

REVIEW ON RESEARCH FOR DESULPHURIZATION OF DIESEL BY ADSORPTION

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Abstract - Desulphurization of diesel fuel by using adsorption is generally used for removal of sulphur using different low cost adsorbents. This paper is review on research carried for study of various types of low cost adsorbents used for sulphur removal. Many investigators studied research on desulfurization process for diesel fuel. Desulphurization was carried out in batch process for the effect of contact time, adsorbent dose, temperature, and concentration and results at different parameters were discussed. Investigators were determined adsorption isotherms and correlated with Langmuir and Freundlich isotherm equations for surface removal. X-ray fluorescence analyzer was generally used by investigators for sulphur content in diesel and adsorptive capacity was examined.

Key Words: Desulphurization, Adsorption, Diesel, Batch process, Sulphur.

1. INTRODUCTION

The use of environmentally benign fuels requires the removal of organosulfur compounds present in various petroleum fractions because these compounds are known to contribute to air pollution and acid rain by sulfur oxides [1]. The issues of gasoline and diesel deep desulfurization are becoming more serious because crude oils refined in various countries are becoming higher in sulfur content and heavier in density, while the regulated sulfur limits are becoming lower and lower [2]. Sulphur and its organic homologues are undesirable in the liquid fuels due to the cause of environmental pollution and hindrance in a variety of refining processes e.g. catalyst poisoning during catalytic hydro treatment, resistance to octane boosting and corrosion of the equipments. Desulphurization has therefore become an unavoidable process for the refineries [3]. Sulfur removal from petroleum and its products is of paramount importance, and adsorption plays an important role in desulfurization of petroleum [5]. The poor quality of crude oil obviously leads to high sulfur contents of oil products, and the technology for desulfurization of crude oil is urgently needed so that the sulfur contents in petroleum product could be reduced from the root [6]. Increasingly stringent environmental protection regulations mean that motor fuel producers must improve their existing technology and to

start considering alternative means of isolating sulphur from crude oil. Adsorption is a process that can be applied for crude oil desulphurization [7]. The removal of organosulfur compound from diesel fuel is an important aspect of all countries to reduce pollution by reducing the emission of toxic gases such as sulphur oxides and other polluted materials [8]. Desulfurization of diesel fuel is gaining worldwide interest among the researchers. This is due to stern regulations and fuel specifications adopted in many countries for checking environmental pollution caused by automobile exhaust gases [9]. In diesel, the primary sulfur compounds that need to be removed in reducing its sulfur content are comprised of benzothiophene (BT), dibenzothiophene (DBT), and their alkyl derivatives [10]. Ultra-low sulfur fuel is needed for several applications in which the total sulfur content should be substantially lower than 10 ppmw. An example of such a process is hydrogen production via reforming of fossil liquid fuel [11]. Desulfurization of hydrocarbon fuels has lately become one of the most important processes in petroleum refining. Increasingly stringent environmental protection regulations mean that motor fuel producers must improve their existing technology and to start considering alternative ways of removing sulfur from fuels [12]. Adsorption is one of the most promising processes for deep desulfurization of diesel fuels. This process is effective in the selective removal of low-concentration materials from liquids. The fuel is brought in contact with a solid adsorbent which selectively adsorbs sulfur containing compounds [13]. The petroleum refining industry, perceived as one of the largest sources of pollution, both direct and indirect via motor exhaust fumes, is on the front line of the battle for achieving environmentally friendly and sustainable operation [14]. Increasing concerns on the air quality regulation have urged the petroleum refining industry to produce cleaner products by removing heteroatoms containing molecules from their major products, diesel and gasoline [15]. Production of diesel oil with low sulfur content in the petroleum refineries is highly driven by the environmental legislations and air quality standards to minimize the environmental hazards and health problems associated with the direct emissions from the diesel powered vehicles. Such emission might contain particulate matter (PM) and toxic gases such as NO_x, SO_x, and CO [16]. Deep desulfurization of liquid hydrocarbon fuels is becoming an important subject worldwide. The desulfurization performance of solid super acid type

adsorbent (sulphated alumina) for commercial kerosene was evaluated on batch system and on continuous flow system [17].

2. Review on research for desulphurization of diesel by adsorption

Desulfurization and Kinetic Study of Diesel Fuel by Batch Adsorption on Activated Carbon was investigated by Neran Ibrahim and Samar Aljanabi. They were used batch adsorption desulfurization process for diesel fuel and activated carbon as adsorbent. Authors were studied effects of time, temperature, and initial sulphur content. Authors were obtained the highest desulfurization efficiency 57% at the best operating conditions of 2.5h, 50°C, 0.8mm AC particle size, and 1000rpm. Investigators were used different kinetic models to fit the experimental data. The experimental adsorption isotherms were correlated by Langmuir and Freundlich models [1]. Reduction of the sulfur content in liquid hydrocarbon fuels by adsorption for removing dimethyl sulfide and propylmercaptan was investigated by Dezhi Yi and Li Shi. Investigators were used bentonite adsorbents modified by CuCl₂ for the desulfurization of model oil. The bentonite adsorbents were characterized by X-ray diffraction and thermal analysis. Authors were studied factors that influence the desulfurization capability, including loading and calcination temperature. Authors were found that maximum sulfur adsorption capacity was obtained at a Cu (II) loading of 15 wt %, and the optimum calcination temperature was 150°C [2]. M. Shakerullah et al. desulfurization of liquid fuels by selective adsorption through mineral clays as adsorbents. Investigators were used different clays collected from local sources, including Kaolinite, Montmorillonite, Palygorskite and Vermiculite for the selective adsorption of sulphur compounds in petroleum products i.e. crude oil, kerosene and diesel oil. They were carried out batch process for desulfurization at different time intervals i.e. 1, 3 and 6 hrs at 40 °C temperature. Authors were investigated that Kaolinite exhibited the maximum desulfurization yield of 60 %, 76 % and 64 % at 6 hrs adsorption in case of crude oil, kerosene and diesel oil respectively and they were used SEM and EDX analysis methods for characterization of mineral clays adsorbents [3]. M.S. Patil et al. Desulfurization of hydrocarbon liquid fuels by adsorption. Authors were investigated batch reactor for desulfurization of hydrocarbons by adsorption using activated carbon prepared from black liquor. They were used phosphoric acid and nitrogen as activating agents. Authors were used scanning electron microscope and X-ray diffraction for the surface morphology of the two activated carbons before and

after sulfur sorption. They were studied parameters effecting adsorption such as Mercaptan feed conc, Stirring speed, Particle size, temperature, and effect of solvent [5]. Comparative Analysis of Adsorptive Desulfurization of Crude Oil by Manganese Dioxide and Zinc Oxide was investigated by Adeyi, Abel Adekanmi and Aberuagba. Authors were compared the desulfurization potentials of two metal oxides-activated manganese dioxide, AM and activated zinc oxide, AZ and the adsorption was conducted on these adsorbents. Investigators were performed batch adsorptive desulfurization experiments were by contacting 2 g of the adsorbent-activated manganese dioxide, AM powder with 20 ml of crude oil for a period of 60, 120, 180, 240, 300 and minutes at a temperature of 300C. The sulphur content of each sample was analyzed by means of X-Ray Fluorescence spectrophotometer [6]. Gaurav Daware et al. desulfurization of diesel by using low cost adsorbent. Investigators were used neem leaves for the preparation of activated carbon for desulfurization of diesel fuel. Authors were used 2 g neem leaves activated carbon and carried out batch experiment using 10 ml diesel at temperature of 200°C for 3.5 hr. They were concluded that with the increase in time and temperature, concentration of sulphur removal also increases & maximum removal of sulphur is 65% at 200C. Authors were studied Kinetic equilibrium of Langmuir and Freundlich isotherms [7]. Adsorptive desulfurization of feed diesel using chemically impregnated coconut coir waste was studied by J. K. Ahmed and M. Ahmaruzzama. Investigators were carried out batch experiments for removal of sulphur from diesel using coconut coir waste activated carbon. Experiments were conducted to optimize the adsorption parameters such as adsorbent dose, temperature, and contact time at optimum temperature 293 K and optimum dose of 1 g/20 mL for 3 h. Freundlich model was studied by investigators for experimental data [8]. Liquid phase adsorptive desulfurization of diesel fuel was proposed by G. Karagiannakis and P. Baltzopoulou, Dolios and A.G. Konstandopoulos. Authors were investigated lab scale process for desulfurization by adsorption using activated carbon as adsorbent. Authors were used organic solvent for washing of adsorbent. They were investigated that the most efficient was the micron-sized AC powder, with low 42µm mean diameter and high surface area 1960-2053 m²/g. The desulfurization process proved to be more efficient under ambient temperature, while the AC performance was essentially independent of the bed geometry and of the LHSV in the range of 7.5 – 35 h⁻¹. [9] Marko Music et al. Kinetic equilibrium and statistical analysis of diesel fuel adsorptive desulfurization. They were used adsorption process for

desulphurization of diesel fuel. Investigators were carried out batch adsorption process using activated carbon and aluminium oxide. Kinetic and equilibrium analysis of the adsorption process was done. Authors were proposed that activated carbon proved to be more efficient during the adsorption of sulfur compounds from diesel fuel when compared to aluminum oxide. And adsorption desulphurization is described by Freundlich model [10]. Analysis of continuous fixed bed adsorptive desulfurization of diesel fuel was proposed by Marko Muzic, Zoran Gomzi, and Katica Sertic Bionda. Fixed bed column was designed for the removal of organic sulfur compounds from diesel fuel by activated carbon. Authors were carried out experiments and studied the effects of process parameters such as flow rate, bed depth and temperature. Investigators were investigated that Sulfur content of less than 0.7 mg/kg was achieved for the lowest flow rate of 1 mL/min and highest bed depth of 28,4 cm at 50 °C [11]. Optimization of diesel fuel desulfurization by adsorption on activated carbon was proposed by Marko Muzic and Katica Sertic. Authors were carried out adsorption in batch adsorber for desulphurization of diesel and Response surface methodology was used for optimizing the adsorption process of organic sulfur compounds. Authors were investigated that optimum sulphur removal achieved was, 6 mg kg⁻¹ at 50 °C and 100 minutes with input sulfur concentration of 16,0 mg kg⁻¹ [12]. Adsorption Process of Sulfur Removal from Diesel Oil Using Sorbent Materials was investigated by Isam Zubaidy and Fatma Bin. They were proposed adsorption desulfurization process of diesel fuel and used carbonized date palm kernel powder as adsorbent in batch process at room temperature. Authors were investigated that the sulfur content was reduced from 410 ppm to 251 ppm using 5% adsorbent material and further reduction and up to 184.6 ppm using 10% sorbent material. [13]. Isam Zubaidy et.al adsorptive desulfurization of commercial diesel oil using granular activated charcoal. Investigators were used granular activated charcoal for adsorption of sulfur compounds from commercial diesel oil. They were carried out different experiments for desulphurization and equilibrium of sulfur adsorption on GAC was examined. Authors were proposed that sulfur content was reduced by 20.9 % compared to the original sample at room temperature [14]. A. Adeyi et.al Kinetics Analysis and Dosage Effects of Manganese Dioxide Adsorbent on Desulphurization of Crude Oil. Authors were carried out batch experiments for adsorptive desulphurization of crude oil using activated manganese dioxide and authors were showed that showed that desulphurization efficiency was increased on increasing

contact time and sorbent dose. Investigators were investigated that 49% reduction of crude oil sulphur and they were found that values of pseudo-first order and pseudo-second order reaction model were 0.8162 and 0.9951 when the experimental data were fitted into them [15]. Desulphurization of Tawke Diesel Fuel by Adsorption on Na-Y Type Zeolite, Local Clay and Active Carbon was studied by Mohammed K. Younis and Sherwan Mohammed Simo. Authors were used of granular Na-Y type zeolite, MOR type zeolite, molecular sieve 3A type, local clay and activated charcoal used for removal of sulfur compounds from Tawke diesel fuel. They were investigated that activated charcoal, is proved to be more efficient than remaining adsorbents and from results it was proposed that the desulfurization by activated charcoal is more efficient than by the clay, zeolite type and almost reach more than 20% [16]. Mohammad Ishaq et.al. adsorptive desulphurization of model oil using untreated acid activated and magnetic nanoparticle loaded bentonite as adsorbent. Investigators were carried out batch process for study the effect of contact time, adsorbent dose, initial dibenzothiophene concentration and temperature. They were found that at different adsorbent doses percentage of adsorption of DBT was increased with increasing adsorbent dose. Authors were investigated that bentonite impregnated with magnetic exhibits better performance in the desulphurization of fuel as compared to bentonite in untreated form as well as activated with HNO₃ [17].

3. CONCLUSIONS

Thus this paper reviews on research for adsorption of diesel fuel for removal of sulphur. Various investigators carried out experiment for desulphurization of diesel by using adsorption in batch process. Different researchers were used different types of adsorbents. Many of authors carried out adsorption experiment for the effect of contact time, adsorbent dose and sulphur concentration. In this way desulphurization was carried for removal of sulphur from activated carbon and compared sulphur content in diesel before and after adsorption.

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