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NOVEL METHODS OF DEEP DESULFURIZATION: A REVIEW

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Abstract

In order to meet the defined standards of sulfur emission, it is an inevitability to develop varied models based on indispensable concepts. Such models can only be created after having robust knowledge about the issue and setups involved in desulfurization. This review presents various criteria for Hydrodesulfurization (HDS) and novel Non-HDS processes with comprehensive information of the catalysts and reactor set up data. In addition, radiation theory concepts and material on novel biocatalyst employed in the process of desulphurization are also elucidated. The recent advancements are in emerging stage, so making feasible improvements on the factors would support the petroleum processes to release a reduced amount of sulfur in the atmosphere. A concerted integrated approach will surely lead the way for a safer and rapid way for the production of zero-sulfur fuels.

***Keywords**: Desulfurization; Catalysts; HDS and Non-HDS; Reactor setup.*

1. Introduction

The rising environmental concerns around the globe have enforced almost all the petroleum process industries to remove the pollutants as much as possible from the light oils. Research on science and technology of deep desulfurization gained momentum during the last decade, due to strict compliance of the standards fixed by the Environmental Protection Agency (EPA) for quality of the fuels that says a minimum allowable sulfur quantity should be < 30ppm. Stringent European standards stipulated a sulfur content of lesser than 10ppm [1-2]. Almost all legislations during the late 1990s were focussing on the removal of sulfur from varied compounds since it has a myriad number of deleterious effects over human lives, variety of refinery equipment, and also on the environment.

The refineries all around the world are developing novel processes to reduce sulfur levels in transportation fuels in order to satisfy the regulations. The research on the removal of sulfur is a primary concern in the process industries. The sulfur basically has adverse effects on engine parts, and metallic joints present in the equipment in addition to the increased corrosion of relevant mechanical parts of the distillation columns. Pollution, greenhouse effect, acid rains are various other reasons behind the removal of it from the fuels.

The removal of sulfur by oxidation is a core process. The experiments presented paradigms for the fact that all the sulfur compounds can be easily converted into separable oxides [3]. The oxidation process has history, which involves the presence of NO_2 was proposed in 1974. Peroxidation of sulfur compounds is one of the best methods used where both adsorption and extraction are followed. The process described as purification of liquid oil in 1988, which was further developed as oxidative desulphurization in 2000 is considered as the most prominent approach for the removal of dibenzothiophene (DBT) and its derivatives at lower temperature and pressure which are complex forms of sulfur and hard to remove by general hydro-desulfurization (HDS). The complexity in treating DBT is due to the substitution of sulfur on the 4 and 6 positions that result in steric hindrance [1]. The hydrogen paucity is majorly responsible for cost rise of ultra-deep desulfurization, which is focused on meeting the need of the ultra-clean fuels.

In recent times, more concerted research through biological route is gaining momentum. One promising short term application of biotechnology is the production of biopetrochemicals from oil. Biodesulfurization of oil was made with resting cells of *Pseudomonas delafieldii* R-8, where the resting cells in the late logarithmic phase harvested from the cultural broth were used [5]. Similarly, Sumedha and Durlubh stated the importance of thermophilic *Klebsiella sp.* as sulfur removing bacteria, which may eventually help biocatalysts to independently desulfurize petroleum oil. *Nocardia globerula R-9* had also shown the potential to remove sulfur content from diesel [6-7].

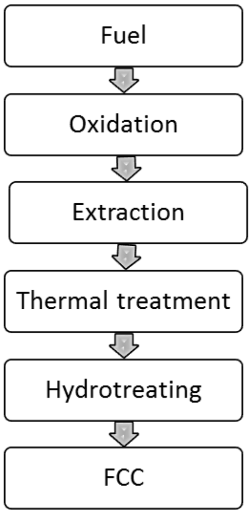


Fig.1. Basic desulfurization process flow

Recent advances in desulfurization involve nanotechnology and polymer sciences. Catalytic properties of the tungsten oxide bronze (TOB) nanoparticles is similar to that of hydrogen peroxide in making a fine desulfurized product [8]. Some compounds of cobalt and molybdenum are used as the metallic catalyst base. Hydroxyl-terminated polybutadiene/ acrylonitrile (HTBN) polymer material was chosen for deep desulphurization of LPG using the solubility parameter method. Despite the fact,that new method developed are unable to compete with traditional desulfurization due to the sturdy nature of the same, various new methods are reported that reduce the production cost and improve the process performance. Basic desulfurization module is illustrated in Fig.1.

2. Fuel components

Nearly 70-80% of the refinery outlets constitute gasoline, diesel, and other non-transportation fuels. These products are under severe investigation for the removal of sulfur [2]. Since oxides of sulfur coming out of various automobiles are noxious, countries like Germany, USA is aiming to squelch these gaseous emissions. Major target is to achieve zero sulfur content of the fuels due to the fact that high content of sulfur hampers the performance of the fuels by a change in the basic intrinsic properties of the fuels like oxygen content, vapor pressure, benzene content and polynuclear aromatic content. Liquid Petroleum Gas (LPG) is one of the most important fractions used all over the world as household and transportation fuel. The LPG obtained from FCC unit or delayed coking process usually contain various kinds of sulfur compounds, including carbonyl sulfide (COS), mercaptan, carbon disulfide (CS_2), dimethyl sulfide (DMS) and dimethyl disulfide (DMDS) and so forth. Out of those DMS and DMDS are intricately dovetailed with the other components, hence very difficult to remove. Gasoline is also treated using the FCC to reduce the sulfur content, but the reduction below 30ppm is very unconventional. The removal of sulfur from straight run diesel is a major concern basically to stabilize the properties like cetane number, density and polyaromatic composition [2] by employing some process that usually reduces sulfur up to 1.5-2.5% by weight. In the case of non-transportation fuels, these factors are not stringent as much as the others.

3. Basic HDS and other processes

Oxidation of the sulfur components is the arcane process, which is simplified and presented using Fig.2. Air is used in various industries for the oxidation process due to its cheap rate and abundance. .The maintenance of 300-380°C temperature under the reaction pressure of 15-90 bar in the reactor is the basic requirement in the HDS process, where the feed gets separated easily as per the component sensitivity. Solvent extraction is developed in sequence with HDS, where the solvent can dissolve and remove up to 90% of the sulfur.

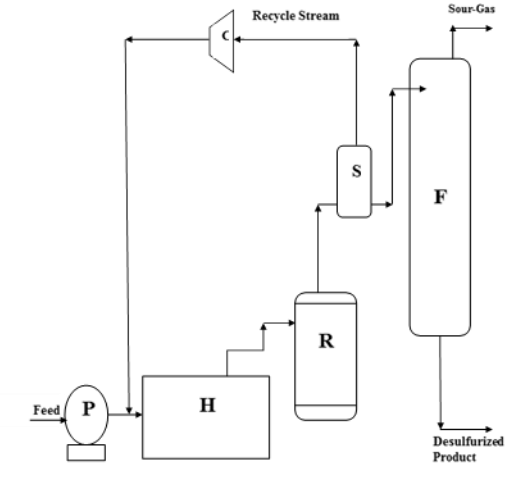


Fig.2. HDS process with catalyst
P - Pump; H - Heat treatment; R - Reactor; S - Separator; F - Fractionator; C - Compressor

Transfer of sulfur from light oil to aqueous polar solvent is the simple step involved. The removal of a very little amount of sulfur present in light oil requires highly extreme temperature, pressure, and catalyst conditions. Hence the development of a cost-effective process with high specificity was the necessity. The Hydrogenation process in the presence of special catalysts combined with irradiation techniques need essential metal supports like Ce; Mo has been used to remove SOx from the gas in petroleum and H_2S from natural gas [9]. A process used tungsten catalysts to convert sulfur compounds to sulfone in the presence of H_2O_2. The catalyst used is tungstophosphoric acid in n-octane and acetonitrile, which has a biphasic system. BDT was quantitatively oxidized within minutes in the presence of tetra octylammonium bromide and phosphor-tungstic acid at 75°C under the influence of ultrasound irradiation [8,10-11]. Application of any form of irradiation has shown positive effects on the process outputs. Atmospheric pressure laser ionization is one of the novel analytical methods employed in the late 2000s for process evaluation. Further research leads to the ESI method, but it was not favoured due to limitations like component polarity and ionization factors. Nowadays, APLI is used to analyse complex crude components and temperature sensitive constituents. APLI effectively detects even non or low polarity compounds such as hydrocarbons, sulfur species, and oxygen species that lead to more advancements in desulfurization processes [12].

NON HDS processes:

3.1. Shifting of boiling point by alkylation

Separation of the sulfur component from the lighter ones simply uses variations in the boiling point, which is derived from British Petroleum using olefin alkylation of the thiophenic sulfur technique [13] (OATS). A general process flowchart is illustrated in Fig.3.

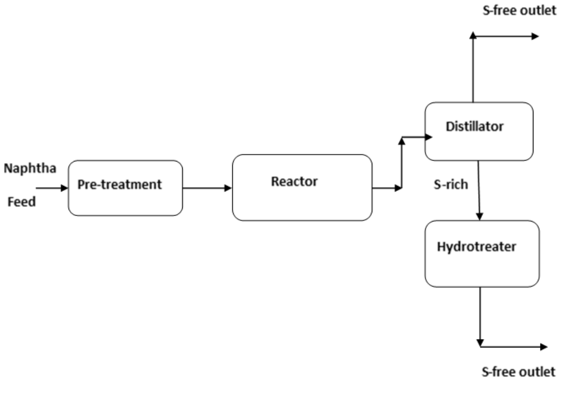


Fig.3 NON-HDS process (OATS reactor)

The mechanism dependent on temperature and catalysts gives rise to side reactions if impurities are present. Hence the pretreatment section is important to remove impurities. Acidic catalysts such as halogenated boron, zinc or aluminum having silica-alumina support are preferred. In many cases, the lighter naphtha is directly sent to gasoline container while the heavy one is sent for hydrotreating. This has the major disadvantage that very severe hydrotreating conditions are required to remove the sulfur further from the heavy components.

OATS reactor followed by distillation and hydrotreating helps in removal of sulfur from the gasoline stream up to 99.5%. But this effectiveness is accompanied by a drawback is that the output of the process has more severe treatment condition requirement than usual. The OATS reactor reduces sulfur from 2 330ppm to 20ppm with only two octane loss [13]. A similar trend was observed using the oxidation of DBT. Using oxygen or any mild oxidizing catalyst the DBT can be converted into DBT sulfone which is poached by H_2O and forms hydroxybiphenyl sulfonate which has a high boiling point. The removal of SO_2 component from the complex results in the formation of hydroxybiphenyl. Analogous to this method, the conversion of thiophene to alkylated thiophenes like 3-hexylthiophenes effects a change in the boiling point to about 85°C [2].

3.2. Desulfurization via extraction

The key reason behind the introduction of this process is that the sulfur constituents present are extensively soluble in various solvents, and their rejection strength for hydrocarbons is notable. The sulfur compounds are transferred from the fuel oil into the mixing tank containing the solvent. These organosulfur compounds are separated from the solvents by the process of distillation [2]. The most vital character of the process is the usage of low pressure and temperature. The mixing can easily occur at ambient temperature and pressure. The solvent must have different boiling temperature than sulfur, and it must be economically feasible. In these processes, if the additional option of the recovery of aromatics is made then a further improvement in the economic efficiency will be the outcome.

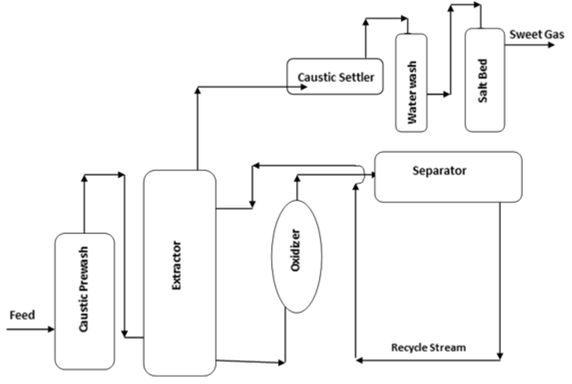


Fig.4 Simplified MEROX as extractive desulfurization

Fig. 4 gives a scheme of the setup for general MEROX process. The basic step is the transfer of sulfur from oil to solvents. Further separations can be done using a separator column or fractionators. Several solvents and a varying number of extraction cycles help in removal of sulfur up to 50-90%. The key limitation of the process is the solubility of the sulfur compounds in the solvent. The higher solubility can be easily obtained by the preparation of 'solvent-cocktail.' Acetones, alcohols, and esters are some of the solvents normally used in the preparation of the cocktail. Conversion of sulfur to sulfones also enhances the solubility parameter [13].

3.3. Desulfurization via conversion and extraction

Petro Starc Inc. first introduced this method in 1996. They presented the combination of conversion and extraction for diesel fuel desulfurization. Before liquid-liquid extraction, the fuel is mixed with an oxidant compound. The process of oxidation was done below 100°C and at atmospheric pressure, thus leading to excellent sulfur removal accompanied by good cetane number. API gravity and aromatics content improvements were achieved. Extensive separation of sulfur and recovery of hydrocarbons to a greater extent were the outcome of the process, then, in turn, enhances the functions of the fuel [12,14]. Proving that the application of the combined processes of oxidation and extraction is very effective. Patented extractive agents that are used in such processes include formamides, sulfoxides, furfurol, and glycols. In case of raw petroleum component and their extraction solvents like glycol derivatives with methyl esters are used to remove the sulfur content up to 94%. Desulfurized yield of lighter oil fractions and straight run gas oil was enhanced using extraction combined with UV radiation catalyzed photochemical reactions.

3.4. SulphCo desulfurization

SulphCo technology uses ultrasound to oxidize sulfur compounds in the water-fuel emulsion, which contains H_2O_2 catalyst. The conditions are maintained at a temperature range of 70-80°C with 1 atmospheric pressure. Bechtel Corp. scientists as a basic estimate put the cost of the process at nearly equal to 50% of one hydrotreater [2,11]. The simple process flow comprises oxidation and extraction phases involving emulsification with ultrasonication. The flow diagram is shown in Fig.5.

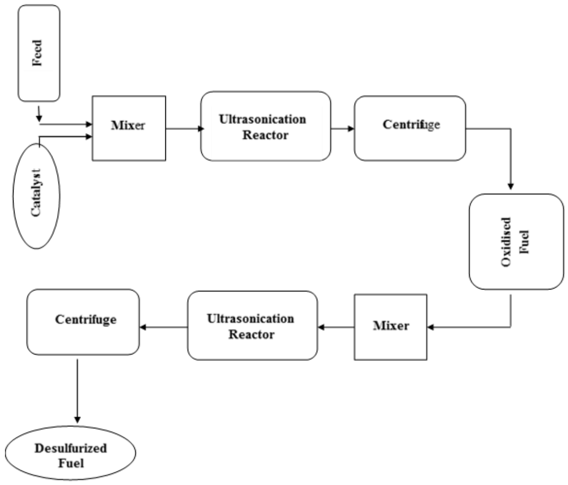


Fig.5. General process-flow of oxidation and extraction involving ultrasound

The basic emulsification process involves a static mixer where suitable pressure and mixing is employed. In this process, the ultrasonication breaks the droplets and produces high hydraulic shear that further divides the constituents into submicron-sized particles. Reduction of droplet diameter influences the reaction kinetics and eliminates the need for phase transfer. Since the contact surface is increased requirement of peroxides is reduced significantly. Ultrasonication process produces intense local heating and enormous pressure. It induces oxidation in the presence of catalysts. The process output confirms the removal of sulfur up to 80-98% thus resulting in sulfur content up to 10ppm.

3.5. Unipure aromatic sulfur reduction

This is based on the oxidation of aromatic sulfur in an aqueous phase before extraction. Mild temperature and pressure conditions are applied to the process. The reduction of sulfur from 270ppm to 2ppm is observed. The basic mechanism is the conversion of sulfide to sulphones with smaller residence time. The analysis of the kinetic study of the reaction suggested a substantial improvement to the process if photons or ultrasound radiations are employed [13].

3.6. Desulfurization by photochemical oxidation and extraction

Desulfurization process combined with photochemical procedures is an advancement to the reported processes. Photodecomposition or photo-oxidation is one of the major discoveries enlisted. Desulfurization involving a combination of photochemical reactions with the extraction of the organosulfur compounds is one of the unconventionality that is specific to this method. Extracted product is further irradiated using UV radiations to form polar compounds; these are then rejected by non-polar hydrocarbons that get concentrated in the solvent. Further removal of the sulfur compounds can be done by using acetonitrile, the best suitable solvent available [15]. Optimization of the combination of solvents and photosensitizer is necessary to increase the rate of the organosulfur compounds by phototransformation. A reduction in the sulfur content almost to 2% in commercial light oil is achieved after 2hrs of irradiations, which has the potential to reduce sulfur content to 1.4% if exposed to 10hrs of radiation. Difficulties in the photosensitizing lead to replacement by H_2O_2, which in turn hinders the energy transfer from DBT to naphthalene. After photo-irradiations solutions are periodically checked for consistency in the amount of carbon present and composition of compounds [15-16].

General oxidative desulfurization (ODS) process achieved under microwave treatment is the most significant application. Microwaves are radiations lying between infrared and radio frequencies. ODS process efficiency is affected by oxidizing agents, catalyst and oil types, microwave power levels, treatment times, temperature and dosage of oxidizing agents [10]. Other essential factors that influence the extent of desulfurization are extraction design and time. The presence of polar molecules like organic sulfides, oxidizing agents, as well as catalysts, significantly help in strengthening and promoting the reactions. Moreover, the sulfur and nitrogen compounds present with a dipole in the crude are also highly sensitive towards microwaves. Operating conditions are less severe, and treatment times are also shorter [16].

Another improvisation in the desulfurization process is the application of ultra-sonication. Various studies suggested that the cavitation phenomenon intervenes in the desulfurization due to the presence of bubbles, which can be made to collapse using ultrasound. Elimination of the usage of the metallic catalysts and maintenance of relatively mild conditions are the other important contributing factors of the method. Comprehensive analysis of the process revealed other parameters that have a positive influence on the outcome include the presence of H_2O_2, glacial acetic acid, number of stages of methanol extraction, temperature control, ultrasound effects, reagents reuse and removal of varied components using mechanical stirring. Increase in sulfur removal requires a higher amount of acetic acid but crossing a certain threshold percentage increase does not affect the sulfur removal. Essentially the ratio of acetic acid and sulfur is maintained at 300:1. Hydrogen peroxide with acetic acid in a proper proportion of approximately 1:5 gives appreciable separation of sulfur, which is accompanied by minimal oil loss. Temperature factor is used to determine the volatile nature of the particles that aid the process efficiency. Ultrasound treatment is applied only for 5mins, which selectively removed up to 90% of the sulfur compound present [11].

3.7. Desulfurization by precipitation

Buildup and subsequent removal of insoluble charge transfer complexes is the basis of this methodology. The sulfur-containing compounds and π-acceptors are charged into batch reactors under agitation at fixed rpm. The reacted components are separated by filtration and further treated for gas oil recovery. Current analysis of the process shows that the efficiency is remarkably low, which can remove only 20% of sulfur. Due to the competitive nature of the reactants, DBTs present have low selectivity towards removal. Excess of TNF provision is required; due to the over stoichiometry, the further removal of the same is necessary [13].

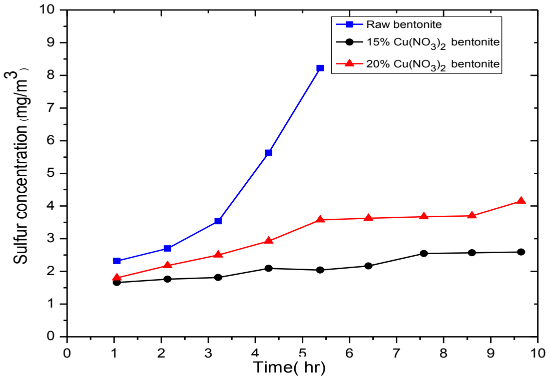
Methylation of DBT using methyl iodide and silver tetrafluoroborate is reported to produce high water-soluble compounds, which lead to the desulfurization. It has also been reported that desulfurization of light gas oils can be catalyzed by adding more alkylation reactors, and it is observed that sulfur content was reduced up to 0.005% w/w basis. Catalytic cracking of naphtha is also a significant process that helps in better desulfurization.

3.8. Selective oxidative desulfurization

As mentioned before, the conversion of sulfur to sulfone form involves oxidation. Acetonitrile was found to be the solvent which helps convert sulfur to the sulfone form. This conversion mainly creates a gradient of temperature among the compounds present by increasing the boiling point, hence a better separation can be achieved [1,13]. The sulfone content is basically dependent upon various factors like nature and consumption of acid catalysts, hydrogen peroxide consumption, temperature, duration of oxidation [17]. Rapid oxidation also helps the refiners in the removal of sulfur selectively from the mixtures, which include heavy aromatics and multi-ring components with DBTs. High activity was obtained for the combination of ammonia tungstate and fluoride complexes [18]. The unique process employs oxidation catalysts in the aqueous phase, where the scope for future development is combining the process with the application of ultrasound or photons [11]. Usage of Cu catalyst in the process has shown enormous separation yields. There are several factors responsible for the desulfurization that include loading, baking temperature, valence state, surface area, pore size, the total pore volume of the catalyst. Based on these observations, the desulfurization breakthrough is deduced and calculated by the following equation:

$$S_t = \frac{q * 10^{-6} * 100\%}{m} \int_0^t (C_0 - C_t)dt$$

where 'S_t' the amount of sulfur adsorbed on the adsorbent (wt percent mg-S/g of adsorbent), 'q' is the flow velocity of the LPG (ml/h), 'C_0' is the inlet concentration of the LPG(mg/m^3) and C_t at any time 't(h)' and the mass of the adsorbent 'g' [19].



The maintenance of the optimum level of the adsorbent is the most crucial factor which is observed in this work. The process must keep 15% of bentonite level at a temperature of 150°C temperature that effects maximum separation of the sulfur. If this level rises to a higher value like 20%, the sulfur removal decreases, as shown in the Fig.6 [19].

Fig.6. Cu bentonite catalyst effects on sulfur

This process is analogous to the normal distillation of organosulfur compounds. Here, SO_2 is predominantly released, but H_2S molecules may also be formed when the decomposition temperature shoots above 300°C. The observed process efficiency is relatively low, which is up to 40%. Usage of higher catalyst strength is found to increase efficiency, which is a major topic of research currently.

3.9. Desulfurization by adsorption on a solid sorbent

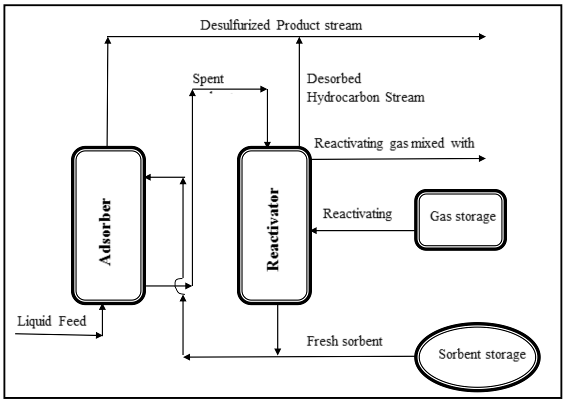


Fig.7. Simplified adsorptive desulfurization process

One of the effective ways to remove numerous organosulfur compounds present in the petroleum fraction is by using adsorption technique. Based on mechanisms of sulfur and use of adsorbent, it can be either desulfurization or desulfurization accompanied by adsorptive desulfurization. Regeneration of the sorbent is an essential factor responsible, which is possible by flushing the spent sorbent with a desorbent. Desorption results in the high flow of organosulfur compound in the desorbed stream. It results in the removal of H_2S, S, or any other sulfur oxides present. Simplified process setup is given in Fig.7.

Salem and Hamid studied adsorptive desulfurization, where two bedded combination of batch reactors were proposed [2], which principally helps in the removal of 4 and 4,6-substituted dibenzothiophenes that are always present in the leftover of the hydrotreatment. In this case, activated carbon, Co-Mo, or silica-alumina like catalysts are employed for the removal of sulfur effectively. Activated carbon is noted for its efficient usage under 100°C [20].

Similarly, IRVAD and Philips S Zorb processes are also widely used. IRVAD is a technology developed by Black and Veatch Pritchard engineering firm, which has a main focus on removing organosulfur compounds. The IRVAD process uses countercurrent moving bed having solid sorbent operating at 240°C, low pressure with a hydrocarbon to the adsorbent ratio of about 1.4 [21]. It further requires additional downstream treatment of the outlet that principally involves high-pressure hydrotreating. The simulations can be done on the sorbent properties to modify the same to gain higher purity [2,14].

Similar flow techniques are applied by IRVAD and S Zorb process, but the nuance of difference is presented in fluidized bed technology. It is mentioned that the process can remove 98% of the sulfur from gasoline, and almost 100% hydrocarbons can be recovered. The key factor of these processes involves octane number maintenance; the loss of the same is observed in the range of 0.5-1.5 of the original [13].

4. Process setups and recent variants

Starting from basic oxidation with/without various ionic or heterogeneous catalysts, the process developments are well documented. Generally, these processes can be divided into two parts; one involves sulfur elimination and another transformation of sulfur into separable compounds. Sulfur elimination majorly includes conventional HDS processes. In the case of sulfur transformation, catalytic distillation, alkylation, extraction, etc. are preferred [2]. Oxidation of sulfur from divalent sulfide to hexavalent sulfone group is one of the major changes that had taken place [3]. In a few models, oil was extracted into the ionic liquid phase and oxidized to their corresponding sulfone by peroxomolybdic compounds.

4.1. Solvent and catalyst engagement

Desulfurization based on adsorptive processes involves solid sorbent which can only absorb or react with the sulfur compounds, which can effectively remove S, SO_2, and H_2S. The efficiency is mostly determined by absorption capacity, reactor area usage, selectivity, removal of aromatics, and durability with regeneration. Selective adsorption is much more effective over HDS. As per the literature, Petro Start Inc. combined conversion and extraction processes in 1996, before extraction fuel mixed with peroxides helps in the advantage of the various factors like cetane number, API gravity and aromatic contents which are accompanied with reduction of sulfur from 4200ppm to 10pmm or even lower [2]. For diesel fuels novel ionic liquids can be used which follow extraction and regeneration simultaneously and helps in removal of sulfur components up to 50ppm. Ionic liquids with the presence of sulfur compounds were able to remove up to 60-70% of the sulfur and aromatic content, which is accepted by industrial standards. Progress of the field is well-known after the application of amorphous silica-alumina (ASA), one of the excellent catalysts used in combination with Pd. This aids in the separation of the aromatics up to 75% also reduces Sulfur to 6ppm. The improvement in the characteristics of catalyst is made by having mainly two types of pore sizes. The catalyst with large pores can adsorb the aromatics and other larger constituents, while the other smaller one which has resistance against the sulfur poisoning can be effectively used for sulfur adsorption and regenerated, so the process efficiency never reduces even if more quantity of sulfur is introduced.

In the case of refinery products, sulfur present in small proportions can be end blended easily for which a lesser quantity of hydrogen is required. Only an integrated approach involving catalyst selection, reactor design, process configuration which will lead to efficient desulfurization, i.e. catalytic desulfurization combined with HDS. Removal of sulfur-containing compounds using H_2O_2 and acetic acid with the presence of sulphuric acid or hydrochloric acid as a supporting catalyst is also one of the core processes. This process is found to remove nearly 90% of the sulfur present, which attracted the attention of the research community. One drawback is the effect on Oxidation efficiency of H_2O_2 by several factors like temperature, pH, and dissolved ions maintained in the process.

4.2. Reactor modules

Reactor modeling and simulation are key factors that bolster the progress of any process setup. Conventional hydrotreating reactors follow co-current streams of oil and hydrogen supply provided one behind another. It leaves traces of these unreacted H_2 and H_2S, that reduces the reactor efficiency [17]. Taking counter current approach is one of the advancements, first invented by Scanraff's Synsat gas treatment process. The process also reported that not only removes sulfur up to 1ppm, but also nitrogen and other aromatic compounds to a very great extent. The major development of the design involves the introduction of co-current and counter-current reactors in a sequential module, which in turn helps in the reduction of the catalyst volume required for desulfurization. Monolithic catalyst preparation and reactor setups involve varied parts including direct extrusion or paste of catalyst, which helps in higher catalyst loading into the reactor. Nowadays monolithic bed reactors are transformed into mobile reactors, which show ideal behaviour and give higher conversion. Monolithic reactors have advantages over normal reactors like larger productivity, better selectivity, and higher efficiency and preclude unsafe conditions. Flow characters of the monolithic reactors are far more superior over the normal reactors that increase its activity. Taking IFP into concern, the process developed by them involves a concept called as T-star catalyst based reactors, characterized by mechanical stability and resistance to attrition. Usage of multi-staged airlift reactors that overcome poor reaction kinetics at low sulfur concentrations with reduction of mixing costs is another development. Mesoporous aluminosilicate molecular sieves are installed in such reactors to direct the space velocity decrease, increase in temperature and Hydrogen pressure, improvement in the vapour liquid contact, scrubbing, and removal of H_2S from the recycle stream. Concerning an article of Oil and Gas Journal wrote in 2001, the Z-sorb process is used for the desulfurization of gasoline as well as diesel. The ultra-deep desulfurization is chosen as the process since it is cost effective and reduces the refinery CO_2, SO_2 emission in comparison to normal processes [13].

The novelty in the alignment of the process catalysts gave rise to multi-bedded catalyst layers separated by gases at lower temperatures. The rise in reactor performance requires an increase in recirculation for heat removal. In the MPCP device process, shown in Fig. 8, liquid, solid mass transfer is majorly involved, that increases the concentration of the hydrogen over the catalyst surface.

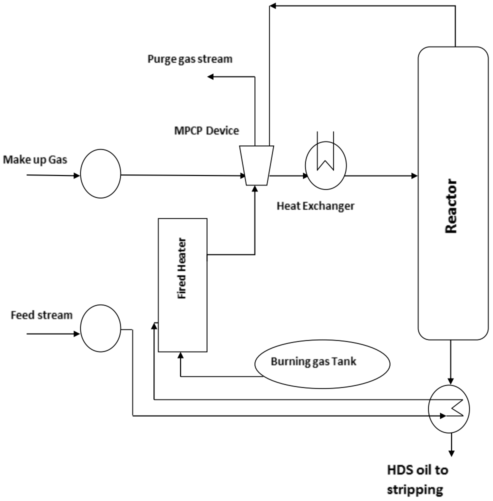


Fig.8. Advanced MPCP unit based process

With decreased catalyst particles size and sudden rise in flow velocity enhancement of the liquid, solid mass transfer is achieved. Lower grade fouling is observed due to the liquid present washes off the corroding constituents present. The most important advantage of the system is the simplification of the heat repercussions, reducing the complications involved in pumping hot oil at 320 - 450°C. In order to array all heat fluxes a common network of recuperates combined with conventional HDS reactor followed by stripper unit increases not only investment costs but also energy expenses for transpiration of a gas-liquid mixture through extremely long pipe-work [22]. Similarly, for natural gas and LPG desulphurization, two methods are employed, first is passive adsorption, and second is catalytic transformation followed by adsorption. Technology developed by Englehard involves a method which combines the fuel with a sub-stoichiometric amount of oxygen and uses a sulfur tolerant monolithic catalyst to oxidize selectively the sulfur compounds to oxides. This is the selective catalytic oxidation. This method is mapped by the author based on catalyst performance as a function of temperature, oxygen-to-carbon ratio, and space velocity. Catalyst deactivation occurs at high temperature, presence of fuel particles in the absence of air, catalyst exposed to fuel-air mixture at ambient temperature [17].

4.3. Novel presence of membranes and nanoparticles

Precursors or solvents are usually immobilized in the membrane pores, hence find critical application in desulfurization. Novel constituent comprises of polymer like, polyoxometalates, that has gained much attention due to their tenability of composition, size, shape and acid-base properties with redox functions. Presence of ionic liquids, which can form π complexes majorly containing chloride ions help to enhance the separation. Desulfurization using metallic compounds over the membrane layers help in the removal of sulfur forming sulfur-metallic bonds or with catalytic decomposition. Various reactions give different products due to the polycrystalline nature of the films with the distribution of surface sites varying from film to film. Hydroxyl-terminated polybutadiene/acrylonitrile(HTBN) polymer material was selected for deep desulphurization of LPG using the solubility parameter method. Interaction between polymer and solvent molecule is used to estimate the separation criteria. Supporting layers like polyacrylonitrile prepared with phase inversion are mainly used below the flat plate composite membranes. Methyl mercaptan is the main substance present inside the LPG, with the sulfur present over which the HTBN membrane proved to be a promising material for separation. The permeability property of methyl mercaptan is also different from other sulfur constituents, which is effectively managed by the membrane [23].

Similar to membranes, the novel field of nanosciences is also applied for the process. Multiwalled CNTs with MnO_x nanocatalyst is used for the desulphurization process where the performance of the same at 25°C and atmospheric pressure indicates the sulfur removal which is up to 99.85% in the first 30 min span [24]. CNTs are chosen for the process because of some unique properties like tube-shaped mesoporous structure, the transmission of reactants and products, resistance towards basic and acidic conditions. They are tested for deep desulfurization for sour naphtha, which is very complicated to remove. In the CNTs, the carbon-carbon double bonds increase their strength at 1560cm^{-1}which further intensifies the oxidation process preventing the aggregation and precipitation of the multi-walled carbon nanotubes [24]. Peroxidation of sulfur compounds is one of the finest methods that are used, followed by adsorption and extraction.

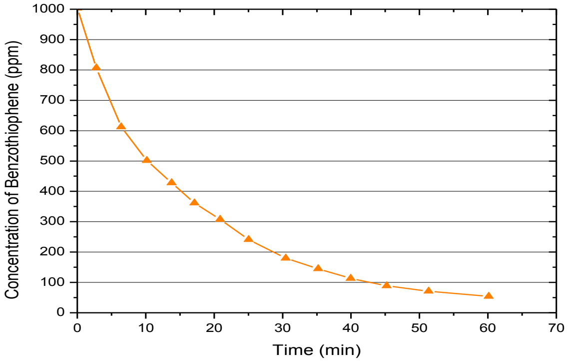


Fig.9. With nanocatalyst presence

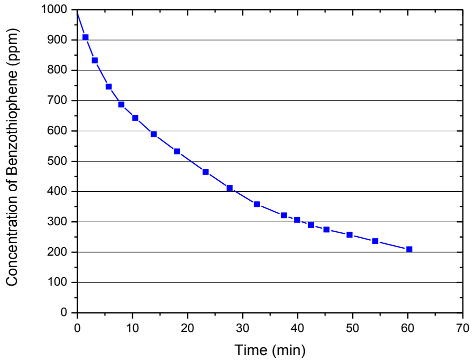


Fig.10. Without catalyst presence

Catalytic properties of the TOB (tungsten oxide bronze) in the nanoparticles size are similar to that of hydrogen peroxide process giving fine desulfurization product. The kinetics of the reaction has directly shown that the concentration dependence of TOB on the oxidation process of benzothiophenes. The chief advantages are high chemical purity, thermal stability even at 800°C. Fig. 9 shows a steep decrease in the concentration of benzothiophene from 242ppm to nearly 12ppm [18]. Similarly, Fig. 10 and Fig. 11 shows the tungsten catalyst based processes where sulfur reduction is observed.

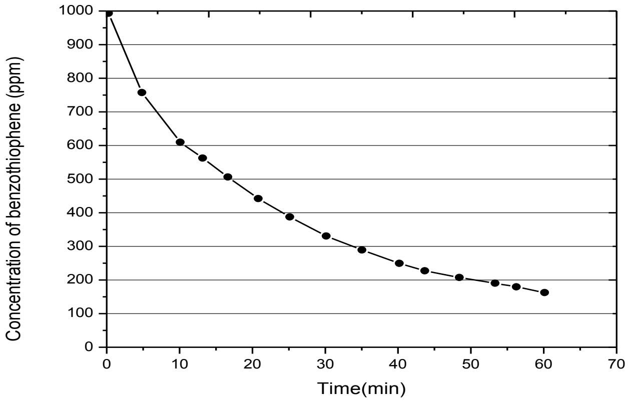


Fig.11. With coarse grade tungsten oxide catalyst

Maintenance of the octane or cetane number is the center of various processes. Philips Petroleum Corporation proposed the pre-aromatization of FCC gasoline that reduces the sulfur content from 300ppm to 10 ppm and augments octane from 89 to 100. Combination of hydrotreating and octane boosting process is known as ISAL process, which basically treats the high naphtha feed and reduces the sulfur from 1450 ppm to 10 ppm without affecting the octane number [2,14]. To avoid octane loss, newer methods follow fractionation before desulfurization for all the components of FCC. It helps in preserving olefins at different selective compound conditions having different boiling points.

4.4. Biocatalyst applications

Nature of sulfur compounds, reaction conditions, the catalyst used are three important factors, and these dominate the reaction pathways of desulfurization. In the near future, the study of polynuclear organic compounds, biocatalysts having complex, abstruse nature are predominantly considered for the deep desulfurization processes. Bio-enzymes are used in the process of desulfurization, and the product resulting from this method is hydroxyphenyl benzene sulphonate which can be commercially used as a feedstock in the surfactant productions. Various research groups have investigated the application of *Nocardia globerula* R-9 for the desulfurization of straight diesel. Its usage graphically follows Michaelis Menten mechanism. It efficiently removes DBT and 4,6-DMDBT at different rates [6]. Desulfurization involves C9-C12 carbon compounds in gasoline and C12-C23 in diesel in diverse ring forms. Pseudomonas and flavin reductase are some initial bio enzymes that are utilized in the process. The basic promoter has been characterized by the presence of sulfur-containing amino acids. Some cases of thermophilic biodesulfurization under high temperature decreases oil viscosity, makes molecular desulfurization easier, improves enzymatic reaction rates, and decreases bacterial contamination.

5. Setbacks of the processes

Initial stages of the process development have problems due to hydrogen deficiencies; especially the HDS process had some difficulties in meeting the demands. Deep HDS problem for diesel stream is exacerbated by the inhibiting effects of co-existing polyaromatics and nitrogen compounds in the feed as well as H_2S in the product. Presence of H_2S usually poisons inorganic catalysts; hence, elimination of the sulfur is highly important. Biocatalysts have fewer disadvantages, but these overweigh disadvantages of all the remaining processes. Cells precipitated at the bottom are an adverse condition for desulfurization. Costly equipment and catalyst preparation methods, skilled labour requirement for supervision are some major pitfalls. Few methods show that desulfurization using old methods precluded the expansion of the reforming unit.

Severe process conditions result in a reduction of the quality of petroleum components and octane number. The temperature required for the process is above 500°C and many causes over cracking of the products. Water is also wasted in the process to clean off the raffinate and remove acetonitrile in case of photo-sensitized processes. Commercial light is also used in the process of removal of sulfur up to the level of 0.05% with 48hrs of rigorous radiations, which is difficult to be used in the industry.

Proper boundary to the application of acidic or basic catalyst must be maintained. The enhancement of reaction becomes less prominent with an increase in phosphotungstic acid.

Sterile Trimethyl Ammonium Bromide (STAB) is a catalyst with high activity and selectivity towards sulfur. The maintenance of STAB at a proper concentration in association with phosphotungstic acid raises the reaction rate.

The increase in mixing speed, interphase mass transfer, and emulsification have a drastic impact on the desulfurization due to larger droplets, presence of high surface area, and high rate of reaction. Formation of stabilized emulsions pose some difficulty in the recovery of oil from water in the BDS, and so one such solution to this problem is the use of destabilizing agents to avoid the formation of the emulsion based bonds. However, a flip side to this method is the higher operating costs and time required.

Grignard reagents are used for separation of thiophenes, benzothiophenes, and DBTs in the presence of nickel/cobalt halide phosphine complexes. Likewise, platinum and molybdenum are the catalysts preferred. However, this is not a cost-effective method. The complex paraffin gets affected by the oxides that need to be suppressed properly. Solvent to oil ratio is the most important bottleneck of the process. Hence proper balance is the major requirement.

The major disadvantage is that they are more expensive than any other reactors. Heavy streams desulfurization is still an enigma in for many scientists where non-reactive sulfur compounds are present. The major problem here is the disposal of the eliminated sulfur and solvent recovery. High chemical purity and thermal stability at 800°C are needed so that the components can thwart the effects of sudden temperature fluctuations. High homogeneity and high reactivity of three-phase reaction system is the most important experimental difficulty in the ionic catalyst process.

The major developments amidst all the processes considered are the design of the reactor – where the introduction of co-current and counter-current reactors in series that in turn helps in the reduction of the catalyst volume required for desulfurization. However, the major disadvantage is that packed bed reactors cannot be used in the process.

6. Concluding remarks

All the above-discussed topics and technologies are revised several times. Such a continuous area of research is present, where numerous permutations and combinations are possible that delivers better and better process setups. To meet the more stringent rules and regulations involved in desulfurization, more and more processes should evolve. New design approaches use enormous chemistry for the production of zero sulfur affordable diesel and gasoline.

Ultra deep desulfurization methods should be challenged now and then, which will focus on the creation of zero sulfur fuels. Liquid hydrocarbon processing, applications of composite membranes are the key sector for future research. Lesser hydrogen requirement, higher efficiency, faster, better, and safer production should be the aim of the processing teams.

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