Increasing of Naphthenes Content in Naphtha by Using Y and β Zeolite Prepared from Iraqi Kaolin

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ABSTRACT

This work dealt with separation of naphthenic hydrocarbons from non-naphthenic hydrocarbons and in particular concerns an improved process for increasing the naphthenes concentration in naphtha, The separation was examined using adsorption by Y and β zeolite in a fixed bed process. The concentration of naphthenes in the influent and effluent streams was determined using PONA classification. The effect of different operating variables such as feed flow rate (2- 4 L/hr); bed length (50 - 80 cm) on the adsorption capacity of Y and β zeolite was studied. Increasing the bed length lead to increase the naphthenes concentration, and increasing the flow rate lead to decrease in the concentration of naphthenes, It was found that the decrease in flow rate to 2 L/hr and increase the bed length to 80 cm lead to increase the naphthenes concentration from 6.2 to 24.8 Wt. %.

Key words: Adsorption, Naphthenes, Naphtha, Y and β zeolite, Iraqi kaolin.

زيادة محتوى النفثينات في مقطع النفثا بإستخدام زيولايت من نوع Yو β محضر من طين الكاؤولين العراقي

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الخلاصة

يتعامل هذا البحث مع فصل المركبات الهيروكربونية النفثينية عن المركبات الهيدروكربونية غير النفثينية، وبصورة خاصة، تحسين عملية زيادة تركيز المركبات النفثينية في مقطع النافثا. تم اجراء العملية بطريقة الامتزاز بواسطة الزيولايت من نوع Y و β في العمود الثابت، تم قياس تراكيز المركبات النفثينية في المجرى الداخل والخارج باستخدام طريقة (PONA). تمت دراسة تأثير متغيرات تشغيلية مختلفة مثل معدل جريان اللقيم (2-4 لتر/ساعة) وارتفاع العمود (50-80 سم) على سعة الامتزاز للزيولايت من نوع Y و β. انَّ زيادة ارتفاع العمود يؤدي الى زيادة تركيز المركبات النفثينية وزيادة معدل الجريان يؤدي الى انخفاض تركيز المركبات النفثينية.

وُجِدَ أن خفض معدل الجريان الى 2 لتر/ساعة وزيادة طول العمود الى 80 سم يؤدي الى زيادة تركيز المركبات النفثينية من 6.2 الى 24.8 % .

1. INTRODUCTION

Environment-related issues nowadays for sure a powerful driving force for the improvement of current refinery processes or the development of new routes for upgrading refinery cuts.

Naphthenes are ring structures where each carbon atom is linked to two hydrogen atoms and to two carbon atoms. This arrangement applies to single–cycle structures. The general formula is (C_nH_{2n}), **Calemma, et al., 2013.**

In the refining of petroleum by modern techniques, complex hydrocarbon mixture of the gasoline boiling range are frequently produce which comprise paraffin and naphthene hydrocarbons. The latter have appreciably higher octane numbers than paraffins of the same boiling range, certain naphthenes, particularly cyclohexane, are also of great value in the production of variety of organic chemicals, **Abbas, 2011**.

Several techniques have been forward to separate naphthenes from paraffins such as azeotropic distillation, membrane extraction and liquid-liquid extraction, **Abdul – Raheem, 2003.** However, these methods for separating naphthenes from complex hydrocarbon mixtures are either economically impractical or are effective only with particular mixtures**, Schreiner et al, 1993, Drzaj, et al., 1985**

Adsorption plays an important role in industry of recovery of valuable substances. It's most important uses in the removal of organic contaminants from polluted sources. The relative advantages of adsorption over other conventional advanced treatment methods as mentioned at **Rashid, 2009,** because it can remove both organic as well as inorganic constituents even at very low concentrations, it is relatively easy and safe to operate, both batch and continuous equipment can be used, no sludge formation, the adsorbent can be regenerated to use again and all adsorption processes involve a decrease in the free energy of the system, **Cassidy, 1951**, **Mohanty et al., 2005**.

Adsorption of material occurs when certain species is selectively retained on the surface, or in the pores or interstices of adsorbent. Forces causing adsorption are the same ones that cause the cohesions in solids and liquids. If these forces are van der Waals then it is physical adsorption or physisorption, if there is an electron transferred or shared then it is chemical adsorption or chemisorption, **Land, 1971.** Adsorbents are natural or synthetic materials of amorphous or microcrystalline structure those need on a long scale include activated carbon, activated alumina, silica gel, and molecular sieve, **Perry and Chilton, 1984**. Zeolites are high capacity selective adsorbents because they separate molecules based upon the size and configuration of the molecule, relative to the size and geometry of the main apertures of the structure, **Mohammed and Abbas, 2014.** Also zeolites adsorb in particular those with permanent which show other interaction effects, with selectivity that it is not found in other solid adsorbents, **Kirk-Othmer, 1983**.

The present study is a trial to increase naphthenes concentration in naphtha fraction by using bed consists of y and β zeolites prepared from Iraqi kaolin.

2. MATERIALS AND EXPERIMENTAL TECHNIQUES

2.1 Materials

2.1.1 Feed

The feed hydrocarbons (naphtha) are obtained from Al – Doura refinery/Iraq. The properties of (naphtha) are given in **Table 1** and the chemical composition of Iraqi kaolin (Doukhla kaolinite) used are given in **Table 2.**

2.1.2 Adsorbent:

2.1.2.1 Synthesis of Y-Zeolite type from Iraqi kaolin

In order to prepare zeolite from kaolin, kaolin was dissolved by the addition of sodium hydroxide (kaolin / NaOH = 1/1.5 by wt.) at 850˚C for three hours. A typical zeolite synthesis procedure from clay was performed as follows:

Ten grams of kaolin powder and 12.67 grams of sodium silicate were dispersed in 150 ml of deionized water under constant stirring for 1 hour. The slurry with a molar composition of

$$6SiO_2:Al_2O_3:9Na_2O:249H_2O$$

and the pH range of (13-14) were aged at 100˚C temperature for 48 hours to form gel slurry. Then the gel slurry was transferred into the polyethylene container to hydrothermally crystallize. Crystallization was carried out at about 100˚C. Subsequently, the resultant precipitate was separated from the mother liquor by filtration. The crystalline mass is then washed with deionized water until a pH range of (9-12) and dried at 100˚C for 16 hours, **Htay and Oo, 2008.**

2.1.2.2 Synthesis of β-Zeolite type from Iraqi kaolin

The kaolin was firstly calcined at 720^{o}C for 4 hours and then was treated with 20 wt% hydrochloric acid HCl solution at 94^{o}C under reflux conditions. The solid with SiO_2/Al_2O_3 molar ratio of 18 was obtained.

In a typical process, 16.0 g of HCl-treated solid was added to a mixture solution composed of 3.2 g sodium hydroxide NaOH and 46.4 g of Tetraethylammonium hydroxide (TEAOH) aqueous solution (15.9 wt%) under stirring. Then the resulted mixture with the following molar chemical composition:

$$4.5Na_2O:Al_2O_3:18SiO_2:6TEAOH:756.8H_2O$$

was transferred into a 200 ml autoclave and placed at 170^{o}C for 30 hours. After crystallization, the solid product was filtered, washed, dried and calcined at100^{o}C and 550^{o}C for 6 hours respectively, **Wan, et al. 2010**.

2.2 Adsorption Equipment and Procedure

Experiments were carried out in cylindrical column (2.54 cm diameter, 100 cm length). Three liters glass container is used for feed and connected to a dosing pump (HB 36) for pumping the feed at desired flow rate to the top of the adsorption column. The column is packed with y and β zeolites.

The bottom of the adsorption column is fitted with a perforated plate to support the zeolite bed with equal volume crystal balls was used in the top to achieve normal distribution and to reduce the channeling. The bottom of adsorption column is fitted with valve. 1L receiver is used to collect the effluent which is analyzed for determining the concentration of naphthens hydrocarbons. The entire apparatus is shown in **Fig.1**.

A certain quantity of y and β zeolite (50% of each) is heated to 110 ^{o}C for three hours to avoid the humidity. The zeolite is put in the adsorption column where it is supported by a perforated plate. The feed is pumped to adsorption bed which is constructed from multiple layers in series depending of the bed length of the experiment using dosing pump at desired product. The feed is passed through the bed and product is collected in 1L glass receiver. The product is analyzed (as described in the following paragraph) at intervals time for obtaining the concentration of naphthene at each time. The feed is continuously flowing through the bed until no change in naphthens concentration between the inlet and outlet streams is observed, which means that the saturation of adsorbent is over.

2.4 Analytical Method

The chemical composition of naphtha is described by PONA classification (i.e. the parrafinic, olefinic, naphthenic, and aromatic composition in the naphtha sample).

PONA analysis is (IP 128) carried out depending on the following measurements:

a- Bromine No. determined by IP 130.

b- Aniline No. determined by IP 2.

c- Sample dearomatization made according to ASTM D 1019 – IP 145.

d- Sample distillation determined by IP 123.

There are four procedures to determine the PONA analysis:

1- Procedure A: used when (50%) boiling point (B.P) below 110^{o}C and Bromine No.below (0.5).

2- Procedure B: used when (50 %) boiling point above 110 ^{o}C and Bromine No. below (0.5).

3- Procedure C: used when (50 %) boiling point below 110 ^{o}C and Bromine No. above (0.5).

4- Procedure D: used when (50 %) boiling point above 110 ^{o}C and Bromine No. above (0.5).

3. RESULTS AND DISCUSSION

3.1 Characterization of Zeolites

3.1.1 X-Ray Diffraction

Powder XRD studies were performed on the calcined samples in order to identify or detect different crystalline phases present in the catalyst. **Figs. 2 - 5** illustrate XRD patterns, HY-Zeolite prepared from kaolin, standard type Y-Zeolite, Hβ-Zeolite prepared from kaolin and standard β-Zeolite. The comparison between the prepared Zeolite and the reference indicates that the preparation method gives good results. This leads to conclusion that our preparation method gives a nearly synthesized indigenous. XRD also shows that there is small reduce in the intensity of the peaks located around differences regions, which can be explained by the nature of the silica materials, which were used in the preparation method, **Treacy and Higgins, 2001.**

3.1.2 Chemical analysis

The chemical analysis composition of the prepared zeolites (Y and β Zeolite) and the commercial zeolites are shown in **Table 3**. The SiO_2/Al_2O_3 molar ratios are 5 and 15.4 which are slightly smaller than that in commercial. However, these ratios are typical of such type of zeolite, the values of SiO_2 /Al_2O_3 molar ratio obtained during the treatment times of dealumination for β zeolite as shown in **Table 4**; it refers to increases of SiO_2 /Al_2O_3 molar ratio of sodium type of Y and β under the same conditions reching 8.92 and 24.85 for Y and β Zeolite respectively, this is due to the higher pore diameter of β zeolite (240 nm) with respect to Y zeolite pore diameter (116 nm) and this improves mass transfer through β zeolite, Y zeolite normally has a SiO_2/Al_2O_3 molar ratio of about 10. However, this can be progressively increased to the point where nearly all the alumina is removed as a work published by Guisnet et al. Nevertheless, the concentration of its strong acidic centers passes through a maximum at a molar ratio of SiO_2/Al_2O_3 of 19-25. The values of SiO_2/Al_2O_3 molar ratio obtained during the treatment times of dealumination for Y zeolite are shown in **Table 4**, on the other hand, β zeolite normally has a SiO_2 /Al_2O_3 molar ratio of about 32.5. This can be progressively increased to the point where nearly all the alumina is removed as a work published by Anthony et al. However, the concentration of its strong acidic centers passes through a maximum at a molar ratio of SiO_2 /Al_2O_3 of 20-30, **Anthony et al., 2001, Hopper and Voorhies, 1972**, **Guisnet et al., 1984 and Karge and Ladebeck, 1980**.

3.1.3 Surface area

The surface areas of the zeolites (H-Y and H-β) were determined by nitrogen physisorption method (BET). The results show that β - Zeolite has higher surface area than Y – Zeolite, i. e. 347 and 334 m^2/g respectively.

3.2 Breakthrough Results

The transient of naphthenes concentration through the adsorption bed is shown in **Fig. 6.** The concentration ratio Co/Ci for naphthenes has its largest value at the beginning of adsorption process and last for a certain time then decreases gradually until the adsorbent becomes saturated with non-naphthenic hydrocarbons feed. At the saturation condition the ratio Co/Ci of naphthenes reaches unity indicating no further separation of naphthenes occurs, on the other hand, the results show that Y-zeolite or β-zeolite beds give lower performance than that of mixed zeolite, this may be due to the relation between adsorbents pore size and non-naphthenic compounds molecular size that occur compilation through adsorption.

3.2.1 Effect of feed flow rate

Adsorption of non-naphthenic compounds is studied at different flow rates. **Fig. 7** shows the transient values of (Co/Ci) at different flow rates.

Results show that increasing the flow rate lead to earlier break points. That is because at high flow rate the quantity of feed mixture to be adsorbed is more and hence break points come early. Also increasing the flow rate will reduce the contact time between the adsorbent and the adsorbate and hence less enriching degree of naphthenes is obtained, maximum concentration ratio for naphthene achieved at earlier time reaching 3.7 at operating conditions of Q=2 L/h, Z= 80 cm, these results are agreement with **Jaber, 2005**.

3.2.2 Effect of bed height

Different runs are made to study the variation of separation affinity with varying the bed height of adsorbent. These are illustrated in **Fig. 8**.

In general, increasing bed height leads to increase the degree of enrichment, (Co/Ci). This is because of two reasons; (1)increasing the bed height means increasing the quantity of adsorbent and hence increase the capacity of adsorption of the bed which leaving more naphthenes components in the raffinate, (2) increasing bed height leads to increase the resident time of feed mixture in the bed which cause high degree of enrichment for naphthenes.

In contrast shows that shorter bed lengths are generally responsible for earlier break point, This is because any increase in bed length will increase adsorption capacity of aromatic or parafinic components, causing slow movement of (MTZ) toward the end of the bed, i.e., earlier saturation of bed with the adsorbate, the naphthenes reaches the break through concentration Co/Ci equal to one at time of about 50 and 70 min for 50 and 80 cm respectively, also these results are compatible with **Jaber, 2005**.

4. CONCLUSIONS

Based on experimental results, the following conclusions are made:

1. Y and β zeolites prepared from Iraqi kaolin gave much closed characteristics to that of commercial types.
2. In general, zeolite is good adsorbent for non-naphthenic compounds. Particularly, bed of mixed types of Y and β zeolite gave higher performance than each separated one.
3. In general, increasing the bed height and decreasing the flow rate lead to increase the separated performance. Increasing bed height to 80 cm (2.5 cm diameter) with flowrate of 2 L/h gave an increase in naphthenic concentration from 6.2 wt % to 24.85 wt %.

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6. NOMENCLATURE AND ABBREVIATIONS:

Nomenclature

Ci	inlet concentration of Naphtha
Co	outlet concentration of Naphtha
Q	volumetric Flow Rate, L/hr
Z	bed length, cm

Abbreviation

ASTM	American Standard Test Method
B.P	Boiling Point

BET	Brunauer, Emmett and Teller
MTZ	Mass Transfer Zone
PH	Acidity
PONA	Parrafinic, Olefinic, Naphthenic, and Aromatic composition in the Naphtha sample
TEAOH	Tetraethylammonium Hydroxide
XRD	X-Ray Diffraction

Table 1. Properties of Naphtha.

Specific gravity at 15.6/15.6 ^{o}c	0.675
R.V.P (kg/cm^2) at 37.8 ^{o}c	0.95
Initial boiling point ^{o}c	76 ^{o}c
End boiling point ^{o}c	186 ^{o}c
Aromater % wt.	11.9
Olefin % wt.	0.1
Naphthene % wt.	6.2
Paraffins % wt.	81.9
Bromine No.	1.2
API	61

Table 2. Chemical omposition of Iraqi Kaolin (Doukhla Kaolinite) used.

Constituent	Weight (%)
SiO_2	50.10
Al_2O_3	32.80
Na_2O	0.27
TiO_2	1.27
Fe_2O_3	1.24
MgO	0.24
CaO	0.28
K_2O	0.66
L.O.I , wt %	12.3

Table 3. Chemical analysis of the two types of prepared zeolites and its references.

Chemical composition (mol. %)	HY-Zeolite		Hβ-Zeolite	
	Kaolin	Reference	Kaolin	Reference
SiO_2	5.65	6	17.25	18
Al_2O_3	1.13	1	1.12	1
Na_2O	9.05	9	4.17	4.5
SiO_2/Al_2O_3 (*molar ratio*)	5	6	15.4	18

Table 4. Comparative ratios of SiO_2/Al_2O_3 for Sodium form of Y zeolite and β zeolite dealuminated by acid leaching method.

Zeolite type	No. of treatment times with Nitric acid HNO_3			
	Prepared	One	Two	Three
	SiO_2 to Al_2O_3 molar ratio			
Y zeolite	5	6.31	7.58	8.92
β zeolite	18.4	20.61	22.02	24.85

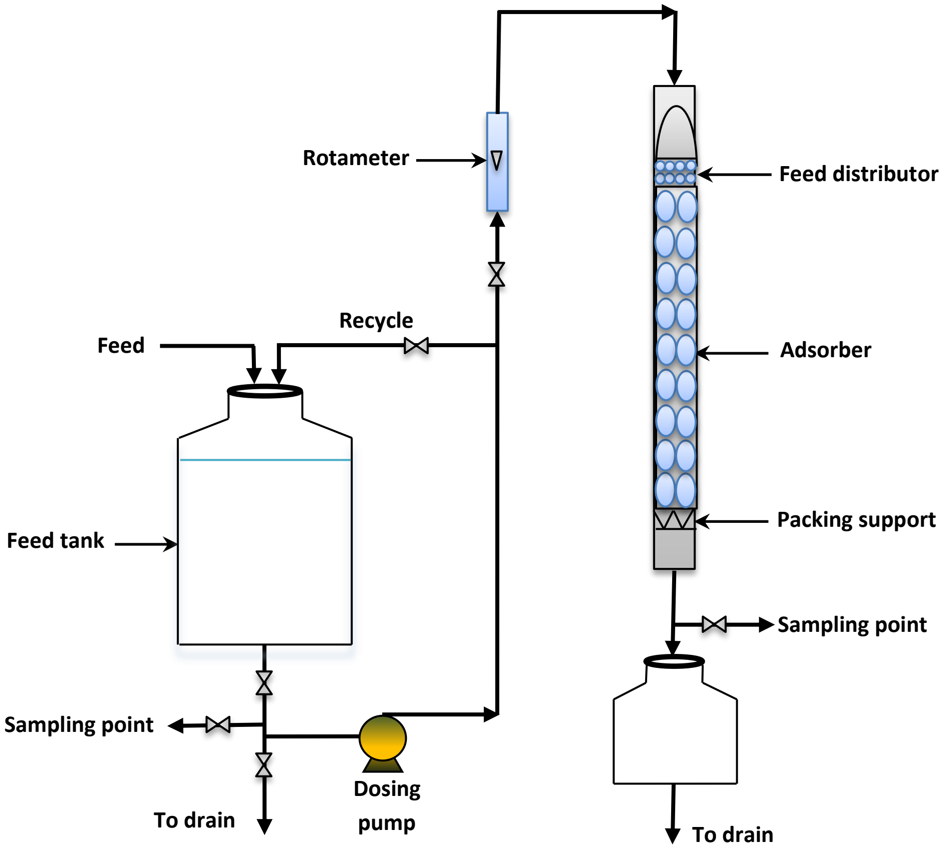

Figure 1. Schematic diagram of the experimental rig.

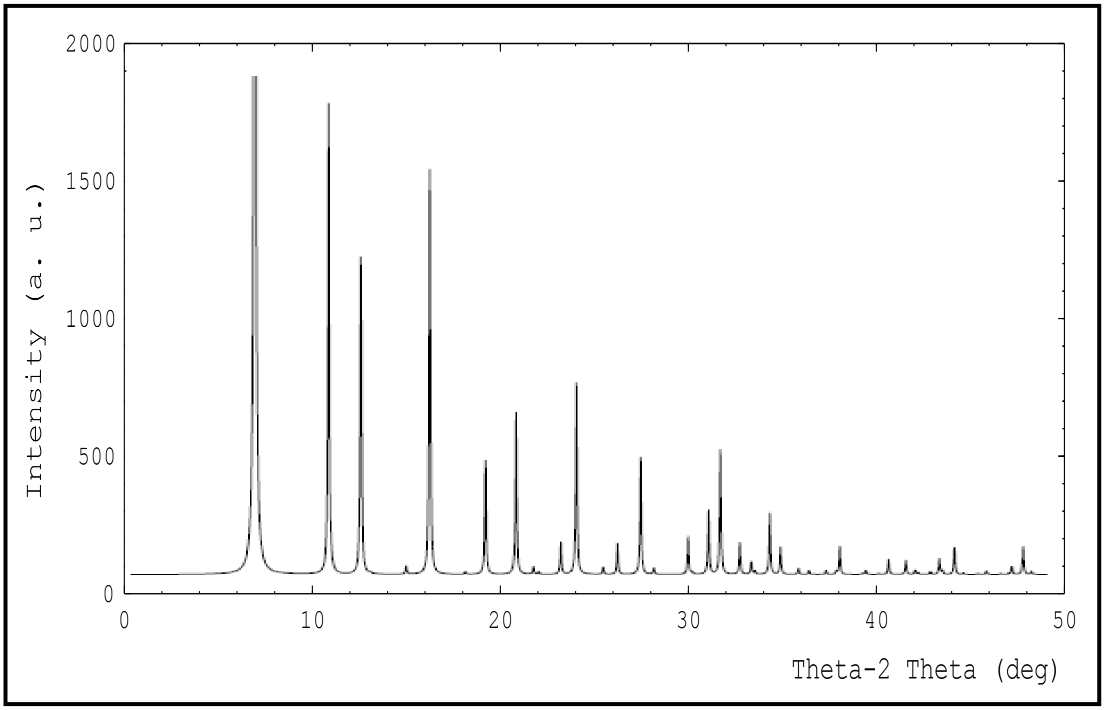

Figure 2. XRD of HY- Zeolite prepared from Kaolin.

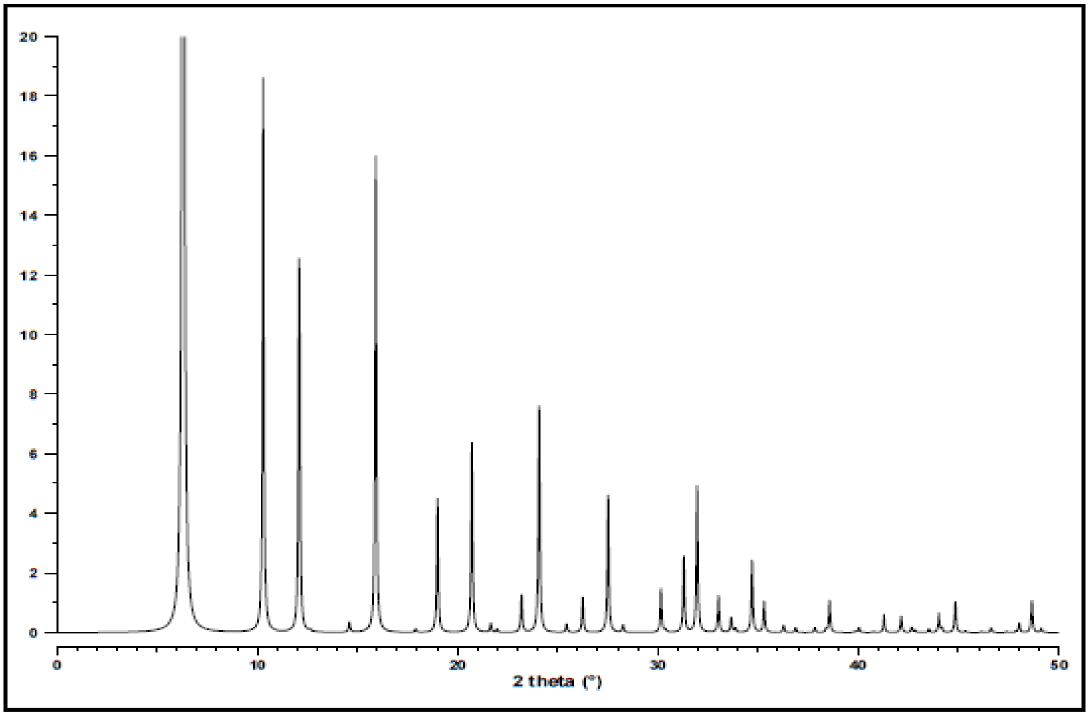

Figure 3. XRD of standard type Y- Zeolite, **Treacy and Higgins, 2001**.

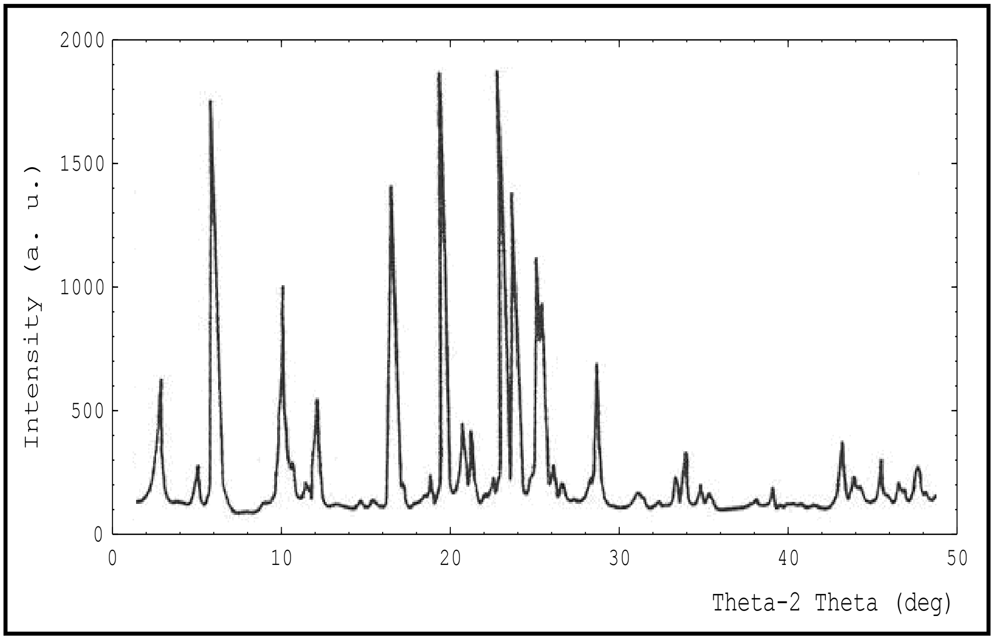

Figure 4. XRD of type Hβ- Zeolite prepared from Kaolin.

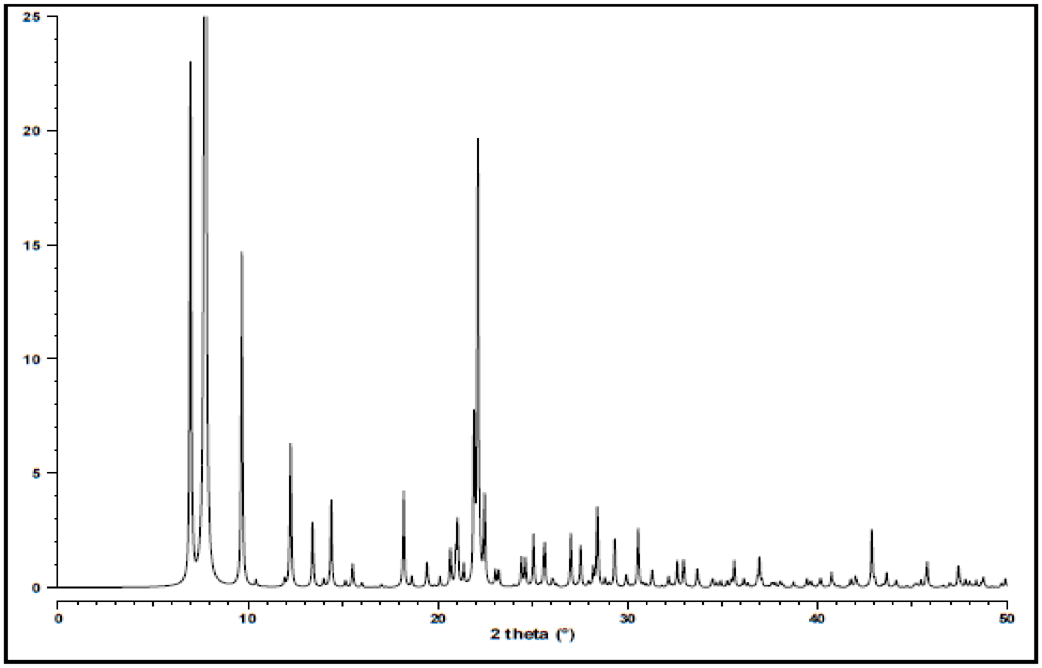

Figure 5. XRD of standard β – Zeolite, **Treacy and Higgins, 2001.**

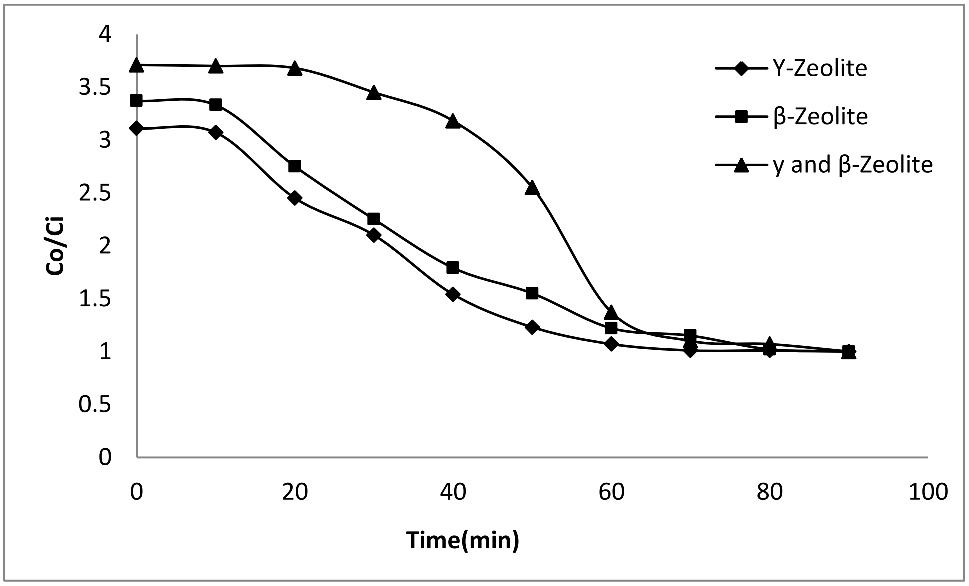

Figure 6. Concentration profile for Naphthenes.

Operating conditions (Ci = 6.2 wt%, Q =2 L/hr and Z = 80 cm).

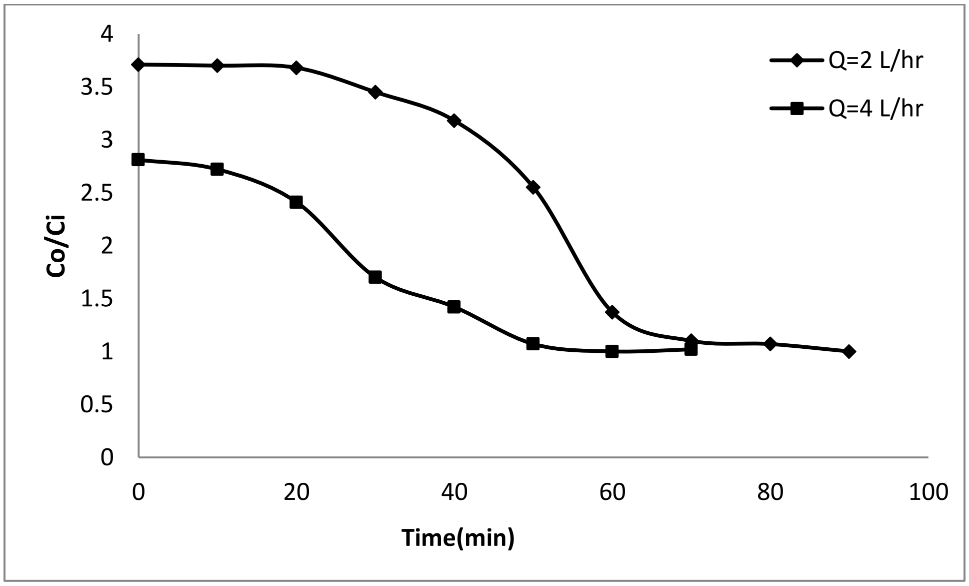

Figure 7. Effect of feed flow rate on the concentration profile of Naphthenes

Operating conditions (Ci = 6.2 wt % and Z = 80 cm).

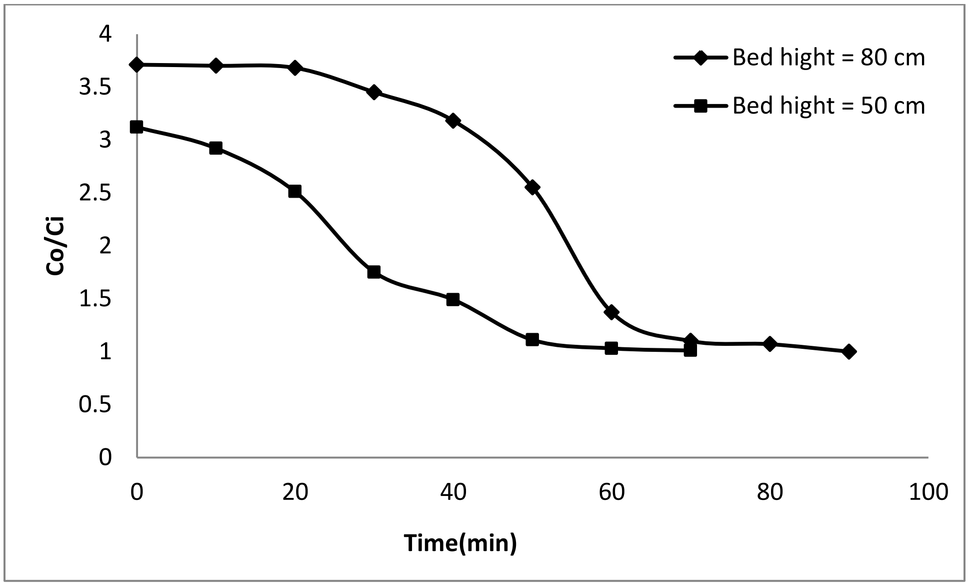

Figure 8. Concentration profile for Naphthenes at

Operating conditions (Ci = 6.2 wt % and Q =2 L/hr).