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Research Article

# Production of High-Octane Number Gasoline from Basra Low Octane-Number Gas Condensate and Ethanol over Modified Zn/ZSM5 Zeolite Catalyst

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## Abstract

Catalytic transformation of a low-octane number stable gas condensate to high-octane number gasoline (RON: research octane number) is an economically and strategically vital process. In this research, modifying ZSM5 zeolite (80 Si/Al ratio) by impregnation with 2% Zn (Zn/ZSM5) was carried out to increase the selectivity for isomerization and aromatization thereby enhance the octane number. The process was conducted by using stable gas condensate 85 vol% with 15 vol% ethanol in a fixed bed reactor. Zn/ZSM5 and ZSM5 were examined in a pilot scale under different conditions temperature 360-420 °C LHSV 1.2-2 $h^{-1}$, pressure 5 bar. Catalysts were characterized before and after Zn loading using Fourier Transform Infra Red (FT-IR), Brunauer-Emmett-Teller (BET), X-ray Diffraction (XRD), Scanning Electron Microscope (SEM), Field Emission Scanning Electron Microscope (FESEM), Transmission Electron Microscope (TEM), and $N_2$-adsorption. The SEM, FESEM, and TEM have shown that no change in morphology and metal distribution. The XRD and FT-IR characterizations revealed the modified catalysts retained their crystallinity after metal impregnation while $N_2$-adsorption isotherm demonstrates no significant change in porosity. The results of Zn/ZSM5 display an optimum result at 420 °C, 1.2 $h^{-1}$, 5 bar with enhancement of RON from 60.5 to 89.0 whereas ZSM5 shows RON enhancement from 60.5 to 82.0. Post Zn loading, PONA test has shown an increase for iso-paraffin from 45.4 to 47.4%, and aromatics from 10.8 to 14.0. The findings translate the effectiveness of using Zn on ZSM5 for gas condensate – gasoline transformation.

***Keywords***: Gas condensate-gasoline transformation; ethanol; Zinc-modified ZSM5; Aromatization; Octane number

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## 1. Introduction

Stable gas condensate transformation to high octane number gasoline is considered as a great deal of investment. Gas condensate is relatively cheap, clean, and widely abundant hydrocarbons primarily made up of hydrocarbons $C_{5+}$ produced as by-products from natural gas production [1–3]. Nowadays, there is a growing interest in stable gas condensate to produce high RON gasoline. RON is described as the ratio of the volume of isooctane in a mixture of normal heptane and isooctane. The octane number (RON) dictates the ability of gasoline to resist knocking during combustion and enable higher efficiency in spark-ignited engines [4]. The depletion of conventional light oil reservoirs with an urgent demand for gasoline has become the main motivation for gas condensate transfor-

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mation not to mention the low cost of gas condensate. As a result, gas condensate is a potential alternative energy source to be converted into high octane grade gasoline in the coming years [5–7]. Associated with extracted gas, gasoline, kerosene, and lesser or higher-boiling fractions are usually present. It is used in producing petrochemicals as well as gasoline or a component of gasoline blends [8,9]. Several quality indicators such as Reid vapor pressure, sulfur content, benzene- aromatics, and isoparaffin are highly taken in consideration in gasoline assessment [10,11].

The kinetic of gas condensate transformation to gasoline requires a catalyst to derive the reaction. Zeolite based catalysts are the most used ones due to their stability, selectivity, and low cost [12,13]. Hajimirzaee *et al.* have studied the effect of Zn or Ga/ZSM5 on LPG conversion to gasoline where they found both have shown the same performance at a low impregnated concentration [14]. Zeoforming is a process where the catalyst is ZSM5 dealing with light hydrocarbons feedstock with a promising pathway [15]. One of the plus points in zeoforming is no need for hydrogen like the conventional reforming process [16–18]. However, two hurdles hinder the commercialization of this technology. One issue is the benzene content in the produced gasoline exceeds the accepted limit of 1 vol% for RON +90. People in this field aim to use zeoforming to blend with another source of gasoline aiming to produce premium grade +90 RON [19]. The second one is the short operation time for ZSM5 catalyst, due to temporary deactivation occurring by coking which obliges the process to operate under high pressure (<25 bar). Another way to produce high-octane gasoline is from methanol, called methanol to gasoline "MTG" on ZSM5 catalysts without hydrogen gas [20,21].

Researchers have found additions of some metals such as Zn, Cu, Ag, Mo, Ga, and Pd to ZSM5 exhibit high performance in term stability, selectivity, and the yield [22–25]. Among these metals, Pt, Ga, and Zn, were reported the best to increase formation of gasoline. The addition of metal ions lower the formation of coke during pyrolysis, boost the yield of aromatic hydrocarbons, and remove oxygenated molecules [26–28]. Unlike Pt, Zn is inexpensive, not sensitive to sulfur components, and does not have a hydrogenolysis restriction [29]. On the other hand, handling gallium carries some health risks, produces coke deposition, and extremely expensive [30,31]. Other studies have shown good results in term the stability, aromatics selectivity and enhancing the octane number of gasoline after Zn incorporation on ZSM5 at the presence of ethanol [32–34]. In similar method, a new gas technology (NGT-synthesis) company has innovated a one-step methaforming process that removes sulfur and converts both naphtha and methanol into a high-octane gasoline with low benzene [19]; in addition, releasing hydrogen with high purity too. Some people have raised the bar finding this process as alternative to the following three processes naphtha desulfurization, reforming, isomerization, and benzene removal. This gives advantages to reduce the capital and the operating costs by 70% [35,36].

This study assesses the performance of 2 wt% of Zn loading ZSM5 zeolite (Si/Al 80) in gas condensate (supplied from Basra) to gasoline conversion tested in a fixed bed reactor in a pilot scale. The feed to the reactor is composed of 85 vol% of stable gas condensate and 15 vol% of ethanol. The Zn loading was carried out using impregnation method. The catalyst examination was done at pressure 5 bar, temperature of 360-420 °C, and space velocity of LHSV 1.2-2.0 $h^{-1}$. The results of Zn/ZSM5 have shown a significant improvement in RON from 60.5 to 89.0 whereas Zn-free catalyst ZSM5 has shown 60.5 to 82.0. We have attributed the RON improvement to the highly dispersed Zn nanoparticles. The Zn and ZSM5 matrix may significantly induce isomerization and aromatization reactions. To authors' best knowledge, no study before has utilized Zn on ZSM5 for gas condensate-gasoline transformation especially when ethanol is incorporated with the gas condensate.

## 2. Materials and Methods

### 2.1 Catalyst Preparation

ZSM5 with silica to alumina ratio ($SiO_2/Al_2O_3$ mole ratio = 80) was purchased from Zeolyst International (product number CBV 8014) as well as normal cation in a form of ammonium. ZSM5 was calcined at 550 °C for 6 h to get acidic ZSM5 powder. Metal precursor salt with a formula of $Zn(NO_3)_2.6H_2O$ (Thomas Baker, India) was used as to load 2 wt% ZnO by impregnation. Zn was impregnated on ZSM5 to obtain a solution containing the metal and ZSM5 in an amount of 80 g/150 ml by using the rotary vacuum evaporator. In the evaporator, the mixture was continuously rotated at 10-30 rpm and heated for drying at 70 °C under vacuumed pressure 100-200 millibar. Catalysts were then oven dried at 80 °C for 20 h and calcined using temperature programmed furnace at 550 °C (ramping step is 10 °C/min) for 5 h to convert zinc present to their respective oxides. Finally, the catalyst powder was shaped by pressing under the pressure of 10-15 TNS for 5-8 min using a tablet (ID = 2 cm) by electromechanical press machine then crushed and sieved by sieve shaker (3-4 mm).

### 2.2 Catalyst Characterizations

FT-IR spectra test was performed using Shimadzu FTIR-1800s spectrophotometer instrument with KBr tablet method and recording range from 400 to 4000 cm$^{-1}$. $N_2$-adsorption was conducted on micrometrics ASAP-2020 machine at 25 °C. after the degassing of sample in a vacuum for 10 h at 250 °C. The catalyst total surface area was measured by the BET model while the micropore (area and volume) was analyzed by *t*-plot method. X-ray diffractometer manufactured by (Philips model PW1730 / Hollande) was used to determine catalyst crystallographic properties. Scanning electron microscopy (SEM or FESEM (MIRA III, Weistron) were used to investigate change in morphology of the surface. Transmission electron microscopy (TEM) was performed to study the morphologies, microstructures, and metals dispersion of the catalyst on the support ZSM5.

### 2.3 Pilot Plant Test

Catalyst performances to examine the RON were carried out in a multipurpose reactor (RTK-1100) that contains a stainless-steel continuous flow reactor. An 80 g of the shaped catalyst covered by two layers upper and down of 50 g of 4 mm diameter ceramic ball to fill the reactor length of 90 cm. The catalysts were degassed at 300 °C under nitrogen and pressurized to 4 bar for 2 h before each test. Gas condensate (obtained from Nuhr Bin Ummar Oil field in Basra) was introduced to flow from a tank on the selected flow rate to get the targeted LHSV. The stream was injected with ethanol sharing of 15 vol% of the total feed entering the reactor. The feed was pre-heated to 350 °C then passed to a high-pressure separator with a cooling jacket and later on to a low-pressure separator. After the reaction reached study state the product was collected to be enough for products test. The volumetric percentage of iso-paraffins, n-paraffin, naphthene, and aromatics of the gas condensate feedstock compounds and product gasoline samples compounds were determined using the gas chromatography device (Agilent 6890N G1540N Network GC System/USA). The obtained data were compared with the atmospheric distillation test according to ASTM D86. RON was tested by using cooperative fuel research (CFR) engine (Waukesha Engine, Dresser, USA) according to ASTM D 2699, 2700. Finally, portable sulfur analyzer of fuel using monochromatic wavelength-dispersive by X-ray Fluorescence (Sindie, OTG, XOS, USA) was used to measure total sulfur content according to ASTM D 7039.

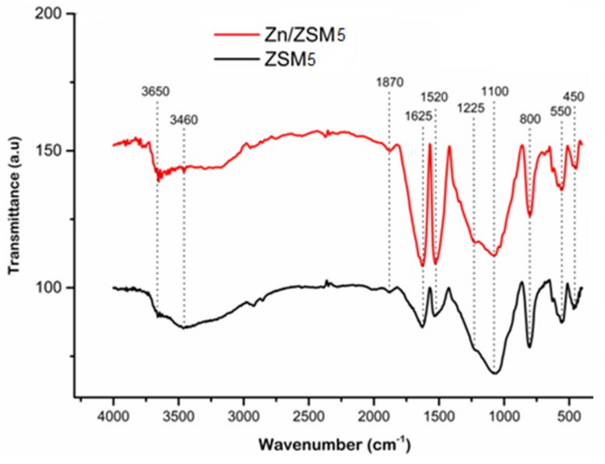

Figure 1. FTIR spectrum ZSM5 and Zn/ZSM5 catalysts.

Table 1. Properties of gas condensate for PONA test, and distillation test.

| General Property | Value |
|---|---|
| CFR (RON) | 60.6 |
| RVP, psi | 14.7 |
| Density at 15 °C, kg/m$^3$ | 0.68 |
| Sulfur content, ppm | 345.4 |
| Gas chromatography | |
| Components | Contents, vol% |
| n-Paraffin | 40.54 |
| i-Paraffin | 35.91 |
| Naphthene | 16.15 |
| Aromatics | 7.4 |
| Distillation test | |
| vol% | Temperature, °C |
| IBP | 34.4 |
| 5 | 43.1 |
| 10 | 44.5 |
| 20 | 47.4 |
| 30 | 50.6 |
| 40 | 54.4 |
| 50 | 59.5 |
| 60 | 66.4 |
| 70 | 76.1 |
| 80 | 91.2 |
| 90 | 128.6 |
| FBP | 167.2 |

## 3. Results and Discussion

### 3.1 Composition and Properties of Gas Condensate

Associated stable gas condensate properties were depicted in Table 1. Table 1 shows the general gas chromatography and distillation test specifications. It is seen that the RON is low 60 with Reid vapor pressure of 14.7 psi and a sulfur content of 345 ppm. Liquid gas chromatography test revealed the major groups of the feed were n-paraffined and i-paraffine with 40.54% and 35.91%, respectively. Figure 1 shows FT-IR spectroscopy analysis for ZSM5 and Zn/ZSM5. In the spectrum, two categories of zeolites are observed. The first category refers to the primary unit of the structure which is linked to oxygen (internal vibrations) (*i.e.*, $AlO_4$ or $SiO_4$) within the wavelength range of 450-1225 $cm^{-1}$. Typically, peaks are in the region 450 and 550 $cm^{-1}$ are recognized to Al−O or Si−O, respectively. The band at around 800 $cm^{-1}$ is attributed to the structure sensitive external tetrahedron, while the 1100 $cm^{-1}$ band

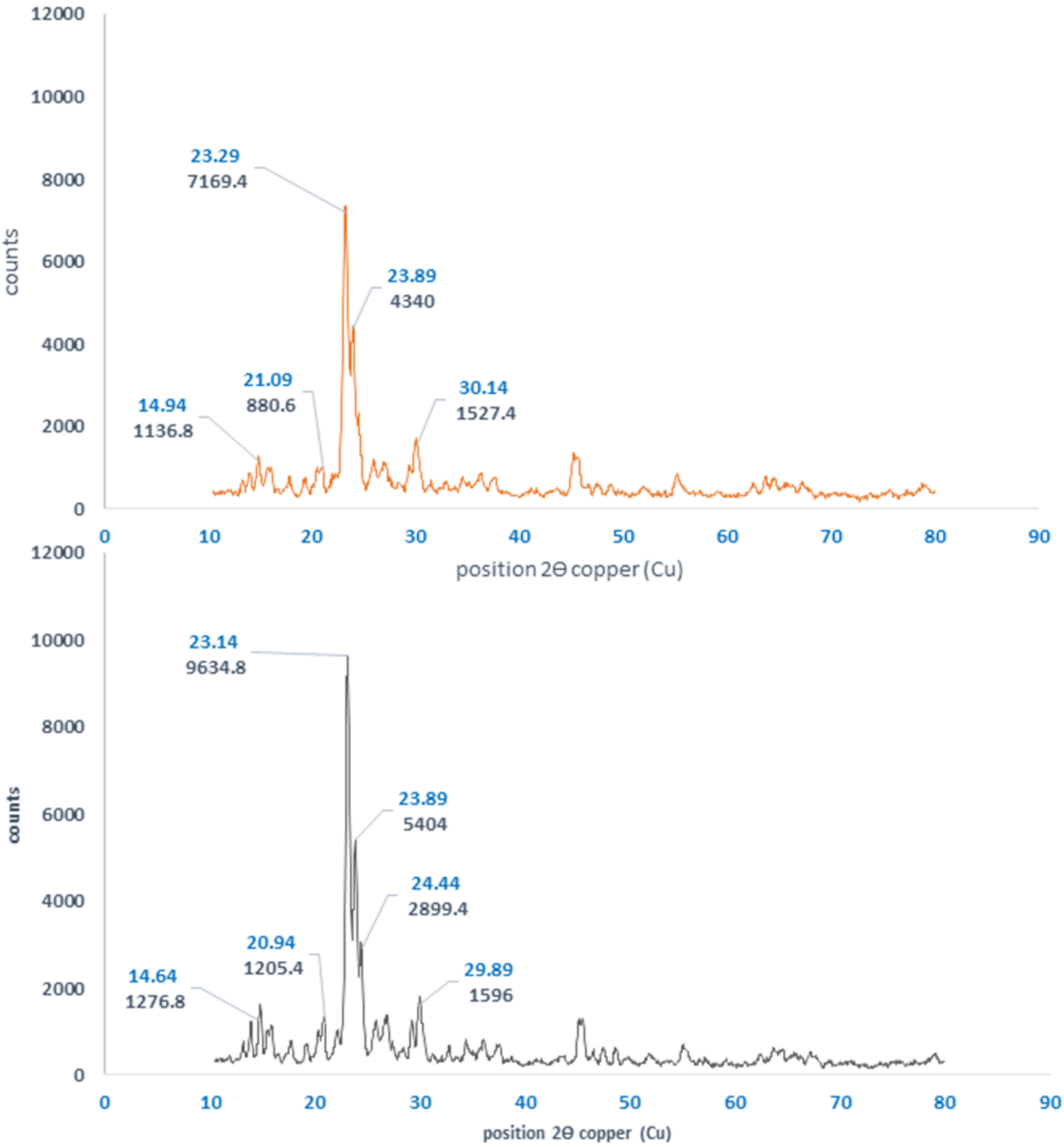

Figure 2. XRD pattern (lower) ZSM5, (upper) Zn/ZSM5 catalysts.

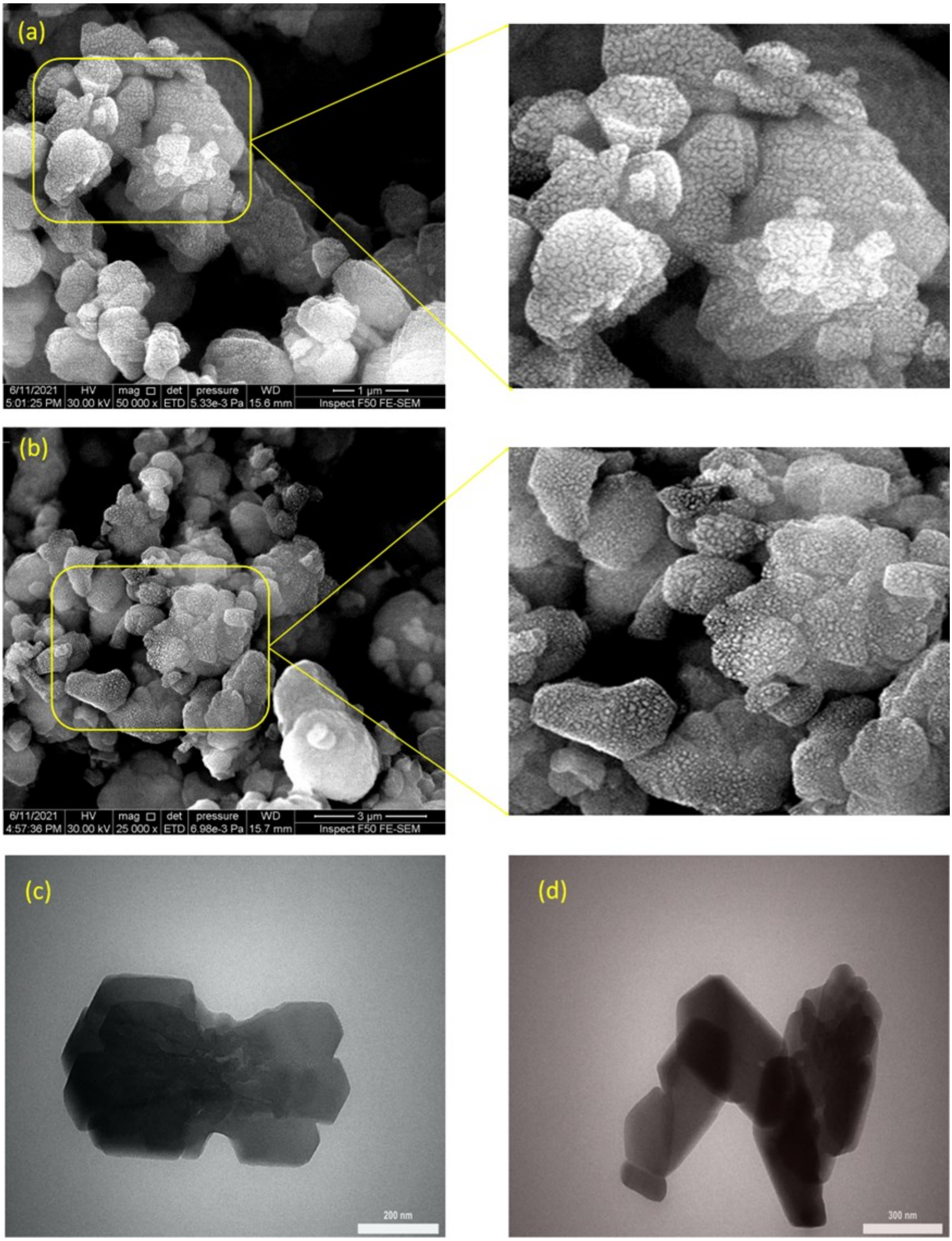

Figure 3. (a) FESEM for ZSM5 with inset, (b) FESEM for Zn/ZSM5 with inset, (c) TEM image of ZSM5 (d) TEM image of Zn/ZSM5.

represents the structure insensitive internal tetrahedron symmetric stretching vibrations, whereas the peak at 1520 cm$^{-1}$ is attributed to Brønsted acid site vibration [37–40].

In the second category, the vibrations connected to tetrahedral connections are observed in the area of 1625 and 3460 cm$^{-1}$ which are associated with hydroxide link (OH group) [41]. The Brønsted acid decreased slightly because H-protons of the zeolite were replaced by the anchored Zn that obvious at acid peak region (3460–3650) [42].

ZSM5 and Zn/ZSM5 samples were examined by XRD to know the crystallographic pattern post Zn loading as in Figure 2. Figure 2 shows the characteristic peaks of ZSM5 with Zn loading. The typical peaks of both curves were observed assuring ZSM5 structure was preserved after Zn impregnated. No recognizable peaks of ZnO and other Zn species were seen, indicating that the Zn species grains are small relative to ZSM5. On the other hand, the crystallinity of the Zn/ZSM5 becomes lower compared with catalyst before Zn loading and that may be caused by Al erupting from the zeolite structure forming a eutectic with Zn during the calcination process [32].

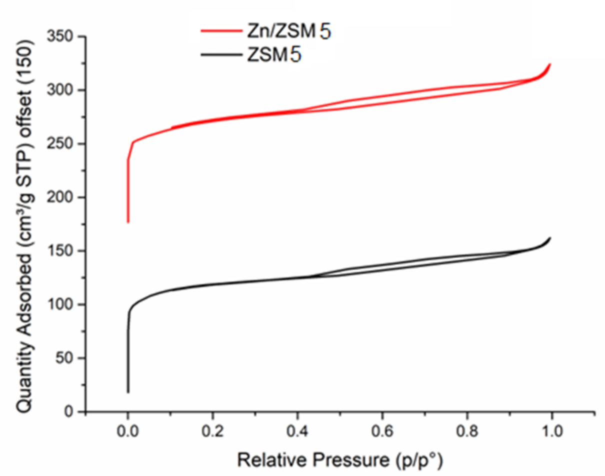

Figure 4. $N_2$ adsorption-desorption isotherm for catalysts (ZSM5, Zn/ ZSM5).

Due to metal obstructions on the surface and inner pores of the zeolite, the monometallic ZSM5 diffraction peaks intensities were decreased when Zn was added. Because of the small quantity of impregnated Zn on the surface of ZSM5, no peaks other than the characteristic peaks of ZSM5 were visible in the X-ray diffractogram pattern. This provides a profound evidence to support the explanation for the pattern of zeolite pore filling and the distribution of zinc [43]. Figure 3(a) and (b) display the FESEM analysis findings for the ZSM5 catalyst before and after Zn loading. Sufficient dispersion was observed in the SEM micrograph. These results are relatively compatible with the crystalline size obtained by XRD data. Also, FESEM images of ZnO impregnated ZSM5 catalysts show no obvious change in the crystal morphology after metal loading. The particles are uniform oval and spherical aggregates in shape [28]. However, there are very slight changes in the good nature of the catalyst surface because the zinc was impregnated on HZSM5 to form metallic Zn/ZSM5 [40]. Figure 3(c) showed the transmission electron microscopy (TEM) images of ZSM5. The absence of any Zn species particles suggests that the Zn species grains are very small and uniformly dispersed throughout the zeolite crystals. Figure 3(d) displays TEM image revealing Zn/ZSM5. Those are well-agreed with the results of XRD characterization.

To assess the effect of Zn loading on the pore structure of ZSM5, the textural properties were measured by the $N_2$ physisorption technique before and after Zn loading as shown in Figure 4. The BET hysteresis shows a relative low pressure ($p/p° < 0.2$) representing micropore filling which is type II based on IUPAC [44]. There is not a noticeable change in microporous textural properties with a long horizontal plateau. This affirms the XRD results of excellent Zn crystal dispersion and negligible micropore channels blockage. While in the mesoporous filling region within (0.4-0.85) rela-

Table 2. Textural properties of catalyst samples before and after loading.

| Textural properties | Samples name | |
|---|---|---|
| | ZSM5 | Zn/ZSM5 |
| BET specific surface area ($S_{BET}$) (m$^2$/g) | 378.07 | 358.87 |
| Micropore surface area ($S_{micro}$) (m$^2$/g) | 274.11 | 201.98 |
| External surface area ($S_{ext}$) (m$^2$/g) | 103.95 | 156.89 |
| Total pore volume ($V_{total}$) | 0.2347 | 0.2328 |
| Micropore volume ($V_{micro}$) | 0.1383 | 0.1535 |
| Mesoporous volume ($V_{meso.}$) | 0.0964 | 0.0793 |
| Average pore size (nm) | 2.4830 | 2.5950 |

tives pressure range, the hysteresis loop of Zn/ZSM5 sample has gotten more wider represent beginning of bottle nick shape formation due to the crystals agglomeration on the mesoporous channel mouth.

Table 2 shows the results textural properties for ZSM5 catalysts before and after Zn loading. The total BET surface area and total pore volume were reduced slightly 5% and 0.81%, respectively. Conversely, for microporous textural there was a sharp decrease for micropore surface area ($S_{micro}$) with 26.31%. This could imply Zn loading forms very small crystals blocked mainly the micropore textural. Meanwhile, the micropore volume ($V_{micro}$) has increased by 10% which may indicate there is some of loaded Zn crystals agglomerate inside the mesoporous texture converting it to be microporous. On the other hand, external surface area was increased by 33.74% due to depositing of Zn crystals on the external surface. Furthermore, average pore size increased after Zn loading representing that a mass portion of Zn crystals goes deep inside micropore structure and block them causing an increase in average pore size by 4.3%.

## 3.3 Catalytic Performance

### 3.3.1 Effects of ethanol on the composition and characteristics of the methylation process

Dehydration of ethanol is the first step to take place to produce light olefins which are intermediate products as shown in Equation (1). Later, produced olefine are transformed in subsequent reactions. The generated water during this reaction turns to steam prolongs the catalyst cycle by removing the coke deposits from the catalyst as soon as they are formed. The percentage of water produced is almost 7-9 vol%.

$$CH_3CH_2OH \rightarrow CH_2{=}CH_2 + 2H_2O \qquad (1)$$

Next, aromatization of olefins occurs to produce the components that dictate the high-grade gasoline. Dehydrocyclization of olefins proceeds to produce naphthene then dehydrogenation of naphthene to produce aromatics as shown in Equation (2). It also releases hydrogen that is used in hydrogenation and desulfurization processes. As it is seen in Table 1, $H_2S$ in gas condensate is 345 ppm, while after methaforminig process the $H_2S$ in product gasoline is 49 ppm. The methaforming is great approach to process feeds with sulfur content without prior hydrotreatment.

$$2CH_2{=}CH_2 + CH_2{=}CH_2 \rightarrow C_6H_6 + 6H_2 \qquad (2)$$

Moreover, alkylation of aromatics takes place when ethanol is dehydrated after ethanol contact with the ZSM5 releasing an ethyl radical. The radical quickly joins the aromatic molecule that is present in the feed to form high-octane alkyl aromatics (benzene in this case) as shown in Equation (3). ZSM5 catalyst promotes alkylation of undesirable benzene into valuable toluene and xylene and blocks formation of heavier molecules. The result of benzene content in the product does not exceed 1.7 for all conditions. There is an effect of ethanol to limit the benzene in the product.

$$CH_3\,CH_2OH + C_6H_6 \rightarrow C_6H_5\,CH_2CH_3 + H_2O \quad (3)$$

Isomerization of paraffins creates iso-paraffins as shown in Equation (4). The reaction process of n-hexane coupling with ethanol

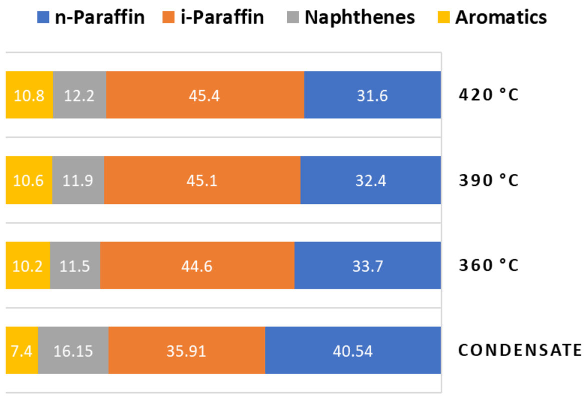

Figure 5. Composition of condensate vs products at different process temperatures over ZSM5.

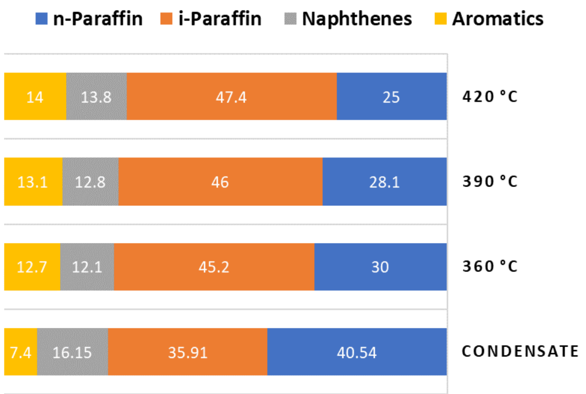

Figure 6. Composition of condensate vs products at different temperatures over Zn/ZSM5.

over ZSM5 at 350 °C using a pulse reaction system. Ethanol induces n-hexane conversion via a bimolecular hydride transfer resulting in intermediate products (ethoxy groups). As it is seen from Table 1 and Figure 6 the iso-paraffin increase from 35.9 in gas condensate to 47.4 in product as well as n-paraffin decrease from 40.5 in feed to 25 in product. This is attributed to isomerization reaction and presence of ethanol with feed.

$$C_6H_{14} + CH_3CH_2OH \rightarrow C_6H_{13}\,CH_2CH_3 + H_2O \quad (4)$$

### 3.3.2 Effects of Zn loading on the composition and the methylation process

Test runs using ZSM5 (Si/Al 80) and Zn/ZSM5 (Si/Al 80) were conducted in a fixed bed reactor. To demonstrate the impact of the Zn loading over ZSM5 on the composition and characteristics of the obtained product, conditions were set to be at varying temperatures in the range of (360 - 420 °C) at 30 °C intervals, pressure = 5 bar and feedstock flow rate was 1.2 $h^{-1}$). Based on selected metals, enhancement in term of stability and selectivity towards aromatics and BTX can be expected. Zn is the focus for this gas condensate feedstock with alcohol as a co-feed. Due to its improved dehydrogenation abilities, success with ethanol dehydro-aromatization, and an oxidized active phase that enables the avoidance of time-consuming reactivation [45–47].

Figures 5 and 6 show the improvement effect of adding 2% ZnO to ZSM5. The performance immediately increases which is attributed to Zn in the activation of ethanol and the dehydrogenation of paraffinic components. Keeping in mind, the produced high-octane gasoline is measured after considering the selectivity and yield of iso- and aromatic paraffins.

Figure 5 shows the components statistics of n-paraffin, i-paraffin, naphthenes, and aromatics on ZSM5. At the sequence of temperature ramping, it is seen the i-paraffin has increased by 26% from 35.91 to different percentages where the maximum value 45.4 spotted at 420 °C. The change in naphthenes content is obvious with a dehydrogenation percent of 24.4%. For the aromatics the enhancement percent was 46%. However, Figure 6 displays a promising approach with 32% in i-paraffin and 89.9 % in aromatics where the naphthenes conversion was 14.5%.

This demonstrates that after Zn loading the aromatic content significantly rises. Overall, it is worth noting that the RON of the product increases by 21.6 points to a greater degree with ZSM5 while the RON of the product increases by 28.5 points with Zn/ZSM5. This is because when processing gas condensate with ethanol as a co-feed, both the aromatization and isomerization reactions are in the active pass.

### 3.3.3 Analyses of the effects of temperature on the composition and characteristics of the methylation process

To demonstrate the temperature influence on the methaforming process, the compositions and characteristics of the resulting gasoline product were carried out in multi-purpose unit (MPU) in fixed bed reactor over ZSM5 (Si/Al 80), Zn/ZSM5 (Si/Al 80) in the range of 360 °C to 420 °C. The temperature step is 30 °C for each experiment at a constant pressure of 5 bar, LHSV 1.2 and 2 $h^{-1}$. The reaction temperature is a very important operating parameter for catalytic gas condensate aromatization and

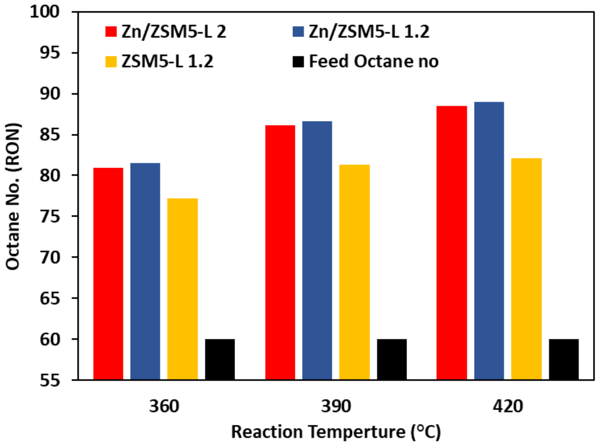

Figure 7. RON results for ZSM5 and Zn/ZSM5 at different temperatures at a constant LHSV.

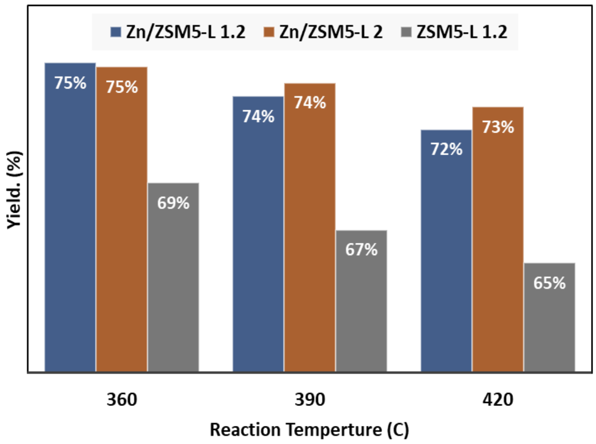

Figure 8. Yield results for ZSM5 and Zn/ZSM5 at different temperatures at a constant LHSV.

isomerization and therefore getting high octane number of product gasoline. Also, RON depends on dehydrogenation of naphthenes and dehydrocyclization or isomerization of n-paraffins. However, raising reaction temperature leads to hydrocracking reactions then causes an increase coke formation on the surface of catalyst [48,49].

Figure 7 demonstrates the RON for each catalyst with constraining factors of the methaorming process. For ZSM5 (Si/Al 80) catalyst, the increasing the temperature of the process increases octane obtained for range (77.2-82.1). At higher temperatures, the major group in the product is iso-paraffin and more effective than aromatics group. Isomerization and aromatization reactions are favored leading to higher-octane number. Meanwhile, for Zn/ZSM-5 (Si/Al: 80) catalyst, the increasing the temperature of the methaforming process increases octane obtained for range (81.5-89). At higher temperatures, aromatization reactions are favored especially for Zn/ZSM5 (Si/Al: 80) leading to the production of a higher volume of aromatics and iso-paraffin in the product and hence higher-octane number. The influence of the Zinc impregnation on ZSM5 is very significant with an increase in the process temperature from 360 °C to 420 °C.

Figure 8 displays the yield of gasoline products in the methaforming process decreases from 69 wt% to 65 wt% for ZSM5 (Si/Al: 80), and from 75 wt% to 72 wt% for Zn/ZSM5 (Si/Al: 80). The effect of cracking reactions is considered as a culprit in in the formation of gaseous products that decrease the product yield as process temperature rises.

## 4. Conclusions

In this work, 2 wt% of Zn was loaded on ZSM5 using the impregnation method aiming to convert the stable gas condensate to high grad gasoline. with the Zn/ZSM was compared with a benchmark ZSM in a fixed bed reactor. The feed is composed of 15 vol% of ethanol and 85 vol% is gas condensates. FT-IR, XRD, FESEM, and TEM analyses were conducted to characterize ZSM5 and Zn/ZSM5 to explain both catalyst performance. Our results have shown the Zn/ZSM5 prefers the aromatization pathway with ~90% increase and ~32% in isomerization pathway. However, ZSM5 does prefer the naphthenes dehydrogenation. Overall, the RON has increased from 60.5 to 89 on Zn/ZSM5 where 60.5 to 82 on ZSM5. Using alcohol as a co-feed in methaforming process increase the selectivity towards toluene and limit the production of benzene. We attribute such performance of Zn/ZSM5 for the good dispersion that bestowed tremendous active surface area. Further investigation is needed to explain why aromatics products increased on Zn/ZSM.

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## CRediT Author Statement

Mohammed A. Salim: Writing – original draft, Software, Methodology, Formal analysis, Resources, Investigation, Conceptualization, Visualization, Project administration, Funding acquisition. Usama A. Saed: Review and editing, Visualization, Validation, Supervision, Investigation, Conceptualization.

## References

[1] Speight, J.G. (2011). Production of Hydrocarbons from Natural Gas. In: *Handbook of Industrial Hydrocarbon Processes*. Elsevier, pp. 127–162. DOI: 10.1016/b978-0-7506-8632-7.10004-0.

[2] Shoaib, A.M., Bhran, A.A., Awad, M.E., El-Sayed, N.A., Fathy, T. (2018). Optimum operating conditions for improving natural gas dew point and condensate throughput. *Journal of Natural Gas Science and Engineering*, 49, 324–330. DOI: 10.1016/j.jngse.2017.11.008.

[3] Hassan, A., Mahmoud, M., Al-Majed, A., Alawi, M.B., Elkatatny, S., BaTaweel, M., Al-Nakhli, A. (2019). Gas condensate treatment: A critical review of materials, methods, field applications, and new solutions. *Journal of Petroleum Science and Engineering*, 177, 602–613. DOI: 10.1016/j.petrol.2019.02.089.

[4] Hammadi, A.N., Shakir, I.K. (2020). Enhancement the octane number of light naphtha by adsorption process. *AIP Conference Proceedings*, 2213, 020044. DOI: 10.1063/5.0000129.

[5] Asgari, A., Dianatirad, M., Ranjbaran, M., Sadeghi, A.R., Rahimpour, M.R. (2014). Methanol treatment in gas condensate reservoirs: A modeling and experimental study. *Chemical Engineering Research and Design*, 92(5), 876–890. DOI: 10.1016/j.cherd.2013.08.015.

[6] Kamari, A., Sattari, M., Mohammadi, A.H., Ramjugernath, D. (2015). Reliable method for the determination of surfactant retention in porous media during chemical flooding oil recovery. *Fuel*, 158, 122–128. DOI: 10.1016/j.fuel.2015.05.013.

[7] Ramirez, J.A., Brown, R.J., Rainey, T.J. (2017). Liquefaction biocrudes and their petroleum crude blends for processing in conventional distillation units. *Fuel Processing Technology*, 167, 674–683. DOI: 10.1016/j.fuproc.2017.08.022.

[8] Heting, H., Baojia, H., Yiwen, H., Xing, L.I., Hui, T. (2017). Condensate origin and hydrocarbon accumulation mechanism of the deepwater giant gas field in western South China Sea : A case study of Lingshui 17-2 gas field in Qiongdongnan Basin. *Petroleum Exploration and Development*, 44(3), 409–417. DOI: 10.1016/S1876-3804(17)30047-2.

[9] Khomyakov, I.S., Gerasina, T.A. (2019). Refinement of Gas Condensate Straight-Run Gasoline on MFI-Type Zeolites Modified with Binary Compounds. *IOP Conference Series: Earth and Environmental Science*, 272(2), 022145. DOI: 10.1088/1755-1315/272/2/022145.

[10] Christensen, E., Yanowitz, J., Ratcli, M., Mccormick, R.L., (2011). Renewable Oxygenate Blending Effects on Gasoline Properties. *Energy & Fuels*, 25(10), 4723–4733. DOI: 10.1021/ef2010089.

[11] Abdellatief, T.M.M., Ershov, M.A., Kapustin, V.M. (2020). New recipes for producing a high-octane gasoline based on naphtha from natural gas condensate. *Fuel*, 276, 118075. DOI: 10.1016/j.fuel.2020.118075.

[12] Primo, A., Garcia, H. (2014). Zeolites as catalysts in oil refining. *Chemical Society Reviews*, 43(22), 7548–7561. DOI: 10.1039/c3cs60394f.

[13] Choudary, N.V., Newalkar, B.L. (2011). Use of zeolites in petroleum refining and petrochemical processes: Recent advances. *Journal of Porous Materials*, 18(6), 685–692. DOI: 10.1007/s10934-010-9427-8.

[14] Hajimirzaee, S., Mehr, A.S., Kianfar, E. (2020). Modified ZSM-5 Zeolite for Conversion of LPG to Aromatics Modified ZSM-5 Zeolite for Conversion of LPG to Aromatics. *Polycyclic Aromatic Compounds*, 42(5), 2334–2347. DOI: 10.1080/10406638.2020.1833048.

[15] Erofeev, V.I., Medvedev, A.S., Khomyakov, I.S., Erofeeva, E. V. (2013). Conversion of gas-condensate straight-run gasolines to high-octane gasolines over zeolite catalysts modified with metal nanopowders. *Russian Journal of Applied Chemistry*, 86(7), 979–985. DOI: 10.1134/S1070427213070069.

[16] Nabgan, W., Rashidzadeh, M., Nabgan, B. (2018). The catalytic naphtha reforming process : hydrodesulfurization, catalysts and zeoforming. *Environmental Chemistry Letters*, 16, 507–522. DOI: 10.1007/s10311-018-0707-x.

[17] Belinskaya, N., Altynov, A., Bogdanov, I., Popok, E., Kirgina, M., Simakov, D.S.A. (2019). Production of Gasoline Using Stable Gas Condensate and Zeoforming Process Products as Blending Components. *Energy and Fuels*, 33(5), 4202–4210. DOI: 10.1021/acs.energyfuels.9b00591.

[18] Nabgan, W., Nabgan, B., Amran, T., Abdullah, T., Wijayanuddin, M. (2021). Development of zeolites for zeoforming reaction of naphtha. *Malaysian Journal of Catalysis*, 5, 10–18.

[19] Kirgina, M., Belinskaya, N., Altynov, A., Bogdanov, I., Temirbolat, A. (2020). Transformations of stable gas condensate hydrocarbons into high-octane gasoline components over ZSM-5 zeolite catalyst. *Journal of Natural Gas Science and Engineering*, 84, 103605. DOI: 10.1016/j.jngse.2020.103605.

[20] Saxena, S.K., Viswanadham, N., Al-muhtaseb, A.H. (2013). Enhanced production of high octane gasoline blending stock from methanol with improved catalyst life on nano-crystalline ZSM-5 catalyst. *Journal of Industrial and Engineering Chemistry*, 20(5), 2876–2882. DOI: 10.1016/j.jiec.2013.11.021.

[21] Wan, Z., Li, G.K., Wang, C., Yang, H., Zhang, D. (2018). Effect of reaction conditions on methanol to gasoline conversion over nano-crystal ZSM-5 zeolite. *Catalysis Today*, 314, 107–113. DOI: 10.1016/j.cattod.2018.01.017.

[22] Bi, Y., Wang, Y., Chen, X., Yu, Z., Xu, L. (2014). Methanol aromatization over HZSM-5 catalysts modified with different zinc salts. *Chinese Journal of Catalysis*, 35(10), 1740–1751. DOI: 10.1016/S1872-2067(14)60145-5.

[23] Jarvis, J., Wong, A., He, P., Li, Q., Song, H. (2018). Catalytic aromatization of naphtha under methane environment: Effect of surface acidity and metal modification of HZSM-5. *Fuel*, 223, 211–221. DOI: 10.1016/j.fuel.2018.03.045.

[24] Godwin, G., Abdulazeez, O., Atta, Y., Mukhtar, B., Yakubu, B. (2020). Highly selective and stable Zn–Fe/ZSM-5 catalyst for aromatization of propane. *Applied Petrochemical Research*, 10, 55–65. DOI: 10.1007/s13203-020-00245-9.

[25] Shim, H., Hong, J., Ha, K.S. (2022). Efficient Utilization of Hydrocarbon Mixture to Produce Aromatics over Zn/ZSM-5 and Physically Mixed with ZSM-5. *Catalysts*, 12(5), 501. DOI: 10.3390/catal12050501.

[26] Vichaphund, S., Aht-Ong, D., Sricharoenchaikul, V., Atong, D. (2015). Production of aromatic compounds from catalytic fast pyrolysis of Jatropha residues using metal/HZSM-5 prepared by ion-exchange and impregnation methods. *Renewable Energy*, 79(1), 28–37. DOI: 10.1016/j.renene.2014.10.013.

[27] Ramos, R., García, A., Botas, J.A., Serrano, D.P. (2016). Enhanced Production of Aromatic Hydrocarbons by Rapeseed Oil Conversion over Ga and Zn Modified ZSM-5 Catalysts. *Industrial and Engineering Chemistry Research*, 55(50), 12723–12732. DOI: 10.1021/acs.iecr.6b03050.

[28] Kianfar, E., Hajimirzaee, S., mousavian, S., Mehr, A.S. (2020). Zeolite-based catalysts for methanol to gasoline process: A review. *Microchemical Journal*, 156, 104822. DOI: 10.1016/j.microc.2020.104822.

[29] Al-Kandari, H., Al-Kandari, S., Al-Kharafi, F., Katrib, A. (2009). Molybdenum-Based Catalysts for Upgrading Light Naphtha Linear Hydrocarbon Compounds. *Energy & Fuels*, 23(12), 5737–5742. DOI: 10.1021/ef900617d.

[30] Ogunronbi, K.E., Al-Yassir, N., Al-Khattaf, S. (2015). New Insights into Hierarchical metal-containing Zeolites; Synthesis and Kinetic Modeling of Mesoporous Gallium-containing ZSM-5 for Propane Aromatization. *Journal of Molecular Catalysis A: Chemical*, 406, 1–18. DOI: 10.1016/j.molcata.2015.05.005.

[31] Dauda, I.B., Yusuf, M., Gbadamasi, S., Bello, M., Atta, A.Y., Aderemi, B.O., Jibril, B.Y. (2020). Highly Selective Hierarchical ZnO/ZSM-5 Catalysts for Propane Aromatization. *ACS Omega*, 5(6), 2725–2733. DOI: 10.1021/acsomega.9b03343.

[32] Wang, X., Gao, X., Dong, M., Zhao, H., Huang, W. (2015). Production of gasoline range hydrocarbons from methanol on hierarchical ZSM-5 and Zn/ZSM-5 catalyst prepared with soft second template. *Journal of Energy Chemistry*, 24(4), 490–496. DOI: 10.1016/j.jechem.2015.06.009.

[33] Niu, X., Gao, J., Wang, K., Miao, Q., Dong, M., Wang, G., Fan, W., Qin, Z., Wang, J. (2017). Influence of crystal size on the catalytic performance of H-ZSM-5 and Zn/H-ZSM-5 in the conversion of methanol to aromatics. *Fuel Processing Technology*, 157, 99–107. DOI: 10.1016/j.fuproc.2016.12.006.

[34] Liu, M., Cui, T., Guo, X., Li, J., Song, C. (2021). Stable Zn@ZSM-5 catalyst via a dry gel conversion process for methanol-to-aromatics reaction. *Microporous and Mesoporous Materials*, 312, 110696. DOI: 10.1016/j.micromeso.2020.110696.

[35] Sims, S., Adebayo, A., Lobichenko, E., Lishchiner, I., Malova, O., Us, S. (2017). *Methaforming: Novel Process for Producing High-Octane Gasoline from Naphtha and Methanol at Lower CAPEX and OPE*X. URL: https://static1.squarespace.com/static/58a254c3c534a53002f008a3/t/58b0f1be579fb3b2015edfc0/1487991236692/NGTS%2BAFPM%2BPaper%2B12.1.2017.pdf (24 Feb 2023).

[36] Soltanali, S., Mohaddecy, S.R.S., Mashayekhi, M., Rashidzadeh, M. (2020). Catalytic upgrading of heavy naphtha to gasoline: Simultaneous operation of reforming and desulfurization in the absence of hydrogen. *Journal of Environmental Chemical Engineering*, 8(6), 104548. DOI: 10.1016/j.jece.2020.104548.

[37] Paquin, F., Rivnay, J., Salleo, A., Stingelin, N., Silva, C. (2015). Multi-phase semicrystalline microstructures drive exciton dissociation in neat plastic semiconductors. *Journal of Materials Chemistry C*, 3, 10715–10722. DOI: 10.1039/C5TC02043C.

[38] Rostamizadeh, M., Yaripour, F., Hazrati, H. (2018). Ni-doped high silica HZSM-5 zeolite (Si/Al = 200) nanocatalyst for the selective production of olefins from methanol. *Journal of Analytical and Applied Pyrolysis*, 132, 1–10. DOI: 10.1016/j.jaap.2018.04.003.

[39] Omar, B.M., Bita, M., Louafi, I., Djouadi, A. (2018). Esterification process catalyzed by ZSM-5 zeolite synthesized via modified hydrothermal method. *MethodsX*, 5, 277–282. DOI: 10.1016/j.mex.2018.03.004.

[40] Oseke, G.G., Atta, A.Y., Mukhtar, B., El-Yakubu, B.J., Aderemi, B.O. (2021). Increasing the catalytic stability of microporous Zn/ZSM-5 with copper for enhanced propane aromatization. *Journal of King Saud University - Engineering Sciences*, 33(8), 531–538. DOI: 10.1016/j.jksues.2020.07.014.

[41] Kianfar, E., Salimi, M., Pirouzfar, V., Koohestani, B. (2018). Synthesis of modified catalyst and stabilization of CuO/NH4-ZSM-5 for conversion of methanol to gasoline. *International Journal of Applied Ceramic Technology*, 15(3), 734–741. DOI: 10.1111/ijac.12830.

[42] Espindola, J.S., Gilbert, C.J., Perez-Lopez, O.W., Trierweiler, J.O., Huber, G.W. (2020). Conversion of furan over gallium and zinc promoted ZSM-5: The effect of metal and acid sites. *Fuel Processing Technology*, 201, 106319. DOI: 10.1016/j.fuproc.2019.106319.

[43] Long, H., Jin, F., Xiong, G., Wang, X. (2014). Effect of lanthanum and phosphorus on the aromatization activity of Zn/ZSM-5 in FCC gasoline upgrading. *Microporous and Mesoporous Materials*, 198, 29–34. DOI: 10.1016/j.micromeso.2014.07.016.

[44] Thommes, M., Kaneko, K., Neimark, A. V., Olivier, J.P., Rodriguez-Reinoso, F., Rouquerol, J., Sing, K.S.W. (2015). Physisorption of gases, with special reference to the evaluation of surface area and pore size distribution (IUPAC Technical Report). *Pure and Applied Chemistry*, 87(9–10), 1051–1069. DOI: 10.1515/pac-2014-1117.

[45] Tshabalala, T.E., Scurrell, M.S. (2015). Aromatization of n-hexane over Ga, Mo and Zn modified H-ZSM-5 zeolite catalysts. *Catalysis Communications*, 72, 49–52. DOI: 10.1016/j.catcom.2015.06.022.

[46] Jarvis, J.S., Harrhy, J.H., He, P., Wang, A., Liu, L., Song, H. (2019). Highly selective aromatization and isomerization of N-alkanes from bimetallic Pt-Zn nanoparticles supported on a uniform aluminosilicate. *Chemical Communications*, 55(23), 3355–3358. DOI: 10.1039/c9cc00338j.

[47] Mahale, R.S., Parikh, P.A. (2020). Aromatization of n-hexane: Synergism afforded by C1 - C3 alcohols. *Chemical Engineering Science*, 217, 115519. DOI: 10.1016/j.ces.2020.115519.

[48] Elsayed, H.A., Menoufy, M.F., Shaban, S.A., Ahmed, H.S., Heakal, B.H. (2017). Optimization of the reaction parameters of heavy naphtha reforming process using Pt-Re/Al2O3 catalyst system. *Egyptian Journal of Petroleum*, 26(4), 885–893. DOI: 10.1016/j.ejpe.2015.03.009.

[49] Yusuf, A.Z., John, Y.M., Aderemi, B.O., Patel, R., Mujtaba, I.M. (2019). Modelling, simulation and sensitivity analysis of naphtha catalytic reforming reactions. *Computers and Chemical Engineering*, 130, 106531. DOI: 10.1016/j.compchemeng.2019.106531.