

RESEARCH PAPER

Vacuum residue upgrading by pyrolysis-catalysis procedure over mesoporous ZSM-5 zeolite

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ABSTRACT

A systematic study of a two-staged upgrading process of vacuum residue for light fuel production was carried out in a semi-batch binary reactor apparatus over Y, ZSM-5 and alkaline treated ZSM-5 zeolites. Prepared catalyst samples were characterized with XRD and BET. Density and Viscosity estimation, as well as GC/SIMDIS analyses were conducted on liquid product to examine the quality of the produced fuels. Solid residual product was observed with SEM pictures. Results of the catalytic cracking of pyrolysis vapors revealed that liquid product viscosity reduced by 40% in the presence of alkaline treated ZSM-5 zeolite. The amount of naphtha+kerosene cut produced was elevated from 14.6% in the absence of catalyst to 21.68% over ZSM-5 and 31.4% over mesoporous ZSM-5 zeolite. In all the experiments 26% solid residue remained in pyrolysis reactor which is desirable since it preserves the catalyst from deactivation by heavy hydrocarbon molecules and coke precursors.

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1. Introduction

One of the main concerns of downstream petroleum industry is to meet the rapidly growing demand of middle distillates (C₁₀-C₂₈). Obviously, the conventional fossil reserves will not last forever, while the demand for light fuels is increasing. On the other hand, very small amounts of unconventional oil reservoirs are currently being used because of the difficulties with refining these crudes. This has caused an essential shift towards the upgrading of heavy fractions such as atmospheric and vacuum distilled residual oils which are generated as byproducts in the refinery processes [1, 2]. Vacuum residue is the heaviest fraction achieved from the fractional distillation of crude oil which is extracted from the bottom of the vacuum distillation tower. This heavy cut is characterized with high density, viscosity and molecular weight and contains large amounts of asphaltenes, heteroatoms and heavy metals [3].

Main routes of upgrading residual hydrocarbons are thermal cracking, catalytic cracking, and hydrocracking. These methods are applied in order to increase the value of heavy oil fractions by generating lighter fractions [4]. Catalytic cracking provides higher yields of target products while softening the reaction conditions such as temperature and pressure compared to the non-catalytic methods. However, high amounts of metal and asphaltenes in vacuum residue (VR), speed up the catalyst deactivation[5]. High viscosity of VR also causes difficulty while processing this feed and inhibits smooth flowing through the streamline. In some researches, solvents such as toluene, gas oil, etc. have been applied for the dilution of the residual oil feedstock in order to overcome this problem [6-8]. However, these methods bring about additional costs of extracting solvents. In another approach, multistage conversion of heavy

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oils has been employed by the researchers from the past to present [9-11]. Conducting pyrolysis on VR as the first stage removes heavy hydrocarbon and asphaltene molecules which are coke precursors, as well as some catalyst poisons and provides lighter feed for the catalytic reaction.

Different zeolites are used as catalysts for the heavy oil upgrading processes such as Y, ZSM-5, Beta, MCM-41, etc. Depending on the feed and target products, these catalysts function differently. Jafari et al. [9] investigated the effect of four different nanoporous zeolites on the catalytic cracking of heavy cracked oil obtained from VR thermal cracking and revealed that the best liquid product quality was obtained over H-SAPO-34 and the highest catalytic activity and light olefin production occurred over Na-ZSM-5. However, the light olefin production accompanied by a satisfactory quality of the liquid product was achieved over Al-MCM-41 catalyst due to the appropriate pore structure and moderate acidity of this catalyst.

ZSM-5 zeolite is one popular catalyst in oil industry due to its unique structure, high thermal stability, shape selectivity, high surface area and activity [12]. However, the microporous structure can be a major drawback while dealing with large hydrocarbon molecules, leading to low liquid product yield and fast deactivation due to the blockage of small pores by the coke deposition. The creation of mesopores in microporous structure of zeolite increases the diffusion rate of reactants and provides better access to the acid sites, where catalytic reaction occurs [13].

Over the past decades, a lot of synthesis methods have been proposed in order to induce mesoporosity in zeolites [14, 15]. Recent studies have also revealed that the desilication by alkaline treatment is a suitable method to produce mesopores in ZSM-5 zeolites, while structural integrity is preserved [16-20]. The effect of different treatment conditions such as the concentration of sodium hydroxide solution, temperature, and

the reaction time on the mesopore creation and structural changes of ZSM-5 have been thoroughly investigated in the literature [13, 21, 22]. The effect of $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio on the results of alkaline treatment has also been studied previously [23, 24]. It was found that the optimal alkaline treatment conditions exist for a certain $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio.

In the present study, the authors employed a pyrolysis-catalysis approach in a binary reactor apparatus for the conversion of vacuum residue to light fuels such as naphtha and diesel over the alkaline treated ZSM-5 zeolite. In-situ catalytic cracking of the pyrolysis vapors has been numerously applied for the two-stage upgrading of plastic wastes such as polyethylene and polystyrene solid pieces [25-27]. However, there are few studies on in-situ catalytic upgrading of VR pyrolysis vapors in the literature [28]. In this research, the two-staged upgrading process of Tehran Refinery vacuum residue over alkaline treated ZSM-5 zeolite was carried out in a binary reactor apparatus for the first time. In-situ catalytic cracking of the pyrolysis vapors of vacuum residue, exiting from a semi-batch reactor takes place in a secondary fixed bed reactor, where the prepared catalyst is located. The effect of alkaline treatment on ZSM-5 zeolite cracking performance compared to the parent ZSM-5 zeolite and Y zeolite was also investigated in this research.

2. Research methods

2.1. Materials

Na-ZSM-5 zeolite ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 38$) and Na-Y zeolite ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 5.2$) were purchased from Tianjin Chemist Scientific company. Sodium hydroxide (NaOH) and ammonium nitrate (NH_4NO_3) provided from Merck were used for alkaline and ion exchange treatments respectively.

The VR sample, obtained from a vacuum distillation unit, was supplied by Tehran oil refinery. The properties of feedstock are presented in Table 1.

Table 1. VR feedstock properties

Characteristics	Value
Density at 15.6°C (g/cm ³)	0.998
Viscosity at 37.8 °C (cSt)	352
n-Heptane insoluble (wt%)	7.5
CCR (wt%)	17.4
Sulfur (wt%)	3.83
Nitrogen (ppmw)	2870
V (ppmw)	60
Ni (ppmw)	20

2.2. Upgrading process

The two-staged, binary reactor apparatus used for VR upgrading is presented in Figure 1. Thermal cracking reactions were carried out in a Pyrex round bottom Quartz flask with an internal capacity of 500 ml. An electric mantle equipped with temperature controller system was employed for providing the reaction temperature. A stainless steel tube with a length of 30 cm and ID of 2 cm, loaded with 0.6 g catalyst diluted with 2.4 g silica bead was placed inside an electrical furnace for the catalysis stage of the process. K-type thermocouple was placed in the middle of the catalyst bed in order to monitor the reaction temperature. Both reactors were

isolated with glass wool to minimize the heat losses. Catalytic cracking reactor was heated to the desired temperature under nitrogen flow with a 10°C/min ramp. Then, the temperature was kept constant and pyrolysis reactor heating started with the same heating speed. At the pyrolysis stage, 30 g of VR was thermally cracked and the produced vapors were directed to the catalysis stage in a sealed and isolated streamline. The amount of pyrolysis vapors entering the second reactor affected the catalytic reaction procedure and was controlled by adjusting the heating rate of the pyrolysis reactor and the amount of the VR loaded as feed.

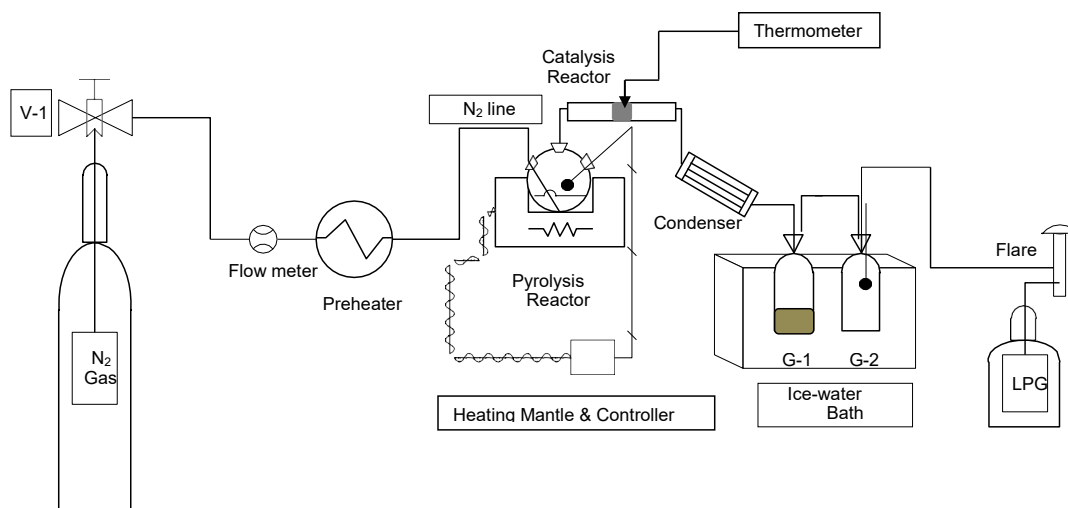


Figure 1. Experimental apparatus used for the two-staged upgrading of VR

Thermal cracking process continued for 120 minutes. The pyrolysis and catalysis reaction temperatures were kept constant at 450 °C during this time. Experiments were conducted under the atmospheric pressure and the nitrogen stream was used for providing an inert environment and the removal of pyrolysis vapors from the pyrolysis stage. Exiting vapors from the second reactor were directed to the condenser and after that to a cold trap, located in an ice-water bath. The cracked vapors were collected after the condensation and the non-condensable gases were burned in a Bunsen burner.

Pyrolysis vapors were subjected to the catalytic upgrading over HY, HZSM-5 and alkaline treated HZSM-5 zeolites.

After the completion of the reaction time, the mantle was turned off and the temperature decreased to 200 °C in about 10 min to confidently

stop the reactions. The liquid product collected in the cold traps was weighed after the reaction. The remaining solid material was also weighed to determine the residual product. The gas yield was eventually calculated from a mass balance. Product yields were calculated from Eq (1) to Eq (3).

$$\text{Liquid product yield } (Y_{\text{Liquid}}) = \text{Eq (1)}$$

$$[(\text{Weight of Liquid Product})/(\text{Weight of Feed})] \times 100$$

$$\text{Solid product yield } (Y_{\text{Solid}}) = \text{Eq (2)}$$

$$[(\text{Weight of Solid Residue})/(\text{Weight of feed})] \times 100$$

$$\text{Gas product yield } (Y_{\text{Gas}}) = 100 - Y_{\text{Liquid}} - Y_{\text{Solid}} \quad \text{Eq (3)}$$

2.3. Catalyst preparation

As received ZSM-5 and Y zeolites were calcined at 550 °C under 60 cc/min air flow for four hours before the treatments. Optimal alkaline treatment conditions (sodium hydroxide concentration, temperature and duration of treatment) were

determined based on the literature, according to $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of the parent sample [13, 23].

Alkaline treatment was performed using 200 cc of 0.2 M NaOH aqueous solution. The solution was heated up to 80 °C, then 5 grams of ZSM-5 zeolite was added and the mixture was stirred under the reflux condition for 2 hours. The slurry was then immediately cooled down to room temperature in an ice bath in order to cease the reaction. Next, it was filtered and washed with deionized water until neutral pH was attained, then dried in an oven overnight at 110 °C.

Alkaline treated ZSM-5 sample was obtained in Na-exchanged form. The protonated form was acquired by ion exchange with 1 M ammonium nitrate solution at 80 °C for 3 hours under the reflux condition. Five grams of the treated sample, were added to 150 cc of 1 M ammonium nitrate solution, filtered and washed with deionized water and dried overnight in an oven at 110 °C. This process was repeated two more times. Ion exchanged ZSM-5 sample was calcinated at 550 °C under 60 cc/min air stream for 4 hours and labeled as "MesoHZ".

Ion exchange treatment was also performed on parent Na-ZSM-5 and Na-Y zeolites as mentioned above and obtained samples were named "HZ" and "HY" respectively.

2.4. Characterization

2.4.1. Thermal analysis

Thermo gravimetric analysis was conducted for VR sample in order to investigate its thermal behavior and determine the minimum temperature required for the thermal cracking with a SDT Q600 V20.9 Build 20 thermal gravimetric (TA Instruments) analyzer under the nitrogen flow.

2.4.2. Catalyst characterization

X-ray diffraction (XRD) patterns of parent and prepared samples were recorded by an X'Pert PRO MPD diffractometer (Philips, Netherland) using Cu K α radiation ($\lambda=0.154056$ Å) at 40 kV and 30 mA in scanned angle range of 5-60 ° (2 θ). The result patterns were compared to the standard compounds reported in JCPDS data base files.

Textural properties of the samples were evaluated from nitrogen adsorption-desorption isotherms recorded by an ASAP 2020 Plus (Micromeritics, USA) instrument. Before conducting the adsorption measurements, samples were degassed for 2 h at 200 °C. Specific surface areas of the samples were

calculated according to the BET isothermal equation, pore size distribution was determined by using Barrett–Joyner–Halenda (BJH) method and micropore surface area, micropore volume and external surface area were calculated using the t-plot method.

2.4.3 Product characterization

Obtained liquid products were analyzed through the simulated distillation method by a GC/SIMDIS analyzer (Agilent ,USA), equipped with flame ionization detector (FID) and a DB-2887 capillary column (10 m \times 530 μm), according to ASTM D2887 standard method. The simulated distillation was performed in order to investigate the boiling point distribution and the amount of light components of the feed and the products of catalytic cracking process. After the fractionations, distillates were classified as the three boiling point ranges including naphtha (30 °C – 150 °C) kerosene (150 °C-250 °C), diesel (250 °C-370 °C) and heavy oil (370 °C+).

Density, refractive index and the viscosity of the liquid products were measured according to the related standard methods. A 10 ml pycnometer (Isolab, Germany) was used to measure the density at 20 °C based on ASTM D1480. Refractive indices of the liquid products were determined by using Abbe Refractometer NAR-1T Liquid (Atago, Japan) as specified by ASTM D1218. Kinematic viscosity was evaluated by a Cannon Fenske Opaque Liquid viscometer, size 75 (Normalab, France) used in a hot bath according to ASTM D445 standard. The H/C (hydrogen-to-carbon atomic ratio) and the molecular weight of the cracked oil product were calculated by using Riazi equation [29]:

$$P = a \times \exp(b \times vis_{37.8^\circ\text{C}} + c \times I + d \times vis_{37.8^\circ\text{C}} \times I) \times (vis_{37.8^\circ\text{C}})^e \times (I)^f \quad \text{Eq (4)}$$

$$I = \frac{n_d^2 - 1}{n_d^2 + 2} \quad \text{Eq (5)}$$

Table 2 represents the constants of Riazi equation for each property.

Table 2. Constants of Riazi equation

Constant	C/H ratio (wt/wt)	Molecular weight (g/mol)
a	2.143×10^{-12}	4×10^{-9}
b	0.2832	-8.9854×10^{-2}
c	53.7316	38.106
d	0.91085	0
e	0.17158	0.6075
f	-10.88065	-10.6

The morphology of the solid residue was observed by scanning electron microscope. FE-SEM images were taken with S4160 (HITACHI, Japan) apparatus.

3. Results and Analysis

3.1. Catalyst characterization

XRD patterns of the samples are presented in Figure 2. Reflection peaks at $2\theta = 7.99^\circ, 9.14^\circ, 23.21^\circ, 23.65^\circ$ and 24.38° which are assigned to ZSM-5 structure framework according to JCPDS 00-044-0002, are observable for the parent and the modified sample. It can be seen that the intrinsic lattice structure of ZSM-5 zeolite has remained unchanged with no new phases being created after modifications for MesoHZ catalyst.

Alkaline treatment may have slightly reduced the relative crystallinity of zeolite structure (93%) but all the characteristic diffraction peaks are observed in the desilicated sample with only minor decreased intensities compared to the parent sample. This result is similar to Zhao et al. [30]. Decreased intensity indicates the presence of mesopores due to the dissolution of silica species in alkali solution and the extraction of them from zeolite framework which causes partial damage to the zeolite structure [31]. HY sample has also exhibited typical pattern of the Y zeolite with diffraction peaks at $2\theta = 6.3^\circ, 10.3^\circ, 12.2^\circ, 16^\circ, 19.1^\circ, 20.7^\circ, 23.3^\circ, 24.1^\circ, 27.6^\circ, 31.4^\circ, 32^\circ$ and 34.8° (JCPDS=01-077-1551), which reveals that ion exchange has not affected the structure of zeolite.

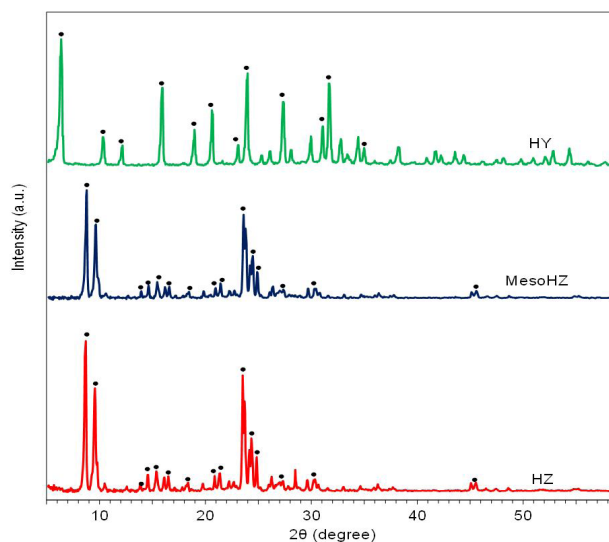


Figure 2. XRD patterns of HY, HZ and MesoHZ samples

Nitrogen adsorption-desorption analysis was also conducted on the parent ZSM-5 and MesoHZ samples in order to investigate the effect of alkaline treatment on the structural properties. Figure 3 displays N_2 adsorption-desorption

isotherms of parent and modified samples. ZSM-5 zeolite has shown a type I isotherm with a plateau at high relative pressures which is the typical isotherm for microporous materials [21]. Alkaline treatment has significantly affected the

adsorption-desorption behavior of ZSM-5 zeolite. Isotherm obtained for MesoHZ catalyst is similar to type IV with H2 like hysteresis loop indicating

the presence of mesopores in the zeolite structure. These results support previous reports on the alkaline treatment of ZSM-5 [32-34].

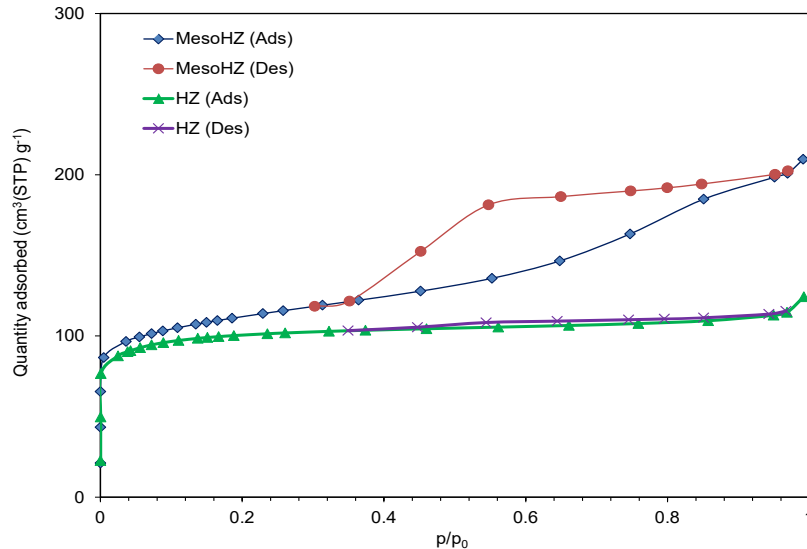


Figure 3. N₂ adsorption-desorption isotherms of HZ and MesoHZ samples

Table 3 represents textural properties of parent and alkaline treated ZSM-5 samples obtained from the nitrogen sorption experiments. S_{BET} , S_{EXT} and V_{total} for HZ sample increased from 380 m²/g, 22 m²/g and 0.191 cm³/g up to 427 m²/g, 175 m²/g and 0.323 cm³/g for MesoHZ sample, respectively.

According to t-plot calculations mesoporous and microporous volumes also increased predictably. Alkaline treatment remarkably improved the

textural properties of ZSM-5 zeolite with the creation of mesopores in the zeolite structure. These mesopores facilitate the diffusion of large sized molecules of heavy oil into the pores where active acidic sites are located [35]. Textural properties of HY sample have also been presented for making comparisons. Performing alkaline treatment has resulted in higher mesoporous volume and external surface area in ZSM-5 zeolite compared to HY.

Table 3. Textural properties of HZ, MesoHZ and HY samples, extracted for N₂ sorption analysis

Sample	S_{BET} (m ² /g)	S_{EXT} ^a (m ² /g)	S_{mic} ^b (m ² /g)	V_t ^c (cm ³ /g)	V_{mic} ^d (cm ³ /g)	V_{meso} ^e (cm ³ /g)
HZ	379.6	5.31	374.3	0.191	0.165	0.026
MesoHZ	406.58	19.9	386.68	0.323	0.272	0.051
HY	812.6	9.1	803.5	0.362	0.324	0.038

^a t-plot external surface area.

^b t-plot micropore surface area.

^c Volume adsorbed at $P/P_0=0.99$.

^d t-plot micropore volume.

^e Mesopore volume ($V_{total}-V_{mic}$).

3.2. Vacuum residue upgrading

3.2.1. VR thermal analysis

Thermal analysis of VR is shown in Figure 4. From the TGA curve, the highest slope of weight

loss has occurred near 350 °C. Based on the obtained results and the previous literature [36], thermal cracking temperatures higher than 400 °C were selected for the upgrading procedure.

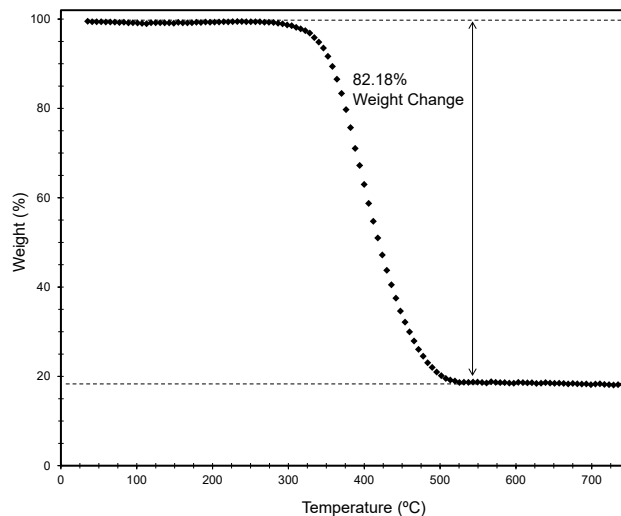


Figure 4. TGA analysis of vacuum residue

3.2.2. Catalytic performance

Pyrolysis-catalysis process was performed on VR at two different temperatures. For an accurate evaluation of the catalyst role, a blank test was implemented where no catalyst was loaded in the second reactor and the pyrolysis vapors were repeatedly thermally cracked in the second stage. Results of this blank test are presented as “Thermal cracking” in the results. Product distribution obtained over different catalyst samples at 400 °C and 450 °C are also presented in Figure 5.

In each temperature, the amount of solid product in all the cases is the same, which proves the validity of our experiments. Since the first stage condition is not altered, the amount of solid residue must be constant independently from the second stage. Second stage could only affect the liquid and gaseous product distribution.

Elevating the temperature from 400 °C to 450 °C resulted in more liquid and gas production in the expense of solid residue product [36]. The amount of solid residual product decreased from 38% to 26% by increasing the reaction temperature. The amounts of gas produced over HZ and MesoHZ samples were higher compared to HY at both temperatures. Catalytic performance leads to the production of lighter components. Further proceed of cracking reactions results in the enhancement of gaseous components as side products of heavy hydrocarbons cracking [37]. The amounts of gaseous products in the absence of catalyst at 400 °C and 450 °C are 18.5% and 25.7% respectively. Employing HY zeolite as the catalyst has increased these values to 20.7% and 28.7%,

which is not noticeable. However, the amount of gaseous product over HZ sample at 450 °C is around 26%, while alkaline treatment has enhanced this value up to 38.26% over MesoHZ sample. Hence, we may conclude that the severity of the reactions over ZSM-5 has been higher than the Y zeolite.

Lower amounts of gas produced over Y zeolite compared to ZSM-5 has also been reported previously in the literature [9]. According to the typical ammonia temperature programmed desorption (TPD) data reported earlier on these catalysts, total acid amount of ZSM-5 zeolite is higher than Y zeolite, however, the overall acid strength of Y zeolite is higher compared to ZSM-5. The lower strength and relatively high amount of acidic sites coupled with cylindrical shaped channels of ZSM-5 with proper width can explain the higher activity provided with this catalyst [9].

Alkaline treatment of ZSM-5 resulted in higher gas production and catalyst activity. Larger pores of MesoHZ sample compared to HZ and HY, improve the hydrocarbons mobility in zeolite structure. The enhanced accessibility of large hydrocarbon species present in the pyrolysis vapors, to the active sites of MesoHZ provides higher catalytic activity and gas production [38]. Temperature elevation noticeably increased the differences between HZ and MesoHZ performances. Higher temperatures employed in the catalytic cracking can activate the penetration of long chain molecules into the large cages via Knudsen diffusion [9]. This phenomenon coupled with the higher accessibility due to larger pores resulted in a remarkable catalytic performance over MesoHZ sample.

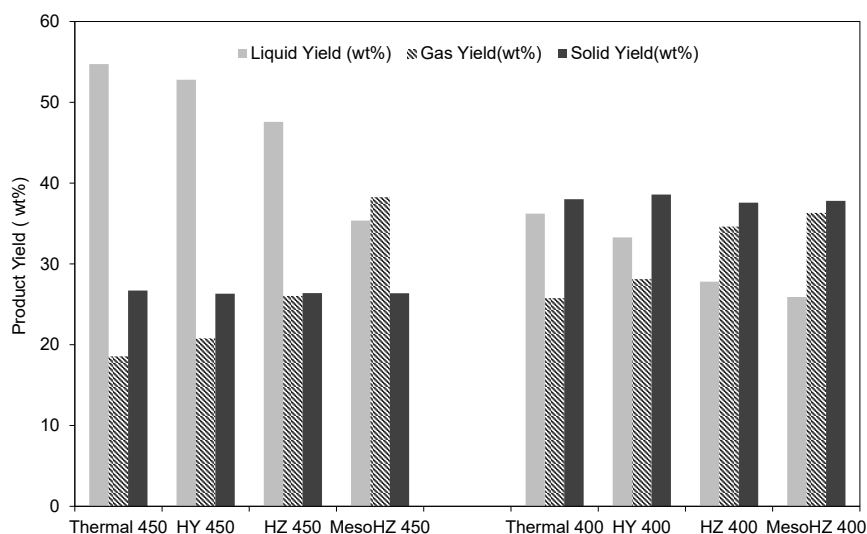


Figure 5. Product distribution over different catalyst samples at 400 °C and 450 °C

3.2.3. Product evaluation

Liquid products obtained over different samples at 450 °C were examined to determine the best quality achieved by upgrading process. Table 4 presents the calculated properties based on the methods mentioned in section 2.4.3. Viscosity of liquid product reduced by 5% and 17% after using HY and HZ samples compared to the blank test, while MesoHZ sample remarkably decreased the viscosity by 40% and the lower the viscosity, the

better the quality of the final liquid product. Also MW, calculated from Eq (4), reduced by 41% over this sample. The higher degree of large hydrocarbon cracking results in the better quality of the obtained product. However, density and refractive indices slightly increased over the catalytic reactions. H/C ratio also increased upon catalytic reaction which may be due to the dehydrogenation reactions occurred over acidic sites.

Table 4. Liquid product properties

Property	Thermal Cracking	HY	HZ	MesoHZ
Density (g.cm ⁻³)	0.86	0.86	0.88	0.87
Viscosity (cSt)	3.5	3.3	2.9	2.1
Refractive Index	1.483	1.482	1.488	1.493
Molecular Weight	531.5	492.1	429.4	310.5
H/C Atomic Ratio	1.64	1.65	1.53	1.51

The simulated distillation analysis was also performed in order to determine the light fractions present in the liquid products in the presence and absence of the catalyst samples. Increasing the cracking reactions by elevating the diffusion to active sites and reducing the mass transfer limits through alkaline treatment has led to an increase in the amount of low boiling point compounds in the liquid product.

According to the results displayed in Figure 6, the lowest amount of heavy oil cut was observed over MesoHZ sample compared to the blank test.

The amount of heavy oil compounds reduced from 50% in the absence of catalyst to 31.4% over MesoHZ sample. The amount of kerosene cut produced in blank test was only 12%. By employing HY catalyst, this value increased to 14%. However, 16% kerosene cut produced over HZ sample was notably enhanced to 23% over MesoHZ by performing the alkaline treatment. A combination of mild acidity and large mesopore volume in MesoHZ sample resulted in a high amount of light fuel production in two-staged VR upgrading process.

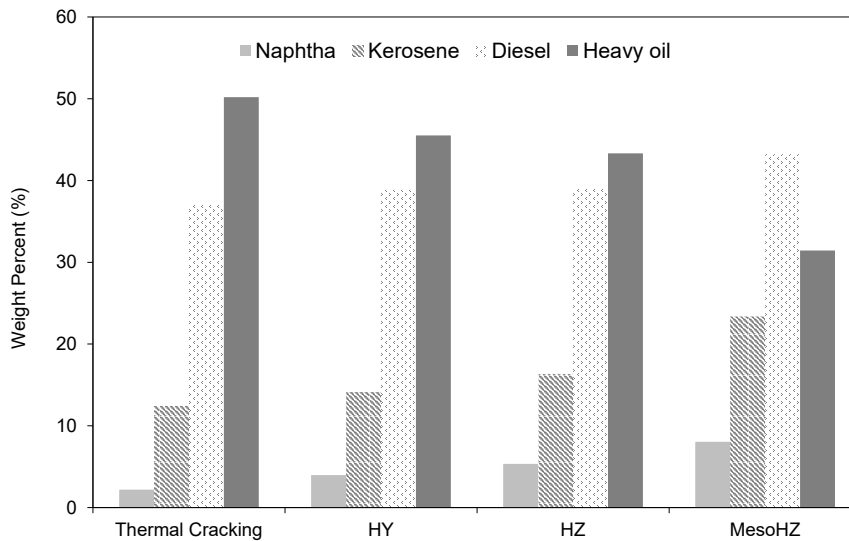


Figure 6. Boiling point distribution of liquid products obtained over catalyst samples at 450 °C

The solid residue product left in the pyrolysis reactor was collected and observed by FE-SEM pictures after the process. SEM images of solid residue obtained at 450 °C; displayed in Figure 7, provide the information about the structure and the morphological characteristics of high-molecular weight residue remained after VR pyrolysis.

During the thermal cracking reaction, lighter fractions are extracted from the vacuum residue

and their concentration decreases in the medium, while the concentration of heavier fractions, especially asphaltenes, increases. The heavy fractions are inclined to aggregate together and form solid residue with coalescent structure made of small coke particles with different sizes. This phenomenon is the reason for the porous structure and rough surface of the solid residue as can be seen in the pictures [39, 40].

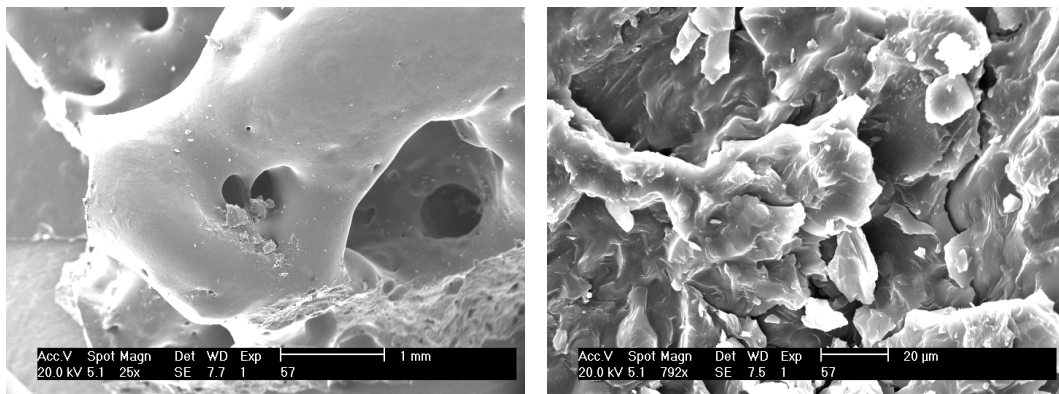


Figure 7. FE-SEM pictures of solid residue product

The extraction of these heavy fractions from VR during pyrolysis, leads to the reduction of catalyst deactivation rate in a pyrolysis-catalysis process compared to the conventional VR upgrading processes. Catalyst is preserved from the direct contact with heavy molecules such as asphaltenes which are the coke precursors since they remain in pyrolysis reactor at the first stage.

4. Conclusion

Findings of this study revealed that in-situ catalytic upgrading of VR pyrolysis vapors in a two-stage apparatus over alkaline treated ZSM-5 zeolite catalysts resulted in light fuel production. A blank test, referred as "Thermal cracking" was performed with silica beads located in the second reactor in order to evaluate the effect of catalyst performance.

Y zeolite did not alter the results significantly compared to the blank test, due to the microporous structure which inhibited the diffusion of large hydrocarbon molecules. ZSM-5 zeolite exhibited slightly higher catalytic activity and more light fuel production compared to Y zeolite; 21.68% and 18.09 production of naphtha+kerosene cut over ZSM-5 and Y zeolite was achieved respectively. However, alkaline treatment performed on ZSM-5 zeolite remarkably enhanced the priority of this zeolite compared to Y zeolite and 31.4% of this cut was produced over alkaline treated ZSM-5, which is remarkable compared to the blank test, where only 14.62% naphtha+kerosene cut was produced. Reduced mass transfer limitation due to the mesopore creation led to a higher degree of heavy hydrocarbon cracking and light fuel production. The amount of solid residue remained in pyrolysis reactor had a similar value (26%) in all the experiments which proved the validity of the experiments.

Pyrolysis-catalysis binary reactor apparatus eliminates the costs and difficulties of using solvent dilution in VR upgrading and results in light fuel production, while heavy hydrocarbon molecules such as asphaltenes and coke remain in pyrolysis stage. Catalyst is also preserved from the consequent damages.

References

- [1] D. Wang, L. Jin, Y. Li, and H. Hu, "Partial oxidation of vacuum residue over Al and Zr-doped α -Fe₂O₃ catalysts," *Fuel*, vol. 210, pp. 803-810, 2017.
- [2] B. Sarkar, W. Kwek, D. Verma, and J. Kim, "Effective vacuum residue upgrading using sacrificial nickel(II) dimethylglyoxime complex in supercritical methanol," *Applied Catalysis A: General*, vol. 545, pp. 148-158, 2017.
- [3] M. Golmohammadi, S. J. Ahmadi, and J. Towfighi, "Catalytic cracking of heavy petroleum residue in supercritical water: Study on the effect of different metal oxide nanoparticles," *The Journal of Supercritical Fluids*, vol. 113, pp. 136-143, 2016.
- [4] C. Nguyen-Huy and E. W. Shin, "Amelioration of catalytic activity in steam catalytic cracking of vacuum residue with ZrO₂-impregnated macro-mesoporous red mud," *Fuel*, vol. 179, pp. 17-24, 2016.
- [5] M. Ghashghaee and S. Shirvani, "Two-Step Thermal Cracking of an Extra-Heavy Fuel Oil: Experimental Evaluation, Characterization, and Kinetics," *Industrial & Engineering Chemistry Research*, vol. 57, pp. 7421-7430, 2018.
- [6] L. T. Do, C. Nguyen-Huy, and E. W. Shin, "NiK/yCexZr1-xO₂-macroporous Al₂O₃ catalysts for cracking of vacuum residual oil with steam," *Applied Catalysis A: General*, vol. 525, pp. 23-30, 2016.
- [7] C. Nguyen-Huy and E. W. Shin, "Oxidative cracking of vacuum residue with steam over NiK/CeZr-Al catalysts," *Fuel*, vol. 192, pp. 149-157, 2017.
- [8] H. Kondoh, K. Tanaka, Y. Nakasaka, T. Tago, and T. Masuda, "Catalytic cracking of heavy oil over TiO₂-ZrO₂ catalysts under superheated steam conditions," *Fuel*, vol. 167, pp. 288-294, 2016.
- [9] M. Jafari Fesharaki, M. Ghashghaee, and R. Karimzadeh, "Comparison of four nanoporous catalysts in thermocatalytic upgrading of vacuum residue," *Journal of Analytical and Applied Pyrolysis*, vol. 102, pp. 97-102, 2013.
- [10] A. S. Krishna and D. J. Bott, "Two-stage nonhydrogenative processing of residua," *Industrial & Engineering Chemistry Process Design and Development*, vol. 24, pp. 1266-1275, 1985.
- [11] I. Mochida, X. Z. Zhao, and K. Sakanishi, "Catalytic two-stage hydrocracking of Arabian vacuum residue at a high conversion level without sludge formation," *Industrial & Engineering Chemistry Research*, vol. 29, pp. 334-337, 1990.
- [12] R. Ravandi, R. Khoshbin, and R. Karimzadeh, "Synthesis of free template ZSM-5 catalyst from rice husk ash and co-modified with lanthanum and phosphorous for catalytic cracking of naphtha," *Journal of Porous Materials*, vol. 25, pp. 451-461, 2018.
- [13] M. Ogura, S.-y. Shinomiya, J. Tateno, Y. Nara, M. Nomura, E. Kikuchi, et al., "Alkali-treatment technique — new method for modification of structural and acid-catalytic properties of ZSM-5 zeolites," *Applied Catalysis A: General*, vol. 219, pp. 33-43, 2001.
- [14] K. Möller and T. Bein, "Mesoporosity — a new dimension for zeolites," *Chemical Society Reviews*, vol. 42, pp. 3689-3707, 2013.
- [15] A. Feliczak-Guzik, "Hierarchical zeolites: Synthesis and catalytic properties," *Microporous and Mesoporous Materials*, vol. 259, pp. 33-45, 2018.
- [16] S. Fathi, M. Sohrabi, and C. Falamaki, "Improvement of HZSM-5 performance by alkaline treatments: Comparative catalytic study in the MTG reactions," *Fuel*, vol. 116, pp. 529-537, 2014.
- [17] J. C. Groen, W. Zhu, S. Brouwer, S. J. Huynink, F. Kapteijn, J. A. Moulijn, et al., "Direct Demonstration of Enhanced Diffusion in Mesoporous ZSM-5 Zeolite Obtained via Controlled Desilication," *Journal of the American Chemical Society*, vol. 129, pp. 355-360, 2007.
- [18] Y. Li, S. Liu, S. Xie, and L. Xu, "Promoted metal utilization capacity of alkali-treated zeolite: Preparation of Zn/ZSM-5 and its application in 1-hexene aromatization," *Applied Catalysis A: General*, vol. 360, pp. 8-16, 2009.
- [19] Y. Song, X. Zhu, Y. Song, Q. Wang, and L. Xu, "An effective method to enhance the stability on-stream of butene aromatization: Post-treatment of ZSM-5 by alkali solution of sodium hydroxide," *Applied Catalysis A: General*, vol. 302, pp. 69-77, 2006.
- [20] L. Zhao, B. Shen, J. Gao, and C. Xu, "Investigation on

the mechanism of diffusion in mesopore structured ZSM-5 and improved heavy oil conversion," *Journal of Catalysis*, vol. 258, pp. 228-234, 2008.

[21] H. Mochizuki, T. Yokoi, H. Imai, S. Namba, J. N. Kondo, and T. Tatsumi, "Effect of desilication of H-ZSM-5 by alkali treatment on catalytic performance in hexane cracking," *Applied Catalysis A: General*, vol. 449, pp. 188-197, 2012.

[22] L. Jin, X. Zhou, H. Hu, and B. Ma, "Synthesis of 2,6-dimethylnaphthalene by methylation of 2-methylnaphthalene on mesoporous ZSM-5 by desilication," *Catalysis Communications*, vol. 10, pp. 336-340, 2008.

[23] L. Zhao, J. Gao, C. Xu, and B. Shen, "Alkali-treatment of ZSM-5 zeolites with different SiO₂/Al₂O₃ ratios and light olefin production by heavy oil cracking," *Fuel Processing Technology*, vol. 92, pp. 414-420, 2011.

[24] J. C. Groen, J. A. Moulijn, and J. Perez-Ramirez, "Desilication: on the controlled generation of mesoporosity in MFI zeolites," *Journal of Materials Chemistry*, vol. 16, pp. 2121-2131, 2006.

[25] C. Ma, J. Yu, Q. Yan, Z. Song, K. Wang, B. Wang, et al., "Pyrolysis-catalytic upgrading of brominated high impact polystyrene over Fe and Ni modified catalysts: Influence of HZSM-5 and MCM-41 catalysts," *Polymer Degradation and Stability*, vol. 146, pp. 1-12, 2017.

[26] C. Santella, L. Cafiero, D. De Angelis, F. La Marca, R. Tuffi, and S. Vecchio Cipriotti, "Thermal and catalytic pyrolysis of a mixture of plastics from small waste electrical and electronic equipment (WEEE)," *Waste Management*, vol. 54, pp. 143-152, 2016.

[27] M. Syamsiro, H. Saptoadi, T. Norsujianto, P. Noviasri, S. Cheng, Z. Alimuddin, et al., "Fuel Oil Production from Municipal Plastic Wastes in Sequential Pyrolysis and Catalytic Reforming Reactors," *Energy Procedia*, vol. 47, pp. 180-188, 2014.

[28] I. Mochida, K. Sakanishi, Y. Korai, and H. Fujitsu, "Two-stage catalytic up-grading of vacuum residue of a Wandoan coal liquid," *Fuel*, vol. 65, pp. 1090-1093, 1986.

[29] M. R. Riazi, *Characterization and Properties of Petroleum Fractions*: ASTM International, 2005.

[30] L. Zhao, C. Xu, S. Gao, and B. Shen, "Effects of concentration on the alkali-treatment of ZSM-5 zeolite: a study on dividing points," *Journal of Materials Science*, vol. 45, pp. 5406-5411, 2010.

[31] S. Asadi, L. Vafi, and R. Karimzadeh, "Catalytic cracking of propane over impregnated mesoporous ZSM-5: A strategy to change product distribution by sequential modification," *Microporous and Mesoporous Materials*, vol. 255, pp. 253-260, 2018.

[32] F. Zhou, Y. Gao, G. Wu, F. Ma, and C. Liu, "Improved catalytic performance and decreased coke formation in post-treated ZSM-5 zeolites for methanol aromatization," *Microporous and Mesoporous Materials*, vol. 240, pp. 96-107, 2017.

[33] H. Sun, P. Peng, Y. Wang, C. Li, F. Subhan, P. Bai, et al., "Preparation, scale-up and application of meso-ZSM-5 zeolite by sequential desilication-dealuminum," *Journal of Porous Materials*, vol. 24, pp. 1513-1525, 2017.

[34] J. Li, X. Li, G. Zhou, W. Wang, C. Wang, S. Komarneni, et al., "Catalytic fast pyrolysis of biomass with mesoporous ZSM-5 zeolites prepared by desilication with NaOH solutions," *Applied Catalysis A: General*, vol. 470, pp. 115-122, 2014.

[35] S. Safari, R. Khoshbin, and R. Karimzadeh, "Beneficial use of ultrasound irradiation in synthesis of beta-clinoptilolite composite used in heavy oil upgrading process," *RSC Advances*, vol. 9, pp. 16797-16811, 2019.

[36] R. Asgharzadeh Shishavan, M. Ghashghaee, and R. Karimzadeh, "Investigation of kinetics and cracked oil structural changes in thermal cracking of Iranian vacuum residues," *Fuel Processing Technology*, vol. 92, pp. 2226-2234, 2011.

[37] S. Oruji, R. Khoshbin, and R. Karimzadeh, "Preparation of hierarchical structure of Y zeolite with ultrasonic-assisted alkaline treatment method used in catalytic cracking of middle distillate cut: The effect of irradiation time," *Fuel Processing Technology*, vol. 176, pp. 283-295, 2018.

[38] R. Khoshbin and R. Karimzadeh, "Synthesis of mesoporous ZSM-5 from rice husk ash with ultrasound assisted alkali-treatment method used in catalytic cracking of light naphtha," *Advanced Powder Technology*, vol. 28, pp. 1888-1897, 2017.

[39] T. Yan, J. Xu, L. Wang, Y. Liu, C. Yang, and T. Fang, "A Review of the Upgrading of Heavy Oils with Supercritical Fluids," *RSC Adv.*, vol. 5, 2015.

[40] A. Boytsova, N. Kondrasheva, and J. Ancheyta, "Thermogravimetric Determination and Pyrolysis Thermodynamic Parameters of Heavy Oils and Asphaltenes," *Energy & Fuels*, vol. 31, pp. 10566-10575, 2017.

ارتقاء باقی مانده خلاء طی فرایند دو مرحله ای پیرولیز-کاتالیز بر روی زئولیت مزوحفره ZSM-5

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چکیده

در این پژوهش ارتقاء باقی مانده خلاء در یک سیستم نیمه پیوسته‌ی دو راکتوری با هدف تولید سوخت های مایع سبک بر روی زئولیت های ZSM-5 و ZSM-5 فراوری شده با محلول سود، مورد بررسی قرار گرفته است. کاتالیست های تهیه شده با آنالیزهای XRD و BET مشخصه یابی شده اند. کیفیت محصول مایع بدست آمده از فرایند ارتقاء، توسط آنالیز GC/SIMDIS و اندازه گیری پارامترهای ویسکوزیته و دانسیته مورد بررسی قرار گرفته است. همچنین محصول جامد باقیمانده از فرایند پیرولیز، توسط عکسبرداری SEM ارزیابی شده است. بر اساس نتایج، ویسکوزیته‌ی محصول مایع در حضور زئولیت ZSM-5 فراوری شده، ۴۰٪ کاهش یافته است. هم چنین برش نفت سفید و نفتای تولید شده، از ۱۴/۶٪ در غیاب کاتالیست، به ۲۱/۶۸٪ در حضور زئولیت ZSM-5 و ۳۱/۴٪ پس از فراوری قلیایی و ایجاد مزوحفرات افزایش یافته است. در آزمایشات انجام شده ۲۶٪ باقی مانده‌ی جامد درون راکتور پیرولیز به جای مانده که موجب حفاظت کاتالیست از هیدروکربن های سنگین و پیش ماده های تشکیل کک، می گردد.

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