

# Adsorption Process of Sulfur Removal from Diesel Oil Using Sorbent Materials

Isam A. H. Al Zubaidy, Fatma Bin Tarsh, Noora Naif Darwish, Balsam Sweidan Sana Abdul Majeed, Aysha Al Sharafi, and Lamis Abu Chacra

**Abstract**—The removal of organo-sulfur compounds (ORS) from diesel fuel is an important aspect of all countries to reduce air pollution by reducing the emission of toxic gases such as sulfur oxides and other polluted materials. One of the easily and fast method to remove sulfur from diesel oil is the adsorption desulfurization process. Adsorption-desulfurization process of diesel fuel was proposed and examined. Local diesel fuel of 410 ppm sulfur content was treated with commercial activated carbon and carbonized date palm kernel powder at room temperature in batch work. The contact time were examined and chosen. The addition of activated carbon caused reduction in sulfur content by more than 54% of the original sulfur content value while carbonized date palm kernel powder without any activation process showed lower performance toward sulfur recovery. This high reduction will definitely improve the emission quality and reduce the harmful effect of the combustion process of diesel fuel to the environment.

**Index Terms**—Activated carbon, adsorption process, desulfurization process, diesel oil.

## I. INTRODUCTION

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 [1]. Although extensive efforts have been made to decrease the sulfur contents of diesel oil, the regulation on the fuel quality is going to be tightened faster than expected. Fruit kernel activated charcoal in batch process was used for desulfurization process [2]. The results revealed the potential for adsorbent as a low cost adsorbent and have a higher capacity for sulfur at gas oil concentrations than in kerosene. Naphtha desulfurization by adsorption was studied [3]. They found that 13X zeolite have the highest capacity for sulfur at low concentration range and activated carbon at higher concentration range. The hydro-desulfurized straight run gas oil having less than 50 ppm sulfur was adsorptivity treated with activated carbon fiber to attain the ultra-low sulfur gas oil having less than 10 ppm sulfur [1]. Deep desulphurization of diesel fuel was studied [4]. The hydro-desulfurized straight run gas oil with 50 ppm sulfur was treated with activated carbon fiber to a low sulfur content of less than 10 ppm. The adsorptive desulphurization of gasoline over nickel based adsorbent, showed high capacity and selectivity for the adsorptive

desulfurization of gasoline. The adsorption involves C-S bond cleavage as evidenced by the formation of ethyl benzene from benzothiophene in the absence of hydrogen gas [5].

This work will focus on the adsorption desulfurization process of local diesel oil using activated carbon.

## II. EXPERIMENTAL WORK

### A. Materials

Diesel oil was collected locally from one petrol station in Sharjah/ UAE. The main physical properties of the diesel oil are shown in Table I. The heavy metals presents in diesel oil are shown in Table II.

TABLE I: PHYSICAL PROPERTIES OF DIESEL FUEL

Properties	Method	Diesel oil
Specific gravity, 15/15 °C	ASTM D 1298	0.8426
API gravity	ASTM D 1298	36.43
Water content, vol%	ASTM D 96	Nil
Ash content, wt%	ASTM D 582	0.0247
Aniline point, °C	ASTM D 611	78
Diesel index	ASTM D 611	62.8
Cetane index	Ref. 6	53.9
Calorific value, joule/g	ASTM D 240	46,000
Flash point, °C	ASTM D 93	85
Sulfur content, µg/g	ASTM D 7220-06	410

TABLE II: HEAVY METALS IN DIESEL OIL

Metal	Units	Diesel Oil	Treated diesel oil
Aluminum(Al)	ppm	< 9.1	10.6
Iron(Fe)	ppm	< 1.2	1.2
Lead(Pb)	ppm	< 1.0	0.1
Barium(Ba)	ppm	< 3.0	0
Calcium (Ca)	ppm	1.3	10.4
Chlorine (Cl)	ppm	25.7	28.1
Chromium(Cr)	ppm	< 1.0	< 1.0
Copper(Cu)	ppm	1.7	0.3
Manganese(Mn)	ppm	< 1.0	< 1.0
Molybdenum(Mo)	ppm	< 0.7	0
Nickel(Ni)	ppm	< 1.0	0
Phosphorous(P)	ppm	6.3	7.5
Silicon(Si)	ppm	16.2	41.1
Potassium (K)	ppm	< 2.2	< 2.2
Vanadium(V)	ppm	< 1.0	< 1.0
Zinc(Zn)	ppm	< 1.0	0.1

Manuscript received December 4, 2012; revised January 8, 2013.

Isam A.H. Al Zubaidy, Fatma Bin Tarsh, Noora Naif Darwish, Balsam Sweidan, Sana Abdul Majeed, Aysha Al Sharafi, and Lamis AbuChacra are with Chemical Engineering Department/ College of Engineering, American University of Sharjah/ UAE (email: izubaidy@aus.edu).

The physical properties showed sulfur content of 410 ppm and high value of diesel index and cetane index.

Commercial activated carbon (NORIT, product number C3445, Sigma Aldrich) was used. The Norit particles, (size 100 and 400-mesh (37 to 149 micron)), were used after heating at 105 °C for two hours prior using. Helium with very high purity was also used for sulfur measurements.

Date palm kernels were collected, washed with tap water, distilled water to be free from dirt and allows drying in an oven at 100 °C for 24 hours, grinded and sieved. Fractions of maximum size of 710 micrometer and lower were collected and kept in close jar.

### B. Thermally Activated

Date palm kernel powder was placed in steel tube with small hole at the top for the ventilation of the gases produced during carbonization and heated in a muffle furnace. The tubes were heated to 650 °C and maintained at the selected temperature for 3 hrs. It is allowed to cool and then grinded using mortar. The powder was sieved using sieve shaker to collect particles of an average size of 710 micrometer and lower. The sample was kept in close jar. The sample was allow to heat to 105 °C for 1 hr prior using for any test.

### C. Method

Diesel oil was mixed with 5 % by mass commercial activated carbon for 1-5 hrs using flask shaker at a rate of 500 oscillations /min at room temperature. 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. The sulfur content was plotted with time (Fig. 1) and it was found that the shaking for two hours is enough to get reasonable sulfur removal.

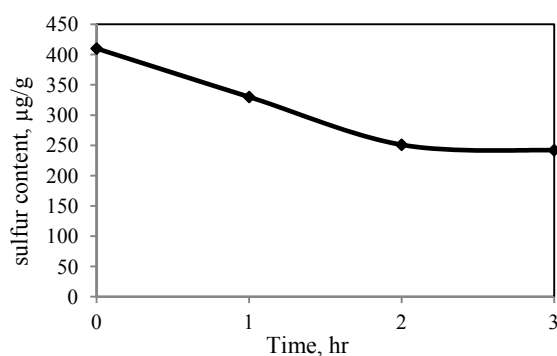


Fig. 1. amount of sulfur with contact time using commercial activated carbon

0-10% by mass of commercial activated carbon were mixed with diesel oil for two hours with continuous mixing and then subjected to filtration process. The filtrate was analyzed for sulfur content. The sulfur content and metal content was measured using Spectro iQ ii X-ray fluorescence analyzer tool which works according to IP532/05 and ASTM D 7220-06.

Samples of diesel oil and treated oil were analyzed for other physical properties. All physical properties were conducted according to ASTM standard methods.

## III. RESULT AND DISCUSSION

The high value of cetane index indicates that this type of diesel has good ignition quality and contain high amount of paraffin's. Cetane index of 53.9 indicates that this type of diesel has a short delay time that allows more time for the fuel combustion process to be completed. Hence, higher speed diesel engines operate more effectively with higher cetane index fuels. This will result in a smoother running and better performing engine with more power and fewer harmful emissions. The contact time was fixed as two hours as shown in Fig. 1.

The amount of commercial activated carbon was varied between 0-10%. The sulfur content was plotted vs. amount of commercial activated carbon as shown in Fig. 2. The curve showed continuous decrease of sulfur content.

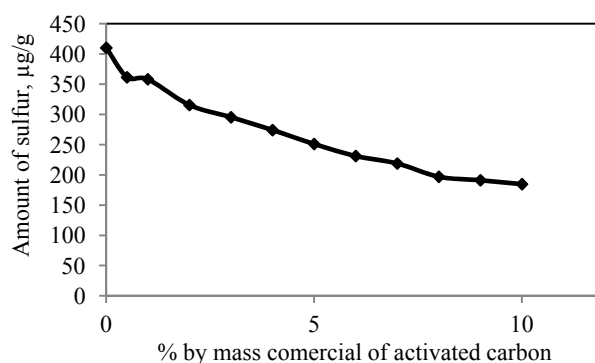


Fig. 2. Amount of commercial activated carbon as adsorbent with sulfur content at room temperature and contact time of two hours

The sulfur breakthrough curve (Fig. 3) showed that the sulfur recovery was 12.68% by adding 1% sorbent material and this removal was increased to about 38.78% by adding 5% sorbent material and further increase to 54.98% by increasing the activated carbon to 10% of the diesel oil quantity. This represents a very important improvement in physical properties and emitted gases to the atmosphere. This means that the sulfur dioxide emitted to the atmosphere was reduced to the half. Further work is ongoing to use active carbon from different local biomass materials base as well as to make this process as an environmentally friendly process.

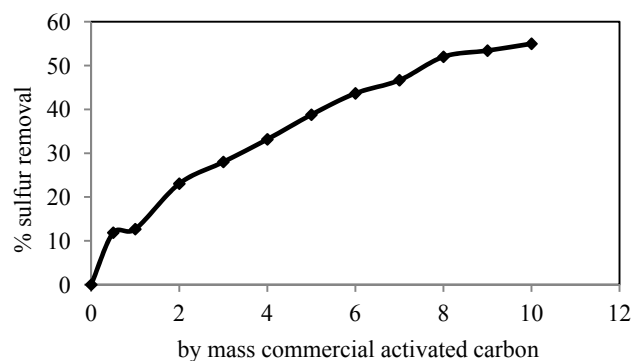


Fig. 3. Sulfur breakthrough curve with amount of adsorbent

The treated oil with 5% activated carbon was analyzed for metal content as shown in Table II.

Carbonized material from date palm kernel was also used but without activation for desulfurization process of diesel fuel as shown in Fig. 4.

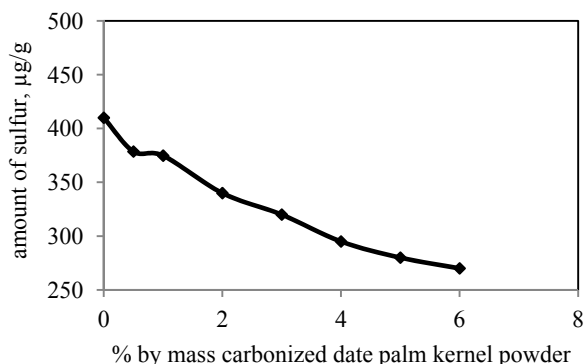


Fig. 4. Adsorption desulfurization process using carbonized date palm kernel powder

It was found that this material was able to reduce sulfur content by 34.15% with the addition of 6% by mass sorbent material. This value is lower than sulfur removal using activated carbon.

#### IV. CONCLUSION

The desulfurization of diesel oil by adsorption process using activated carbon showed a reduction in the amount of sulfur by more than half of the original amount of sulfur. 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. This will definitely reduce the environmental impact of using diesel fuel in buses and other heavy duty machineries by reducing the

amount of sulfur dioxide emitted to the atmosphere.

#### ACKNOWLEDGMENT

The authors would like to thank the American University of Sharjah/UAE for providing the equipment to perform this work.

#### REFERENCES

- [1] S. Yosuke, S. Kazuom, C. Ki-Hyouk, K. Yozo, and M. Isao., "Two-step adsorption process for deep desulphurization of diesel oil," *Fuel*, vol. 84, issues 7-8, pp. 903-910, 2005.
- [2] M. H. R. Gamil and M. M. Nasser, "Desulphurization of Um Al Nar refinery straight run kerosene and gas oil using pal fruit kernel activated charcoal: a locally made adsorbent," *Adsorption science and technology*, vol. 15, no. 4, pp. 311-321, 1997.
- [3] S. H. Abu baker Salem, "Naphtha desulphurization by adsorption," *Ind. Eng. Chem. Res.*, vol. 33, pp. 336-340, 1994.
- [4] Y. Toida, "Adsorption desulphurization agent for desulphurizing petroleum fraction and desulphurization method using the same," *USA Patent*, 20050173297, 2005.
- [5] X. L. Ma, M. Sprague, and C. Song, "Deep desulphurization of gasoline by selective adsorption over Nickel-based adsorbent for fuel cell application," *Ind. Eng. Chem. Res.*, vol. 44, no. 15, pp. 5768-5775, 2005.
- [6] W. J. Pierre, T. Pierre, and F. J. Pierre, "Petroleum products, Refining, Petroleum," Institut français du pétrole publications, vol. 1, 1995.



**Isam Al Zubaidy** earned BSc in Chemical Engineering from Baghdad University/ Iraq in 1976 and MSc in Chemical and Petroleum Processing Engineering from Herriot- Watt University, Scotland-UK 1981 with thesis titled "Kinetic studies of the Desulfurization of thiophene in the presence of desulfurized gas-oil over a cobalt-molybdate catalyst". He worked with Institute of Technology and College of Engineering in Baghdad/ Iraq from 1977-1998 as assistant professor. He worked as technical manager in waste oil recycling in UAE for the period 1999-2000. He joined the American University of Sharjah/UAE since 2000. His areas of research interest is the waste oil recycling, oil spill to soil and water, oil sludge treatment, desulfurization process of oil products, and corrosion. He is the author of more than 35 published papers and many textbooks and handouts for chemical engineering students.