Al-Khwarizmi Engineering Journal, Vol. 11, No. 1, P.P. 73- 83 (2015)

Al-Khwarizmi Engineering Journal

Catalytic Cracking of Iraqi Vacuum Gasoil Using Large and Medium Pore Size of Zeolite Catalysts

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(Received 12 January 2014; accepted 17 December 2014)

Abstract

The catalytic cracking conversion of Iraqi vacuum gas oil was studied on large and medium pore size (HY, HX, ZSM-22 and ZSM-11) of zeolite catalysts. These catalysts were prepared locally and used in the present work. The catalytic conversion performed on a continuous fixed-bed laboratory reaction unit. Experiments were performed in the temperature range of 673 to 823K, pressure range of 3 to 15bar, and LHSV range of 0.5-3h^{-1}. The results show that the catalytic conversion of vacuum gas oil increases with increase in reaction temperature and decreases with increase in LHSV. The catalytic activity for the proposed catalysts arranged in the following order:

HY>HX>ZSM-11>ZSM-22

The product distribution depends greatly on the temperature and on the catalyst type. A higher hydrocarbon yields was obtained for HY zeolite catalyst. The selectivity towards high octane number compounds for the proposed catalysts are arranged in the following order:

HY>HX>ZSM-11>ZSM-22

The cracking conversion is improved by increasing reaction pressure up to 15 bar. The simulated experiments of the catalytic cracking process show that the higher conversion and more desired products can be achieved to conventional feeds.

Keywords: *catalytic cracking, vacuum gas oil, Zeolite, HY, HX, ZSM-11, ZSM-22.*

1. Introduction

With the continuously increasing in demands for light hydrocarbon products due to the increases in industrialization and population as well as crude oil resources limitations, have caused a strong interest for the development of new and alternative methods for liquid fuels production. Currently, the catalytic cracking units are available and become more prevalent due to the declining availability and higher price for light crudes (Jorge Ancheyta, 2011; Lawrie 2011; Fonseca et al, 2011; Siddiqui et al., 2011; Mario L. 2010). It is the most used process in the production of LPG and gasoline from vacuum gas oil or atmospheric residue (Samar et al., 2008; Caeiro et al., 2007).

The process of catalytic cracking of a hydrocarbon feedstock comprises the catalytically scission of the C-C bonds cracked in a reactor by contact with a cracking catalyst to produce cracked products and unconverted cracked products and feed are withdrawn as a vapor stream and fractionated in a fractionator column to produce a plurality of products including a liquid slurry oil product containing hydrocarbons (Al-Hassani, 2007; Gauw et al., 2002; Mohsen et al., 1995).

The formation of products in catalytic cracking process is accomplished by both primary and secondary reactions. Primary reactions are designed as those involving the initial carbon-carbon bond scission and the immediate neutralization of carbonium ion (Samar et al., 2008; Occelli, 2007; laxmi et al., 2003; Gauw et al., 2002). The mechanism of carbonium ions formation initially beginning by a small amount of thermal cracking of n-paraffins to form olefins. These olefins add a proton from the catalyst to form large carbonium ions which decompose according to the beta rule (carbon-carbon bond scission takes place at the carbon in the position beta to the carbonium ions and olefins) to form small carbonium ions and olefins. The small carbonium ions propagate the chain reaction by transferring a hydrogen ion from an n-paraffin to form a small paraffin molecule and new large carbonium ion. Thus the chain repeats itself continuously (Corma et al., 1995; Samar et al., 2008; Thomas, 1949; Mohan et al., 2004). Even through the basic mechanism is essentially the same, the manner and extent of response to catalytic cracking differs greatly among the various hydrocarbons types and type of catalyst used.

Cracking catalysts are divided into three classes: (1) acid-treated natural aluminosilicates, (2) amorphous synthetic silica-alumina combinations, and (3) crystalline synthetic silica-alumina catalysts called zeolites or molecular sieves (Mario, 2010; Jiří et al., 2011).

Zeolites are widely used as catalysts for cracking of petroleum feedstocks. The advantages of the zeolite catalysts are: (1) higher activity, (2) higher gasoline yields at a given conversion, (3) production of gasoline containing a larger percentage of paraffinic and aromatic hydrocarbons, (4) lower coke yield (and therefore usually a larger throughput at a given conversion level), (5) increased isobutane production and (6) ability to go to higher conversions per pass without over cracking (Lawrie, 2011; Gary, 2001; Ibrasheva and Zhubanov, 2000).

Zeolites such as ZSM-11, ZSM-12, mordenite, Y-zeolite, L-zeolite, b-zeolite and silicoaluminophosphates (SAPO-n), as well as ZSM-22, have been studied extensively as the catalysts for catalytic cracking (Graça et al., 2011, 2009; Gang et al., 2008; Samar et al., 2008; Laxmi; et al., 2003; Arthur et al., 2002; Muñoz et al., 2000;).

The dimensions and shape of zeolite pores is strongly influenced the activity and selectivity of catalytic conversion. The shape selectivity exhibited by zeolites can be classified as (i) reactant shape selectivity, (ii) product shape selectivity, and (iii) transition state shape selectivity depending upon whether reactant diffusion, product diffusion, or the transition state is a limiting step. Besides these classic shape selectivity mechanisms inside the zeolite micropores, pore mouth catalysis is a special type of transition state shape selectivity involving adsorption and catalysis in the pore openings only (Laxmi et al., 2003; Al-Khattaf et al., 1999-2002).

Generally, large and medium pore sizes are widely used as cracking catalysts. The catalyst composition comprising a primary cracking component, such as zeolite Y, and a mesoporous aluminophosphate material which includes a solid aluminophosphate composition modified with at least one element selected from zirconium, cerium, lanthanum, manganese, cobalt, zinc, and vanadium (Al-Hassany, 2009; Mohan et al., 2004). The mesoporous aluminophosphate material has a specific surface area of at least 100 m^2/g, an average pore size less than or equal to 100Å, and a pore size distribution such that at least 50% of the pores have a pore diameter less than 100Å (Arthur et al., 2002). Corma et al., 1995 explained that the size of the catalyst pores which are larger than 6 Å diameter allows to process relatively high-boiling oil fractions and petrochemical bases. Also he concluded that faujasite is used for carrying out the cracking and hydrocracking of vacuum gasoil. Zeolite pores size is strongly effect the product distribution, and this property has been studied extensively by many authors (Al-Hassany, 2009; Al-Khattaf et al., 1999-2002; Schwan et al., 2000; Henrique et al., 1997).

The main objective of the present work is to study the cracking activity and selectivity as well as products distribution of ZSM-11, ZSM-22, HY and HX catalysts and the effect of limited ranges of operating conditions (temperature, LHSV, and operating pressure) on the vacuum gas oil transformation in a fixed bed continuous laboratory reaction unit.

2. Experimental Work

2.1. Materials

2.1.1. Feedstock

Vacuum gas oil (VCO) supplied from Al-Dura Refinery was used as a feedstock in transformation experiments. The properties of VCO are listed in Table 1.

Table 1,
Properties of Straight Run Light Naphtha.

Specific gravity @ 15°C	0.893
Pour point, °C	48
Vanadium Content, ppm	3
Nickel Content	2
Aniline point, °C	70
CCR, wt%	1
Sulfur Content, wt%	1.5
IBP, °C	320
FBP, °C	550
Composition	wt.%
Saturated/ non-cyclic	46.9
Cyclic/ non aromatics	22.5
Monoaromatic	25.1
Diaromatic	4.6
Triaromatic	0.6
Tetraaromatic	0.3

2.1.2. Nitrogen Gas

High purity (99.999 vol.%) of nitrogen gas supplied from the local market was used in the present work.

2.1.3. Ammonium ZSM-11, ZSM-22, HY and HX Zeolites

Ammonium ZSM-11, ZSM-22, HY and HX zeolites supplied as a powder from Zeolyst International Company. They were used in the preparation of the proposed catalysts. The properties of these zeolites are listed in Table 2.

Table 2,
Properties of ammonium zeolite powder.

	SiO_2/Al_2O_3 Mole Ratio	**Nominal Cation Form**	**Na_2O Weight %**	**Surface Area, m^2/g**
HY	5	Ammonium	0.08	660
HX	2.5	Ammonium	0.02	352
ZSM-11	21	Ammonium	0.01	387
ZSM-22	31	Ammonium	0.05	395

2.2. Catalyst Pelleting

100 g of ammonium ZSM-11, ZSM-22, HY and HX zeolites powders were shaped as pelletes with dimensions of 3mm×5mm using a laboratory scale pelleting machine (model TDP-1.5 from MINHUA PHARMACEUTICAL MACHINERY CO., LIMITED). The final forms were dried at 110°C and stored in an evacuated place.

2.3. HY Zeolite Preparation

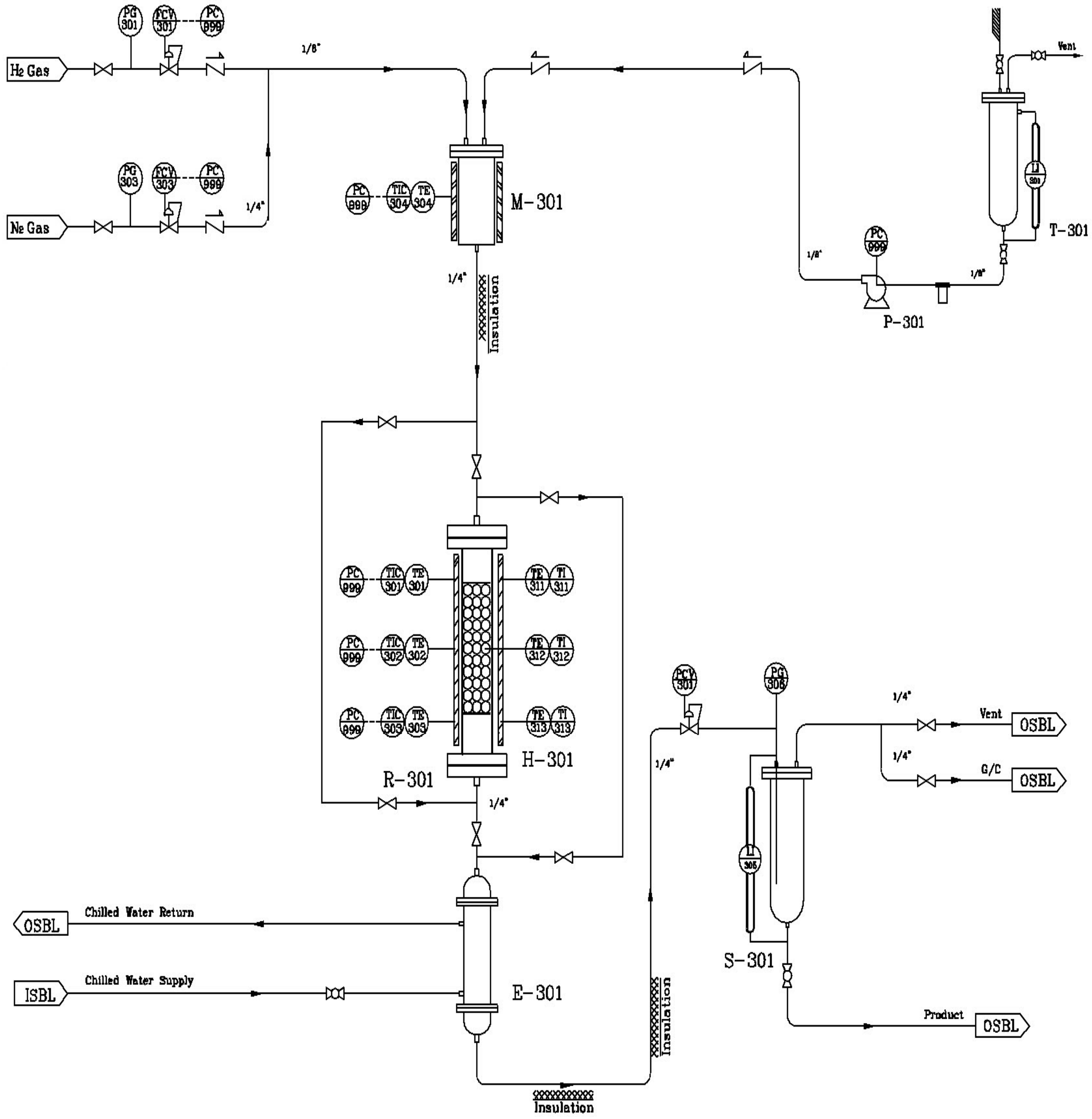
The dried zeolite pellets were calcinated at 500°C for 3 hrs in a furnace with nitrogen. The calcinated catalyst pellets were then reduced with hydrogen at 350°C for 3 hrs (Al-Hassani, 2007). The properties of the prepared ZSM-22, ZSM-11, HY and HX zeolite catalysts are listed in Table 3.

Table 3,
Properties of the ZSM-11, ZSM-22, HY and HX zeolites.

	Surface Area m^2/g	**Bulk density g/cm^3**	**Pore volume, cm^3/g**
ZSM-22	399	0.510	0.37
ZSM-11	332	0.532	0.115
HY	662	0.592	0.96
HX	425	0.588	0.521

2.4. Catalytic Cracking Reaction Unit

Catalytic cracking experiments were conducted in a continuous fixed bed reactor laboratory scale unit. Figure 1 shows the schematic diagram of this unit. It consist of feed tank (T-301), gas flow meter and controller (FCV), feed pump (P-301), evaporator (M-301), fixed bed reactor (R-301), high pressure separator (E-301), low pressure separator (S-301), and an appropriate heating system (H-301). The reactor was heated and controlled automatically with computer control software and by four steel-jacket heaters using chromal alumel thermocouple (type k).



R-301	**Tubular Reactor**	**P-301**	**Feed Pump**	FCV-301 FCV-302 FCV-303 FCV-304	Mass flow controller
T-301	Feed Tank	E-301	Condenser		
S-301	Separator	M-301	Mixer		
H-301	Heater	PRV-301	Pressure Relief Valve		

Piping and Instrument Flow Diagram

Laboratory Reaction Unit

University of Baghdad

Al-Khawarizmi College of Engineering

Department of Biochemical Engineering

Fig. 1. Schematic Diagram of Laboratory Continuous Fixed Bed Reaction Unit.

2.5. Catalytic Cracking Experiments

The catalytic activity experiment was performed by charging 30 cm^3 of fresh catalyst in the reactor and between two layers of inert material (glass balls). In the beginning of each experiment, the reactor was flashed with nitrogen 2 l/h for 1 h to purge the air from the system, then the reactor is heated to the desired temperature. The reaction pressure was adjusted by regulating nitrogen pressure. A pre-specified flow rate of vacuum gas oil was set on, vaporized in the evaporator and the vapor was mixed with the nitrogen in the mixing unit at a specified flow rates. The mixture entered the reactor from the top, distributed uniformly and reacted on the catalyst. The gaseous products passed through the high pressure separator and the final condensates were collected in the low pressure separator only after steady state operation was established and the initial products were discarded. The catalytic cracking reaction conditions employed are temperature range 400-550°C, liquid hourly space velocity (LHVS) range 0.5-3h^{-1}, the pressure was ranging from 3-15 bar.

2.6. Gas Chromatographic Analysis

The collected products (liquid and gas) were analysis into their components by gas chromatographic (GC) analysis using SHIMADZU GC model 2014A with FID detector.

3. Results and Discussion

The results of catalytic conversion runs of Iraqi vacuum gas oil (IVGO) are discussed in this section in order to evaluate the catalyst performance. The purpose of the present work is to choose the study the effect of operating conditions on the proposed catalysts activity and stability. The catalytic cracking conversion involves six main reactions, gaseous product formation, isomerizaation, n-paraffin formation, olefination, cycalization and aromatization. In this section, discussions were built upon the results of these reactions.

3.1. Effect of Temperature

The effect of temperature on IVGO transformation is shown in Figs. 2-5. It is clearly temperature dependent. In the temperature range of 673 to 823K the conversion is increases over the prepared ZSM-22, ZSM-11, HY, and HX catalysts.

The increases in the activity may be due to the increases in the concentration of the active sites and as the reaction temperature increases the concentration increases leads to increase in the cracking rate. This phenomenon was observed also by other researchers (Samar, 2008; Al-Khattaf et al., 1999-2002; Schwan et al., 2000; Corma et al., 1995).

It can also be observed that the values of the cracking conversion over the prepared catalysts take the following order:

HY > HX > ZSM-22 > ZSM-11

The higher activity for HY catalyst compared with the other prepared catalyst may be due to the effect of catalyst acidity. HY zeolite has a high acidity as reported by many studied (Al-Hassany, 2009; Gauw et al., 2002; Al-Khattaf et al., 2002) and the order of acidity decreases in the same manner so a lower conversion is observed for ZSM-11 catalyst.

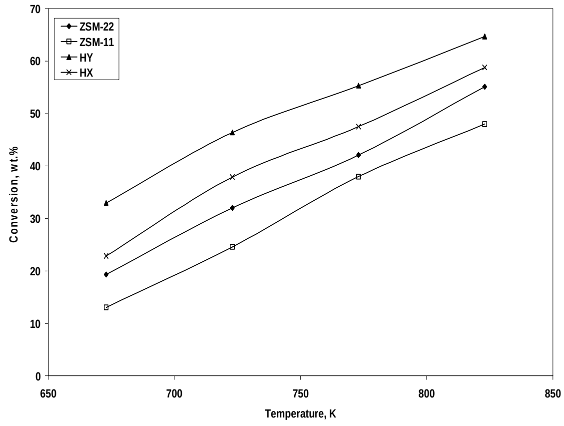


Fig. 2. Catalytic cracking conversion vs. temperature at LHSV of 0.5h^{-1} and pressure of 3bar.

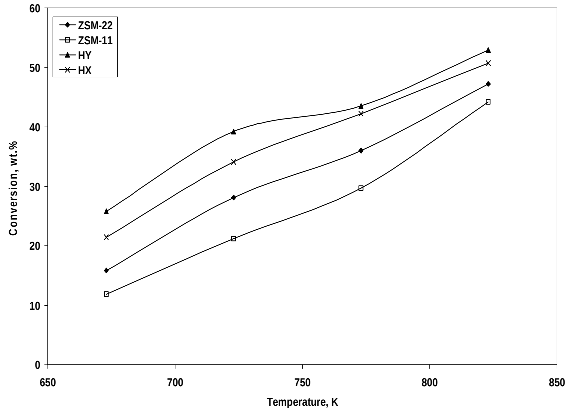


Fig. 3. Catalytic cracking conversion vs. temperature at LHSV of 1h^{-1} and pressure of 3bar.

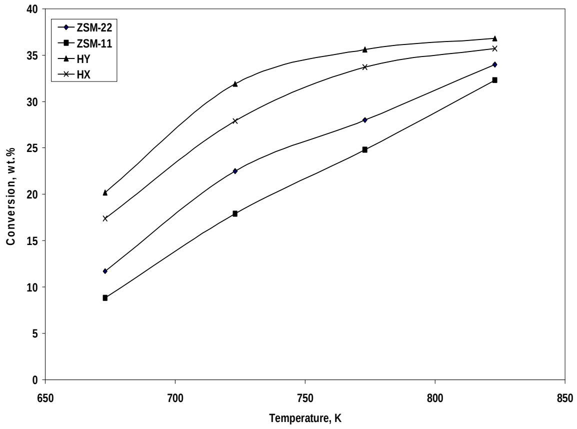


Fig. 4. Catalytic cracking conversion vs. temperature at LHSV of 2h^{-1} and pressure of 3bar.

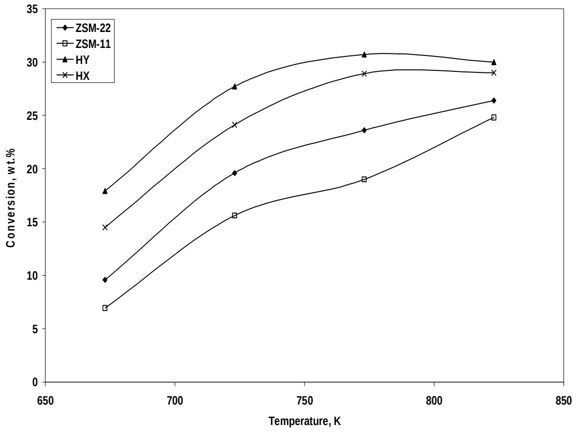


Fig. 5. Catalytic cracking conversion vs. temperature at LHSV of 3h^{-1} and pressure of 3bar.

3.2. Effect of LHSV

Figures 6 - 9 show the change in IVGO transformation as a function of LHSV. The liquid hourly space velocity taken as the ratio between the volumetric flow rate of IVGO and catalyst volume (the contact time is 1/LHSV). It can be observed from these figures that as the LHSV increases the catalytic conversion decreases so the rates of cracking decreases. This many be attributed to the fact that with decreasing LHSV more time is exerted to the molecules of IVGO to react on the active sites. The same order is observed for the prepared catalyst and this is may be attributed to the effect of pore diffusion. A high pore volume was measured for HY zeolite and lower value was measured for ZSM-11 and as listed in Table 2. The same observations were reported in other works (Graça et al., 2009; Caeiro et al., 2007; Laxmi et al., 2003; Arthur et al., 2002; Al-Khattaf et al., 1999-2002).

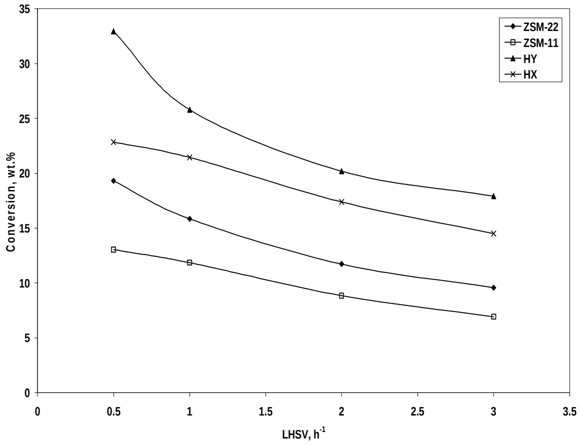


Fig. 6. Catalytic cracking conversion vs. LHSV at temperature of 673K and pressure of 3bar.

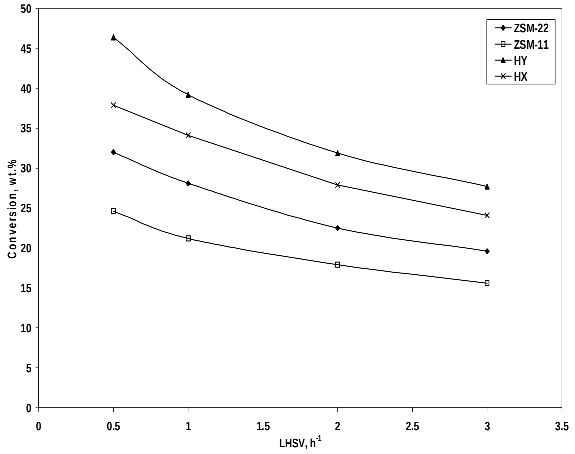


Fig. 7. Catalytic cracking conversion vs. LHSV at temperature of 723K and pressure of 3bar.

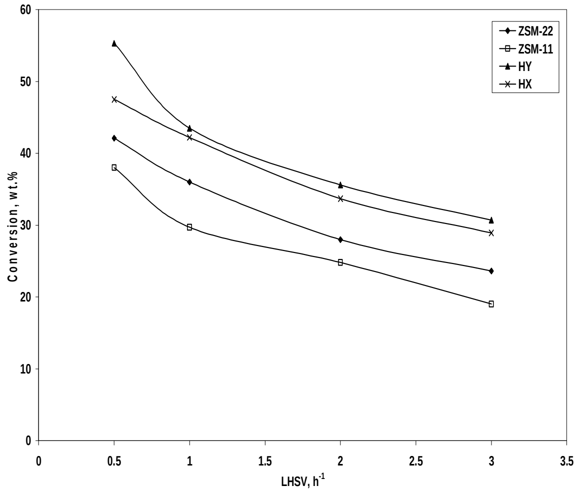


Fig. 8. Catalytic cracking conversion vs. LHSV at temperature of 773K and pressure of 3bar.

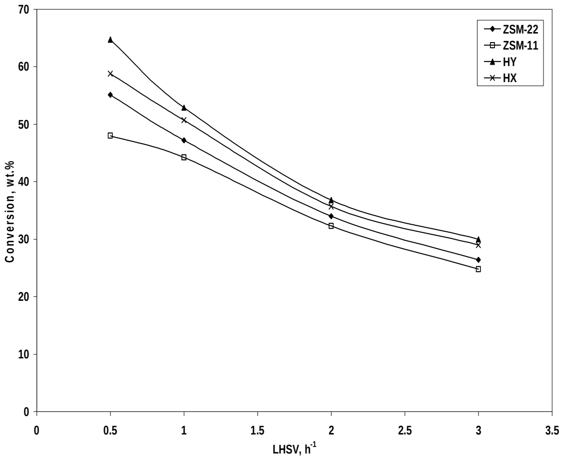


Fig. 9. Catalytic cracking conversion vs. LHSV at temperature of 823K and pressure of 3bar.

3.3. Effect of Pressure

The effect of reaction pressure on the IVGO catalytic conversion is shown in Fig. 10. As the reaction pressure increases IVGO conversion increases and over the four prepared catalysts.

The increase in operating pressure is probably leads to increase in hydrocarbon surface coverage area leading to increasing the concentration of carbenium ions i.e. more cracking activity. On the other hand, increasing pressure means minimizing the formation of coke which can be due to a shorter intermediate hydrocarbon residence time inside the catalyst, and thus minimizing the coking activity. These observations are agree well with the results reported by Siddiqui et al., 2011; Al-Hassany, 2009; Gauw et al., 2002, Al-Khattaf et al., 1999-2002; Ibrasheva et al., 2000.

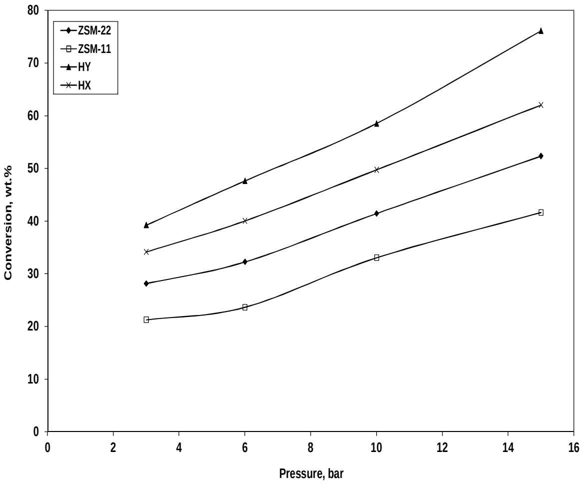


Fig. 10. Catalytic cracking conversion vs. pressure at LHSV of 1h^{-1} and temperature of 723K.

4.4. Catalytic cracking products distribution

Figures 11 to 16 show the cracking product yields were obtained over the proposed catalysts and in the temperature range of 673 to 823K while LHSV and reaction pressure were kept constant at 1h^{-1} and 3bar respectively.

As mentioned above, six types of reactions are proposed. It can be observed that the rate of reactions increase with the increased in reaction temperature over the proposed catalysts. The difference can be further illustrated by the effect on the yield of hydrocarbons. Generally, it can be observed that the selectivity towards high octane number compounds for the proposed catalysts are arranged in the following order:

HY>HX>ZSM-11>ZSM-22

Also a high yields were found for the high octane products. This many be attributed to acidity of the active sites in the catalysts and also to the effect of pore size of the catalyst. The acidity increases from ZSM-22 to HY since the formation of carbenium ions favor the high acidity catalysts. These ions then will decompose to produce isomers or high octane number hydrocarbon products as mentioned above in the mechanism of cracking. These results are agree well with other observation reported by Siddiqui et al., 2011; Fonseca et al., 2011; Graça et al., 2011, 2009; Gang et al., 2008; Caeiro et al., 2007; Corma et al. 1995; Mohan et al., 2004.

Al-Khattaf S. and Lasa H. de, et al., (1999, 2001 and 2002) have been proposed the criteria of the effect of pore size on the diffusion of hydrocarbon molecules inside HY-zeolite structure. They stayed that the critical diameter of HY-zeolite as large as 10.2Å. For, *iso*-propyl-benzene family, these molecules can diffuse and eventually crack inside the Y-zeolite structure as follows: (a) if the molecule critical diameter is smaller than 7.4Å (e.g. cumene) hydrocarbon molecules may evolve under kinetically controlled regime, (b) if the molecule critical diameter is larger than 7.4 Å, but smaller than 10.2 Å, case of 1,3-DIPB and 1,3,5-TIPB, with 8.4 and 9.5Å critical diameters, diffusional transport may affect the overall rate of cracking. The same phenomenon has been observed by Al-Hassany (2009). She illustrated the diffusion of n-hexane inside HY-zeolite. She stated that the molecular diameter of hexane is 4.8Å, with an increase of about 0.7Å for every additional increase in branch length.

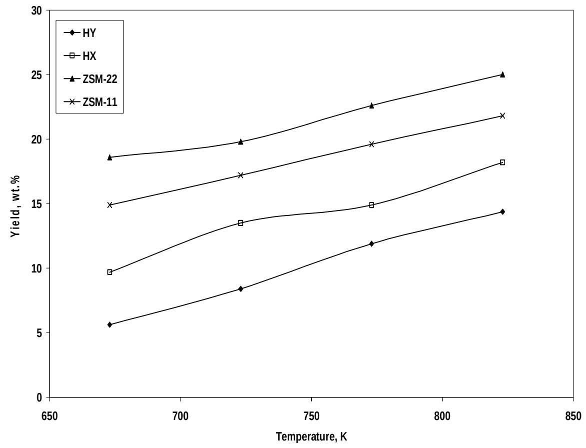


Fig. 11. Gaseous products yield vs. temperature at LHSV of 1h^{-1} and pressure of 3bar.

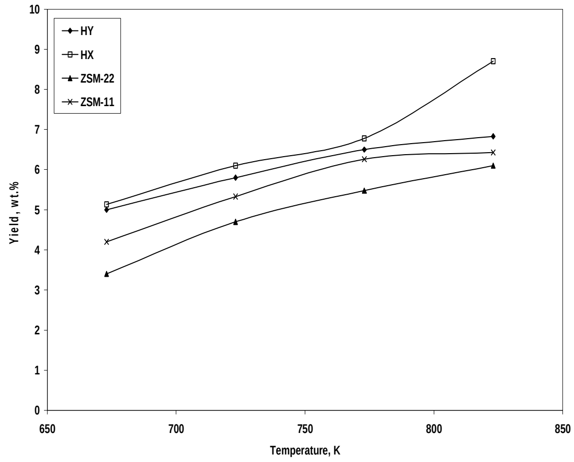


Fig. 14. Cyclo-compounds yield vs. temperature at LHSV of 1h^{-1} and pressure of 3bar.

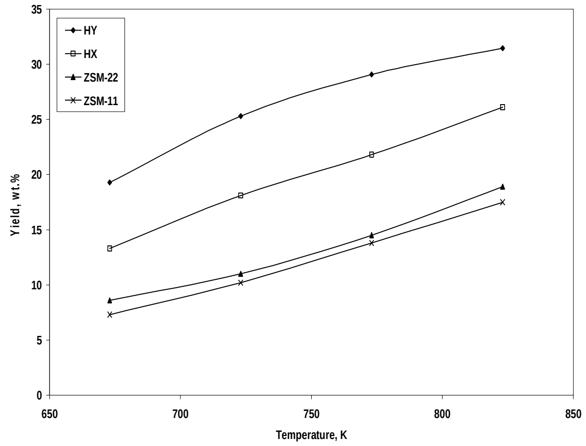


Fig. 12. Isomeres yield vs. temperature at LHSV of 1h^{-1} and pressure of 3bar.

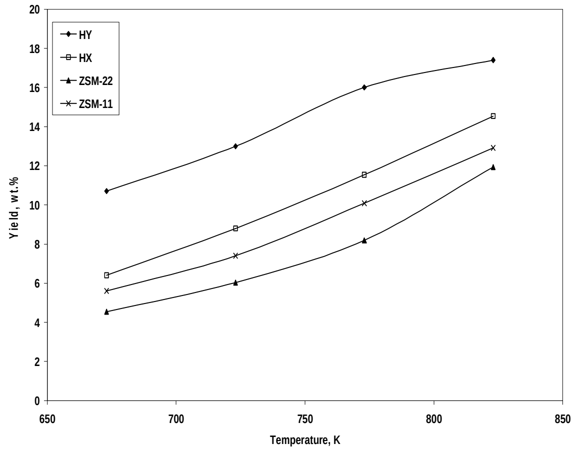


Fig. 15. Olefins yield vs. temperature at LHSV of 1h^{-1} and pressure of 3bar.

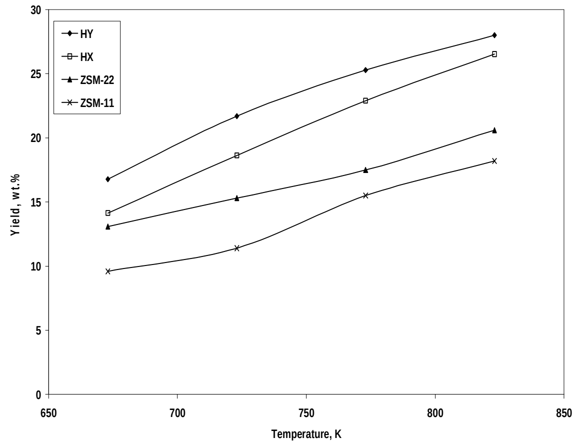


Fig. 13. n-Paraffins yield vs. temperature at LHSV of 1h^{-1} and pressure of 3bar.

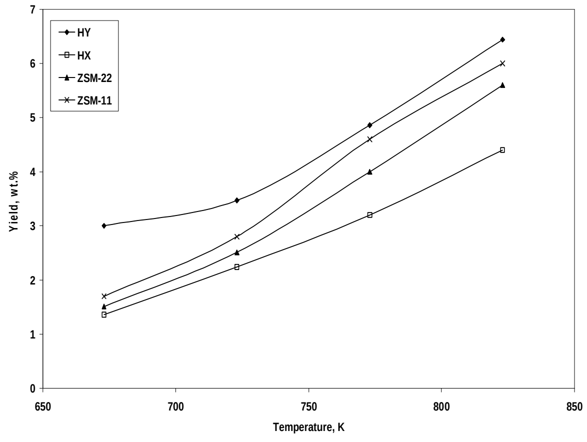


Fig. 16. Aromatics yield vs. temperature at LHSV of 1h^{-1} and pressure of 3bar.

4. Conclusions

The transformation of IVGO was evaluated in a laboratory fixed bed reaction unit using HY, HX, zsm-11, zsm-22 zeolite catalysts. The following conclusions were drawn from the experimental results:
The prepared catalysts exhibit a catalytic cracking activity within the studied range of operating conditions. The catalytic activity for the proposed catalysts arranged in the following order:

HY>HX>ZSM-11>ZSM-22.

The catalytic cracking reaction is temperature dependent, and increases with the increase in temperature. The cracking activity decreases with the increase in LHSV over the proposed catalysts. The catalytic conversion is improved by increasing operating pressure from 3 to 15 bar. The cracking product distribution dependent on the temperature and on the catalyst used. The cracking products yields increases with the increase in temperature. HY exhibit a higher octan number hydrocarbon products yields. The selectivity towards high octane number compounds for the proposed catalysts are arranged in the following order:

HY>HX>ZSM-11>ZSM-22

Acknowledgement

This study was supported by a grand provided by the Ministry of Higher Education and Scientific Research/ Research and Development Department. Authors gratefully acknowledge this contribution and supporting.

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التكسير الحفاز لزيت الوقود العراقي باستعمال الزيولايت ذي الحجم المسامي الكبير والمتوسط

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الخلاصة

تمت دراسة تحويل التكسير الحفاز لزيت الغاز العراقي الناتج من الوحدات الفراغية باستعمال عدة أنواع من الزيولايت ذات الحجم المسامي الكبيرة والمتوسط (HY، HX، ZSM-22 و ZSM-11). تم تحضير هذه العوامل مختبريا واستعملت في العمل الحالي. جرت تفاعلات التحول الحفاز في وحدة تفاعل مختبرية ومستمرة ومن نوع الحشوة الثابتة. أجريت التجارب بدرجات الحرارة تراوحت من ٦٧٣ إلى ٨٢٣ كلفن، وضغط تراوح من ٣ إلى ١٥ بار، وبسرع فراغية تراوحت ٠.٥ الى ٣ ساعة$^{-١}$. بينت النتائج أن التحول الحفاز لزيت الغاز يزداد مع زيادة درجة حرارة التفاعل ويتناقص مع زيادة السرعة الفراغية. ان ترتيب الفعالية التحفيزية للعوامل المساعدة المستخدمة يمكن ترتيبها بالشكل الآتي:

HY> HX> ZSM-11> ZSM-22

ان توزيع نواتج التفاعل يعتمد الى حد كبيرة على درجة الحرارة وعلى نوع العامل المساعد. تم الحصول على أعلى معدلات لنسبة النواتج للعامل المساعد HY. ان انتقائية التفاعل باتجاه تكوين مركبات ذات رقم اوكتاني عالٍ بالنسبة للعوامل المساعدة المستخدمة يمكن ترتيبها بالشكل الآتي:

HY> HX> ZSM-11> ZSM-22

يمكن تحسين تحول التكسير الحفاز بزيادة الضغط. ان تجارب المحاكاة لعملية التكسير الحفاز أظهرت بأنه بالإمكان الحصول على تحول عالٍ وتحسين معدلات إنتاج المنتجات المطلوبة من المواد الأولية التقليدية.