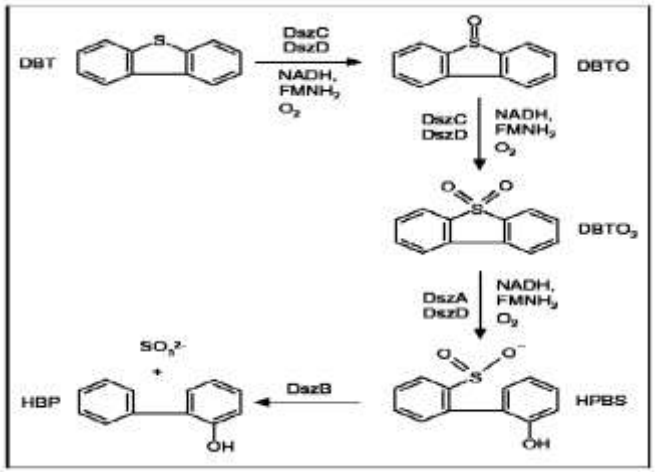

Fig1: 4S direction in R-Erythropilis IGIS8

Until now various aerobic bacteriaes are reported to perform di sulfurization from di-benzo thiofen and alkali derivatives based on 4S direction, some of them include of R-erythropolis H-2, R-erythropolis IGIS81 is bacteria to di sulfurization of di-benzo thiofen and its derivatives without change of carbon structure. Now, we evaluated di

sulfurization of di-benzo thiofen and 4-methyl di-benzo thiofen and 4,6-di -methyl di-benzo thiofen that are very much in gas oil this is the first in Iran.

Bacteriaes specifications:

RIPI-S-81bactri is new type to di sulfurization that is extracted from oil field and have been evaluated by oil industry research center RIPIs 81 is gram positive, mandatory aerobic, without spore and cocobacil bacteria colory is pale pinx at agar culture dish as circle, smooth and requalar, concave and transparent. This is mesophyll that grow under 30C temperature (Shennan 2015).

Chemical materials:

Material is not produced in Iran.
di-benzo thiofen (DBT) should be provided by Merck company, Germany with specified punty level 4-methyl di-benzo thiofen is provided by aldrich -sisma company with high purity and 4,6 di-methyl benzo thiofen is synthesised by aldrich company, USA, other chemicals are provided through valid companies as solvents with appropriate analytical degree bacteria culture environment, culture dish as 1 lit have been pronded to grow RIPI-S81 bacteria with two parts. First part include of KH2 PO4 6gr NA2 NO3 4gr, NH4 NO3 1.2gr, C2H5 NA2 2gr (sodium benzoat) without ion in water (deionzed PH=7/8)

Second part:

Minerals that is solved in deionized water 150 mllitr. it is include of $MgCO_2$, $6H_2O$ 0.75gr Mn CO2 $4H_2O$, 0.004gr , $CaCl_2$, $2H_2O$, 0.001gr , $FeCl_3$ 0.001gr.
all organic silpured composition have been solved in DMF (di-methyl formamide) and added to culture dish as source of sulfur to grow bacteria.

Analysis Methods:

chemical structure metabolits of bacteria di sulfurization have been determined on de-benzo thiofen 4-methyl di-benzo thiofen and 4,6- dimethyl di-benzo thiofen using mass spectrophotometry gas chromatography analysis (GC.MS) that include of GC device (varion 3400 made by USA-Germany) and mass spectrophotometry (sa turn II (MS) type of telionic. Cell growth is measured using spectrophotometer (UV mini 1240 CE schimadzai company) by 660 km frequency. Amount of gathered phenolic composition of culture should be determined by Gibs test.
Firstly 100 ml of Gibson indicator is mixed to 5 ml bacteria reaction environment (0.1 gr 2,6- di cholorokinon chloramid in 10 ml ethanol).
Positive reaction would be occurred after 1hr from warming at 30 C accumulation of phenolic compositions would be measured by spectrophoto meter at 610 nm frequency start time and production extent of phenolic compositions have been evaluated using UV device (Germany UVG-45) by 254 nm frequency positive reaction maybe occurred when using UV device, the colors of violet-blue is created with flourcence properties in sample to evaluate and determinate to metabolites of bacteria di sulfurization on sulfur resources, the samples would be extracted with ethyl acetate solvent firstly PH would be decreased to 2 and with equal volume, ethyl acetate would be added and mixed. Then the surface layer would be separate and analyzed.
Reaction of active without growth:
Primary culture of RIPI- S81 is performed under 30 C temperature using flask 500 ml include of 300 ml culture and 20 ppm di-benzo thiofen and dimethyl formamide solvent (1000 ppm) during 78 hours.
By achievement to end of logarithmic phase of growth, centrifuge (4000 ppm) has been performed during 8 minutes using phosphate buffer 0.1 mol (PH=7.8), washing has been performed two times. Then said buffer has been added to produce cell suspension. It's cellular density was 30 at 560 nm frequency. Then 6 covered small vials has been prepared with capacity of 2mp lit then 0.5 ml lit cell suspension has been added to vials also 200 ppm di-benzo thiofen solution and di-methyl formamide solvent (20000ppm) has been added to two vials. At the other need 4-methyl di-benzo thiofen and di-methyl formamide solvent (20000 ppm) as 200 ppm has been added to two other vials. Finally solution of 4, 6-dimethyl formamide solvent (20000 ppm) has been added next two vials. Then 3 covers

has been prepared and with 0.4ml lit bupper and 200ppm sulfur resources as control. The shaker system is used as reciprocal to a vials (225 rpm) in warming room under 30C temperature (Shenan 2015).

Evaluation of di sulfurization activity (water phase reaction system):

Using style flasks with capacity of 100 ml and 50 ml lit culture materials evaluation has been performed 4.5 ml lit microbial suspension has been added to as op-them. To two p-rst flasks, 20ppm di-benzo thiofen solution and dimethyl formamide solvent (100000 ppm) has been added and two next flasks, 20ppm of 4-methyl di-methyl formamide (1000ppm) has been added to next flasks, 20 ppm of solution of 4,6-dimethyl formamide (10000ppm) has been added. Finally to two other flasks 10ppm of suffer resources have been added. All flasks have been adjusted on shaker as 120rpm in warming room with 30c temperature.
Evaluation of di sulfurization process of said Bacteria on sulfur resources have been provided as below. Growth delay phase of bacteria on 4,6-dimethyl di-benzo thiofen is predicted as 18 hours di-benzo thiofen. Samples including di-benzo thiofen or 4,6-dimethy di-benzo thiofen are just sulfur resource that has been evaluated after 14 days.
Therefore, desulfurization process of bacteria on 4-methyl benzo thiofen has been performed with delay phase of 10 days. After that bacteria would entered to logharitmic phase of growth during 10 days, no growth is seen in culture bed including 4-methyl di-benzo thiofen. Therefore, samples including 4-methyl di-benzo thiofin have been evaluated after 17 days .

Table1: test results of simples including specified sulfur reservoirs

Test UV	Gibbs Test OD	OD	PH	Sulfur Sources
Very positive	1/265	1/415	7/15	DBT
positive	0/813	1/32	7/25	4-MDBT
positive	0/739	1/362	7/2	4,6-DMDBT
Very positive	1/235	1/723	7/19	4,6-DMDBT, 4-MDBT, DBT

To evaluate desulfurization process of active bacteria cells without growth , samples have been analyzed including active cells without growth and sulfur resources after 24 hours to perform this, GC-MS device has been used, results show ability of active cells without growth to perform desulfurization from alkali derivatives of di-benzo thiofin.

Elimination of mercaptan from oil patches:

Production of crude oil and gas liquidity including mercaptan have been increased in the world. There's extensive oil resources in Russia, USA, north sea, Iran and Qatar including high content of sulfur. Basic specification of patches including mercaptan is presence of sulfur in hydrocarbon chain. Various group of mercaptans as most toxic and volatile (methyl and ethyl mercaptan with low molecule weight) to heavy mercaptan (branched hydrocarbon chain) are present. Hydrdogen sulfide and light mercaptans of C1-C3 are toxic, volatile, odorous and corresive. During treatment of patches including mercaptan, toxic sulfured-alkaline sludge would be produced. Therefore, production, transfer storage and treatment process include of technological and environmental problems.
To solve this problem, oil industry research center acted to provide technology to eliminate mercaptan from oil patches by DMD and DMC methods .
Recently pilot designs of DMD and DMC is provided and performed in oil industry research center and Iran industrial sectors acted to install them.

DMD:

DMD process is elimination of mercaptan from oil patches using caustic solution, light mercaptan would be eliminated beside to H2S, CO2 and CS2 from oil patch and corrosive heavy and active mercaptans would be transformed to disulfid.

DMD history:

First industrial sector acted to eliminate mercaptan from pentan using catalyst IVKAZ at 1974 in Russia.

Advantages of DMD process:
Comparing DMD to similar processes, there is significant difference and similarities:

A. During DMD process, hemogen, stable and active catalyst of IVKAZ is used that is more active and stable than other catalysts.
B. Using DMD process, feed treatment and purification would be performed during first stage (H2S+ RSH + CS2). To eliminate CS2, special additives should be used during extraction.
C. DMD process based on serox process include sulfur - alkaline water- using serox process , toxic sodium would be transformed to neutral salts of sulfate and thio sulfate sodium.
DMD process and serox unit creat process to treat light hydrocarbon feed from toxic sulfur compositions without harmful sewage and environmental damages.
D. Cost of DMD process is lower than similar processes but DMD is more effective and efficient.

DMD process introduction:

Various DMD processes have been developed based on oil patches, mercaptan percent in feed and products.
1) DMD-1 to eliminate mercaptan from kerosene.
2) DMD-2 to produce edorant (pure mercaptan) from LPG and light Nafta.
3) DMD-2K to eliminate mercaptan from propane and butane.
4) DMD-3 to eliminate mercaptan from heavy Nafta and petroleum.

Below items show under performance projects in Iran:

1) Khark petrochemical: oil industry research center is committed against design, engineering and sale of 3 industrial units of desulfurization to petrochemical products.
In this project, Marta, propane and butane of Khark petrochemical company have been purified in 3 units. The products would be exported. The capacities are as below:
Nafta desulfurization unit: 4000 t/day
Propane desulfurization unit: 500 ton/day
Butane desulfurization unit: 500 ton/day
Amount of sulfur in feeds is 1000 ppm
After desulfurization, it is expected to decrease mercaptan as lower than 5 ppm and total sulfur of propane and butane desulfurization units to 35 ppm and to Nafta unit as 50 ppm.

DMC:

DMC process include elimination of mercaptan from crude oil and gas liquidity. Using caustic solution with viscosity of 5-15%, mercaptan, H2S, CS2 would be eliminated and active heavy mercaptan would be transformed to stable organic and non-toxic composition.

DMC process:

DMC process advantages:

A) During process, hemogen catalyst of IVKAZ may be used as non-toxic, stable and non-expensive sample.
B) This process is unique
C) Cost of this process is very low and its installation is economic based on value added.

DMC process introduction:

1. DMC is used to decrease mercaptan and acidity of crude oil and gas liquidity.

2. DMC-IM:

During these processes, H2S of heavy crude oil would be decreased from 100 ppm to 5 ppm and light mercaptan would be decreased from 300 ppm to 20 ppm (C1-C2).

2-3-DMC:

During this process light mercaptan C1-C2 of crude oil would be decreased from 2000 ppm to 20 ppm.

3-4-DMC:

During this process beside to H2S decrease to 5 ppm, mercaptan would be decreased from 4000 ppm to 50 ppm in crude oil and gas liquidity. Total mercaptan would be decreased to lower than 75 ppm.

Under performance projects:

Now, preliminary design of DMC-3 construction is provided to decrease mercaptan of gas liquidity of phases 4,5 of south pars from 1650 ppm to 50 ppm by research center - As soon as possible EPC project, unit of DMC-3 would be performed with capacity of 80000 barrel in oil industry research center.

- Construction of two treatment units of gas liquidity with capacity of 60000 b/d to gas liquidity of phases 12 of south pars that is one the plans of research center and contract phases is performed (Mohebal, 2014).

Conclusion:

According to contamination environmental standards that are limited and based on global demand to oil and products, sulfur of oil reservoirs would be increased globally di sulfurization from oil patches is very important. Due to presence of sulfur in fuel SO2 would be produced during combustion that is important environmental contamination and would lead to acidic rain. Therefore, fuel di sulfurization from oil products is important.Elimination of sulfur by bio method is lead to importance of bio technology in oil industry.

During bio di sulfurization, sulfur atom of organic composition would be separated by bacteria without breaking carbon structure. This process may be performed by presence of water and oxygen and in absent condition without need to hydrogen. In this research importance of bio di sulfurization and its advantages compared to other methods have been evaluated and aerobic bio di sulfurization and bio di sulfurization as destructive have been defined.

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