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Research Article

Sustainable Development in the Field of Automobiles with low Sulfur Fuels

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Abstract

In today's world where pollution levels have raised to such an extent that if immediate control isn't achieved than it could lead to the fallout of various species and ecosystems. One of the leading contributors is air pollution, which is greatly caused by the immense amount of vehicular emissions from the tailpipes of millions of vehicles across the globe. A detailed analysis leads to the fact that the presence of sulfur in the fuels used to power vehicles is a hazardous pollutant and furthermore allows for the increase in volume of other pollutants released. Thus removal of this element from fuel is the best way to cut down drastically on vehicular emissions and provide for sustainable development along with conservation of environment. In this paper we will be discussing about the various benefits of Low Sulfur fuels, the environmental impact they have. Complications that are caused by the presence of sulfur in fuels and how Sulfur prevents the proper functioning of many catalysts are also discussed in detail. Also, the impact of using Low Sulfur fuels in various types of engines is important. Low Sulfur fuels have a positive impact of the emissions of gasoline and diesel engines and Fuel Cell Vehicles, which are the future of Automobile Engineering with reduced emissions and eco friendly. Types and manufacturing processes involved in the production of Low Sulfur fuels are being dealt with exhaustively. Benefits of Low Sulfur fuels far outweigh the costs. They are far less polluting and have a much smaller environmental footprint.

Keywords: *Sulfur, Smog, Desulfurization, Adsorption and Bio desulfurization*

1. Introduction

Crude oil consists of millions of components with the major component being hydrocarbons, along with traces of other compounds, such as Nitrogen, Sulphur, Oxygen and Metals etc. We will be stressing upon the presence of Sulfur element, which is a hazardous material. When the fossil fuels are burnt, oxides of sulfur such as SO_2, and SO_3, (SO_x) are released in significant quantities. These gases are extremely toxic and cause irreversible damage to the environment and living beings on the earth. Thus, our primary aim is to reduce the sulfur content to the maximum extent to ensure that we live in a cleaner and greener world.

2. Impact of sulfur compounds on environment and human health

The presence of sulfur in the atmosphere is dangerous because it promotes formation of smog. Cold, humid air in light windy conditions facilitates fog formation. When sulfur dioxide is present in the lower regions of the atmosphere; it gets trapped within the fog and reacts with it to give sulfuric acid, which forms Smog. This smog then condenses as acid rain, which causes serious soil degradation and destruction of flora.

The presence of Sulfur compounds in air also has adverse effects on human health. They are responsible for severe respiratory infections, (Bert Brunekreef *et al*, 1997), internal organ poisoning, nausea, and permanent damage to the brain and eyes, diarrhea and many infections, premature deaths, allergies and disorders. Upon prolonged exposure it will cause death.

Figure 1 Visibility reduced to just a few meters during The Great Smog of London 1952

An example is "The Great Smog of 1952" which occurred in England which resulted in the loss of about 4000 lives due to inhalation of the smog. The improper burning of huge amounts of coal also causes smog. This type of smog contains soot and oxides of carbon and sulfur. There is another type of smog known as Photochemical smog, which forms as a result of vehicular emissions and

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industrial fumes. These in the presence of sunlight react with the surrounding atmosphere to form smog.

3. Complications caused by sulfur

Presence of significant quantities of Sulfur in the fuel becomes a major deterrent in the implementation and functioning of vehicular emission control technologies. Due to this, control over the emission of other pollutants like oxides of nitrogen and carbon and also particulate matter etc. becomes and additional problem. Hence reduction of sulfur quantity in the fuel is of paramount importance, which paves the way for cleaner emissions and also aids for engines to run more efficiently.

3.1 Problems confronted by the presence of sulfur in typical fuels

Innumerable problems arise due to the presence of sulfur in fuels. The first and foremost is that it prevents the effective functioning of catalytic converters fitted to vehicles. The sulfur in the exhaust forms a layer on the catalyst and poisoning of the catalyst takes place. Due to this phenomenon the catalyst becomes ineffective in treating the exhaust gases, as exhaust-catalyst contact is cut off. Due to this there is an increase in the emission of CO_2 and CH_4 gases. It also impedes the application of emission control technologies in the case of Diesel, Gasoline and also Fuel cell powered vehicles.

3.1.1 Diesel powered Vehicles

Diesel powered vehicles have a greater fuel economy than gasoline engines. Due to this reason they can bring down CO_2 emissions by about 30%. This percentage can be boosted to 45% by turbo jet injection diesel engines. As pollution reduction is the target, emission standards in the USA and Europe are being revised, the diesel engines currently in use need to be fitted with advanced exhaust after-treatment devices. These technologies can be implemented on a large scale only when there is maximum sulfur removal from the diesel fuel. In case of diesel fuels presence of sulfur increases the fuel consumption of vehicles. Particulate matter also released can be controlled by use of near zero sulfur fuels, which is achieved by the removal of carbon compound emissions from the exhaust stream.

3.1.2 Gasoline powered Vehicles

When it comes to gasoline-powered vehicles, N_2O and CH_4 are the gases emitted in higher amounts. As methane is a difficult gas to combust (as the reaction requires application of very high pressures of ~1000atm), the role of the catalyst becomes vital in controlling the amount of methane exhaust. (Maricq, M. M *et al*, 2002) As discussed above the presence of sulfur hinders the functioning of catalyst by increasing the catalyst regeneration temperature. It has been shown that using low-sulfur gasoline having reduced sulfur content from 330 ppm to 1 ppm decreases methane emissions by 20-50% and N_2O emissions by 70-90%. It also results in an increase of fuel efficiency by 20-25%. This is seen in the case of a direct-injection gasoline engine. To achieve a greater reduction of NO_x in the exhaust stream an advanced catalyst system is required. Implementation of the above methods require low sulfur fuels or near zero sulfur fuels, the latter being required for the effective functioning of fuel-lean NO_x traps or storage type catalysts. Both types of after treatment technology require low or near-zero sulfur fuel. Fuel-lean NOx storage catalysts or traps, require near-zero sulfur fuel to perform with maximum efficiency as even the presence of 50 ppm of sulfur in the gasoline can cut down efficiencies by almost 50%.

3.1.3 Fuel Cell powered Vehicles

Fuel cell vehicles are touted to be the future of transport as it can drastically reduce the amount of harmful emissions. Current fuel cells are being powered by pure Hydrogen; but hydrogen has found to be difficult to store and provides a very low mileage, which is not feasible. Extensive research is being carried out to generate to generate fuel from reforming of petroleum fuels and natural gas. Fuel cells and reforming catalysts require feedstock's devoid of sulfur, as their presence is detrimental to their performance.

4. Classification of low sulfur fuels

The classification of Low Sulfur Fuels is based on the sulfur content present in the fuel in ppm.

4.1 Low sulfur fuel

A fuel is said to be a low sulfur fuel when its sulfur content is around 50 ppm. The prominent effects of using this type of fuel can be seen in the case of diesel fuel vehicles where the particulate filters fitted can control the emissions produced, by 50%. This can be increased to 80% by employing a technique known as "Selective Catalytic Reduction"; where the oxides of nitrogen are being converted into water and nitrogen; both of which are totally harmless. Catalysts such as Zeolites or Titanium oxide are required. The process involves the adsorption of exhaust gases on to the catalyst by the addition of a gaseous reducing agent such as Urea or anhydrous NH_3.

4.2 Near-zero sulfur fuel

The sulfur content in this type of fuel is around 10 ppm. Using this type of fuel increases the performance of NO_x adsorbers employed in both gasoline and diesel powered vehicles. They can achieve over 90% control over these emissions. Nearly 100% of particulate matter control can be achieved by using near zero sulfur fuels.

5. Manufacturing processes used in the production of low sulfur fuels

Conventional diesel and gasoline are first extracted which are then subjected to additional processing where in which the sulfur content is reduced in the fuel. Two processes that are generally employed in the production of low sulfur fuels are discussed below in detail.

5.1 Sulfur Adsorption Process

This process uses an adsorbent such as Cu (I) Y-Zeolite or a Nickel based adsorbent. The sulfur molecules get adsorbed on it and thus are selectively removed from the feedstock. The adsorbent is regenerated and recycled for greater efficiency of the process. The sulfur content in the product stream is reduced to 10 ppm. (Xiaoliang Ma *et al*, 2005).

Figure 2 The CITGO Petroleum Corporation, a subsidiary of Petroles de Venezuela, S.A. at Corpus Christi Texas Refinery, which is capable of producing 100%ULSD

As shown in figure 4, the process is carried out in a fluidized bed reactor. The feedstock is heated and sent into the reactor from the bottom. The adsorbent present selectively adsorbs sulfur in the feedstock. When the adsorbent is exhausted, it is sent in to a regeneration unit where the sulfur is stripped off as sulfur dioxide by passing a current of air in counter direction. The sorbent is activated and recycled back into the reactor where further sulfur removal from feed will take place. The product is obtained at the top of the reactor. This method can be applied to both gasoline and diesel fuels. The merits of this method are, low cost of operation and high degree of sulfur removal.

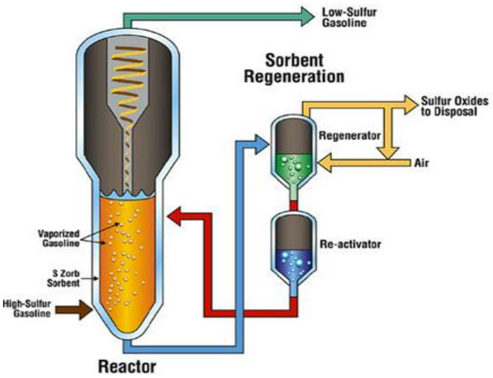

Figure 3 Flow diagram for Sulfur Adsorption process

5.2 Naphtha Hydro desulfurization (HDS) Process

Hydro desulfurization reaction is characterized by the removal of sulfur molecule from the fuel by passing a stream of hydrogen gas, which removes sulfur as hydrogen sulfide. The removal of sulfur from ethanethiol (C_2H_5SH) to give ethane (C_2H_6) is an example of a hydro desulfurization reaction.

$$C_2H_5SH + H_2 \rightarrow C_2H_6 + H_2S$$

Cracking naphtha in a Fluid Catalytic Cracking Unit produces gasoline. (Gary, J.H. and Handwerk, G.E. 1984, S.Ramraj; C.Anandaraj, 2014) As shown in figure 4 the gasoline stream-containing sulfur along with a steam of recycle gas that is rich in hydrogen is heated to reaction temperature in a heat exchanger followed vaporization process by a heater and is then sent into a fixed bed reactor (Hydrotreater). The entering feed is between 300-400^{0}C and compressed to a pressure of 30-130 atm. Catalyst is an alumina base impregnated with cobalt and molybdenum. The reaction products exchange heat with the heat exchanger, which is used to heat the incoming feed. The reaction product is then cooled and sent into a gas-separating chamber where the gas and liquid phases separate out. Liquid phase obtained at the bottom is sent into a stripper (Distillation column) where the liquid obtained at the bottom is reboiled to get desulfurized product. Unconverted gases in the stripper are sent into a condenser and then the condensate is sent back into the column as reflux. The uncondensed gas is called as Sour Gas**.**

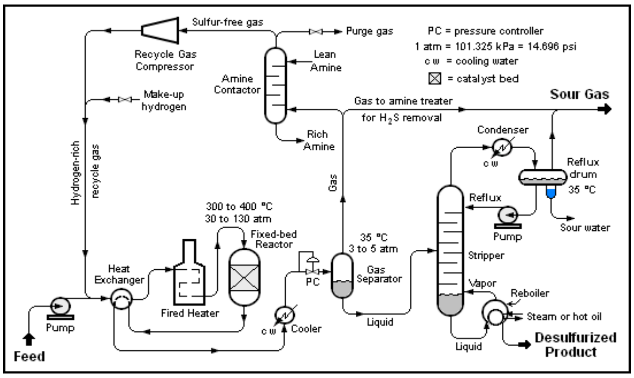

Figure 4 Process flow sheet for Naphtha Hydro desulfurization process

The gas that has been separated from the liquid phase in the gas-separating chamber is sent to an amine contactor where hydrogen sulfide is taken out. The product thus being sulfur free gas that is rich in hydrogen, which is channeled to enter along with the feed stream. If excessive gas formation takes place in the gas separating chamber (which suggest the presence of a greater quantity of lower alkanes and alkenes) it is sent out as sour gas. This gas joins the sour gas stream released after distillation of liquid phase of product. The sour gas usually consists of lower alkanes and alkenes along with H_2S, which is then sent into another amine gas treating unit where again H_2S is separated. The sulfur free stream containing lower alkanes and/or alkenes are recovered by distillation in series based on volatilities. The H_2S obtained is either used to manufacture sulfuric acid or is converted to elemental sulfur.

5.3 Bio desulfurization

This is one of the most promising technologies that can be used to remove sulfur from crude oil and has attracted many researchers towards it in a bid to commercialize the process. Although most of the sulfur can be removed by the above two mentioned processes there are certain aromatic sulfur compounds like dibenzothiophenes which show resistance towards desulfurization. This method can handle high-density bituminous fuels and remove sulfur from them. In Bio desulfurization, bacteria *Rhodococcus* sp. strain ECRD-1 is employed as a biocatalyst. The process involves the mixture of the catalyst and water in a continuous stirred tank bioreactor in which nutrients and NaOH are added and slurry is prepared known as biocatalyst slurry. Additional chemicals and p^H controlling compounds are added into the bioreactor, as they are crucial for the survival and effective action of bacteria. Feed containing high sulfur amount and the biocatalyst slurry are also added. The reaction is allowed to take place; enzymatic action of the bacteria upon the fuel causes the oxidation of sulfur and then cleavage of sulfur-carbon bonds. Air is passed into the bioreactor for oxidation process. The vapors emanated are collected. The reaction product is sent into a phase separating unit where the desulfurized product is obtained as top product. The bottom aqueous phase is sent into a separation unit from which biocatalyst slurry is recovered along with the extraction of sulfate byproduct. (Xiaoliang Ma, Subramani Velu *et al*, 2005)

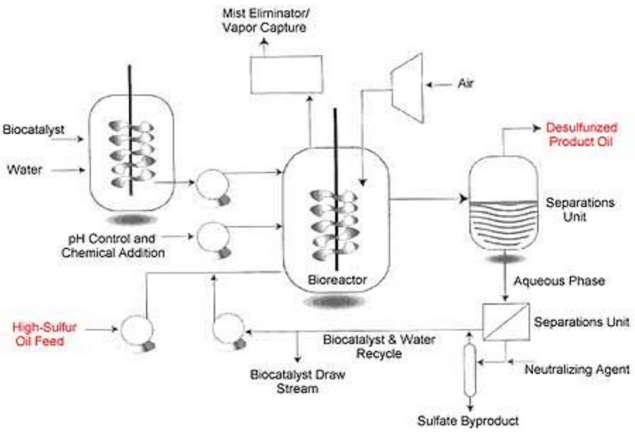

Figure 5 Process flow sheet for Bio desulfurization process

6. Advantages associated with the use of low sulfur fuels

The production of low sulfur fuel can be carried out in existing refineries by the addition of desulfurization equipment. Though significant initial setup cost is a tad on the higher side; the long term benefits of using low sulfur fuels, which result in lower emissions are way higher than the initial production costs. Usage of these fuels has numerous advantages such as;

- Although sulfur in fuel helps with lubrication enhancement, its presence causes acid formation, which is responsible for engine damage. Sulfur compounds in the exhaust also contribute to the formation of acid rain. Thus using low sulfur fuels with additives for enhancing lubricity can mitigate the above problems. (B.K. Bhaskara Rao, 2009)
- Using low sulfur fuels not only eliminates the emission of sulfur based compounds but also allows for effective function of various emission control technologies such as Diesel Particulate Filters, Lean NO_X Traps, Selective Catalytic Reduction (SCR) units etc. which control emissions of oxides of nitrogen and carbon and other harmful hydrocarbons. (See section III).
- The use of Low sulfur fuels have an increased capacity to keep components clean such as fuel injectors and systems, which contribute to, increased fuel economy.
- There has been a significant decline in the number of health issues in regions, which have shifted to low sulfur fuels combined with tighter emission standards. Cases of allergies, lung infections, vision impairment, nausea, diarrhea and many other diseases, which are caused by, air pollution and presence of particulate matter have come down by good numbers. Based on the results of a study, after the introduction of low sulfur fuels in Hong Kong it has been seen that there was a decrease in the premature mortality rate. (Bert Brunekreef *et al*, 1997)

Conclusions

With air pollution reaching alarming levels more and more newer technologies are coming up which alleviate the damage already caused. The harmful effects of sulfur and its compounds were being discussed and how it was impending the functioning of existing emission control technologies. Thus elimination of sulfur to the maximum extent will ensure that emissions of SO_X, NO_X, Particulate matter etc. are controlled as much as possible. Although, it is practically impossible to completely remove all the sulfur from a particular fuel (0% Sulfur), what can be done is to remove sulfur to a large extent by the application of the above discussed processes such as Sulfur Adsorption, Naphtha Hydro desulfurization or Bio desulfurization process so that the emissions are reduced to an acceptable level, which results in a smaller environmental footprint, lower greenhouse gas emissions and possible elimination of toxic SOx gas emissions which will ensure that the air we breathe will be cleaner and life enriching.

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