Production of Green Fuel: A Digital Baffle Batch Reactor for Enhanced Oxidative Desulfurization of Light Gas Oil Using Nano-Catalyst

Hameed, Shaymaa Ali
Chemical Engineering Department, College of Engineering, Tikrit University, Tikrit, IRAQ

Nawaf, Amer T.; Mahmood, Qahtan A.
Petroleum and Gas Refinery Engineering, College of Petroleum Process Engineering, Tikrit University, Tikrit, IRAQ

Abdulateef, Layth Talib
Chemical Engineering Department, Middle Technical University, Baghdad, IRAQ

Jarullah, Aysar Talib*[+]
Chemical Engineering Department, College of Engineering, Tikrit University, Tikrit, IRAQ

Mujtaba, Iqbal M.
Chemical Engineering Department, Faculty of Engineering & Informatics, University of Bradford, Bradford BD7 1DP, UK

ABSTRACT: *A Digital Baffle Batch Reactor (DBBR) for oxidative desulfurization (ODS) reactions is designed and applied here to reduce the sulfur concentration presented in Light Gas Oil (LGO) based on a novel homemade nano-catalyst (Copper Oxide (CuO)/Activated Carbon (AC)). With efficient impregnation, good pore size distribution, high activity, and higher surface area, the designed nanocatalyst (CuO/AC) demonstrated excellent catalytic efficiency. To evaluate the effectiveness of nanocatalyst (prepared experimentally), several experiments related to ODS reactions using the digital baffle batch reactor are carried out under moderate process conditions (reaction temperature (100, 120 and 140 °C), contact time (15, 30, and 45 min) and oxidant (H_2O_2) amount (2, 3 and 5 mL)). The experimental outcomes indicated that increasing the reaction temperature, batch time, and oxidant amount led to the reduced sulfur concentration of oil feedstock leading to a greener fuel. The efficiency of sulfur conversion is reported to be 83.1 % using the modified nano-catalysts and new reactor (DBBR) at reaction temperature 140 ^oC, batch time 45 min, and H_2O_2 amount of 5 mL. So, such new results using DBBR for ODS reactions based on CuO/AC as a new modified nanocatalyst have not been reported in the public domain and it is considered new results.*

KEYWORDS: *Nanocatalyst; Copper oxide; Oxidative desulfurization; DBBR reactor; H_2O_2.*

***** *To whom correspondence should be addressed.*
+ *E-mail: A.T.Jarllah@tu.edu.iq*
1021-9986/2023/3/740- 12/$/6.02

INTRODUCTION

The crude oil feedstock or its derivatives is considered to be a global source of energy. The majority of crude oil is used to make transportation fuels including gasoline, diesel (light or heavy gas oil) and jet fuel. Such oil feedstock contains a complex blend of gaseous, liquids and solid organic components such as S, N_2, and O_2 in addition to metallic compounds (mainly vanadium, nickel, copper and iron). The sulfur content of crude oil and the specific gravity are regarded as the main factors limiting the quality of crude oil [1,2]. Crude oil or oil fractions have high sulfur components namely R–SH, R–S–R', R–S–S–R' and C_4H_4S. These compounds are unwanted compounds owing to several problems which pollute the environment, corrode the machines, pipes and equipment. Furthermore, their emissions are extremely hazardous to human health and the environment. Moreover, these contaminants poison the catalysts and decrease the catalytic performance [3-5]. Therefore, new techniques (new catalyst, new configuration of the reactor or new process) are developed, designed, applied or proposed for the purpose of removing sulfur under moderate operating conditions, low cost, and reduced environmental pollution. ODS is a desirable and preferred process to remove refractory sulfuric compounds which are difficult to remove by HDS [6-7]. Due to the prescribed level of low sulfur requirement oxidative desulfurization (ODS) process receives huge attention due to the low cost and safe operating conditions used in such process. In ODS process, mild reaction conditions can be used for the oxidation reaction of sulfur compounds with low temperatures (<373K), low pressure (~1 bar), and without requiring hydrogen as in the Hydro Desulfurization Process (HDS) [8-9]. In (ODS) process, the organic sulfur-containing compounds can be oxidized to their corresponding sulfone or sulfoxide using the appropriate oxidant and catalyst, then the oxidized products can easily be separated due to high polarity [10]. *Argam* and *Leonid* [11] have investigated the oxidation reaction of dibenzothiophene (DBT) found in real fuel (gas oil) by using porous aromatic frameworks modified by sulfonic groups (PAFs) as catalysts, hydroperoxide (H_2O_2) as an oxidant for ODS process under moderate operation conditions (70°C of temperature, 60 min of duration time and 1 atm of pressure). DBT has completely oxidized and sulfur content in fuel reduced up to ultra-low values (7 ppm). *Rezvani et al.* [12] have studied the oxidation reaction of total sulfur that presented in the gasoline by using $PMoCu/MgCu_2O_4$-PVA as catalyst, hydrogen peroxide + acetic acid (H_2O_2/AcOH) as an oxidant under mild operation conditions (temperature 25-40°C, 1 atm pressure). They founded that increasing the temperature to 35°C, higher sulfur conversion could be obtained, while considerable changes were not obtained at 40°C. Also, sulfur removal was increased with increasing the reaction time. *Nawaf Et Al.* [13] Have Investigated The ODS process f Light Gas Oil (LGO) with (2% Co_3O_4/γ-Al_2O_3) as composite catalyst in the presence of air as an oxidant with moderate operating conditions (temperature of 403–473 K, liquid hourly space velocity (LHSV) = 1–3 h^{-1}, initial concentration of sulfur = 500–1000 ppm). They observed that at low temperature, the DBT conversion was very low, then increased gradually with increasing reaction temperature from 403 K to 473 K and the rate of DBT oxidation increased to 78% at 473 K, LHSV = 1 h^{-1} and 1000 ppm (optimal condition of sulfur conversion). Also, they pointed that increasing the LHSV has an adverse impact on DBT conversion (the DBT conversion at 1000 ppm and 473 K is 75.1%). Note that, at LHSV = 2 and 3 h^{-1} DBT conversions were reported to be 55.9% and 43.7%, respectively. *Guo et al.* [14] have investigated the oxidation reaction of diesel fuel by using air as an oxidant, tert-butyl hydroperoxide (TBHP) as a radical initiator at moderate conditions (ambient temperature and atmospheric pressure) in the presence of isobutyl aldehyde. They observed that at 5 mmol of a molar fraction of TBHP used, the DBT conversion has increased. *Jian* and *Wei Ding* [15] have studied the effectiveness of oxidative desulfurization for the removal of dibenzothiophene from diesel fuel (500ppm of sulfur content) by using the metal-organic frameworks HPW/MOFs as a catalyst combined with oxidant O_2. The oxidative process applied under operation conditions of (90°C of temperature, 180 min of reaction time, and 1 atm of pressure) leads to 90% removal of DBT from fuel oil. *Kobotaeva et al.* [16] have studied the oxidative desulfurization catalytic of fuel oil containing 1–1.3 wt% of sulfur occurred under mild operation conditions (the temperature is 50°C, reaction time is 90 min at atmospheric pressure) by using a nano-composite catalyst of multi-wall Carbon Nano Tube (CNTs) activated by nickel and cobalt. The molar ratio of sulfur of the feed to the oxidizing agent is 1:4. The achieved level of sulfur removal was higher than 75%. *Ahamd et al.* [17] studied

the oxidative desulfurization (ODS) of modeled and real oil samples was investigated using manganese-dioxide supported, nano-magnetic graphene oxide. Nano composite catalyst (MnO_2/ MrGO) is utilized in the presence of H_2O_2/HCOOH as oxidation system. The best conditions for maximum removal of dibenzothiophene (DBT) from modeled oil samples were found to be efficient at (40 °C temperature, 60 min reaction time, 0.8 g catalyst dose/100 mL of feedstock, 2 mL of H_2O_2 /formic acid), which MnO_2/MrGO exhibited intense the desulfurization activity up to 80% in modeled sample. Under the same set of conditions, the removal observed was 41% DBT in the presence of Graphene Oxide (GO) as the catalyst without nano-magnetic graphene oxide which clearly indicated that the advantage of wing MrGO in the composite catalyst. Under above conditions, sulfur removal in real oil samples including diesel oil, gasoline, and kerosene was found to be 67.8%, 59.5%, and 51.9%, respectively. *Cedeno et al.* [18] have studied the ODS catalytic reactions of benzothiophene in diesel conducted with the presence of various catalysts using a model diesel (hexadecane) and actual diesel fuel. ODS activities in model diesel for a series of V_2O_5 catalysts supported on alumina, titania, ceria, niobia and silica, were evaluated. Results showed that the oxidation activity of DBTs depends on the type of the support used. Such behaviour is attributed to the support used in the following order: alumina > titania > niobia > Al–Ti mixed oxide > SBA-15. While the oxidation activity of DBTs for V catalyst supported on niobia or alumina presented had higher catalytic activity than all the other catalysts (niobia > alumina > SBA-15 > titania > ceria > Al– Ti mixed oxide). *Rivoira et al.* [19] have studied the ODS catalytic activity of sulfur removal found in the gas oil by using Fe-modified mesoporous catalysts, different materials such as SBA-15, MCM-48, CMK-3 and CMK-1 as a catalyst supports. The catalysts tested in the oxidative desulfurization of different sulfur compounds were, benzothiophene, dibenzothiophene and 4,6-dimethyl dibenzothiophene. The catalyst prepared using CMK-3 as support was the most active for the ODS reaction. Also, the results obtained here, pointed that the Fe-CMK-3 and Fe-SBA-15 showed to be potential catalysts for the ODS of refractory sulfur compounds. *Ugal et al.* [20] investigated the oxidative catalytic activity of sulfur compounds found in the gas oil by using new types of nano-composite catalysts of (Fe_2O_3/ (Ac) and Pd/ (Ac)). They found that the catalytic activity of sulfur removal in the gas oil reached to 71.20% and 66.0% by wing Fe_2O_3/Ac and Pd/Ac respectively.

The oxidative desulfurization (ODS) operation is classified as one of the most significant process that has recently been utilized for these purposes. In this process, organic sulfur components (RSH, R–SH, R–S–R', R–S–S–R' and C_4H_4S) are transformed into identical oxidized sulfur compounds (RSO_2R, R−S(=O)−R' and R_2S_2) which remain in the product. Oxidants used related to the oxidative desulfurization operation were carried out utilizing several oxidants materials, manly H_2O_2, ozone, O_2 and air. All of these oxidants have been employed due to lowest environmental impact and cost compared to other oxidants [21-23].

In addition to the selection of oxidants, the catalysts used to remove sulfur components should be chosen carefully in the oxidative desulfurization operation. For instance, MnO or CuO based catalysts have better activity toward sulfur removal during ODS reactions than other active metals based on its high adsorption performance [24-26]. As a result, nano-catalysts that have high activity than bulk substance have recently attracted a lot of attention by many authors and several industrial studies [27-28]. Finally, the reactor design/configuration is very important for efficient reduction of sulfur components from the fuel.

The novelty of this research can be summarized as follows: copper oxide (II) or cupric oxide (CuO) is a strong active component with excellent metals. Cupric has the ability to increase the pore volume and pore size of the catalyst and more hardness can be generated providing enough active sites for the reaction. In this study, a new nano-catalyst (CuO/nano-AC) loaded with metal oxide as an active component over nano-activated carbon (that has not been reported in the public domain for sulfur removal) from light gas oil by hydrogen peroxide H_2O_2 (as oxidant) for ODS reactions, will be prepared and studied. CuO/nano-AC is expected to have a high performance toward oxidation desulfurization process. Cupric oxide has an excellent high activity and reusability owing to its useful effects upon the surface area and the acidic-site strength of the appropriate heat treatment temperature at moderate operating condition giving high conversion of sulfur compounds. New reactor design (DBBR) is designed

to evaluate the catalyst prepared via oxidative desulfurization process and getting high removal of sulfur resulting green fuel. As well as, all the above points described above (new reactor, new nano-catalyst and using ODS process) have not been met together in one process and it is considered to be the first study in such area.

With the above backdrop, the present study is mainly focused to combine the issues mentioned above (new reactor and new nano-catalyst) in order to reduce the concentration of sulfur existent in LGO fuel to produce green fuel. Copper oxide loaded on activated carbon (CuO/AC) as a synthetic modified nano-catalyst is locally prepared and used in a digital baffle batch reactor to carry out the ODS reactions under mild operating conditions using H_2O_2 as an oxidizer agent (reaction temperature (100-140 ^oC), time of oxidation (15-45 min), dosing of oxidant (H_2O_2) (2-5 mL) and speed of impeller is 650 rpm with initial sulfur concentration of 1200 ppm.). Note, the homemade nano-catalyst is novel and has not been used in the past and the digital baffle batch reactor had seen limited use in the past [24].

EXPERIMENTAL SECTION

Substances

Dibenzothiophene (obtained from BDH Chemicals Ltd) is used for evaluating the sulfur components' reactivity by ODS operation and dissolved in the oil feedstock (model light gas oil). Activated Carbon (AC) nanoparticle is employed as a support material to build the nano-catalyst. Table 1 below displays the main characteristics of AC (bulk density (Bd), pore size (Pz), surface area (Sa), pore volume (Pv) and particle shape (Psh)). The main physical properties of the oil feedstock (LGO) that has been obtained from Erbil north refinery (KAR Company)-Iraq are illustrated in Table 2.

H_2O_2 is utilized as an oxidizer source (supplied from Sinopharm Chemical Reagent). Copper(II) acetate with a purity of 99 percent was employed as an active material in this research which has been obtained from Sigma Aldrich.

Table 1: Activated carbon nanoparticle specifications.

Characteristics	Unit	Activated carbon
Bulk density (Bd)	g/cm^3	0.544
particle shape (Psh)	-	Sphere
Pore size (Pz)	nm	2.5987
Surface area (Sa)	m^2/g	557.543
pore volume (Pv)	cm^3/g	0.37543

Table 2: Characteristics of the model oil feedstock (LGO).

Properties	Values
Vapor pressure at 37.8 ^oC (Kpa)	69
Specific gravity at 15.5 ^oC	0.872
Octane number, Motor	73.2
Octane number, Research	78.4
Sulfur concentration (ppm)	0.34
Fractionation Properties	(^oC)
IBP (^oC)	200
Volume Distilled (10%)	220
Volume Distilled (50%)	261
Volume Distilled (90%)	310
EP	323

Preparation of Catalyst

The following steps were followed for making copper oxide over activated carbon (5 % CuO/ AC): 1.45 g copper (II) acetate $Cu(COCH_3)_2$ is dissolved in 65 mL deionized water during the dissolution process (provided by *Samarra Company*-Iraq). The solution is agitated with a magnetic stirrer at 550 rpm for 90 minutes without being heated to ensure salt solubility in deionized water. 15 g of AC is placed in a beaker, and the produced mixture is added to the activated carbon and stirred for 90 minutes at ambient temperature by a magnetic stirrer to obtain a homogeneous mixture of impregnated active carbon. After that, the impregnated mixture is placed in a crucible and placed in the furnace to be dried and calcined issue. To begin the drying and calcination process, the temperature is raised to 160°C for 2.5 hours, then to 300°C for 1.5 hours, 450°C for 1 hour, and finally to 590°C for 3 hours. Figs. 1 and 2 depict the flow chart and catalyst preparation stages.

Procedure for oxidative desulfurization in DBBR

The digital baffle batch reactor is domestically built to enhance the mass and heat transport through the oxidative desulfurization process. The College of Engineering at Tikrit University in Iraq has constructed such new design. The design of DBBR can be pointed as follows:

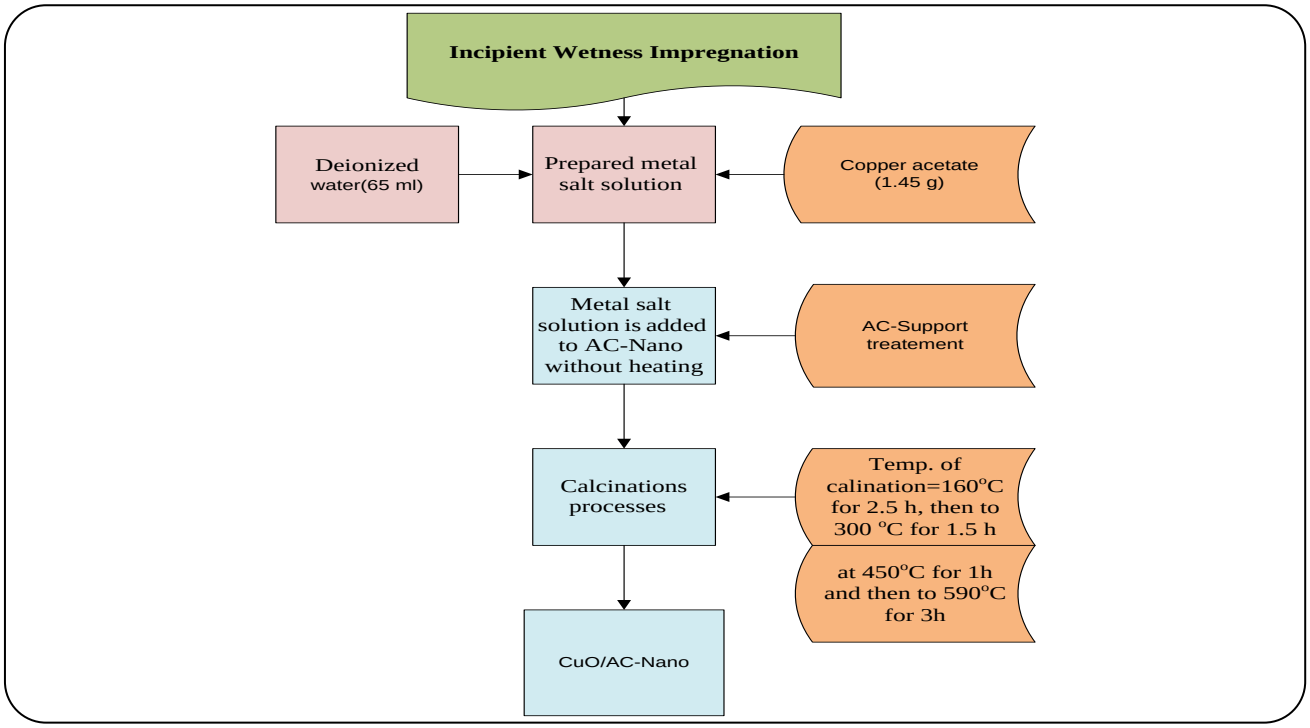

Fig. 1: Catalyst preparation procedure

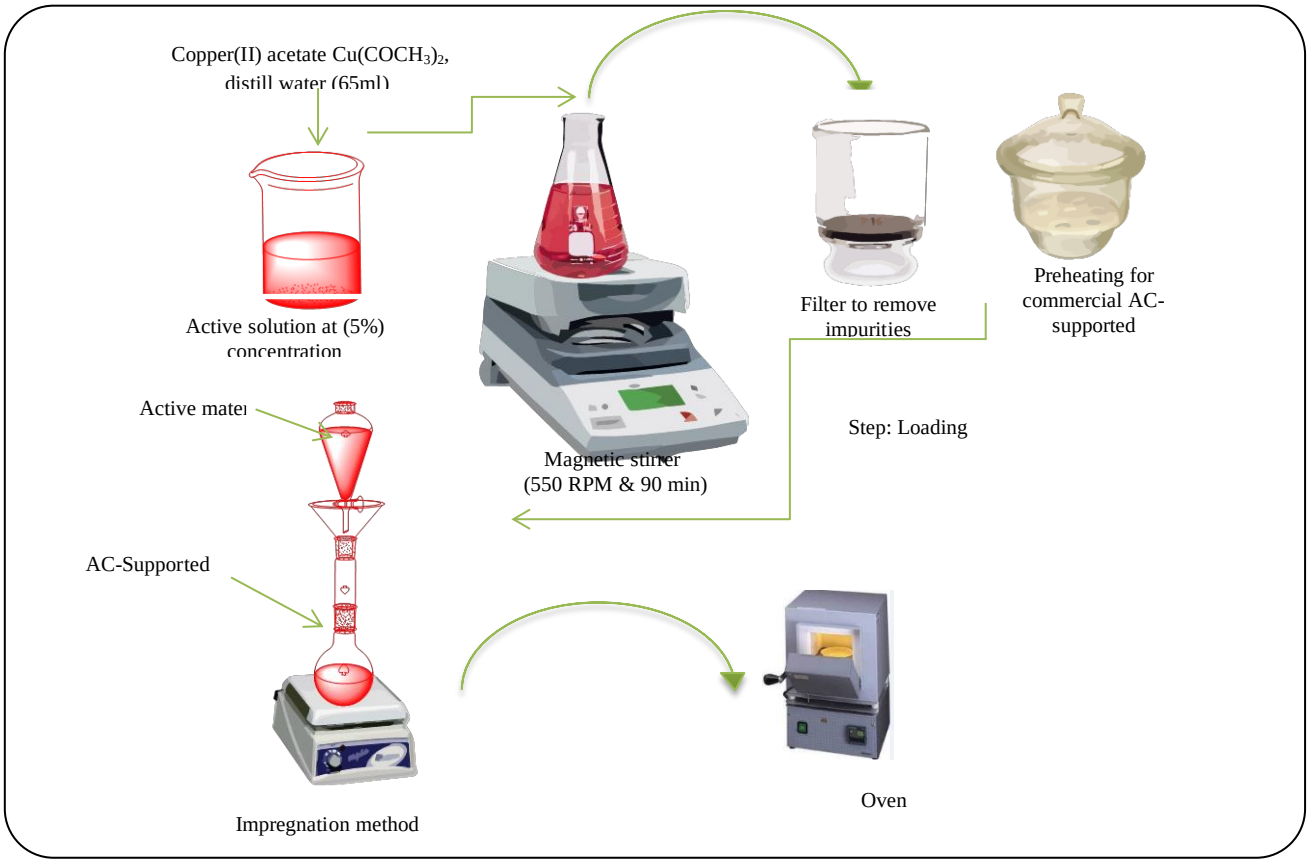

Fig. 2: Catalyst manufacturing procedures and equipment

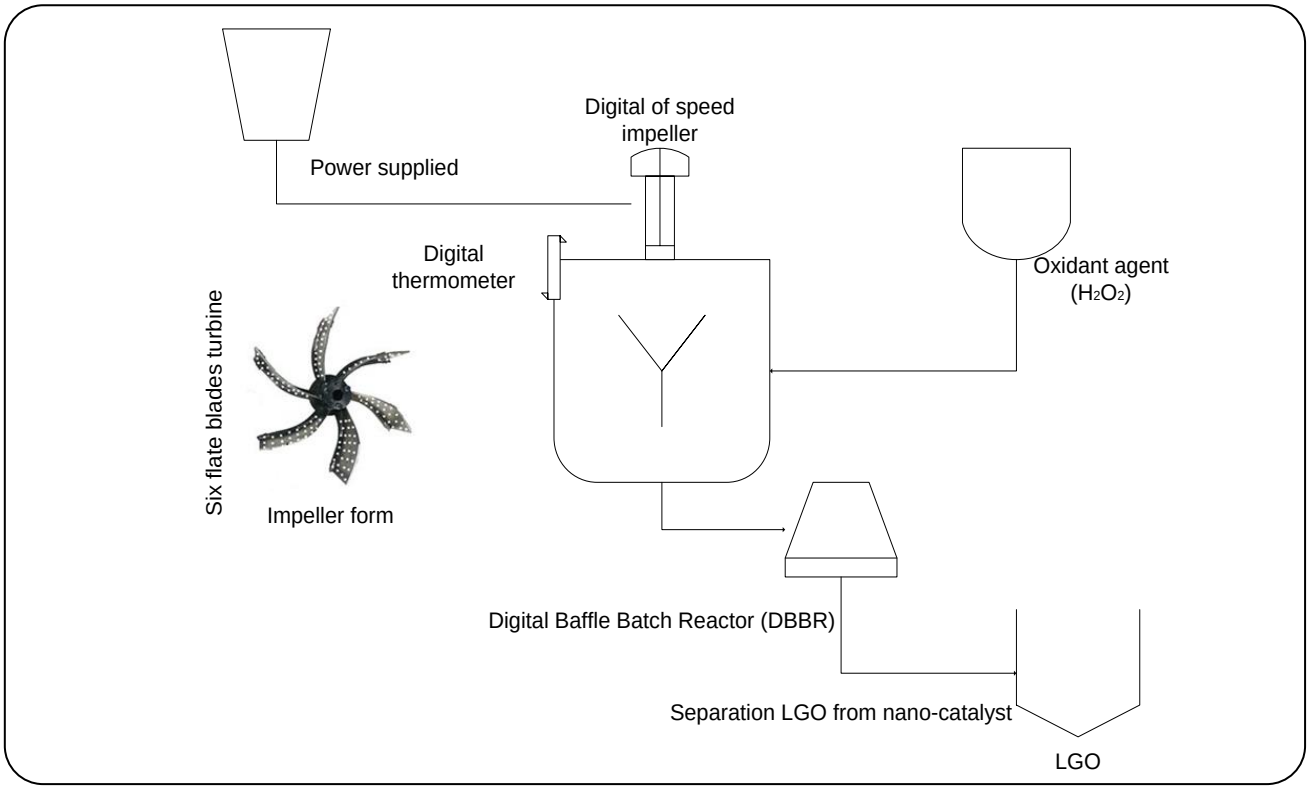

Fig. 3: Experimental diagram of DBBR unit.

1- The DBBR is made up of a digital mixer (with 5000 rev/min).

2- Connect a digital mixer to a cylinder with a length of 145 mm and a diameter of 80 mm for the impeller (six flat-blade turbine based on the impeller's dimensions of 5 cm in length and 5 cm in depth.).

3- A new six-blades turbine have been built with circular holes that are uniformly dispersed throughout the metal's surface in a hexagonal pattern for the purpose of increasing the number of mixing channels within the reactor and enhancing the sulfur removal *via* the oil feedstock, catalyst and oxidant.

4- A stainless steel reactor with a capacity of 200 mL was constructed with 4 baffles (20 cm in a high and 2.5 cm in a width). Within the reactor, baffles have been placed in equal sizes over the reactor's surface (approximately 38 cm between the baffles), with a 2.5 cm protrusion going from each baffle. The reactor is covered from the outside perimeter by woolen material and powered by an electrical motor with 5000 rev/min and able to function higher temperatures (above 1000 °C). The experimental setup is depicted in Fig. 3, and the system specifications are listed in Table 3.

ODS reactions

Experimental conditions

The experimental study in this paper involves various ODS process tests under the following process conditions:

- Homemade catalyst: (CuO/ Activated carbon nanoparticles).
- The reaction temperature of oxidation: 100, 120 and 140 ^oC.
- The time of oxidation: 15, 30 and 45 min.
- Initial DBT concentration: 1200 ppm.
- Dosing of H_2O_2: 2, 3.5 and 5 mL.
- Speed of impeller 650 rpm.

The experiments have been chosen based on the highest and lowest levels, as well as the safe and moderate conditions that existed among them.

Procedure for ODS process

The oil feedstock is created by adding dibenzothiophene to light gas oil (clean). Each run of the experiment includes the following steps:

The sulfur content (represented by DBT type) is added to the oil feedstock (LGO) with a concentration of 1200ppm as a model sulfur compound. H_2O_2 was used

Table 3: DBBR system characteristics.

No.	System Characterization	Property
1	Diameter of impeller	80 mm
2	Preheater	Heater powered by electricity
3	Isolation of the reactor	Glass wool
4	Internal diameter of mixing chamber (cylinder diameter)	110 mm
5	Stainless steel batch reactor	The material is glass (200 mL)
6	Stainless steel baffle	3 distribution on the batch's wall
7	Height of stainless steel cylinder	145 mm
8	Stainless steel impeller kind	Six flat-blades turbine

as an oxidant and the ODS reactions are conducted utilizing the digital baffle batch reactor (DBBR) designed here. To perform the oxidative desulfurization reactions, 150 mL of light gas oil is used in every test. In all of the experiments, the amount of H_2O_2 required for the oxidative desulfurization reactions were (2, 3.5, and 5 mL) under fixed pressure of 0.5 bar. The modified new nano-catalyst (CuO/ AC-nanoparticles) is individually charged into the DBBR including the oil feedstock (LGO). The ODS reactions are carried out under moderate process conditions. These are as follow: for the goal of establishing a good mixing and preventing segregation (stagnant zones within the DBBR), the reaction temperature was set to 100, 120 and 140 °C, and the contact time was set to 15, 30 and 45 minutes at a continuous stirring rate of 650 rpm. During the ODS processes, the gases generated by the oxidative desulfurization reactions are vaporized and subsequently condensed via the condensation operation coupled to the process.

Sample analysis

The output concentration of sulfur compounds is determined for each experiment to test the performance of the catalyst designed under each ODS conditions. Where, the sulfur content was determined using the ASTM-D4294 technique and X-ray fluorescence. All of the analytical procedures used to determine the specifications of the oil feedstock and oil products were precise, quick, and reproducible. To confirm the correctness of the results, the experimental results related to sulfur content and for each sample, the analysis was done twice under the same operating conditions.

Table 4: Nano-catalyst properties

Properties	Unit	Values
Pore volume (Pv)	cm^3/g	0.3876
Pore size (Pz)	nm	2.765
Surface area (Sa)	m^2/g	512.33
Bulk density (Bd)	g/cm^3	0.589
Calcination temperature	K	590

RESULTS AND DISCUSSIONS

Specifications of the prepared nano-catalyst

The prepared homemade catalyst was examined at the Iraqi Ministry of Oil's Petroleum Research and Development Center in Baghdad to determine the main characteristics, including Pv, Pz, Sa and Bd as illustrated in Table 4.

Elemental composition and morphology of nano CuO/AC produced

SEM analysis, as shown in Fig. 4, provides direct proof of the creation of CuO nanoparticles on the plane and edges of activated carbon. CuO nanoparticles with an average size of 20 nm have been used to cover the activated carbon. CuO nanoparticles are well separated from one another and strewn throughout the activated carbon in a random pattern. Additionally, surface of (CuO/Nano-AC) prepared in this research represents the distribution of CuO over the support (AC), where the metal oxides are represented by white regions while the support (AC) is described by dark regions.

The CuO nanoparticles within nano composite CuO/Nano-AC have a spherical structure, which is

conceivable since the addition of OH- induced a fast reaction rate, which might lead to the formation of additional nuclei in a short period of time. So, CuO nano crystals with a spherical shape are formed. Surface of CuO/Nano-AC prepared refers to the distribution of CuO over the support (AC). It has also been noticed from Fig. 4 that the copper oxide is evenly distributed across the support's surface. The triangular marks are the typical varied pore of CuO, and the SEM image clearly displays randomly scattered grains of lesser size. The production of nanoparticles has a homogeneous shape framework, and it is formed by extremely high density with almost uniform spherical forms according to the SEM study. Such high effectiveness of the designed catalyst (CuO/Nano-AC) will positively be reflected during the oxidative desulfurization process according to the good distribution of active compounds, high surface area, high catalyst's particle size, shape, and porosity that contribute to be as a significant role in the reaction activity after the loading process.

XRD behavior (X-ray diffraction)

The XRD results of the generated catalyst is shown in Fig. 5. Based on the results presented in this Figure, it was observed an increase the diffraction peak intensities of the support AC. After loading of CuO over the AC support, the peaks intensity of AC reduced while the diffraction peak intensities corresponding to CuO (at 34.1º, 36.2º, 49.7º, 53.8º, 61.9º and 64.2º) was increased as presented in this Figure. On the other hand, the diffractgram of commercial copper oxide shows the characteristic peaks of CuO at 34.1º, 36.2º, 49.7º, 53.8º, 61.9º and 64.2º. When impregnated AC with CuO, it is seen that the intensity of the peaks corresponding to AC drops and the peaks corresponding to CuO start appearing as shown in the Figure. Such behavior indicates that a high dispersion of CuO on the catalyst surface (over AC supported) is obtained.

ODS reactions

The experiments were conducted in a DBBR reactor employing the modified nano- catalyst (5 % CuO/AC-nanoparticle) that was experimentally manufactured in this research. The following are the effects of the main process conditions upon the sulfur removal (oxidant amount, reaction temperature and contact reaction time).

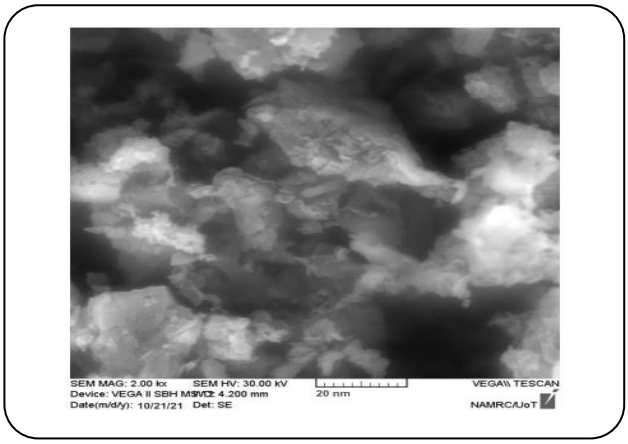

Fig. 4: SEM image of the catalyst prepared.

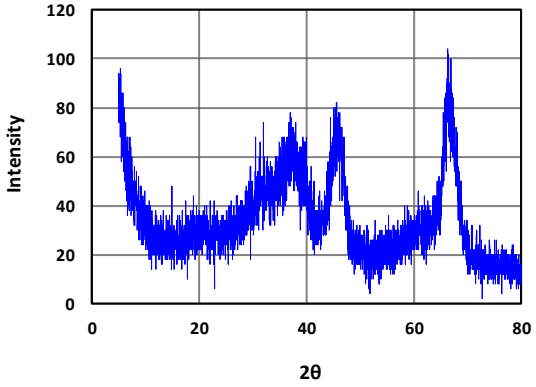

Fig. 5: XRD behavior of the catalyst prepared.

Influence of reaction temperature on sulfur removal

In the DBBR, the effect reaction of temperature on the oxidation desulfurization process for sulfur removal from light gas oil was studied at different temperatures (100 ºC, 120ºC and 140ºC), several contact times (15 min, 30 min and 45 min) and various dosing of hydrogen peroxide (2 mL, 3.5mL and 5 mL). Figs. 6 and 7 illustrated the impact of reaction temperature upon the conversion of sulfur compound for dosing of H_2O_2= 3.5 and 5 mL, respectively at different time of oxidation. According to the results presented in these Figures, increases the reaction temperature lead to reduce the sulfur concentration in the output product. The conversion increases from 31.5% to77.3% as the reaction temperature raised from 100 ºC to 140 ºC at 45 min and 3.5 mL dosing of H_2O_2 as shown in the Fig. 7. The sulfur removal is improved from 42.1% to 83.1% when the reaction temperature rises from 100 ºC to 140 ºC at H_2O_2 dosing of 5 mL and 45 min contact time. These observations can be attributed to the following. The rising oxidation temperature leads to a higher activation

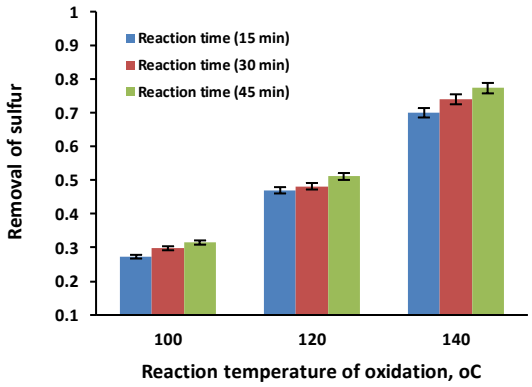

Fig. 6: Impact of reaction temperature on the conversion of sulfur compound for dosing of H_2O_2= 3.5 mL at different.

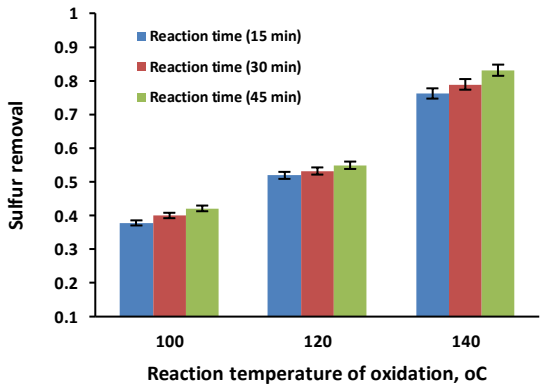

Fig. 7: Impact of reaction temperature on the conversion of sulfur compound for dosing of H_2O_2= 5 mL different time of oxidation.

energy of such reactions [28-30]. The diffusion and osmoses within the pores of the generated nano-catalyst (5 % CuO/AC-nanoparticle) is also increased due to increase in the reaction temperature. Furthermore, rising reaction temperatures reduces the surface tension and viscosity but increases the diffusivity and Henry's constant. The absorption rate of oxidant molecules into oil feedstock and the diffusion rate of sulfur component, as well as the dissolution rate of oxidant into the catalyst pores (where the oxidative desulfurization reaction occurs), increase as the contact time increases with the reaction temperature [31,32].

Influence of contact time for ODS reactions in DBBR reactor

The effect of contact time on the sulfur removal has been studied in the digital baffle batch reactor (DBBR) through the oxidation reaction utilizing the modified homemade nano-catalyst (5%CuO/AC-nanoparticle) at moderate operating condition (shown in Figs. 8 and 9). The sulfur conversion increases as the contact reaction time between the catalyst, LGO (oil feedstock), and hydrogen peroxide (H_2O_2) increases, generating an increase in O_2 atom transfer and dibenzothiophene in the pore site of the catalyst [33-35]. Fig. 8 shows that when the contact time is increased from 15 to 45 minutes at 5 mL of oxidant (H_2O_2) and 120 °C, the sulfur conversion increases from 51.9 to 54.9 %. With the increase in the contact time from 15 to 45 minutes at 140 °C and 5 mL of H_2O_2 (Fig. 9), the removal of sulfur component raises from 76.2 to 83.1 %. It can be shown that extending the contact time leads to better conversion since the contact time between the reactants increases, allowing more contact with the catalyst's active site. [36,37]. The diffusivity of the adsorbate substances (nano-catalyst) and the oil feedstock (light gas oil) has also played a key role in accelerating the desulfurization process (increasing the adsorption process) [38].

Influence of H_2O_2 concentration for ODS reactions in DBBR reactor

The influence of H_2O_2 amount for sulfur removal found in light gas oil was studied at 2 mL, 3.5 mL and 5 mL. The impact of the amount of oxidizer source (H_2O_2) on the sulfur removal based on the modified nano-catalyst (5%CuO/AC-nanoparticle) via oxidation desulfurization process utilizing the DBBR. The efficiency of the sulfur removal is raised with rising the amount of the oxidant (H_2O_2) from 2 to 5 mL. Increasing such amount of the oxidant from 2 to 5 mL (at contact time 45 min and reaction temperature 100 °C), the conversion process has raised from 24.4% to 42.1% (as presented in Fig. 10). Bigger improving of the oil feedstock (light gas oil) in terms of the sulfur content is noted (Fig. 11) through the effect of the oxidizer amount (the sulfur removal increased from 67.1% to 83.1% at reaction temperature 140 °C, contact time 45 min and H_2O_2 of 5 mL), which is regarded the best operating conditions investigated in this study. It is worth noting that the oxidation reaction increases the amount of oxidizer, resulting in more sulfur removal. The addition of a hydrogen peroxide (H_2O_2) as an oxidant to the adsorbent had a noticeable influence on the efficiency of sulfur removal utilizing the new modified

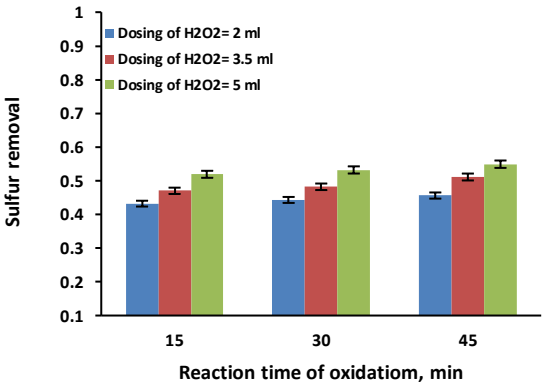

Fig. 8: Impact of contact time on the conversion of sulfur component at reaction temperature = 120°C and different amount of oxidant

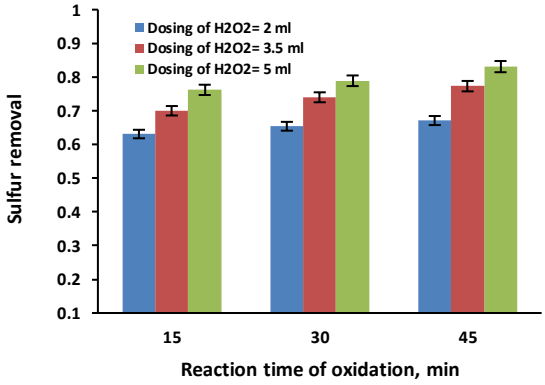

Fig. 9: Impact of contact time on the conversion of sulfur component at reaction temperature = 140°C and different amount of oxidant.

handmade nano-catalysts (5 % CuO/AC). These good active components (active materials) and carrier can be drawn to the significant reaction between hindered sulfur components and H_2O_2, which results in high sulfur removal by transforming them to sulfones that are simply adsorbed upon the catalysts [39,40]. At high temperature (above 140 C), the oxidant will be decomposed and has not got to work as an oxidant in the process. Thus, the process conversion will be decreased and there will be no impact of sulfur removal.

Effect of new design of the reactor on the conversion process

The new design of reactor was Digital Baffle Batch Reactor (DBBR) is locally designed to give the best mass transfer through the oxidation desulfurization process (ODS). The digital baffle batch reactor includes digital mixer, cylinder with a length of 145 mm and the impeller (six flat-blades turbine) with a diameter of 90 mm (the dimension of the impeller were: 5 cm in length and 5 cm in depth). Six flat blades turbine has been designed in a new shape to contain circular holes which are equally distributed over the surface of the metal in a hexagonal manner leading to increase the mixing channels inside the reactor and increasing the conversion process through the path (model light gas oil), catalyst and oxidant. New design of reactor its good where getting high conversion and too easy design large-scale production and get high mixing by use baffle in the wall. Comparison the results obtained in this study and other published results as shown in the Table 5.

Reusability of the Nano-catalyst (Cu/AC) in ODS process

The CuO/AC nano-catalyst used here has reused in the oxidative desulfurization process of the light gas oil under the best operating conditions for removal sulfur evaluated in this work. The conversion of sulfur (DBT) from LGO in the first cycle of the ODS reaction and the efficiently reduced the level of sulfur in the model LGO with DBT conversion reaching 83.1% at a best operating conditions (reaction temperature of 140°C, amount of oxidant 5 mL and reaction time 45 min) reaction as shown in the Fig. 12. The active component (CuO) embedded in the nano-support was better dispersion of active metals (CuO) as well as high surface area, pore volume, and homogenous distribution for the support. The conversion of sulfur also indicated good reusability of the nano-catalyst (CuO /AC) with conversion reaching 86.65% after five cycles.

CONCLUSIONS

Production of green and an environmentally friendly fuel is recently considered the major goal in petroleum refining industries to meet the environmental regulations with respect to sulfur content and to achieve cleaner air, lower emissions and a sustainable environment around the world. Continuing with the challenges facing the investigators in this field and getting a suitable catalyst of such impurity creating clean fuel is regarded a vital issue in fuel quality development and a primary purpose for developing of increasingly productive innovations on new oxidative nano-catalyst. So, the new homemade nano-catalyst (CuO/) over support (AC) nanoparticles is

Table 5: Comparison results obtained by this study and other published results.

Catalyst	Oxidant	Operating conditions	Solvent	Conversion	Reference
Autoxidation	air	Temperature 145-175oC Time=360 min	water	46-47%	[41]
ZnO/nano-Al_2O_3	air	Temperature= 190°C Time=50 min	Without solvent	70.52%	[4]
Ti/MM	H_2O_2	Temperature= 60°C Time=120 min	Acetonitrile	64%	[42]
CuO/Nano-AC	H_2O_2	Temperature= 140°C Time=40 min, H_2O_2=5 mL	Without solvent	83.1%	This work

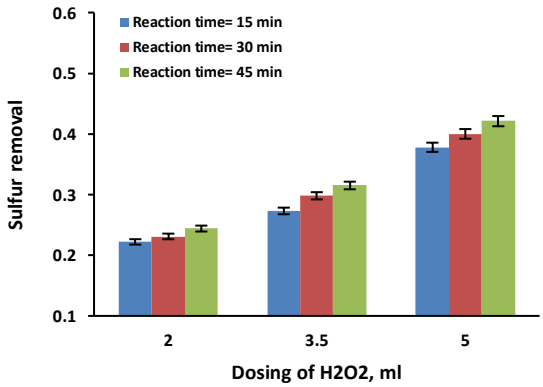

Fig. 10: Effect of H_2O_2 on sulfur removal at reaction temperature = 100 °C and different reaction time.

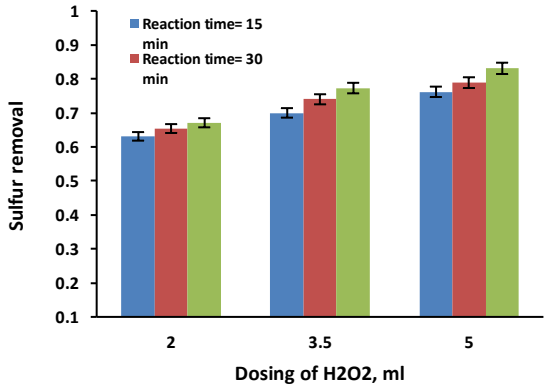

Fig. 11: Effect of H_2O_2 on sulfur removal at reaction temperature = 140 °C and different reaction time.

extensively studied here to get a suitable nano-catalyst creating clean fuel (light gas oil) by reducing the sulfur content through high effectiveness of the catalyst via oxidation reaction in a new digital baffle batch reactor - DBBR that has been investigated here.

Based on the results reported in this study, the new homemade nano-catalyst (5%CuO/AC-nanoparticle) can be utilized confidently to ODS reactions and it has been

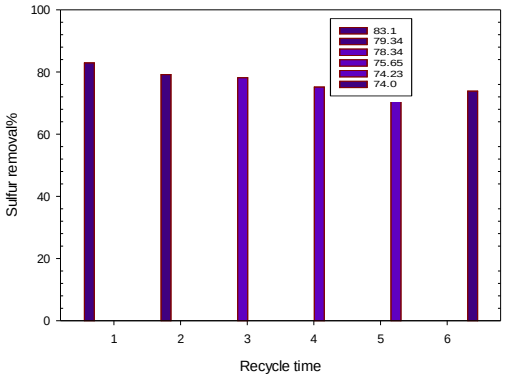

Fig. 12: Reusability of the nano-calalyst (CuO/AC) for oxidative desulfurization.

reported to be one of the most significant catalysts to get a green fuel and reducing the sulfur content under moderate operating conditions. In the catalyzed process of the oxidation reaction, it was noted that using of nano-particles for preparation of the catalyst exhibits high effectiveness. The method of impregnation is a good way for preparation of nano catalyst due to the excellent distribution of the active metals beside the high surface area and pore volume. The catalyst activity and the process conversion depends mainly on the active and the reactor type. A good sulfur removal from light gas oil can be accomplished using the DBBR via ODS reactions over a new homemade nano catalyst (5 % CuO/AC-nanoparticle) under mild operational conditions (reaction temperature = 140 °C, contact time = 45 min, and amount of H_2O_2 = 5 mL), resulting in excellent ODS reactions and higher conversion of 83.1 % of sulfur compound resulting in good fuel quality and lower pollution.

Received : Mar. 27, 2022 ; Accepted : June 13, 2022

REFERENCES

[1] Bhatia S., "Zeolite Catalysts: Principles and Applications", CRC Press INC, Florida (2020).

[2] Srivastava V.C., An evaluation of Desulfurization Technologies for Sulfur Removal from Liquid Fuels, *The Royal Society of Chemistry*, **2**: 759-783 (2012).

[3] Gokhale S., Khare M., A Review of Deterministic, Stochastic and Hybrid Vehicular Exhaust Emission Models, *International Journal of Transport Management*, **2**: 59-7 (2004).

[4] Nawaf A.T., Jarullah A.T., Abdulateef L.T., Design of a Synthetic Zinc Oxide Catalyst over Nano-Alumina for Sulfur Removal by Air in a Batch Reactor, *Bulletin of Chemical Reaction Engineering and Catalysis*, **14**: 79-92 (2019).

[5] Palaić N., Setrić-Bionda K., Margeta D., Podolski Š., Oxidative Desulphurization of Diesel Fuels, *Chemical-Biochemical Engineering*, **29**: 323-327 (2015).

[6] Zhang M., Weia Y., Li R., Zhu W., Li H., Zhang Q., Wang, M., Chen X., Li H., Magnetic POM-Based Mesoporous Silica for Fast Oxidation of Aromatic Sulfur Compounds, *Fuel*, **209**: 545-551 (2017).

[7] Zhang M., Liu J., Yang J., Chen X., Wang M., Li H., Zhu W., Li H., Molybdenum-Containing Dendritic Mesoporous Silica Spheres for Fast Oxidative Desulfurization in Fuel, *Inorganic Chemistry Frontiers*, **6**: 451-458 (2019).

[8] Qian E.W., Development of Novel Non-Hydrogenation Desulfurization Process-Oxidative Desulfurization of Distillate, *Journal of The Japan Petroleum Institute*, **51**: 14-31 (2008).

[9] Zhang, G., Yu, F., Wang, R., Research Advance in Oxidative Desulfurization Technologies for the Production of Low Sulfur Fuel Oils, *Petroleum & Coal*, **51**: 196-207 (2009).

[10] Rezvani, M.A., Khandan, S., Aghmasheh, M., Synthesis and Characterization of New Nanocomposite TBA-PW11Ni@NiO as an Efficient and Reusable Heterogeneous Catalyst in Oxidative Desulfurization of Gasoline, *Journal of the Taiwan Institute of Chemical Engineers*, **77**: 321-328 (2017).

[11] Argam, V.A., Leonid, A.K., Polina, D.P., Anna, O.S., Alexander, V.A., Anton, L.M., Eduard A.K., Metal-Free Oxidative Desulfurization Catalysts Based on Porous Aromatic Frameworks, *Industrial & Engineering Chemistry Research*, **60**: 9049–9058 (2021).

[12] Rezvani, Khandan S., Synthesis and Characterization of a New Nanocomposite (FeW11V/CTAB-MMT) as an Efficient Heterogeneous Catalyst for Oxidative Desulfurization of Gasoline, *Applied Organometallic Chemistry*, **32**: 1-13 (2018).

[13] Nawaf A.T, Jarullah A.T, Gheni S.A., Development of Kinetic and Process Models for the Oxidative Desulfurization of Light Fuel Using Experiments and the Parameter Estimation Technique, *Industrial & Engineering Chemistry Research*, **54**: 12503–12515 (2015).

[14] Guo W., Wang C., Lin P., Lu X., Oxidative Desulfurization of Diesel with TBHP/isobutyl Aldehyde/Air Oxidation System, *Appl. Energy*, **88**: 175–179 (2011).

[15] Jian, Wei, Ding, Wang., A New Green System of HPW@MOFs Catalyzed Desulfurization Using O_2 as Oxidant, *Chinese Chemical Letters*, **27**: 655-658 (2015).

[16] Cedeño-Caero, Gomez-Bernal H., Fraustro A., Oxidative Desulfurization of Synthetic Diesel Using Supported Catalysts: Part III. Support Effect on Vanadium-Based Catalysts, *Catalyst Today*, **133–135**: 244-25 (2008).

[17] Kobotaeva N.S., Skorokhodova T.S., Transition Metal Activated Multi-Walled Carbon Nanotubes as a Catalyst for the Oxidative Desulfurization of Fuel Oils, *AIP Conference Proceedings*, **2310**: 020152 (2020).

[18] Ahmad W., Ur Rahman A., Ahmad, Yaseen., Oxidative Desulfurization of Petroleum Distillate Fractions Using Manganese Dioxide Supported on Magnetic Reduced Graphene Oxide as Catalyst, *Journals Nanomaterials*, **11**: 1-16 (2021).

[19] Rivoira L., Juárez J., Martínez M.L., Andrea, B., Iron Modified Mesoporous Materials as Catalysts for ODS of Sulfur Compounds, *Catalysis Today*, **349**: 98-105 (2020).

[20] Ugal J.R., Jima'a R.B., Al-Jubori W.M.K., Oxidative Desulfurization of Hydrotreated Gas Oil Using Fe_2O_3 and Pd Loaded over Activated Carbon as Catalysts, *Oriental Journal of Chemistry*, **34**: 1091-1097 (2018).

[21] Zhang G., Yu F., Wang, R., Research Advance in Oxidative Desulfurization Technologies for the Production of Low Sulfur Fuel Oils, *Petroleum & Coal*, **51**: 196-207 (2009).

[22] Al-Maliki A., "Desulfurization of Gasoline and Diesel Fuels Using Non-Hydrogen Consuming Techniques", MSc Thesis, Chemistry Department, King Fahad University of Petroleum and Minerals (2004).

[23] Nawaf A.T., Hameed S.A., Abdulateef L.T, Jarullah A.T., Kadhim M.S., Mujtaba I.M., A Novel Synthetic Nano-Catalyst (Ag_2O_3/Zeolite) for High Quality of Light Naphtha by Batch Oxidative Desulfurization Reactor, *Bulletin of Chemical Reaction Engineering and Catalysis*, **16**: 716-732 (2021).

[24] Nawaf A.T., Hamed H.H., Hameed S.A., Jarullah A.T., Abdulateef L.T.; Mujtaba I.M., Performance Enhancement of Adsorption Desulfurization Process Via Different New Nano-Catalysts Using Digital Baffle Batch Reactor and Mathematical Modeling, *Chemical Engineering Science*, **232**: 116384 (2021).

[25] Qian E.W., Development of Novel Non-Hydrogenation Desulfurization Process-Oxidative Desulfurization of Distillate, *Journal of the Japan Petroleum Institute*, **51**: 14-31 (2008).

[26] Jarullah A.T., Ghazwan S.A., Al-Tabbakh B., Mujtaba I.M., Enhancement of Light Naphtha Quality and Environment using New Synthetic Nano-catalyst for Oxidative Desulfurization: Experiments and Process Modeling, *Computers & Chemical Engineering*, **140**: 106869 (2020).

[27] Nawaf, A.T., Gheni S.A., Jarullah A.T., Mujtaba I.M., Improvement of Fuel Quality by Oxidative Desulfurization: Design of Synthetic Catalyst for the Process, *Fuel Processing Technology*, **138**: 337–343 (2015).

[28] Xun S., Jiang W., Guo T., He M., Zhu R.W., Li H., Magnetic Mesoporous Nanospheres Supported Phosphomolybdate-Based Ionic Liquid for Aerobic Oxidative Desulfurization of Fuel, *Journal of Colloid and Interface Science*, **534**: 239-247 (2019).

[29] Nawaf A.T., Jarullah A.T., Saba A.G., Mujtaba I.M., Development of Kinetic and Process Models for the Oxidative Desulfurization of Light Fuel, Using Experiments and the Parameter Estimation Technique, *Industrial and Engineering Chemistry Research*, **54**: 12503−12515 (2015).

[30] Leitao A., Rodrigues A., Studies on the MEROX Process: Kinetics of n-butyl Mercaptane Oxidation, *Chemical Engineering Science*, **44**: 1245-1253 (1989).

[31] Paniv P.M., Pysh'ev S.V., Gaivanovich V.I., Lazorko O.I., Nan-Catalytic Oxidation Desulfurization of the Kerosene Cut, *Chemistry and Technology of Fuels and Oils*, **42**: 159-166 (2006).

[32] Jarullah A.T., Aldulaimi S.K., Al-Tabbakh B.A., Mujtaba I.M., A New Synthetic Composite Nano-Catalyst Achieving an Environmentally Friendly Fuel by Batch Oxidative Desulfurization, *Chemical Engineering Research and Design*, **160**: 405-416 (2020).

[33] Zhang L., Wang J., Sun Y., Jiang B., Yang H., Deep Oxidative Desulfurization of Fuels by Superbase-Derived Lewis Acidic Ionic Liquids, *Chemical Engineering Journal*, **328**: 445-453 (2017).

[34] Shihab M.A., Nawaf A.T., Mohamedali S.A., Alsalmaney M.N., Improving Porosity of Activated Carbon Nanotubes via Alkali Agents for the Enhancement of Adsorptive Desulfurization Process, *Materials Science Forum*, **1002**: 423-434 (2020).

[35] Abdulateef L.T., Nawaf A.T., Al-Janabi O.Y., Peter J.S., Qahtan A.M., Batch Oxidative Desulfurization of Model Light Gasoil over a Bimetallic Nanocatalyst, *Chem. Eng. Technol.*, **44**: 1708–1715 (2021).

[36] Saleh A.T., Sulaiman O.K., AL-Hammadi A.S., Dafalla H., Danmaliki I.G., Adsorptive Desulfurization of Thiophene, Ben-Zothiophene and Dibenzothiophene over Acti-Vated Carbon Manganese Oxide Nanocompo-Site: with Column System Evaluation, *J. Cleaner Prod.*, **17**: 959-6526 (2017).

[37] Sarda K.K., Bhandari A., Pant K.K., Jain S., Deep Desulfurization of Diesel Fuel by Selective Adsorption over Ni/Al_2O_3 and Ni/ZSM-5 Extrudates, *Fuel*, **93**: 86–91 (2012).

[38] Nawaf A.T., Hameed S.A., Jarullah A.T., Mujtaba I.M., Design of New Activated Carbon Based Adsorbents for Improved Desulfurization of Heavy Gas Oil: Experiments and Kinetic Modeling, *Chemical Product and Process Modeling*, **16**: 229–249 (2021).

[39] Ugal J., Jimaa RB., Al-Jubori W.M., Abbas B.F., Al-Jubori N.M., Oxidative Desulfurization of Hydrotreated Gas Oil using Fe2O3 and Palladium Loaded over Activated Carbon as Catalyst, *Oriental Journal of Chemistry*, **34**: 1091-1097 (2018).

[40] Ghazwan S.A., Jarullah A.T., Al-Tabbakh B., Mujtaba I.M., Design of An Environmentally Friendly Reactor for Naphtha Oxidative Desulfurization by Air Employing a New Synthetic Nano-Catalyst Based on Experiments and Modelling, *Journal of Cleaner Production*, **257**: 120436 (2020).

[41] Javadli, R., and de Klerk, A., Desulfurization of Heavy Oil- Oxidative Desulfurization(ODS) as Potential Upgrading Pathway for Oil Sands Derived Bitumen, *Energy Fuels*, **26**: 594–602 (2012).

[42] Leng K., Sun Y., Zhang X., Yu M., Xu W., Ti-Modified Hierarchical Mordenite as Highly Active Catalyst for Oxidative Desulfurization of Dibenzothiophene, *Fuel*, **174**: 9–16 (2016).