Production of Activated Carbon from Spent Lubricating Oils by Chemical Treatment

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Abstract

In this work activated carbon of a good quality prepared from spent lubricating oils using oxidation condensation process. The oxidation of the spent lubricating oils conducted using 2% (wt%) of ($CoCl_2$, $ZnCl_2$ & $FeCl_3$) and in the presence of a stream of air or oxygen. The reaction mixture was heated at 350°C for (12, 24 & 36) hr, this followed by removal of uncarbonized materials under reduced pressure. The carbonization and activation was conducted at 550±25°C for 3 hrs and the ratio of the feedstock to NaOH (1:2). After the carbonization was completed, the reaction mixture was subjected to purification by treatment with distilled water, 10% HCl and distilled water till it gives neutral test to litmus paper. The samples were dried at 120°C for 24 hr and its physical properties were determined, the research work indicated that a good quality activated carbon was obtained when the oxidation of sample was conducted using 2% $FeCl_3$ for 36 hr.

الخلاصة

يتضمن البحث تحضير الكاربون المنشط من الزيوت المستهلكة عن طريق اجراء عملية اكسدة تكاثفية باستخدام 2% وزناً من ($CoCl_2$، $ZnCl_2$ و $FeCl_3$) وامرار تيار من الهواء عند 350°م لمدة (12، 24 و 36) ساعة، يلي ذلك عملية ازالة للمواد غير المكربنة باستخدام التقطير الفراغي. بعد ذلك يتم مفاعلة مخلفات التقطير الفراغي مع زيادة من هيدروكسيد الصوديوم [(2:1)، مادة اولية: هيدروكسيد الصوديوم] عند 550±25°م لمدة 3 ساعات. يتم تنقية المادة الناتجة عن طريق الغسل بالماء المقطر لحين التعادل ومن ثم المعاملة مع محلول 10% حامض الهيدروكلوريك وباستخدام عملية التصعيد الحراري لمدة ساعة واحدة، يلي ذلك عملية ترشيح للمادة الكاربونية وغسلها بالماء المقطر لحين التعادل. تجفف النماذج عند 120°م لمدة 24 ساعة، يلي ذلك عملية تحديد مواصفات الكاربون المنشط المحضر ومقارنتها مع كاربون منشط تجاري من انتاج شركة B.D.H.

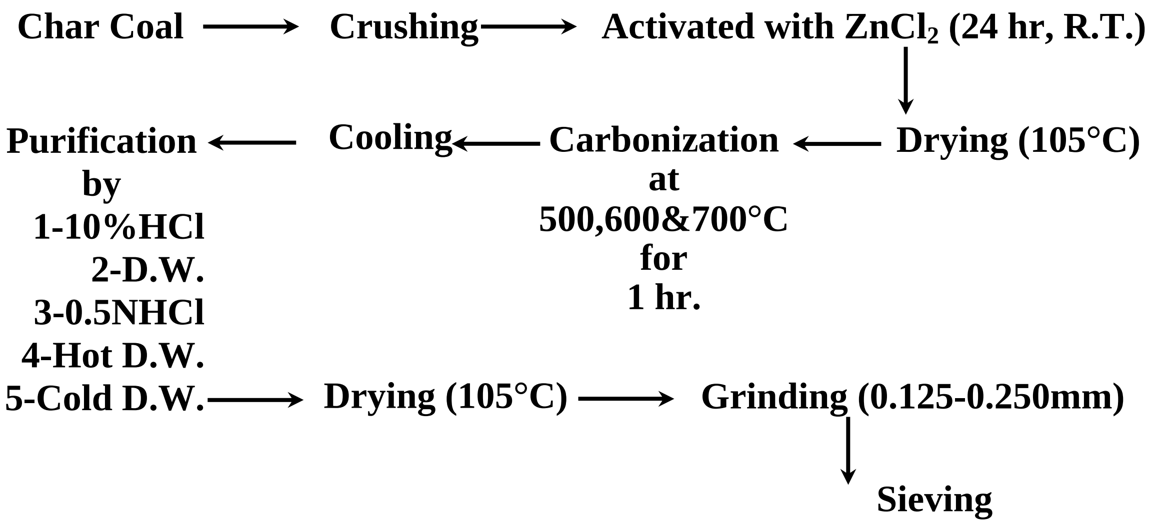
Introduction

Activated carbon, also called charcoal, is greatly involved in recent civilization. It is employed in the production of many products of great need every day; to remove impurities that cause an objectionable colour, taste, odour, heavy metals from drinking water and nutrients. Removal of leathal gas in the chemical ware fare (gas masks) and to separate/purify products in the chemical and pharmaceutical industries. Activated carbon covers a family of materials made from carbon which have the ability to attract and hold certain substance on the carbon surface. This ability is called “adsorption”. The adsorption process is an example of what is termed “chemical filtration”, where certain dissolved substance are removed from the water. Filter floss, on the other hand performs “mechanical filtration” by trapping solid particles suspended in the water.

The Feedstock most commonly used to produce the carbon are coal, petroleum residue and asphaltenes, peat, lignite, wood and other plants harvesting products. These feedstock containing recognizable amount of carbon. The hydrogen and other unrequired components are driven of by heating the feedstock under vacuum to produce a “char”. The char is then activated by exposure to an extremely hot gas, usually at about 800-1000°C, which may help to open the pores of all its type, by reaction with unrequired atom in the structure. The feedstock selected plus the manner in which it’s carbonized and activated, determines the characteristics of the finished activated carbon product and its cost. There are dozens. Of different kinds of activated carbon produced; of these only a handful will be well valuable to any particular application(1).

The literature contains many research work concerning activated carbon, which may include source of the feedstock, nature of carbonization processes, type of activation methods and texture of the product activated carbon which is given as follow;

O’Grady and Wennerbery, prepared activated carbon having exceptionally high surface area over 2500 m^2/gm and extraordinary adsorptive capacities. The carbon is made by a direct chemical activation in which petroleum coke and other carbonaceous sources are reacted with excess KOH at 400-600°C(2). Gercia *et. al.*, prepared activated carbon from mixing pine wastes with KOH in a pilot gasifier, without any previous treatment. They employ different alkali/char ratios varied from 1:1 to 1:4 at 725-800°C. After the activation process, the sample was cooled under N_2 and washed sequentially five times with (5%) NHCl and finally with distilled water till neutral litmus paper is indicated. Then the sample dried at 110°C for 24 hr(3). Ceren and Meral, prepared Activated Carbon as given below(4);



Chipofy and McConnachie prepared activated carbon from agricultural waste. Production involved carbonization of set quantity of the precursors in stainless steel trays that were in turn placed in a stainless steel box and heated in a steam atmosphere at 600, 650, 700, 750 and 800°C, ± 10°C for 30 minutes. Steam was generated by pumping water from a 20 liter jar into the steel box at different feed rates(5). Teng and Weng, prepared activated carbon from mesophase pitch powders by heat treatment and KOH etching at temperature 427°C. The activated carbon obtained has a surface area and pore volumes as high as 2900 m^2/gm and 1.7 cm^3/gm, respectively with high yields of approximate 30% Wt(6). Kobayashi *et. al.*, prepared activated carbon from brown coal and weathered coal with a relatively large quantities of sodium hydroxide or potassium hydroxide (alkali ratio to coal 2-2.5) under low temperature (500-700)°C than the conventional steam activated (900-1000)°C. For instance, active carbon with specific surface area of more than 1000m^2/gm were obtained with high yield (33-36%), when weathered coal was activated by NaOH (ratio 2.5-3.0) at

700°C. the effect of alkali could be, improved significantly by pre-heating at 500°C of coals, affording the active carbon with higher values of specific surface area (1300m^2/gm) at 550°C$^{(7)}$. Aweed, prepared activated carbon from residual petroleum products such as that of qaiyarah heavy crude oil (S about 7.45%) by employing direct oxidation with and/or by using certain type of catalysts ($CoCl_2$, $ZnCl_2$ and $FeCl_3$) at 350°C. Activation of the carbon after oxidation carried out at about 550±25°C by using different percentage of KOH. Catalysts used in the research ($CoCl_2$ & $ZnCl_2$) give a good result but not as the same as that of $FeCl_3$$^{(8)}$.

Prinsloo and Jiger, prepared activated carbon by the chemical and physical activation. Coke precursors (uncalcined) produced from waxy oil and medium temperature pitch were activated between 0.5 & 9 base coke ratio, 600-800°C heat treatment temperature (HTT) and 1.5 and 12 hr heat treatment time (HTt). All activation and cooling cycles were carried out under a constant flow of nitrogen$^{(9)}$. Rhamadhan *et. al.*, prepared activated carbon from (Beje asphalt) using several percentage of V_2O_5 and in the presence of a stream of air or oxygen at 350°C for 3 hrs. The carbonization and activation was conducted at 550±25°C for 3 hrs using excess NaOH$^{(10)}$. Al-Ghanam, *et. al.*, prepared activated carbon from (Heet asphalt) using several percentage of poly ethylene in the presence of air at 350°C for 3 hrs and then complete the carbonization and activation at 550±25°C using excess NaOH$^{(11)}$. Al-Ghanam, *et. al.*, prepared activated carbon from heavy petroleum residue using chemical treatment. The activity of carbon was performed through adsorption of acids in aqueous$^{(12)}$.

Experimental

1- Treatment of Spent Lubricating Oils

Exactly weighed (100gm) from spent lubricating oils were treated with 2% (Wt%) of ($CoCl_2$, $ZnCl_2$ & $FeCl_3$). The mixture was heated gradually till 350°C and kept for a period of 12,24 & 36 hr. Air was continuously passes during the heating period. The product from the oxidation was allowed to cool to room temperature. Unreacted part of the spent lubricating oils were removed by distillation under vacuum. The residual materials left behind were used as a feedstock for the activated carbon preparation.

2- Carbonization of The Oxidized Spent Lubricating Oils

The materials from above step were mixed with twice its weight of the carbonizing agent (Ca: NaOH) and (30-50) ml of distilled water. The mixture was heated gradually with continuous stirring till a thick bulk of the oxidized product were obtained. The heating was continued at 550±25°C for a period of 3 hrs. The product was cooled to room temperature and purified as in the next step.

3- Purification of The Carbonized Product

The carbonized materials were crushed carefully and washed with large amount of distilled water till it gives neutral test for litmus paper. The carbonized materials were mixed with a sufficient amount of 10% HCl solution. The mixture was heated under reflux for 1 hr, cooled, filtered and washed with distilled water. The washing continued till a negative litmus paper was indicated. The sample obtained was dried at 120°C for 24 hr and kept for property measurements.

4- Activated Carbon Measurements:

A- Measurement of Density

The density of the prepared activated carbon were determined by weighing 10 cm^3 of the carbon sample using graduated cylinder(20).

B- Determination of Ash Content

The ash content was measured by heating burning one gram of the prepared activated carbon sample in a porcelain crucible using an electrical furnace for five hours at temperature of 1000-1100^{o}C. the remained residue was considered as the ash content.(21)

C- Measurement of Humidity

One gram (exactly weighed) of the activated carbon was heated in an oven at 150^{o}C for 3hr. The difference in weight before and after heating operation was calculated as H_2O vapour in the sample(22).

D- Determination of Carbon Activity by Methylene Blue Adsorption Method

An exactly weight (0.1 gm) of the prepared activated carbon sample was added to an aqueous solution of 20 ppm methylene blue pigment in a conical flask. The solution was shacked by an electrical shaker for 24 hr at a temperature of 25°C till adsorption of methylene blue from its aqueous solution was completed a state of equilibrium was reached. The absorbance of the solution was determined using (UV-Visible Spectrophotometer) at λmax 665 nm. The procedure was carried out for the different types of the prepared samples for comparison purposes. The final concentration of methylene blue value for each activated carbon sample was calculated as the number at milligrams of methylene blue adsorbed by one gram of carbon(23).

E- Determination of Carbon Activity by Iodine Adsorption Method

The iodine number (In), which is the amount (in milligrams) of iodine adsorbed from its aqueous solution by one gram of activated carbon. The method involve:

1- One gram of the dried activated carbon transferred to 250 ml Erlenmeyer flask.
2- To the flask, add 10 ml of 5% HCl and swirl until the carbon is wetted.
3- Place the flask on a hot plate, bring the contents to a boil and allow to boil for exactly 30 minute.
4- Allowing the flask and contents to cool to room temperature add 100 ml of standardized 0.1 N iodine solution to the flask.
5- Immediately stopper flask and shake the contents vigorously for 30 minute.
6- Filter by gravity immediately after the 30 minute shaking period through filter paper.
7- Mix the filtrate in the beaker with a stirring rod and pipette 50 ml of the filtrate into 250 ml Erlenmeyer flask.
8- Titrate the 50 ml sample with standardized 0.1N sodium thiosulfate solution until the yellow color has almost disappeared. Add about 1 ml of starch solution and continue titration until the blue indicator color just disappears. Record the volume of sodium thiosulfate solution used(24).

$$\textbf{Iodine number} = \frac{\mathbf{X}}{\mathbf{m}} \qquad \mathbf{D}$$

Where:

m = is the weight of the activated carbon in grams

X = A – [2.2 Bx ml of thiosulfate solution used]

A = $N_1 \times 1269.0$

B = $N_2 \times 126.93$

N_1 = normality of iodine solution.

N_2 = normality of sodium thiosulfate solution.

D = correction factor.

Results and Discussion

Production of activated carbon usually carried out by carbonization of any organic compound that have high carbon content by a routine carbonizing method or modified ones. The choice of feedstock for carbonization processes is of a vital important to the uses and application since activated carbon is used in the removal of pollutants and support for catalysts, therefore in this research work liquid spent lubricating oils which have no economical value has been used. Lubricating oils contain a large molecules and various molecular structure that may include aromatic, naphthenic in a free form or condense and in some cases waxes is present. The carbonization process was conducted by direct oxidation of the material till solidification. The condensation process was conducted by using catalysts of different molecular weight and ions. Application of the catalysts aimed to increase the molecular weight (condensation and oxidation increase the oxygen functionality).

Condensation oxidation of lubricant as given by other worker may processed throw the the following reaction(18):

$$\text{Lubricants} \longrightarrow \text{resins} \longrightarrow \text{Asphaltenes}$$

The results of using Zinc Chloride for different period of times using the same feed stock showed little effect which could be explained in term of low activity of $ZnCl_2$ as lewis acid in the presence of lubricant addatives. The polymerization and oxidation reactions could be poisoned by side reactions and no increase in the carbon content as recognized. This appeared little change of the density and adsorptive properties.

On the other hand when Cobalt Chloride substituted Zinc Chloride for the same period of times and the same amount of lubricant, a certain improvement was recognized especially in the Iodine number and slight reduction in the density which may refer to a certain polymerization-oxidation reaction took place. The results also indicated a slight intensity in the feed stock after treatment.

However application of Ferric Chloride as lewis acid in the presence of oxygen gave a great polymerization-oxidation process which is recognized by the low density and high adsorptive for Iodine number and Methylene blue.

In addition the ability of condenseation and oxidation using different lewis acids is greatly affected by the molecular size of the cation and the effective charge (i.e. $FeCl_3$ > $CoCl_2$ > $ZnCl_2$).

The results of the investigation were given in table below.

Table: Properties of the Prepared Activated Carbon

Sample	**Cat.**	**Time hr**	**Density g/cm^3**	**Ash %**	**Humidity %**	**Iodine Number mg/g**	**Methylene Blue Mg/g**
1	-	12	0.441	1.610	0.821	150	15
2	-	24	0.440	1.521	0.800	200	19
3	-	36	0.440	1.512	0.790	225	22
4	$ZnCl_2$	12	0.432	1.471	1.101	450	60
5	$ZnCl_2$	24	0.431	1.521	1.001	525	63
6	$ZnCl_2$	36	0.431	1.621	1.231	575	65
7	$CoCl_2$	12	0.421	1.521	1.521	475	65
8	$CoCl_2$	24	0.401	1.550	1.201	560	68
9	$CoCl_2$	36	0.400	1.561	1.761	625	70
10	$FeCl_3$	12	0.322	1.521	1.201	750	73
11	$FeCl_3$	24	0.321	1.501	1.810	880	85
12	$FeCl_3$	36	0.301	1.536	0.981	950	93
B.D.H	-	-	0.345	3.200	0.800	908	90

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