

Catalytic Oxidative Desulfurization of Heavy Naphtha with Hydrogen Peroxide in the presence of Catalyst (PMN550)

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Abstract:

Catalytic oxidative desulfurization of the heavy naphtha fractions has been researched with the use of the air-assisted formic acid and H₂O₂ oxidation in the presence of the natural zeolite (PMN 550) as the catalyst. The catalyst used was synthesized in the lab. and identified through FT-IR, AFM, BET, XRD, XRF, SEM, and TGA thermal analyses showed that the prepared catalyst has an efficient catalyst characteristic. The yield of the desulfurization in the cases of HN has been increased in the presence of the natural zeolite (PMN-550) and HN's sulfur content has been decreased from 651.3 ppm to < 10 ppm in a 60 min period at a temperature of 90 Co, which has resulted in subsequent removal of sulfur compounds from octane phase. This oxidative treatment effectively reduced the sulfur content of heavy naphtha, and adsorption with PMN550 further reduced the sulfur content to below 9 mass ppm. A batch reactor was used to evaluate the performance of the prepared catalyst at different reaction temperatures (20-120 °C), and batch time (20-140 min.) with different amounts of natural zeolite (PMN550) catalyst. Numerous parameters of the design have been utilized for the determination of factors giving the optimal sulfur content removal from the HN in the batch modes. The studied operating conditions were the ratio of H₂O₂ to heavy naphtha, temperature, solution pH, catalyst weight and contact time.

Keywords: Catalytic oxidative desulfurization (CODS), Catalyst (PMN550), hydrodesulfurization (HDS), organosulfur compounds, extraction.

1. Introduction

Removing sulfur from the petroleum fractions is a transaction that was performed already

with the use of some processes, like hydrodesulfurization (HDS), using the catalysts operating in the removal of the sulfur. On the other hand, this procedure needs high pressure and temperature levels, in addition to consuming high hydrogen amounts. Oxidative desulfurization, which is related to using catalysts via the electronic affinity and the selectivity, performs sulfur molecules' removal, which was the subject of the scientific studies that aim to reduce the amount of sulfur present in the fractions of petroleum [1][2]. The organosulfur compounds in the petroleum-derived fuel types are typically eliminated through the use of the HDS process. However, the traditional HDS process is unable to economically produce ultra-clean fuels with very low content of sulfur, in particular for the fuel cell vehicles. Based on that, substitute processes like adsorptive desulfurization, oxidative desulfurization (ODS), bio-desulfurization, and others were researched [3][4]. Naphtha, which is a promising fuel candidate for fuel cell vehicles, includes considerable amounts of organosulfur compounds like sulfides, thiols, disulfides, benzothiophenes and thiophenes. Amongst organosulfur compounds, the thiophenes have been considered as the most refractory compounds in the process of the ODS as a result of their low reactivity to the oxidations [5]. Which is why, developing effective approaches of oxidation for the thiophenes is quite significant to produce ultraclean naphtha. Due to the mild operating conditions and low cost required, the ODS has been defined as the most appropriate substitute to industrial HDS [6]. This process also has the benefit of the high effectiveness in the treatment of refractory S compounds that are difficult to treat using the HDS under the normal operating conditions [7]. In this procedure, the compounds of the sulfur in the petroleum are oxidized selectively, with the increase of their polarity by catalytic oxidative desulfurization (CODS) [8]. A novel method for oxidative desulfurization of liquid hydrocarbon fuels based on catalytic oxidation using molecular oxygen coupled with selective adsorption [9]. The oxidized compounds of the sulfur are separated from the non-polar phase by adsorption or extraction (liquid-liquid extraction). ODS is gaining increasing popularity as one of the alternative techniques to hydrodesulfurization for liquid fuels due to its cost-effectiveness, mild operation and promising efficiency [10]. The organic peracids [11]. have been studied extensively for this purpose due to the fact that they provide a sufficient route for the selective oxidations of the compounds of sulfur, however, as a result of their explosive natures, those are mainly produced in situ through the H_2O_2 reaction with the organic acids such as the acetic and formic acids [12]. Springer Science & Business Media). Nonetheless, to attain deep desulfurization, excess organic acid and hydrogen peroxide amounts are required. Several catalysts have been utilized for assisting this process of oxidation and for enhancing the efficiency of the ODS with minimal peracid consumption [13]. As it has been reported elsewhere, the oxidative desulfurization of the fuel oil utilizing formic acid and H_2O_2 without using a catalyst resulted in approximately 60% removal of the sulfur that has been

increased up to 95% with the use of the activated carbon as the catalyst [14]. The other catalysts that have been utilized include the sodium and magnesium silicates and EDTA [15]. Metal oxides loaded on molecular sieves [16], transition metal salts [17], silica gel [18], and sodium bicarbonate [19]. Have stated light gas oil ODS with the use of the hydrogen peroxide as the oxidant in the presence of the Zn/hydroxyapatite produced through the ion exchange approach; the results have shown that a maximal value of 68% of the S has been removed. However, such a type of catalyst (i.e., transition metal cation exchange) has not been reported for the ODS of heavy oil [20]. It has been concluded from those researches that those catalysts have in fact, promoted the peroxy species' formation that resulted in additionally increasing the organosulfur compounds' oxidation, which has given yields of desulfurization. the Molecular oxygen, O₂, was utilized as well, as a preferred low-cost oxidant combined with a variety of the initiators such as the aldehydes in the presence of various catalysts in the ODS with high-potential results [21][22][23][24]. It's clear that in the case of the feed that contains high sulfur amounts, the efficiency of desulfurization utilizing those reported catalysts has been quite poor. The heavy feed stock desulfurization, like the bitumen, atmospheric residue, and so on, by the ODS was taken under consideration quite rarely so far. A small number of the reports have shown non-catalytic ODS of some heavy of the oil types, like the Athabasca bitumen, however, sulfur removal attained has been very small (about 50%) [25][26]. The ODS of the heavy fractions was less efficient due to several factors, like their high content of sulfur, high viscosity and density, in addition to the limitations of the phase transfer throughout the process. It was shown that in the heavy fractions, the present S has been mainly in a form of the complex alkylated benzothiophenes; treating those compounds with the process of the commercial HDS has been difficult as a result of steric hindrance that is posed by the side chains of the alkyl around the atoms of the sulfur because of which those have been referred to as the refractory S compounds. None-the-less, those compounds' reactivity toward the oxidation has been high due to the alkyl groups' electron-donating effects, increasing electron density on S atom, as a result facilitating electrophilic attacks of the Sulphur on the atom of the oxygen throughout the oxidation [27]. In the present work, we carried out ODS of heavy naphtha fraction using air-assisted performic acid oxidation system in the presence of PMN550 catalyst. The reaction conditions (temperature, time and concentration of oxidants, i.e., H₂O₂ and formic acid) at atmospheric pressure in a batch shaking unit were optimized. This method introduces a novel method in the treatment of petroleum fractions, especially crude oil in general and the disposal of toxic sulfur and contaminated using the adsorption technology by cheap and efficient catalysts.

2. Experimental

2.1. Materials

Semi-flexible Formic acid (HCOOH) from (Shanghai Macklin Biochemical Co.,Ltd); Hydrogen Peroxide H₂O₂ from (PanReacAppliChem); Acetic acid Glacial C₂H₄O₂ were obtained from Biosolve (Biosolve B.V., Valkenswaard, The Netherlands)), Malic acid C₄H₆O₅ (BDH Company), Phthalic acid C₈H₆O₄ (MERCK), Sulfuric acid H₂SO₄ (THOMMAS BAKER), Methanol CH₃OH from (PubChem), Ethanol C₂H₅OH from (MERCK) & Distilled water (Iraqi local product).

2.2. Heavy Naphtha

The Experimental work was carried out on sample of Midland Refineries Company/ Daura refinery Heavy Naphtha. Table 1 presents the physical characteristics of Heavy Naphtha.

Table 1 Real true boiling point (TBP distillation) of Al Daura refinery

Expected ASTM Distillation D86	
Vol. %	Time
I.B. P	80 min
5%	92
10%	100
20%	106
30%	111
40%	116
50%	122
60%	127
70%	132
80%	138
90%	146
95%	154
E.B.P.	176
T.B. P	98
RES.	0.8

Table 2 Properties of heavy naphtha (HN) feedstock Daura refinery

Physical Properties	
Spec. gravity at 15 Co	0.7377
Crude TBP cut points Co	100-170
Sulfur content PPM	651.3
RON	40-50

2.3. Preparation and Characterization of Catalyst (PMN550)

Natural zeolite is abundant in the Iraqi local markets, many confiscations India, Yemen, China and others. Where the focus in this research is on the natural zeolite that is exported (India). After it has been prepared, developed and activated to be suitable for the catalytic oxidation process, for several reasons. First: its abundance, second: its low cost, and third: the nature of its composition. The natural Indian zeolite consists of Anorthite, Albite & Hematite rocks. As shown in the X-ray diffraction (XRD) examination. The method of its preparation, development and activation as a suitable catalyst for catalytic oxidation process (CODS) The raw natural zeolite was milled in the laboratory. The crushed natural zeolite was cross-linked by an electric sieve shaker for 10 minutes. To obtain 10 mesh. Then, it was dried overnight in an oven at 40°C, then (10g) natural zeolite was calcined for (4 h) at 550°C. The powder was cooled to room temperature by turning off the furnace before the catalytic oxidation process. The synthesized catalysts were characterized by elemental analysis Via XRD surface properties and XRF, FTIR, BET, TGA and AFM analysis.

2.4. Activity tests of the catalysts for ODS reactions

The batch reactor has been utilized for carrying out the sulfur compound reaction of oxidation. In addition, this reaction is carried out in a 500 mL flask with 3 necks and a round bottom. The middle neck is linked to a vertical condenser that condenses oil feedstock' vapours, allowing only air to get out. The other neck has been utilized as an air inlet that's connected to the compressor, and the air is going to reach the flask bottom via a glass tube. In contrast, the 3rd neck has been utilized for measuring flask temperature through the insertion of a thermometer into solution inside the flask and for withdrawing sample reaction in the case when the time has approached. The batch reactor is heated and mixed with the help of a heating mantle stirrer. The process diagram, as well as the experimental device of ODS, are shown in the two Figures 1 and 2

3. Oxidation of experimental sulfur procedure

3.1. Catalytic oxidation of desulphurization (CODS) of Heavy Naphtha

Heavy Naphtha ODS experiments were carried out using 20 mL of real heavy naphtha in a 3-neck flask that has a condenser, which was placed in an oil bath that is mounted on a magnetic stirring hot plate. The sample was treated with 2.5ml formic acid, 2 ml H₂O₂, and 0.2g PMN550 catalyst. Utilizing Pyrex glass air bubbler, dry air has been bubbled through the reaction mix at a 150 ml/min flow rate and stirred for (20,40,60,80,100,120,140) min. with constant air bubbling and temperature maintained at (20,30,50,70,80,90,120) C. Following oxidation, the sample has been mixed with an equal extraction solution volume (20:80 methanol/distilled water) and

transferred into a separating funnel, where oil layer has been separated. To achieve maximum sulfur removal, the temperature of the reaction and the time have been enhanced. The reactivity regarding various sulfur compounds has been studied via conducting reactions at various temperatures and withdrawing small aliquots from the reaction sump at various times. The kinetics of oxidation were also investigated. Hydrogen peroxide and performic acid concentrations were optimized. It was also looked into the impact of extraction number on total desulfurization yields.

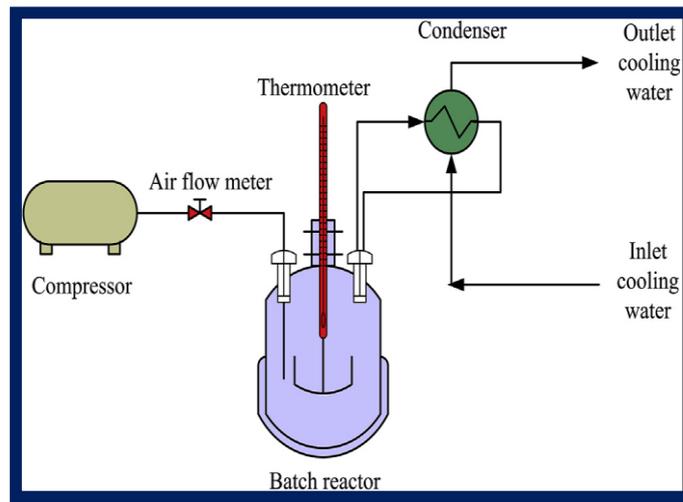


Figure 1 Process diagram of batch reactor system.

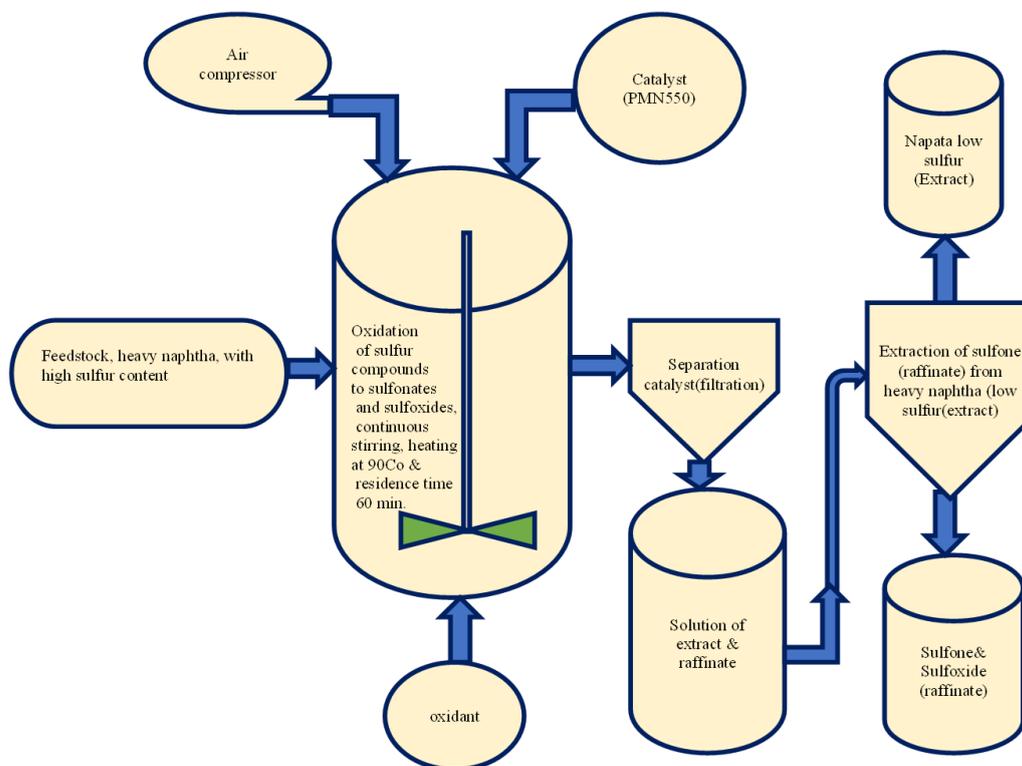


Figure 2 Schematic representation of the ODS system

3.2. Measure Sulfur concentration ASTM D7039

The sulfur concentration has been determined through SINDIE OTG sulfur analyzer using the ASTM D7039 method. The SINDIE device provides enhanced accuracy and precision when measuring ultralow sulfur diesel and gasoline, as well as crudes and heavy fuel oil. Because ASTM D7039 approach is optimum for refining industries, in which performance, reliability and detection are crucial. The device is located at the Ministry of Oils' Researches and Development Oil Centre as shown in Figure 3, 4 and 5.



Figure 3 Experimental device of ODS reactions

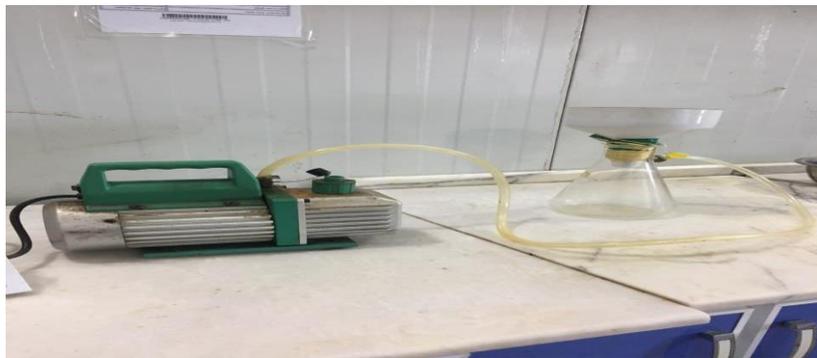


Figure 4 Filtration stage by vacuum



Figure 5 Changing the color of raffinate due to changing operational conditions and the amount of sulfur content also varies

3.3 Total Sulfur Analyses

The total sulfur concentration in the samples has been determined using an SN analyzer (Antek by PAL) with chemi-luminescence and a vacuum ultraviolet detector. As a carrier gas, argon was used, and pure oxygen was used as an oxidant. Analyses have been carried out in triplicates, with the average result indicated for every μl of injected samples. Using the next relation, the desulfurization yield related to the real heavy naphtha has been calculated as %desulfurization.:

$$\% \text{Desulfurization} = \frac{(S_o - S_t)}{S_o} \times 100 \quad (1)$$

where the S_o represents the sulfur concentration of the original heavy naphtha and S_t represents the treated oil's sulfur concentration.

3. Results And Discussion

4.1 Characterizations of the catalysts

The characterization of composite supports and the prepared catalysts provides information regarding morphology, structure, and chemical composition. The data is vital to explain the relations between their physiochemical and chemical properties as well as on the catalytic activity.

4.4.1 Fourier transform infrared (FTIR) -Spectrum

In FTIR spectra illustrates that Sharp feature appearing corresponds to hydroxyl groups of our PMN550 peak at 3400 cm^{-1} [28]. It might be identified. Also, the peak at the value of 1183 cm^{-1} represents Si-O-Al and Si-O-Si bonds in a stretching mode. In addition, TiO_2 showed strong absorption peaks at 1402 & 1654 cm^{-1} , FTIR bands at 780 cm^{-1} and 1100 cm^{-1} might be allocated to asymmetric and symmetric stretching vibration values of Si-O-Si linkage regarding the model of the zeolite [29][30]. The vibration modes of 1046 cm^{-1} and 793 cm^{-1} have been assigned to the internal vibration of SiO_4 . The H-OH bending vibrations related to molecules of water that were adsorbed have been identified at 1625 cm^{-1} . FTIR spectroscopy thoroughly detects the acidic groups of the hydroxyl OH of solid catalysts as shown in Figure 6 [31][32].

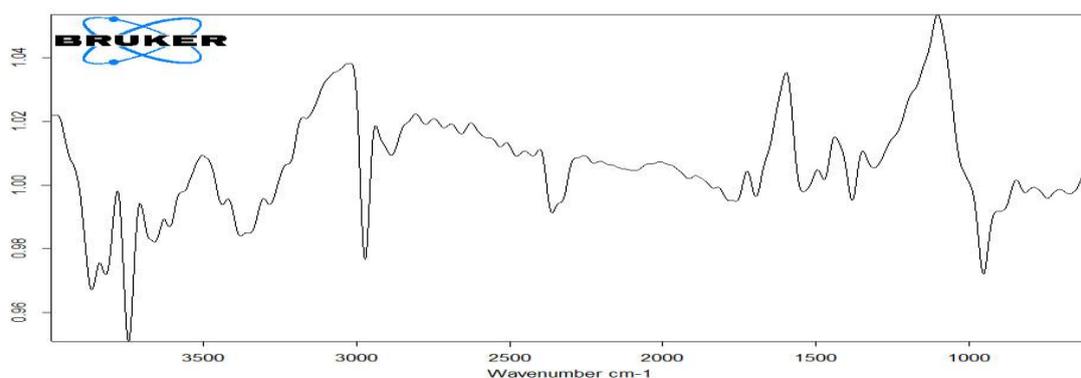
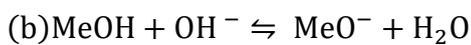
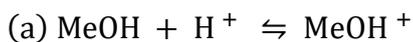


Figure 6 FTIR-Spectrum

4.4.2 Chemical composition

XRF was applied for determining the structural formula related to prepared samples. XRF analyses have indicated that Natural Zeolites has been majorly composed of Al_2O_3 (11.437%) and SiO_2 (45.104 %) succeeded by Fe_2O_3 (8.449%), CaO (7.276%), MgO (4.183%), Na_2O (2.432%), K_2O (2.18%), TiO_2 (1.257%), MnO (0.086%), and P_2O_5 (0.851%). In the existence of aqueous solutions, surface OH groups were developed on such oxide types. Results have exhibited that 0.270mmol/g surface OH groups have been present on pumice catalyst surface. OH groups that have been formed on the surfaces of the metal oxide have played the role of Brnsted acid sites



In which, MeOH_2^+ , MeOH , and MeO^- represent the protonated, neutral, and de-protonated surface OH groups.

4.4.3 X-ray diffraction (XRD)

XRD has been defined as the major analytical method that is used to determine the grain size, phase composition, and crystal structures of materials as shown in Figure 7. Based on pigments' distribution, the material composition might be analyzed (qualitatively) by comparing the powder diffraction. In addition, the catalysts' XRD analysis was conducted at the temperature of the room within a range of Bragg angle $10^\circ \leq 2\theta \leq 90^\circ$ at 2°min^{-1} scanning speed via X-ray diffract meter, with the use of $\text{Cu K } \alpha$ - radiation ($\lambda=3.44690 \text{ \AA}$).

The analysis results indicate that the main PMN550 sample phases have been anorthite, albite, and hematite. PMN550 catalyst exhibited many patterns of XRD as shown in Figure 8.

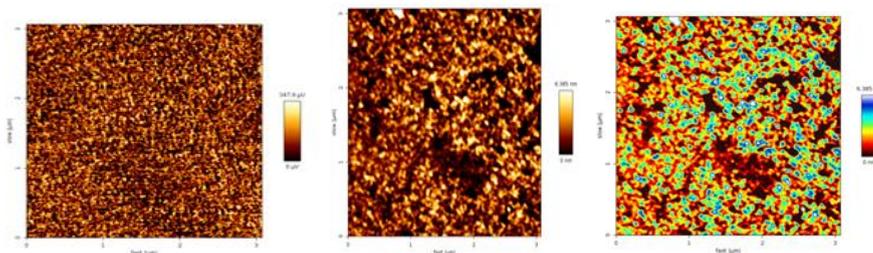


Figure 7 AFM particle size distribution with average diameter

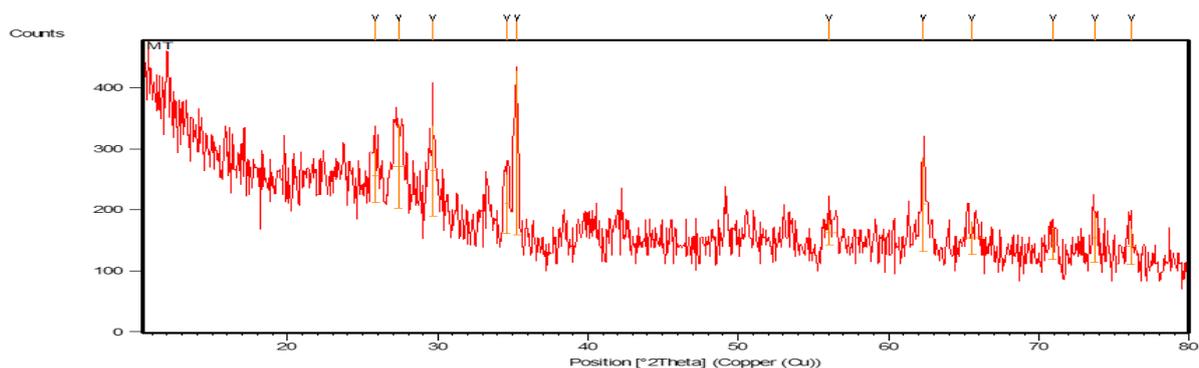


Figure 8 XRD Diagram

4.4.4 Pore volume and Surface area analyses

The pore volume and surface area have been measured for prepared PMN550. Table 3 shows the pore volume, surface area, and pore sizes of synthesized PMN550. It may as well be observed that after calcination, surface area and pore volume have been slightly decreased because of the occupation regarding active components in certain spaces within samples. The micrographs showed that the particles of the catalyst had higher agglomeration, while individual granules corroded and rough surfaces that which might be because of particles' attrition throughout the reaction and the reacting materials' settling on the surface of the catalyst.

Table 3 Summary of pore volume, surface area, and pore size of PMN550 catalyst

Catalyst	Surface area (m ² /gm)	Pore size (nm)	Pore volume (cm ³ /gm)
PMN550	0.4703	12.71315	0.001495

4.4.5 Thermal gravimetric analysis (TGA)

Figure 9 shows the TGA profiles of the catalyst PMN550 sample. From this figure, the curve showed two regions regarding the mass loss: the first one (between 110-290oC), with mass loss values about 10%, associated with the evaporations of the physically-adsorbed water on a solid [33][34]. In the range of 420-790oC, it comes from releasing the chemisorbed water that occurs at 590oC [35]. At temperatures above 790 °C, the weight of the sample tends to remain stable. The mass loss values identified in TGA experiments at (4.7526%) for the catalysts. Such good results indicated that the catalyst PMN550 has a good thermal stability. The highest thermal stability is achieved for PMN550, where the total mass change equals 4.7526%. From 130°C to 790 °C, there was a decrease in the mass-loss rate, i.e., again in thermal stability because of the char. lastly, starting at a temperature of 790 °C, the decomposition regarding such intumescent layer and thus of composite might be identified.

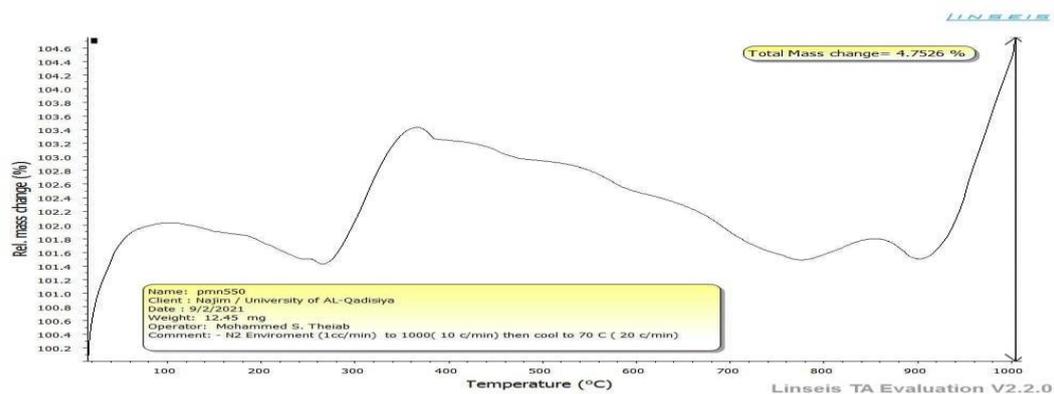


Figure 9 Thermal gravimetric analysis (TGA)

4.4.5 Scanning Electron Microscopy (SEM)

The surface morphology of the prepared PMN550 has been displayed by the SEM. Figure show SEM image with three magnification size 50 μ m, 20 μ m 10 μ m and 5 μ m. the average particle size and practice size distribution at any range has increased after calcined at 550 °C. It was observed that Natural Zeolites surface morphology had been changed. The SEM of the catalysts showed the particle size at 164.5 nm as shown in Figure 10. Also, the shape of the particles that are presented in these Figures is in spherical form.

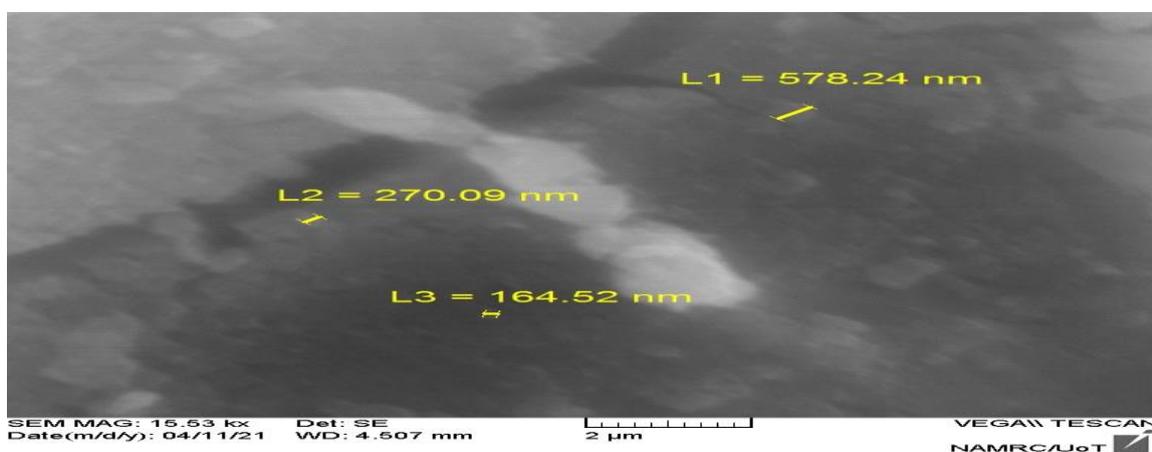


Figure 10 SEM images of the catalyst prepared with different scales

5. Oxidative desulfurization results

Organ sulfur components in naphtha include sulfides, thiols, thiophenes, disulfides and benzothiophenes. The reactivities of the oxidation regarding other organ sulfur compounds existing in naphtha have been investigated because the traditional HDS approach might result in efficiently removing the sulfides, aliphatic thiols, and di-sulfides from naphtha [36]. Model and actual oil samples were desulfurized with the use of oxidation with HCOOH and H₂O₂ as oxidants and air as a co-oxidant in the existence of PMN550 as a catalyst. The model oil's ODS has been first examined

in the existence of catalysts using 2ml HCOOH and 2ml H₂O₂ at 80°C for one hr, after which the real heavy naphtha has been extracted using an 80% methanol (aq) solution. The activity of the prepared catalyst is tested by employing the oxidative desulfurization process. Heavy Naphtha (HN) is used as an oil feedstock and air as an oxidant in a batch reactor. Several operating conditions affecting the reduction of sulfur content such as reaction time, reaction temperature, the catalyst amount, type of acid, the content of Hydrogen Peroxide, the content of formic Acid, and the Extraction cycle are studied. The effectiveness of catalytic and thermal desulfurization processes in batch mode with the use of a water bath shaker for removing sulfur from heavy naphtha fractions at different parameters is listed in the procedure section. As a result, the following explanations are given for the obtained results.

5.1 Effect of temperature

As can be seen in Figure 11, when there is an increase in the system's temperature, the efficiency of the percentage desulfurization increases as well. At the same time, all the rest of the variables remained constant at the optimal levels. As the reaction temperature rises, so does the rate of production of the active species of oxygen in addition to sulfur compounds' oxidation. As a result, choosing an adequate high reaction temperature is advantageous. In the case where the temperature of the reaction has been raised from 25C° to 90 C°, the active oxygen species' formation might speed up the sulfur oxidation reaction. The impact of temperature, on the other hand, is common, the increase of mobility that is related to acidic ion solution. In addition to that, rising temperatures could cause the swelling of the internal catalyst media structure, allowing further penetration of the ions of the sulfur. It has been discovered that increasing the temperature of the feed from 25C° to 90 C° or more increased sulfur conversion by oxidation. This impact could be because at higher temperature degrees, the rupture of the bond results in causing an increase of the active sites. As a result, the sulfur compounds' removal efficiency from the heavy naphtha will improve [30][31].

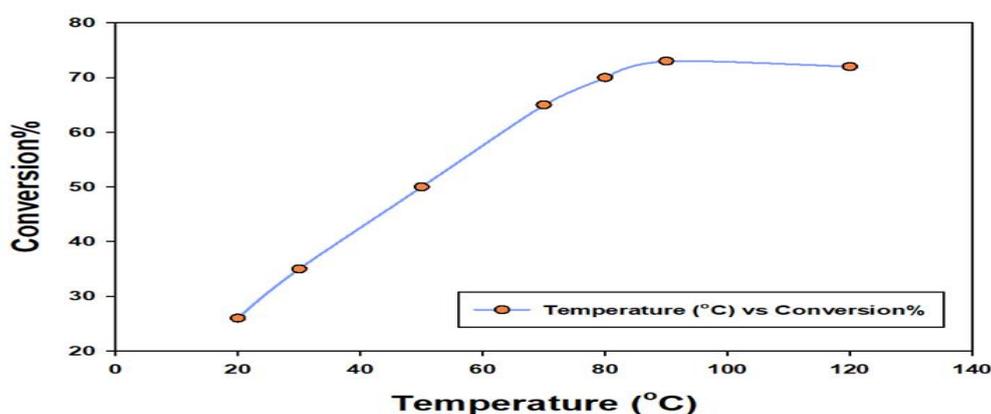


Figure 11 Effects of the temperature on the efficiency of the percentage desulfurization at the optimal conditions.

5.2 Effect of contact time

As shown in Figure 12, in the case where the time of the process of the sulfur desulfurization in heavy naphtha was raised, the efficiency of the percentage desulfurization has been increased in the case where the rest of the variables stay constant. This could be because the desulfurization time increases while the rest of the variables remain constant (at the optimal values), the solution spends more time compared to it in the case where time decreases, causing sulfur contents to be thermally-treated or in contact with the surface of catalysts for a longer period of time. As a result, the catalyst may convert more S molecules or uptake more S from the solution. As a result, the efficiency of the desulfurization of heavy naphtha solution will increase as a percentage.

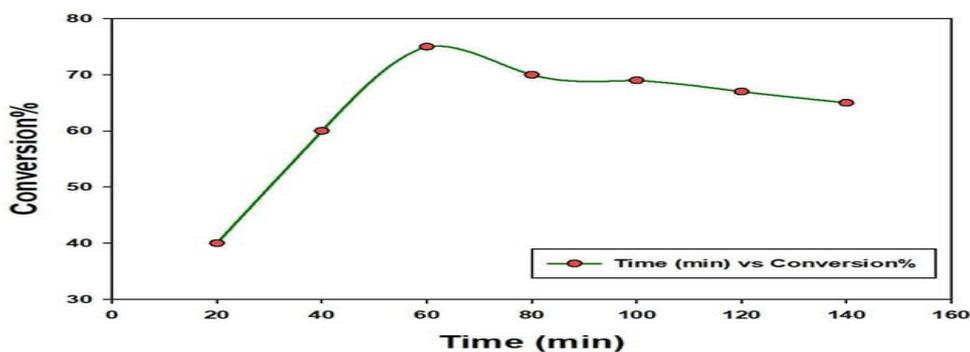


Figure 12 Effects of the time of the contact on the efficiency of the percentage desulfurization at optimal conditions.

5.3 Effect of catalyst amount

As can be seen in Figure 13, in the case when there is an increase in the catalyst amounts, the efficiency of percentage desulfurization has been increased as well, while the rest of the variables remained constant. The increased weight of PMN550 means that the surface area related to the catalyst for adsorptions and thus reaction has been increased. Therefore, the number of the active sites on the surface of the catalyst has been increased, increasing availability regarding reaction binding sites and, as a result, increasing the efficiency of sulfur compound conversion on the two catalyst types. Furthermore, the catalyst's ability for adsorbing and reacting a greater number of sulfur molecules from the light naphtha has been increased, resulting in higher efficiency of the percentage desulfurization from liquid solutions and lower sulfur content in heavy naphtha.

5.4 Effect of the content of hydrogen peroxide

The results reported that there was increased percentage desulfurization with the increase in a ratio of hydrogen peroxide to heavy naphtha (H_2O_2/HN) (an increase in H_2O_2 volume with a constant volume of HN 20 ml) till (12ml in catalytic desulfurization and 2.0ml in thermal desulfurization) in the case where all of the other variables have been constant at the optimal values, whereas Figure 14

shows that there is a decrease in the conversion of sulfur after those values. These results might be explained because of the considerable impact of (H_2O_2/HN) ratio upon producing more ions of OH^- and CH_2O_3 that are increased with an increase in H_2O_2 volume.

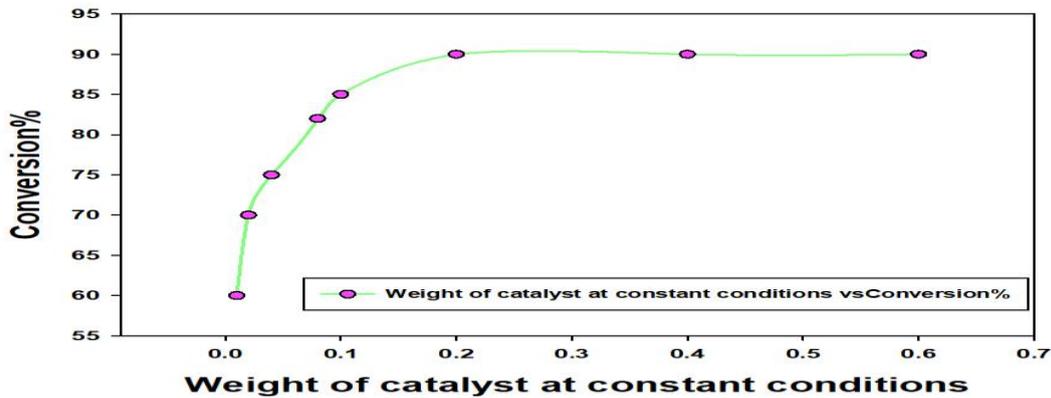


Figure 13 Effects of the catalyst weight upon the efficiency of the percentage desulfurization at the optimal conditions.

Thus, the oxidation process related to sulfur complexes in light naphtha fraction is going to be increased in the 2 processes of desulfurization. The sulfur concentration in HN will be reduced and result in an increase in desulfurization process efficiency. Yet increasing H_2O_2/HN ratio beyond (more than 12ml in catalytic desulfurization and more than 2.0ml for thermal desulfurization via PMN550 catalyst) will cause an increase in the solution's acidity because of the high H_2O_2 concentration and simultaneously result in cleavage H_2O_2 into oxygen. The formic acid formations is going to be influenced, and sulfurs conversion effectiveness is going to be reduced. Thus, the ratio of H_2O_2/HN has been considered as one of the significant factors impacting the catalytic and thermal desulfurization process, and the well observations regarding H_2O_2/HN ratio should be considered as shown in Figure 15. Those results are in accordance with the results of [37][38][39].

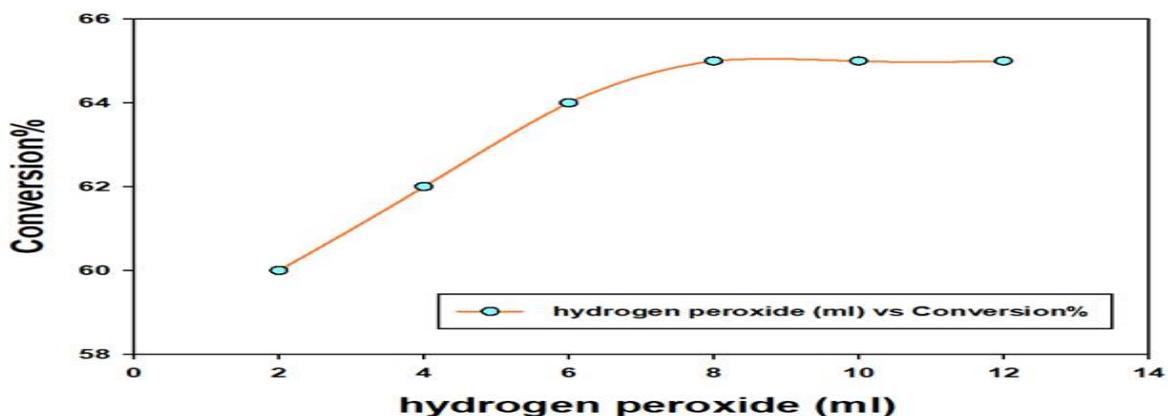


Figure 14 Effects of the hydrogen H_2O_2 to the ratio of the light naphtha (H_2O_2/HN) on efficiency of percentage desulfurization at optimal conditions.

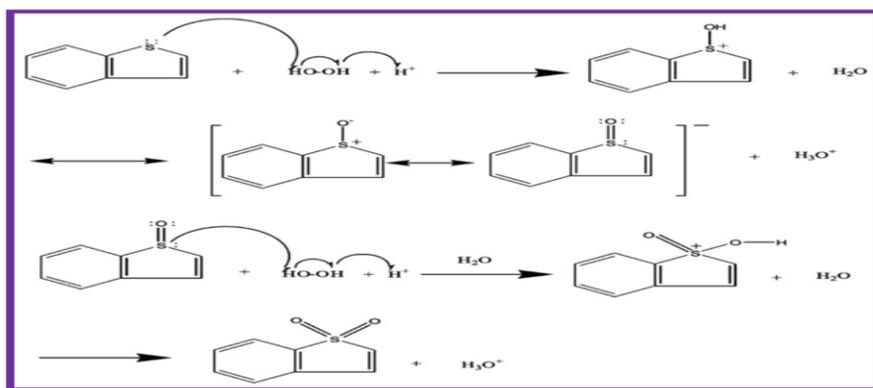


Figure 15 Oxidation mechanism with H₂O₂ in presence of a proton.

5.5 Effect of formic acid content

The results have shown that the content of the desulfurization efficiency from the heavy naphtha in the catalytic as well as the desulfurization procedures have been increased in the case of the increase in the content of the formic acid, maintaining all of the other variables constant at the optimal levels, as can be seen from Figure 16. such decrease in the conversion of the sulfur may be clarified below:

An increase in formic acid content values is favorable for sulfur oxidation, which is why the reaction of the oxidation will have the optimal behavior and present more sufficient sulfur compounds' conversion. Nonetheless, the high formic acid content value has provided a proper surrounding for the reaction between the HCOOH and the H_2O_2 for the purpose of producing the pre formic acid that promotes the process of sulfur oxidation. Moreover, the performic acid's concentration has been increased in solution leading to catalyzing H_2O_2 to form pre formic acid through the free radical of the active oxygen on the surface of PMN550 catalyst that has been considered as a promoter for the process of sulfur oxidation. These results have been perfectly in agreement with the results by [28].

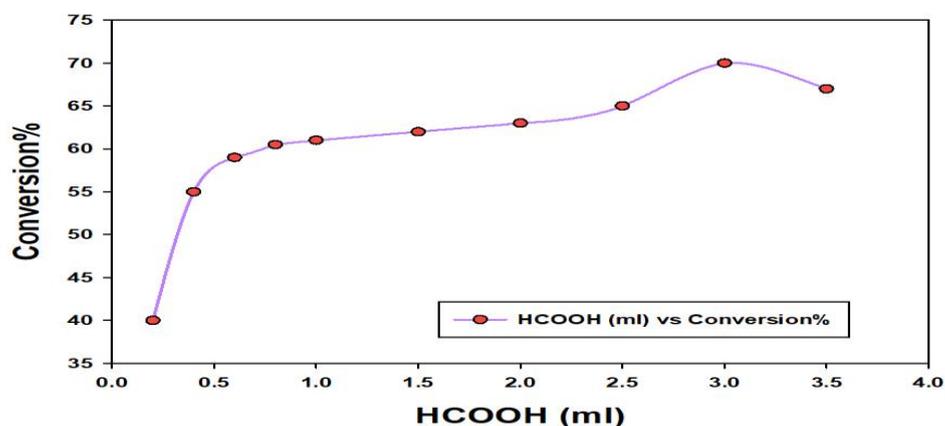


Figure 16 Effects of the pH of the solution on the efficiency of the percentage desulfurization at the optimal conditions.

6. Extraction of Oxidized Real heavy naphtha(Heavy Naphtha)

The polar solvents were utilized in order to extract oxidized oil in the process of the ODS. In this research, the solution of the methanol-water (80: 20) has been utilized to extract the real heavy naphtha that has been oxidized in the presence of the PMN 550. For the purpose of investigating the solution of methanol-water (80: 20) extraction efficiency, extracted sulfur compounds' concentration has been researched. The sulfur concentration balance in the extract of the heavy naphtha, following catalytic oxidation, has been illustrated in Figure 17 data has revealed that the model S compounds might be extracted slightly by the solution of the methanol-water with the oxidization of heavy naphtha. On the other hand, in the cases of the catalytic oxidation that is followed by heavy naphtha extraction, about 90% of S has been eliminated. Throughout the step of the extraction, all compounds of oxidized sulfur have been shifted to the solution of the methanol-water. The results that have been listed in Table 4 have shown that the desulfurization yield of 1st, 2nd, 3rd and 4rd extraction stages was 90, 92, 95 and 99%. It has been observed from results that following the 2nd extraction, there have not been many changes in the efficiency of the desulfurization, which suggests that the extractions in the 4 stages have been helpful in the maximal oxidized sulfur compounds' removal. Due to the high solvent system polarity, the heavy naphtha recovery yield has been very good, approximately 98% - 99%, the minor yield loss could result from the handling throughout the process of the extraction.

Table 4 desulfurization Extraction cycles.

Extraction cycles	Conversion %	Sulfur content (ppm)
1	90	64.83
2	92	51.804
3	95	32.265
4	99	8.07

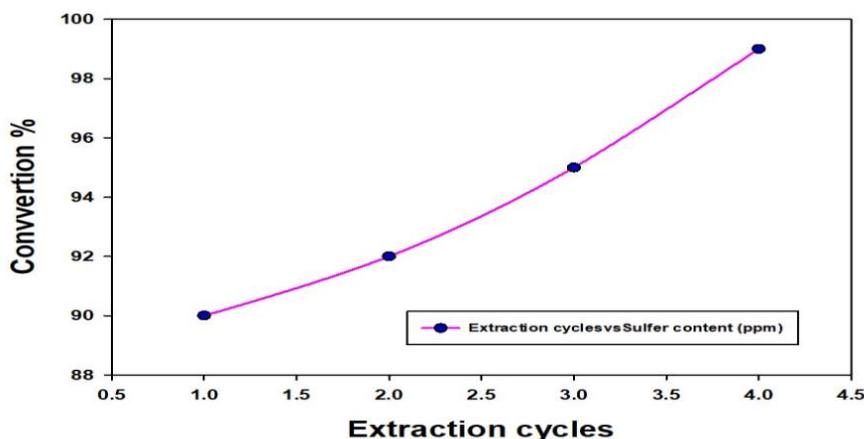


Figure 17 Desulfurization of heavy naphtha in presence of the PMN550 catalyst with several extractions with the methanol-water

6. Conclusions

The following conclusions could be obtained:

1. An efficient catalyst has been prepared according to catalyst characterization tests (XRD, XRF, AFM, SEM, BET, and TGA).
2. Catalytic ODS of heavy naphtha was studied in the presence of PMN550 catalyst, utilizing air assisted oxidation of the performic acid. Catalysts have been synthesized and characterized in lab. The maximal removal of the sulfur of the heavy naphtha has occurred at 90°C, ambient pressure, 60min., and 150mL/min air flow rate.
3. The sulfur content of the heavy naphtha was reduced from 651.3 ppm to less than 10 ppm in 60 min at 90 °C temperature.
4. The increase in the amounts of solid catalyst-adsorbent results in the enhancement of the procedure of the desulfurization as a result of increasing surface area and active sites for the adsorption as well as the catalytic processes.
5. The increase of pH has resulted in decreasing the efficiency of the removal due to the fact that low value of the pH that has resulted from the formic acid has been favorable for the oxidation of the sulfur. Moreover, low pH provides a proper environment for the reactions between the hydrogen peroxide and the formic acid, producing and promoting the process of sulfur oxidation.
6. The temperature has a significant impact on the procedure of desulfurization. The increase of the degree of temperature to 90°C results in the enhancement of active oxygen species' production rate and sulfur compounds' oxidation. Active oxygen species' formation is capable of accelerating sulfur's oxidation reaction. In addition to that, the increase of temperature results in decreasing the viscosity, and that could result in increasing the heavy liquid penetration within solid pores and enhancing adsorption and catalytic reactivities.
7. The maximal efficiency of the desulfurization for the catalytic desulfurization has been 99% with the use of the PMN-550 as the catalyst respectively at a ratio of the (H₂O₂/ Heavy naphtha) at low pH and a 90°C temperature and 60 min contact time.
8. The increase of the contact time between liquid reactants enhances the procedure of desulfurization through the rise in the percentage of the oxygenation of the compounds of sulfur. In addition to that, the increase of processing time results in increasing the contact time between the adsorbent, PMN-550 catalyst and the compounds of the sulfur, resulting in the increase of the efficiency of the adsorption.
9. The results have shown that the desulfurization yield of 1st, 2nd, 3rd and 4rd extraction stages was 90, 92, 95 and 99%. It has been observed from results that following the 2nd extraction, there have not been many changes in the desulfurization efficiency.

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الأكسدة التحفيزية لازالة الكبريت من النفط الثقيل مع بيروكسيد الهيدروجين والعامل المساعد (PMN550)

الخلاصة: في هذا البحث تمت دراسة عملية ازالة الكبريت التأكسدي الحفاز من كسور النافثا الثقيلة باستخدام حمض الفورميك ومساعدة الهواء وأوكسيد H₂O₂ في وجود الزيوليت الطبيعي (PMN 550) كمحفز. تم تصنيع المحفز المستخدم في المختبر. وأظهرت التحليلات ل BET ، AFM ، FT-IR ، XRD ، XRF ، SEM ، و TGA أن المحفز المحضر له خاصية محفز فعالة. وقد زاد محصول ازالة الكبريت في حال استخدام ال HN في وجود الزيوليت الطبيعي (PMN-550) وانخفض محتوى الكبريت في HN من 51.3 6 جزء في المليون إلى اقل من 10 جزء في المليون في فترة 60 دقيقة عند درجة حرارة Co 90 ، مما أدى إلى ازالة مركبات الكبريت لاحقا من مرحلة الأوكتان. هذا العلاج التأكسدي قلل بشكل فعال من محتوى الكبريت في النافثا الثقيلة ، والامتزاز مع PMN550 قلل من محتوى الكبريت إلى أقل من 9 كتلة في الدقيقة. تم استخدام مفاعل دفعي لتقييم أداء المحفز المحضر في درجات حرارة تفاعل مختلفة تراوحت بين 20 و 120 درجة مئوية ولفترات زمنية مختلفة تراوحت بين 20 إلى 140 دقيقة مع كميات مختلفة من محفز الزيوليت الطبيعي (PMN550). تم استخدام العديد من مقاييس التصميم لتحديد العوامل التي تعطي ازالة محتوى الكبريت الأمثل من HN . كانت ظروف التشغيل المدروسة هي نسبة H₂O₂ إلى النافثا الثقيلة ودرجة الحرارة ودرجة الحموضة في المحلول ووزن المحفز ووقت الاتصال.