

Original Research Article

Desulfurization of Tawke diesel fuel Using Na-Y type zeolite and active carbon

ABSTRACT

The removal of sulfur compounds from Tawke diesel fuel were done with granular Na-Y type zeolite, MOR type zeolite, molecular sieve desiccant NO 17-1159 and activated charcoal, the results were characterized by sulfur meter to ensure before and after desulfurization, GC analysis also used to enhance the characterization of sulfur removal. It's clear from our results that the desulfurization by activated charcoal more efficient than the zeolite type and almost reach more than 19%.

Keywords: desulfurization, diesel, adsorbitive desulfurization, Na-Y type zeolite, active carbon

1. INTRODUCTION

Sulfur and its compounds are undesirable in petroleum generally and in diesel especially due to fear of environmental pollution and corrosion of the refinery equipments. Removal of these compounds is of great concern today. During combustion sulphur compounds are converted mainly to sulphur dioxide (SO₂), which is a major cause of air pollution and acid rains [1, 2]. In order to prevent air pollution caused by exhaust gases, governments of many countries all over the world have assign sulphur removal from transportation fuels since the last twenty years ago. For example, from 2009 in the USA the sulphur maximal content in on-road fuels has to be 15 ppm [3,4]. Identical or even stronger demands were made for the fuels produced in the European Union as 10 ppm [5]. Demands for clean diesel fuels in Iraq generally and in Kurdistan region especially are high. The removal of organic sulfur compounds from transportation fuels is becoming a more important issue in recent years not only for environmental regulations but also because of the possibility that these fuels can be re-formed on-board to produce hydrogen-rich gas as a fuel for fuel cells for mobile, portable, and stationary applications. To reform these liquid fuels for fuel cell applications, the sulfur level should be further reduced close to zero ppm because the presence of even traces of sulfur is a poison to the reforming catalysts as well as electrode catalysts [6].

Hydrodesulphurization (HDS) is currently being used in the petroleum industry. HDS is the only one widely used industrial technology. This method had some disadvantages due to the expensive catalysts and using valuable hydrogen for this process. HDS also has limited effectiveness at removing thiophenes, benzothiophene, dibenzothiophene and its derivatives from diesel [7,8].

Adsorption is the most common HDS alternative method currently used to achieve ultra clean fuels [9]. Adsorption is a mass transfer process wherein molecules in a free phase become bound to a surface by intermolecular forces. It can be done under ambient conditions, such as room temperature and normal pressure. The reaction rate is very high. Sulfur compounds in diesel can be removed by physical adsorption, chemisorption and π -complexation adsorption. Physisorbed sulfur compounds can be easily removed from adsorbents. So, it is easy to regenerate the adsorbents. The zeolite-based adsorbents have

been used as promising materials for selectively removing the sulfur derivatives from diesel . Metal ion exchanged Y zeolites showed high selectivity and capacity for sulfur compounds using π -complexation between metal ion and sulfur compounds [10]. The selectivity of the zeolite-based adsorbents varies according to fuel composition such as aromatic and moisture concentrations[11].

This paper discusses the non hydrodesulfurization processes, by zeolite and activated carbon. The development of the mentioned processes is given, along with a discussion of recent studies in this field.

2. MATERIAL AND METHODS

Diesel sample used in this study was obtained by fractional distillation from Tawke crude oil -Zakho KRG-Iraq. Typical physical and chemical properties of diesel fuels that was used are presented in Table 1.

Table 1 Physical and Chemical Properties of Diesel Products

Tests	Diesel Fuel	Method
B.P, °C	185-320	ASTM D86
Density at 15.6°C	0.8235	ASTM D1217
API Gravity at 15.6 °C	40.18	Calculate
Water content,	133.122	-
Cetane index	56.5	ASTM D976
Diesel index	49.7	Calculate
Cloud Point , °C	-15.5	-
Sulphur content	1.0092	ASTM D4294
Flash Point , °C	63.6	ASTM D93
Aniline Point , °C	65	ASTM D611
Refractive Index (RI) at	1.462687	ASTM D1218

The adsorbent materials used in this study were commercial activated charcoal p.a., powder from Carl Roth GmbH + Co. KG, (Melting point 3550 °C, Bulk density of 150-250 kg/m³), granular Na-Y type zeolite having SiO₂/Al₂O₃ molar ratio of 5.4 , granular MOR type zeolite without binder having SiO₂/Al₂O₃ molar ratio of 9 and molecular sieve desiccant NO 17-1159. Commercial activated charcoal was used after calcining at 700 °C for 4h.

H-form of Y and H-MOR without binder zeolites was prepared by ion exchanging with NH₄NO₃ solution at 70 °C to obtain NH₄-form of zeolite. After ion exchange and then filtered the solution, samples washed with distilled water, dried at 120 °C for 4 hrs, and then calcined at 550 °C for 4 hours to obtain H-form of each Y and MOR type zeolite. The ion exchange process was repeated four times, each time for one hour to complete the required level of ion exchange.

All adsorbent materials present in this study were used after heating at 120 °C for 2hours prior using.

2.1. METHOD

Diesel fuel was mixed with 5 % and 10% by mass commercial activated charcoal for 1-6 hrs using flask shaker at a rate of 60 round /min at 30 °C and ambient pressure. The resulting solution was filtered to separate the solid adsorbent material from filtrate. The filtrate was

analyzed for sulfur content. This step is to choose the proper contact time that gives highest sulfur removal.

Diesel oil also mixed with 5% by weight each of the following adsorbent materials: activated charcoal, granular H-Y type zeolite having $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio of 5.4, granular H-MOR type zeolite without binder having $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio of 9 and molecular sieve desiccant NO 17-1159 at 30°C and 60°C and ambient pressure for 3 hrs. The filtrate was analyzed for sulfur content. The sulfur content was measured using EDXRF Sulfur Meter RX-360SH.

Also the analysis for samples were performed using Perkin Elmer Clarus 580 Gas Chromatograph (GC). The chromatographic analysis was conducted according to the following program-Initial temperature of 30°C maintained for 5min, increase at the rate of 4°C per min to 250°C and maintained for 30 min at 250°C . Helium was used as a carrier gas at a pressure 48psi during the analysis.

3. RESULTS AND DISCUSSION

The sulfur content was plotted with time hours using 5%wt and 10%wt activated charcoal at 30°C .

Fig. 1. sulfur content %wt contact with time using 5% activated charcoal at 30°C

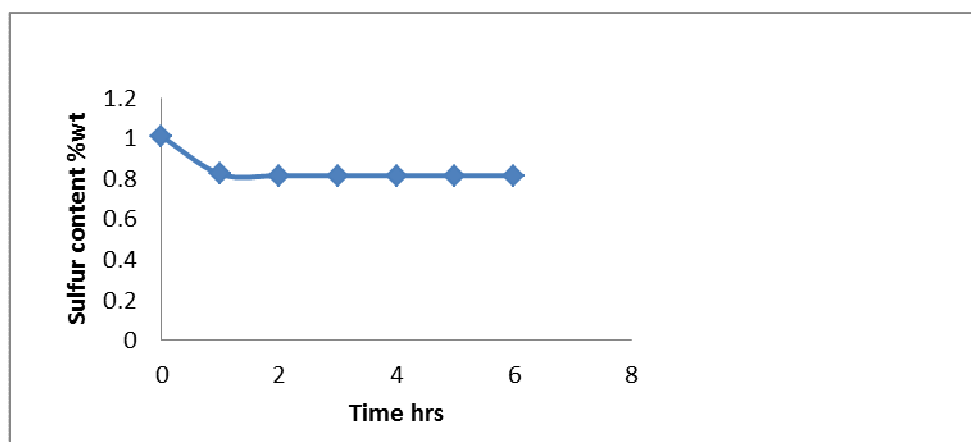
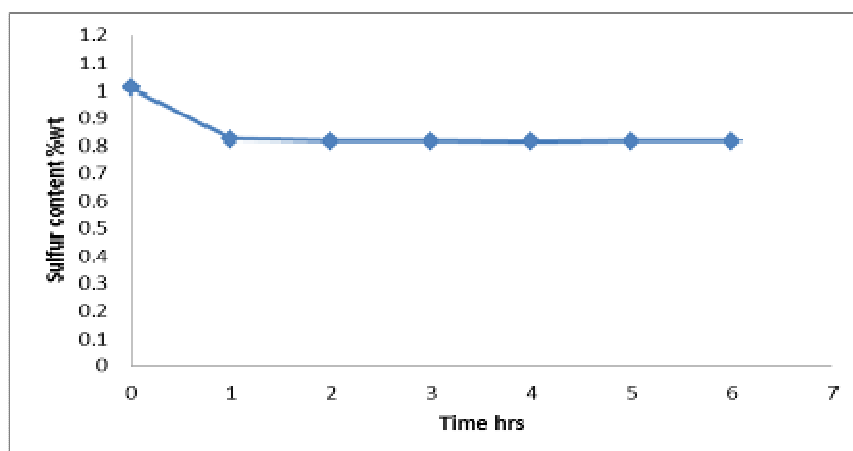


Fig. 2. sulfur content %wt contact with time using 10% activated charcoal at 30°C



It is clear from figures 1. and 2. that the three hours shaking enough for used activated charcoal to remove good amount of sulfur from Tawke diesel fuel. In other word It can be seen that the most of the sulfur compounds are adsorbed within 3hrs. indicating that all adsorption sites are saturated.

The result showed that the sulfur content recovery was 5.73% after one hour shaking with 5% activated charcoal and this removal was increased to about 8.2% by shaking for 3 hrs with activated charcoal. By increasing the percentage of activated charcoal to 10% the sulfur recovery was 19.2% after 3 hrs shaking.

Thus, by increasing of the amount of commercial activated carbon from 5% to 10%wt Fig. 2. The curve showed continuous decrease of sulfur content.

Desulfurization of Tawke diesel fuel containing about 1.0092%wt sulfur was studied over used adsorbent materials for three hours at 30 °C; 60 °C and ambient pressure.

The results of adsorption studies on the desulfurization of Tawke diesel fuel over ion exchanged zeolites granular H-Y , granular H-MOR without binder , desiccant and activated charcoal are summarized in table 2. The results show that under present experimental conditions the adsorption capacity varied among activated charcoal, granular H-Y , granular H-MOR without binder and desiccant depending upon the nature of exchanged capacity, pore size and the acidity of each adsorbent used in this process.

Table 2. Effect of temperature on Sulfur content %wt after 3 hours sorption

Samples	Sulfur content %wt30 °C	Sulfur content %wt60 °C
Mother	1.0092	1.0092
Treated with granular H-	0.9992	0.9991
Treated with granular H-Y	0.9638	0.9433
Treated with desiccant NO	0.9810	0.9851
Treated with activated	0.9262	0.9103

The activated charcoal exhibited better performance in desulfurization of diesel and the sulfur content treated with granular H-MOR type zeolite without binder is less than that treated with granular H-Y type zeolite this due to the adsorption on MOR without binder affected by method of synthesis (clay particles) and MOR type zeolite more sensitive than Y type zeolite to the impurities (poisoning).

The color of diesel sample treated at 30 °C turned from red to light yellow, probably due to the adsorption properties of used adsorbent materials which enable it to remove dyes.

GC chromatogram of diesel fuel after treatment with 5%w activated charcoal at 30 °C Figure 3. shows the clear increase of intensity of some beaks In comparison with chromatogram of diesel fuel before treatment Figure 4. especially at the time of 15 and 16 min. this due to the sorption activity of used adsorbent material .

However, this was not a critical variable because of the complexity of diesel fuel, and there is no standard solutions for calibration, it is very difficult for us to use GC analysis to give more explanation.

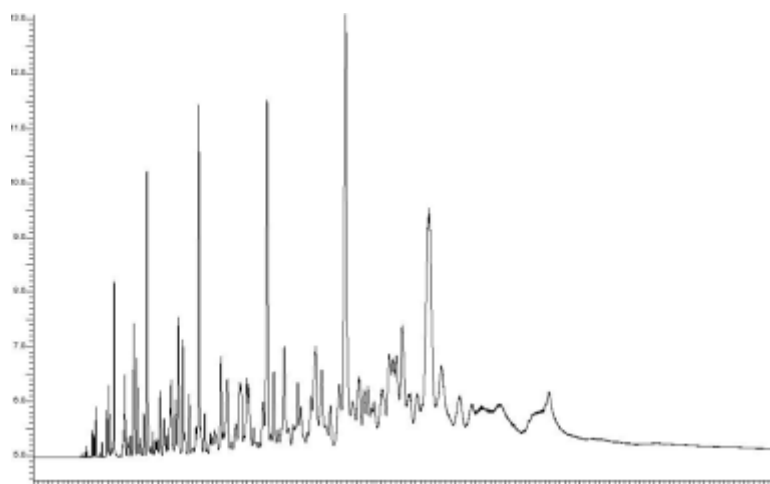


Figure 3. Chromatogram of diesel fuel after treatment with 5%wt activated charcoal at 30 °C

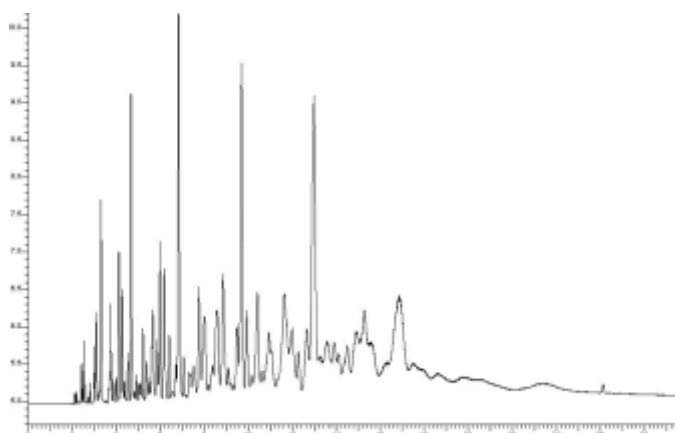


Figure 4. Chromatogram of diesel fuel before treatment

4. CONCLUSION

Based on our experiments it may be concluded that it is impossible obtain low sulfur content in desulfurization process only with adsorption on used adsorbent materials. desulfurization by activated charcoal more efficient than the other adsorbents and give us a future perspective to focus on this type mainly and made some modification to increase the activity of the adsorbent.

REFERENCES

1. Speight, J.G.; The Chemistry and Technology of Petroleum, (1999), 3rd Ed., Marcel Dekker, New York, 1-937.
2. Song C., Xiaoliang Ma, Ultra-deep desulphurization of liquid hydrocarbon fuels-chemistry and process, Int. J. Green Eng., 1(2) (2004), 167–191.
3. Babich, I. V., Moulijn, J. V. Science and technology of novel processes for deepdesulfurization of oil refinery streams: a review // Fuel. 2003. Vol. 82, No. 6.P. 607–631.

- 173 4. Song, C. An overview of new approaches to deep desulfurization for ultra-clean
174 gasoline, diesel fuel and jet fuel // Catal. Today. 2003. Vol. 86. P. 211–263.
- 175 5. Tailleux R G, Ravigli J, Quenza S, Valencia N. Catalyst for ultra-low sulfur
176 and aromatic diesel. ApplCatal A-Gen, 2005, 282: 227–235
- 177 6. Parkinson, G., “Diesel Desulfurization Puts Refiners in a Quandary,”
178 Chem. Eng., 108, 37 (2001).
- 179 7. Fujikawa T, Kimura H, Kiriya K, Hagiwara K. Development of ultra-deep HDS
180 catalyst for production of clean diesels. Catal Today, 2006, 111 (3–4): 188–193.
- 181 8. Hernández-Maldonado A J, Yang R T. Desulfurization of transporta-
182 tion fuels by adsorption. Catal Rev, 2004, 46(2): 111–150
- 183 9. R.T. Yang, A.J. Hernandez-Maldonado, W. Cannella, Desulfurization of trans-
184 portation fuels with zeolite under ambient conditions, Science 301 (2003)
185 79–81.
- 186 10. A.J. Hernandez-Maldonado, R.T. Yang, J. Am. Chem. Soc. 126 (2004)
187 992.
- 188 11. V.M. Bhandari, C.H. Ko, J.G. Park, S.-S. Han, S.-H. Cho, J.-N. Kim,
189 Chem. Eng. Sci. 61 (2006) 2599.

190
191