

**EFFECT OF OPERATING VARIABLES ON THE
PERFORMANCE OF Pt -Re /AL₂O₃ CATALYST IN HEAVY
NAPHTHA REFORMING**

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ABSTRACT

The influence of operating conditions on the yield and quality of reformat was studied for naphtha reforming, using a bi-metallic Pt-Re/Al₂O₃ catalyst. The experiments were carried out in a high pressure micro-reactor unit under various conditions. The results showed that, increasing the reaction temperature or lowering the liquid hourly space velocity (LHSV) led to an increase in the yield of aromatics at the expense of reformat. The hydrogen pressure requirement for attaining the best product quality research octane number (RON) was 15 bar. The transformations of naphthenes and paraffines to aromatics are mainly responsible for improving the antiknock property of the reformates via the dehydrogenation and dehydrocyclization reactions. The optimum conditions for producing a reformat rich in aromatics (79.9 wt.%) and has a high RON value (100), were found to be 500°C reaction temperature, 15 bar hydrogen pressure and 1 h⁻¹ LHSV at fixed H₂: HC ratio.

Key words: Heavy Naphtha, Reforming, Catalyst.

1- INTRODUCTION

Catalytic reforming is one of the most significant processes in petroleum refining and petrochemical industries. It occupies the leading place in upgrading the octane number of naphthas to the level that makes the reformat suitable as a gasoline blend stock (Ntos, et al., 1995; Tore

& Sigurd, 2007 and Meyers, 2006). Besides, it is considered to be a very important source of hydrogen, and also for aromatic production (**Pieck, et al., 2005 and Silvana, et al., 2008**).

Several principle reactions take place during the catalytic reforming operation, including dehydrocyclization, dehydrogenation, isomerization and hydrocracking of the hydrocarbon molecules (**James, 1989**). These reactions occur on acid and/or metal sites; hence, they demand the use of bifunctional catalysts. The acid function with a certain acid strength is typically provided by a solid carrier such as alumina promoted by fluorine or chlorine and is mainly responsible for isomerization and cracking reactions; whereas the metal function, usually a noble metal, acts as active sites for hydrogenation-dehydrogenation reactions (**Meyers, 2006; Viviana, et al., 2007 and Vanina et al., 2009**).

Early, a bifunctional reforming catalyst composed of Pt supported on an acidic oxide was introduced (**Ntos, et al., 1995; Macleod, et al., 1998; Carvalho, et al., 2004 and Carvalho, et al., 2004**). Later on, the catalyst was modified by adding a second metal such as rhenium or cadmium to platinum; Pt alone or combined with other metals supported on chlorinated or fluorinated alumina are employed in the industry. The use of bi- or tri-metallic catalysts have several advantages (**Pieck, et al., 2005; Viviana, et al., 2007 and Mohammed & Hussein 2004**). They can reduce the working pressure with greater activity, selectivity and has a lower coking rate and higher resistance to deactivation than the mono-metallic catalyst. These factors enable the process to be operated with smaller regeneration frequencies leading to a subsequent reduction of operating costs (**Silvana, et al., 2008; Morteza Baghalha, 2010 and Guryev, 2007**).

The anti-knock improvement obtained from the reforming of petroleum naphtha is attributed principally to the formation of aromatic compounds (**Jorge & Akshat, 2008**). Lesser contribution results from isomerization of straight chain paraffins to branched chains. Therefore, the most desired reactions taking place are the dehydrogenation of naphthenes, dehydrocyclization and isomerization of paraffins. The undesirable hydrocracking reaction is also involved, particularly at high temperature and allow the yield of the valuable product to be lowered. Paraffinic hydrocarbons are more susceptible to hydrocracking than

naphthenes under reforming conditions. The rates of hydrocracking as well as the dehydrocyclization reactions are usually low (**Ali & Siddiqui, 2006 and UOP, 1997**), while dehydrogenation of naphthenes and paraffins occurs rapidly.

Gasoline fractions in the range of 60°C, not over than 180°C, are employed as the catalytic reforming feedstock. Lighter fractions, with less than six carbon atoms, are not recommended for reforming, since it contains neither cyclo- hexane, nor alkanes capable of transforming to aromatics. On the other hand, when the fractional composition of the stock is raised to above 180°C, more coke is deposited on the catalyst, which reduces its service life under the reaction conditions (**UOP Apr, 1997; Chevron Products Company, a division of Chevron USA Inc. Chapter 4, 1 2001; Chevron Products Company, a division of Chevron USA Inc. Chapter 2, 1. 200); Chemical Engineering Resources. Com, 1 (1999).**

Several factors affected the converted yield and hydrocarbons distribution of the reformat, among these, reaction temperature, pressure and LHSV. The main object of this investigation is to elucidate the influence of process variables on the performance of the bimetallic Pt-Re/Al₂O₃ catalyst on heavy_naphtha reforming, in order to get maximum product ratio with high octane number.

2. EXPERIMENTAL

2.1. Feedstock

In this study a hydrotreated heavy straight-run naphtha, provided from Cairo Oil Refinery Company, with specifications depicted in **Table (1)**, has been used as a feedstock.

2. 2 Catalyst

The experimental work was carried out using a commercial platforming catalyst with alumina base. The main constituents of this catalyst are: 0.3 wt % Pt, 0.3wt% Re and 1 wt % Cl.

Table (1): Feed Specifications

Test	Result
1- ASTM Distillation; vol. %	
10%	68 °C
20%	80 °C
30%	90 °C
40%	100 °C
50%	109 °C
60%	118 °C
70%	127 °C
80%	137 °C
90%	148 °C
Final Poling Point (F.B.P)	167 °C
2- Density @ 15°C, gm/cm³	0.7264
3- Reid Vapor Pressure, psi @ 100°F	5.85
4-Total Sulphur, ppm	100
5- Octane Number (Research method)	52
6- GC Analysis: %wt.	29.5
Paraffins (P)	37.94
Iso-Paraffins (I)	0.25
Olefins (O)	20.41
Naphthenes (N)	11.7
Aromatics (A)	

2. 3. Experimental set up and analysis

A high pressure micro-reactor unit (cata-test unit) was used. The unit consists of a stainless steel reactor (internal diameter 19 mm, external diameter 27 mm and length 50 cm). It is divided into three zones, each of them is heated and separately temperature controlled. 50 cc of the catalyst were charged in the middle zone of the reactor

(El Kady, et al., 2010). The hydroconversion reactions of the heavy naphtha have been carried out at different operating conditions. The feed and the collected liquid products were analyzed by gas chromatography. The gas chromatographic analyzer used in this study has the specifications declared in **Table (2)**.

Table (2): GC Specifications

Model	Varian GC – 450 (Fast DHA)
Carrier gas	Helium, linear velocity=29 cm/sec 35°C
Detector	Flame Ionization Detector, (F.I.D) @300°C
Injection temperature	250°C
Initial Boiling Point (I. B.P)	35°C
Final Boiling Point (F.B.P)	200°C
Column	Length: 100cm diameter: 0.25mm Name: fused silica coated with 0.5 microm methyl silicon powdered.

3. RESULTS AND DISCUSSION

The optimization of reforming process parameters depends on how to get maximum product ratios with high octane number components. To realize this intention, the following operating conditions have been applied to upgrade the antiknock property of low octane naphtha by using Pt-Re/Al₂O₃ catalyst: temperature: ranges from 300-500°C; hydrogen pressure: started from 5 up to 35 bar and liquid hourly space velocity (LHSV): varying from 1-4 h⁻¹, at a constant H₂/HC ratio of 350 L/L.

3.1. Effect of Temperature:

Reaction temperature is one of the most substantial parameter influencing the reforming process. This can be observed clearly from the obtained data depicted in **Table (3)** and **Fig (1)**.

Gas chromatographic analysis of the hydrotreated straight-run naphtha, that is used as a feed, contains 11.7 wt % aromatics, besides 20.41 wt% naphthenes and the rest are paraffinic hydrocarbons (n-and iso-), with traces of olefins. The results reveal that, the obtained yield, the distribution of the hydroconverted products and consequently the octane number, are temperature dependant. Lowering the applied

reaction temperature, increases the liquid product and reduces the gas yield but simultaneously reduces the conversion to aromatics. Paraffins and cycloparaffins composed the main constituents of the reformat, while the concentration of the most desired aromatic components, having the higher octane number, do not exceeds 16.8 wt% at 300°C. This led to a slight improvement in the research octane number (RON) from 52 to 57.9 at this temperature.

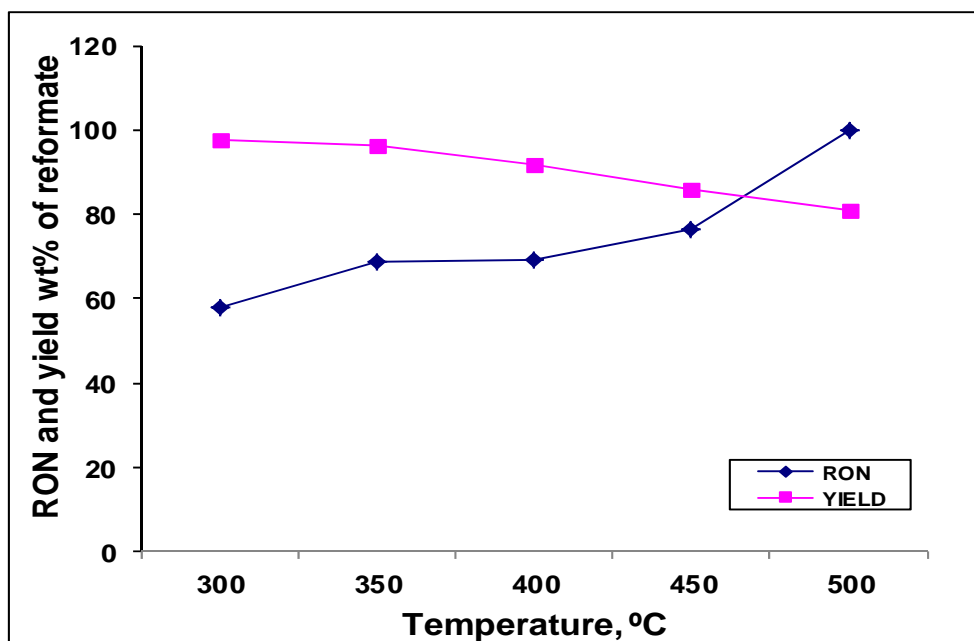
Upon the gradual raising the reactor temperature, keeping the other conditions constant, the amount of liquid yields dropped steadily from 97.7 wt% at 300°C to 81 wt% at 500°C. This diminution resulted from the formation of light gases due to the procession of the endothermic cracking reaction that becomes more at elevated temperatures. Nevertheless, reformat with high RON, reaching 100, can be attained at the highest temperature applied i.e (500°C). This improvement in the antiknock property issues principally from the predomination of the high RON components, particularly aromatics, in the hydroconverted product.

Dehydrocyclization of paraffins and dehydrogenation of naphthenes are the two main reactions responsible for the substantial increase of aromatic yield. It is known that, both reactions are endothermic requiring high energy of activation to proceed. Consequently, they are enhanced enormously at high temperatures and accounting for the increase of aromatic yield in the liquid product. Data in **Table (3)** confirm this fact. Upon increasing the reaction temperature, paraffins and naphthenes concentrations are distinctly reduced from 67.44 to 16.8 wt% and from 20.41 to 3.27 wt%, respectively, whereas aromatics amounts to 79.85 wt% are detected at 500°C.

It can be recognized that isomerization of straight chain hydrocarbons to isoproffins is slightly involved at 350°C.

Table (3): The effect of Temperature(@ Pressure=15kg/cm², Space velocity=1h⁻¹ H₂/Hc=350 L/L).

Temperature, °C	Feed	300	350	400	450	500
Density@15°C, g/ml		0.7420	0.7423	0.7430	0.7590	0.8328
R.O.N	52	57.9	68.8	69	76.4	100
Aromatics, wt%	11.7	16.77	18.26	20	39.68	79.85
Naphthenes, wt%	20.41	21.94	17.36	20.75	9.57	3.27
Olefins, wt%	0.25	0.14	0.39	0.75	0.40	0.08
n-Paraffins, wt%	29.5	23.50	21.22	25	11.66	5.30
Iso-paraffins, wt%	37.94	37.65	42.97	33.50	38.69	11.50
Total Paraffins, wt%	67.44	61.15	64.19	56	50.35	16.80
Product Liquid Yield wt.%		97.72	96.29	91.66	86.00	81.00

**Fig. (1):** Effect of reaction temperature on the yield and RON of the reformate.

3.2. Effect of Pressure:

Data given in **Table (4)** and shown in **Fig. (2)** reflect the influence of the pressure on the hydrocarbon distribution and RON of the obtained reformat. Upon raising the hydrogen pressure under constant experimental conditions, RON can be boosted to attain its maximum value of 100 at 15 bar. This can be ascribed to the predominance of aromatic compounds that amount to 79.85 wt%, in the liquid product. The concentration of the unconverted naphthenes and paraffins (n-and iso-) were diminished from 20.41 to 3.27 wt% and from 67.44 to 16.8 wt% as a result of their transformation to aromatics via dehydrogenation and dehydrocyclization reactions, respectively. This may be imputed to the promotion of hydrogenolysis of coke precursors, thereby reducing coke formation that deposited on the catalyst surface on sites preferred for those previously mentioned reactions and lead to its partial deactivation. Therefore, it preserves the activity of sites responsible for aromatic formation that attended by RON improvement. However, aromatic content and consequently RON, are dropped on further increase of hydrogen pressure beyond 15 bar to be 32.58 wt% and 71, respectively, at 35 bar; whereas the unreacted naphthenes and paraffins are steadily increased to become 11.55 wt% and 62.9 wt%, respectively, at hydrogen pressure of 35 bar. Hence, too high hydrogen pressure does not favor both the dehydrocyclization and dehydrogenation reactions (**Kjel, 1996 and Bishara 1984**). This result can be explained through the fact that dehydrogenation is a reversible reaction and the presence of large amount of hydrogen will reverse the direction of the reaction, since hydrogen will be considered as a reactant. Therefore, dehydrogenation of naphthenes can not proceed efficiently and leads to the inhibition of aromatic formation.

Moreover, it is known that, dehydrocyclization of paraffins is a two –step process, involving dehydrogenation step prior to ring closure. Therefore, at a sufficiently high hydrogen pressure (> 15 bar), the dehydrocyclization rate is also decreased due to the suppression of the preliminary dehydrogenation reaction at high hydrogen pressures.

On the other hand, at lower pressure (< 15 bar) dehydrogenation of paraffins to olefins and their subsequent polymerization to coke precursors are faster reactions and lead to extensive coverage of the Pt surface by carbonaceous residues which inhibit the reaction rate. As cited in literatures, the amount of carbon deposited on the catalyst surface

increases with decreasing pressure, and aromatic concentration in the produced reformate diminished rapidly (**Bishara, 1984**).

The data indicate that the rate of hydrocracking reaction is enhanced by pressure resulting in a considerable loss of reformate. The liquid product diminished from 90.80 wt% to 62.90 wt% throughout the entire range of hydrogen pressures applied i.e (from 5 to 35 bar).

As shown in **Table (4)**, Pt-Re/Al₂O₃ catalyst can enhance the conversion of naphthenes and paraffins to aromatics to attain 79.85 wt% at a hydrogen pressure amount to 15 bar, 500°C, 1h⁻¹ LHSV and H₂/HC ratio equal to 350 L/L. This will improve the RON to become 100 at such conditions.

Table (4): The effect of Pressure

(@ Temperature=500°C, Space velocity=1h⁻¹ H₂/Hc=350 L/L

Pressure, bar	Feed	5	15	25	35
Density@15°C, g/ml	0.7264	0.8057	0.8328	0.7567	0.7451
R.O.N	52	79	100	72	71
Aromatics, wt%	11.7	61.27	79.85	37.26	32.58
Naphthenes, wt%	20.41	5.10	3.27	9.87	11.55
Olefins, wt%	0.25	0.50	0.08	0.51	0.20
n-Paraffins, wt%	29.5	10.31	5.30	17.61	19.05
Iso-paraffins, wt%	37.94	22.82	11.50	34.75	36.62
Total Paraffins, wt%	67.44	33.13	16.80	52.36	62
Product Liquid Yield wt. %		90.8	81.00	70.6	62.9

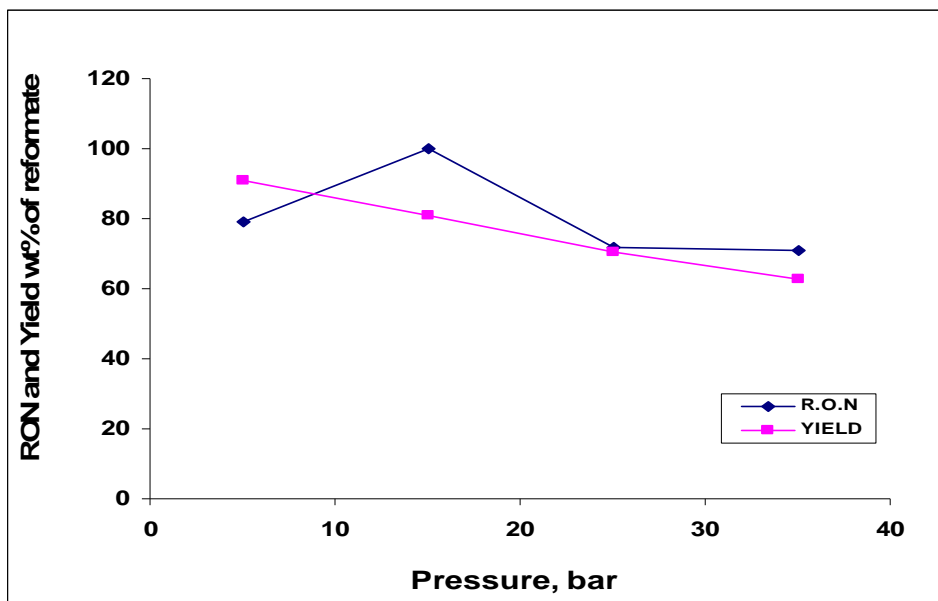


Fig. (2): Effect of pressure on the yield and RON of the reformat.

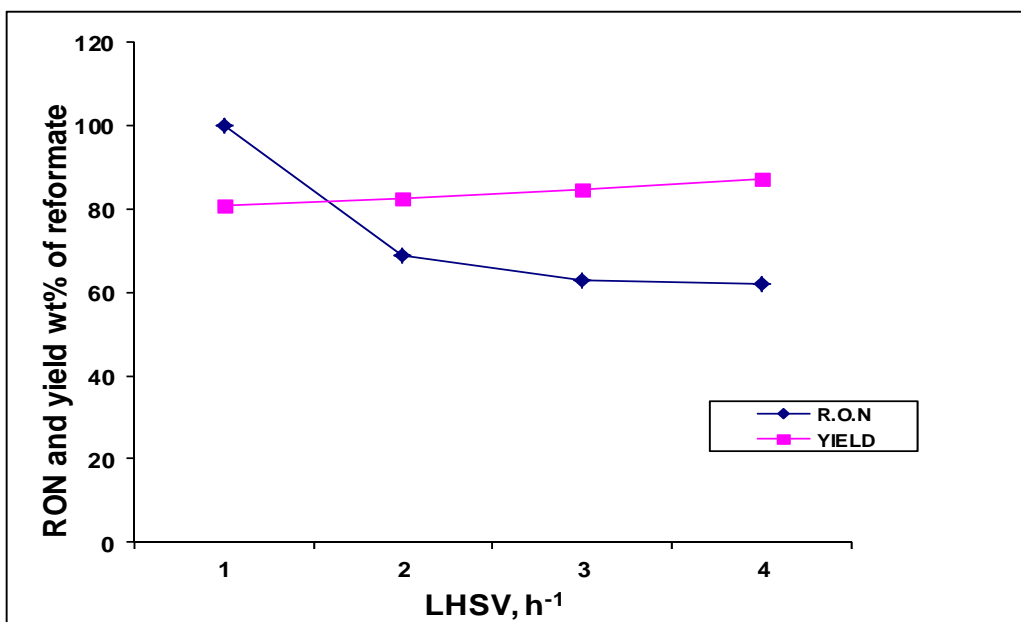
3.3 Effect of LHSV

The effect of liquid hourly space velocity (LHSV) on the yield and quality of the produced reformat was also investigated in the range of 1-4 h⁻¹, at 500°C, 15 bar and H₂/HC ratio, 350 L/L. The obtained results are listed in **Table (5)** and **Fig. (3)**. Increasing the contact time by lowering of the velocity gives the same effect as the elevation of the reaction temperature, namely a lower reformat liquid product and higher gas yield, as a result of hydrocracking reaction. However, the RON is improved owing to the enhancement of naphthenes and paraffins conversion to aromatics. Too low velocities are not recommended from the economical point of view; also longer residence time leads to coke deposition on the catalyst.

The product distributions in **Table (5)** illustrate that the highest aromatic content amount to 79.85 wt% was obtained at LHSV of 1 h⁻¹ with simultaneous improvement of RON to exhibit the upmost value of 100, at the same applied reaction conditions mentioned above. Increasing the LHSV to be 2 h⁻¹ up to 4 h⁻¹, leads to a remarkable reduction of aromatic content to become in the range of 34.36-18 wt% accompanied by sharp declination of RON value to be 69-62 in the range of 1-4 h⁻¹, at 500°C, 15 bar and H₂/HC ratio, 350 L/L.

Table (5): The effect of LHSV(@ Temperature=500°C, Pressure=15 bar, H₂/Hc=350 L/L)

LHSV, h ⁻¹	Feed	1	2	3	4
Density@15°C, g/ml	0.7264	0.8328	0.7532	0.7480	0.7403
R.O.N	52	100	69	63	62
Aromatics, wt%	11.7	79.85	34.36	20.48	18
Naphthenes, wt. %	20.41	3.27	13.08	16.84	14.5
Olefins, wt%	0.25	0.08	1.27	1.32	1.50
n-Paraffins, wt%	29.5	5.30	20.89	24.82	26.00
Iso-paraffins, wt%	37.94	11.50	30.40	36.54	40.00
Total Paraffins, wt%	67.44	16.80	57.02	60.36	66.00
Product Liquid Yield wt. %		81.00	82.7	84.5	87.3

**Fig. (3):** Effect of LHSV on the yield and RON of the reformate

CONCLUSION

The bimetallic Pt-Re \ Al₂O₃ can be visualized as a promising catalyst for heavy naphtha reforming.

The pronounced improvement in the antiknock property is principally ascribed to the enhancement of aromatic content in the produced reformate.

The concentration of aromatic compounds, which have a high research octane number (RON), were significantly increased in the reformate as a result of transformation of cyclo- and n-paraffins to aromatics via dehydrogenation reactions, respectively.

A significant increase in the RON value of heavy naphtha can be achieved at high reaction temperature and low liquid hourly space velocity (LHSV).

The best product quality with high RON value can be obtained at a pressure of 15 bar.

Therefore, the optimum operating conditions for heavy naphtha reforming was found to be 500°C reaction temperature, 15 bar hydrogen pressure and 1 h⁻¹ LHSV. These leads to produce a reformate rich in aromatics (79.85 wt %), and consequently has a high RON value of (100).

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تأثير عوامل التشغيل علي اداء حفاز البلاتين والرينيوم المحملين
علي الالومينا علي عملية اصلاح النافا فتا الثقيله .

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تمت دراسة تأثير عوامل التشغيل علي كمية ونوعية النافا الناتجه عن عملية الاصلاح باستخدام حفاز البلاتين - والرينيوم المحملين علي الالومينا وأجريت التجارب باستخدام مفاعل صغير بوحدة الضغط العالي ، وذلك تحت ظروف مختلفه . وأسفرت النتائج عن ان زيادة كل من درجة حرارة التشغيل وتقليل السرعة الفراغيه قد أدت الي زيادة تكوين المركبات العطريه علي حساب كمية المنتج . وباستخدام ضغط هيدروجيني قدره ١٥ بار أدي الي الحصول علي أفضل منتج ذو أعلى رقم أوكسيني .

ويعتبر إزالة الهيدروجين وايضا ذلك المصحوب بتكوين المركبات الحلقية لكل من البرافينات الحلقية والعاديه (علي التوالي) ، وتكوين العطريات هي المسئولة عن تحسين الخاصية المضادة للخبط (anti-nock) للنافتا المعالجه .

وتبين النتائج أن أفضل ظروف تشغيل لانتاج النافتا المعالجه الغنيه بالمواد العطريه (٧٩.٨٥%) والتي لها أعلى رقم أوكسيني (١٠٠) هي درجة حرارة ٥٠٠م° ، وضغط ١٥ بار وسرعه فراغيه ١ساعه وذلك عند نسبه ثابتة من الهيدروجين الي الهيدروكربونات .