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Improving the Quality and Production of Reformate

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Abstract

One of the primary and most crucial units in Iraqi refineries is the gasoline reforming unit. In order to simulate and upgrade the conventional unit to the other unit configuration (Continuous Catalytic Regeneration Reformer Process (CCRRP)), it was suggested in this study to develop the gasoline reforming unit (Semi-Regenerative Catalytic Reformer Process (SRCRP)) by adding a fourth reactor (fixed bed reactor) of the same size and configuration for the last reactor of the unit that is currently used in the refinery. This study aims to investigate the effect of increasing the number of reactors on product quality. Several variables were studied in the unit, including temperature (490, 500, 510, 520, 530, and 540 °C), pressure (8 & 12 bar), Liquid Hourly Space Velocity (LHSV) 1.5 & 4.5 hr-1, catalyst type (spent and fresh), and catalyst regeneration and pre-preparation steps (carbon burning + drying + oxychlorination + calcination + reduction + sulfiding). The results showed that the maximum increasing of RON values is 10 degrees under 12 bar and 4.5 hr-1 by applying all the regeneration and pre-preparation steps with exception of oxychlorination (for spent catalyst) but with short life period of this catalyst comparing with fresh catalyst which have high activity for long interval with 8 grades increasing in RON. In addition, the RON of the reformate at (12 bar) was higher than the octane number at (8 bar). Otherwise, the RON does not differ significantly between the two LHSV values tested (1.5 and 4.5 hr-1), indicating that the LHSV had no major influence on the product's octane number for reformate improvement by adding fourth reactor. According to the catalyst regeneration and pre-preparation method, the results indicate that the highest and longest improving of octane number was obtained when a fresh catalyst was applied in the unit by performing the pre- preparation processes which include (drying + reduction + sulfiding) for it, followed by spent catalyst with all the activation steps which include (carbon burning + drying + oxychlorination + calcination+ reduction + sulfiding).

Keywords: Reforming unit, Reformate, Semi-Regenerative Catalytic Reformer Process (SRCRP), Catalyst.

تحسين نوعية وانتاج الريفورميت

الخلاصة:

تعتبر وحدة تحسين البنزين إحدى الوحدات الأساسية والأكثر أهمية في مصافي العراق. ولمحاكاة الوحدة التقليدية وتطويرها إلى وحدة مطورة أخرى والمتمثلة بوحدة (Continuous Catalytic Regeneration Reformer Process (CCRRP)، اقترحت هذه الدراسة الى تطوير وحدة تحسين البنزين التقليدية (Semi-Regenerative Catalytic Reformer Process (SRCRP)) وذلك بإضافة مفاعل رابع (مفاعل الطبقة الثابتة) بنفس حجم وتصميم المفاعل الأخير في الوحدة المستخدمة حاليًا في المصفى. بالاضافة إلى دراسة تأثير زيادة عدد المفاعلات على جودة المنتج.

حيث تم دراسة العديد من المتغيرات في الوحدة، بما في ذلك درجة الحرارة (490، 500، 510، 520، 530، و540 درجة مئوية)، والضغط (8 و12 بار)، وسرعة السائل (1.5 & 4.5 hr^{-1})، ونوع العامل المساعد (المستعمل والجديد)، وطريقة تنشيط العامل المساعد وخطوات التحضير المسبق والتي تشمل (حرق الكربون المترسب + التجفيف +oxychlorination + الكلسنة + الاختزال + الكبرتة). أظهرت النتائج أن أقصى زيادة لقيم RON هي 10 درجات تحت ضغط 12 بار و4.5 hr^{-1} من خلال تطبيق جميع خطوات التنشيط والتحضير المسبق باستثناء oxychlorination (للعامل المساعد المستعمل) ولكن مع عمر تشغيلي قصير لهذا العامل المساعد مقارنة بالعامل المساعد الجديد الذي يتمتع بفعالية عالية لفترة زمنية طويلة مع زيادة 8 درجات في قيم RON. بالإضافة إلى ذلك، كان العدد الاوكتاني لمادة الريفورميت الناتجة من المفاعل الرابع تحت ضغط (12 بار) أعلى من العدد الأوكتاني للمنتج من التفاعلات تحت ضغط (8 بار). بخلاف ذلك، لم يلاحظ تغيير كبير في العدد الاوكتاني RON بين قيمتي LHSV (1.5 & 4.5 hr-1)، مما يشير إلى أن LHSV لم يكن له تأثير كبير على العدد الأوكتاني لمادة الريفورميت بإضافة المفاعل الرابع. اما بالنسبة لطريقة تنشيط وتحضير العامل المساعد، فان النتائج تشير إلى أنه تم الحصول على أعلى وافضل تحسين للعدد الأوكتاني عند استخدام عامل مساعد جديد في الوحدة من خلال إجراء عمليات التنشيط والتحضير المسبق التي تشمل (التجفيف + الاختزال + الكبرتة) لها، متبوعة بالعامل المساعد المستعمل مع المحافظة على اتباع جميع خطوات التنشيط والتي تشمل (حرق الكربون المترسب + التجفيف + + oxychlorinationالكلسنة + الاختزال + الكبرتة).

1. Introduction

The catalytic reforming process of naphtha is considered as one of the most important chemical processes in petroleum refineries because it implies the transformation of low-octane heavy naphtha into higher-octane reformates that are used as a major blending component for transportation engines, which are called gasoline. Therefore, reforming units are applied to produce more than 37% of gasoline around the world. In addition, hydrogen gas is produced from this process as a desirable product that is used as an energy source in many fields in the future and in the refinery for the crude oil conversion processes [1]. The naphtha cut that is produced directly from the atmospheric distillation unit contains 40–70 wt% paraffin, 20–50 wt% naphthenes, 5–20 wt% aromatics, and only 0–2 wt% olefins. However, 30–50 wt% of the olefins in naphtha are produced by Fluid Catalytic Cracking (FCC) units, coking, or visbreaking processes [1]. As a result, naphtha composition has an effect on the performance and quality of the final product of the catalytic reforming unit [1-3].

There are numerous principle reactions that occur along the catalytic reforming process, such as dehydrocyclization, dehydrogenation, isomerization, and hydrocracking of the hydrocarbon molecules. On the other side, there are many types of reforming catalysts that include bi-metals and tri-metals-supported catalysts according to the required properties of the final product, which is related to the use of this product. In addition, using the bi-functional catalyst is preferred in this process because the above reactions could occur over the acid and/or metal sites represented by alumina and Pt, respectively. Each site is responsible for specific reactions throughout the process [1][4][5].

Furthermore, some of these reactions are preferable and others are considered undesirable reactions depending on the reaction chemistry and how it effects on the octane number of the reformate from one side and the purity of the hydrogen generated from the reaction on the other side [6]. Desirable reactions are responsible for high-octane production, of which include the dehydrogenation, dehydrocyclization, and isomerization reactions that considered preferable reactions. The main selected reaction among the desirable reactions is dehydrogenation due to the hydrogen gas generation and because it is the main source of aromatic production with a high octane number. In contrast, dealkylation and cracking reactions are classified as undesirable reactions. Otherwise, the most critical and predominant reaction that occurs in the first reactor of the reforming unit (depending on the unit configurations) is naphthene dehydrogenation. Therefore, reforming reactions are highly endothermic, which required extra heating during the operation to keep the reaction going in the right way. According to the classification of reactions and depending on the reaction rate, the dehydrogenation of paraffin and naphthene can be considered as a very fast reaction that generally happens in the first reactor over the metallic side of the reforming catalyst. In addition, paraffin and naphthene isomerization reactions take place with a minor difference in the reaction time within the same reactor [7]. However, hydrocracking takes a long time and occurs in the final reactor that contains the reforming catalyst. Meanwhile, the operators are adjusting the operating conditions (temperature and pressure) as a function of reactions to make sure to minimize the unwanted side reactions as much as possible that reflecting on the decreasing the catalyst life time [8].

Platinum-based catalysts supported by an alumina and promoted with chlorine (sometimes with fluorine) that are used in catalytic reforming. Most often, rhenium and platinum are mixed to create a more stable catalyst that allows for lower pressure operation. The bi-functional catalyst for the reforming is manufactured with a high surface area. The metal site (Pt) is responsible for the desirable reactions, which include hydrogenation and dehydrogenation. On the other side, isomerization is occurring over the acid (solid acid site) that is presenting with alumina; cyclization, and cracking are taking place over both sites [9]. During the run, the acid concentration will decline and the catalyst activity will decrease. As a result, enhancing the catalyst with chlorine or fluorine is critical for maintaining the acceptable percentage of acid throughout the reaction to ensure the reaction stability which reflected on the reformate production grade. In special cases, fluorine is applied to processes that deal with feedstock without hydrotreatment. The main function of adding chlorine during the reaction is considered a "dynamic promoter," which provides a stable catalyst throughout the reaction time under harsh conditions [10].

The most common designs of catalytic reforming processes are [11]:

(i) Semi-Regenerative Catalytic Reformer Process (SRCRP).
(ii) Cyclic Regenerative Catalytic Reformer Process (CRCRP).
(iii) Continuous Catalytic Regeneration Reformer Process (CCRRP).

There are few parameters that should be studied and monitoring during the reforming operation because they are considered as an indicator of the rate of reaction and quality of the products such as: temperature, pressure, space velocity, H_2/Hc ratio, catalyst type and feed quality, these parameters are all relevant to all modes of operation, including semi, cyclic, and continuous regeneration process [12] [13]. The most important operating parameters are temperature, pressure, and space velocity. Whenever the temperature increases, the RON range increases. On the other hand, pressure and space velocity are inversely related to the RON rate.

2. Materials and Methods

2.1. Materials

Reformate product was supplied from the semi regeneration catalytic unit (reforming unit) in Mid Refineries Company (MRC) which was applied as a feedstock in this project. Table (1) shows the specification properties of reformate product.

PR-9 (PROCATALYST) spent which is used for 9 years and fresh catalysts were supplied from the semi regeneration catalytic unit (reforming unit) in MRC which were applied as a plant catalyst in this project. Table (2) shows the physical and chemical properties of fresh and spent PR-9 catalyst. In addition, the specification of regenerated catalyst was shown in the same Table. More details about the regeneration steps will explain later.

Hydrogen, nitrogen, and oxygen gases were used during the catalyst pre-preparation steps (regeneration steps) and the actual runs. All gases with purity (99.9999%) were supplied from local markets with exception of H_2 gas that was supplied from the H_2 generator unit in PRDC.

Propylene Di Chloride (PDC) was supplied from MRC, Di Methyl Di Sulfide (DMDS) was supplied from south refineries company and ceramic ball was bought from local markets.

Table (1): The specifications of Iraqi-reformate (final product) from semi regeneration catalytic unit in MRC

Specifications	**Unit**	**Measurement**
API. at 15.6 °C		54
Density at 15.6 °C	g/cm^3	0.76280
Sulfur Content	ppm	0.6
Research Octane Number (RON)		91
Distillation I.B.P.	°C	43.2
5 Vol.% distilled	°C	65.5
10 Vol.% distilled	°C	72.3
20 Vol.% distilled	°C	83.4
30 Vol.% distilled	°C	93.6
40 Vol.% distilled	°C	103.3
50 Vol.% distilled	°C	114.4
60 Vol.% distilled	°C	126
70 Vol.% distilled	°C	138.2
80 Vol.% distilled	°C	151
90 Vol.% distilled	°C	167.7
EBP	°C	192
Recovery	%	93.8
Residue	%	5.7
Losses	%	0.5
RVP	psi	7.11
Calorific value	Kcal/g	11.247
n-paraffins	Vol%	13.53
Iso-paraffins	Vol%	40.49

Olefins	Vol%	8.46
Naphthanes	Vol%	1.58
Aromatics	Vol%	34.65
Oxygenates	Vol%	0
Un-known	Vol%	1.28

Tables (2): The physical and chemical properties of PR-9 (spent and fresh).

Properties	**unit**	**Spent catalyst**	**Fresh catalyst**	**Regenerated catalyst**
Pt content	Wt%	0.159	0.25	0.208
Re content	Wt%	0.118	0.25	0.118
BET Surface area	m^2/g	158.96	200	198.04
Bulk density	g/cm^3	0.824	0.74	0.736
Pore volume	cm^3/g	0.3875	0.55	0.5038
Pore size	nm	9.7524	9.5964	10.1759
Grain crushing strength	N/mm	8.93	7.06	7.06
Carbon content	%	9.5	-	3.1
Loss of ignition	%	10.8	1.7	2.1

2.2.2. Equipment

There were different equipment inside the laboratories of PRDC that used to evaluate and characterize the feed, products and catalysts for example: CFR machine (Waukesha ASTM D-2699) that used to evaluate the Research Octane Number RON which is considered as a crucial parameter for gasoline property, density (Auton paar ASTM D-4052 18a), GC analysis (Type, 1300 Thermo ASTM D-6729) to evaluate PIONAX composition, atmospheric distillation (ASTM D-86), RVP (eralytics ASTM D-5191), digital calorific value (CAL3K-AP ASTM D-240), bulk density (Autotap ASTM D-4164), metal content (ICP ASTM D7260), sulfur content (Sindieota ASTM D-7039), [carbon content, loss of ignition and grain crushing strength (MA.TEC ASTM D-6175], [BET surface area, pore size and pore volume (micromeritics ISO-9277-2010)] which will be mentioned in the discussion part.

2.3. Catalytic Reforming Pilot Plant Unit

In the laboratory of refining research section/ refining and gas research department/ Petroleum Research & Development Center (PRDC) /ministry of oil, a catalytic reforming pilot plant unit (VINCI Technology / France) was used to develop a new research concept that related by adding a fourth reactor compared with the conventional reforming process which is used three reactors (semi-regenerative catalytic reformer process) and trying to investigate the impact of this modification step on the quality of reformate and how to improve the octane number of product.

The pilot unit is designed to perform catalytic reactions under high temperature and pressure using a fixed bed reactor under hydrogen flow with the down flow operating mode of feedstock. The reactor consisted of 0.6 m long with an outer diameter 2.5 cm and 1.75 cm internal diameter of fixed bed carbon steel reactor connected with control system that attached with the unit to control the reaction parameters. There are three heating zones in the reactor and was controlled using the temperature controller in the control panel. Pilot plant unit was designed to work under operating conditions include: reactor maximum working pressure 50 bar and maximum working temperature 550 C. There is a cooling and separation zones to convert the product from the gas to liquid phase for collecting the sample and to separate liquid product from gas phase product. All the operating conditions, such as pressure, temperature, feed and gas flow, and LHSV were controlled via the control panel, the pressure, and temperature gauges that were attached to the unit. The reforming unit and all attachments are shown in Figure (1).

Fig. (1): A photograph of reforming pilot plant in PRDC

2.4. Catalytic Reforming Pilot Plant Unit Operating Procedure

Two types of PR-9 catalysts (spent and fresh) were applied in the pilot plant reactor, which was supplied from MRC; 91 gm with a 1.2 mm diameter of catalyst and 46 cm height of catalyst in reactor was loaded inside the reactor with an extra weight of ceramic balls that were applied at the top and lower ports of the reactor to maintain a regular and homogenous diffusion of feed and to prevent the channeling phenomenon of the feed.

Prior the unit start up step, make sure that there is no leak in the unit for safety issues and to maintain the operating conditions stable during the runs. Furthermore, pre-treatment steps were applied to qualify the reforming catalyst activity before the actual run and to get an active catalyst with a specific properties nearly similar to the fresh catalyst properties. So, regeneration and pre-preparation methods performed through several sequential steps which include the following:

A- Catalyst regeneration process that applied outside the reforming reactor.

B- Drying, oxychlorination, calcination, reduction and sulfiding that carried out after loading the catalyst inside the reforming reactor.

All these processes are explained below [10] [13]:

1. Spent catalyst regeneration process (coke burning) and (re-dispersion of metal sites): this process was applied to remove the carbon deposit over the outer shell of catalyst that lead to decrease the catalyst activity during the process and that could be reflected on the porous structure and mechanical strength of the applied catalyst.

   This process includes the regeneration of the spent catalyst by heating it using heating furnace with heating rate of 3-5 ^oC/min until the temperature reach to 350 ^oC and stay on this temperature for 30 minutes. After that, the heating was resumed to ramp the temperature up to 500 ^oC and hold on this temperature for 2-3 hours.
2. Drying process: this process was applied after the catalyst was loaded inside the reactor to remove the residual amount of moisture, this step includes N_2 purging at 10 bar and heating the catalyst with heating rate 30-40 ^oC/hr until the temperature was reached to 205 ^oC and keep the temperature on this value for 10 hours.
3. Oxy-chlorination process: this process was applied to prevent sintering, re-dispersion the metal clusters over the alumina surface and to improve the acid content for acid site that reduced during the operation. Gradually, increase the reactor temperature up to 510^{o}C.

   When the reactor temperature reaches to this value, the mixture of oxygen/nitrogen stream is starting to introduce into the reactor at 6% O_2 flow from N_2 Flow, after maintaining the above conditions for 3 hours start the injection of PDC with (0.75%wt of chlorine from catalyst weight) gradually using the micro syringe until the PDC volume will consumed.

4. Calcination process: this process is a complement to the oxy-chlorination process. Calcination step was applied to verify the acid content in the catalyst. By running the process under the same conditions that mentioned in step 3 except flow of N_2 at the same flowrate (in step 3) and O_2 at 7-10% flow from N_2 Flow.
5. Reduction process: this process was applied to remove the amount of oxygen that obtained from the oxychlorination and calcination steps and to prevent the catalyst agglomeration due to the moisture formation. This process includes the catalyst heating using the reactor heaters with heating rate of 40 ^{o}C/hr with continues H_2 flow until the temperature reach to 510 ^{o}C and remain on this temperature for 1-2 hours under 10 bar of hydrogen pressure. Meanwhile, the drain section was evacuated during the operation to discharge the water that obtained during the reduction operation.
6. Sulfiding process: used to partially poison the platinum catalyst or reduce its activity because the metal catalyst function has a high activity that related with the formation of hydrocarbons through the hydrogenolysis reactions. In addition, this treatment was used to reduce the metal-catalyzed cracking reactions that lead to decline the properties of the product.

   Sulfiding process was done using DMDS (0.05%wt of sulfur from catalyst weight) that mixed with hydrotreated heavy naphtha and this mixture was pumped to the reactor. The process conditions include: pumping hydrogen gas at 10 bar and increasing temperature up to 370 ^{o}C and hold on this value for 1 hour.

By the end of sulfiding reaction, the temperature was increased to 480 ^{o}C with pumping of pure reformate. After completing the regeneration process, the reformate was pumped and mixed with hydrogen with the down flow operating mode, then flowed over the catalyst bed to start the reactions. The reaction was monitored by control cabinet to adjust the reaction conditions that include: pressure, temperature and reaction flow rate. The final product was chilled before being separated in the separator. Different analyses were applied as mentioned previously.

Note: the chlorine injection process is continuous with the feed throughout the work period and for all types of catalysts, as in refineries, to compensate for the acidity drift of the catalyst during work.

The reaction was carried out under different operating conditions include:

C- Temperature range 490, 500, 510, 520, 530 and 540 °C
D- Pressure applied 8, 12 bar.
E- LHSV 1.5, 4.5 hr^{-1}
F- Catalyst: includes used and fresh catalyst.
G- H_2/HC= 6 mole ratio

Regarding to catalyst pre-treatment steps, different scenarios were tested to inspect the effect of these steps on the reformate quality that related to the catalyst performance which include the following:

- Applying all the regeneration and pre-preparation steps which include (carbon burning + drying + oxychlorination + calcination + reduction + sulfiding) for spent catalyst
- Applying all the regeneration and pre-preparation steps which include (carbon burning + drying + calcination + reduction + sulfiding) for spent catalyst with exception of oxychlorination
- Applying all the regeneration and pre-preparation steps which include (carbon burning + drying + oxychlorination + calcination + reduction) for spent catalyst with exception of sulfiding.
- Applying the pre-preparation steps which include (drying + reduction + sulfiding) for new catalyst.

3. Results and Discussion

3.1. Experimental Results Under Different Catalyst Treatment Methods

Table (3) shows the RON degree at different ranges of temperature (490, 500, 510, 520, 530, and 540 °C), pressure (8 & 12 bar) and LHSV (1.5, 4.5 hr^{-1}) by using different catalyst types which were regenerated at different methods as follows:

Table (3): Experimental results under different catalyst treatment methods which include: (A)- Spent catalyst (without oxychlorination + sulfiding), (B)- Spent catalyst (oxychlorination + without sulfiding), (C)- Spent catalyst (oxychlorination + sulfiding) and (D)-New catalyst (without oxychlorination + sulfiding)

1- Spent catalyst (without oxychlorination + sulfiding)

T/°C	12bar/ 4.5hr^{-1}	12bar/1.5hr^{-1}	8bar/ 4.5hr^{-1}	8bar/1.5hr^{-1}
490	91.2	91	89.6	89.4
500	91.9	91.7	89.8	89.6
510	92.5	92.2	90.1	89.7
520	93.7	93.5	90.9	90.6
530	95	94	92.5	91.9
540	94.3	93.3	91.3	91.1

A

2- Spent catalyst (oxychlorination + without sulfiding)

T/°C	12bar/ 4.5hr^{-1}	12bar/1.5hr^{-1}	8bar/ 4.5hr^{-1}	8bar/1.5hr^{-1}
490	98.5	93	91.8	91
500	100.7	94.7	92.1	91.8
510	100.7	96.6	93.5	92.5
520	98.4	94.9	92.6	91.7
530	96.8	93	91.9	91
540	95.5	92.7	91	90.3

B

3- Spent catalyst (oxychlorination + sulfiding)

T/°C	12bar/ 4.5hr^{-1}	12bar/1.5hr^{-1}	8bar/ 4.5hr^{-1}	8bar/1.5hr^{-1}
490	91.5	90.9	90.4	90
500	92.4	92	91.1	90.6
510	94.6	92.4	92	91.5
520	96.6	95.5	94	92.5
530	95.4	93.8	91.8	91
540	93.3	92.5	91.4	90.3

C

4- New catalyst (without oxychlorination + sulfiding)

T/°C	12bar/ 4.5hr^{-1}	12bar/1.5hr^{-1}	8bar/ 4.5hr^{-1}	8bar/1.5hr^{-1}
490	92	89.6	89	89
500	93.6	90.4	90	89.3
510	95	91.5	90.8	89.5
520	96.5	93	92	90.4
530	98.6	95	93	91
540	96	92	90	89.1

D

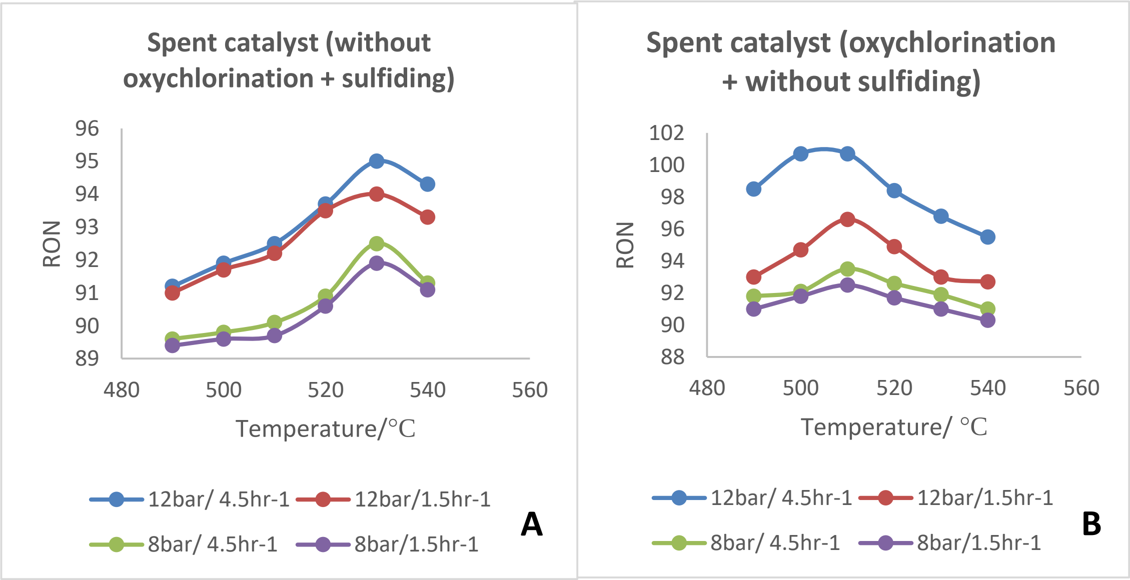
3.2. Discussion of Different Parameters

3.2.1. The Effect of Temperature

Temperature is a constraint parameter in the reforming process. The temperature was raised from 490 to 540 °C in order to simulate the temperature rates that can be applied in the semi-regeneration units [14] [15], and adopted with the applicable temperatures in the pilot plant unit located in the PRDC center. Figures (2) show the effect of temperature on the octane number. The effect of six different temperatures (490, 500, 510, 520, 530, and 540 ºC) was tested on the behaviour and change of the octane number, by fixing the other operating conditions such as pressure (at 12 & 8 bar), liquid hourly space velocity LHSV (1.5 & 4.5), and (H_2 / HC = 6 mole ratio). It is noted that all Figures follow the same behaviour for all tests, which is increasing the octane number by increasing the temperature, this is a natural phenomenon and it is like with what is mentioned in the literature of the positive effect of temperature on the reactions of the reforming unit and lead to increase the octane number. In addition, RON values are directly proportional to temperature up to a specific limit because after this limit, the reactions move in the reverse direction. The RON rates of the products enhanced with increasing temperatures due to an increase in the rates of aromatic substances in them and declining the paraffin and naphthenic percent s due to the dehydrogenation reaction along the process, but improving the RON rates varied depending on the type of catalyst and the methods of regeneration under different pressures and LHSV. Therefore, for spent catalyst, it can be noticed that by applying the sulfiding step without oxychlorination and using oxychlorination without the sulfiding step; the RON values increased at a rate of 4 degrees at 530 ºC and 10 degrees at 510 ºC under 12 bar and 4.5 hr^{-1}, respectively. However, in the case of applying the catalyst regeneration and pre-preparation conditions in the complete way, which include (sulfiding and oxychlorination), it was observed that the RON values improved by 6 degrees when the temperature was increased up to 520 ºC at the same operating conditions as mentioned above (12 bar and 4.5 hr^{-1}). In the case of the new catalyst test, at 530 ºC the value of RON was improved by 8 degrees under 12 bar and 4.5 hr^{-1}.

Overall, we conclude that as temperature rises, the RON value rises because most of the reforming reactions are endothermic reactions as a result of increasing the reactions speed which include (hydrocracking, isomerization, cyclization, naphthane isomerization, naphthane dehydrogenation) that lead to improve the branching structures and aromatics which increase the RON, but as heating rates rise to extremely high levels, the RON value falls, which may be attributed to the formation of a coke layer on the surface of the catalyst [6], resulting in a decrease in its efficiency in chemical transformations of the feedstock, which has a negative impact on the quality of the resulting reformate.

These results were in partial agreement with the results that were confirmed by [15]. This deviation is totally true which attributed to the feedstock changing from conventional heavy naphtha to modified reformate [16] and that lead to change in the reforming chemistry.



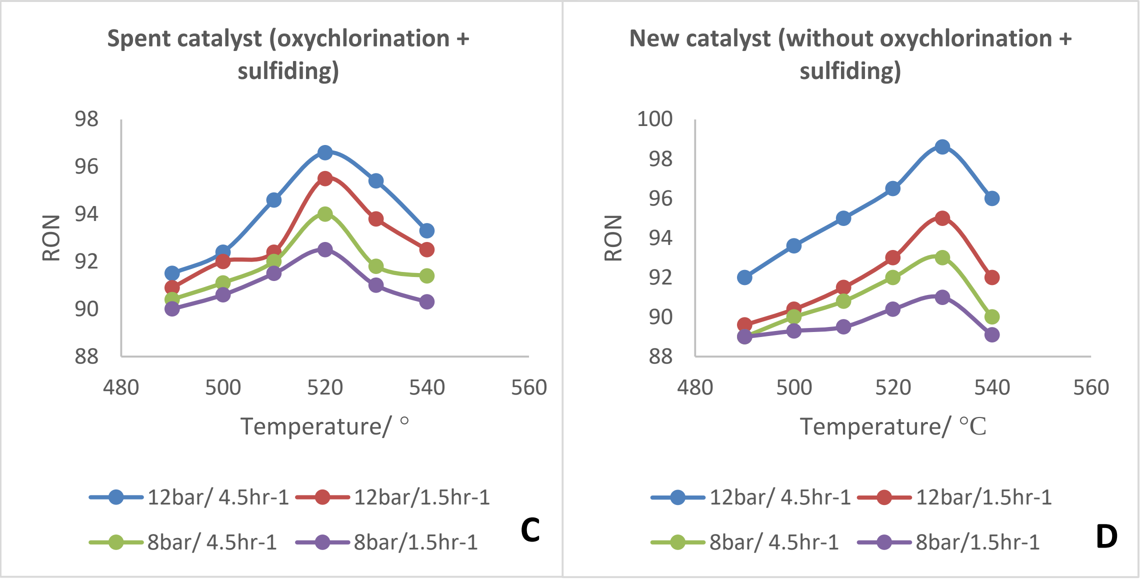


Fig. (2): The effect of temperature on RON at different regeneration & pre-preparation conditions and type of catalyst: **A** (Spent catalyst (without oxychlorination + sulfiding), **B** (Spent catalyst (oxychlorination + without sulfiding), **C** (Spent catalyst (oxychlorination + sulfiding) and **D** (New catalyst (without oxychlorination + sulfiding) at temperature range of (490, 500, 510, 520, 530, and 540 ºC), pressure (at 12 & 8 bar), LHSV (1.5 & 4.5), and (H_2 / HC = 6 mole ratio).

3.2.2. Effect of Pressure

Two values of pressure (12 and 8 bar) were tested on the change in the octane number with fixing the remaining operation conditions represented by temperature (490, 500, 510, 520, 530, and 540˚C), LHSV (1.5 & 4.5 hr^{-1}), (H_2/HC = 6 mole ratio) and two types of reforming catalyst.

Pressure is considered as one of the important variables in the reactions and has positive effect on some reactions and negative effect on others in reforming unit reactions [6]. For instance, the hydrocracking reactions are increased by pressure while (cyclization, naphthane dehydrogenation) reaction are decreased by increasing pressure and this reaction is the main reactions for creation of aromatic materials that have high octane number, while pressure does not affect the isomerization reactions (isomerization, naphthane isomerization), meaning, increasing pressure will negatively affect the octane number [6] [17]. However, it was observed in this research the opposite, that is, it was noted that the octane number of the products from reactions operating at (12 bar) pressure was higher than the octane number of the reactions operating at (8 bar) pressure, as shown in the Figures (3), and the reason for this is that all of these experiments were conducted on the same catalyst, and the reactions that were carried out at a pressure of (12 bar) were done before the reactions that were carried out at a pressure of (8 bar) and therefore, as it is known, the catalyst is at the start of operations with the highest levels of activity, as well as it is known that the presence of high pressure is one of the main conditions that protect the catalyst from rapid loss of activity and carbon deposition, thus keeping the longest operation life of the catalyst, and since the pressure of (8 bar) is considered a relatively low pressure, and therefore the catalyst will lose its activity faster when working at this pressure after the pressure (12 bar) and it will not give a clear indication of pressure comparison, so in the case of pressure comparison for such conditions, the test must be done for an separate experiment for the same catalyst, that is, the catalyst is divided into two parts, each section is tested separately for the same operating conditions and different pressures (12 and 8 bar) to clearly give the results of the pressure effect.

According to the Figures and results, the RON rates improved by 3 degrees at 8 bar, 4.5 hr^{-1} and 520 ^{o}C for spent catalyst (oxychlorination and sulfiding); in addition, 10 degrees at 12 bar & 4.5 hr^{-1} for the same type of catalyst by applying oxychlorination and without sulfiding process as shown in Figures (3 A & C). On the other hand, RON grade was upgraded by 1.5 and 6 points, respectively, for oxychlorination and without sulfiding spent catalyst regeneration steps under 1.5 hr^{-1} at different pressures (8 and 12 bar), as shown in the Figures (3 B & D). As a result, the higher RON increasing was caused by applying oxychlorination without sulfiding regeneration steps for spent catalyst at 12 bar and 4.5 hr^{-1} as a result of reasons that mentioned above which refers to the effect of oxychlorination process that increase the catalyst acid site and to maintain the acidity level along the run [13]. On the other hand, the activity of this type of catalyst under the above treatment procedures was maintained for a short time comparing with the fresh catalyst. Therefore, it can’t be considered that this upgrading of RON is permanent; and the catalyst activity was temporary comparing with the fresh catalyst.

3.2.3. The Effect of Liquid Hourly Space Velocity LHSV

Liquid hourly space velocity LHSV is defined as the speed of feedstock (the reactants) over the catalyst, and it has a reverse effect on all the reactions of the reforming unit (hydrocracking, isomerization, cyclization, naphthane isomerization, naphthane dehydrogenation), meaning that in the case of reducing the liquid hourly space velocity LHSV, the octane number will increase due to giving more time for the reactants to complete the reaction process on the surface of the catalyst [6].

In this research, two values of the Liquid Hourly Space Velocity LHSV were tested on the change in the octane number, which are (1.5 & 4.5 hr^{-1}) when fixing the other operating conditions represented by temperature, pressure, the ratio of hydrogen to the hydrocarbon and catalyst type, as follows (490, 500, 510, 520, 530, and 540 ˚C), (12 and 8 bar), (H_2/HC = 6 mole ratio) and (spent & fresh catalyst) respectively. In this research, we noticed that the octane number is not change too much of the results between the two LHSV values that were tested (1.5 & 4.5 hr^{-1}), meaning that there was no significant effect of the hourly space velocity LHSV on the octane number of the product, and the reason for that is the feedstock in these experiments is reformate and not heavy naphtha, because as mentioned previously that the purpose of this research is to evaluate the installation of a fourth reactor in the conventional reforming unit (three reactors), and since the reformate coming out of the third reactor is already rich in aromatic and branching substances, therefore, keeping it for a longer period than necessary on the surface of the catalyst did not affect the result. From that the best speed for it, is the higher speed at LHSV (4.5 hr^{-1}), which gave results nearly similar to the lower speed (1.5 hr^{-1}), and from that we conclude that the speed at 4.5hr^{-1} is the best, less value of coke deposition, and most economically, considering the increase in production quantities for the same number of produced octane. Figures (4) illustrate the behavior of using fresh catalyst at various LHSV. Other results for other regeneration modes are followed the same trends of results as shown in Figure (4).

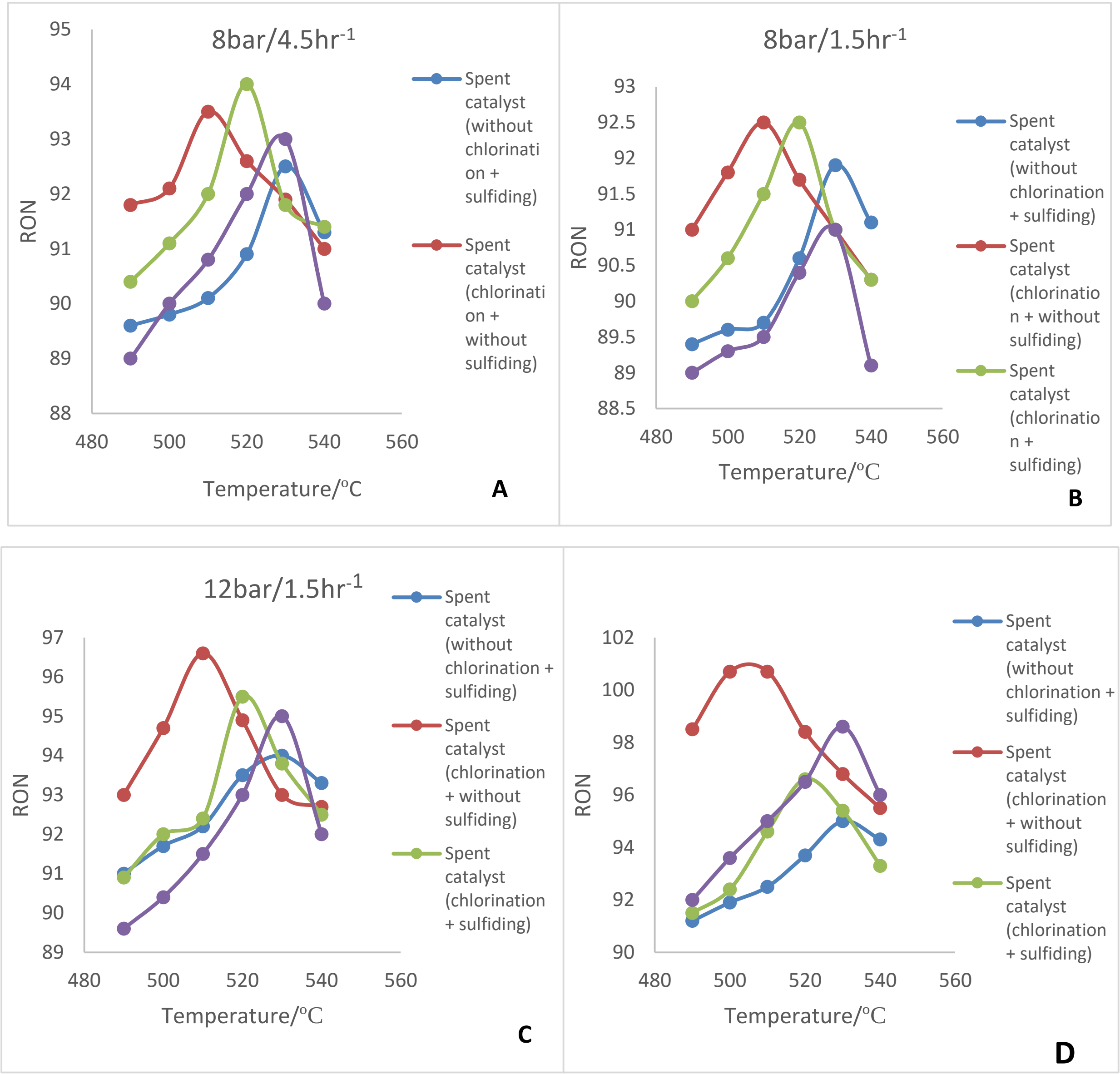


Fig. (3): The effect of pressure on RON at different regeneration & pre-preparation conditions and type of catalyst: A (8 bar 4.5 hr^{-1}), B (8 bar 1.5 hr^{-1}), C (8 bar 4.5 hr^{-1}) and D (8 bar 1.5 hr^{-1}) at temperature range of (490, 500, 510, 520, 530, and 540 °C), and (H_2 / HC = 6 mole ratio).

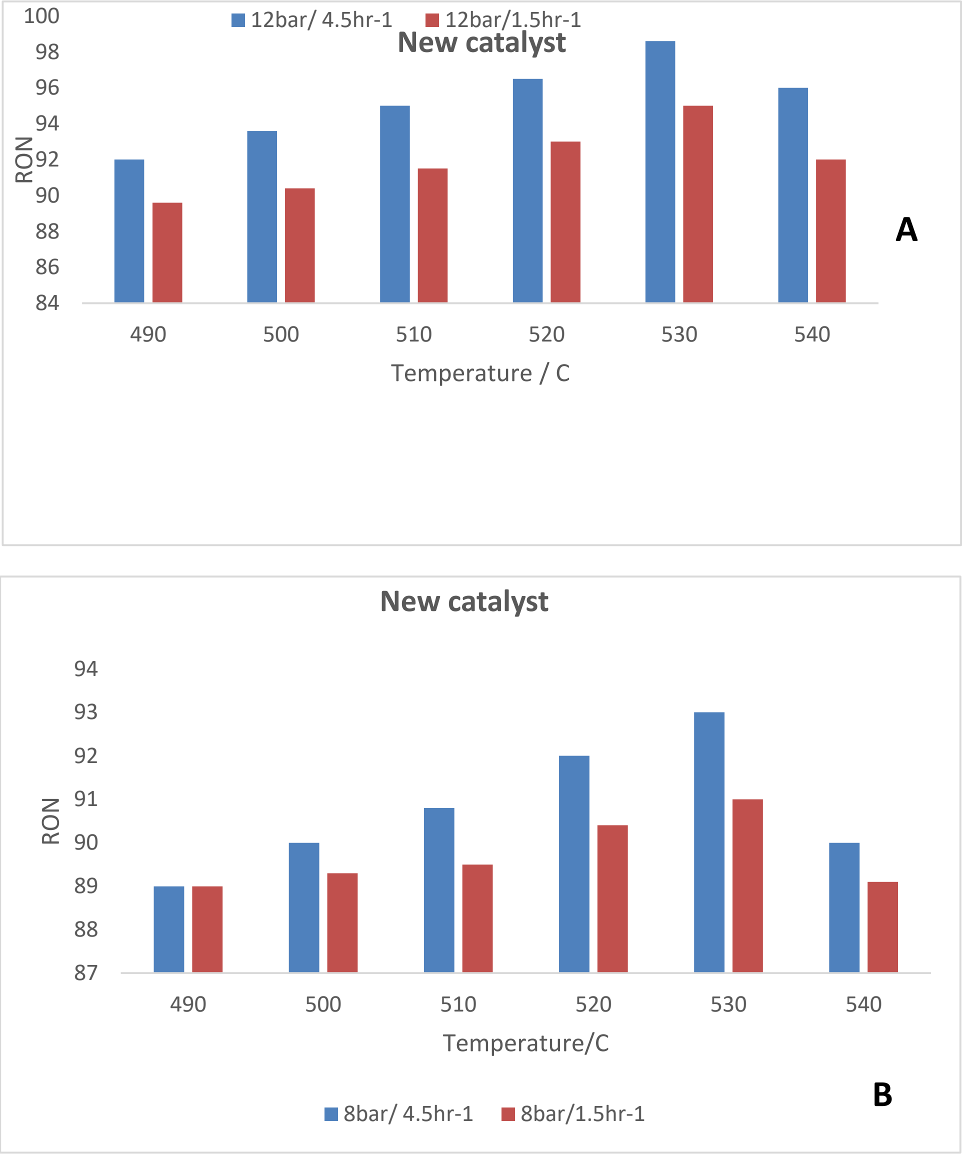


Fig. (4): The effect of LHSV on RON for fresh catalyst (without oxychlorination + sulfiding) at temperature range of (490, 500, 510, 520, 530, and 540 ºC and (H_2 / HC = 6 mole ratio) at A: pressure 12 and B: 8 bar respectively.

3.2.4. The Effect of Catalyst and Method of Regeneration

The catalyst (PR9), which are industrial catalysts used in many reforming units, and currently used in the Daura refinery, which was tested at different operating conditions of temperature (490, 500, 510, 520, 530, and 540˚C), pressure (12 & 8 bar), Liquid hourly space velocity LHSV (1.5 & 4.5 hr^{-1}), and the hydrogen-to- feed ratio (H_2/HC = 6 mole ratio); and compared with new catalyst and different procedure of regeneration methods of spent catalyst (used for nine years in reforming units in the Daura refinery), but it was tested after regeneration with different regeneration conditions from oxychlorination and sulfiding etc., to choose the best conditions.

The results in Table (3) showed that the highest octane number obtained was in the case of using a used catalyst that was regenerated with applying all the regeneration steps which include (carbon burning + drying + oxychlorination + calcination + reduction) were performed for it during the regeneration process, with exception of sulfiding (for spent catalyst), and this is a natural behavior, that this type of catalyst has the highest value of improvement in the number of octane, because the catalyst is very active after regeneration, and usually the sulfiding process takes place after the regeneration process in order to reduce its initial high activity, so that it help it to prevent activity quickly lose and thus leads to increase the life of the catalyst, so this step is strongly recommended in the unit's operating manual to prevent the fast poisoning of catalyst after regeneration and extend its operational life.

While the lowest improvement in the octane number was obtained for the catalyst that was regenerated but without the oxychlorination step (carbon burning + reduction + sulfiding), and this was what was expected, because the oxychlorination step is used to compensate for the acidity that was lost on the catalyst used, which should be (1%) for the new catalyst, and therefore the cancellation of this step (oxychlorination) led to not compensate the acidity of catalyst to the normal value, which led to reducing its activity below the level required. While, in the case of the new catalyst with (reduction + sulfiding), it was noted that it gave the best rate of improvement in the octane number followed by using the used catalyst which was regenerated at (carbon burning + oxychlorination + reduction + sulfiding), with the application of all conditions recommended in the operating manual as a function of life time. From that it is concluded that the best catalyst in this work are ranked as follow:

- New catalyst (drying+ reduction + sulfiding).
- Spent catalyst by regeneration at (carbon burning + drying + oxychlorination + calcination+ reduction + sulfiding).
- Spent catalyst by regeneration at (carbon burning + drying+ calcination + reduction + sulfiding).
- Spent catalyst by regeneration at (carbon burning + drying + oxychlorination + calcination + reduction).

4. Conclusion

It was proposed to add a fourth reactor to the semi-regenerative naphtha reforming unit with the same size of the last reactor of the unit as an idea to improve and to simulate the configuration of the continuous catalytic regeneration reformer process as an idea to increase the octane number, and study the effect of the variables affecting the quality of the product, which include (temperature, pressure, LHSV, H_2/HC, catalyst type and the effect of regeneration and pre-preparation methods). The results showed that:

1. The influence of temperature on the octane number was investigated, and it was discovered that the effect of temperature is rather positive, leading to an increase in the fraction of aromatic and light compounds due to the increasing of hydrocracking and aromatization reactions. The results demonstrated that by using used catalyst and the activation conditions (sulfiding and oxychlorination) were applied in their totality way, the RON values grew at a rate of 10 degrees at 510 ^{o}C under 12 bar and 4.5 hr^{-1} for short running time. On the other hand, for the new catalyst tests, the value of RON was enhanced by 8 degrees under 12 bar and 4.5 hr^{-1} using a sulfiding phase as a catalyst preparation step at 530 ^{o}C.
2. As for the effect of pressure, different pressures have been applied consistently 8 & 12 bar. The application of a higher pressure of 12 bar improved RON values compared to the lowest pressure of 8 bar for spent and fresh catalysts because it used directly after 12 bar pressure.
3. As regard to the effect of LHSV, it was observed that the increase in LHSV at 4.5 hr^{-1}has a positive effect on RON values, but with a slightly higher percentage compared with the lower LHSV 1.5 hr^{-1}, and this is the opposite results of the expected behavior in the traditional units because it was used the reformate as feed.
4. With regard to the effect of the quality of the catalyst with various regeneration and pre-preparation processes, which include (carbon burning + drying + oxychlorination + calcination+ reduction + sulfiding). It was observed that the new catalyst is the best in terms of efficiency for improving the RON values. In contrast, spent catalyst that regenerated without an oxy-chlorination step followed the opposite behaviour compared with fresh catalyst, with the lowest RON upgrading around 4 degrees.

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