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Preparation of Activated Carbon by Chemical Treatment of Spent Lubricant Oil with Residual Wastes (Blow-Down) of Mishraq Sulfur Company

K. S. Tawfiq, A. A. Hamdon and A. A. Thanoon
Chemistry Department, College of Education, University of Mosul, Mosul

(NJC)

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Abstract

The aim of this study is to prepare activated carbon from waste materials characterized by their environmental hazardous and polluted effect; those are spent lubricant oil (SLO) and Mishraq blow down (Mbd) the side product from Mishraq Sulfur Company. Those two materials were chosen as starting materials for activated carbon preparation.

The laboratory work include the preparation of the activated carbon via two treatments, the first includes thermal treatment of (SLO) that was already oxidized under certain experimental conditions with certain percentages of (Mbd). Sample mixtures were heated at 170^{o}C for different time intervals using 1%(wt/wt) anhydrous aluminum chloride as catalyst. The second treatment includes thermal treatment of oxidized (SLO) with different percentages of (Mbd), the mixtures were heated at 300^{o}C for certain time intervals under additionally air stream oxidation condition. Products possessing highest asphaltene contents were chosen as starting matters for activated carbon preparation. They were simply and vacuum distilled respectively. The remained heavy material was treated with potassium hydroxide in (1:2) at 550±50^{o}C for 3hrs. The prepared carbonaceous product was then purified and its activity was determined by adsorption ability, ash content, bulk density and humidity content.

الخلاصة

تهدف الدراسة الى تحضير الكاربون المنشط المستخدم في مجالات صناعية وتطبيقية واسعة باستخدام زيوت التزييت المستهلكة والناتج العرضي من عملية استخراج وتنقية الكبريت (البلوداون) من حقل المشراق والحاوي على ما يقرب من 92% وزناً من الكبريت . ان كلا المادتين تطرحان الى البيئة بشكل غير مسؤول ويسببان ضرراً بيئياً بالغ الخطورة.

حضر الكاربون المنشط عن طريق اجراء معاملتان حراريتان اولهما تتضمن معاملة زيوت التزييت المستهلكة والمؤكسدة بالهواء عند ظروف عملية تم اعتمادها مسبقاً مع نسب محددة من مادة البلوداون ومن ثم تسخين النماذج عند درجة حرارة 170^{o}م ولفترات زمنية معينة باستخدام حفاز كلوريد الالمنيوم اللامائي بنسبة 1% وزناً . أما

المعاملة الحرارية الثانية فقد تضمنت معاملة نماذج زيوت التزييت المستهلكة المؤكسدة مسبقاً مع نفس النسب من مضاف البلوداون المستخدمة في المعاملة الاولى ومن ثم أكسدة النماذج اضافياً بالهواء عند درجة حرارة 300^{o}م ولفترات زمنية معينة وبدون استخدام حفاز.

تم اختيار افضل النماذج من المعاملات الحرارية اعلاه من حيث المحتوى الاسفلتيني لها وجرى تقطيرها اعتيادياً ثم فراغياً لاجل ازالة المواد الهيدروكاربونية المتبقية القابلة للازالة . بعدها تم معاملة المخلفات الثقيلة المتبقية كيميائياً مع زيادة من هيدروكسيد البوتاسيوم عند درجة حرارة 550 ± 50^{o}م ولمدة 3 ساعات .

تم تنقية نماذج الكاربون الناتج ومن ثم تقييم خواصه باجراء بعض القياسات الفيزيائية اللازمة لذلك . أظهر الفحم المنشط المحضر بهذه الطريقة خواصاً امتزازية جيدة جداً.

Introduction

The oxidation of lubricant oil takes place in highly complicated systems. For example, in an internal combustion engine, the catalysis by metal surfaces and soaps as well as complex variation in temperature and oil-air agitation through out the oil stream will affect the stability and lead to lubricant oil oxidation (1), besides the deposition of carbonaceous material within engine parts.

The oxidation of (SLO) was studied by many workers, different oxygenated compounds were formed. It is believed that the oxidation of hydrocarbon fraction is chain reaction in which peroxides play an essential rule in the process. Oxidative–dehydrogenation reaction of hydrocarbons results in asphaltene increasement (2,3). On the other hands, the dehydrogenating property of sulfur reclaims it to be used in converting simple hydrocarbonic system to polycyclic aromatic one from the corresponding aliphatic, resinous and hydro aromatic derivatives (4). Such processes could be performed under certain suitable experimental conditions lead to the introduction of sulfur atoms in such amount causing sulfur-dehydrogenation reaction and the final products are macromolecules of polymeric carbon-sulfur, tar like material and carbon substances, or even may be carbon-sulfur-bulk complexes that could be obtained at high temperature (400 ^{o}C) in the absence of oxygen (5).

Most of the oxygenated compounds like esters of saturated carboxylic acids (6), aromatic carboxylic acids (7) and ketones (8) can be easily sulfurized ordinarily under mild conditions. Sulfurization and sulfur-dehydrogenation reactions are considered to be the bases for various sulfur-containing compounds formation accompanied with hydrogen sulfide liberation leading to polycyclic aromatic compounds and unsaturated sulfur-heterocyclic compounds formation from the corresponding oxygen-hydrocarbon containing compounds (9,10).

Activated carbon is black material having pores of non crystalline texture. It could be granular or powder. Active carbon differs from most adsorbent in terms of surface area and capacity. Active carbon can be obtained by wide range of high carbonaceous materials such as coal, bitumen…etc. Preparation of activated carbon can be carried out employing a certain type of compounds that have an ability of hydrogen removing from the hydro-carbonic structure in the form of H_2S, NH_3 and some times H_2O(11).

Looking back to the knowledge available in the literature we find many workers in the field of activated carbon production and some of them are:-

Garcia (12) et. al. prepared activated carbon from pine wastes gasified the pilot reactor in the presence of potassium hydroxide using different alkali/char ratio from 1:1 to 1:4 (wt:wt) at 800°C.

Hamdon (13) prepared activated carbon from (SLO) using oxidation-condensation process. The oxidation of (SLO) conduct- ed using 2% (wt/wt) of cobalt chloride, zinc chloride and ferric chloride in the presence of stream of air. The resulted product was treated with sodium hydroxide at 550°C for 3 hrs.

Shawabkch(14) et. al. prepared activated carbon by oxidizing (SLO) using nitric and sulfuric acid.

AL-Rahho(15) prepared activated carbon from oxidized (SLO) using different additives (polystyrene, polyethylene, melamine, rubber and asphaltene) at different treatment conditions. The resulted activated carbon possesses good adsorption properties.

Experimental

1-Used Materials

1-Spent lubricant oil.
2-Blowdown.
3-Petroleum spirt.
4-Iodine solution.
5-Sodium thiosulfate.
6-Methylene blue.
7-Hydrochloric acid.

2-Used Apparatuses.

1-Electrical oven.
2-Electrical furnace.
3-Electrical shaker.
4-Spectrophotometer
5-Air blowing apparatus.

3-Thermal air oxidation of (SLO)

To optimize the oxidation conditions of (SLO) that give rise to max asphaltene content, known weights of (SLO) samples were oxidized by air thermally at 100, 200, and 300±25°C for 24, 48 and 72 hrs at flow rate 120 cm^3/min. Asphaltene content for the all oxidized (SLO) samples was determined according to the procedure given by (16). The (SLO) sample (L_8) oxidized at 300±25°C for 48 hrs gives rise highest asphaltene content, see table (1).

4-Treatment of oxidized (SLO) with (Mbd)

Two thermal treatments have been performed applying oxidized (SLO) product having max asphlatene content, the treatments are:-

a-Thermal catalyzed treatment of oxidized (SLO) with (Mbd) using anhydrous aluminum chloride catalyst

Samples of oxidized (SLO)(L_8 sample table (1)) contain- ing different percents 2, 4, 6, 8, and 10% of (Mbd) whose compositional contents given in table (2) were heated at 170°C for 5, 6 and 7 hrs in presence of 1% anhydrous aluminum chloride. Asphaltene content was determined for each resulted treatment product.

Another treatment was carried out too under similar above mentioned conditions using (SLO) mixed with 8% of (Mbd) conditions which give rise to max asphaltene content, table (3).

b-Thermal treatment of oxidized (SLO) with (Mbd) under additional air oxidation condition

Samples of oxidized (SLO)(L_8 sample table (1)) containing 2, 4, 6, 8, and 10% of (Mbd) were oxidized additionally by air at 300±25°C for 5, 6 and 7 hrs. Another thermal treatment was performed using (SLO) sample mixed with 6% of (Mbd) condition which give rise to max asphaltene content, table(4).

5-Preparation of activated carbon

Thermal treatments products containing highest asphaltene content were chosen for this purpose. They were distilled simply and vacuum respectively. The remained heavy hydro-carbonic matter was considered to be the starting matter for activated carbon preparation as follows:-

a-Primary carbonization

The heavy residual product from vacuum distillation was mixed with potassium hydroxide in ratio1:2(wt:wt) respectively. The sample was heated at 350^{o}C for 2hrs with continuous stirring.

b-Final carbonization and activation

The resulted matter from primary carbonization was heated to 550±50^{o}C for 3hrs, and then cooled to room temperature.

c-Purification of the prepared activated carbon

The prepared samples were washed with distilled water several times to remove the free alkalinility till neutral washing water was got. Reactivation step was done by mixing activated carbon sample with 100ml of 10% hydrochloric acid solution, refluxed for 2hrs to minimize metal contents. The resulted product was filtered and washed with distilled water several times to remove the acidity effect till neutrality. The sample was then filtered, dried at 100-120^{o}C for 24hrs, crashed, sieved (20-40) mesh and stored in a desiccator's.

6-Assessment of activated carbon activity

The activity of activated carbon was determined by measuring the internal and external surface area by measuring iodine (17) and methylene blue (18) adsorption from its aqueous solution. Other determined physical assessments like apparent density (19), ash content (20) and humidity (21) were measured.

Results and Discussion

The results given in table (1) show the asphaltene contents obtained from oxidation processes of (SLO). The best oxidation condition which gives rise to max asphaltene quantity via oxidative-condensation reaction of hydro carbonic molecules is for the reaction performed at 300±25^{o}C for 48 hrs.

Asphaltene amount was found to be decrease on increasing treatment time from 48 to 72 hrs this may be attributed to the possibility of thermal decomposition of such alkyl aromatic groups, in other words the thermal decomposition of large asphaltene molecules to smaller species(15).

Several experiments have been carried out to deduce the sulfur effect addition on asphaltene formation using anhydrous aluminum chloride as catalyst. Maximum asphaltene amount 17.801% was obtained from the treatment of oxidized (SLO) with 8% (Mbd) at 170^{o}C for 6 hrs using 1% aluminum chloride (table (3)). On adding 10% (Mbd) to the reaction mixture asphaltene has been failed to separated and calculated, this could be explained to the absence of system homogeneity, i.e. phase separation caused by the insoluble of added (Mbd) containing sulfur. Meanwhile, the treatment of previously oxidized (SLO) with 6% (Mbd) under continuous air stream oxidation at 300±25^{o}C(additionally oxidized) for 5 hrs gives rise max aphaltene content 46.371%, but it seems that asphaltene content decreases on increasing the percents of added (Mbd) to 8 and 10% respectively, table (4).

In other words the main reaction behind low asphaltene contents given in table (3) is attributed to the sulfurization reaction that could happen at moderate temperature range 170^{o}C in the presence of 1% aluminum chloride catalyst. Meanwhile, high temperature sulfur-dehydrogenation reactions for the treated hydro carbonic system are thought to be the predominant reactions behind asphaltene increasement as shown in table (4), while as sulfur content in reaction mixture increases by increasing of added (Mbd) percents (increasing of sulfur: hydrocarbon ratio) thus will increase the formation possibility of lower molecular weight sulfurized products rather than condensed aromatic macromolecules formation [22,23] as the seen effect of added (Mbd) in table (4).

Carbon activity assessment represented by methylene blue adsorption, iodine number, apparent density and humidity content and ash content are given in table (5). The given results indicate that the prepared activated carbon samples (C_1&C_2) posse's excellent adsorption properties and they are better than that of the comercial sample (C_{BDH}). This explains the capability of preparation of activated carbon possessing good specific properties from (SLO) as confirmed by Shawabkch [14] et. al. study.

On comparing the production yields of the prepared activated carbon samples (C_1&C_2) it seems that the production yield is directly proportional to asphaltene content, besides that (C_1&C_2) samples having lower ash content as a result of washing by 10% hydrochloric acid solution.

Table (1): Asphaltene percents for oxidized (SLO) different temperatures and treatment times.

Sample	Time (hr)	Temperature (±25^{o}C)	Asphaltene (wt%)
*L_o	0.0		0.0
L_1	24	100	1.210
L_2	48	100	1.831
L_3	72	100	2.210
L_4	24	200	2.510
L_5	48	200	3.101
L_6	72	200	4.501
L_7	24	300	5.010
L_8	48	300	7.500
L_9	72	300	5.321

*L_o-Spent lubricant oil.

Table (2): Compositional contents percentages of blow down material as given by Mishraq Sulfur Company[24].

Content	(wt%)
Total sulfur	92.3
Free sulfur	79.02
Combined sulfur with carbon	13.28
Total carbon	7.63
Bitumen	0.029
Ash	0.0693
Carbonized matter	20.98
Combined carbon with sulfur	7.60

Table (3): Asphaltene percents for oxidized (SLO) treated with different percents of (Mbd) at (170°C) using (1%) anhydrous aluminum chloride catalyst.

Sample	Mbd (wt%)	Asphaltene (wt%)		
		5hrs	6hrs	7hrs
L_1	2	9.510	13.010	8.632
L_2	4	9.560	13.590	13.001
L_3	6	11.781	14.753	12.211
L_4	8	12.10	17.801	14.021
L_5	10	---	---	---
$^*L_6$	8	0.0	0.0	0.0

$^*L_6$ - Spent lubricant oil treated thermally with (8%) (Mbd)

Table(4):Asphaltene percents for oxidized(SLO)additionally oxidized at (300°C) at different treatment times.

Sample	Mbd (wt%)	Asphaltene (wt%)		
		5hrs	6hrs	7hrs
L_7	2	4.021	13.271	31.101
L_8	4	10.421	11.051	33.211
L_9	6	46.371	35.391	33.091
L_{10}	8	18.621	15.012	17.631
L_{11}	10	8.011	7.511	10.412
$^*L_{12}$	6	5.000	5.620	8.671

$^*L_{12}$- Spent lubricant oil treated thermally with (6%) (Mbd)

Table (5): The properties of activated carbon prepared from the first and second treatment samples having maximum asphaltene content.

Sample	Asphaltene (wt%)	Density gm/cm^3	Ash (%)	Humidity (%)	I.N. mg/gm	M.B. mg/gm	Yield (%)
C_1	*17.801	0.262	2.09	2.14	1082	340	15
C_2	*46.371	0.387	1.15	1.08	1012	300	25
C_{BDH}	---	0.345	3.20	0.80	908	90	---

* Values from table 3 and 4

References

1- G. H. Dension and O. L. Harle, "Oxidation of Lubricant Oils at High Temperature", ***Ind. Eng. Chem***., 1949, **4(5),** 934-937.

2- Y. H. Ichikawa, ***Soc. Chem. Ind. Jpn. Suppl. Binding***, 1939, **39**, 405.

3- J. J. Knoterus**,** ***Inst. Petroleum, London***, 1956, **42**, 355.

4- M. G. Voronkov, N. S. Vyazankin, E. N. Deryagina, A. S. Nakhmanovich and V. A. Usov, "Reactions of Sulfur with Organic Compounds", Institute of Organic Chemistry, (1987), pp. 49-56.

5- Y. A. Shahab, A. A. Siddiq and K. S. Tawfiq, "The Synthesis of Carbon-Sulfur Bulk Compounds", ***Carbon***, 1988, **26(6),** 801-802.

6- M. Meyer, R. Beer and G. Lersch, ***Montash. Chem***., 1913, **34**, 1665.

7-Wm. G. Toland, Jr. J. B. Wilkens and F. J. Brutschy, ***J. Am.Chem. Soc***., 1953, **75**, 2263.

8- R. P. Napfer, H. A. Kaufman and P. R. Driscoll, ***J. Hetero- cycl. Chem.,*** 1970, **7**, 393.

9- L. F. Fieser and E. B. Hershberg. ***J. Am. Chem. Soc***., 1935, **57**, 1508.

10-L. F. Fieser and E. B. Hershberg. ***J. Am. Chem. Soc***.,1935, **57**, 1851.

11- M. W. Ahmedra, W. E. Marsh and R. M. Raw, L. S. U. Ag Center, Bulettin, (2001), 869.

12-A. Gracia, A. Gregorio, D. Boavida and I. Gulyurtlu, "Preparation and Characterization of Activated Carbon from Pine wastes Gasified in Pilot Reactor" Department of Inorganic Chemistry, University of Alicante, Spain (2003)

13-A. A. Hamdon, ***National Journal of Chemistry***, 2005, **18**, 216-155.

14-R. Shawabkch, A. Khaifaty, O. Khashman and Tarawnch, "Combined and Hybrid Adsorbents" 1st. ed., Springer Netherlands, pp. 195-200, (2006).

15-M. S. Al-Rhoo, "Preaparation of Activated Carbon from Spent Lubricant Oil by Chemical Traetment", M. Sc, Thesis, College of Education, Mosul University, (2009).

16-L. A. Ali and K. A. Al-Ghannam, (1981), "Investigation of Asphaltene in Heavy Crude Oils", ***J. Fuel***, 1981, **60**, 1043-1046.

17-AWWA Standard for Granular Activated Carbon, (1974), B604-74, Sec. 7, Approved by J. of American Water Work Association Board of Directors on Jan. 28.

18-"Test Methods for Activated Carbon" Rosterbau Int. Engine- ering GMBH, W. Germany Devtschos Arzeneibuch, 6th. ed.

19-ASTM D2854-70, "Standard Test Method for Apparent Density of Activated Carbon".

20-ASTM D2866-70, "Total Ash Content of Activated Carbon".

21-ISO, 5. 62, (1981), "Determination of Volatile Matter Content of Hard Coal and Coke".

22- G, Dougherty and P. D. Hammond, ***J. Am. Chem.. Soc***., 1935, **57**, 117.

23- D. B. Clapp***, J. Am. Chem. Soc.,*** 1939, **61,** 2733.

24- M. O. Al-Gobore, (1999)," Study of Sulfur Waste Obtained From Raw Sulfur Purification by Thermal Method,