THE EFFECT OF OPERATING CONDITION FOR CUMENE CRACKING ON THE PERFORMANCE OF PREPARED HX - ZEOLITE CATALYST

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ABSTRACT

The present study reports the effect of temperature and liquid hourly space velocity (LHSV) on the cumene cracking reaction rate and selectivity by using a laboratory continuous flow unit with fixed bed reactor operating at atmospheric pressure. The prepared HX zeolite was made from Iraqi kaolin with good crystallinity .The activity and selectivity of prepared HX-zeolite was compared with standard HY zeolite and HX zeolite catalysts in the temperature range of 673-823K and LHSV of 0.7-2.5 h^{-1}. It was found that the cumene conversion increases with increasing temperature and decreasing LHSV at 823K and LHSV of 0.7 h^{-1} the conversions 65.32, 42.88 and 59.42 mol% for HY, HX and prepared HX catalysts respectively and at LHSV of 2.5 h^{-1} and the same temperature the conversions decrease to 29.24, 12.53 and 22.89 mol%, respectively .It also found that the benzene yield increases with increasing temperature at 823K and LHSV of 0.7 h^{-1} the benzene yields were 58.79, 38.56 and 54.56 mol% for HY zeolite , HX zeolite and prepared HX zeolite, respectively and the selectivity to benzene is nearly constant over the studied temperatures range. The kinetics of cumene cracking (the kinetics parameters-rate constant)and activation energy are used in this study to characterize differences between various catalysts. The reaction was found to be first order with activation energy equal to 78.58 , 89.10 and 97.77 kJ/mol for HY, prepared HX and HX , respectively.

الخلاصة

تبحث الدراسة الحالية تأثير درجة الحرارة و السرعة الفراغية على معدل تفاعل التكسير للكيومين و الانتقائية باستخدام وحدة جريان مستمر مختبرية تحتوي على مفاعل ذو حشوة ثابتة تعمل تحت الضغط الجوي . HX zeolite المحضر صنع من الكأولين العراقي و يمتلك نسبة تبلور جيدة .تم مقارنة الفعالية و الانتقائية لل HX zeolite المحضر مع عوامل مساعدة قياسية HY zeoilte و HX zeolite ضمن مدى درجات حرارة 673-823 ك ولسرع فراغية 0.7 -2.5 سا$^{-1}$.وقد لوحظ زياده تحول الكيومين مع زيادة درجة الحرارة ونقصان السرعة الفراغية في درجة حرارة 823 ك وسرع فراغية0.7 سا$^{-1}$ كان التحول 65.32، 42.90 و 59.42 مول% لكل من HY ، HX و Prepared HX على التوالي و بسرعة فراغية2.5 سا$^{-1}$ و نفس درجة الحرارة كان التحول 29.24 ، 12.53 و 22.89 على التوالي و كما لوحظ ان نواتج البنزين تزداد بزياده درجة الحرارة عند درجة 823 ك وسرعة فراغيه 0.7 سا$^{-1}$ نواتج البنزين كانت 58.79 ،38.56 و54.56 مول% لكل من HY ، HX و Prepared HX على التوالي . وقد لوحظ ان انتقائيه البنزين هي تقريبا ثابته على مدى درجات الحرارة المدروسة لكافه العوامل الساعدة المدروسة. اما حركية التفاعل لتكسير الكيومين وثابت معدل التفاعل وطاقه التنشيط استخدمت في هذه الدراسة لتشخيص الاختلافات بين العوامل المساعدة المختلفه.ولقد لوحظ بان التفاعل من المرتبه الاولى مع طاقات تنشيط 78.58 ،89.10 و 97.77كيلو جول / مول لكل من HY، prepared HX و HX على التوالي .

INTRODUCTION

The cracking of pure hydrocarbon and in particularly the dealkylation of cumene can provide important method for investigation the nature of catalyst [Prater and Lago,1956]. The dealkylation of cumene has been recognized as suitable rapid method for screening catalysts as compared with the gas oil method because it is possible to analyze the reaction products with a gas chromatographic analysis rather than by distillation, effecting an appreciable saving in time [Nicholson D. E. ,1955].

Donald and Wojciechowski (1977a) studied the catalytic cracking of cumene and they observed over 60 reaction products and the selectivity behavior of the major ones has been examined. They used a fixed bed reactor charged with LaY zeolite catalyst. A total of 67 compounds have been isolated in the reaction products. Twenty-eight of these have been found to be light hydrocarbons up to a boiling point of 80°C and include most isomers of C_4, C_5, and C_6. The remaining fractions contain phenyl compounds, 29 of which have higher boiling points than dipropyl benzene and comprise less than 0.1% of the total products.

Cumene dealkylation reaction on fresh catalyst had been reported to be promoted by Bröӧnsted acid sites [Tanabe K.,1970]. The high selectivity of the reaction over acid catalysts is related to the high proton affinity of the benzene ring and to the stability of the ejected carbonium ion [Peter A. J.,1977].

The catalytic cracking of cumene commences with chemisorption of cumene on a single active site. This is followed by splitting the molecules to propylene and benzene. The reverse reaction, the alkylation of benzene to cumene requires the adsorption of either benzene or propylene on an active site followed by a radical mechanism [Donald and Wojciechowski,1977b].

The knowledge of the kinetics of the reaction at the active sites is of primary importance in determining the nature and the difference between catalytic action in heterogeneous catalysis [Prater and Lago,1956].

Haensel V.(1951) has used cumene as a test for cracking catalyst (silica-alumina) at a reaction temperature between 350-550^oC and LHSV 5 h^{-1} in fixed bed reactor. He found that the yields of benzene are ranging from 5- 39 wt%, and found that the reaction is partly reversible in the lower temperature range.

Plank and Nace (1955) studied the cumene cracking and coke formation over silica-alumina at 800-1000 F^o (699.66-810.77 k) and 2-6 h^{-1} LHSV in fixed bed reactor and found that when temperature increases the conversion of cumene increases, and decreases as LHSV increases.

Schwab and Sieb (1964) studied the catalytic activity and the activation energy in the cracking of cumene, and they found that the replacement of the Na ion by divalent cations Ca or Mg decreased the activation energy of 231 kJ/mole by a factor of 2.

Pansing and Malloy (1965) reported, the cracking rates which are inferred from the rate of appearance of propylene gas are thus liable to serious error; however rates determined from benzene appearance are more reliable. The value of activation energy obtained by Pansing and Malloy was 86.52 kJ/mole.

Donald and Wojciechowski (1977b) used cumene cracking reaction to evaluate the activity of 100/140 mesh of LaY zeolite catalyst. And they studied the kinetic of cumene dealkylation over LaY at three reaction temperature 360, 430, and 500°C in tubular reactor and they assumed that the endothermic chemisorption of cumene must be in order to construct a plausible picture of the reaction energy surface, and they were also shown that the diffusion limitations affects the rate of catalyst decay to a different extent than the rate of reaction ,and they also found the activation energy for the dealkylation of cumene to be 94.5 kJ /mole .

Corma and Wojciechowski (1980) studied the initial selectivities for primary products in the catalytic cracking of cumene on HY and LaY zeolite catalysts in an integral fixed bed glass tubular reactor . It was observed that the reaction products and their characteristics behavior have been found to be the same for both LaY and HY zeolites at 360, 430 and 500 °C, which is due to the similarity in the nature of the active sites in both catalysts. At a temperature range 360-500°C the obtained selectivity for benzene ranged from 0.16 to 0.94 and from 0.65 to 0.94 mol% over HY and LaY zeolites, respectively.

Selim et al. (1992) studied the activities of different Nd-zeolite prepared from the original NaX and NaY zeolites by ion exchange at reaction temperature between 300-420^{o}C by using microcatalytic technique. Cumene cracking was used as a reaction model and found that NdY-zeolite was more active than NdX-zeolite, and the reaction is a first order with an activation energy of 67.2 kJ/mol. Also it was observed that the catalytic activity at the same temperature was found to be higher for Y-zeolites than that corresponding X-zeolite.

Al-Kattaf and de Lase (2001) used a riser simulator to study the kinetics of cumene cracking over two sizes of zeolite crystals (0.4 and 0.9 µm). It was shown that the kinetics follows first order reaction and the main reaction pathway of cumene cracking involves the cleavage of the isopropyl group to produce benzene and propene.

Samar, K. Dh. (2008) prepared HX-zeolite from Iraqi kaolin . The catalytic activity of catalyst prepared from local kaolin was studied by using cumene cracking as a model for catalytic cracking and compared with standard HY zeolite and HX zeolite catalysts. The activity test was carried out in a laboratory continuous flow unit with fixed bed reactor at duration time in the range 10-240 minutes, temperature 823 K , and LHSV 1 h^{-1} .

This work deal with the study of the effect of temperature and LHSV on the cumene cracking reaction rate and selectivity by using prepared and standard catalysts and the study of kinetic of dealkylation process .

MATERIALS AND CATALYSTS PREPARATION

-Cumene

Cumene supplied by BDH with 98% purity was use as a feedstock in this work. It has molecular weight 120.20 g/mol, density of 0.860 g/cm^3 and boiling point of 423K.

-HY-Zeolite

HY-Zeolite (CBV600) was supplied from Zeolyst International (UWE Ohlrogge (VF)) as a powder. This zeolite has 0.2 wt% of Na_2O, SiO_2/Al_2O_3 mole ratio of 5, unit cell of 24.3 Å, pore volume of 0.92 and surface area of 660 m^2/g. A 70 g of HY-zeolite as a powder was mixed with 30 g montmorillonite clay as binder. The chemical composition of montmorillonite is: 51.3%SiO_2, 28.73%Al_2O_3, 1.3%Na_2O, 3.4% CaO, and 3.3 % MgO. The resulting mixture was mixed with water to form a paste. The paste was placed in a cylindrical cavity of 2 cm inside diameter, and 10 cm long. Extrudates shapes were obtained when the paste was compressed manually. Very uniform spaghetti shaped paste was ejected and put in a porcelain crucible at room temperature overnight. Extrudates were dried in a programmable electrical furnace at 120°C for 2 hr. The calcination was done at

550°C for 2 hr. Then the calcined extrudates were cut into 4-8 mm long [Samar, K. Dh.,2008] .

NAX-ZEOLITE

Synthetic crystalline zeolite type 13X was delivered by Linde Company as a pellets (3×5) mm. This catalyst has 14 wt% of Na, SiO_2/Al_2O_3 mole ratio of 2.2, unit cell of 24.9 Å, pore volume of 0.35, and surface area of 340 of m^2/g. Hydrogen-form from standard Na-X zeolite was prepared by ion exchange method of the original Na-X catalyst with ammonium nitrite solution [Samar, K. Dh.,2008].

PREPARED HX-ZEOLITE

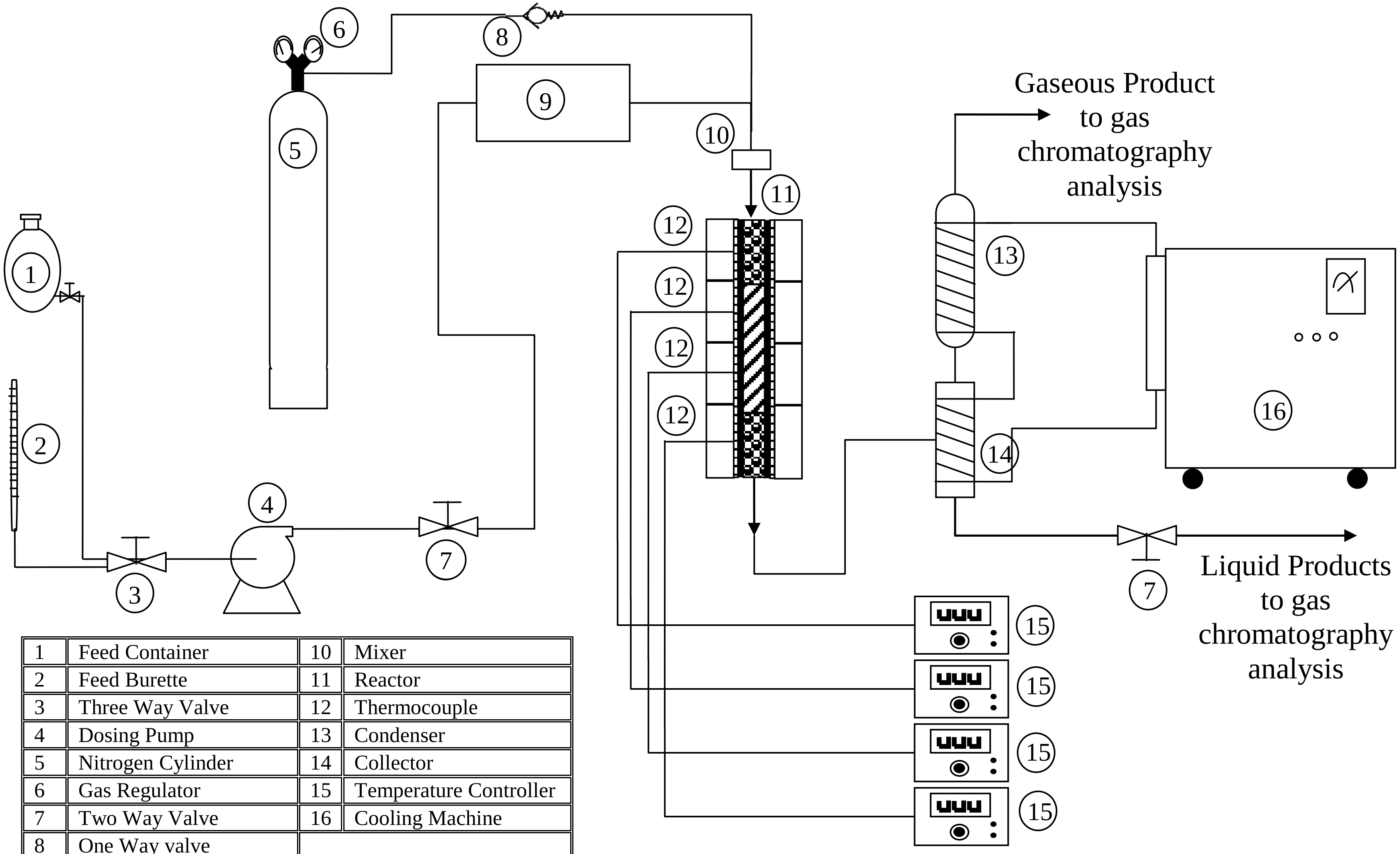
The prepared HX-zeolite from Iraqi kaolin was prepared by steps consisting from; a gel formation step of metakaolin in alkaline medium in presence of additional silica to crystallize the zeolite was achieved at 60 ^oC for 1 hr, and with stirring. In ageing step of the reactants at room temperature for 5 days and crystallization step at 87±2 ^oC for 24 hr. The next steps were decantation, washing, filtration and drying. A 100 g of catalyst powder was prepared by mixing 25 g of the binding material which is kaolin with 75g of catalyst powder and the paste was placed in a cylindrical cavity a extrudates shapes were obtained when the paste was compressed manually then the extrudates were dried and calcined . The hydrogen-form catalyst was prepared by ion exchange method of the original catalyst with ammonium nitrite solution .This catalyst has 0.848 % Na_2O, SiO_2/Al_2O_3 mole ratio of 2.8,pore volume 0.318 cm^3/gm and surface area 290.19 m^2/g after ion exchange [Samar, K. Dh.,2008] .

ACTIVITY TEST

The cracking activity tests were performed in a continuous laboratory unit . Figure 1 shows the process flow diagram of this unit. The unit consists of feed tank, flow meter, feed pump, evaporator, reactor, separator, collector and cooler with appropriate control system for heating. The reactor was a carbon steel tube with an outside diameter of 1.9 cm, 2 mm thickness and 80 cm length. A 30 cm^3 (17 cm height) fresh catalyst was charged to the reactor between two layers of inert materials (glass balls). The catalytic cracking reaction conditions, employed are temperature 673-823K, liquid hourly space velocity of 0.7-2.5 h^{-1} (0.35-1.25 ml/min of cumene)and the pressure kept atmospheric. The charged catalyst was replaced of each temperature. Liquid products were trapped by condenser at -5 ^oC , collected periodically and analyzed by using gas chromatography.The gas chromatography model Packard 438A was used for the analysis .This device equipped with column of 0.25mm diameter, 50 m length and FID detector.

CATALYST ACTIVITY

Cumene cracking was chosen as a model to evaluate the activity of the prepared HX-zeolite and to compare the results with the activity of the standard catalysts HY and HX Zeolite. Cumene conversions over the prepared and standard catalysts were determined after the first 10 minutes of each run.



1	Feed Container	10	Mixer
2	Feed Burette	11	Reactor
3	Three Way Valve	12	Thermocouple
4	Dosing Pump	13	Condenser
5	Nitrogen Cylinder	14	Collector
6	Gas Regulator	15	Temperature Controller
7	Two Way Valve	16	Cooling Machine
8	One Way valve		
9	Evaporator/Preheater		

Figure 1. Flow Diagram of The Laboratory Reaction Unit**.**

RESULTS AND DISCUSSION

Effect of LHSV and Temperature

Figures 2,3 and 4 show the effect of LHSV on conversion at different temperatures using HY- zeolite , HX- zeolite and prepared HX-zeolite .

From these figures the changes of cumene conversion are function of LHSV (which is inverse of space time). At LHSV of 0.7 h^{-1} and temperature 823K, the conversions of cumene are 65.32, 42.88 and 59.42 mol% for HY, HX and prepared HX catalysts, respectively and at LHSV of 2.5 h^{-1} and the same temperature the conversions decrease to 29.24, 12.53 and 22.89 mol%, respectively.

As the LHSV increases cumene conversion decreases which means that decreasing in the residence time offers a less of contact time for cumene with catalysts.

The above mentioned figures show that the cracking rates favor low LHSV. These observations agree well with the previous investigation reported by Plank and Nace (1955) and Selim et al. (1992).

The conversion increases as the temperature increases over the studied catalysts (fig. 2-4). At 673K and LHSV of 0.7 h^{-1}, the conversions are 9.0, 1.4 and 5.9 mol% for HY, HX and prepared HX catalysts respectively, while at 823K using the same LHSV the conversions reach 65.32, 42.90 and 59.42 mole% respectively.

This is attributed to the increase of active sites that can be used for the reaction when the temperature increases. These observations are well agreed with the results reported by Plank and Nace (1955), Ahmed J. A. (1982), Emad F.M. (1985) , Selim et al.(1992) and Al-Khattaf and de Lasa (2001).

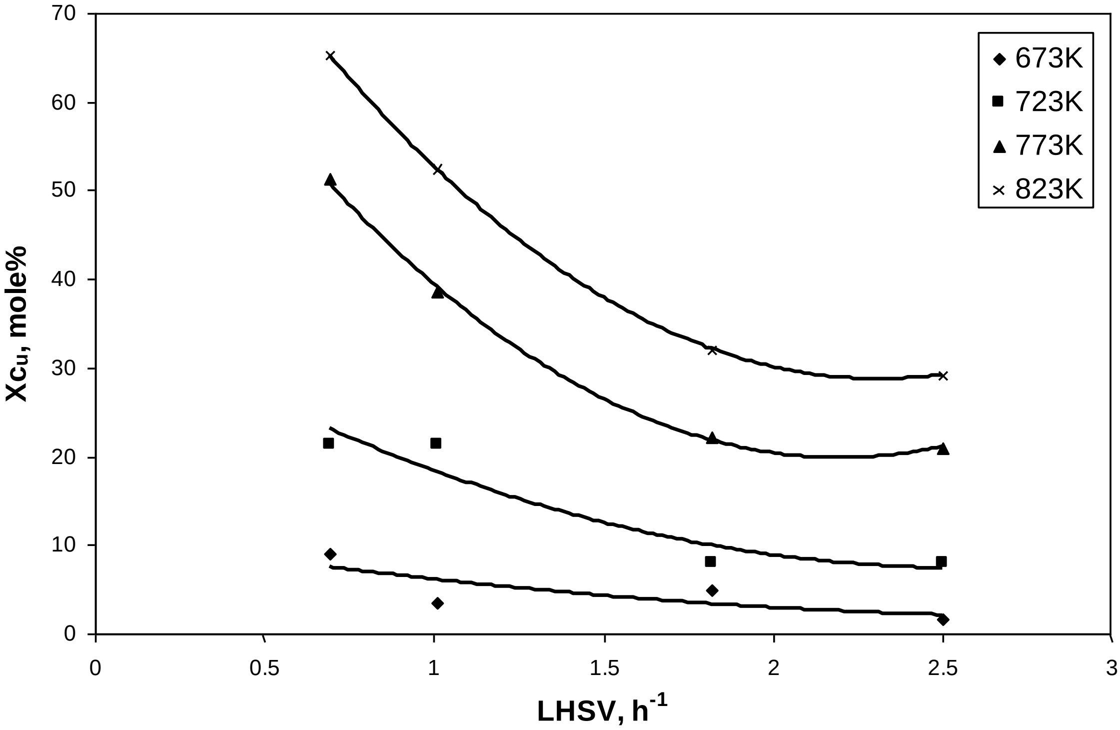


Figure 2 Effect of LHSV on Cumene Conversion at Different Temperatures Using HY Catalyst.

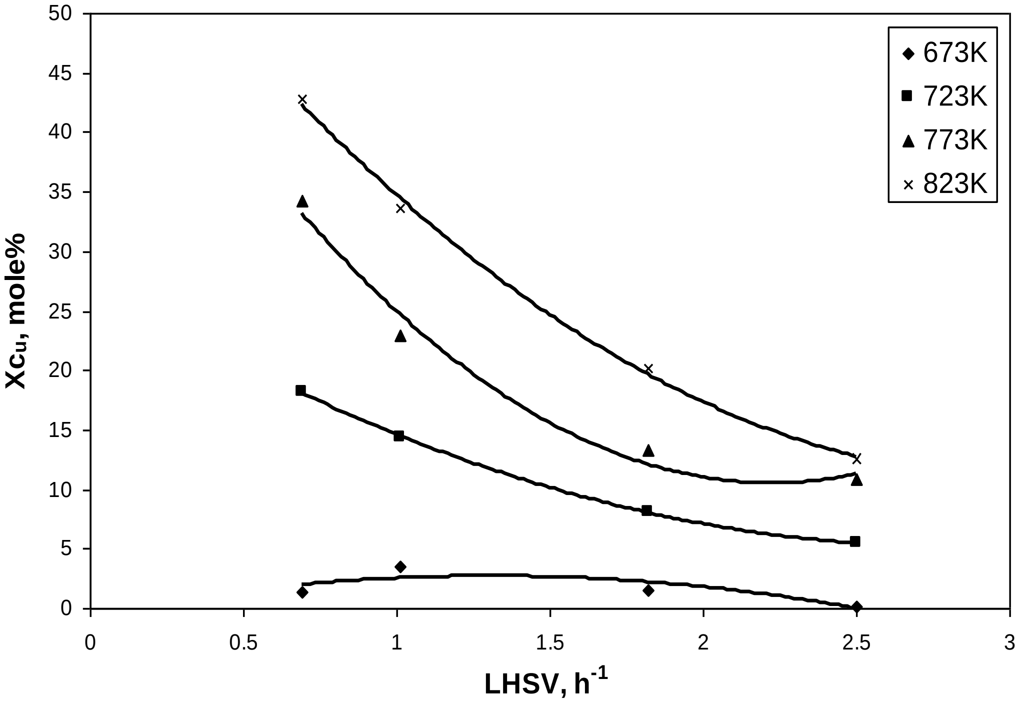


Figure 3 Effect of LHSV on Cumene Conversion at Different Temperatures Using HX Catalyst.

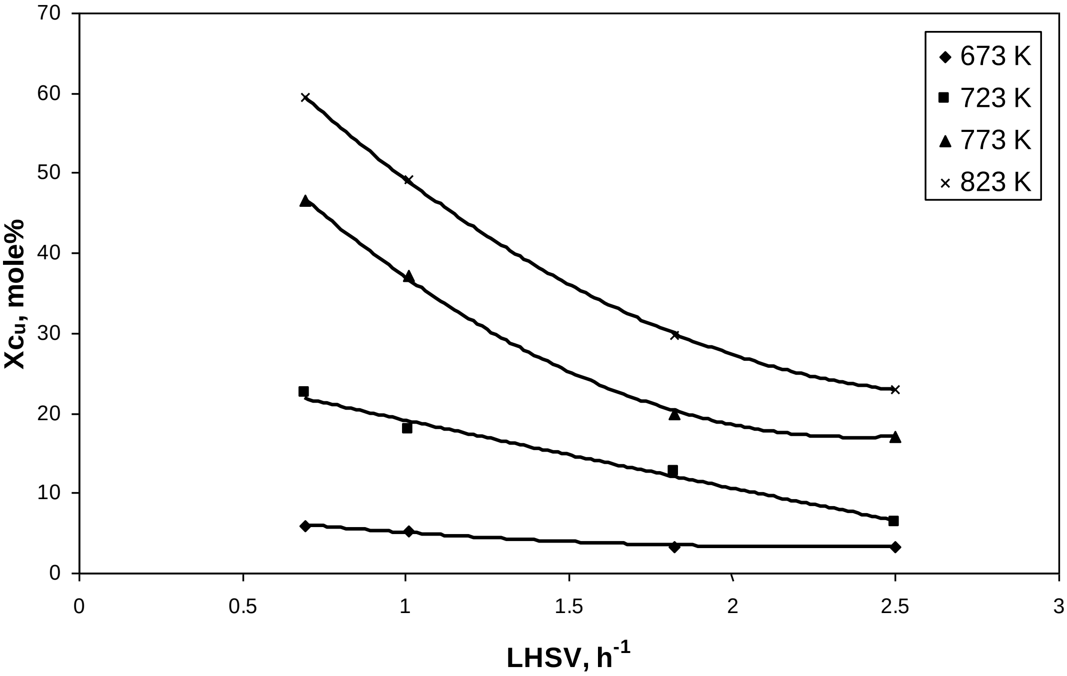


Figure 4 Effect of LHSV on Cumene Conversion at Different Temperatures Using Prepared HX-zeolite.

KINETICS OF CUMENE CRACKING

The obtained results from the laboratory reaction unit of cumene cracking were analyzed by the available kinetic models.

The results correlated with zero, first and second order kinetic equations (eq. 1,2 and 3)assuming ideal plug flow models[Prater and Lago,1956 and Levenspiel,1999].

$$X_{cu} = \frac{k}{Ccu_{in} LHSV} \qquad \ldots(1)$$

$$-\ln\left(1 - X_{cu}\right) = \frac{k}{LHSV} \qquad \ldots(2)$$

$$\frac{1}{Ccu_{in}} \frac{X_{cu}}{1 - X_{cu}} = \frac{k}{LHSV} \qquad \ldots(3)$$

The results show that cumene conversion data have a deviation from the zero and second order kinetic models and well correlated with first order kinetic model as shown in figures 5-7, and that in agreement with Prater and Lago(1956), Lyandres et al.(1969) , Corma and Wojciechowski (1982), Selim et al. (1992), Al-Khattaf and de Lase (2001) and Jennifer et al. (2006) .

Plots of conversion vs. 1/LHSV shown in figures 5-7 give straight lines with slopes equal to rate constants. The results of the rate constant at different temperatures for the three catalysts are given in table 1 .These values decreases in the following order: HY>Prepared HX > HX, which is may be due to the effect of pore volume, Si/Al mole ratio and acidity difference among the studied catalysts.

Table 1, Values of Rate Constant for 1st Order Reaction Rate.

Temperature, K	**HY**	**HX**	**Prepared HX**
		k, h^{-1}	
673	**0.060**	**0.016**	**0.040**
723	**0.186**	**0.141**	**0.217**
773	**0.491**	**0.281**	**0.477**
823	**0.729**	**0.396**	**0.634**

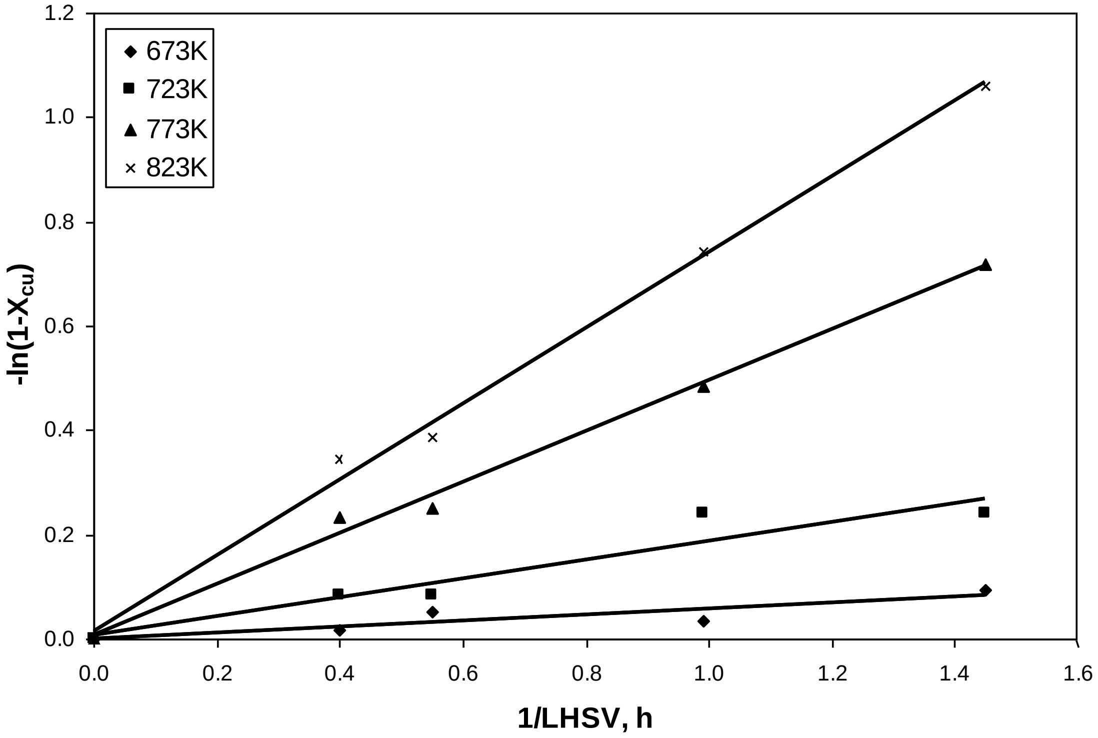


Figure 5 First Order Test of HY Catalyst.

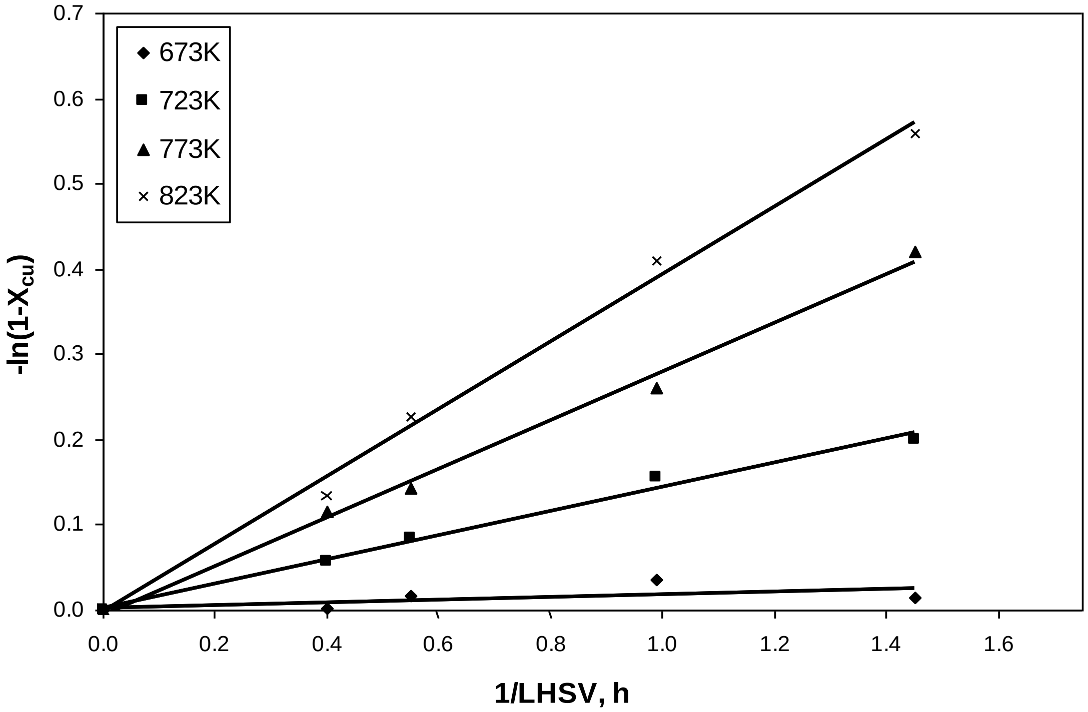


Figure 6 First order Test of HX Catalyst.

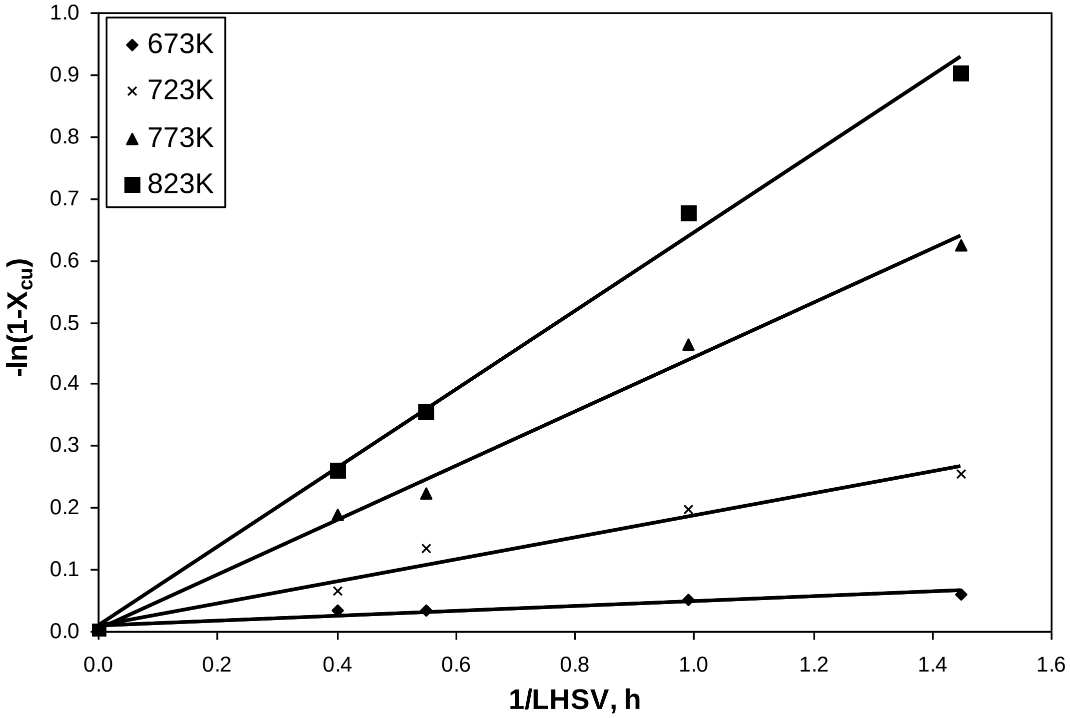


Figure 7 First Order Test of Prepared HX.

THERMODYNAMICS OF CUMENE CRACKING

The apparent activation energy for the cumene cracking reactions was calculated by using the Arrhenius equation(4), which satisfies the relationship between rate constant and the reaction temperature.

$$k = k_o e^{\left(-\frac{E_a}{RT}\right)} \qquad \ldots(4)$$

The plot of ln k vs. (1/T) shown in figures 8-10 used for activation energy calculation using HY, HX and prepared HX.

The values of apparent activation energy for HY, HX and prepared HX catalysts are78.58 , 97.77 and 89.01 kJ/mol, respectively .

The role of catalyst is the reduction of the energy barrier for the reactants to reach the complex state which then decomposes to product. As the apparent activation energy decreases the reaction rate increases and catalyst activity increases.

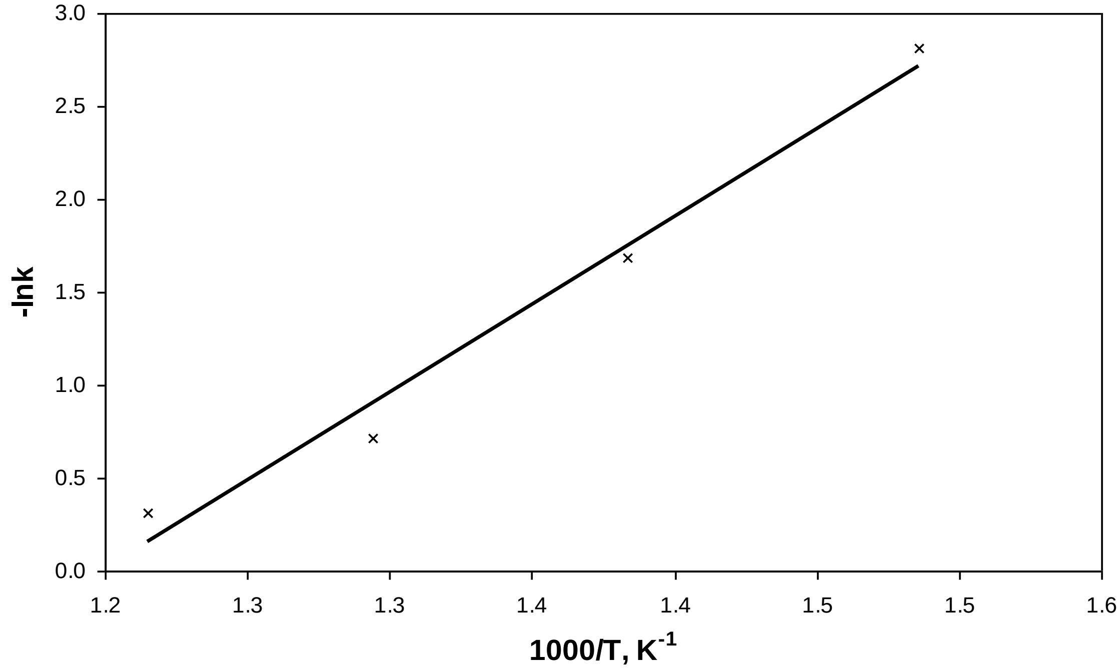


Figure 8 Plot of –lnk vs 1/T for HY Catalyst**.**

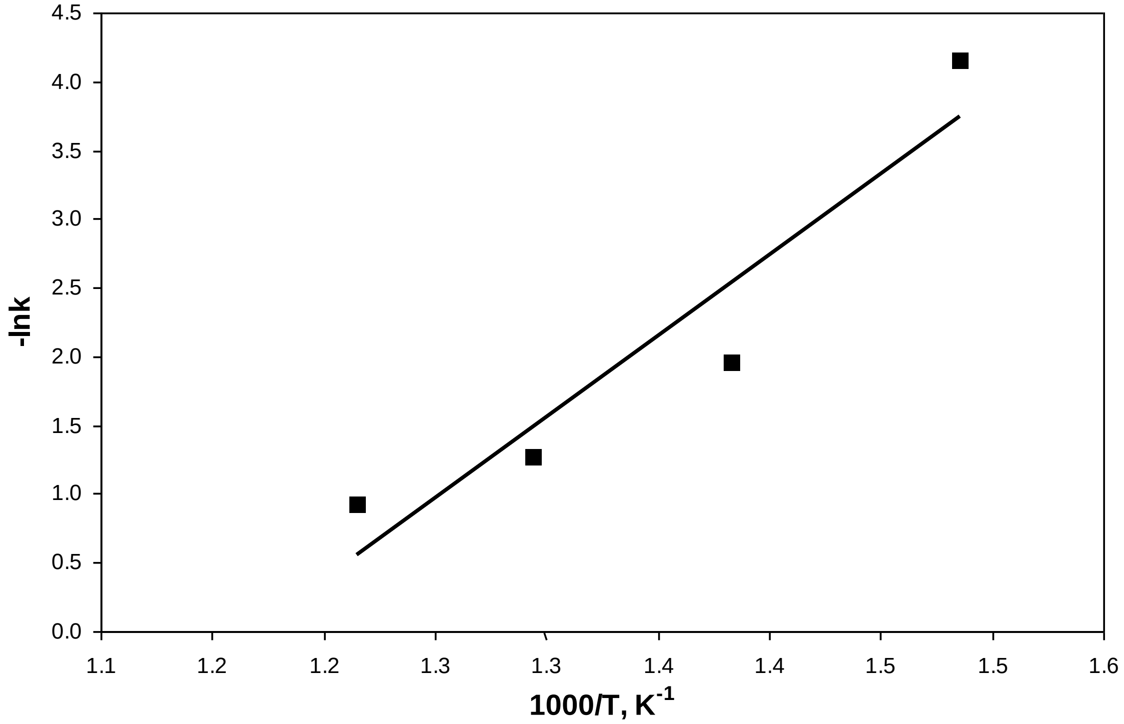


Figure 9 Plot of –lnk vs 1/T for HX Catalyst.

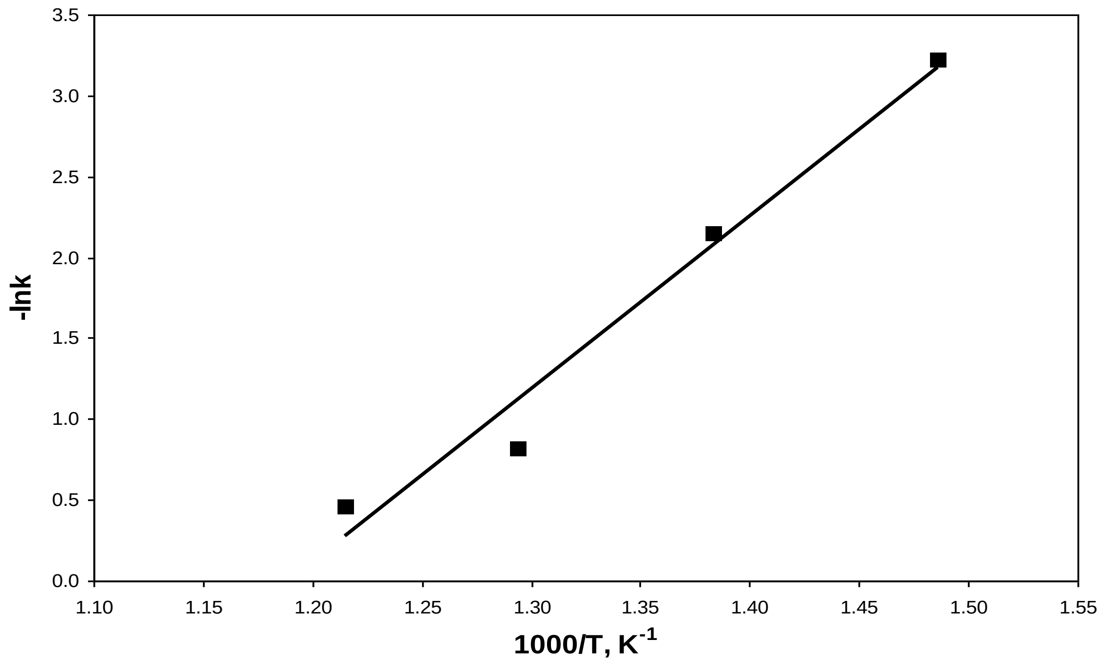


Figure 10 Plot of –lnk vs 1/T for Prepared HX Catalyst**.**

YIELD AND SELECTIVITY

By plotting cumene conversion vs. benzene yield a straight line is obtained with a slope equal to benzene selectivity and as shown in figures 11-13.

It was found that the benzene yield increases with increasing temperature. At 823K and 0.7 hr^{-1} the benzene yields were 58.79, 38.56 and 54.56 mol% for HY zeolite , HX zeolite and prepared HX zeolite, respectively. And at the same LHSV and at 673K the benzene yields were decreased to 6.53, 1.00 and 4.40 mol%, respectively.

Benzene selectivity is nearly constant over the studied temperature range for HY, HX and prepared HX . This is also observed by Peter et al. (1974) ,Donald and Wojciechowski (1977a)and Corma and Wojciechowski (1980).

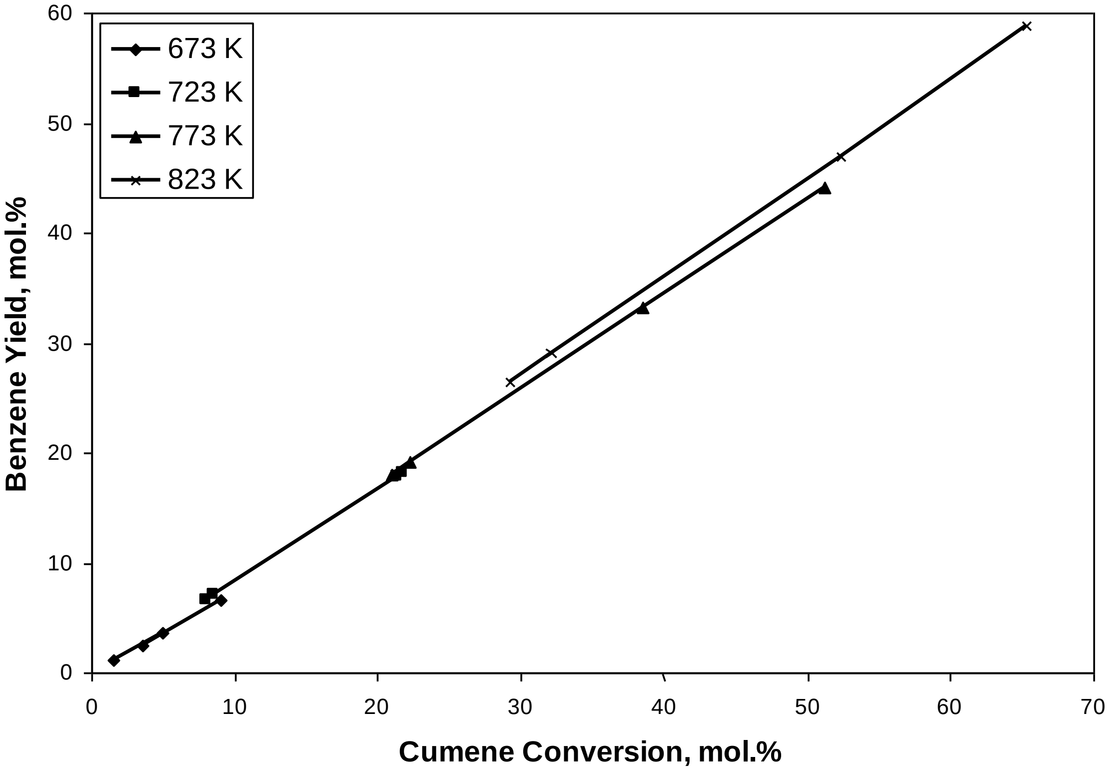


Figure 11 Benzene Yield as a Function of Cumene Conversion for HY Catalyst at Different Temperatures.

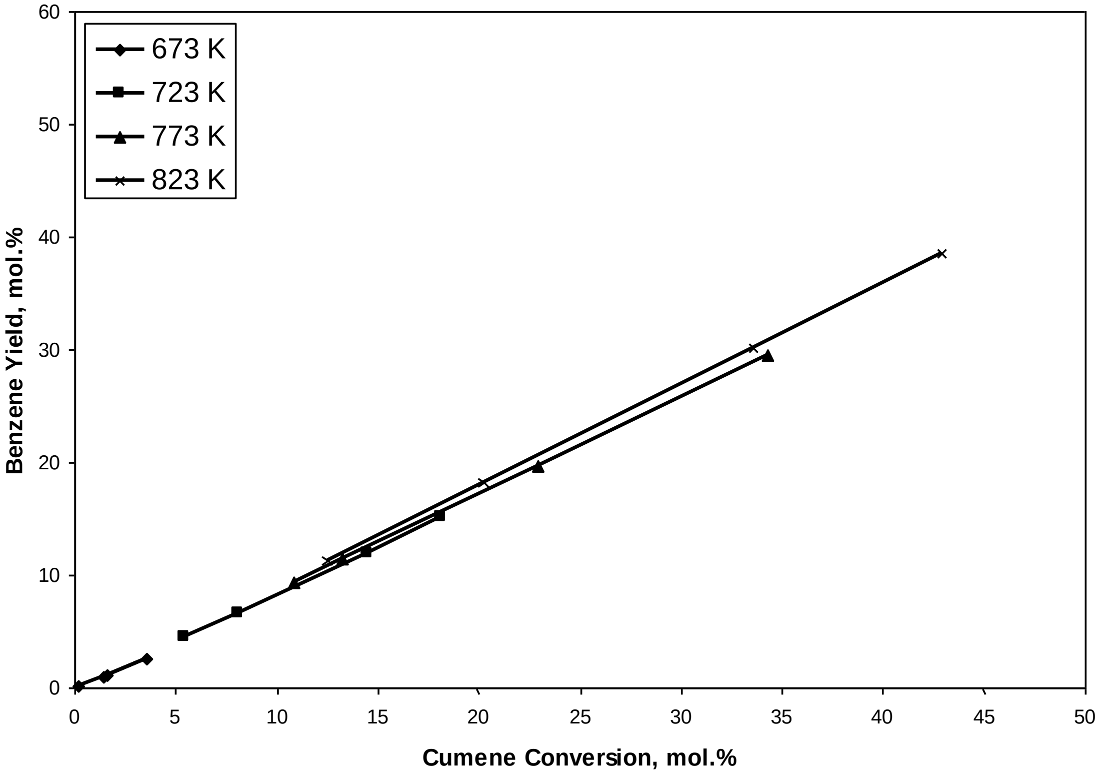


Figure 12 Benzene Yield as a Function of Cumene Conversion for HX Catalyst at Different Temperatures.

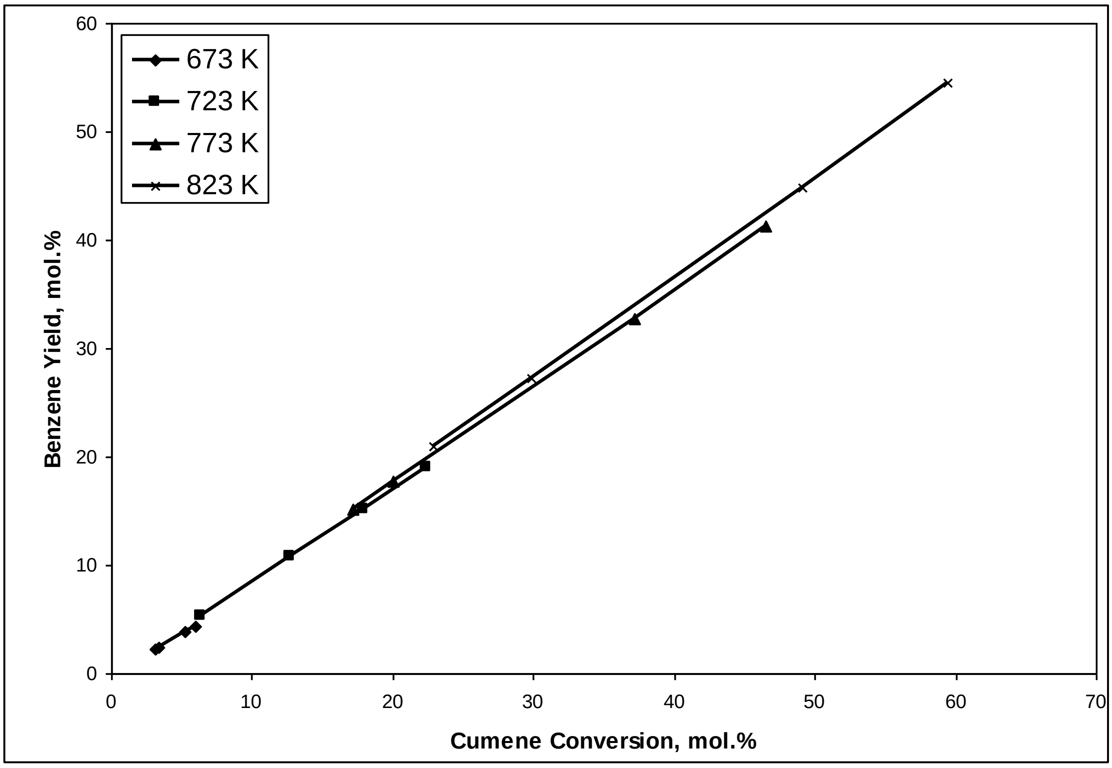


Figure 13 Benzene Yield as a Function of Cumene Conversion for prepared HX at Different Temperatures.

CONCLUSIONS

- Cumene conversion increases with temperature increasing from 673 to 823K and decreases with the LHSV increasing from 0.7 to 2.5 h^{-1}.
- From the kinetic study for cumene cracking over the studied catalysts, it was found that the reaction follow first order reaction model.
- It was observed that the values of activation energy(E_{act}) for catalytic cracking of cumene over the standard and prepared catalysts take the following order:
- E_{act} of HX-zeolite> E_{act} of Prepared HX-zeolite >E_{act} of HY-zeolite.
- 4. All the standard and prepared catalysts gave high benzene selectivity, and no significant change in selectivity was observed. While the yield exhibits a variation between the catalysts activity, and increases with the temperature increasing from 673 to 823K.

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