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Maximizing High Value Light Products by Catalytic Cracking of VGO Produced by Iraqi Refinery over Formulated FCC Catalyst

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Abstract. Prototype of FCC catalyst were formulated by mixing the stabilised Y zeolites (68*wt%*) with polyvinal alcohol (PVA) (7%) as a solution binder and bentonite (25%). The Y zeolite including the original HY with Si/Al of 2.6 (*cat.-2.6*) and dealuminated HY with Si/Al of 30 (*cat.-30*) were used and tested for catalytic cracking of Iraqi vacuum gas oil (VGO) obtained from Al-Dura refinery using a pilot plant. The cracking process was carried out at a temperature of 520 °C and atmospheric pressure, The weight ratio of catalyst / oil ratio was 3 and 5. The results show that higher conversion of 77 wt. % and better product distribution (gasoline, kerosene and gas oil) could be obtained over *cat.30* resulting to a good liquid product yield. The catalytic activity, in terms of VGO conversion was not affected over *cat.-30* in spite of its lower acidity, suggesting the determinate of mesoporosity in the Y zeolite (*cat.-30*) catalysed cracking reactions. A higher yield of ~ 67 wt% to mid-distillates (*i.e.*Naphtha and kerosene) was as a result of the improvements in the diffusion to and from catalyst structure.

Introduction

In the petrochemical industry, the demand for useful light fuels such as gasoline, kerosene and gas oil has increased with time due to the formidable growth of world population, industry and economy across the globe.[1,2] Approximately half of the primitive petroleum deposits have been consumed.[3] The production of conventional oils, including both light and medium oils with high market value, has reached the maximum capacity in the early 1960s then followed a constant decrease due to the depletion of resources.[3,4]

Unconventional oil resources, including the heavy oil, extra heavy oil and bitumen, represent about 70% of the world's oil fields.[5] With the current technologies such as enhanced oil recovery (EOR), thermal methods, miscible displacement and chemical flooding, the technically recoverable amounts of heavy oil have been estimated at 430 billion barrels which means that large deposits of heavy oil has to be available for further exploitation.[5,6]

In order to obtain useful light hydrocarbons from the residual oil, common refinery techniques such as hydrocracking, thermal cracking and catalytic cracking have been used.[7] Catalytic cracking is a class of conversion processes which can process a wide range of feed stocks. This process is used to break down the high boiling, high molecular weight of hydrocarbons into lighter valuable products in the presence of catalyst.[7,8,9] The catalyst used by the catalytic cracking is usually the solid acid catalyst such as zeolites, amorphous silica-alumina combinations and natural aluminosilicates.[10] Zeolite is a very important class of microporous catalysts used in the catalytic cracking process. The function of zeolites is to improve the process efficiency and product selectivity through breaking the long chain molecules into shorter valuable products molecules (*i.e.* gasoline range organics). Thus, high activity in terms of conversion (recovery of more useful gasoline products from the feedstock), less residuum and insignificant amount of coke formation can be obtained by employing the zeolites as catalyst.[9,10,11,12]

Catalytic cracking has a number of advantages. By catalytic cracking, high yields of gasoline with the high octane number are produced. Furthermore, catalytic cracking yields substantial quantities of gaseous light olefins, which are important platform chemicals for the polymer industry. Finally, the catalytic cracking process owns large flexibility and improved selectivity, being able to (*i*) produce both aviation turbine kerosene (ATK) and motor gasoline and (*ii*) accommodate the variation in the market demand for the production of gas oil.[9]

Sonthisawate et al.,[13] investigated the catalytic cracking of vacuum gas (VGO) oil and atmospheric residue (AR) using of composite catalysts of silica-alumina and zeolites containing microporous and mesoporous to form catalyst with hierarchical structure. The reaction temperature was 500 °C under a stream of He. They concluded that selectivity of cracking for gas product in AR was higher than that in VGO, which indicated that dealkylation of aromatic components, proceeded. Their result also showed that improved in conversion due to increase diffusion rate of raw materials with increasing pore size for both Y and β zeolite containing catalysts. In the concerning on type of zeolite included more than 70% of gasoline selectivity from both VGO and AR was obtained by using Y zeolite containing catalysts.

Catalytic cracking of VGO over zeolite type Y, mordenite, zeolite Y / alumina and mordenite / alumina have been performed by Hwan Lee et al.[14] with a different pore size distribution for cracking activity of VGO and the selectivity of the products such as kerosene, gasoline and diesel. The cracking temperature was 500 °C for 75 sec. The result indicated that the conversion of VGO over zeolite Y/alumina catalysts with a wide pore size distribution is about the same as that over pure zeolites Y butless coke was formed over zeolite / alumina compared to those over pure zeolites, also the catalysts containing zeolite Y show higher conversion of VGO than these on the catalysts containing mordenite. The selectivity of olefin is smaller on the catalyst containing Y zeolite compared to the catalyst containing mordenites because of low-bimolecular hydrogen-transfer reaction rates.[14]

Scherzer and McArthur [15] studied a series of fluid catalytic cracking (FCC) catalysts with a particular composition and physical properties for cracking high nitrogen feedstock. A higher content of zeolite together with the presence of high surface, area acid sites and a high pore size distribution in the catalyst matrix was suitable for cracking high nitrogen feedstock.

This research project is suggested by the Technical directorate, Ministry of Oil due to the incessant high demand for gasoline range products. Particularly, this research project will perform catalytic cracking of VGO which is produced by Iraqi refineries using commercial catalysts (*i.e.* zeolites or FCC catalysts). The present work has two main novel points including, firstly, the formulation of the catalyst using Y zeolite and polyvinal alcohol (PVA) and bentonite, which was done in the petroleum research and development centre labs after several attempts to find out the suitable percentage of each component, secondly, tested the catalytic performance of the prepared catalyst for catalytic cracking of VGO fraction obtained from local refinery. Catalytic cracking of VGO was carried out over the prepared catalysts formulated with Y zeolites having different degree of Si/Al ratio and mesoporosity in order to process the heavy feedstocks in FCC and increase the mid – distillates yield. A comprehensive analysis regarding characterisations for the two commercial Y zeolites (Si/Al of 2.6 and 30) was also accomplished. Catalytic products will be then distilled to assess their boiling point ranges. Additionally, the products yield will be discussed. Therefore, the research project is expected to play a pivotal role in enabling the exploitation/conversion of heavy hydrocarbons into useful light hydrocarbons products.

Experimental

Chemicals and materials

Commercial Y zeolites (CBV600 and CVB760) were obtained from Zeolyst International. CBV600 (H form) has a silicon to aluminium ratio (Si/Al) of 2.6. CVB760 (H form) has the Si/Al of 30. Polyvinyl Alcohol (PVA) solution and Bentonite were used as binder.

For the catalytic cracking reaction, vacuum gas oil (VGO) as a feedstock with density of 0.88 g/cm^3 was obtained from Dura refinery.

Preparation of catalysts

To prepare the catalysts, 68 *wt%* of zeolites Y (CBV – 600 or CBV – 760 types) were mixed with 7 *wt%* of Polyvinyl Alcohol (PVA) as a solution binder and 25 *wt%* of Bentonite.

The PVA was dissolved in deionized water using heater magnetic stirrer with continuous heating up to 90 ºC and stirring for about 2 h. The Y zeolite powder was mixed with bentonite and PVA in order prepare the catalyst paste. The obtained paste was then added inside the Mini Screw Extruder to obtain the extruded shape of the catalyst. Average size of the prepared catalysts is ~10 mm in length and their diameter is around 2 mm. The extruded catalysts were finally dried at 110 ºC for 5 h followed by calcination at 550 ºC for 4 h. The final extruded catalyst after drying and calcination. The catalysts were named cat.-2.6 and cat.-30 according to the Si/Al ratio of the parent samples (Y zeolites).

Characterisation of materials

Powder X-ray diffraction (PXRD) patterns of the both Y zeolites were recorded in the range of $5° < 2\theta < 50°$ on a shimadzu-6000, Japan X-ray diffractometer – 6000 with the conditions of Cu$K\alpha_1$ radiation operating, 40 kV, 40 mA.

Fourier transform infrared spectroscopy (FTIR) (type Shimadzu, Japan) was used to characterise the obtained Y zeolites using KBr tablets. The spectra were obtained at ambient temperature by 56 scans at 4 cm^{-1} resolution in the wavelength range of 400–1,200 cm^{-1}.

The textural properties were assessed after nitrogen (N_2) adsorption – desorption at –196 °C using a Micromeritics ASAP 2020 instrument. Prior to the N_2 physisorption measurement, ~100 mg sample was degassed at 250 °C under vacuum for 5 h. The specific surface area of the zeolites was measured according to Brunauer-Emmett-Teller (BET) method. Mesopore size distribution analysis was determined with the Barrett-Joyner-Halenda (BJH) model on the adsorption branch of the isotherm.

The grain crushing strength of formed Y zeolite was carried out using (Crush SP –50) from MA.TEC materials technologies, USA. The crushing device is in compliant with ASTM D4197 and ASTM D6175. Calcination of formed catalysts was performed using Muffle furnace “Carbolite”1500 ºC, UK, While drying were carried out using “memmert” dryer 300 ºC, Germany.

Catalytic experiments

The catalytic cracking of VGO was performed in a Multi-Purpose Unit (MPU) (as shown in Fig. 1 a and b) fixed- bed reactor at 520°C, with a feed time of 60 sec, and the weight ratio of catalyst to oil (g/g) was changed in a range of 3 and 5 keeping the amount of catalyst constant (62 g), and changing the amount of oil fed, in order to vary the conversion. The relevant calculation of weight hourly space velocity (WHSV) was 20 h-1 and 12 h-1, corresponding to catalyst /oil weight ratio (g/g) 3 and 5, respectively. Table 1 shows the properties of the VGO.

Prior to each experiment, the system was purged with N_2 flow for 15 min at the reaction temperature. After reaction, stripping of the catalyst was carried out for 15 min using a N_2 flow .During the reaction and stripping steps, the liquid products were collected in the corresponding glass receivers located at the exit of low pressure separator.

Table 1: VGO feedstock properties

Properties	**Value**
Density @15 °C (gm/ml)	0.91
Viscosity @ 40 °C (cSt)	48
Sulfur Content wt.%	1.4
Initial Boiling Point °C	307
Final Boiling Point °C	532

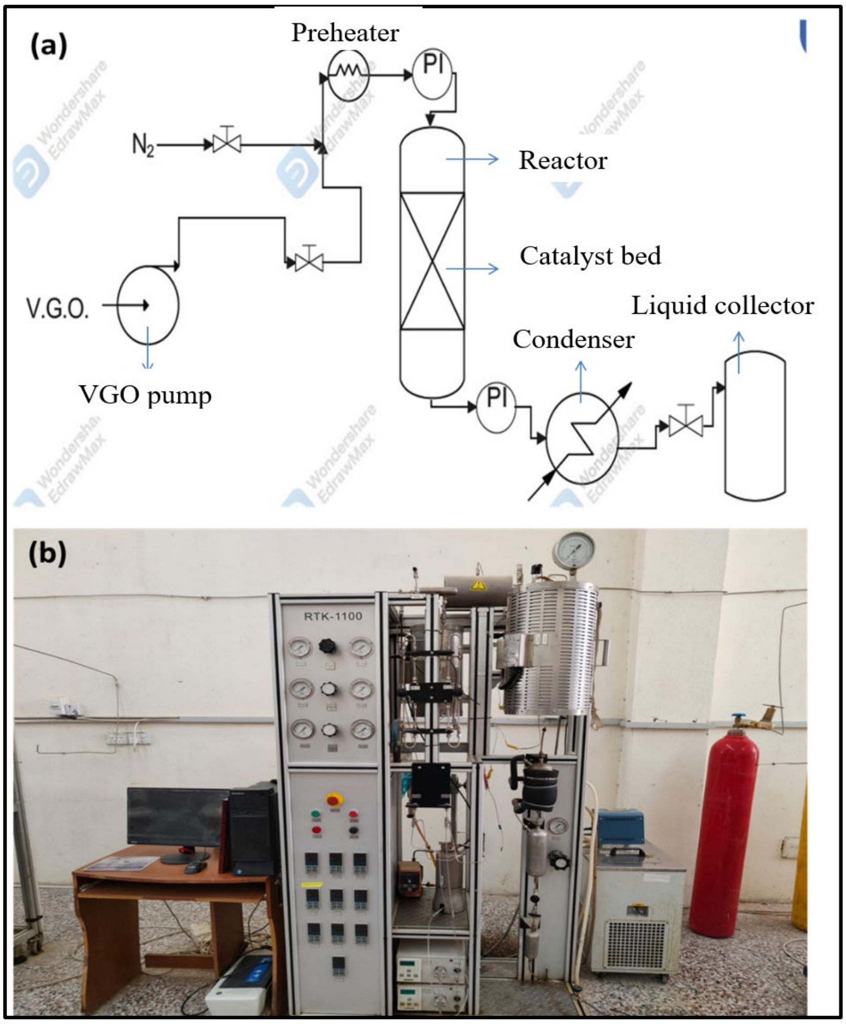


Fig. 1: (a) Schematic diagram and (b) photo of a technical pilot scale catalytic cracking apparatus (**Multi-purpose unit**) fixed bed reactor.

Product analysis

Collected liquid products were weighted and then analyzed by a distillation method using petroleum fraction distillation apparatus. The amounts of gasoline, kerosene and gas oil were also weighted and quantified considering boiling point temperature ranges from initial boiling point (IBP) to 175, 176 − 250, and 251 – 292 °C, respectively.

Results and Discussion

Properties comparison of the Y zeolite catalysts.

Both XRD patterns and FTIR spectra of the two catalysts as shown in Fig. 2 displayed the characteristic features of FAU type zeolite. XRD analysis of the Y zeolite catalysts (Fig. 2 a) exhibits the identical characteristic diffraction peaks of FAU zeolite in the wide angle range of 15.5-34.8° 2θ. FTIR was performed to measure the characteristic vibration bands of Y zeolites catalysts (Fig. 2b). The band at around 452 cm^{-1} can be attributed the structure-insensitive Si–O and/or Al–O bending vibration of the internal tetrahedral aluminosilicate framework.[16] The band at 571 cm^{-1} is assigned to the double six membered ring external linkage peak of Y zeolites (FAU structure). The bands between 693–785 cm^{-1} are associated with the internal symmetrical stretching vibrations of Y zeolites. The other two distinct peaks at 977 cm^{-1} and 1,150 cm^{-1} are assigned to internal tetrahedral asymmetrical stretching and external linkage asymmetrical stretching, respectively.[16,17]

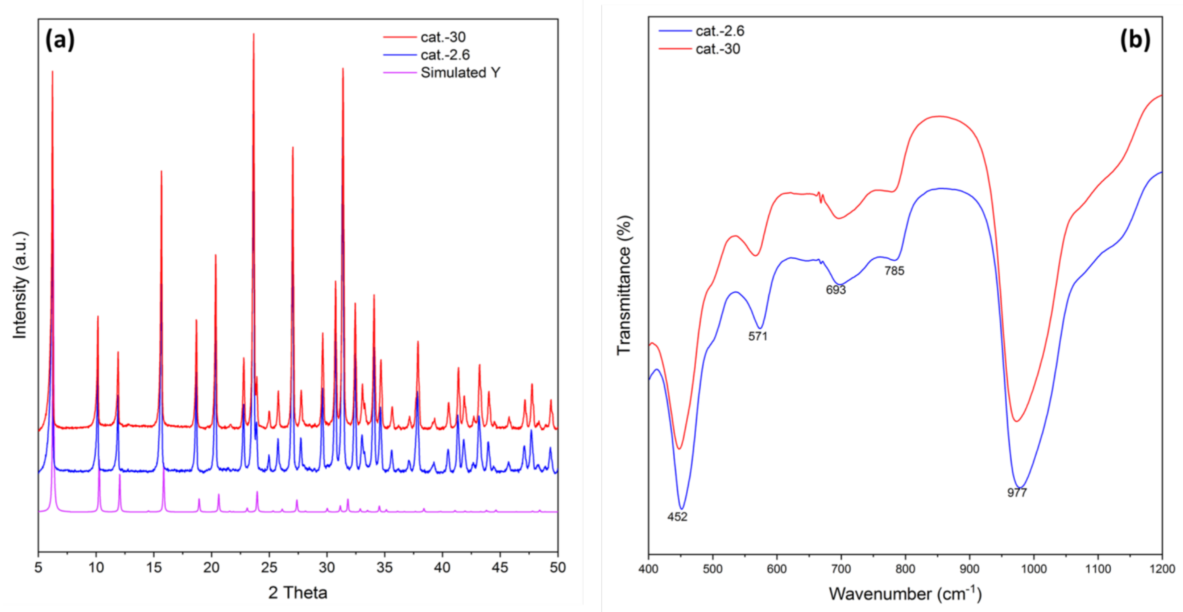


Fig. 2: a) XRD patterns and b) FT-IR spectra of Y zeolite catalysts.

Table 2: Crushing strength of the Y zeolite catalysts

Sample	Crush Strength (N/mm)
Cat.-2.6	3.22
Cat.-30	5.61

The N_2 adsorption-desorption isotherms of the Y zeolite catalysts are showed in Fig. 3. The cat.-2.6 displays a type I isotherm corresponding to the microporous nature of the cat.2,6.[18] On the other hand, the cat.-30 zeolite catalyst shows the typical IV behaviours with the H2 hysteresis loop, suggesting the presence of mesopores in the catalyst. The textural properties of the catalyst prepared by this work is summarised in

Table 3 The cat.-2.6 displays insignificant mesoporous features concerning the specific external surface area (S_{external}) of 10 m^2 g^{-1} and specific mesopore volume (V_{meso}).

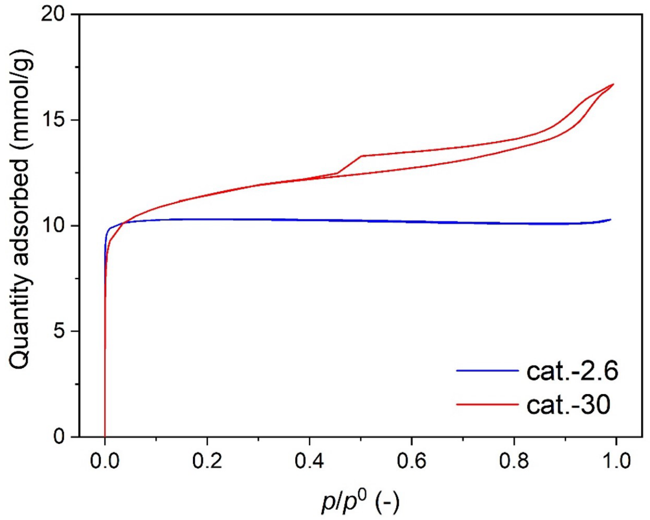


Fig. 3. N_2 adsorption-desorption isotherms of Y zeolite catalysts.

In comparison with cat.-2.6, the cat.-30 has more mesoporous features. For example, regarding the external surface area, cat-30 possess values of S_{external} at ~282 m^2 g^{-1} which is higher than that recorded for cat.-2.6 at ~10 m^2 g^{-1}. Cat.-30 exhibits a comparable BET surface areas (S_{BET} = 798 m^2 g^{-1}), indicating the well preservation of intrinsic zeolite structure and presence of mesoporous structures.

Micropore and mesopore size distributions (PSDs) of the prepared materials are shown in Fig. 4. Micropore PSDs of both catalysts (Fig. 4a) exhibit the mean distribution centred at around 0.74 nm which is the intrinsic micropore size of zeolite Y. Mesopore PSDs (Fig. 4b) display the distribution of well-developed mesopores in a range of 2–20 nm for cat.-30 while cat 2.6 did not show any mesopores.

Table 3: Textural properties of the Y zeolite catalysts.

Sample	V_{total}[a] [cm^3 g^{-1}]	V_{micro}[b] [cm^3 g^{-1}]	V_{meso}[c] [cm^3 g^{-1}]	S_{BET} [m^2 g^{-1}]	S_{micro}[b] [m^2 g^{-1}]	S_{external}[b] [m^2 g^{-1}]
Cat.-2.6	0.35	0.35	0	858	848	10
Cat.-30	0.54	0.28	0.26	798	516	282

[a] total volume adsorbed at $p/p^0 = 0.99$; [b] based on the t-plot method; [c] $V_{\text{meso}} = V_{\text{total}} - V_{\text{micro}}$.

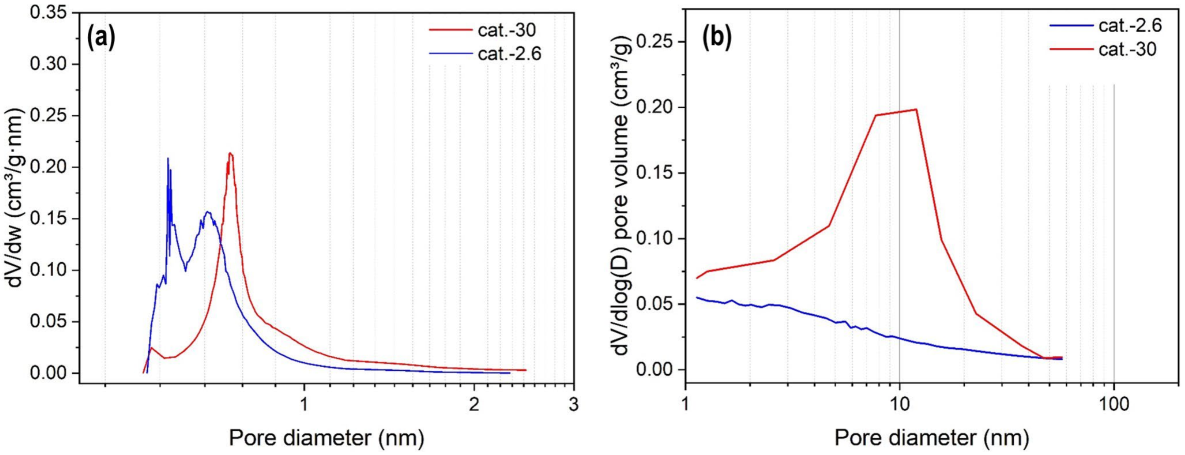


Fig. 4: (a) Micropore PSDs by the Horváth-Kawazoe (HK) method and (b) mesopores PSDs by the Barrett-Joyner-Halenda (BJH) method for the Y zeolite catalysts.

Catalytic cracking of vacuum gas oil (VGO)

Fluid catalytic cracking process which is used in petrochemical industry, is one of the largest acid-based catalytic reactions. The FCC process is used to transform the heavy oil into valuable products such as gasoline, kerosene and other products in the presence of zeolite composed catalyst.

In related catalysts, zeolites have been used in many industrial catalysis, particularly petrochemical conversion processes such as fluid catalytic cracking (FCC), alkylation and isomerisation, because zeolites have a good hydrothermal stability, high surface area, strong acidity and well shape selectivity.[1,2] In particular, the faujasite (FAU) Y has a three dimensional pore structure with a window aperture of ~0.74 nm and a spherical supercage with a diameter of 1.3 nm,[4,19] and it is considered as the most important active additives in FCC catalysts for gasoline range organics.

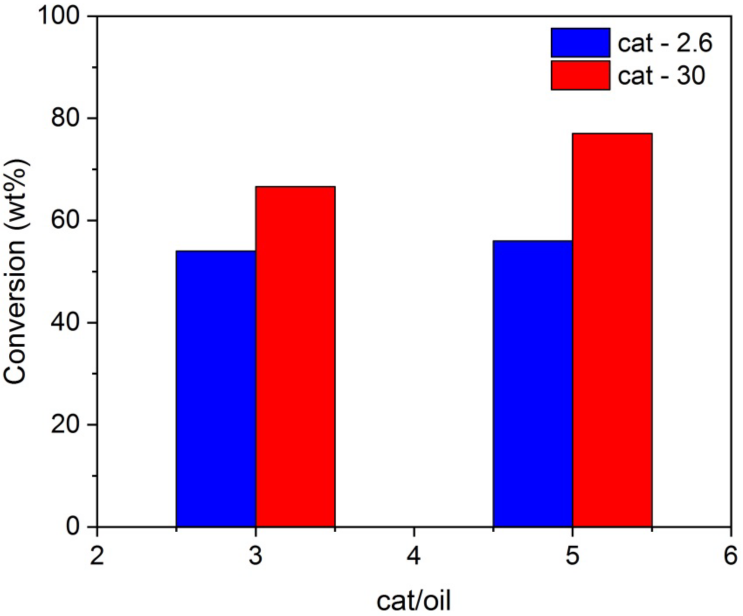


Fig. 5: Conversion of VGO feedstock over Y zeolite catalysts at different catalyst/VGO ratios.

Catalytic cracking of VGO (obtained from Daura refinery) was carried out at a range of conversion achieved by changing the catalyst to VGO ratio (cat/oil) 3 and 5, corresponding to WHSV of 20 h^{-1} and 12 h^{-1}, respectively. Zeolites Y and USY with Si/Al of 2.6 and 30 respectively were used. As shown in Fig. 5, the conversion profile of VGO over both cat-2.6 and cat-30 are increased when increasing the cat/oil ratio (*i.e.* decreasing space velocities). This finding proves that the conversion is a function of reaction time for all catalyst. This is in agreement with previous studies.[20] They observed that the total conversion increased when space velocities decreased. Increasing the contact time (*i.e.* reducing WHSV) of the feed molecules is boosting the VGO conversion. Similar finding for the effect of WHSV on the VGO conversion is obtained by previous work. [20]

As the utmost important additive in FCC catalyst, Y zeolites with mesoporosity have been proved to be extremely beneficial for refineries.[24] The catalytic cracking activity of cat-30 was evaluated in reference to the cat-2.6 (parent Y). In general terms, acidity and porosity of zeolites are equally important for cracking reactions. However, with huge molecules such as VGO, the cracking of VGO requires a catalyst with the accessible acidic sites.[22] The accessibility of the bulky molecules to the acidic sites depends on the porous framework of the zeolitic catalyst. Cat-2.6 has the lower VGO conversion over the course of reaction (*i.e.* about 50% and 54% for both cat/oil of 3 and 5, respectively); while cat-30 exhibits higher cracking activity (*i.e.* about 69% and 77%) for cat/oil of 3 and 5, respectively. The superior cracking performance of cat-30 over the course of the catalytic cracking tests can be assigned to presence of abundant intracrystalline mesoporosity, enhancing an excellent molecular diffusion to the acidic sites.

The yields of various hydrocarbons fractions in FCC are shown in Fig. 6. The hydrocarbons fractions were noticed in the VGO conversions over both catalysts. Generally, gasoline and kerosene are the products with the highest yields. Cat-30 promoted the yield to gasoline at ~20 wt%, which is higher than cat-2.6 (~4), suggesting that cat-30 has a good cracking activity than cat-2.6. The well activity of cat-30 could be assigned to its intracrystalline mesoporosity. The hierarchical feature of cat-30 improves the accessibility to and diffusion through zeolite framework. In all cases, the yield of kerosene displayed utmost as a function of the conversion. This is identification to its well-known intermediate role in the conversion mechanism of FCC process.[23]

It can be observed in Fig. 6 a, that gasoline fraction yields are steadily rising as a function of conversion. Interestingly, cracking of VGO over cat-30 produced a lower yield of gas oil than kerosene and gasoline. It can be concluded that cat-30 favours a lighter petroleum fraction with a high market value (*i.e.* gasoline and kerosene). It is worth mentioning that gas oil which is contributed significantly to diesel pool is also demanded by the market.

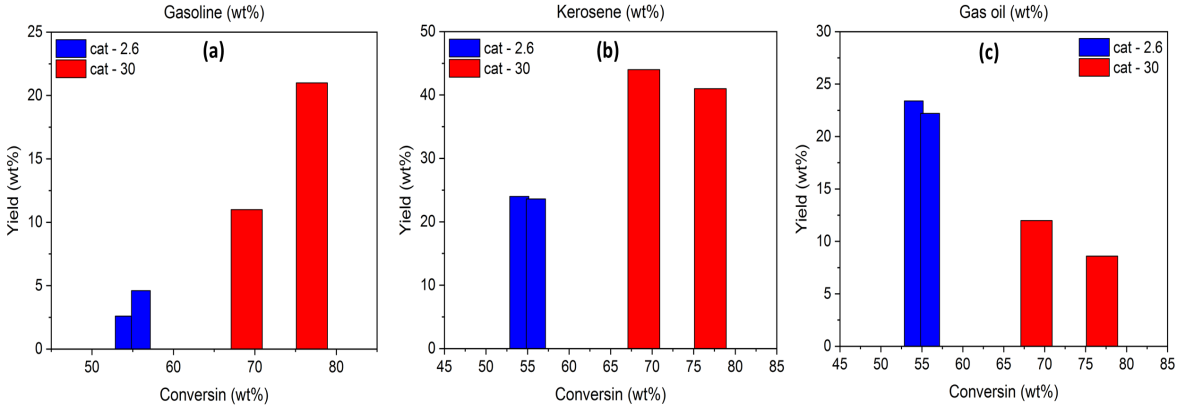
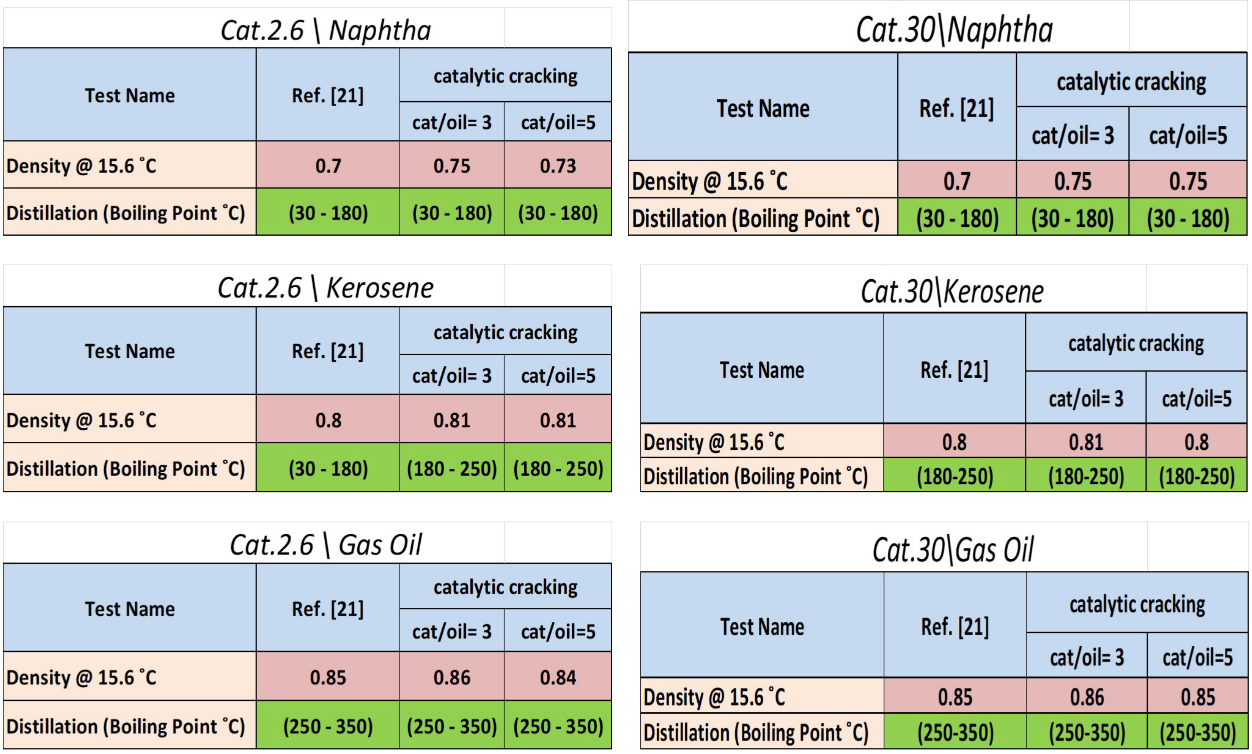


Fig. 6: Hydrocarbon yields as a function of the conversion of VGO feedstock over Y zeolite catalysts (a) gasoline, (b) kerosene, (c) gas oil.

Table 4: Properties of hydrocarbon yields



Cat.2.6 \ Naphtha

Test Name	Ref. [21]	catalytic cracking	
		cat/oil= 3	cat/oil=5
Density @ 15.6 ˚C	0.7	0.75	0.73
Distillation (Boiling Point ˚C)	(30 - 180)	(30 - 180)	(30 - 180)

Cat.30\Naphtha

Test Name	Ref. [21]	catalytic cracking	
		cat/oil= 3	cat/oil=5
Density @ 15.6 ˚C	0.7	0.75	0.75
Distillation (Boiling Point ˚C)	(30 - 180)	(30 - 180)	(30 - 180)

Cat.2.6 \ Kerosene

Test Name	Ref. [21]	catalytic cracking	
		cat/oil= 3	cat/oil=5
Density @ 15.6 ˚C	0.8	0.81	0.81
Distillation (Boiling Point ˚C)	(30 - 180)	(180 - 250)	(180 - 250)

Cat.30\Kerosene

Test Name	Ref. [21]	catalytic cracking	
		cat/oil= 3	cat/oil=5
Density @ 15.6 ˚C	0.8	0.81	0.8
Distillation (Boiling Point ˚C)	(180-250)	(180-250)	(180-250)

Cat.2.6 \ Gas Oil

Test Name	Ref. [21]	catalytic cracking	
		cat/oil= 3	cat/oil=5
Density @ 15.6 ˚C	0.85	0.86	0.84
Distillation (Boiling Point ˚C)	(250 - 350)	(250 - 350)	(250 - 350)

Cat.30\Gas Oil

Test Name	Ref. [21]	catalytic cracking	
		cat/oil= 3	cat/oil=5
Density @ 15.6 ˚C	0.85	0.86	0.85
Distillation (Boiling Point ˚C)	(250-350)	(250-350)	(250-350)

Table 4 lists the density values and relevant boiling points ranges of the hydrocarbon yields obtained over the two comparative catalysts (*i.e. cat.-2.6* and *cat.-30*) for both cat/oil ratios of 3 and 5. The density of the cracking fractions have been measured and compared with the marketing specifications guide of Iraqi petroleum products as the reference. By comparing the measured densities of obtained fraction for both catalysts with the reference, it can be seen that the petroleum fractions density is comparable to the reference within the similar boiling points ranges, indicating that the obtained cracking fractions were successfully produced. In details, the naphtha produced from vgo cracking was with a density of ~ 0.75 g/cm^3 which is comparable to the referenced one (*i.e.* 0.75 g/cm^3). VGO cracking over both cat.-2.6 and cat.-30 produced kerosene and gas oil with a density of ~ 0.8 g/cm^3 and ~ 0.85 g/cm^3, respectively. Both recorded densities of kerosene and gas oil are similar to the one recorded in the reference.

Conclusions

Two commercials FAU Y zeolite were formulated as FCC catalyst and analysed comprehensively for their porous and acidic properties, aiming at exploring their catalytic performance in the catalytic cracking of VGO. The obtained results by N_2 sorption displayed the hierarchical feature of mesoporosity in zeolite. For example, in comparison to cat.-2.6, cat.-30 has a higher intercrystal mesopososity with relatively high moesopore volume of 0.26 cm^3 g^{-1} and external surface area of 282 m^2 g^{-1}. The hierarchical mesoposrosity in cat.-30 showed significantly improved catalytic performance compared to cat.-2.6 in the cracking reactions. Independently of the catalyst, the conversion of VGO over cat.-30 at the same condition was higher than that over cat.-2.6. The catalyst with higher mesoporosity exhibited a higher observed activity that the microporous catalyst (*i.e.* 2.6). As a result, a better diffusion transport of bulky molecules in the feedstock (VGO) could be obtained leading to improve the accessibility to the active sites, and the higher density of acid sites catalysing the cracking reactions. The catalytic results show that higher conversion of ~ 77 wt. % and better product distribution (gasoline, kerosene and gas oil) could be obtained resulting to a good liquid product yield.The yield of gasoline (22 wt. %) and kerosene (45 wt. %) obtained over cat.-30 was considerably higher than the cat.-2.6. The cat.-30 with intracrystalline mesoporosity promoted a good yield to gasoline and kerosene, which is higher than the reference catalyst cat.-2.6 (*i.e.* gasoline at ~ 4 wt. % and kerosene ~ 22 wt. %). Despite the lower acidity of cat.-30, the catalytic activity, in terms of vgo conversion were not affected, suggesting the determinate of mesoporosity in the Y zeolite (cat.-30) catalysed cracking reactions. A higher yield to mid-distillates was as a result of the improvements in the diffusion to and from catalyst structure.

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