

FLUID CATALYTIC CRACKING OF PETROLEUM FRACTION (VACUUM GAS OIL) TO PRODUCE GASOLINE

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ABSTRACT

In this work, fluid catalytic cracking of vacuum gas oil to produce gasoline over prepared faujasite type Y zeolite was investigated using experimental laboratory plant scale of fluidized bed reactor.

The catalytic activity of prepared faujasite type NaY, NaNH₄Y and NaHY zeolites was investigated. The cracking process was carried out in the temperature range 440 to 500 °C, weight hourly space velocity (WHSV) range 10 to 25 h⁻¹, and atmospheric pressure. The catalytic activities of the prepared faujasite type NaY, NaNH₄Y and NaHY zeolites were determined in terms of vacuum gas oil (VGO) conversion, and gasoline yield. The conversion at 500°C and WHSV 10 hr⁻¹ by using faujasite type NaY, NaNH₄Y and NaHY zeolite were 50.2%, 64.1% and 69.5wt% respectively. The gasoline yield using the same operating conditions were 24.8%, 30.5% and 36.8wt% respectively. Gas chromatographic analysis of produced gasoline shows that the paraffin, olefin, and aromatic content change considerably with the end point temperature of gasoline fraction.

Keywords : Fluid catalytic cracking ; gasoline production ; vacuum gasoil cracking

INTRODUCTION

The catalytic cracking unit is the most important conversion facility in a modern refinery. This process consists of the scission of the hydrocarbon C–C bonds present in the feedstock (usually vacuum gas oils or residues) in order to obtain gasoline, light alkenes or other low molecular weight hydrocarbons [1]. This process produces

about 45% of the total gasoline pool either directly or indirectly [2].

Catalytic cracking was truly revolutionized in the early 1960s with the advent of zeolite containing fluid cracking catalysts. Catalyst activities were raised by an order of magnitude and units needed to be redesigned to take full advantage of the new catalyst technology [3]. These design changes

included the elimination of reactor dense beds and the use of the feed riser as the sole conversion vessel. Recycle was greatly reduced and replaced with more fresh feed. It was found that coke left on the regenerated catalyst impaired the catalyst activity and selectivity and the average carbons on regenerated catalyst were reduced [4].

The two main components of cracking catalysts are the zeolite Y and the matrix. The main functions of the matrix are to pre-crack large molecules and adsorb Ni and V preferentially in order to protect the zeolite Y of the catalyst particle [5].

Most studies in fluidized catalytic cracking have focused on zeolite Y, as this is still the dominant zeolite used in FCC. Besides the acid properties of this zeolite, the unique pore architecture of Y zeolite is ideal for cracking gas oil components into gasoline molecules [6]. In this respect, Y zeolites dealuminated by steaming (USY) create a secondary porosity formed during the partial destruction of the zeolite framework and forming mesopores which facilitate diffusion of larger molecules into the zeolitic channels. The obtained USY type zeolites show, a much better hydrothermal stability [7]. This zeolite can significantly improve the octane number of gasoline in catalytic cracking. Addition of a few percent ZSM-5 to a conventional FCC catalyst gives an equivalent octane number increase [8]. The light olefins for petrochemicals are a valuable product, often exceeding the revenue obtained for transportation fuels. As a consequence, distinctive processes for making much larger amounts of propylene than a normal FCC unit have been developed. The Deep Catalytic Cracking Process was the first commercial scale process that was designed to maximize propylene. Specially formulated catalysts, more severe process conditions and equipment made to handle the unique product distribution are all components of this technology [9].

A modified Deep Catalytic Cracking (DCC) process has been offered by

SINOPEC, termed as Catalytic Pyrolysis Process (CPP), in which vacuum gas oils and atmospheric residues are converted to produce all petrochemical products, i.e. ethylene, propylene, butenes, and aromatics. This process is really a substitute for a steam cracking furnace in an ethylene plant. It allows the operator to use cheaper feedstocks and vary the ratio of ethylene to propylene over a wider range than is possible with only thermal cracking [10].

The aim of the present work is to design and construct a fluid catalytic cracking unit to study the performance of the prepared catalyst to produce gasoline from vacuum gas oil. The effect of the gasoline end point on the produced gasoline composition was also investigated.

Experimental

Feedstock and catalyst

Vacuum gas oil with boiling range 265°C to 400°C supplied from vacuum distillation unit of Al-Duara refinery was used as a raw material for fluidized catalytic cracking process. The cracking catalyst (faujasite type Y zeolite catalyst) was prepared from locally available kaolin. The properties of catalyst type NaY and vacuum gas oil are reported in table 1 and 2, respectively.

The prepared faujasite type NaY zeolite was modified by exchanging sodium ion with ammonium ion to obtain NaNH_4Y zeolite. Hydrogen-form zeolite catalyst prepared by calcinations $\text{Na NH}_4\text{-Y}$.

Table 1 Prepared catalyst properties .

Specific area (m^2/g)	360
Pore volume (cm^3/g)	0.39
Silica to alumina mole ratio	3.85
Unit cell size (UCS) (Å)	24.73

Table 2 Properties of vacuum gas oil.

Specific gravity at 60/60 °F	0.8739
Pour point, °C	5
Viscosity at 37.8 °C,SSU	51.22
Viscosity at 98.8 °C,SSU	33.54
Aniline point , °C	70
Molecular weight	278
Refractive index at 20 °C	1.4875
K _{uop} -factor	11.70
K _w -factor	11.67
ASTM distillation(D-86), °C	
IBP	265
10%	281
30%	304
50%	316
70%	334
90%	381
FBP	400

FCC experiment

The FCC experiments were carried out at temperature range 440 to 500 °C, WHSV range 10 to 25 h⁻¹, catalyst particle size between 75 to 150 micrometer, and atmospheric pressure using prepared catalyst NaY form, NH₄Y form, and NaHY form. Fig 1 represents the schematic flow diagram of the fluidized catalytic cracking system.

Analytical method

Catalytic cracking products include gases C₁-C₅, and gasoline were analyzed by gas Chromatography method.

Gas Chromatograph Agilent Technologies 6890N located in Al- Duara Refinery. This analysis was used to measure the volume percentage of components in the gas product. The equation of state for ideal gases converts the volume data to mass .

This GC column type was porapak Q, length 1.8m ,diameter 3mm ,and mesh 80-100 was used to measure the gas product from fluidized catalytic cracking unit. The operating condition of gas chromatograph were inlet temperature 80°C, oven temperature 140°C , air flow rate 300 ml/min., hydrogen flow rate 5ml/min., and flow rate in column 30 ml/min.

The gasoline product was analyzed with simulated distillation gas-chromatographic column using other gas chromatograph Agilent Technologies 6890N located in Al- Duara Refinery. The column type was HP 1 capillaries column ,length 100m, diameter 0.25mm, and film thickness 0.5µm was used to measure the gasoline composition produced from fluidized catalytic cracking unit. The operating condition of gas chromatograph were : initial temperature 35°C, final temperature 300°C , hydrogen flow rate 30 ml/min., air flow rate 400 ml/min., and nitrogen make - up 30 ml/min. Analysis of produced gases and gasoline were carried out according to ASTM 1945.

Olefin content in catalytic cracking gasoline was determined using IROX 2000 located in Al- Duara Refinery.

The concentration of the hydrogen sulfide in the cracked gases was determined using chemical analysis according to UOP Method 172- 59 in Al-Duara Refinery.

Hydrogen gas produced from catalytic cracking was monitored using Gas Chromatograph 373 GASUKURD KDGYO located in Al-Duara Refinery according to UOP 539- 73.

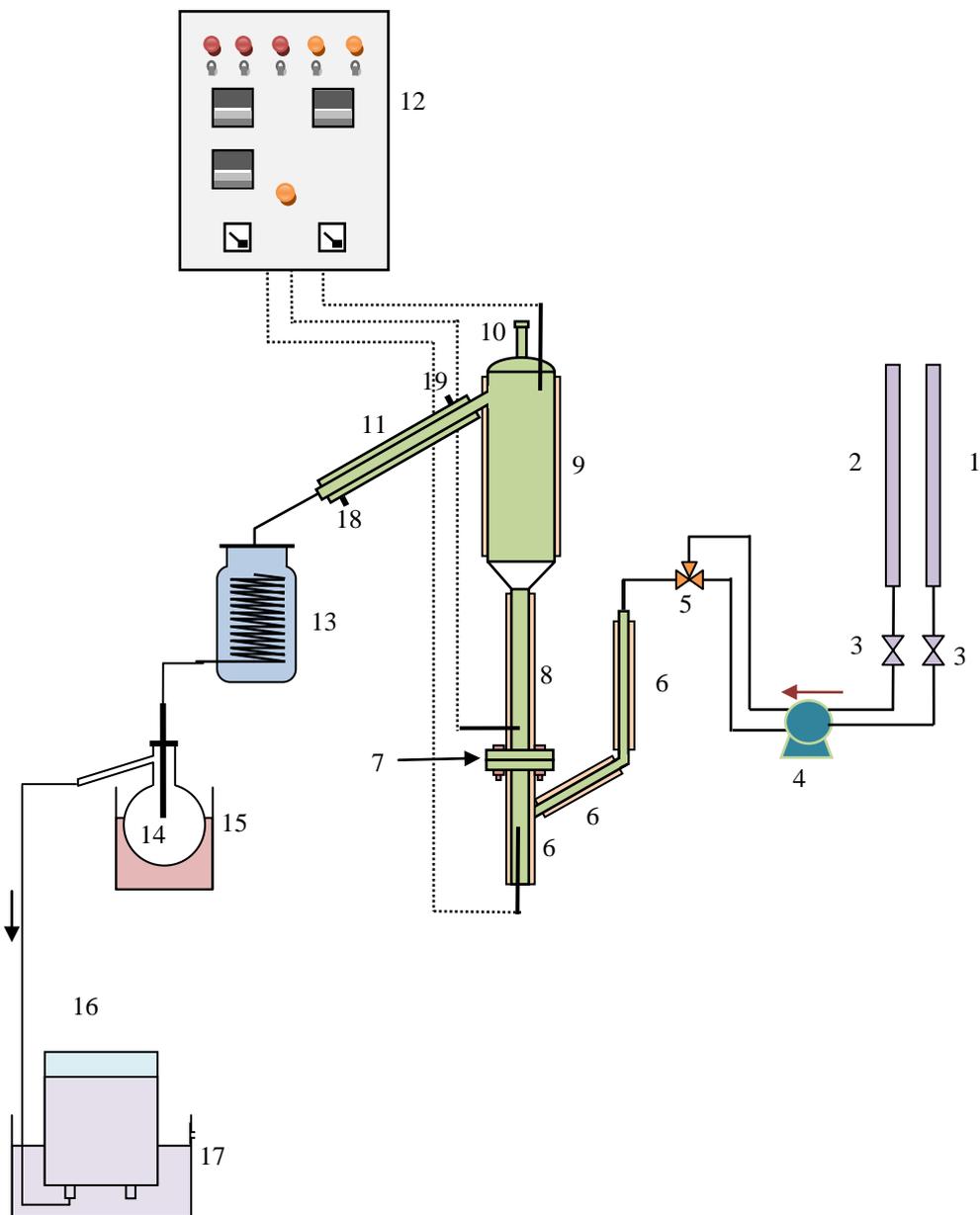


Fig. 1 Schematic flow diagram of the fluidized catalytic cracking system:

(1) Burette VGO feeding; (2) Burette water feeding; (3) Valve; (4) Dosing pump; (5) Three way valve; (6) Preheated section; (7)Distributor (8)Fluidized bed reactor section; (9)Reactor separation section; (10) Catalyst charge inlet; (11) Double pipe heat exchanger; (12) Control panel; (13) Internal tube ice water bath; (14) Separation and collection flask; (15) Ice water bath ; (16) Gas collection ; (17) Water tank; (18) Chilled water in; (19) Chilled water out.

RESULTS AND DISCUSSION

Effect of superficial gas velocity on conversion and gasoline yield

The effect of the ratio of superficial gas velocity to minimum fluidization velocity (u_o/u_{mf}) on the VGO conversion and the gasoline yield was investigated in the range of 2 - 7. Experiments were performed at different weights of prepared NaY catalyst to vary the u_o/u_{mf} ratio at constant weight hour space velocity. The experimental conditions of these tests are WHSV of 10 hr^{-1} , reaction temperature of $480 \text{ }^\circ\text{C}$, and atmospheric pressure.

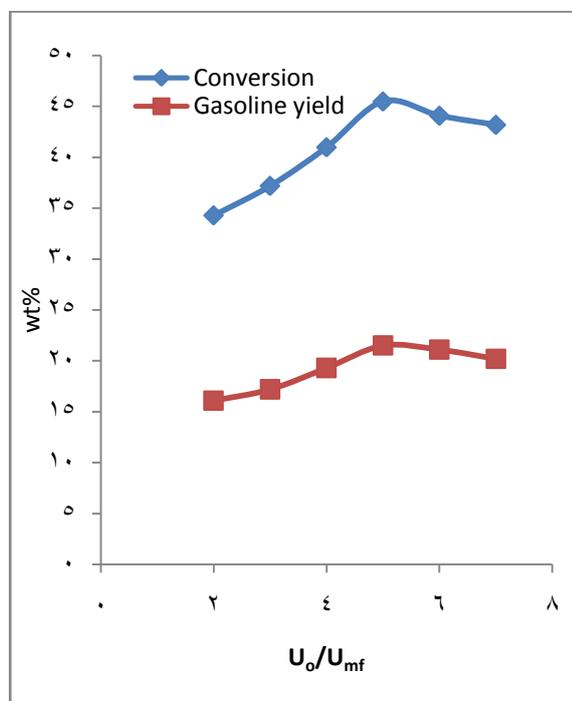


Fig. 2 Effect of u_o/u_{mf} ratio on the VGO conversion and gasoline yield

Fig. 2 shows the effect of the ratio u_o/u_{mf} on the conversion and gasoline yield. It is seen from this figure that the VGO conversion and the gasoline yield are affected by the inlet gas velocity, when the u_o/u_{mf} ratio increases the VGO conversion and gasoline yield also increase up to u_o/u_{mf} equals 5, after that the

conversion and gasoline yield slightly decrease. Therefore the value of u_o/u_{mf} equal five will be selected for the study of the variation of WHSV and temperature experiments.

Effect of WHSV

The effect of WHSV on the VGO conversion and the yield of gasoline, gases, and coke was studied at different reaction temperatures, and u_o/u_{mf} equals 5. Figs. 3, 4, and 5 show the effect of WHSV on the VGO conversion at different reaction temperature for Na form catalyst, NaNH_4 form catalyst, and NaH form catalyst, respectively. As shown from these figures, the VGO conversion increases with decreasing of WHSV at constant temperature. This means that the conversion of VGO is a function of reaction time for all catalysts, the increasing of the contact time of the feed molecules with the catalyst increases the VGO conversion in direct proportion to the amount of the catalyst and inversely proportional to the feed flow rate. The lower WHSV increases the contact time and favors VGO conversion (Figs. 3 to 5) and gasoline yield Figs. 6 – 8.

The lower WHSV not only denotes to contact condition between oil vapor and catalyst, but also indicates the average activity of catalyst. With decreasing WHSV, the contact opportunity between oil vapor and active sites increases, but the ratio of active sites contact with oil vapor to the overall active center decreases, and correspondingly, less active center on the surface per unit catalyst would be covered by coke.

The gases produced from fluidized catalytic cracking unit at $500 \text{ }^\circ\text{C}$, 10 WHSV h^{-1} and Na form catalyst was analyzed by gas chromatography and the components analysis of the gases is presented in Table 3. This table shows that the percent of C_3 and lighter gases were present 8.78 wt%, these include hydrogen, methane, ethane, ethylene, propane

,and propylene .While the percent of iso-butane ,n-butane, and butene was 8.1 wt%.

To check the amount of thermal cracking of vacuum gas oil, experiments were performed without catalyst at temperature of 500°C. The gasoline yield from thermal cracking was only 2.9 wt%.

Table 3 Chemical analysis of gases

Gases	Volume % from gas product	Yield (wt%) from total product
Hydrogen	2.75	0.026
Hydrogen sulfide	0.63	0.099
Methane	14.38	1.388
Ethane	16.42	1.823
Ethylene	12.36	1.362
Propane	14.31	2.754
Propylene	11.21	2.135
Iso Butane	5.43	1.462
N. Butene	13.65	3.589
N. Butane	7.6	2.049
Iso Pentane	0.94	0.307
N. Pentane	0.32	0.113

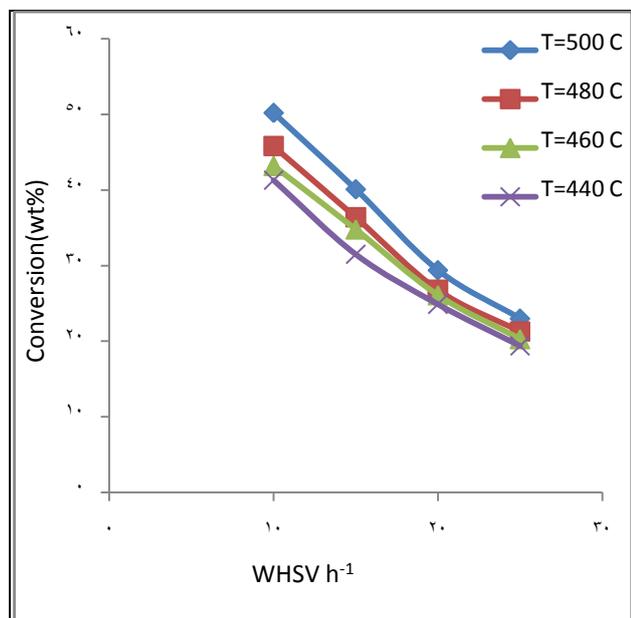


Fig. 3 Effect of WHSV on the VGO conversion at different temperatures for Na-form zeolite

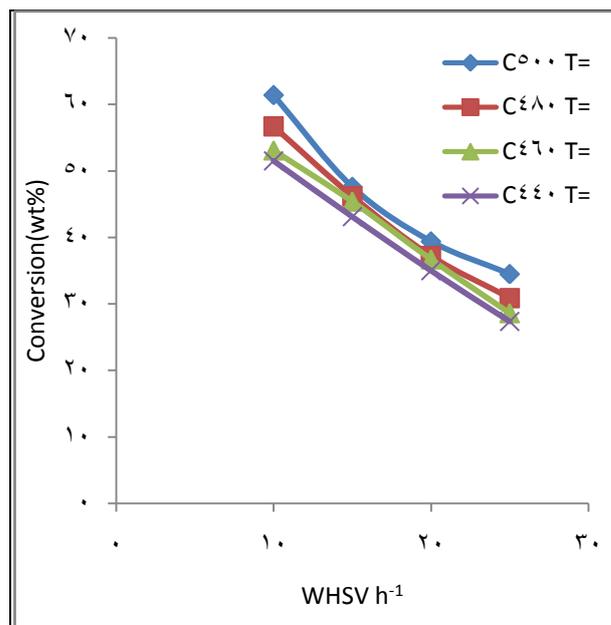


Fig. 4 Effect of WHSV on the VGO conversion at different temperatures for NaNH₄-form

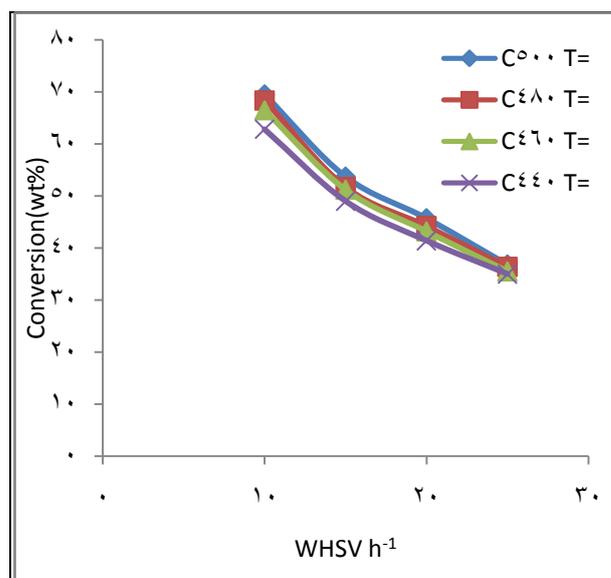


Fig. 5 Effect of WHSV on the VGO conversion at different temperatures for NaH form zeolite

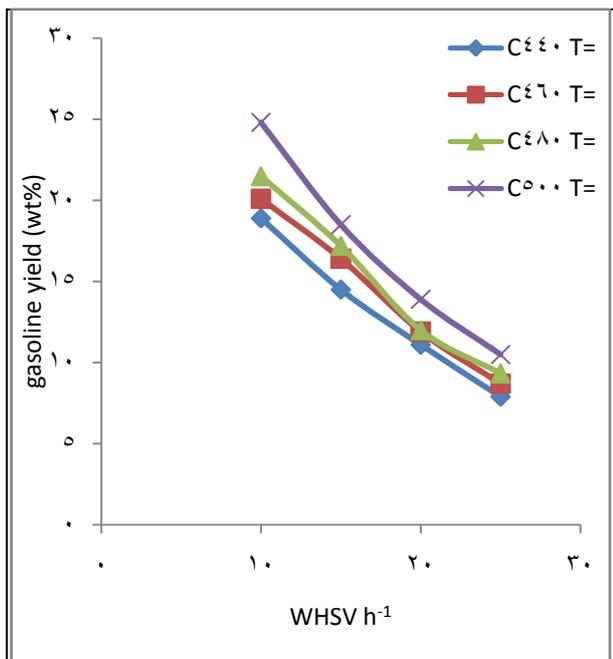


Fig. 6 Effect of WHSV on the yield of gasoline at different temperatures for Na –form zeolite

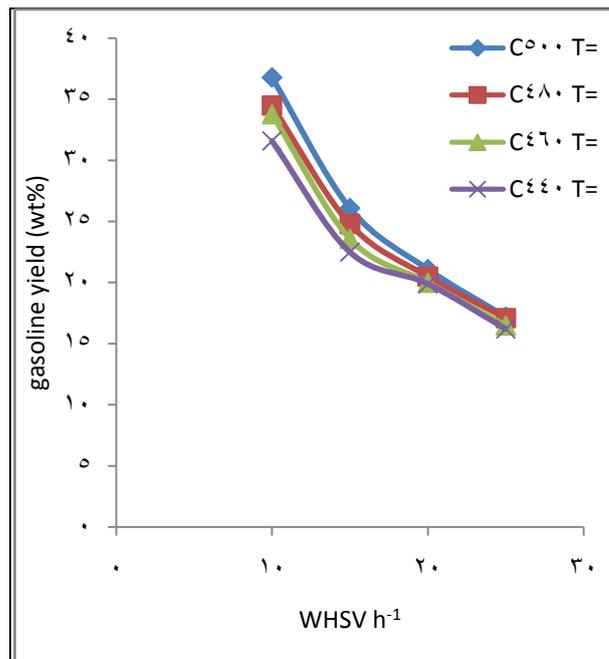


Fig. 8 Effect of WHSV on the yield of gasoline at different temperatures for NaH-form zeolite

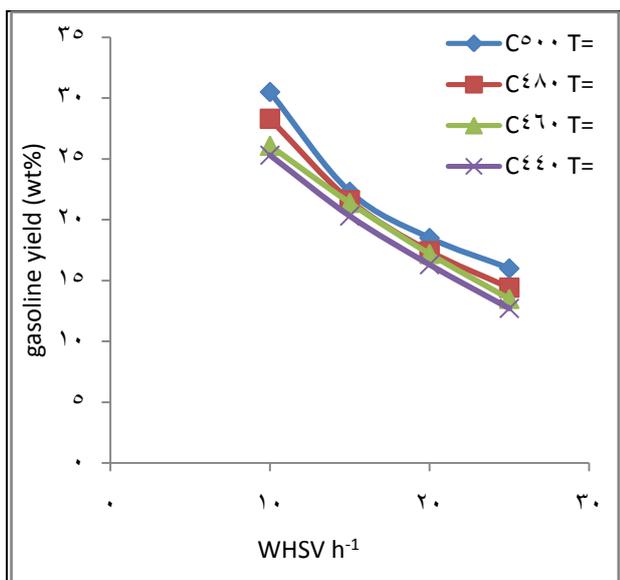


Fig. 7 Effect of WHSV on the yield of gasoline at different temperatures for NaNH₄-form zeolite

Effect of Temperature

The effect of temperature on the VGO conversion and the yield of gasoline, gases, and delta coke was studied at WHSV 10 to 25h⁻¹.

Figs. 9 – 11 show the effect of temperature on the VGO conversion for Na form catalyst, NaNH₄ form catalyst, and NaH form catalyst respectively. As shown in these figures, the VGO conversion increases with increasing the temperature. This may be attributed to the increase of temperature which accelerates intermolecular motions, assists the transformations of the reactants into new compounds and thus enhances the rate of chemical reaction. It is thermal activation which in the present case acts in conjunction with catalytic activation as mentioned by Decroocq [11]. The higher temperature provided advantages in terms of a better feed vaporization which reduced coke formation by condensation reactions of poorly vaporized feed molecules. Both the higher temperature and the resulting lower coke formation enhanced the diffusion of feed

molecules. Also increased temperature enhances the overall conversion of gas-oils by enhancing the rates of protolysis of paraffins and decomposition reactions as α - and β -scission.

Increasing the reaction temperature increases the gasoline yield as shown in Figs. 12 - 14.

Figs. 9 – 14 show the NaH form zeolite catalyst gives a highest VGO conversion and gasoline yield among Na form, NaNH_4 form and NaH form zeolite catalyst. The VGO conversion at 500°C and $\text{WHSV} 10 \text{ hr}^{-1}$ by using faujasite type NaY, NaNH_4Y and NaHY zeolite were 50.2%, 64.1% and 69.5wt% respectively, the gasoline yield were 24.8%, 30.5% and 36.8wt% respectively using the same operating condition.

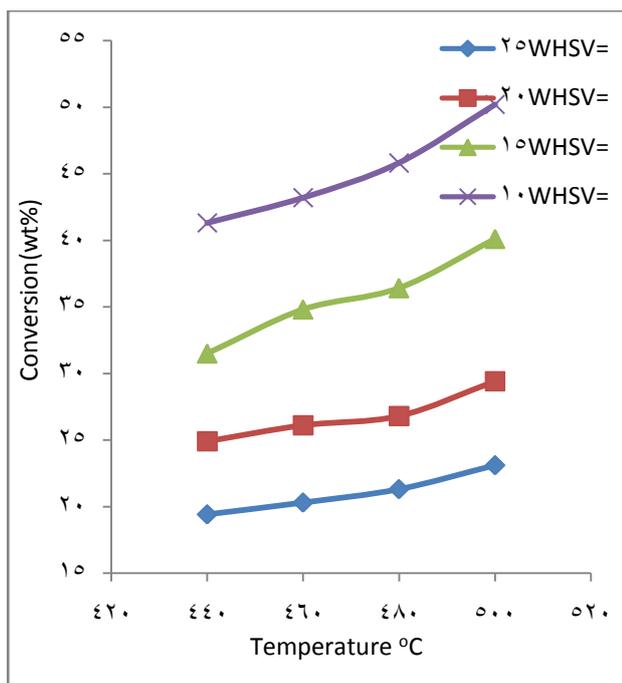


Fig. 9 Effect of temperature on the VGO conversion at different WHSV for Na-form zeolite catalyst

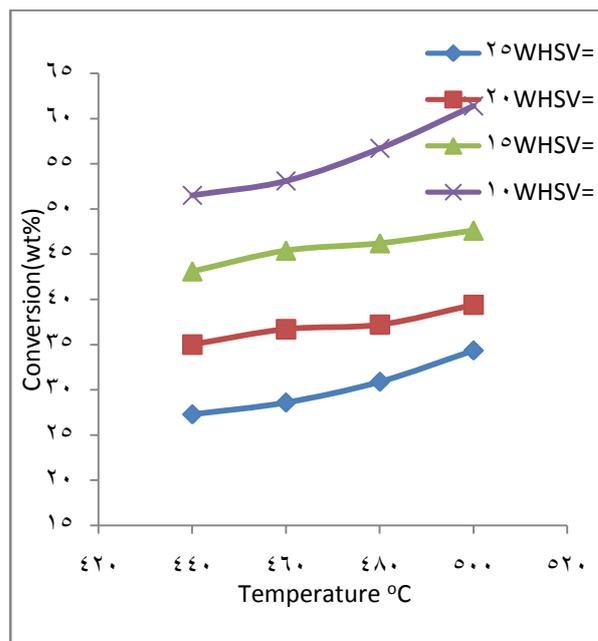


Fig. 10 Effect of temperature on the VGO conversion At different WHSV for NaNH_4 - form zeolite catalyst

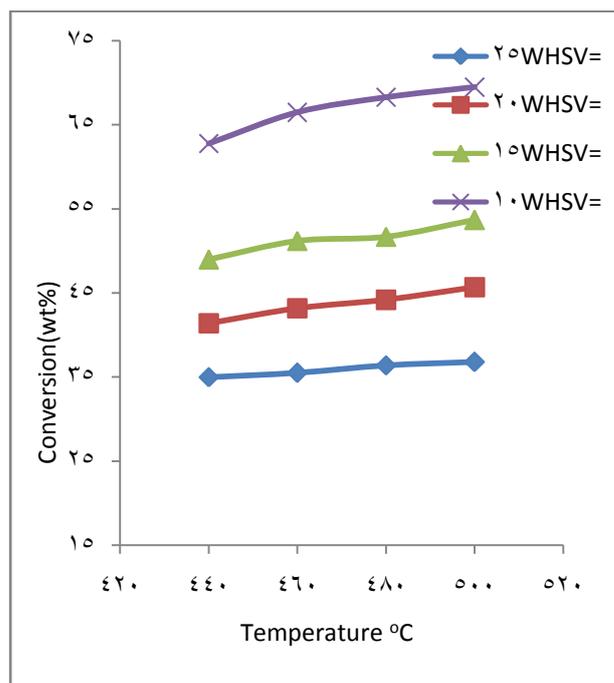


Fig. 11 Effect of temperature on the VGO conversion at different WHSV for NaH- form zeolite catalyst

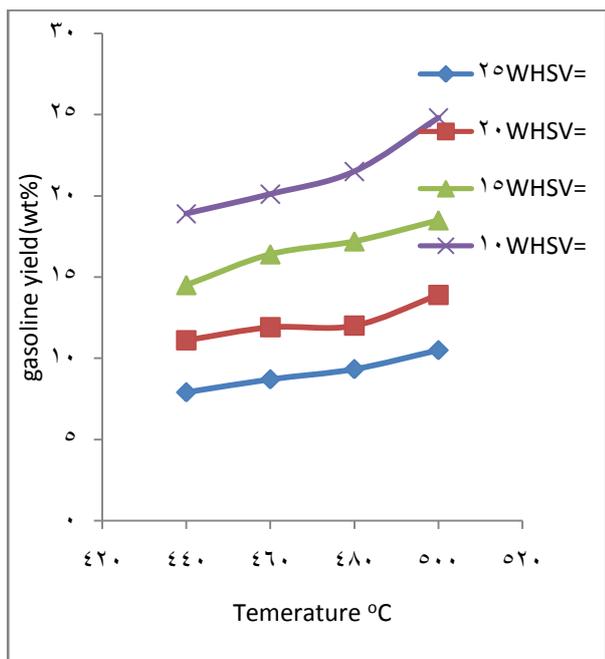


Fig. 12 Effect of temperature on the yield of gasoline at different WHSV for Na-form zeolite catalyst

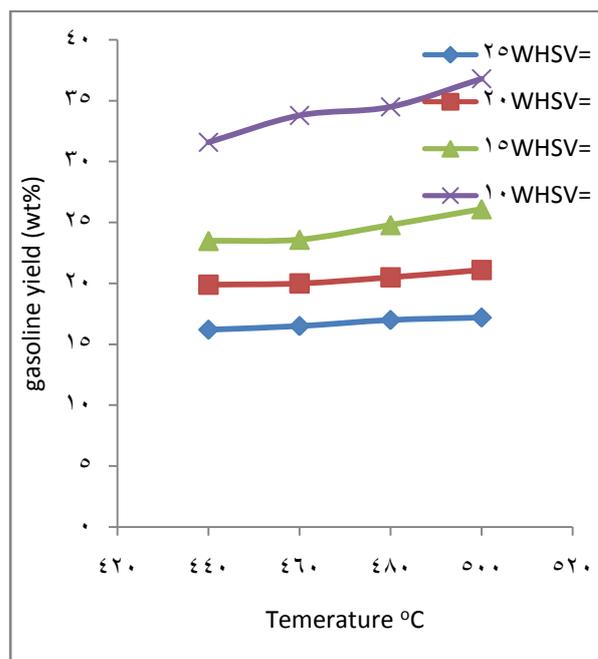


Fig. 14 Effect of temperature on the yield of gasoline at different WHSV for NaH-form zeolite catalyst

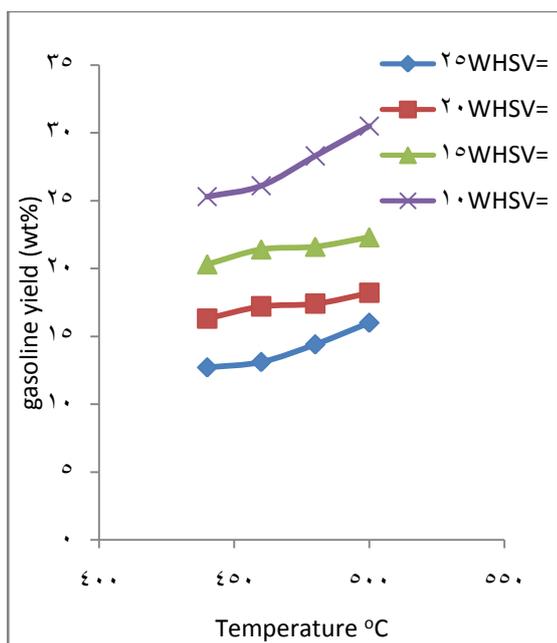


Fig. 13 Effect of temperature on the yield of gasoline at different WHSV for NaNH₄- form zeolite catalyst

Relation between VGO conversion and gasoline yield

Figs. 15, 16 and 17 show the relation between VGO conversion and gasoline yield using Na form, NaNH₄ form, and NaH form zeolite catalysts respectively. As shown in these figures, the gasoline yield increases with increasing the VGO conversion.

In general, it may be noted that when a vacuum gas oil is processed in a fluidized bed over zeolite catalyst the yield of gasoline first increases, then passes through a maximum, and finally decreases, whereas the weight yield of gases keeps increasing with the degree of conversion of the feed. This situation is commonly observed in catalytic cracking because a set of consecutive reaction. The primary cracking of the vacuum gas oil constituting the feed, produces an unsaturated gasoline, which is usually the wanted product.

However this gasoline may also react, either by undergoing a secondary cracking (usually referred to as over cracking) to gases compounds or oligomerization and cyclo-addition of its unsaturated components to dehydrogenated products and coke [11].

Thus, if the degree of the conversion of the feed is high ,the gasoline formed as an intermediate product is partially transformed to light secondary products and to coke deposits, both of which reduce the gasoline yield of the unit .To prevent the occurrence of this degradation process, which seriously impairs the profitability of the operation , the degree of the conversion is usually set at a value corresponding to the maximum yield of gasoline .To obtain an overall maximum gasoline yield, the design of reaction section to be modified, the incompletely converted or unconverted fraction of the feed is separated from light products for subsequent incorporation in various heavy fuel, are replaced by recycle reactors in which the unconverted feed is processed again [12].

From Figs. 15 ,16, and 17 it can be seen that gasoline yield and VGO conversion are always increased by WHSV decrease. It means that the reaction is below the secondary cracking (over cracking).

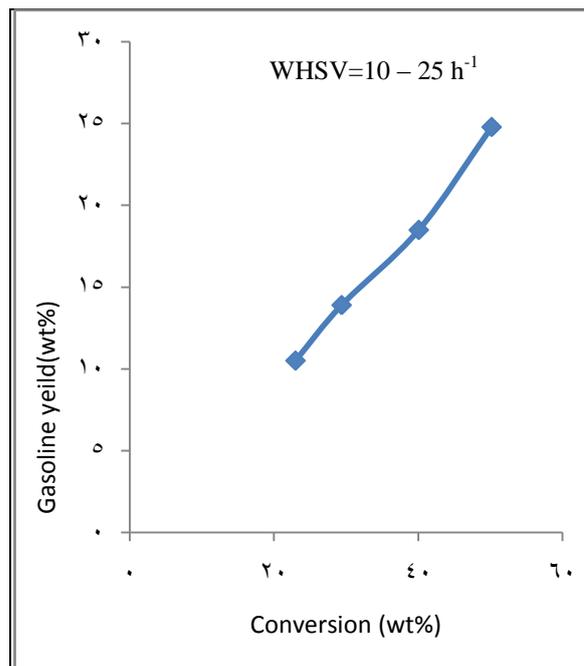


Fig. 15 Relation between conversion (wt%) and gasoline (wt%) at 500°C for Na –form zeolite catalyst.

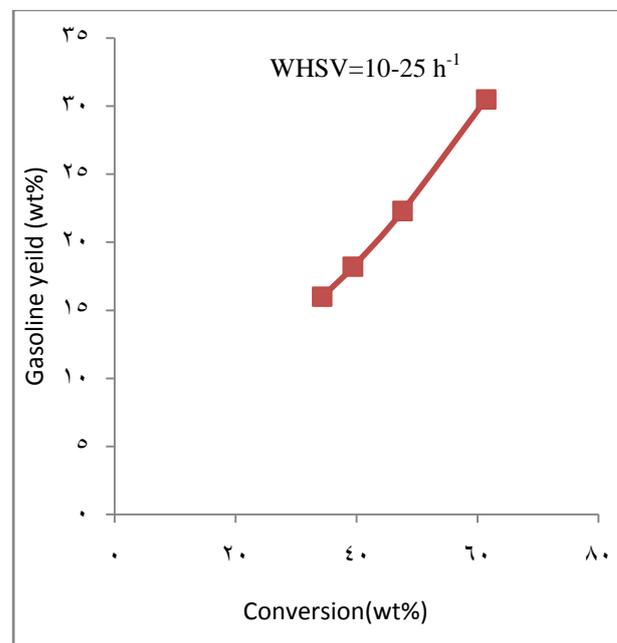


Fig. 16 Relation between conversion (wt%) and gasoline (wt%) at 500°C for NaNH₄ -form zeolite catalyst

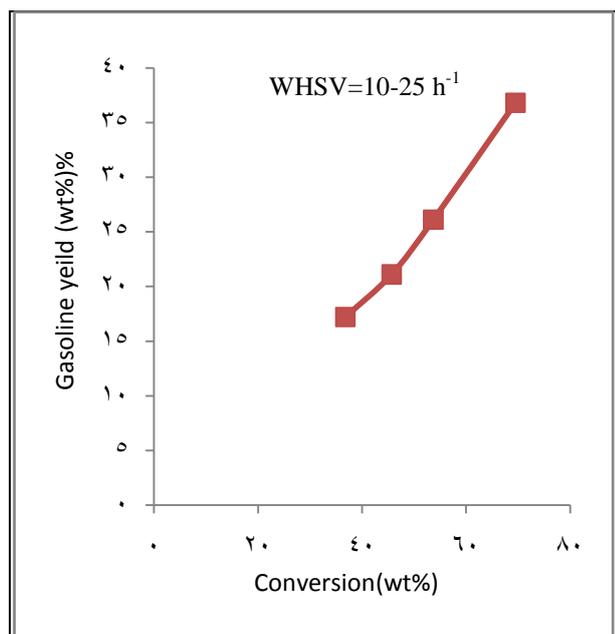


Fig. 17 Relation between conversion (wt%) and gasoline (wt%) at 500°C for NaH form zeolite catalyst

The chemical composition of the gasoline

The chemical composition of the catalytic cracking gasoline fractions was analyzed using simulated distillation gas chromatography depending on the end point temperatures of distillation step. These fractions are IBP - 110°C, IBP - 180°C, IBP - 200°C, and IBP - 220°C.

Table 4 shows a comparison between the chemical composition of cracked gasoline fraction produced in this work with those obtained from California gas oil and Gachsaran gas oil studied by Eastwood et al

[13].

This table shows that the paraffins and olefins decreases with increasing the end point temperature, naphthenes approximately kept constant with the end point change, while aromatics increases with increasing the end point temperature. This table also shows the high concentration of olefins in all fractions, and this may be due to the decreasing

hydrogen transfer reactions within catalytic cracking reactions.

Baker [14] and Whittington et al [15] measured the chemical composition and research octane number of cracked gasoline produced from different feedstock and found that the RON depended mainly on the aromatic content as shown in figure 18.

Fig. 18 was used for the estimation of the RON of gasoline produced at 500 °C and 10 h⁻¹ WHSV. The estimation value of RON was 97 which means that the produced gasoline could be used as high octane basic automobile gasoline.

Table 4 A comparison between the chemical compositions of gasoline fractions

Chemical Composition of cracked gasoline(vol. %)	Paraffins	Naphthenes	Olefins	Aromatics
C ₅ -110°C	36.40	3.00	43.1	17.5
C ₅ -180°C	22.69	3.01	41.60	32.7
C ₅ -200°C	15.70	3.00	40.2	41.1
C ₅ -220°C	12.08	3.03	34.1	50.79
C ₅ -220°C from California gas oil [17]	8.70	10.40	43.70	37.30
C ₅ -220°C from Gachsaran gas oil [17]	21.20	15.70	30.20	33.10

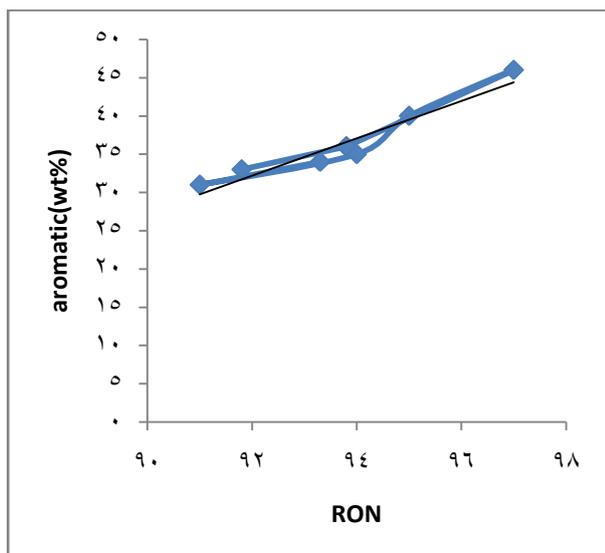


Fig. 18 Relation between RON and aromatic content for cracked gasoline

CONCLUSIONS

The experimental results indicate that higher temperature 500°C was favorable for conversion of vacuum gas oil to gasoline and other product.

- 1- The experimental results indicate that the gasoline yield increased from 17.2 to 36.8 wt% when the WHSV decreases from 25 to 10 h⁻¹ for NaH form zeolite at 500°C.
- 2- The results indicate that the effect of WHSV is higher than the effect of temperature on the VGO conversion and gasoline yield within the process variables.
- 3- The best operation condition was 500°C and WHSV 10 h⁻¹ which gave a VGO conversion 69.5wt% and gasoline yield 36.8wt% for NaH form zeolite.
- 4- The estimated research octane number of produced gasoline at 220 °C was 97.
- 5- The composition of cracked gasoline is a function of its end point temperature .The

aromatic content of gasoline produced increases from 17.5 to 50.79wt% while paraffins decrease from 36.40 to 12.08wt%, olefins decrease from 43.10 to 34.10 wt% with end point temperature increases from 110 to 220 °C. The naphthene remain approximately constant with end point increasing.

- 6- The activity of faujasite type Y zeolite NaH form is a highest among Na form, NaNH₄ form and NaH form.

REFERENCES

- [1]Barajasa,J.R.H., Roma´na,R.V., and Sotelob,D.S., (2006),“ Multiplicity of steady states in FCC units: effect of operating conditions ”, Fuel, 85, 849–859.
- [2]Reza Sadeghbeigi, (2000), “Fluid Catalytic Cracking Handbook Design, Operation and Troubleshooting of FCC Facilities”, Elsevier Inc.
- [3]Magee, J. S., and Mitchell, M. M., (1993), “Fluid Catalytic Cracking Science and Technology”, Elsevier, Amsterdam,.
- [4]Wilson, J.W., (1997), “Fluid Catalytic Cracking Technology and Operation”, Pennwell, Tulsa,.
- [5]Habib, E.T., Zhao, X., Yaluris, G., Cheng, W.C., Boock, L.T., Gilson, J.-P., in: Guisnet, M., Gilson, J.-P.(Eds.), (2002), “Zeolites for Cleaner Technologies”, Imperial College Press, London, , p. 105.
- [6]Corma, A., Forne´s, V., Martinez, A. , Melo, F.V. , Pallota, O. , in: Grobet, P., Mortier, W.J., Vansant, E.F., Schulz-Ekloff, G. (Eds.), (1988), “Innovation in Zeolite Materials Science”, Studies in Surface Science and Catalysis, vol. 37, Elsevier, Amsterdam, , p. 495.
- [7]Sie, S.T., in: Jansen, J.C., Sto¨cker, M., Karge, H.G., Weitkamp, J. (Eds.), (1994), “Advanced Zeolite Science and Applications”, Studies in Surface Science

and Catalysis, vol. 85, Elsevier, Amsterdam, , p. 587.

[8]Dwyer, F.G., Degnan, T.F., in: Magee, J.S., Mitchell M.M., (Eds.), (1993), "Shape Selectivity in Catalytic Cracking in FCC: Science and Technology", Studies in Surface Science and Catalysis, vol. 76, Elsevier, Amsterdam, p. 499.

[9]Fu, A., Hunt, D., Bonilla, J. A., and Batachari, A., (1998), "Deep catalytic cracking plant produces propylene in Thailand", Oil and Gas Journal, January 12, 49–53.

[10]Michael Stocker, (2005), "Gas phase catalysis by zeolites", Microporous and Mesoporous Materials, 82, 257–292

[11]Danial Decroocq , ,(1984) , "Catalytic Cracking of Heavy Petroleum Fractions", Imprimerir Louis-Jean, Paris.

[12]Weitkamp, J. , Traa, Y. , in: Ertl, G. , Kno' zinger, H., Weitkamp, J. (Eds.), (1997) "Handbook of Heterogeneous Catalysis", Wiley-VCH, Weinheim, , p. 2039.

[13]Eastwood B.,S.C., Plank,C.J., and Weisz.P., ,(1971). "Proceedings of the eight word petroleum congress", vol. 4 p.245 .Applied science publishers, London.

[14]Baker,R.W., (1972) " Presentation at the Davison – Crosfield catalyst symposium" Great British, April 10-11.

[15]Whittington, F.L., Murphy,J.R., and Lutz,I.K., ,(1972) ,Oil and Gas journal , Oct.3059.

التكسير الحفازي المائع لمقطع نفطي (زيت الغاز الفراغي) لانتاج الكازولين

الخلاصة:

تم استخدام التكسير الحفازي المائع لزيت الغاز الذي حصل عليه من التقطير الفراغي لمتبقي التقطير الجوي في وحدة الزيوت في مصفى الدورة باستخدام العامل المساعد فايوجاسيت نوع Y زيولايت المحضر . درست الفعالية الحفازية للفيوجيسايت بصيغة الصوديوم NaY ، و صيغة الامونيوم NaNH_4Y و صيغة الهيدروجين NaHY زيولايت باستخدام وحدة تجريبية بحدود درجات الحرارة بين $440 - 500^\circ\text{C}$ وسرعة فراغية بين $10 - 25$ سا⁻¹ . تم تعيين الفعالية الحفازية للفيوجيسايت بصيغة الصوديوم NaY ، و صيغة الامونيوم NaNH_4Y و صيغة الهيدروجين NaHY زيولايت بصيغة تحويل المتفاعلات الى مختلف النواتج ونسبة الكازولين الناتج . لقد كانت نسبة تحويل المتفاعلات الى نواتج عند درجة حرارة 500°C وسرعة فراغية 10 سا⁻¹ 50.2% و 64.1% و 69.5% على التوالي. وان انتاجية الكازولين لنفس الظروف التشغيلية كانت 24.8% و 30.5% و 36.8% على التوالي . بينت تحليل الغاز الكروماتوغرافي Gas Chromatography للكازولين المنتج بان نسبة البرافينات ، الاولييفينات والاروماتيات تتغير تبعا لتغير درجة حرارة نهاية التقطير لمقطع الكازولين .