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Hydrocracking of N-Heptane with a NiO-MoO$_3$/Y Zeolite as catalyst. The Network of Reaction.

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Abstract

The hydrocracking of n-heptane has been carried out in a fixed bed reactor at 20 bar pressure and with H_2/n-heptane molar ratio of 5 using 4wt%NiO-8wt%MoO$_3$/Y zeolite as a catalyst. The W/Fo ratio was varied between 5-30kg.h./kmol at different reaction temperature 325, 350, 375, 400 and 425^{0}C. The product was analyzed by gas chromatography. The following activity order was obtained:

HY>CuY>CrHY>CrY>MnY.

All forms of Zeolites (HY, CuY, CrHY, CrY, and MnY) were prepared from mono valent cationic sodium type by means of ion exchange process. This modification was carried out to improve the catalytic properties of NiO-MoO$_3$/Y zeolite catalyst. The ion exchange with Cr, Mn, Cu and CrH, were resulted the lowest rate comparing with NH_4^+. The reaction temperature influenced the activity of NiO-MoO$_3$/Y zeolite catalyst. The isomerization of n-heptane attains a maximum at 375 ^{0}C, it drops sharply at higher temperatures. In addition the NiO-MoO$_3$/CrHY catalyst has good activity toward isomerization compared with other types of catalysts. The kinetics of the reaction has been studied using the conversion and yield values explorated at time on stream to zero. The experimental data were fit well by a pseudo-first order kinetic equation and the kinetic constant values obtained. The kinetic parameters of the 2-methyl hexane and 3-methyl hexane have been obtained from the initial selectivities.

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التكسير بوجود الهيدروجين للهبتان الاعتيادي باستخدام اوكسيد النيكل – موليبيديوم المحمل على الزيولايت شبكة التفاعل.

الخلاصة

تضمن هذا البحث دراسة تحضير الحفازات من نوع اوكسيد النيكل مع ثلاثي اوكسيد الموليبديوم المحملان على زيولايت الفوجاسايت نوع (Y) بنسبة 4% وزنا و 8% وزنا على التوالي ومن ثم التحقق من فعاليتهما في تفاعلات التكسير بوجود الهيدروجين للهبتان الاعتيادي.

تم اجراء عملية الاستبدال الايوني لايون الصوديوم احادي الشحنة بايونات كل من الامونيوم والكروم والنحاس والمنغنيز والكروم – هيدروجين. لقد تم استخدام طريقة التطوير هذه لتحسين خواص ومواصفات هذه الحفازات. ان معدل الاستبدال الايوني لايونات لايونات الكروم والنحاس والمنغنيز والكروم – هيدروجين اقل مقارنة مع معدل الاستبدال الايوني لايونات الامونيوم.

اجري تحميل اوكسيد النيكل بنسبة 4% وزنا وثلاثي اوكسيد الموليبديوم بنسبة 8% وزنا على الزيولايت باستخام نترات النيكل وموليبدات الامونيوم بطريقة التشبع. اتبعها عمليات التجفيف والكلسنة تحت ظروف ثابتة.

اجريت دراسة سلوكية للحفازات المحضرة على تفاعلات التكسير بوجود الهيدروجين للهبتان الاعتيادي في مفاعل انبوبي صغير وقد تم تحليل النواتج بجهاز كروموتوغرافيا الغاز. لقد شملت الدراسة السلوكية دراسة فعالية تلك الحفازات تحت متغيرات عديدة شملت درجة حرارة التفاعل (325–425 ^{0}م) ونسبة وزن الحفاز الى المعدل المولي للهبتان الاعتيادي (W/F_0) بين (5–30) كغم.ساعة/كيلومول وبنسبة مولية ثابته من الهيدروجين الى الهيدروكربون (5) اضافة الى دراسة تاثير نوع الايون الموجب ونسبة تبادله مع ايون الصوديوم. اظهرت النتائج ان فعالية تلك الحفازات كانت كما يلي: HY>CuY>CrHY>CrY>MnY

بينت النتائج ان تاثير درجة الحرارة على فعالية الحفازات قوي، حيث ان هذه الحفازات اظهرت فعالية اكبر تجاه الازمرة بدرجات الحرارة المنخفضة فيما يزداد التفاعل باتجاه التكسير عندما تزداد درجة الحرارة حيث كانت اعلى نسبة ازمرة عند درجة الحرارة 375 ^{0}م اضافة الى ذلك اظهر الحفاز نوع ($NiO\text{-}MoO_3/CrHY$) فعالية جيدة تجاه الازمرة مقارنة مع بقية انواع الحفازات.

لقد تم دراسة الموديل الحركي للتفاعل باستخدام قيم التحول والانتاجية بعد حساب قيم التحول عند الزمن صفر. البيانات العملية التي تم ادخالها الى معادلة من الدرجة الاولى حيث تم من خلالها حساب ثوابت التفاعل، ومن ثم حساب ثابت التفاعل للمنتجين 2–مثيل الهكسان و 3–مثيل الهكسان باستخدام قيم الانتقائية الابتدائية .(Initial Selectivity)

1. Introduction

Hydrocracking is one of the most important processes of the modern petro-chemical industry used to convert heavy oils into more valuable products. It does the work by converting large high boiling point molecules into lower boiling product by simultaneous hydrotreating and cracking carbon-carbon bonds(1).

Hydrocracking is a very flexible process which allows to obtain a broad range of saturated products ranging from high yields of liquid petroleum gas to middle distillate with a high octane number. This flexibility is due to not only to the process itself but mostly to the catalyst design.

Hydrocracking requires bifunctional catalysts, exhibiting a cracking function and a hydrogenation function, which have to be suitably balanced, according to the feeds and final desired product (2).

Concerning the cracking function, it is well known that cracking is an acid-catalyzed reaction; hence, it is desirable to have one acid function in which the strength and number of acid sites could be controlled. This is achieved actually, by using some zeolites such as Y, ZSM-5, erionite, and mordenite. Among them, Y zeolites are the most widely used, while the others are used in the cases, which require reactions controlled by pore geometry (3,4).

The hydrogenation-dehydrogenation function is given by either noble metals such as platinum and palladium or combinations of non noble metals such as (Co, Ni, Mo). When choosing appropriate hydrogenation-dehydrogenation function, it must be considered if the feed contains catalyst poisons such as sulfur, nitrogen, and oxygen, which make infeasible the use of noble metals (5).

Aucejo and co-workers (6) studied the hydrocracking of n-heptane using $NiO-MoO_3/HY$ zeolite as a catalyst and they varied the W/Fo (weight of catalyst/molar flow of n-heptane) ratio at different reaction temperature. They studied the kinetics of the reaction by two different procedures, one of them uses the conversion and yield values and the other uses a kinetic equation where the deactivation of the catalyst has been included.

Isabel (7) studied the hydrocracking of n-heptane using ($NiO-MoO_3/HY$) zeolite as catalyst, to try to obtain a net work of reactions to account for the formation of the various products observed. They concluded that the parameters of these reactions have been obtained from the initial selectivities of the products. They found that the values of the apparent activation energies obtained for the isomerization, hydrogenolysis, cracking and disproportionation reactions were 99.1, 169.6, 221.4, 195.9 kJ/mol, respectively. While Riberio et al (8) studied the n-hexane hydrocracking reaction using Pt/HY zeolite catalyst, and they calculated an apparent activation energy for the cracking reaction of 146kJ/mol.

Corma and co-workers (9) studied the cracking of n-heptane on H-Y zeolites at atmospheric pressure and up to 470^0C. The selectivity curves in the absence of decay have been obtained for each reaction product. The initial selectivities to the primary products have been calculated, and from them the values of the initial selectivities to the three main reactions, i.e., cracking, isomerization, and disproportionation have been obtained. The kinetic parameters have been calculated.

In a previous work the results obtained comparing the activity of different catalyst with zeolite as the cracking component in the n-heptane hydrocracking reaction have been reported by Vazues et al. (10). The best results have been obtained with a catalyst prepared with an ultrastable zeolite impregnated with 4wt%NiO and 8wt%MoO_3 (hydrogenating component). This catalyst is more economical than those formed by noble metals. An additional number of experiments have been carried out in order to obtain information about the kinetics of the hydrocracking process, necessary for the design of industrial hydrocracking reactors.

2. *Experimental work*

2.1. Materials

The sodium Y zeolite, SK-40 was purchased from AKZO-chemi-B-V-Ketjen as a powder without a binder and with the following composition: 63.2wt% SiO_2, 20.2wt% Al_2O_3, 14.1wt% Na_2O. Its particle size range within YSNM.

(HY, CuY, MnY, CrY) zeolites were prepared by exchanging the original sodium form with ammonium chloride, cupric chloride, manganese chloride and chromium chloride respectively, CrH-Y zeolite was prepared by exchanging the original sodium form firstly with nitrate, and secondly with ammonium chloride.

The nickel and molybdenum were incorporated into the zeolite by vacuum impregnation at 70^0C from an aqueous solution of nickel nitrate $Ni(No_3)_2.6H_2O$ and ammonium heptamolybdate $(NH_4)6Mo_7O_{24}.4H_2O$, respectively, after each impregnation, the zeolite were formed as extrudates (3mm by 2mm). Then the sample was dried at 110^0C for (6hrs) and then calcined at 550^0C for (5hrs).

2.2. Apparatus

The experiments were carried out in continuous tubular, plug flow, stainless steel reactor of (2.4cm) in internal diameter and (17cm) length. A drawing of the apparatus and its components is presented in Sketch 1.

The reactor was divided into three zones, upper, middle, and lower zones, which was charged for each experiment with 5g of the catalyst pellets located in the reaction zone (middle zone).

2.3 Operating procedure

The catalyst experiments were performed under a wide range of temperature between 325-4250C, 2x106 Pa total pressure, hydrogen / hydrocarbon mole ratio (H2/HC) was kept constant at 5. The W/Fo (weight of catalyst / molar flow of n-heptane feed) was varied between 5-30 kg.h/kmol.

The total time for each run at certain temperature was typically 1.5hrs. The first sample was taken 10min. after initiation of n-heptane flow, then the subsequent samples were taken at 30 min. intervals.

The products analysis was carried out by gas chromatographic analysis using FID on Varian 6000 (flame ionization detector). A porapak Q stainless steel column with an inside diameter of (1/8in) and length of 3m was used to separate the products.

3. Study of the kinetics of the process using the values extrapolated to zero time on stream

3.1 kinetics of the global reaction

It was assumed that the reactor used was an integral plug flow reactor. By making a mass balance on a differential element of the reactor and assuming for the process a pseudo-first order kinetic equation, the following differential equation was obtained:

$$Fo\frac{dx}{dw}=\frac{K.P}{1+R_M}.(1-x)\ldots\ldots\ldots\ldots\ldots\ldots(1)$$

By integration of this expression between the inlet and the outlet conditions of the catalyst bed, the following relation between the conversation and the operation variables was obtained:

$$-\ln(1-x)=\frac{K.P}{1+R_M}.\frac{W}{F_o}\ldots\ldots\ldots\ldots\ldots\ldots(2)$$

Where k is the rate constant of the reaction, P the total pressure, R_M the H_2/n-heptane molar ratio and W/Fo the weight of the catalyst/molar flow of n-heptane. The results obtained and the operating conditions used in each experiment are given in Table (1).

Since in all the experiments the pressure and RM values were maintained constant, fitting the experimental conversion and W/Fo ratio according to equation (2) the rate constant of the reaction, K, could be calculated if the conversion values were non-accumulated.

Nevertheless, due to the characteristics of the experimental apparatus used and the slow deactivation of the catalyst the experimental conversion values obtained were accumulated between the initial moment and different time on stream. The relation between the experimental conversion and time on stream is given in Figs. (1) to (5).

As has been said before, to try to eliminate this difficulty, values extrapolated to zero time on stream obtained by fitting the experimental conversion and time on stream to the following equation (Newton-Quasi equation/Statistica Program-version 5).

$$x=a_0+\exp[b_0+c_0(t)]\ldots\ldots\ldots\ldots\ldots\ldots(3)$$

Where a_0, b_0, c_0 are constant and x, t referring to the experimental conversion and time on stream respectively. The a_0, b_0, c_0 values and the conversion at zero time on stream are given in Table (2). At these conditions it could be accepted that the catalyst was not yet deactivated and that the extrapolated conversion value was quite representative of the conversion obtained in all the experiment if the catalyst was not deactivated.

To check the validity of this model the $-\ln(1-x|_{TOS=0})$ values are plotted versus the W/F0 as shown in Figs. (6) to (10).

For the five types of catalyst studied the values fit to a linear well, that is to say, the experimental data agree well with the assumed pseudo-first order kinetic equation.

The rate constant values obtained from the slope of the straight lines are given in Table (3).

3.2 The path way of the reaction

In view of the type of the products obtained, the reaction network proposed should include isomerization reaction, to explain the formation of n-heptane isomers; cracking reactions, because fraction shorter than C7 are present in the products; and hydrogenolysis reaction, to account for the formation of methane.

The formation of methane as a primary product is difficult to explain by an acid catalyzed mechanism if we take into account that the production of methane involves primary carbonium ions and, moreover, no methane is observed as a primary product when the reaction is carried out on the purely acid H-Y zeolite (corma et al)(9).

On the other hand, the results obtained show that the formation of C6, C5, and C4 fractions is greater than that of C1, C2 and C3 fractions. In order to explain these results, it could be that disproportionation followed by cracking reactions also occurs, as suggested by other authors (Bolton and Bujalski)(11).

Among all the possible disproportionation-cracking reactions the following ones, being the most probable, have been considered:

$$2C_7 \rightarrow [C_{14}] \rightarrow C_6 + 2C_4 \ldots\ldots\ldots\ldots (4)$$

$$2C_7 \rightarrow [C_{14}] \rightarrow C_6 + C_5 + C_3 \ldots\ldots\ldots\ldots (5)$$

$$2C_7 \rightarrow [C_{14}] \rightarrow 2C_5 + C_4 \ldots\ldots\ldots\ldots (6)$$

Therefore, the network of the reaction proposed to explain the product distribution observed experimentally could be:

$$C_7 \xrightarrow{isomerization} i\text{-}C_7 \ldots\ldots\ldots\ldots (7)$$

$$C_7 \xrightarrow{Cracking} C_2 + C_5 \ldots\ldots\ldots\ldots (8)$$

$$C_7 \xrightarrow{Cracking} C_3 + C_4 \ldots\ldots\ldots\ldots (9)$$

$$C_7 \xrightarrow{Hydrogenolysis} C_1 + C_6 \ldots\ldots\ldots\ldots (10)$$

$$2C_7 \xrightarrow{Disproportionation} C_6 + 2C_4 \ldots\ldots\ldots (11)$$

$$2C_7 \xrightarrow{Disproportionation} C_6 + C_5 + C_3 \ldots\ldots (12)$$

$$2C_7 \xrightarrow{Disproportionation} 2C_5 + C_4 \ldots\ldots\ldots (13)$$

3.3 Kinetic of the 2-Methyl Hexane and 3-Methyl Hexane Formation Reactions

the experimental results obtained in this work show that the range of operating conditions studied the reaction for the formation of 2-methyl hexane and 3-methyl hexane are very important and their contribution of the total conversion is greater than 70%. For this reason the kinetics of these reactions have been studied individually.

The reaction proposed is

$$C_7 \xrightarrow{K1} A_1 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (14)$$

$$C_7 \xrightarrow{K2} A_2 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (15)$$

Where A1, A2 are 3-methyl hexane and 2-methyl hexane respectively. In Figs. (11) to (15) the variation of the molar yields of 3-methyl hexane and 2-methyl hexane is plotted versus the corresponding conversion at 3250C and different W/Fo molar ratio versus the time on the stream. From the shape of these curves we can obtain the initial selectivity value (no. of moles obtained from each n-heptane mole reacted) for each product as the slope of the tangent of these curves. These values are given in Table (4).

The initial selectivity of a given reaction is defined as the ratio between the initial rate of the given reaction and the initial rate of the global reaction (12):

$$(IS)_i = \frac{r_{io}}{r_o} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (16)$$

In accordance with definition, the rate constant of a reaction can be calculated if the initial selectivity and rate equation of the reaction as well as the rate constant and the rate equation of the global reaction are known.

Therefore, the initial selectivity of each reaction can be expressed as:

$$(IS)A_1 = \frac{K_1[So]}{K[So]} \ldots\ldots\ldots\ldots\ldots\ldots (17)$$

$$(IS)A_2 = \frac{K_2[So]}{K[So]} \ldots\ldots\ldots\ldots\ldots\ldots (18)$$

Where K is the rate constant for a reaction and [So] is the initial concentration of active centers in the catalyst.

Table (5) shows the rate constant obtained by this procedure for the two reactions considered.

4. *Results and Discussion*

4.1 effect of ion exchange

Extrudates of the initial zeolite NaY was exchanged with different cations (H. Cr, Cu, Mn, CrH). The exchange technique used in this process was the one step- batch impregnation under constant temperature. In which only one fresh salt solution was used.

The ion exchange reaction reached equilibrium in which there is no further replacement occurs, because of the diffusion difficulties of the exchanged ions into the zeolite structure. The ion exchange could be reached a maximum into the sodalite cages and then hexagonal prisms, which are the main components of zeolite structure. For this reason, it was not expected a complete exchange occur.

The highest percentage of ion exchange can be achieved with ammonium ions.

The ion exchange with (Cr, Mn, Cu, CrH) were resulted the lowest rate

Comparing with ammonium ion. This is due to the fact that the rate of exchange of cations increases as the radius of the cations increases. This conclusion is in a good agreement with the work of Brayant (13) .Table (6) summarized the achieved percentage of ion exchange and radius of the different cations

4.2 Effect of Reaction Temperature

The effect of reaction temperature on the conversion of n-heptane is shown in Figs. (16) to (20). It shows increase in conversion as reaction temperature increases for all types of catalyst at constant pressure that is considered as an ordinary result between reaction temperature and the conversion. The continuity increase refers to the fact that the equilibrium conversions are not attained at this range of temperature (325-425^0 C).

The effect of reaction temperature on the isomerization and cracking yield is shown in Figs. (16) to (20) at W/Fo=30 kg.h/kmol. The isomerization yield shows an increase as reaction temperature goes up from 325 to 375^0C. At temperature higher than 375^0C the degree of isomerization decreases rapidly and this may be attributed to two causes; firstly, the desorption of hydrocarbons from very strong acid sites is hindered and secondly, the decrease in isomerization is matched by an increase in cracking reactions. The cracked products increase as reaction temperature increases. Since that both the isomerization and cracking reactions occur on acid sites, it would appear that as the temperature is raised there is a greater tendency for cracking to occur rather than isomerization. This conclusion is in a good agreement with the work of El-Kady et. al. (14).

From comparison of the yield of isoheptane obtained on NiO-MoO_3/CrHY and NiO-MoO_3/HY samples as shown in Figs. (18) and (20), it can be suggested that such a reaction is related with the acid sites of the catalyst rather than with the chromium ions, since the values are not very different. At 375°C the small difference of isoheptane yield observed could be explained by considering that the level of total conversion of the NiO-MoO_3/HY sample is higher, and it means that more cracking reactions would occur, with disappearance of the primary isoheptane formed. This comparison is in accord with work of Lopez et al (15).

By comparing the results of the hydrocracking of n-heptane for NiO-MoO_3/HY with other types of catalyst, it can be concluded that the NiO-MoO_3/HY catalyst has a higher activity for hydrocracking than other types of catalyst at all different operating conditions. The negatively charged AlO_4 tetrahedral, three-coordinated aluminum oxide and Lewis acid site resulting during the decationization may explain this. In addition the decrease in percentage of ion exchange of other cations compared with decationized form may be explaining the small reduction of catalyst activity.

The activity order for the five types of cations is H>Cu>CrH>Cr>Mn. This can be attributed to the difference in the ion exchange, ionic radius and the acidity of each cation.

4.3 Effect of W/Fo

The effect of W/Fo within the range of 5-30 kg.h/kmol on the hydrocracking of n-heptane has been discussed at five-reaction temperature, namely, 325, 350, 375, 400 and 425°C.

The results shown in Figs. (21) to (25) indicate that when W/Fo increases the conversion of n-heptane catalyst increases. This indicates that whenever the contact time increases, the chance of reaction of n-heptane on the active site increases, therefore the conversion will increase. This conclusion is in a good agreement with the work published by El-Kady et al (16).

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The reaction temperature influences the cracking activity of the catalyst to a comparatively higher extent than the W/Fo.

Besides, it controls the competitive cracking-isomerization reactions of n-heptane more than the W/Fo. At low reaction temperature, 325°C, the cracking activity is evidently low, while isomerization of n-heptane is relatively high.

Finally, the Ni-Mo/Y catalysts present an intermediate behavior between that of a monofuctional cracking HY zeolite catalyst (11) and an ideal bifunctional pt/Y catalyst(17). This can be due to the lower hydrogenating activity of the Ni-Mo with respect to the noble metals. The consequence of this lower hydrogenation capacity is the presence of small amounts of olefins in the products, never detected on pt/Y catalyst, which, on the other hand, are the origin of the disproportionation reactions observed in the Ni-Mo/Y catalyst.

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NOMENCLATURE

Crack.%	Cracked products
Fo	Molar flow rate of n –heptane in the feed kmol/h
Iso.%	Isomerized n – heptane
(IS)I	Initial selectivity of component I
K	Kinetic rate constant of the global process (kmol/kg. h.Pa)
K_1	Kinetic rate constant for the 3-methyl hexane formation reaction (kmol/kg. h.Pa).
K_2	Kinetic rate constant for the 2-methyl hexane formation reaction (kmol/kg.kg.h.Pa)
P	Total pressure(Pa)
R_m	Hydrogen/n-heptant molar ratio in the feed
T	Time on stream (hr) = T.O.S
W/Fo	Weight of catalyst/molar flow of n – heptane (kg.h./kmol)
X%	Percentage conversion of n- heptane
X%	Percentage conversion of n- heptane at zero time on stream

Table (1): Experimental Values of the Conversion for Different W/F_0 and Time on Strea at 325^0C.

W/F_0 (kg.h/kmol)	Type of catalyst	NiMo-MnY	NiMo-CrY	NiMo-CrHY	NiMo-CuY	NiMo-HyY
	Time on Stream (h)	Conversion (x%)				
5	0.167	3.9	7	8.1	9.5	11.5
	0.5	3.5	6	7	8.8	10.1
	1	3.2	5.4	6.1	8.1	9.3
	1.5	2.9	5	5.4	7.5	8.5
10	0.167	12.2	13	15.1	17	20
	0.5	10.8	11.5	14	15.8	18.1
	1	9.9	10.3	13.2	14.9	16.5
	1.5	9	9.5	11.9	13.7	15.6
15	0.167	16.5	18.9	23.3	24.7	28.2
	0.5	14.2	17.8	21	23.3	26.3
	1	12.7	16.8	19.4	22.3	24.7
	1.5	12	15.9	18.1	20.5	23.5
20	0.167	21	23.7	26.1	32.5	35.5
	0.5	18.9	21.1	24.5	30.2	33.3
	1	18	19.4	23.4	29	31.2
	1.5	17.2	18.5	22.4	28	30
25	0.167	23.2	26.7	32.3	36.3	40
	0.5	21.5	23	30.5	33.8	37.5
	1	20.5	22	29	32.6	36.2
	1.5	18.9	21.2	27.5	31.2	35.5

Table (2): Results of constant values and the conversion at zero time on stream.

Type of catalyst	W/F_0 (kg.h/kmol)	a_0	b_0	c_0	x_0%
NiMo-MnY	5	2.4376	0.50995	-0.83237	4.1
	10	8.1132	1.5778	-1.0848	12.95
	15	11.6265	1.8946	-1.8727	18.3
	20	17.071	1.7015	-2.0494	22.55
	30	14.7538	2.20404	-0.50503	23.8
NiMo-CrY	5	4.806	1.0633	-1.6984	7.7
	10	8.673	1.664	-1.2146	13.95
	15	13.972	1.705	-0.6898	19.47
	20	18.005	2.031	-1.7639	25.62
	30	21.352	2.226	-3.3171	30.62
NiMo-CrHY	5	4.4982	1.4453	-1.0133	8.74
	10	-3.087	2.9192	-0.1389	15.44
	15	16.931	2.0469	-1.2172	24.67
	20	21.381	1.7257	-1.0975	27
	30	24.354	2.1781	-0.6755	33.18
NiMo-CuY	5	5.9904	1.3563	-0.6245	9.87
	10	9.444	2.0824	-0.4142	17.47
	15	-131.061	5.051	-0.01955	25.1
	20	27.619	1.862	-1.7134	34.1
	30	30.497	1.9801	-1.4157	37.74
NiMo-HY	5	7.951	1.4714	-1.29717	12.31
	10	14.675	1.8885	-1.3021	21.3
	15	21.916	2.0024	-1.0121	29.3
	20	28.3804	2.1485	-1.1121	36.95
	30	35.316	1.9042	-2.1798	42

Table (3): Rate constant for the n-heptane hydrocracking reaction at 325^{0}C.

Type of catalyst	K(kmol/kg.h.pa)
NiMo-MnY	$3x10^{-8}$
NiMo-CrY	$3.4x10^{-8}$
NiMo-CrHY	$4.1x10^{-8}$
NiMo-CuY	$4.9x10^{-8}$
NiMo-HY	$5.7x10^{-8}$

Table (4): initial selectivities for the 3-methyl hexane and 2-methyl hexane at 325^{0}C.

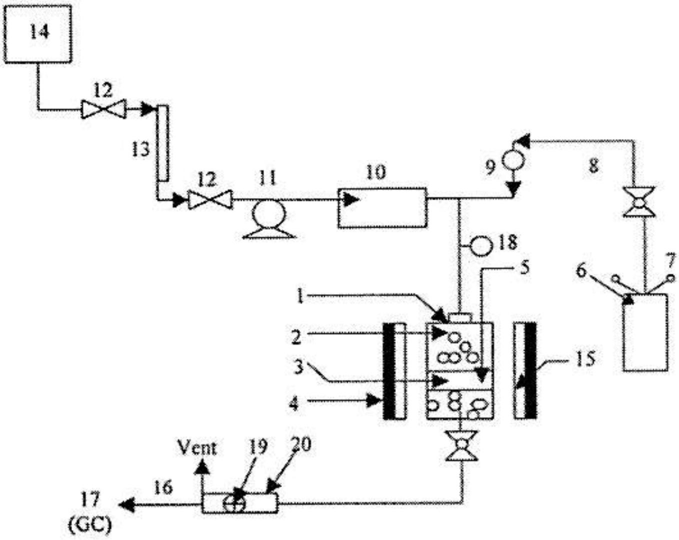
Type of catalyst	(IS) A_1	(IS) A_2
NiMo-MnY	0.3	0.23
NiMo-CrY	0.41	0.3
NiMo-CrHY	0.43	0.35
NiMo-CuY	0.44	0.38
NiMo-HY	0.46	0.41

Table (5): Rate constant for the 3-methyl hexane and 2-methyl hexane formation reactions at 325^{0}C.

Type of catalyst	K_1(kmol/kg.h.pa)	K_2(kmol/kg.h.pa)
NiMo-MnY	$9x10^{-9}$	$6.9x10^{-9}$
NiMo-CrY	$1.36x10^{-8}$	$1.02x10^{-8}$
NiMo-CrHY	$1.76x10^{-8}$	$1.44x10^{-8}$
NiMo-CuY	$2.16x10^{-8}$	$1.86x10^{-8}$
NiMo-HY	$2.62x10^{-8}$	$2.3x10^{-8}$

Table (6): Ion exchange results

Cation	Exchange %	Ionic radius
NH^+_4	90.5	1.43
Mn	82.5	1.29
Cr	70.1	1.25
Cu	77	1.28
Cr-H	85.1	-



1-reactor	11-Feed pump
2-glass	12-Valve
3-Catalyst bed	13-Metering burette
4-Insulation	14-Feed tank
5-Thermocouple and temperature indicator	15-Heater
6-H_2 gas cylinder	16- Gas sample trap
7-Pressure regulator	17-Gas chromatography
8-Needle valve	18-Gage pressure
9-Flow meter	19-Cooling machine
10-One way valve	20-Condenser and Collector

Sketch (1) Schematic flow diagram of catalytic experimental rig.

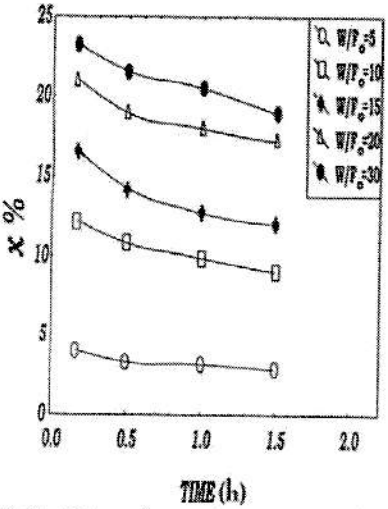


Fig.(1): Change of conversion as a function of time on stream on a NiO-MoO$_3$/MnY catalyst at 325 °C .

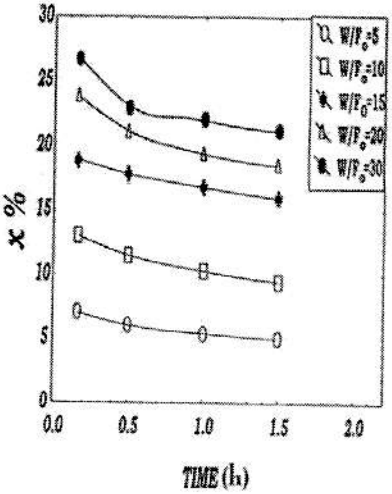


Fig.(2): Change of conversion as a function of time on stream on a NiO-MoO$_3$/CrY catalyst at 325 °C .

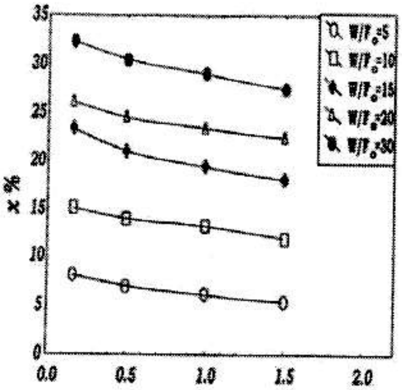


Fig.(3): Change of conversion as a function of time on stream on a NiO-MoO$_3$/CrHY catalyst at 325 °C .

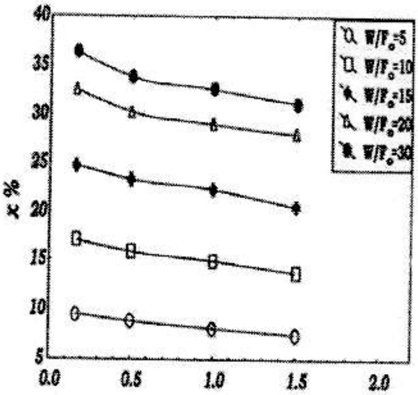


Fig.(4): Change of conversion as a function of time on stream on a NiO-MoO$_3$/CuY catalyst at 325 °C .

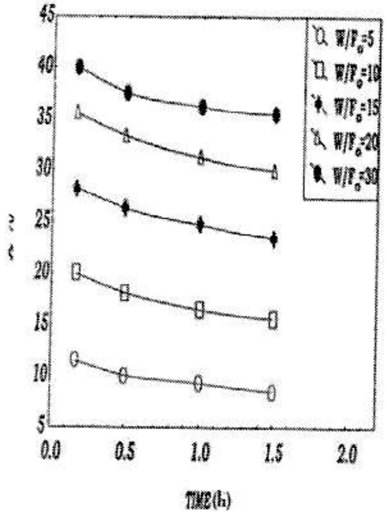


Fig.(5): Change of conversion as a function of time on stream on a NiO-MoO$_3$/HY catalyst at 325 °C .

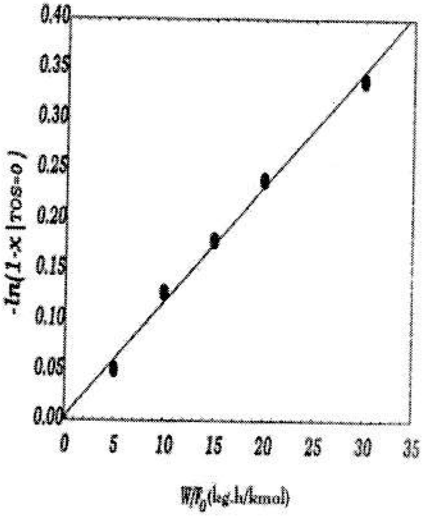


Fig.(6):Plot of first order equation for n-heptane hydrocracking on a NiO-MoO$_3$/MnY catalyst at 325 °C .

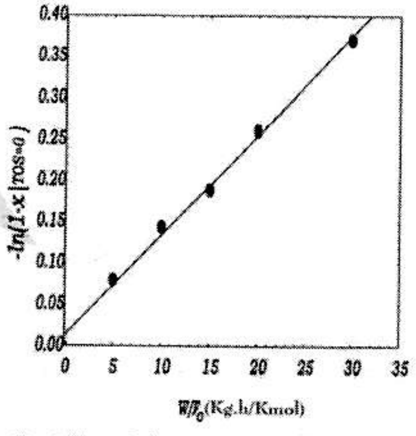


Fig.(7):Plot of first order equation for n-heptane hydrocracking on a NiO-MoO$_3$/CrY catalyst at 325 °C .

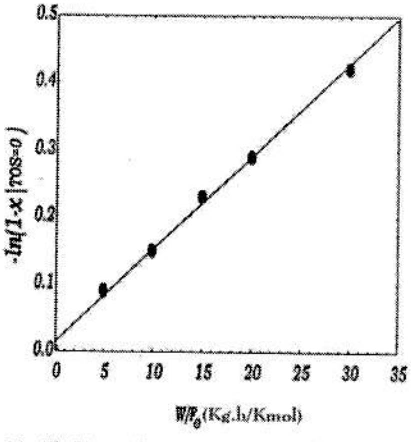


Fig.(8): Plot of first order equation for n-heptane hydrocracking on a NiO-MoO$_3$/CrHY catalyst at 325 °C .

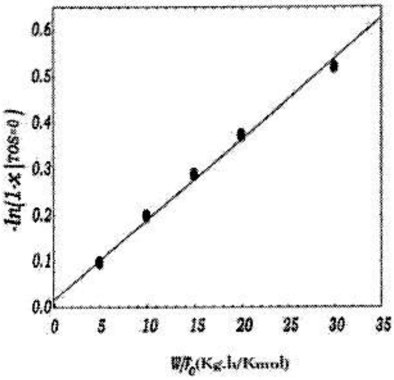


Fig.(9): Plot of first order equation for n-heptane hydrocracking on a NiO-MoO_3/CuY catalyst at 325 °C .

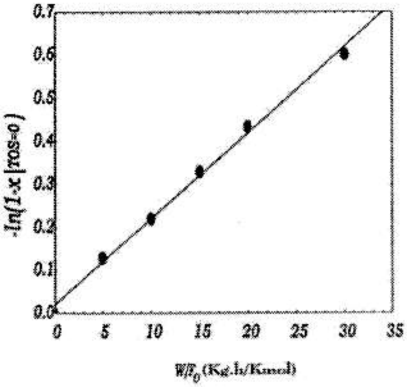
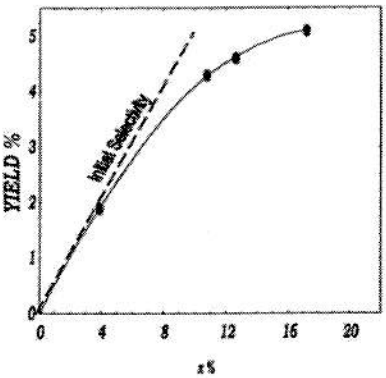


Fig.(10): Plot of first order equation for n-heptane hydrocracking on a NiO-MoO_3/HY catalyst at 325 °C .



Fig(11-a): Selectivity plot for 3-methyl hexane obtained during hydrocracking of n-heptane on a NiO-MoO_3/MnY catalyst at 325 °C .

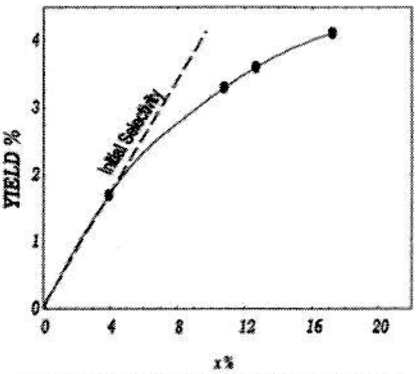


Fig.(11-b): Selectivity plot for 2-methyl hexane obtained during hydrocracking of n-heptane on a NiO-MoO_3/MnY catalyst at 325 °C .

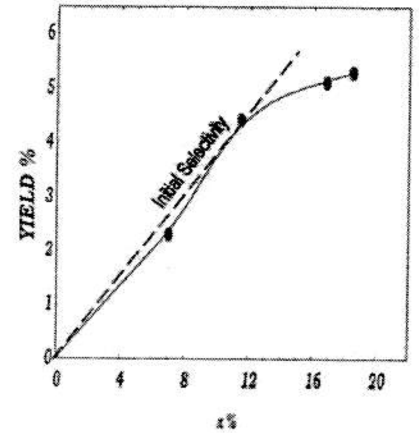


Fig.(12-a): Selectivity plot for 3-methyl hexane obtained during hydrocracking of n-heptane on a NiO-MoO$_3$/CrY catalyst at 325 °C .

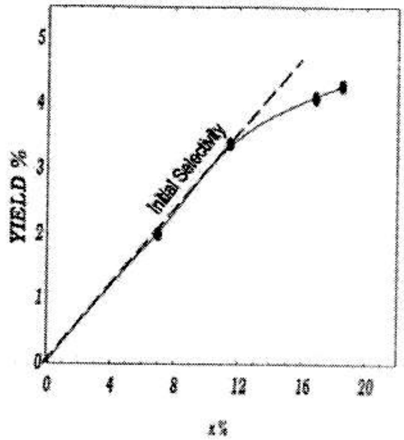


Fig.(12-b): Selectivity plot for 2-methyl hexane obtained during hydrocracking of n-heptane on a NiO-MoO$_3$/CrY catalyst at 325 °C .

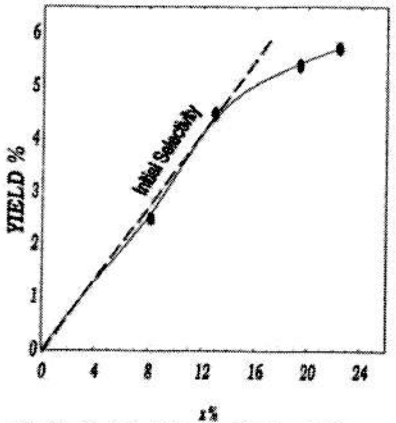


Fig.(13-a): Selectivity plot for 3-methyl hexane obtained during hydrocracking of n-heptane on a NiO-MoO$_3$/CrHY catalyst at 325 °C .

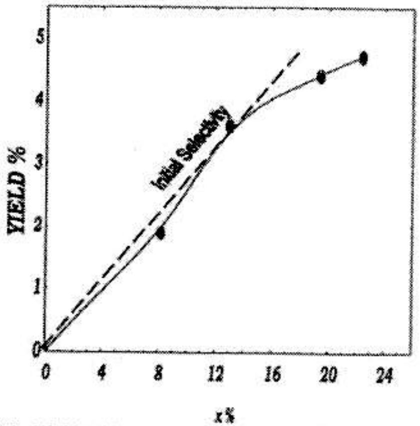


Fig.(13-b): Selectivity plot for 2-methyl hexane obtained during hydrocracking of n-heptane on a NiO-MoO$_3$/CrHY catalyst at 325 °C .

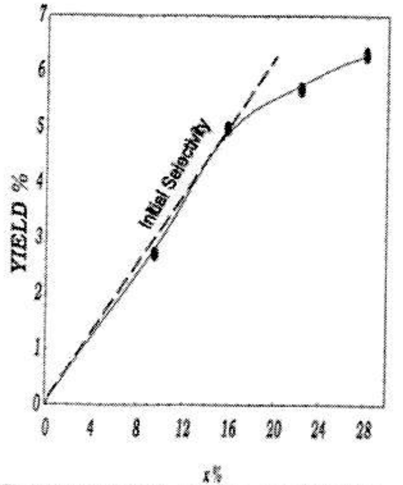


Fig.(14-a): Selectivity plot for 3-methyl hexane obtained during hydrocracking of n-heptane on a NiO-MoO$_3$/CuY catalyst at 325 °C .

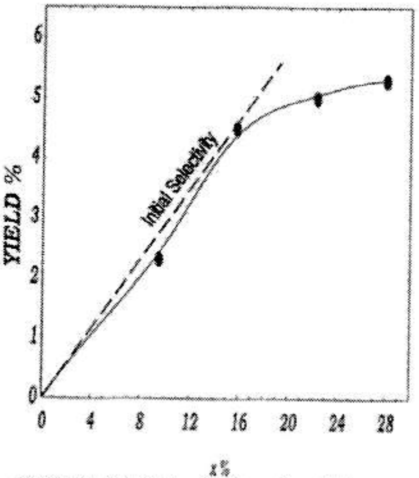


Fig.(14-b): Selectivity plot for 2-methyl hexane obtained during hydrocracking of n-heptane on a NiO-MoO$_3$/CuY catalyst at 325 °C .

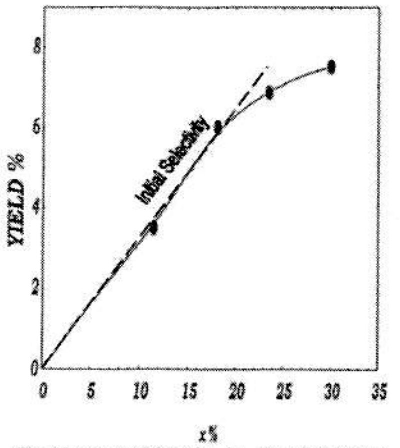


Fig.(15-a): Selectivity plot for 3-methyl hexane obtained during hydrocracking of n-heptane on a NiO-MoO$_3$/HY catalyst at 325 °C .

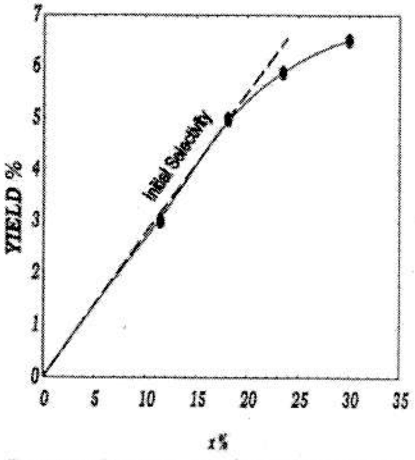


Fig.(15-b): Selectivity plot for 2-methyl hexane obtained during hydrocracking of n-heptane on a NiO-MoO$_3$/HY catalyst at 325 °C .

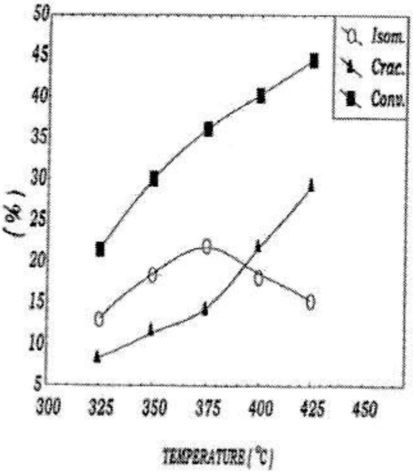


Fig.(16): Effect of reaction temperature on the conversion of n-heptane and the yield of isomerization and cracking for NiO-MoO$_3$/MnY catalyst at W/F$_O$= 30 (Kg.h/Kmol)

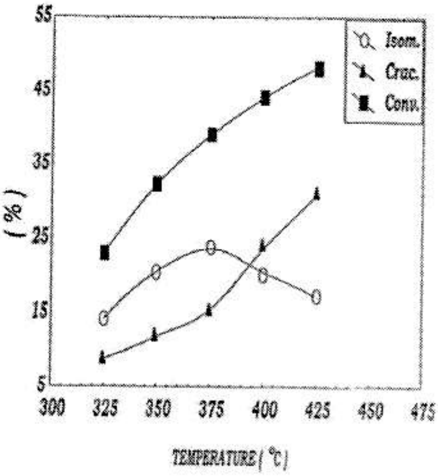


Fig.(17):Effect of reaction temperature on the conversion of n-heptane and the yield of isomerization and cracking for NiO-MoO$_3$/CrY catalyst at W/F$_O$= 30 (Kg.h/Kmol)

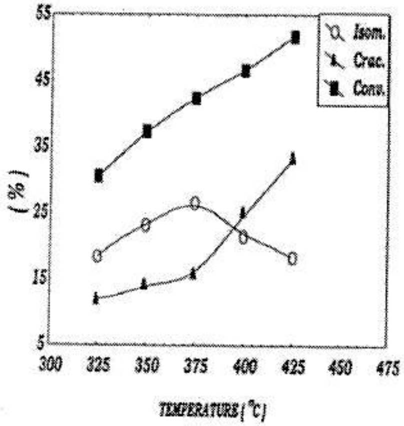


Fig.(18):Effect of reaction temperature on the conversion of n-heptane and the yield of isomerization and cracking for NiO-MoO$_3$/CrHY catalyst at W/F$_O$= 30 (Kg.h/Kmol)

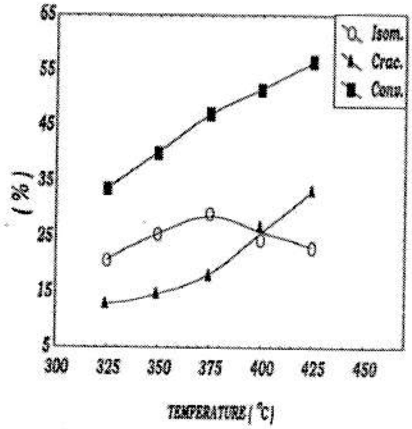


Fig.(19):Effect of reaction temperature on the conversion of n-heptane and the yield of isomerization and cracking for NiO-MoO$_3$/CuY catalyst at W/F$_O$= 30 (Kg.h/Kmol)

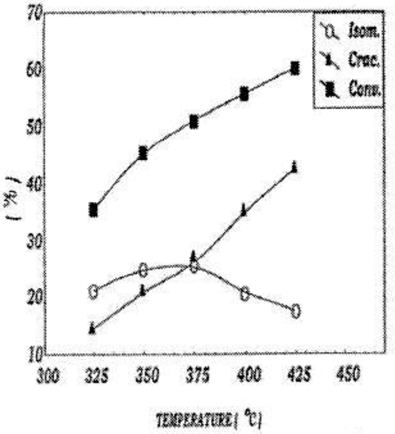


Fig.(20):Effect of reaction temperature on the conversion of n-heptane and the yield of isomerization and cracking for NiO-MoO$_3$/HY catalyst at W/F$_0$= 30 (Kg.h/Kmol)

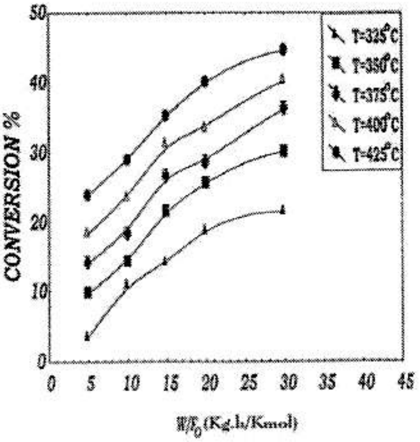


Fig.(21): Effect of W/F$_0$ on the conversion of n-heptane for NiO-MoO$_3$/MnY catalyst.

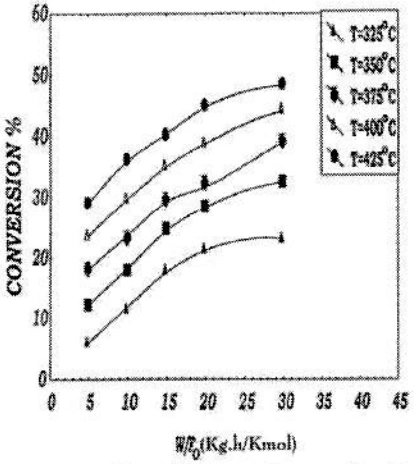


Fig.(22):Effect of W/F$_0$ on the conversion of heptane for NiO-MoO$_3$/CrY catalyst.

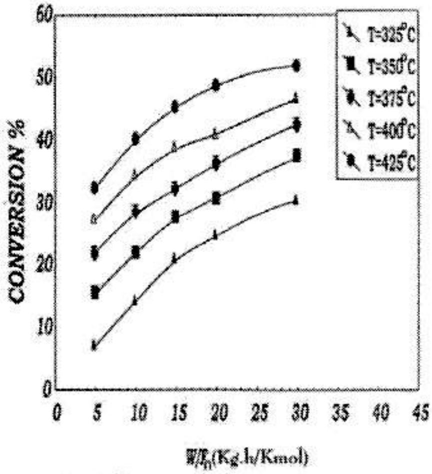


Fig.(23): Effect of W/F$_0$ on the conversion of heptane for NiO-MoO$_3$/CrHY catalyst.

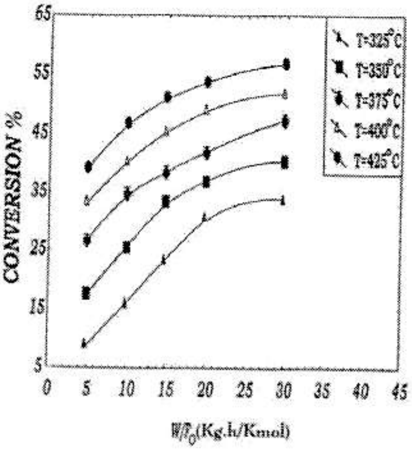


Fig.(24): Effect of W/F_O on the conversion of n-heptane for NiO-MoO_3/CuY catalyst.

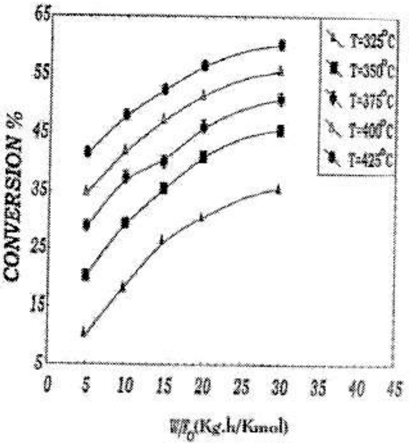


Fig.(25): Effect of W/F_O on the conversion of n-heptanefor NiO-MoO_3/HYcatalyst.