

OXIDATIVE DESULFURIZATION OF GASOIL USING IMPROVING SELECTIVITY FOR ACTIVE CARBON OF RICE HUSK

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ABSTRACT

In view of the impact and risks of Sulfur in Gasoil on the combustion processes and Environmental pollution, A study was conducted to eliminated or reduce the percentage of sulfur in the Gasoil (bejji refinery),by Oxidative Desulfurization (ODS) procedure with hydrogen peroxide/acetic acid as oxidized reagent using active carbon of (Iraq rice Husk) as supported catalysts has been studied, active carbon for rice husk was activated chemically with (ZnCl₂, NaOH) and physically by (CO₂, N₂). The experimental results indicated that the oxidation desulfurization gave of a significantly reduced the value of sulfur (from 0.954 to 0.310)% and The maximum observed sulfur removal in the present oxidative desulfurization system was 77.3%. The rates of the catalytic oxidative desulfurization reaction were found to be increase with the temperature, hydrogen peroxide and surface area of active carbon increase.

Key Words : Desulfurization , Rice Husk , Active Carbon , Gasoil.

INTRODUCTION

The production of transportation fuel with low sulfur content has been a major concern in petroleum industry due to the stringent statutory environmental regulations Imposed by the government worldwide [1]. 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. Catalytic Oxidation Desulfurization is commonly used for sulfur removal from fuels . [2]

At present, the conventional industrial process for removing sulfur-containing compounds from middle distillate fuels is hydrodesulfurization (HDS). To meet new sulfur standards with (HDS) process, operation at higher temperature and higher pressure with more active catalysts is indispensable. Therefore, several new works have been continued for the removal of these refractory sulfur-containing compounds satisfactorily .such alternative processes include selective adsorption, biodesulfurization, oxidative desulfurization (ODS) and photo oxidation.[3], [4]

Among these alternative processes, the (ODS) process has received much attention as an alternative process for the desulfurization because of its two main advantages relative to the (HDS) process. The greatest advantage of ODS is its capability to carry out in the liquid phase under very mild temperature and pressure conditions. Another important feature of (ODS) is that the most refractory sulfur-containing compounds (which have less reactivity toward the (HDS) process. (ODS) generally lead to the formation of sulfoxide or sulfones that can be subsequently removal by conventional separation method such as extraction, adsorption or distillation, [5].

However, (ODS) is an attractive alternative to (HDS) technology due to its lower energy requirement for the removal of refractory sulfur species such as dibenzothiophene (DBS)..[6]. The (ODS) process has been studied in various promising systems of thiophenic compounds in the presence of H_2O_2 /organic acid system, H_2O_2 / heteropolyacid system , H_2O_2 / MoO system, H_2O_2 /Ti-zeolite system, Non-hydrogen peroxide systems and Emulsion catalysis systems [7].

Activated carbons are widely used as adsorbents. They represent extremely versatile adsorbents of industrial significance and are widely used in many applications which concern principally with the removal of undesirable species from liquids or gases. they are also used as catalysts or catalyst supports or gas storages the surface functional groups anchored on within carbons were found to be responsible for the variety in physicochemical and catalytic properties of the matters considered. Oxidation increases the selectivity of organo-sulfurs adsorption via an increase in the number of specific adsorption centers, **[8]**.



Rice husk (RH) are an agricultural waste produced as by-product of the rice milling industry in Iraq, since, the main components of rice husk are carbon and silica (15-22%) SiO2 in hydrated amorphous form like silica gel, it has the potential to be used as an adsorbent, when rice husk is burnt, about 20 wt% of the husk remains as ash. The rice husk ash has more than 95 wt.% of silica with high porosity and large surface area, Using adsorbents to selectively remove the sulfur compounds in liquid hydrocarbon fuels is one of the promising approaches, as the process can be conducted at ambient conditions without using costly hydrogen. [9], [10].

In the present study, Activated Carbon of Rice Husk (ACRH) were examined for (ODS) of a Gasoil fuel (bejji refinery), in the presence of atmospheric oxygen, with the oxidized agent was also conducted at ambient conditions. This method combines the oxidation of the sulfur compounds and adsorption method , and adsorptive desulfurization of the oxidationtreated fuel over (ACRH).

EXPERIMENTAL

Materials and Procedure

Chemical : All chemicals were commercially obtained and used as they received without further purification. Rice husks from aldiwanigah governorate mills- Iraq, gasoil (beji refinery), acitic acid, hydrogen peroxide (30%), sodium hydroxide (BDH), zinc chloride, magnesium acetate and sodium carbonate (fluka).

Instruments : FTIR -8400 spectrophotometer (BRUKER) was used for ACRH Study. XR analyzes (thermo electronic) was used for determinate the S% conversion quality control laboratory (Beji refinery), furnace (carblat) u.k, and molecular sieves (Japan).

Preparation of activated carbon (ACRH) :

Chemical activation of carbon carried out by using zinc chloride (ZnCl₂) and sodium hydroxide (NaOH). Physical activation were carried out via nitrogen gas (N₂), carbon dioxide gas (CO₂) and atmospheric oxygen. type of activated for carbon were influenced due to increasing the surface area with activated process.



Preparation of active carbon AC in presence of atmospheric oxygen :

Ten grams of rice husks was purified by washing with distilled water twice to remove the dust and other impurities then dried at 90 c^0 for 24 hours in oven .The chemical activation started by immersion in zinc chloride solution (20%) for 72 hours. The rice husks were washed later many time with water to remove chlorine. Physical activation processes were carried out by gradual ignition starting **at 200** c^0 for an hour , 300 c^0 for another hour and finally at 400 c^0 for two hours .then kept till usage.

Activation of active carbon in the presence of zinc chloride at N2 atmosphere :

The active carbon prepared and treated as described previously and treated as in like as well ,but in the presence of N_2 which used after purification from moisture and impurities using a system pre - constructed for this purpose .

Activation of active carbon in the presence of zinc chloride at CO₂ atmosphere :

The active carbon prepared as described previously and treated as the same as well, but in the presence of CO_2 which used after purification from moisture and impurities using a system pre- constructed for this purpose.

Activation of active carbon in the presence of sodium hydroxide (NaOH). At an inert atmosphere of nitrogen (N₂) and CO₂ :

Activated carbon was immersion in sodium hydroxide of 2M concentration for 72 hours. them treated with distilled water till got a PH = 7 The treatment carried out as in previously. **The other step** is the activation of active carbon in the presence of (NaOH + CO2) as described in the Previously.

Activation of active carbon in the presences magnesium acetate $(CH3COO)_2Mg$ at atmosphere N_2 .

4 grams of active carbon dried at $90C^0$ for 24 hours . 2grams of magnesium acetate was added and mixed with active carbon by using mechanically stirrer at moderate speed . Them ignited at $200C^0$ for half an hour and at $300C^0$ for half an hour also while at $400C^0$ for 3 hours. under Nitrogen atmospheric and keep till use .

Oxidative desulfurization procedure: 100 ml of gasoil (bejji refinery) were placed at around -bottom flask of capacity 250 c.c. The sample content of sulphre was of 0.954%. 1gm of



activated carbon was charged to the sample, 10 ml of 30% H₂O₂ as an oxidizing agent was added to the flask followed by 5ml of CH₃COOH as a co-catalyst .The mixture was refluxed for 3 hrs at room temperature using a magnetic stirrer at moderate speed(700 rpm/minute), while stirring 2grams of Na₂CO₃ was added to the mixture . The mixture after reflux was transferred to separating funnel to isolate the aqueous layer from the organic layer . The former process was repeated many times for the purpose of desulfurization using oxidation via many types of activated carbon which are prepared as described previously

Ash - content determination at activated carbon

Activated carbon was dried at 100 C^0 for 2 hrs . 1gm of activated dry carbon was ignited at 950 C^0 for 30 minute. ash-content was calculated via the following relationship :

%A sh= $\frac{\text{Ash wt}}{\text{Active carbon wt}} \times 100$

Density Evaluation :

Estimated using the following expression

Totaldensity= sample.wt wt.ofdisplacedwater

FT-IR spectroscopy Study :

FT–IR spectra for **ACRH** before and after carbonize Samples were recorded using KBr disc, AC loading of 0.3wt .

	ULL	
Properties	Method	Result
Sp.G in 15 C⁰	D-1298	0.840
Flash. Point C ⁰	D-93	54.
API - Gravity		37
Total sulfur content Wt%	D-1266	0.954
Diesel Index	IP- 21	55.0
Cetane Index	D- 976	53.0
Pour Point DEG C ⁰	D-9 7	-9
Roms Bottom C.RES Wt%	D-524	0.2
Colour ASTM	D-1500	2.0
Copper Strip Corrosion	D- 130	2.0

 Table 1. Some physical and Chemical Properties for the Gasoil Fuel sample used.



Determination of Surface area : Specific surface area was measured using ethylene glycol and mono ethyl ether method (EGME). [11,12]

RESULTS AND DISCUSSION

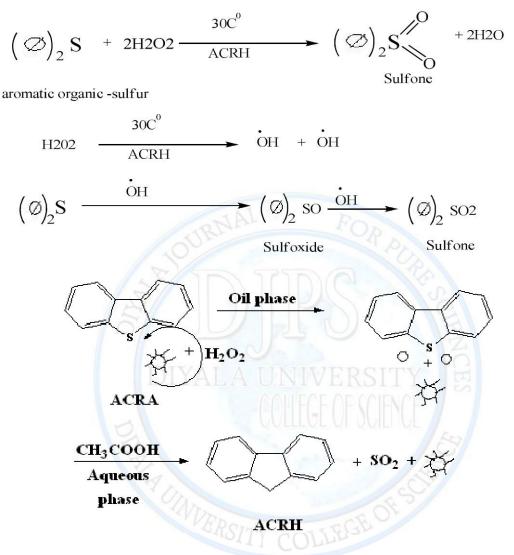
Mechanism of removal of sulfur: The removal of sulfur from petroleum and other fossil feed stocks is a very important global issue in order to decrease atmospheric pollution caused . The (ODS) process has been studied in various systems, including oxidant (Hydrogen Peroxide) with organic acids the catalytic oxidation of the sulfur compounds existing in the liquid hydrocarbons to form the corresponding sulfones and/ or sulfoxides improves significantly the adsorptivity of the sulfur compounds over activated carbon Scheme (1), because the activated carbon has higher adsorption affinity for the sulfones and sulfoxides compounds due to the higher polarity of the former than the latter. This (ODS) method is be more energy efficient ,cost effective and environment friendly in comparison with other (ODS) methods reported in literature and thus could be a more promising process for deep desulfurization of the liquid hydrocarbon fuels.[13]



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Scheme 1. Mechanism of Organo- Sulfur Oxidation

Type of Activated Carbon on Oxidation of Gasoil :

The Composition and properties of the (ACRH) are summarized in the Table 2. Activated carbon is a material with well-developed porous structure, large specific surface area and many surface oxygen-containing functional groups .To elucidate the effect of activated carbon pore structure on the adsorption of gasoil in acetic acid and hydrogen peroxide solution [14],six activated carbons sample were obtained and characterized. The structural



characteristics of the selected activated carbons were calculated from N_2 and CO_2 adsorption isotherms at 450 C^0 and they are summarized in Table 2. In order to understand the role of adsorption of gasoil in the oxidation reaction on activated carbon . Adsorption capacity of the selected activated carbons for gasoil in solution was also summarized in Table 4.

Activated	Chemical	Physical	Surface area	Ash	Density	PH
Carbon	Activated	Activated		%		
ACRH	ZnCl ₂	O 2	446 m ² /g	27	0.42	6.65
ACRH	ZnCl ₂	N2	567 m ² /g	17	0.48	6.64
ACRH	ZnCl ₂	CO ₂	$540 \mathrm{m}^2/\mathrm{g}$	20	0.44	6.44
ACRH	NaOH	N2	$548 \mathrm{m}^2/\mathrm{g}$	22	0.45	10.45
ACRH	NaOH	CO ₂	512 m ² /g	20	0.43	10.10
ACRH	Mg (CH3C00)2	N2	485 m ² /g	22	0.40	10.00

Table 2. Properties of Active carbon from Rice Husk

Effected of Hydrogen Peroxide (H2O2) on Gasoil Desulfurization: The oxidation of Gasoil was carried out with hydrogen peroxide (H₂O₂) as catalyzed by different amount (5, 10 15, 20) ml, in previous studies (H₂O₂) was found to be effective in the oxidation of organic sulfur. Changes of the reaction results are depending on the amount of (H₂O₂). However, the Gasoil conversion (removal sulfur) increased markedly until H₂O₂ =10 ml, which is the best. Table 3. and Fig 1.

Table 3. % Conversion of Sulphur in Different amount of H₂O₂

H ₂ O ₂ ml	% Conversion		
0	0.954		
5	0.582		
10	0.380		
15	0.301		
20	0.463		
ACRH with : ZnCl ₂ + N ₂ 1			



 $\begin{array}{c} 1.2\\ 1\\ 0.8\\ 0.6\\ 0.6\\ 0.2\\ 0\\ 0\\ 0\\ 5\\ 10\\ 15\\ 20\\ 25\\ H2O2 \text{ ml} \end{array}$

Fig 1. Impact of H₂O₂ on the S% Conversion

Chemical activation of Carbon: Carbon has been activated chemically by (ZnCl₂) Solutions , NaOH and Mg (CH₃COO) . Which leads to impregnation in the raw material (lignocellulose) largely . Due to an increased surface area because volatile material immigration .Fig (2) , Table (2)

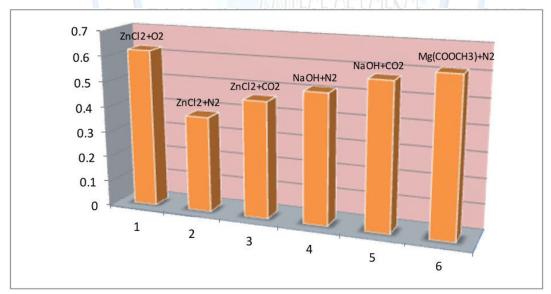


Fig 2. Impact of activated system kind on S% conversion



Physical activation of Carbon:

Stream of N2 and CO2 gases through active carbon at high temperature lead to increased of surface area . Besides an expiration of particles size. Via expelling the carbonic gases from raw material. Fig (3) ,Table (2)

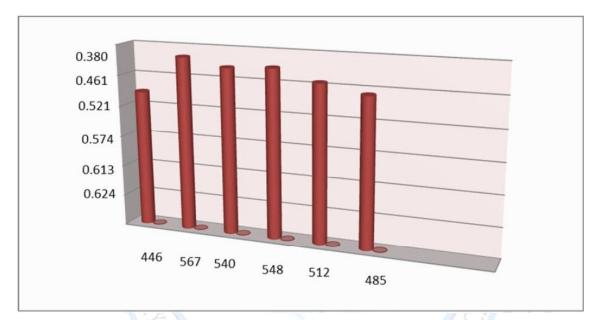


Fig 3. Relationship between S% Conversion and Surface area of (ACRH)

Oxidative Desulfurization of Gasoil :

Sulphide removal has been done by coupled processes include Chemical Oxidation by Hydrogen Peroxide and after it was adsorption on active carbon . The Result of their study shows high efficiency of sulpher removal from (0.954 to 0.380) with short time , low cost . Temperature effect and PH effect were investigation $50C^0$ and PH 6.64 was the optimized conditions , using 10ml Oxidized agent with 567 m² / g surface area in ZnCl₂ + N₂ . Table 4, Fig 4.



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NO	ACRA Activated System	PH	Surface area	% Conversion S	
1	ZnCl2+O2	6.65	446 m2/g	0.624	
2	ZnCl2+N2	6.63	567 m2/g	0.380	
3	ZnCl2+CO2	6.45	540 m2/g	0.461	
4	NaOH + N ₂	10.06	548 m2/g	0.512	
5	NaOH + CO2	10.43	512 m2/g	0.574	
6	Mg (COOCH3)2 + N2	10.21	485 m2/g	0.613	
1 Oxidative at 50 C ⁰ temperature 1					

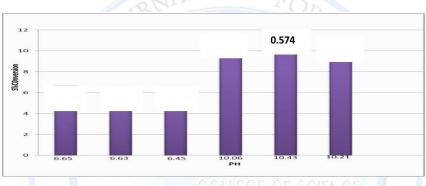


Fig 4. Relationship between S% Conversion and PH

Effected of temperature on oxidation reaction:

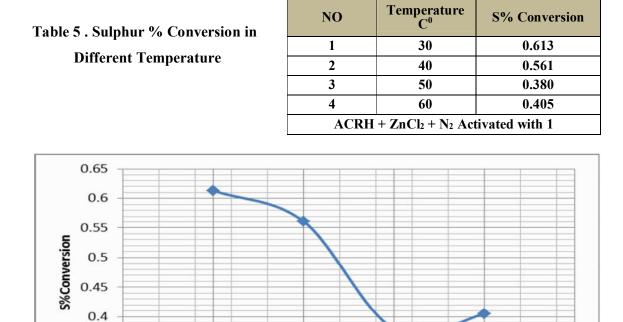
To examine the effect of reaction temperature on the performance of the desulfurization process. The effect of temperature on removal of the organo-sulfurs was studied at different temperatures. Table 5. Fig.5 shows the efficiency of desulfurization in the (ODS) reaction versus the reaction time at four different temperatures (30 40 , 50 , 60) C⁰. An increase in the reaction temperature from 30°C to 50°C led to a remarkable increase in the reaction rate, but oxidation at higher temperature 60 C0 was unfavorable due to the decomposition of hydrogen peroxide to undesirable side products other than hydroxyl radicals which decreases the efficiency of gasoil desulfurization process and affects the quality diesel fuel , In view of these results, the optimum reaction temperature was at $50C^0$. [15]



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40

Temp.c

50

60

FT-IR Spectra of (ACRH) :

20

30

0.35

0.3

FT-IR technique was used for the evaluation of active groups added to the activated carbon in such way that to indicate the effect of activations processes and ignitions ones upon the viability of active carbon an active surface agent . Fig (6). show that there is no much difference between the surface chemistry of the (ACRH) in different activated. A shoulder peak appears at3423 cm- which can be a scribed to O-H stretching vibrations of carboxyl groups. The peaks at 1848cm- . And 2921cm- due to the presence of aliphatic CH , CH₂ and CH₃ groups can be found for both different AC samples, also the Present Peaks in the region 1718cm to the C=O stretching vibrations due to the Presence of carboxyl groups, The peak at 1617cm- is indicative of the Carbonyl groups such as Quinone or Ionoradical structure **[16]**.

70



100 BRUKER 8 Transmittance [%] B 09 20 8 BRUKER 96 Transmittance [%] 85 90 A 85 8 15 2924.63 379 29 3423.85 465.24 508.4 500 3500 3000 2500 2000 1500 1000 Wavenumber cm-1

Fig 6. FT- IR Spectral A: AC before carbonize B: ACRH after carbonize at 400C⁰

CONCLUSIONS

The oxidative desulfurization of Gasoil using oxidizing agent H_2O_2 and organic acid CH₃COOH on (ACRH) as supported catalyst was studied. The various operating parameters such as kind of activation of carbon , reaction temperature , surface area , amount of oxidized agent and PH influences on the performance of the (ODS) process. which examined, it was found that the sulfur removal increases with increasing surface area due to an increase in oxidation reaction rate of sulfur containing compounds. Sulfur removal increases by increasing H_2O_2 which favorites for using 10ml , also the optimum temperatures for oxidative reaction is $50C^0$ and kind of physical and chemical activation, the maximum observed sulfur removal in the ZnCl₂ - N₂ of activated system , which have more surface area at $50C^0$.



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الإزالة الكبريتية بالأكسدة من زيت الغاز بواسطة تحسين الانتقائية للكاربون الفعال من

قشور الرز

د بطارق عبدالجليل منديل السيد لؤي فلاح حسن قسم الكيمياء – كلية العلوم – جامعة الأنبار E-Mail : tarik <u>jm@yahoo.com</u>

نظر التأثير وخطورة الكبريت في زيت الغاز) الديزل (في التلوث البيئي و عمليات احتراق الوقود ، أنجزت هذه الدراسة لأزالة الكبريت أو تقليل نسبته في وقود زيت الغاز) مصافي بيجي (بعملية الأكسدة للأزالة الكبريتية بأستخدام بيروكسيد الهيدروجين كعامل مؤكسد وحامض الخليك كعامل مساعد، وبوجود الكاربون الفعال المحضر من قشور الرز العراقي كعامل مساعد ساند

الخلاصة DIYAL A الخلاصة

تم تنشيط الكاربون الفعال بالطريقة الكيميائية بواسطة (ZnCl₂, NaOH) وفيزيائيا بواسطة (CO₂, N₂) . أظهرت نتائج البحث انخفاض نسبة الكبريت بمقدار 77.3 % من (0.909 to 0.310) ، وأفضت الدراسة الى أن زيادة الأزالة للكبريت من وقود زيت الغاز تزداد مع زيادة درجة الحرارة للتفاعل ،العامل المؤكسد والمساحة السطحية للكاربون الفعال . كما بينت الدراسة امكانية استخدام قشور الرز في المساعدة على تقليل التلوث البيئي من خلال إزالة الكبريت من وقود الديزل بأستخدام مواد على شكل الى الجدوى الأقتصادية لهذة الطريقة في المساهمة بتقليل التلوث البيئي وزيادة كفاءة وقود الديزل بأستخدام مواد على شكل فضلات.

كلمات مفتاحية : الأزالة الكبريتية ، الكاربون الفعال ، كاز أويل ، قشور الرز