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Catalytic Cracking of Furfural Extract-40 over Ni/HY-Zeolite Catalyst.

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ABSTRACT

Modifying of HY/Zeolite is by loading nickel for applying catalyst in thermal catalytic cracking of furfural extract-40 from the lubricating base oil unit. The study involved the characterizing of HY-zeolite and promoted catalyst with nickel by X-ray diffraction analysis, Scanning electron microscopy (SEM), BET (Brunauer, Emmett, and Teller), and infrared ray analyses FTIR. The catalytic thermal cracking tubular reactor with a fixed bed with two type catalysts; HY/zeolite and Ni HY/zeolite, individually at a temperature of 580°C with LHSV 5h^{-1} was investigated. The results indicated that increase the conversion of catalytic cracking of furfural extract-40 also increases the yield of useful petroleum products and decreases the coke depsite on the Ni HY-Zeolite catalyst.

Keywords: Catalytic cracking, oil waste- furfural extract, zeolite, packed bed tubular reactor.

التكسير بالعامل المساعد باستخدام الزيولايت المحفز بالنيكل

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الخلاصة

تم دراسة تاثير تحميل النيكل على الزيولايت و مقارنة العمل مع زيولايت غير المعدل من خلال تطبيق التكسير المحفز لمخلفات (مستخلص الفورفورال) الناتج من وحدة تنقية الزيوت الخفيفة بعد استخدام الفورفرال كمذيب حيث تضمنت الدراسة تقييم الزيولايت من نوع *HY* قبل و بعد التعديل واضافة النيكل. تم دراسة توصيف المحفز المحضر من خلال اجراء فحص حيود الاشعة السينية(XRD)والمسح الكهروضوئي الالكتروني *(SEM)* و المساحة السطحية والجم المسامي بطريقة ال(*BET*)و فحص الاشعة القريبة من الحمراء(*FTIR*). تم تنفيذ تكسير بالعامل المساعد لمستخلص الفورفور باستخدام HY-Zeolite و Ni / HY-zeolite بدرجات حرارة 580 درجة مئوية و سرعة 5 ساعة$^{-1}$ في مفاعل مختبري محشو ثابت.. أظهرت النتائج التجريبية أن تحويل التكسير للمستخلص والانتاجية للمقاطع النفطية المفيدة قد زاد بينما قل الفحم المترسب على العامل المساعد المدعم بالنيكل (Ni / HY-zeolite) .

الكلمات الرئيسية: تكسير الحفاز، مخلفات مستخلص الزيوت-فورفورال، الزيولايت، مفاعل ذو حشوة ثابتة.

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1. INTRODUCTION

The process of cracking is the disintegration of heavy petroleum fractions and residue. To obtain the low molecular weight of hydrocarbons, this process consists of breaking the C-C bond in the feedstock. The catalytic cracking feedstock is usually part of crude oil, with a high boiling point and high molecular weight. The prevalent feedstock is a petroleum fraction of the boiling point between 350-550°C, such as vacuum gas oil, reduced crude, and all cycle oils **(Fahim, 2010).** The value of feedstock determines the value of catalytic cracking. In the catalytic cracking process, the raw materials react with catalyst and cracks into different hydrocarbons **(Alan 2001, Speight 1999).** The product of the unit is generally gasoline and other petroleum products **(Alan, 2001).** Furfural extract is the byproduct of extraction units, which is used to improve the viscosity index of different kinds of lubricating oil fractions and reduce the product's cost. It has a high viscosity, concentrated on high aromatics hydrocarbon **(Esgair, 2018)**. Zeolite Y is one of the most widely useful catalysts in petroleum refinery. It has been the essential developments in intermediate products, octane number, and lubricants and improved the properties **(Chen 1969, Bhatia 1990).** The acidity is one of the important advantages of zeolites, making them the most important catalyst in catalytic cracking because it gives zeolite of high selectivity **(Mu Mu and Mya 2008, Occlli and Connor 2001).** For different petroleum and petrochemical applications, metal catalysts based on transition metals are used in catalytic cracking. In catalyst for cracking, usually include the metal site that reflects on the catalyst's active site **(Esgair,2016)**. The catalytic cracking's support material is applied for improving and defending against attrition the catalyst's mechanical strength. It is also an advocate for enhancing the electronic properties and the essential characteristic acid and acid, such as alkaline or alkali earth metals **(Abu El-Rub et al., 2004 and Bartholomew and Farrauto, 2011).** A standard promotional catalyst includes acid-supported metals such as silica/alumina, alumina, or acidic zeolite. The catalyst dependent on the optimal level of metal load **(Bartholomew and Farrauto 2011)** took up the process's effectiveness

In the present work, the catalytic cracking of furfural extract-40 over HY-Zeolite and prepared NiHY-Zeolite to produce useful petroleum products such as gasoline, kerosene, gas oil, and lubricating oil was investigated to improve the conversion of furfural extract in catalytic cracking.

2. EXPERIMENTAL WORK

The furfural extract- 40 obtained from Al-Dora Refinery is the byproduct from the medium lubricating oil extraction unit and was used as a feed for catalytic cracking feedstock. The properties of furfural extract-40 are shown in **Table 1.**

Table 1. Physical properties of furfural extract 40

Characteristics	value
Specific gravity at $60^0/60\ ^0F$	0.978
API gravity	12.52
Kinematic viscosity, (c.st.) at 100 ^0C	31
Sulfur content, wt.%	5.2
Initial Boiling point, ^0C	350

2.1 Catalysts Preparation:

NiHY-Zeolite catalyst was prepared by impregnating 25 g of HY-Zeolite catalyst with Nickle nitrate aqueous 2M (Ni (NO3)2.2H2O) fa lask with vacuum as shown in **Fig. 1**, then mixing for 2 hours at 250 rpm. The slurry was filtered, and the resulting filter cake was dried overnight at 110^{o}C. Then the obtained dried material was calcined at 600^{o}C for 4 hours.

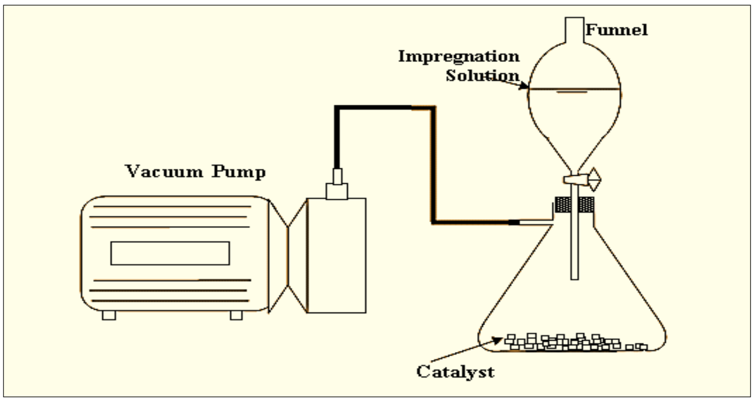

Figure 1. The scheme of impregnation apparatus.

Bentonite (3 wt. %) has been used as a binder for the formation of zeolite extrudates. The formation of the paste of zeolite and binders was done using a syringe (2cm inside diameter ended with hole 2mm diameter). The paste was manually compressed, extruded forms collected. Extrude left at room temperature until the next day so that excess water in the paste gradually vaporized. In order to prevent pores from collapsing, careful care of the drying stage must be taken. The structure will collapse with the surface loss by the high internal vapor pressure in the pores. The catalyst extrude was dried the next day (24 hours) at 100 °C in the oven. The dried extrude was cut into pieces of (2-4 mm long). The calcination process was carried out under controlled conditions with a low heating rate (3°C/min) **(Kriha, 2006).** Zeolite extrudes were calcined at 600°C for 4 hours.

2.2 The catalytic cracking unit.

The catalytic cracking of furfural extract 40 was done by using a fixed packed bed reactor in a continuous laboratory unit, as shown in **Fig. 3.** This unit contains a feeding drum, feed pump, preheater, reactor, chiller and condensing system, gas flow meter, and valve and power box.

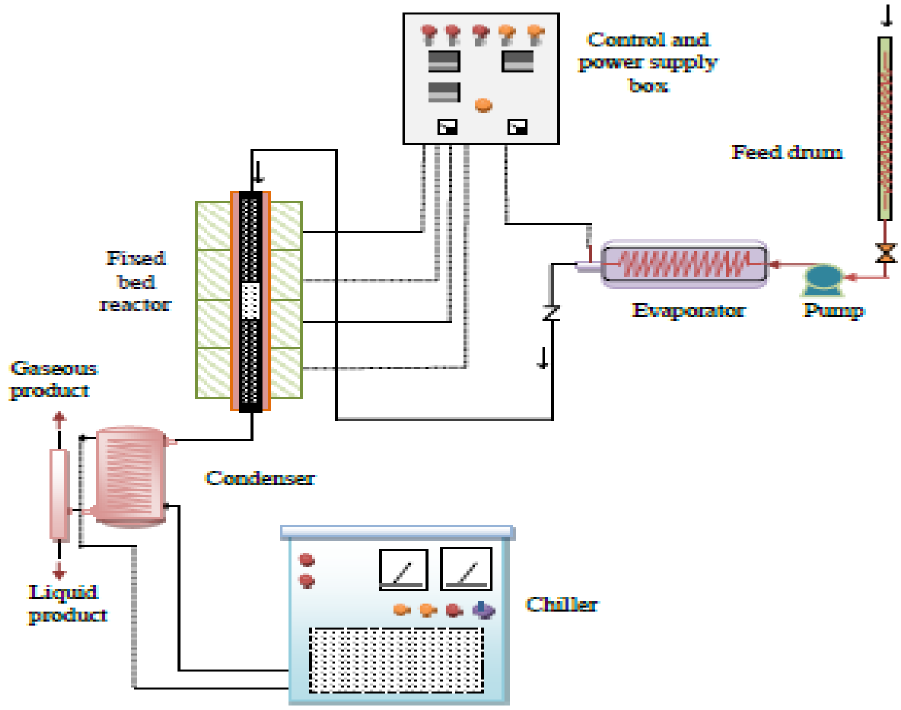

Figure 3. The catalytic experimental unit process flow diagram.

The reactor has dimensions of 20 mm inner diameter and 620 mm long stainless-steel tube, as illustrated in **Fig. 4**. Four separate jackets heated and powered the reactor automatically. Three thermocouples in the reactor were tested at three different locations within the reactor. The reactor was filled with the required quantity of catalytic cracking in the middle zone while the inert ceramic in the top and bottom areas was used to support the catalyst. The bottom area is connected to the cooling and condensing device by a 5 mm diameter tube and then to the separator.

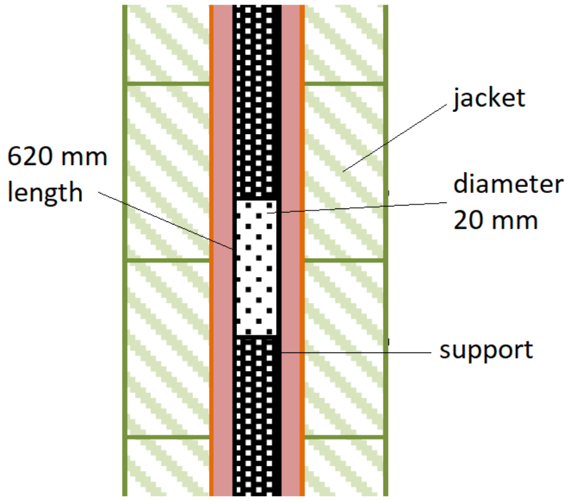

Figure 4. Schematic diagram of the catalytic cracking reactor.

2.3 The experimental procedure

A suitable amount of prepared catalyst was put in the reactor (reaction zone), and then the reactor was linked to the cracking system. The temperature in the reaction zone was 480°C. After the reactor arriving at the desired temperature, the appropriate amount of feed furfural extract pumped from the feed drum by a dosing pump adjusted manually to the desired flow to the preheater. The LHSV was (5 l/h). The vapor and liquid products were discharged to the condenser and then to the separator. Liquid products were transferred to the distillation unit for separating petroleum products.

3. Result and discussion

3.1Characterization of catalyst:

3.1.1 X-ray Diffraction (XRD):

The purity of solid crystal of HY-Zeolite obtained by comparing the x-ray diffraction pattern of prepared zeolite with x–ray diffraction pattern of the standard obtained from the International Zeolite Association **(Baerlocher et al., 2007)**. **Fig. 5** presents the x–ray diffraction for HY zeolite. A comparison between lattice spacing and angle of prepared HY- zeolite with standard HY zeolite is shown in **Table 2**. This comparison shows that the HY zeolite has approximately the same crystal structures as the standard. By summarizing the intensity of 10 major peaks of prepared and standard zeolite, a relative crystallinity of HY-zeolite could be obtained according to Eq. (1) **(Treacy and Higgin, 2001).** It was equal to 97.6 % for the prepared HY zeolite.

$$\text{Relative Crystallinity} = \left(\frac{\text{XPcat}}{\text{Rp ref.}}\right) * 100 \tag{1}$$

XPcat = the sum of peak intensity for the catalyst.

Rp ref. = the sum of peaks intensity for reference catalyst.

Fig. 5 shows the XRD for the HY-Zeolite and prepared Ni HY-Zeolite catalyst. The peaks of 2ɵ=30.07, 34.5, 37.14, 43.2, and 62.7 indicated to appear of Ni_2O_3, NiO [200], NiO[111], NiO[111], and NiO[220] respectively on the surface of the HY-Zeolite catalyst as shown in **Fig. 5**. This result indicated that the prepared catalysts have a good distribution and have suitable crystallinity of promoters on the surface of the catalyst, which reflected the activity for the catalytic cracking of furfural extract-40.

Table 2. Comparison of spacing and angle between prepared and standard catalyst

HY-Zeolite catalyst		*Standard of HY-Zeolite catalyst*	
Angle (2Theta)deg.	*d, spacing(Å)*	*Angle (2Theta)deg.*	*d, spacing(Å)*
7.1	12.402	7.18	12.41
10.05	9.205	10.172	9.210
15.98	5.501	16.103	5.503
21.7952	3.881	21.901	3.890
22.98	3.721	23.532	3.701
27.23	3.284	27.251	3.279
32.001	2.824	32.120	2.830

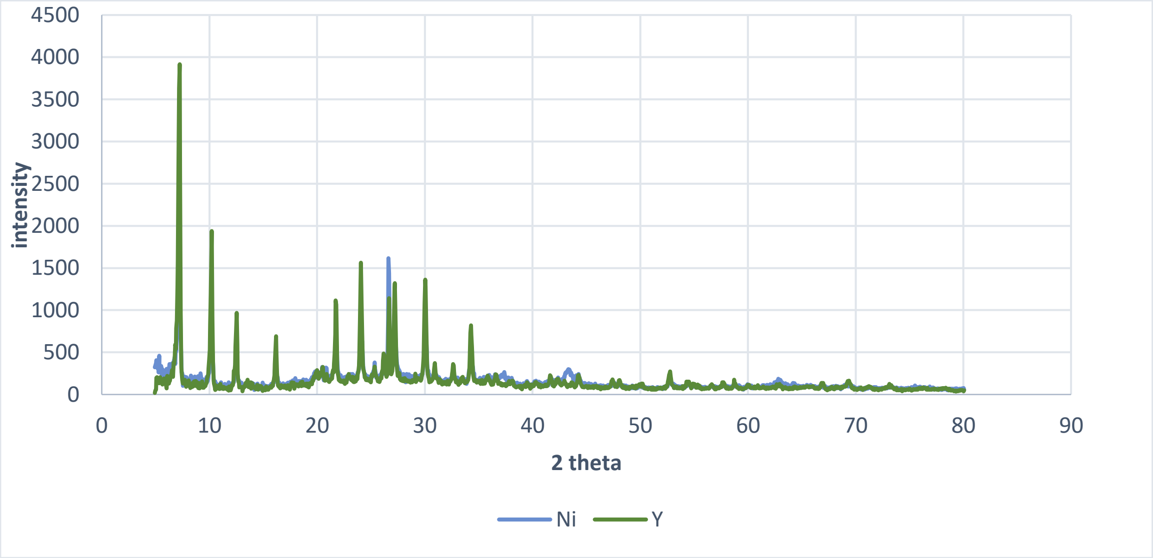

Figure 5. X–Ray diffraction spectrum for HY and Ni HY zeolite catalyst.

3.1.2 Scanning electron microscopy (SEM):

The scanning electron microscopy (SEM) provides knowledge about the crystal morphology and crystal sizes of catalyst. SEM images of the HY-zeolite and promoted prepared catalyst are shown in **Figs 6** and **7**. **Fig 6** displays the morphology of the crystals, the thickness, and the representation of the zeolite catalyst's gel structure. It could also be seen from these images of HY-zeolite and promoted prepared catalysts that the catalysts have good porosity, which may be suitable for the catalytic cracking of large molecular like furfural extract-40 of high polyaromatic molecules. The SEM image of Ni HY-Zeolite of **Fig. 7** shows NiO's distribution particles on the surface of the HY-Zeolite.

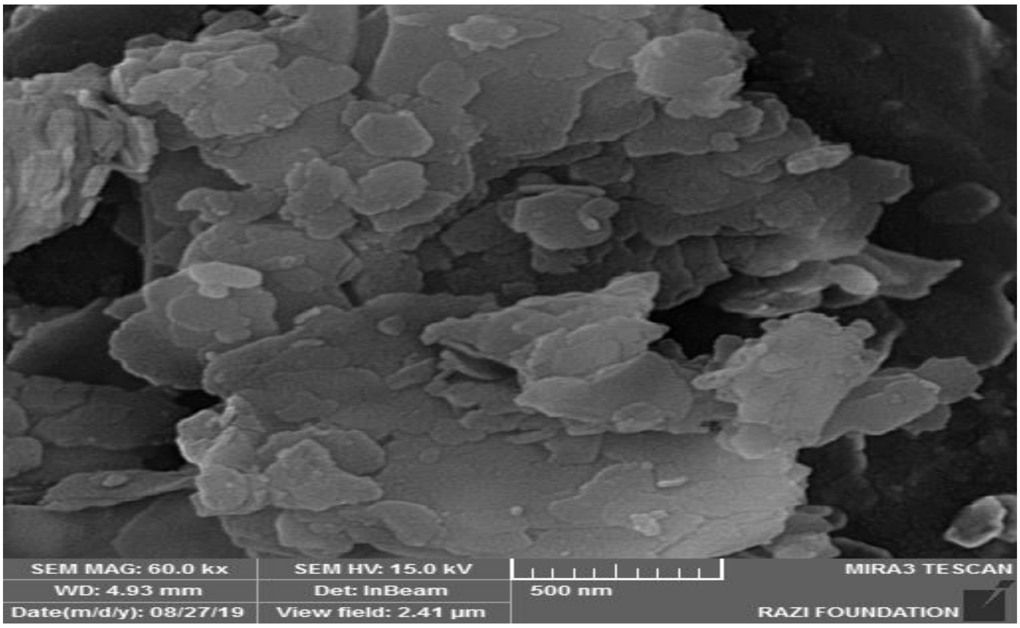

Figure 6. SEM image of HY-Zeolite.

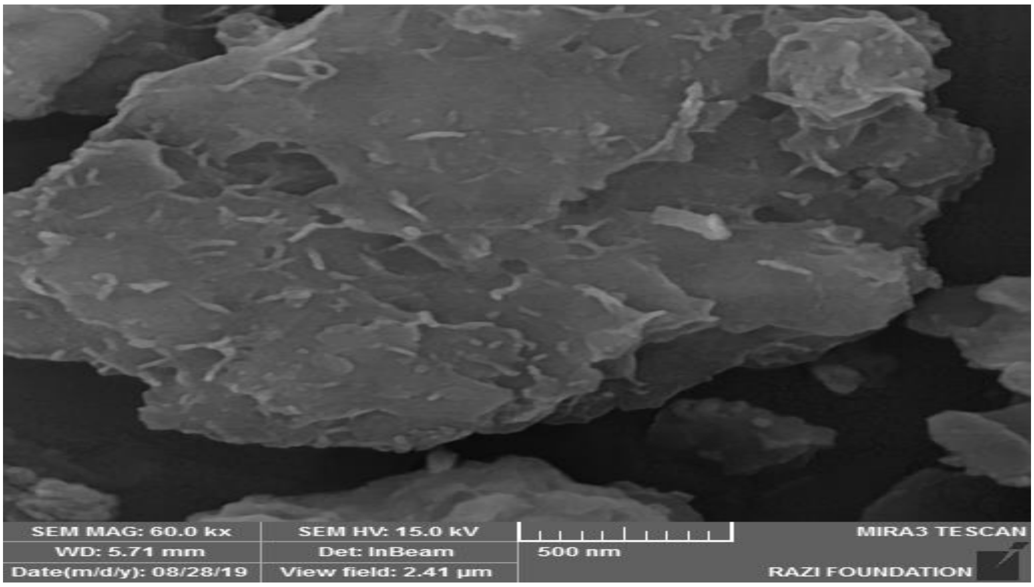

Figure 7. SEM of Ni HY-Zeolite.

3.1.3 Surface area and pore volume:

The HY catalyst's surface area was determined using the BET (Brunauer, Emmett, and Teller) method by physical adsorption of nitrogen at liquid nitrogen temperature. Pore volume is a measure of the catalyst's void-space. It is measured by adsorption of nitrogen, which is expressed in cm^3/g. For the HY catalyst, the surface area obtained was 291.2 m^2/g, and pore volume was 0.1196 cm^3/g. The result is shown in **Table 3**. The surface area of Ni HY-Zeolite was less than of the HY-Zeolite. This is maybe due to that the particles of metal oxide blocked some of the porous, which was reflected on decreasing the surface area and the pore volume.

Table 3. Surface area and pour volume of the catalysts.

Catalyst	**Surface area (m^2/g)**	**Pour volume (cm^3/g)**
HY-Zeolite	289.6	0.118
Ni HY-Zeolite	278.5	0.113

3.1.4 Fourier Transform Infrared Spectroscopy analysis:

The study of zeolite samples by infrared spectroscopy FTIR aims to determine the different chemical functions present on these catalysts' surface. A complementary technique focuses on the study of samples at the molecular level. The FTIR images are shown in **Figs 8** and **9**. The selected FTIR peaks are given in **Table 3**. As reported earlier for rare earth metals, nickel metals' impregnation brings only small changes to HY Zeolite structure. The insertion of cations leads to a small change of band located around 729–1018 cm^{-1}, which corresponds to asymmetric stretching of SiAO (Al) vibration in tetrahedral or alumina- and Silicon-Oxygen bridges **(Shiyun et al., 2006)**. **(Rahdar et al., 2016**) reported for Nickel oxide (NiO) that the absorption bonds at 470 and 522 cm-^{1} are associated to Ni-O vibration bond, but the absorption bond at 619 cm^{-1} is assigned to Ni-O-H stretching bond. The absorption bonds at 447 cm^{-1} are associated with Ni-O vibration bond but the absorption bond at 607 cm-1 is assigned to NiO-H stretching bonds. The IR band at 3444 to 3504 cm^{-1} is due to the stretching vibration of H_2O molecules. Correspondingly, the IR band around 1600 cm^{-1} is due to the bending vibration of H_2O molecules. The presence of the Si-OH group is provided as bonded water. The very strong and broad IR band at around 1000∓50 cm^{-1} is usually assigned to the Si-O-Si asymmetric stretching vibrations. The IR band at 700∓50 cm^{-1} can be assigned to Si-O-Si symmetric stretching vibrations, whereas the IR band at 450∓50 cm^{-1} is due to O-Si-O bending vibrations (**Murry and Greytak, 1997).** Therefore, it was concluded that the FTIR spectra of the HY zeolite match the typical absorption peaks of the commercial HY zeolite.

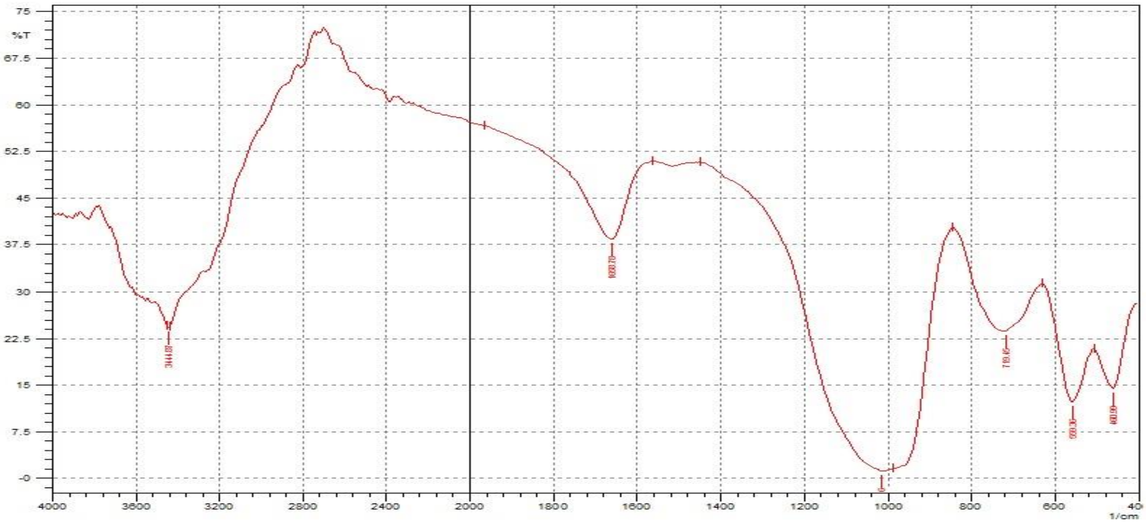

Figure 8. FTIR spectra of HY/Zeolite.

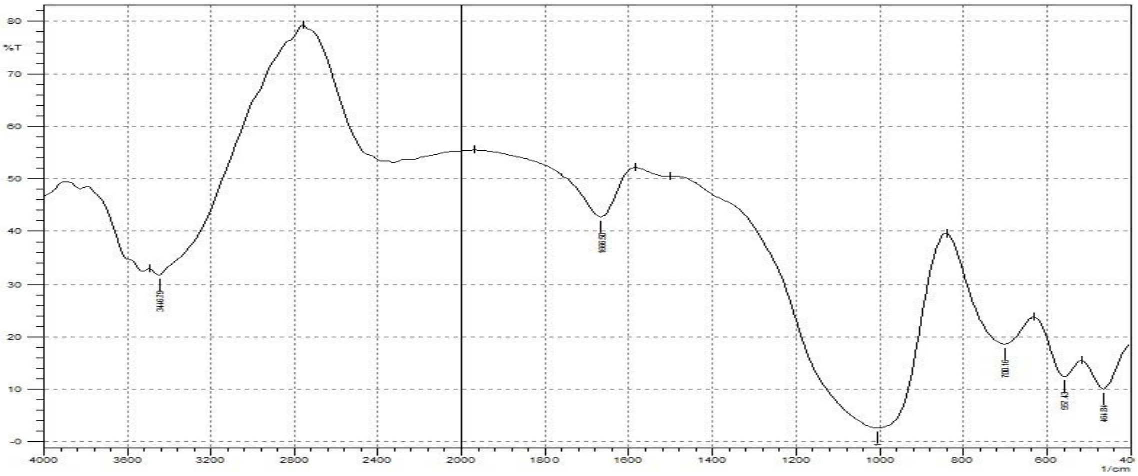

Figure 9. FTIR spectra of Ni HY/Zeolite.

Table 4. FTIR peaks for the HY and promoted zeolite catalyst.

Wave Peaks(cm^{-1})	HY/Zeolite	Ni HY/Zeolite
450-500	460.99	464.84
560	559.36	557.43
670-750	719.43	700.16
970-1100	1014	1004.91
1618-1647	1658	1666.5
3430-3590	3444.87	3446

3.2 Effect of Nickle on the activity HY-Zeolite catalyst for cracking of furfural extract:

Nickle's effect on the activity of HY-Zeolite catalyst for conversion of furfural extract-40 at 580 ^{o}C and LHSV of 5 h^{-1} is shown in **Fig. 10**. The total conversion of furfural extract-40 to produce the petroleum products of light naphtha, heavy naphtha, kerosene, gas oil, and lubricating oil in addition to gases and coke deposited on the catalyst, was 63 and 68% for HY-Zeolite and Ni HY-Zeolite, respectively. In addition, **Fig. 10** shows the percentage yield of petroleum fractions produced from the catalytic cracking of furfural extract-40 at 580^{o}C and LHSV 5 h^{-1} using HY-Zeolite and prepared promoted catalysts. The percentage yield of light and heavy naphtha was 0.7, 0.95 wt. % and 6, 7.81 wt. % for HY-Zeolite and Ni HY-Zeolite catalysts, respectively. While the percentage yield of kerosene, gas oil and lubricating oil were 1.6, 12, 30 wt. % and 1.8, 15, 32 wt. % for HY-Zeolite and Ni HY-Zeolite catalysts, respectively. At the same time, the coke deposit on the Ni HY-Zeolite (3 wt. %) was lower than that for HY-Zeolite. The presence of Nickle on the surface of HY-Zeolite improved the activity of HY-Zeolite toward the conversion of furfural extract-40 to useful petroleum products. This maybe attributed to the introduction of Nickle oxide with good distribution, as shown from the image of SEM, **Fig. 9** on the surface of HY-Zeolite increases the acidic active sites on the HY-Zeolite, which effected the increasing of the cracking of furfural extract. This indicated that the promoted catalyst with Ni on the HY-Zeolite catalyst increases the percent yield of petroleum products and improves the conversion of furfural extract-40 and the yields of petroleum products by decreasing coke formation, deposit on the HY-Zeolite catalyst.

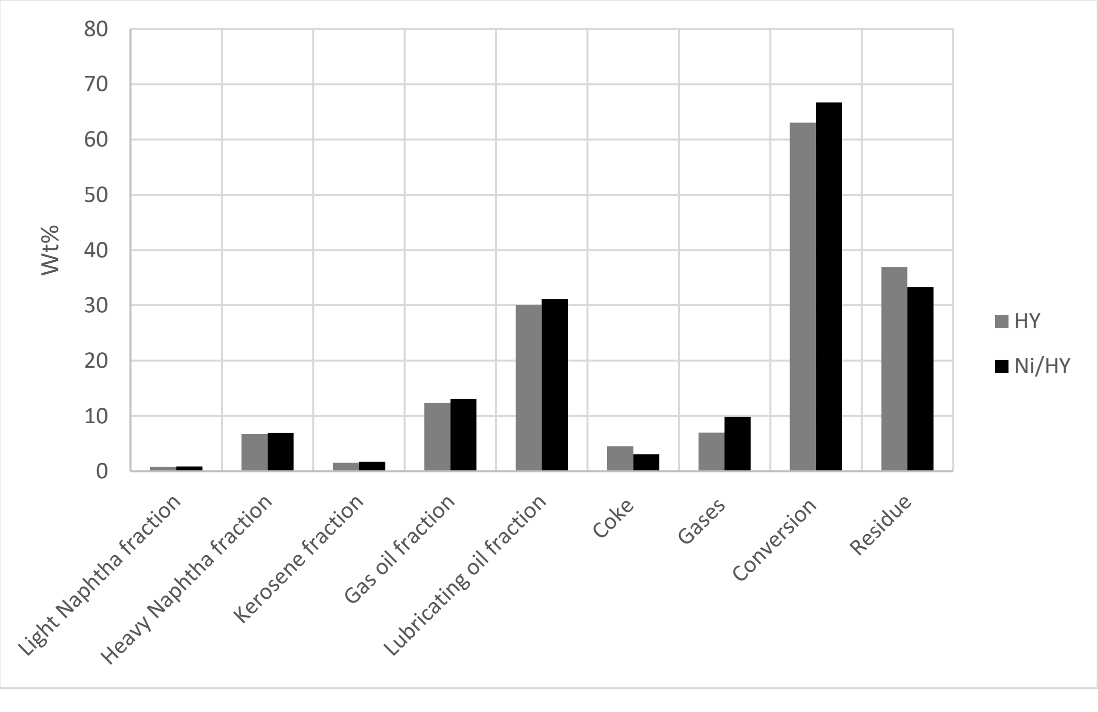

Figure 10. Material balance of wide range fractional distillation products.

4. CONCLUSIONS:

From the present work, using promoted catalyst preparation of zeolite catalyst by loading Ni, and by studying the performance of the prepared catalyst in cracking of furfural extract. Displays product distribution at 580°C after cracking. It is shown that the zeolite catalysts promoted worked as a catalyst for furfural extract cracking. The best observed result using zeolite catalysts with Ni, where the feedstock conversion, light, and middle fraction yields were higher, heavy fraction, bottom, and grown coke amounts lower than the experiment using HY/Zeolite catalyst.

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