



Direct catalytic cracking of crude oil-to-chemicals: Impact of steam catalytic cracking on petrochemicals yield

Aaron C. Akah^{a,*}, Emad Al-Shafei^{b,*}, Qi Xu^a, Mansour AlHerz^a, Ziyauddin S. Qureshi^{c,d,*}, M.Abdul Bari Siddiqui^c, Abdullah Aitani^{b,e}

^a Fuels & Chemicals Division, Research & Development Center, Saudi Aramco, Dhahran, Saudi Arabia

^b Catalyst Center of Excellence, Research & Development Center, Saudi Aramco, Dhahran, Saudi Arabia

^c Interdisciplinary Research Center for Refining and Advanced Chemicals, King Fahd University of Petroleum & Minerals, Dhahran, Saudi Arabia

^d Chemistry Department, King Fahd University of Petroleum & Minerals, Dhahran, Saudi Arabia

^e Chemical Engineering Department, King Fahd University of Petroleum & Minerals, Dhahran, Saudi Arabia

ARTICLE INFO

Keywords:

Direct crude oil-to-olefin
One-step crude oil-to-chemical
Steam catalytic cracking
ZSM-5
ECAT

ABSTRACT

The direct catalytic cracking of crude oil to valuable petrochemicals has drawn significant attention due to its potential to streamline refinery processes as a way of reducing the carbon footprint of petrochemicals production. Petrochemicals like light olefins and BTX are essential feedstocks for the petrochemical industry. This study extends the scope of FCC technology by exploring the direct catalytic cracking of Arabian Extra Light (AXL) crude oil, using spray dried FCC-ZSM-5 modified with La and Ce oxides, in non-steam and steam conditions. The performance of the catalysts was evaluated based on the yield and selectivity of light olefins and BTX. The yield of light olefins for thermal cracking, catalytic cracking and steam catalytic cracking at 675 °C was 36.0 wt%, 43.3 wt% and 51.5 wt%, respectively. The study demonstrated that steam catalytic cracking using FCC-ZSM-5 (impregnated with 1 %La and 1 %Ce oxides) offered significant advantage over non-steam catalytic cracking. The presence of steam enhanced the conversion and shifts product distribution towards light olefins. Steam also modified the cracking mechanism by minimizing secondary reactions, reducing coke formation, and enhancing selectivity toward olefins. The findings in this study contribute to the development of efficient catalyst and process for the direct conversion of crude oil into high-value petrochemicals.

1. Introduction

The refining industry plays a crucial role in the supply of transportation fuels and petrochemicals by transforming raw crude into a vast array of essential products. As a result of global growth in population and urbanization, the demand for petrochemicals is forecast to increase, and more crude oil is expected to be directed towards the production of petrochemicals [1]. Light olefins (ethylene and propylene) are mainly produced by the energy-intensive steam cracking of naphtha, dehydrogenation of paraffins and as byproducts from the fluid catalytic cracking (FCC) of vacuum gas oil (VGO). Benzene, toluene, and xylenes (BTX) aromatics are mainly produced by catalytic reforming of naphtha and byproducts from the steam cracking of naphtha. Light olefins, particularly C₂-C₄ compounds, are the backbone of the petrochemical industry [2] since they serve as raw materials for the production of polymers such

as polyethylene and polypropylene, as well as styrene, cumene-phenol, and methyl tert-butyl ether (MTBE). The growing global demand for these feedstocks has driven innovations in catalytic cracking technologies, with the aim of maximizing their yield and quality [3].

The direct conversion of whole crude oil into high value light olefins and BTX aromatics has gained considerable interest in recent years [1, 2]. This innovative approach offers an opportunity to streamline refinery operations by bypassing intermediate steps and producing high-value petrochemical feedstocks directly from crude oil [4,5]. Furthermore, this direct conversion route offers enhanced feedstock flexibility for the petrochemical sector, potentially reducing reliance on specific refinery streams.

While the majority of light olefins, such as ethylene and propylene, are currently produced via the well-established steam cracking process, this technology appears to be approaching a plateau, where further

* Corresponding authors.

E-mail addresses: aaron.akah@aramco.com (A.C. Akah), emadnaji@gmail.com, emad.alshafei@conscatsys.com (E. Al-Shafei), zqureshi@kfupm.edu.sa (Z.S. Qureshi).

<https://doi.org/10.1016/j.cej.2025.100794>

substantial improvements in product yield and selectivity are becoming increasingly challenging to achieve [6]. For instance, increasing ethylene yields typically requires elevating the cracking temperature; however, this is severely constrained by the high-temperature limitations of the cracking tube metallurgy and the tendency for rapid coke formation within the cracking coils. The FCC is the second source of light olefins and it provides an alternative route to steam cracking with the use of lower activation energy for C—C bonds rupture. Consequently, the temperatures of FCC processes are lower than those for steam crackers. However, the FCC process is specifically designed to upgrade low-value feeds such as VGO and residues to produce predominantly gasoline, with light olefins as byproducts. The feed profile for FCC has been changing from narrow range boiling feeds (such as VGO) to that of a wide range boiling feed, such as whole crude [2,7,8].

Several studies have employed zeolite-based catalysts in steam-assisted catalytic cracking to enhance both the performance and durability of the catalysts during the conversion of paraffinic hydrocarbons into valuable light olefins. Corma et al [9] examined the catalytic cracking of naphtha, rich in paraffins, over ZSM-5 zeolites in the presence of steam, reporting a notable reduction in coke deposition and a lower yield of methane [9,10]. Steam was found to improve the olefin selectivity while simultaneously limiting the undesirable side reactions, including aromatization and subsequent coke precursors, as discussed in prior work by Corma et al [9–11]. Consequently, steam promotes monomolecular cracking mechanisms that favor light olefin production. Additional investigations [12,13] involving phosphorus-modified ZSM-5 catalysts have further confirmed that increasing the steam-to-hydrocarbon ratio during hexane cracking significantly reduces coke formation and extends catalyst time-on-stream, thereby improving overall catalytic efficiency.

Steam catalytic cracking (SCC), an innovative hybrid process, strategically integrates the inherent advantages of both catalytic cracking and traditional steam cracking [14,15] with the aim of significantly increasing the yields of light olefins, while simultaneously expanding feedstock flexibility. SCC typically operates at intermediate temperatures, lower than those typical of steam cracking but higher than those employed in conventional FCC processes. As a result, SCC has emerged as a particularly promising and actively investigated technique for enhancing the direct conversion of crude oil into valuable olefins and aromatics [3]. The introduction of steam into the catalytic cracking environment provides several key advantages over purely catalytic approaches, especially facilitating a series of β -scission reactions that preferentially favor the formation of light olefins [4]. By minimizing the secondary reactions such as cyclization, hydrogenation and alkylation, steam helps to promote the yield of olefins. In addition, coke formation is a significant issue in conventional catalytic cracking and crude oil as feedstock, as it deactivates catalysts and reduces process efficiency [16]. Steam potentially reduces the deposition of carbonaceous materials by reacting with coke precursors and enhancing catalyst regeneration [10]. Under SCC conditions, the utilization of steam minimizes secondary reactions that would otherwise convert valuable olefins into less desirable products, such as dry gas or heavy aromatics, thus enhancing the selectivity of the process towards high-value chemicals. Additionally, the presence of steam improves heat transfer characteristics within the reactor and mitigates localized overheating, enabling more uniform and efficient cracking across the catalyst bed [17].

The selection and design of the catalyst play a pivotal role in the SCC process, profoundly influencing both the product distribution and the optimal operating conditions. Given the inherent characteristics of the SCC process, an effective catalyst should exhibit high activity and selectivity specifically for the production of light olefins, while concurrently minimizing the formation of less desirable byproducts such as hydrogen, methane, and coke. Moreover, the catalyst must possess exceptional hydrothermal stability to withstand the steam-rich environment and robust mechanical strength to endure the process conditions [18]. To mitigate the problem of catalyst deactivation, rare earths

are used to improve the hydrothermal stability of catalysts [18–25]. Lanthanum (La) and cerium (Ce) are the two main rare earths used in FCC catalysts [26–29]. These metals contribute to stabilize the zeolite structure under hydrothermal conditions by limiting the extent of dealumination. Other metals have been used to impact the catalytic performance of zeolites to improve product selectivity. As illustrated in the study by Qu et al [30,31] and Zhang et al [32], introducing certain metals can modify the number and strength of Bronsted and Lewis acids which are crucial for catalytic cracking reactions. In a study on the effect of Ni loading in ZSM-5 on catalytic cracking of polyethylene, Zhang et al [32] showed that as the metallic nickel loading increased the concentration of BTX aromatics in the pyrolysis oil also increased. There was also the corresponding increase in hydrogen production.

The incorporation of ZSM-5 in SCC catalysts has been widely studied and demonstrated to significantly enhance the yield of valuable light olefins [14,33–36]. ZSM-5 is a promising catalyst for steam catalytic cracking of crude oil due to its unique structure, high surface area, and shape-selective properties, which enhance cracking reactions and produce a high yield of light olefins aromatics [37]. The internal pores, high surface area, and shape-selective properties of ZSM-5 make it effective for cracking and aromatization reactions, particularly for light hydrocarbons [38]. ZSM-5 was chosen as the active catalyst component to further enhance light olefin production, as it is more effective than other zeolite catalysts in maximizing light olefin yields. ZSM-5 has a unique ten-membered ring pore structure, which allows it to selectively catalyze reactions of smaller molecules [39]. This means it favors the cracking of larger molecules into smaller, more valuable products like light olefins. ZSM-5 has a high surface area, providing a large number of active sites for cracking reactions [37,40]. This leads to higher conversion rates and increased yields of desired products.

The main objective of this research endeavor is to investigate and elucidate the impact of both steam introduction and the utilization of a specifically formulated metal-modified ZSM-5 catalyst on the direct conversion of crude oil, with a particular emphasis on maximizing the yields of light olefins and BTX aromatics as the primary products. This study extends the boundaries of conventional FCC technology by exploring the direct catalytic cracking of crude oil utilizing spray-dried lanthanum (La) and cerium (Ce) oxide modified ZSM-5 catalysts under both non-steam and steam-rich conditions. The performance of the synthesized catalysts is evaluated based on the resulting yield and selectivity towards light olefins and BTX aromatics. The findings of this investigation are expected to contribute valuable insights towards the development of more efficient catalytic systems and optimized process conditions for the direct and selective conversion of crude oil into high-value petrochemicals. This approach offers a more sustainable alternative to the high-temperature steam cracking process and allows for greater control over the composition of the product stream, particularly the yield of valuable light olefins like ethylene and propylene. Steam catalytic cracking of crude oil can contribute to a more sustainable approach to petrochemical production by reducing energy consumption and minimizing greenhouse gas emissions compared to conventional steam cracking.

2. Experimental

2.1. Material

Commercial fluid catalytic cracking (FCC) equilibrium catalyst (ECAT) and in-house formulated ZSM-5 catalyst (FCC-ZSM-5) were used for catalytic cracking evaluation. FCC-ZSM-5 was formulated using ZSM-5 ($\text{SiO}_2/\text{Al}_2\text{O}_3$: 30 CBV3024E, Zeolyst International), alumina binder Catapal B (Sasol), kaolin clay (Fisher), formic acid (70 wt%, Fisher), phosphoric acid (85wt %, Fisher), lanthanum(III) nitrate hexahydrate (Merck) and cerium(III) nitrate hexahydrate (Merck).

Arabian Extra Light (AXL) crude oil was utilized for direct conversion to chemicals, and its physical and distillation properties are shown in

Table 1
Crude oil chemicals, physical and distillation properties.

Property	Value
Gravity, ° API	39.3
Density at 15 °C, kg/m ³	828
Sulfur (wt. %)	1.6
Vanadium (ppm)	2.7
Nickel (ppm)	<1
Microcarbon residue (wt. %)	2.2
Kinematic Viscosity, @ 21 °C (cSt)	5.8
Elemental analysis (wt. %)	
Carbon	84.3
Hydrogen	12.6
Nitrogen	0.7
Simulated distillation(°C)	
Initial boiling point	25
50 %	287
Final boiling point	577
Distillation cuts (wt. %)	
Naphtha (C ₅ –221 °C)	40.8
Middle distillates (221–343 °C)	26.3
Heavy oil (343 °C+)	32.9
UOP K-Factor	12.0

Table 1 below.

2.2. Catalyst preparation

ZSM-5 was impregnated with 1 % La₂O₃ and 1 % CeO₂ used for catalyst formulations. The formulated catalysts were prepared utilizing the Mobile Minor® R&D Spray Dryer using the following procedure: 300 g of kaolin clay powder was mixed with deionized water to make a kaolin slurry, made-up of 30 % solids. In a separate step, 100 g of La₂O₃ and CeO₂ ZSM-5 were made into a slurry using deionized water and stirred for 10 mins. The zeolite slurry was added to the kaolin slurry and mixed for a further 5 mins. In a separate step, a slurry of 100 g alumina binder (Catapal B alumina) was made by mixing with deionized water and peptized by adding 8.24 g concentrated formic acid (70 wt%). The peptized alumina Catapal B binder slurry was mixed for 15 mins and added to the zeolite-kaolin slurry, followed by further mixing for 10 mins. The catalyst slurry containing 30 % solids was then spray-dried to generate particles of 20–100 µm. The spray dried catalyst was then calcined in the oven at 550 °C for 6 h. The obtained catalyst denoted FCC-ZSM-5 was then steam deactivated and tested in a fixed bed reactor for catalytic cracking of crude oil. The synthesis of FCC-ZSM-5(P) followed the same procedure described above, with the exception that no metals (La or Ce) were incorporated.

2.3. Catalyst characterization

The synthesized FCC zeolite catalysts were characterized using X-ray diffraction (XRD) utilizing Rigaku X-ray diffractometer model Miniflex II. The XRD was equipped with Cu K α radiation at $\lambda = 1.5406 \text{ \AA}$, 30 kV and a current of 15 mA. Furthermore, a XRD scan 2 theta angles between 5° and 55° was utilized at a speed of 2° min⁻¹ and a step size of 0.02°. The textural properties of catalysts were characterized using N₂-adsorption, using a Micromeritics ASAP 2420 instrument.

The scanning electron microscopy (SEM) was utilized to determine the morphology of the spray dried FCC catalysts, using a Jeol CM-7000 scanning electron microscope. SEM provides valuable insights into the morphology, FCC particle size, and surface structure of FCC-ZSM-5 and ECAT catalysts. This information is needed to understand the catalyst morphology for catalytic performance for crude oil cracking into light olefins under both steam and non-steam conditions. SEM characterization complements other analytical techniques by revealing surface roughness, particle size distribution, and the accessibility of active components, which collectively influence olefins yields and overall catalyst efficiency. The FCC zeolite acidity was analyzed by NH₃

temperature-programmed desorption (NH₃-TPD) using Micromeritics Autochem 2910.

2.4. Steam catalytic cracking of AXL crude

Fig. 1 presents the schematics of the fixed-bed continuous flow reactor used in the steam catalytic cracking of AXL crude oil. The reactor system comprises a feed section, a pre-heating section, a once-through reactor, and a separator section. The feed section includes two metering pumps for the delivery of AXL crude oil and water, as well as a mass flow meter to measure the nitrogen gas input. In the pre-heating section, water was heated to 250 °C and mixed with nitrogen prior to entering the reactor tube. A three-zone electrical furnace was utilized to heat the Hastelloy reactor tube, measuring 40 cm in length and 1.3 cm in internal diameter. A stainless-steel tube was heated by an electrical furnace in the pre-heater zone. AXL crude oil was introduced at the upper section of the reactor and mixed with steam in the upper two-thirds of the reactor tube prior to entering the catalyst bed. Prior to the reaction, catalysts were steam deactivated at 810 °C for 6 h. After steam deactivation, 1 g of catalyst with a mesh size of 30–40 was positioned at the center of the reactor tube, atop quartz wool, and inserted into the reactor and purged with nitrogen. The height of catalyst bed measured 2 cm as shown in Table 2. The system was heated to the desired reaction temperature at atmospheric pressure before initiating the cracking of the AXL feed. The performance of crude oil conversion was investigated under three conditions. (i) Thermal cracking (without catalyst), (ii) steam catalytic cracking using ECAT (equilibrium catalyst), FCC with ZSM-5 (P) without metal modification, and (iii) catalytic cracking and steam catalytic cracking with FCC-ZSM-5 impregnated with 1 % La and 1 % Ce oxides.

In a typical cracking experiment, 2.0 g/h of AXL crude oil, 1.0 g/h of water, and 3.9 l/h of nitrogen were utilized. The catalysts were evaluated at atmospheric pressure, 600–675 °C and a residence time of 10.0 s as shown in Table 2. The gaseous feed rate was converted to mol/h using the molecular weight and to cm³/h by applying the gas constant. The space velocity was calculated by dividing the total of the oil feed rate and water feed rate by the catalyst weight. The experiment was performed continuously for 4 h following the attainment of a steady state (40–60 min). At the end of the run, nitrogen was allowed to flow for 30 mins.

The reaction products, consisting of liquid and gas fractions, were passed through a cooled liquid/gas separator. The liquid fraction was collected and analyzed to determine petroleum fractions using the Simulated Distillation (SimDis) method in accordance with ASTM D2887, utilizing a Shimadzu GC 2010 Plus gas chromatograph. The gaseous products were analyzed online using a Micro GC FUSION® Gas Analyzer from INFICON, equipped with a thermal conductivity detector, and programmed according to the ASTM D7833 method for refinery gas analysis.

The coke content in the catalysts was analyzed using the EMIA-220 V Horiba Carbon-Sulfur Analyzer Model. In the furnace, about 10–20 mg of catalyst (with tungsten added as a combustion promoter) was burned at high temperatures. The CO₂ produced was measured using an infrared analyzer and expressed as a percentage of the catalyst's weight. The conversion (wt %) is defined as the sum of total gas and coke yields.

$$\text{Conversion (wt\%)} = \frac{\text{Total gas} + \text{Coke}}{\text{Total feed}} \quad (\text{Eq (1)})$$

3. Results and discussion

3.1. Catalyst characterization

The XRD patterns of FCC-ZSM-5, ECAT, and the binder (Fig. 2A) revealed the crystalline phases and structural integrity of the materials. FCC-ZSM-5 exhibited sharp and well-defined peaks characteristic at 2 θ of 7–10° and 22–25° [41] of the MFI structure of ZSM-5 zeolite, indicating high crystallinity essential for selective hydrocarbon cracking. In

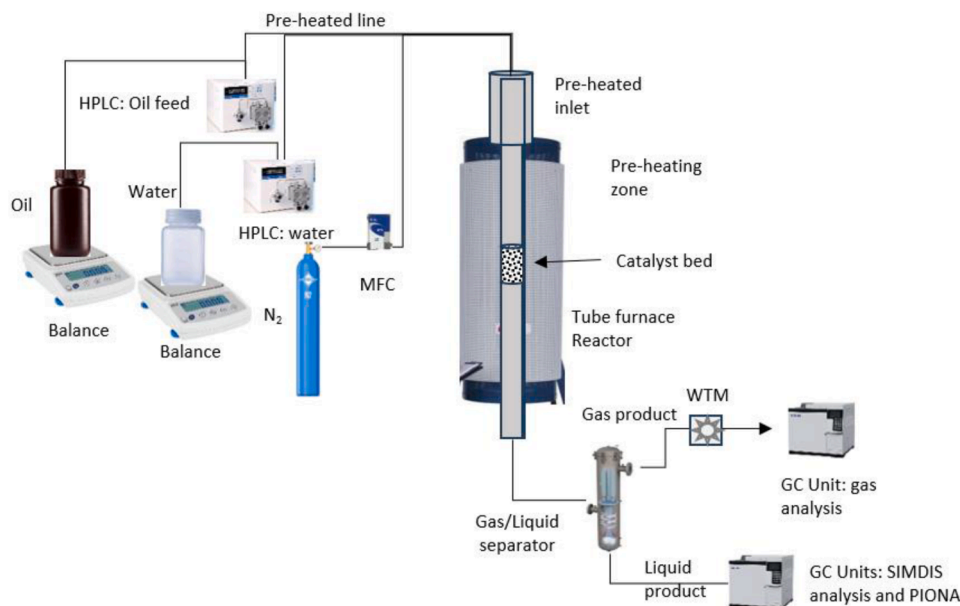


Fig. 1. Schematic diagram of the fixed bed reactor used for steam and non-steam catalytic cracking of crude oil (WTM = wet test meter).

Table 2

Operating conditions of the fixed-bed microscale flow reactor system.

Parameter	Value
Catalyst steaming, °C @ h	810 @ 6
Catalyst weight, g (30–40 mesh)	1
Catalyst bed height, cm	2
Reactor length/ID, cm	40/1.3
Water flowrate, g/h	1
Crude oil flowrate, g/h	2
Nitrogen flowrate, L/h	3.9
Preheater temperature, °C	250
Steam/oil ratio, g/g	0.5
Reactor temperature, °C	600–675
Residence time, s	10
Time on stream (TPS), h	4

contrast, ECAT showed the characteristic peaks at 2θ of 6° , 15.9° , and $23\text{--}25^\circ$ [41], of faujasite-type Y-zeolite, but the intensity of the peaks was lower, reflecting a partial loss of crystallinity due to prolonged use and thermal deactivation. Meanwhile, the binder displayed broad and weak peak at 26.7° , indicative of its predominantly amorphous structure. While the binder contributes little to catalytic activity, it provides essential mechanical support to the catalyst. The XRD results confirm that FCC-ZSM-5 and ECAT retain their respective zeolite frameworks, important for effective catalytic cracking.

The BET isotherms as shown in Fig. 3B and textural properties data in Table 3 offer insights into the surface area, pore volume, and pore size of the catalysts. FCC-ZSM-5 exhibited a surface area of $105.4\text{ m}^2/\text{g}$, with a significant mesopore area of $83.9\text{ m}^2/\text{g}$ and a micropore area of $21.6\text{ m}^2/\text{g}$. The total pore volume was $0.125\text{ cm}^3/\text{g}$, and the average pore size was 4.7 nm , indicating hierarchical porosity [42]. This structure enhances hydrocarbon diffusion and supports cracking reactions, especially under severe conditions. In comparison, ECAT displayed a higher surface area of $208.7\text{ m}^2/\text{g}$, with a mesopore area of $121.7\text{ m}^2/\text{g}$ and a micropore area of $87.0\text{ m}^2/\text{g}$. The pore volume was $0.202\text{ cm}^3/\text{g}$, and the average pore size was 3.9 nm . While its high surface area and mesopores make ECAT effective for cracking smaller hydrocarbons, the smaller average pore size may limit its ability to handle larger molecules [43] present in crude oil. The binder, on the other hand, had the lowest surface area ($50.4\text{ m}^2/\text{g}$) and pore volume ($0.107\text{ cm}^3/\text{g}$), with a broad average pore size of 8.5 nm . Its primary role is to provide structural stability, contributing

minimally to catalytic activity.

The BJH pore size distribution profiles (Fig. 3C) further differentiate the catalysts abilities to process hydrocarbons of varying sizes. FCC-ZSM-5 demonstrated a bimodal pore size distribution with contributions from both mesopores and micropores, enabling efficient cracking of heavy hydrocarbons into light olefins [44,45]. ECAT exhibited a narrower pore size distribution, with a peak around 3.9 nm . This also makes ECAT suitable for cracking smaller hydrocarbons in addition to cracking larger molecules. The binder displayed a broad distribution with larger pores ($>8\text{ nm}$), which supports catalyst integrity but offers little catalytic functionality. These findings highlight the superior hierarchical porosity of FCC-ZSM-5, making it the most suitable for cracking crude oil into light olefins.

The acidity, as measured by $\text{NH}_3\text{-TPD}$ (Fig. 3D, Table 3), is an essential factor influencing cracking performance. FCC-ZSM-5 exhibited a total acidity of $453.3\text{ }\mu\text{mol/g}$, with high-temperature (HT) acidity [46] accounting for $128.8\text{ }\mu\text{mol/g}$. This strong acidity, particularly at elevated temperatures, facilitates the formation of carbocations and promotes β -scission reactions that produce light olefins [47]. While ECAT demonstrated a slightly lower total acidity ($431.6\text{ }\mu\text{mol/g}$) but a higher HT acidity of $155.4\text{ }\mu\text{mol/g}$. The higher HT acidity made the ECAT effective under severe cracking conditions [48], but its smaller pore size may limit large molecule accessibility to active sites. The binder exhibited negligible HT acidity ($40\text{ }\mu\text{mol/g}$) and limited total acidity ($452.7\text{ }\mu\text{mol/g}$), confirming its inert nature in catalytic reactions. These results emphasize the strong acidity of FCC-ZSM-5 and ECAT, with FCC-ZSM-5 offering a balance of both acidity and porosity for efficient catalytic performance.

The SEM images of FCC-ZSM-5 revealed a well-defined crystalline structure with angular and uniform particles, characteristic of its MFI zeolite topology (Fig. 3A). The particles exhibited sharp edges and surfaces, indicating high crystallinity, which aligns with the XRD results (Fig. 2A). The particle size of FCC-ZSM-5 ranged between 25 and $125\text{ }\mu\text{m}$, with minimal agglomeration, ensuring a homogeneous dispersion of active sites during catalytic reactions [49]. Additionally, the SEM analysis highlighted the hierarchical porosity of FCC-ZSM-5, as evidenced by visible micro- and mesoporous channels on the particle surfaces. These features probably facilitate the diffusion of hydrocarbons into the active sites. Furthermore, the uniform particle size supports even heat transfer during catalytic cracking, ensuring stable and efficient performance in both steam and non-steam environments. The SEM

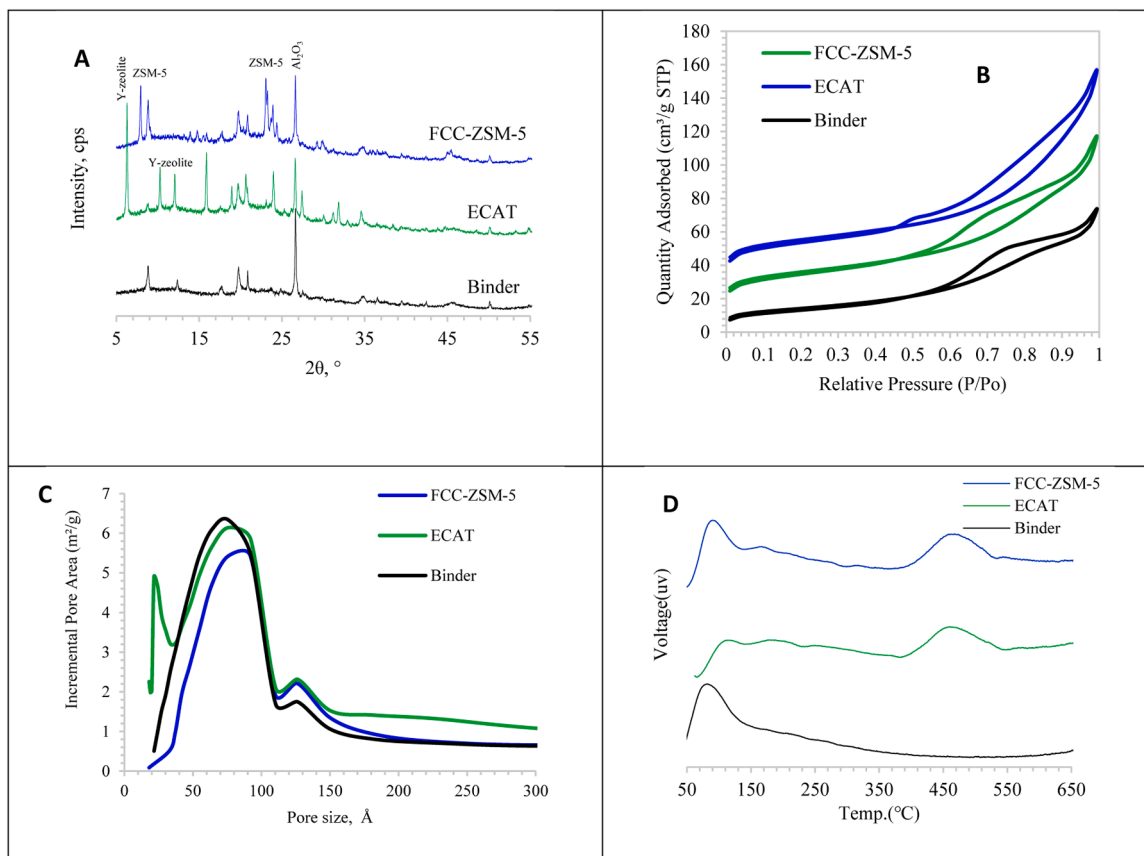


Fig. 2. Characterization of FCC-ZSM-5, ECAT and binder (A) X-ray diffraction pattern (B) isotherm plot, (C) pore size distribution, (D) acidity by NH_3 -TPD.

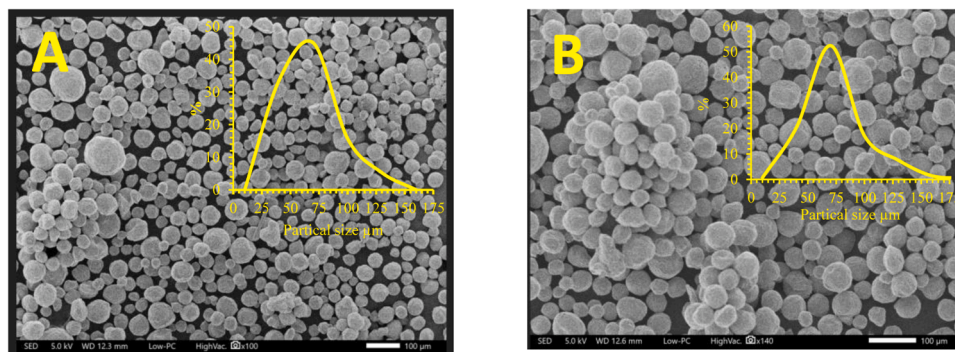


Fig. 3. FCC-ZSM-5 (A) and ECAT (B) topologies and particle size distribution (insert).

Table 3

FCC-ZSM-5, ECAT and binder texture priorities and acidity.

Zeolite	Surface area, m^2/g ⁱ	Mesopore surface area, m^2/g ⁱⁱ	Micropore surface area, m^2/g ⁱⁱ	Pore Volume, cm^3/g ⁱ	Pore Size, nm ⁱ	NH_3 -TPD ⁱⁱⁱ , $\mu\text{mol}/\text{g}$	HT ^{iv} TPD, $\mu\text{mol}/\text{g}$
FCC-ZSM-5	105.4	83.9	21.6	0.125	4.7	453.3	128.8
ECAT ^v	208.7	121.7	87.0	0.202	3.9	431.6	155.4
Binder	50.4	5.5	45.0	0.107	8.5	452.7	40

(i) BET equation, (ii) t -plot, (iii) total acidity (iv) HT: high temperature acidity, (v) ECAT: Equilibrium catalyst.

images of ECAT, which is derived from Y-zeolite, showed notable differences compared to FCC-ZSM-5 (Fig. 3B).

The ECAT particles exhibited an irregular and rounded morphology with evidence of surface roughness and particle agglomeration [50]. These features are indicative of the thermal and mechanical deactivation

that ECAT undergoes during prolonged use in industrial FCC units. The particle size of ECAT ranged from 25–150 μm , which is larger than that of FCC-ZSM-5. Additionally, the rough surface of ECAT particles, as observed in SEM images, suggests partial degradation of the zeolitic framework, which is consistent with the lower crystallinity observed in

XRD patterns. Despite these limitations, the high surface area and strong acidity of ECAT, as shown in BET and NH_3 -TPD data, enable effective cracking of smaller hydrocarbons under high-severity conditions.

3.2. Impact of steam on catalytic cracking of AXL crude oil

The catalytic cracking of AXL crude oil in the absence and presence of steam is compared, as illustrated in Fig. 4 and Tables S1-S2 (supporting information), highlighting the differences in conversion and product yield. Catalytic cracking (with and without steam) of AXL crude oil using FCC-ZSM-5 (impregnated with 1 %La and 1 %Ce oxides) demonstrated a strong temperature dependence. As the temperature increased from 600 °C to 675 °C, the overall conversion of AXL crude oil in the absence of steam increased from 32.4 % to 67.8 %. There was also an associated increase in the yield of light olefins from 22.3 % to 43.2 % as the temperature increased from 600 °C to 675 °C.

The cracking mechanism is primarily driven by the intrinsic acidic properties of ZSM-5. The high acidity of the FCC-ZSM-5 framework and wide mesopores of ECAT facilitated the cracking of large hydrocarbons through a Brønsted acid catalyzed mechanism, which involved in protonation of hydrocarbons on the ZSM-5 acidic sites [51], leading to the formation of carbocations. In β -scission reactions, the carbocations undergo cleavage to produce smaller hydrocarbon fragments, such as olefins and paraffins [10]. Whereas hydride transfer and cyclization reactions promote secondary products formation such as aromatics and isoparaffins as shown Fig. 7. The absence of steam also saw high yields of coke increased from 4.8 % to 9.8 % as temperatures increased [10,52]. This is due to the polymerization of heavy hydrocarbons and aromatics and the buildup of carbonaceous deposits on the catalyst surface [53]. Despite the high coke content, conversion increased because thermal cracking contribution became more evident as the temperature increased. The continuous increase in temperature leads to thermal cracking becoming more predominant, and the catalyst may lose of selectivity to desired products [54].

Fig. 4 also shows the impact steam catalytic cracking has on conversion and product distribution over FCC-ZSM-5 (impregnated with 1 %La and 1 %Ce oxides). The introduction of steam during the catalytic cracking process significantly altered the reaction pathways and products distribution. As seen in Fig. 4, the presence of steam not only enhanced the conversion but also shifted the product selectivity towards more light olefins from 24.4 % to 51.5 % of ethylene, propylene, and butenes. This effect of steam was pronounced at higher temperatures, where the selectivity to light olefins dominated, and the yields of heavier

hydrocarbons such as naphtha and distillates reduced. This is in line with the observations made by Meng et al [55] who investigated the influence of steam on the product distribution for heavy oil catalytic pyrolysis process in a fixed bed reactor. The authors found that when the fluidizing gas was changed from nitrogen to steam, the product distribution improved, and the yields of propylene, butenes, and the total light olefins increased. Under the same operating conditions, they showed that the yields of light olefins were about 6 % higher than those when nitrogen was used as the fluidizing gas.

Steam plays several important roles in modifying the catalytic behavior of ZSM-5 in FCC and mitigates coke formation from crude oil and delays coke precursors formation on the catalyst surface, reducing carbon deposition and maintaining catalyst activity [10]. This is apparent from the slightly lower coke yield 4.9 % to 7.6 % in the presence of steam compared to non-steam conditions at equivalent temperatures (Fig. 4). In addition, the steam environment suppresses the secondary reactions of hydrogen transfer and alkylation [10], that would otherwise convert light olefins into heavier hydrocarbons. As a result, more β -scission of hydrocarbon to olefins are preserved in the product stream. Additionally, steam enhanced the cracking efficiency by increasing the availability of protons on the ZSM-5 acidic sites [56]. Therefore, the cracking mechanism involves steam-assisted catalytic reactions, enhance β -scission of hydrocarbon and cleavage of C—C bonds in large hydrocarbons, favoring the formation of smaller olefins like ethylene and propylene. Overall, the presence of steam facilitated a higher conversion (from 35.9 % to 81.8 %) at all temperatures and enhanced selectivity towards light olefins, as evident in Fig. 4 where ethylene, propylene, and butenes yields are significantly higher compared to non-steam conditions.

3.3. Comparison of steam catalytic cracking vs. thermal cracking

The performance of direct steam catalytic cracking of crude oil to light olefins under three conditions were studied. Results for thermal cracking (no catalyst), and steam catalytic cracking using ECAT (equilibrium catalyst), FCC-ZSM-5(P) without metals and FCC-ZSM-5 (impregnated with 1 %La and 1 %Ce oxides) are shown in Fig. 5 and Table 3S (supporting information). The data demonstrated the advantages of steam catalytic cracking, particularly with FCC-ZSM-5 (impregnated with 1 %La and 1 %Ce oxides) in enhancing the conversion and selectivity toward light olefins [57] compared to thermal cracking. In the absence of any catalyst loading, the conversion for thermal cracking achieved 52.0 %, with moderate yields of light olefins

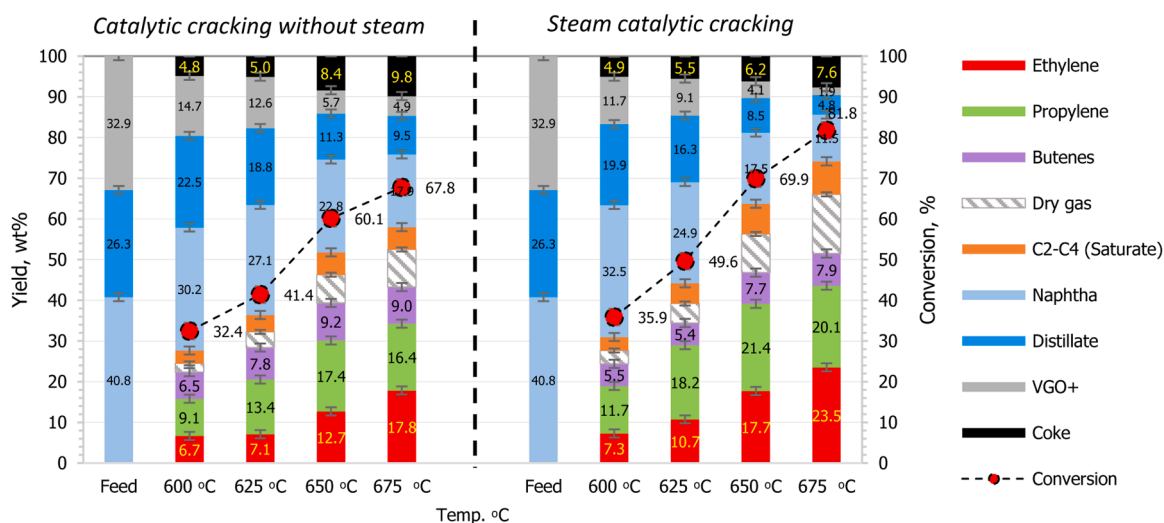


Fig. 4. Performance of FCC-ZSM-5 catalyst as a function of temperature during catalytic cracking and steam catalytic cracking (steam/oil ratio 0.5) at a residence time of 10 s.

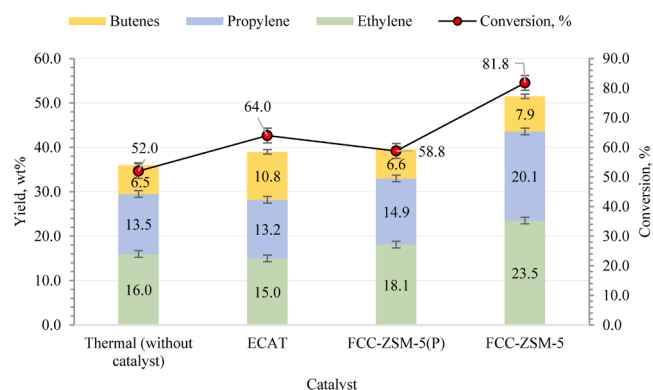


Fig. 5. Comparison of thermal cracking vs catalytic cracking: Product distribution for Thermal without catalyst, ECAT, FCC-ZSM-5(P) and FCC-ZSM-5 with 1 %La and 1 %Ce catalysts at a steam/oil ratio 0.5, 675 °C, residence time of 10 s.

of 16.0 % ethylene, 13.5 % propylene, and 6.5 % butenes. The process is driven solely by high temperatures, leading to cracking of hydrocarbons into smaller molecules. However, the lack of catalytic assistance limits the efficiency and selectivity of the process. While the use of ECAT and FCC-ZSM-5(P) improved the conversion to 58.8 %–64.0 %, indicating enhanced cracking efficiency compared to thermal cracking. The light olefins yield achieved with ECAT was 15.0 % ethylene, 13.2 % propylene, and 10.8 % butenes.

Notably, ECAT demonstrates better selectivity toward butenes (10.8 % compared to 6.5 % for thermal cracking). However, its performance remains moderate, as ECAT is primarily designed for conventional FCC processes and lacks the specialized pore structure and acidity required for maximizing light olefins production in high-severity steam environments. While FCC-ZSM-5(P) show lower conversion than ECAT with a higher yield of ethylene (18.1 %) and propylene (14.9 %) than ECAT. In contrast, the FCC-ZSM-5 (impregnated with 1 %La and 1 %Ce oxides) achieved the highest conversion and olefins yields, with a total conversion of 81.8 %. The light olefins yield was 23.5 % ethylene, 20.1 % propylene, and 7.9 % butenes. This significant improvement is attributed to the unique properties of ZSM-5 and the presence of steam. This suggests that the modified catalyst is more effective at breaking down larger hydrocarbons into valuable light olefins via the well-defined microporous framework enhances cracking reactions while minimizing secondary reactions, such as hydrogen transfer and cyclization. Furthermore, the strong Brønsted acidity of ZSM-5 facilitates the formation of carbocations [58], promoting β -scission reactions that selectively produce light olefins [59]. The presence of steam further enhances the process by delaying secondary reactions, minimizing coke formation [10], and enabling tandem cracking reactions, ensuring high selectivity for olefins. The efficiency and selectivity advantages of FCC-ZSM-5 in

steam catalytic cracking, make it a preferred choice for converting crude oil directly into high-value light olefins.

3.4. Effect of residence time on steam catalytic cracking

The effect of residence time on the catalytic activity and cracking of crude oil using steam was investigated at 650 °C with a steam/oil ratio of 0.5 using FCC-ZSM-5 (impregnated with 1 %La and 1 %Ce oxides). Fig. 6 shows the effect of residence time on AXL conversion and yield of light olefins, heavier hydrocarbons, dry gas, and coke. These trends underline the importance of residence time in influencing the product distribution and catalytic performance. A longer residence time indicates that there is more time for catalytic pyrolysis of hydrocarbons, and therefore the pyrolysis extent is more thorough. LPG can undergo secondary cracking reactions to produce dry gas, and can undergo polyreaction and aromatization to form gasoline and diesel oil. Similar conclusions were reached by Basu and Kunzru [60].

The conversion of crude oil improves progressively with an increase in residence time, as shown in Fig. 6 and Table S3 (supporting information). At a residence time of 7 s, the conversion is 62.6 %, which increases to 76.3 % at 25 s. This enhancement occurred because the longer residence times allow larger hydrocarbon molecules more time to interact with the catalyst surface, facilitating their breakdown into lighter fractions. The light olefins yield, mainly ethylene, propylene, and butenes, show a consistent upward trend with longer residence times. While ethylene and propylene yield increased from 14.2 % and 19.1 % at 7 s to 16.4 % and 19.4 % at 25 s, respectively, the butenes yield decreased slightly, from 7.3 % to 6.2 %. This is likely due to further cracking of butene into lighter olefins such as ethylene and propylene [11]. This behavior is attributed to the bifunctional nature of ZSM-5 catalyst [61], where the acidic framework promotes cracking reactions, while the unique pore structure favors the production and stabilization of smaller hydrocarbons like light olefins [2].

The steam catalytic cracking data also revealed a steady decline in the yields of heavier hydrocarbons like naphtha, distillates, and VGO+ with increasing residence time. This trend indicates that longer residence times enable more cracking of heavy hydrocarbons into lighter products [2]. Furthermore, the minimizing of secondary reactions by steam reduces the likelihood of recombination and polymerization [10], which would otherwise result in heavier products or coke. Coke formation also decreases slightly with residence time, from 6.8 % at 7 s to 6.3 % at 25 s. This reduction is facilitated by steam, which reacts with coke precursors, oxidizing them into gaseous products such as CO and CO₂ [62]. On the other hand, the dry gas yield increased with residence time, from 4.5 % at 7 s to 8.8 % at 25 s. This is consistent with the extended cracking of hydrocarbons and steam reforming reactions, which produce additional hydrogen and light gases under longer residence times and elevated temperatures [2]. The results demonstrate several key advantages of using steam catalytic cracking with ZSM-5

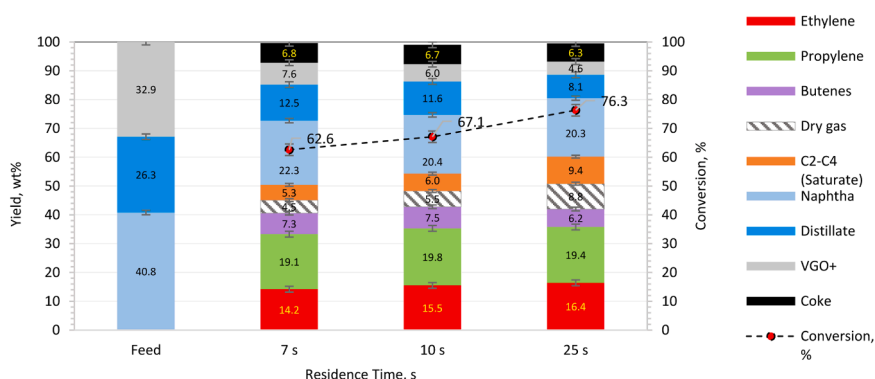


Fig. 6. Effect of residence time at 650 °C and a steam/oil ratio 0.5 over FCC-ZSM-5.

catalysts at extended residence times. These include higher overall conversion, more β -scission to generate smaller hydrocarbons [59], higher light olefins yield (ethylene and propylene), and higher conversion of heavy hydrocarbons into more valuable light products.

3.5. Effect of temperature and steam catalytic cracking

3.5.1. Effect on light olefins

The effect of steam on the yield of light olefins as a function of temperature is shown in Fig. 7. At a steam-to-oil ratio of 0.5, the yield of light olefins was improved compared to catalytic cracking without steam. For both cases of catalytic cracking, the yields of propylene and butenes go through maximum, while ethylene production continuously increases with an increase in temperature. A similar observation was made by Meng et al [55] when they studied the effect of steam on the catalytic pyrolysis of heavy oils. Also, Qi et al [63] arrived at the same conclusion when they developed the kinetic model for the steam catalytic cracking of AXL crude. Steam catalytic cracking over zeolite-based catalysts involves catalytic cracking reactions and thermal cracking reactions both on catalyst surfaces and in the interspaces between catalyst particles.

Propylene and butenes are mainly generated from catalytic cracking reactions following the carbonium ion mechanism, and they are intermediate products, which can undergo such secondary reactions as reforming, hydrogen transfer, aromatization, cracking and polyreaction. Ethylene is primarily formed from thermal cracking reactions following the free radical mechanism, and it is close to an end product, so it is unlikely to undergo any other secondary reaction, apart from hydrogenation to ethane. The increase in reaction temperature helps accelerate secondary reactions of propylene and butenes, which explains the yield patterns go through maxima [33,64].

3.5.2. Effect on BTX yield

The conversion of crude oil into high value products such as BTX aromatics product of benzene, toluene, and xylenes using FCC-ZSM-5 catalysts was affected by temperatures under steam and non-steam catalytic cracking conditions. Figs. 8 and 9 show the PIONA consisted of paraffins, isoparaffins, olefins, naphthenes, and aromatics distribution and BTX yields in naphtha fractions, with a residence time of 10 s. These results highlighted the influence of temperature and the reaction condition on product distribution and reveals the effect of on the yield and quality of naphtha-derived products. Fig. 8 shows that the aromatic fraction increased steadily with temperature in both non-steam and steam catalytic cracking conditions. In the absence of steam, the

selectivity to aromatics in the naphtha fraction increased from 31.5 % at 600 °C to 53.9 % at 675 °C, while under steam conditions, it increased to 59.3 % at 675 °C. The non-steam conditions resulted in higher yields of n-paraffins and isoparaffins compared to steam cracking. While steam promotes the formation of olefins, the selectivity to naphtha range olefins remained consistent at about 18.4 % under steam conditions at 675 °C, compared to 5.9 % without steam. However, the naphthenes yield decreased as temperature increased, indicating that higher temperatures favor cracking reactions that convert cyclic hydrocarbons into BTX aromatics and light olefins. Steam further reduced naphthenes production, with yields declining from 13.4 % at 600 °C to 5 % at 675 °C. The overall naphtha generated from crude oil catalytic cracking raised RON (research octane number) [51] with temperature in both cases, with a sharper increase under steam conditions reflecting higher selectivity to aromatics and olefins, which are desirable for producing high-octane fuels.

The total BTX yield increased significantly with temperature under both conditions as shown in Fig. 9. In the case of non-steam, the BTX yield increased from 7.6 % at 600 °C to 37.5 % at 675 °C, while under steam catalytic cracking, the BTX yield was consistently higher, rising from 7.6 % at 600 °C to 43.3 % at 675 °C. This enhancement is due to steam ability to minimize the secondary hydrogenation reactions [65], and to promote higher cracking of alkylated aromatics into small fractions including BTX product. The overall steam catalytic cracking significantly enhanced the selectivity to aromatics with high RON of naphtha, BTX, and naphtha range olefins, while minimizing paraffin and naphthenes yields and producing a more suitable high-performance fuel.

4. Conclusion

This study successfully demonstrates that Arabian Extra Light (AXL) crude oil can be converted directly into valuable petrochemicals such as light olefins and BTX (benzene, toluene, and xylenes). The research highlighted that steam catalytic cracking using a specially formulated FCC-ZSM-5 catalyst, impregnated with 1 % Lanthanum (La) and 1 % Cerium (Ce) oxides, offered significant advantages over both non-steam catalytic cracking and thermal cracking. At a temperature of 675 °C, steam catalytic cracking achieved a light olefin yield of 51.5 wt%, compared to 43.3 wt% for catalytic cracking without steam, and 36.0 wt % for thermal cracking. The La and Ce modified FCC-ZSM-5 catalyst showed superior performance due to its unique three-dimensional intersecting channel system of 10-membered ring pores. The distinct pore structure of ZSM-5 impacts shape selectivity and favors pathways that lead to the formation of smaller, less branched products, resulting in

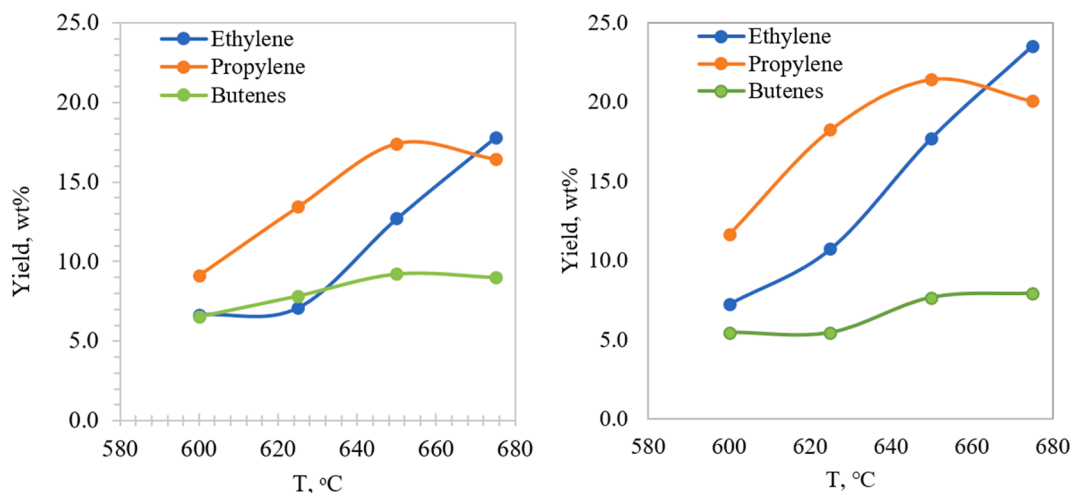


Fig. 7. Effect of temperature and steam on light olefins yield: (A) light olefins yield without steam, (B) light olefins yield with steam catalytic cracking a steam/oil ratio 0.5.

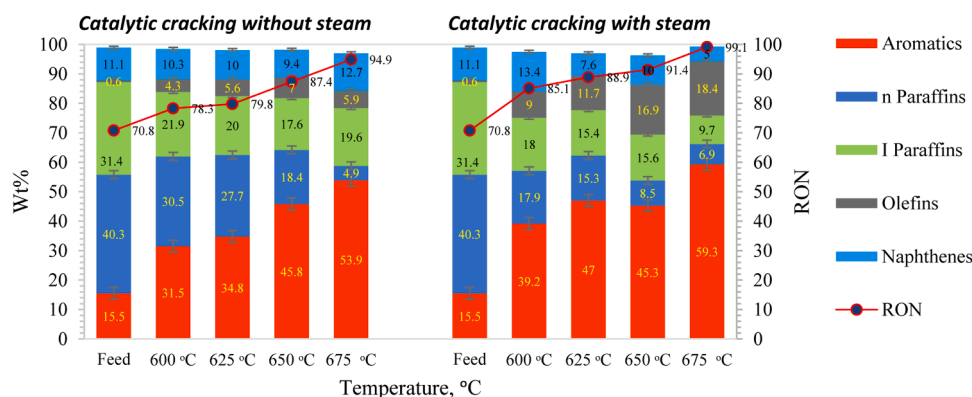


Fig. 8. PIONA fraction yield from FCC-ZSM-5 catalyst, residence time, 10 s, effect of temperature and absence of steam and vs steam cracking (steam/oil ratio 1:2).

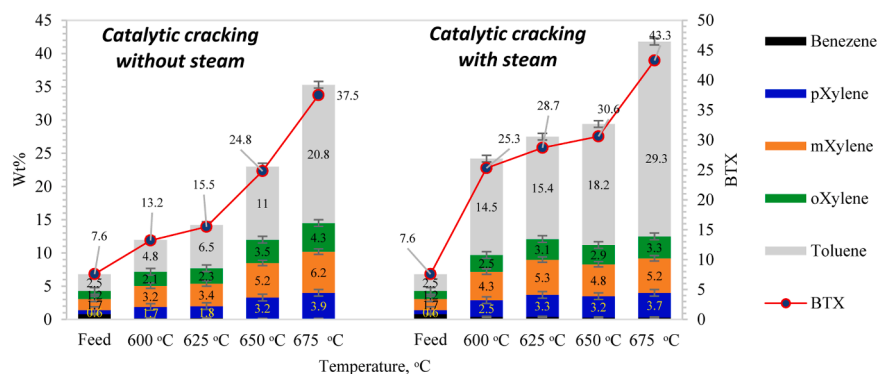


Fig. 9. BTX yield from FCC-ZSM-5 based catalyst, residence time, 10 s, effect of temperature and absence of steam and vs steam cracking (steam/oil ratio 1:2).

a significantly higher yield of light olefins, particularly propylene. The restricted environment also limits the formation of coke and larger aromatic compounds compared to the conventional equilibrium catalyst. The larger, more open structure of USY zeolite in convention equilibrium catalyst (ECAT) makes it more effective for the conversion of bulky and heavy oils into gasoline due to three-dimensional network of large supercages interconnected by 12-membered ring pores. This open-pore structure allows for the diffusion and cracking of bulky hydrocarbon molecules found in heavy gas oils and vacuum gas oils. While some light olefins are produced, the spacious nature of the supercages and the high acidity of USY also promote hydrogen transfer reactions. These reactions lead to the saturation of olefins into paraffins and the formation of aromatics and coke, thus limiting the overall yield of light olefins. At a temperature range of 600 °C - 675 °C, steam catalytic cracking over FCC-ZSM-5 catalyst resulted in a total conversion of 35.9 % - 81.8 % and light olefins yield of 24.5 % - 51.5 % and coke yield of 4.9 - 7.6 %, compared to total conversion of 32.4 % - 67.8 % light olefins yield of 22.3 % - 43.2 % and coke yield of 4.8 - 9.8 % for catalytic cracking without steam. Optimizing reaction conditions, such as temperature and residence time can further improve product selectivity. Higher temperature promotes dehydrogenation reactions and increases BTX production while minimizing undesirable paraffins and naphthenes. Longer residence time enables more effective hydrocarbon cracking while minimizing coke formation. The direct crude oil conversion-to-chemicals emphasized the role of steam in modifying reaction pathways and highlighted La-Ce impregnated FCC-ZSM-5 as an ideal catalyst for efficient and selective conversion of crude oil into valuable petrochemical feedstocks.

CRediT authorship contribution statement

Aaron C. Akah: Writing – review & editing, Writing – original draft, Methodology, Investigation, Conceptualization. **Emad Al-Shafei:**

Writing – review & editing, Writing – original draft, Validation, Methodology, Investigation. **Qi Xu:** Software, Methodology, Investigation, Data curation. **Mansour AlHerz:** Validation, Methodology, Investigation, Data curation, Conceptualization. **Ziyouddin S. Qureshi:** Writing – original draft, Validation, Methodology, Investigation. **M.Abdul Bari Siddiqui:** Resources, Methodology, Investigation, Formal analysis, Data curation. **Abdullah Aitani:** Writing – original draft, Validation, Investigation.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

The study was supported by Saudi Aramco and King Fahd University of Petroleum & Minerals (KFUPM), Dhahran, Saudi Arabia.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at [doi:10.1016/j.cej.2025.100794](https://doi.org/10.1016/j.cej.2025.100794).

Data availability

Data will be made available on request.

References

- [1] P. Giorgi, Reinventing the refinery through the energy transition and refining petrochemical integration, *S&P Glob. Febr.* 11 (2021).

- [2] A. Corma, et al., Crude oil to chemicals: light olefins from crude oil, *Catal. Sci. Technol.* 7 (1) (2017) 12–46.
- [3] Y.K. Park, et al., Catalytic cracking of lower-valued hydrocarbons for producing light olefins, *Catal. Surv. Asia* 14 (2010) 75–84.
- [4] A. Akah, J. Williams, M. Ghrami, An overview of light olefins production via steam enhanced catalytic cracking, *Catal. Surv. Asia* 23 (4) (2019) 265–276.
- [5] M. Alabdullah, et al., Composition-performance relationships in catalysts formulation for the direct conversion of crude oil to chemicals, *ChemCatChem* 13 (7) (2021) 1806–1813.
- [6] Y. Yoshimura, et al., Catalytic cracking of naphtha to light olefins, *Catal. Surv. Jpn.* 4 (2) (2001) 157–167, <https://doi.org/10.1023/A:1011463606189>.
- [7] F.M. Alotaibi, et al., Enhancing the production of light olefins from heavy crude oils: turning challenges into opportunities, *Catal. Today* 317 (2018) 86–98.
- [8] A. Usman, M.A.B. Siddiqui, A. Hussain, A. Aitani, S. Al-Khattaf, Catalytic cracking of crude oil to light olefins and naphtha: experimental and kinetic modeling, *Chem. Eng. Res. Des.* 120 (2017) 121–137.
- [9] A. Corma, J. Mengual, P.J. Miguel, Catalytic cracking of n-alkane naphtha: the impact of olefin addition and active sites differentiation, *J. Catal.* 330 (2015) 520–532.
- [10] A. Corma, J. Mengual, P.J. Miguel, Steam catalytic cracking of naphtha over ZSM-5 zeolite for production of propene and ethene: micro and macroscopic implications of the presence of steam, *Appl. Catal. Gen.* 417 (2012) 220–235.
- [11] A. Corma, V. Fornes, J.B. Monton, A.V. Orchilles, Catalytic activity of large-pore high SiAl zeolites: cracking of heptane on H-beta and dealuminated HY zeolites, *J. Catal.* 107 (2) (1987) 288–295.
- [12] A. Yamaguchi, et al., P-ZSM-5 pretreated by high-temperature calcination as durable catalysts for steam cracking of n-hexane, *Catal. Lett.* 144 (1) (2014) 44–49.
- [13] A. Yamaguchi, et al., Effect of steam during catalytic cracking of n-hexane using P-ZSM-5 catalyst, *Catal. Commun.* 69 (2015) 20–24.
- [14] X. Meng, J. Gao, L. Li, C. Xu, Advances in catalytic pyrolysis of hydrocarbons, *Pet. Sci. Technol.* 22 (9–10) (2004) 1327–1341.
- [15] A. Akah, M. Al-Ghrami, Maximizing propylene production via FCC technology, *Appl. Petrochem. Res.* 5 (4) (2015) 377–392.
- [16] P. Bai, et al., Fluid catalytic cracking technology: current status and recent discoveries on catalyst contamination, *Catal. Rev.* 61 (3) (2019) 333–405.
- [17] A. Olorunfoba, Y. Zhang, C.S. Hsu, State-of-the-art review of fluid catalytic cracking (FCC) catalyst regeneration intensification technologies, *Energies* 15 (6) (2022) 2061.
- [18] A. Akah, Application of rare earths in fluid catalytic cracking: a review, *J. Rare Earths* 35 (10) (2017) 941–956.
- [19] H.S. Cerqueira, G. Caeiro, L. Costa, and F.R. Ribeiro, “Deactivation of FCC catalysts,” *J. Mol. Catal. Chem.*, vol. 292, no. 1–2, pp. 1–13.
- [20] F. Maugé, P. Gallezot, J.C. Courcelle, P. Engelhard, and J. Grosmangin, “Hydrothermal aging of cracking catalysts,” *II. Effect of steam and sodium on the structure of LaHY zeolites*, *Zeolites*, vol. 6, no. 4, pp. 261–266.
- [21] F. Lemos, F.R. Ribeiro, M. Kern, G. Giannetto, M. Guisnet, Influence of the cerium content of CeHY catalysts on their physicochemical and catalytic properties, *Appl. Catal.* 29 (1) (1987) 43–54.
- [22] F. Lemos, F.R. Ribeiro, M. Kern, G. Giannetto, M. Guisnet, Influence of lanthanum content of LaHY catalysts on their physico-chemical and catalytic properties, *Appl. Catal.* 39 (1988) 227–237.
- [23] J. Scherzer and Octane-Enhancing, “Zeolitic FCC catalysts: scientific and technical aspects,” *Catal. Rev.*, vol. 31, no. 3, pp. 215–354.
- [24] N. Rahimi and R. Karimzadeh, “Catalytic cracking of hydrocarbons over modified ZSM-5 zeolites to produce light olefins: a review,” *Appl. Catal. Gen.*, vol. 398, pp. 1–17.
- [25] I. Shimada, K. Takizawa, H. Fukunaga, N. Takahashi, and T. Takatsuka, “Catalytic cracking of polycyclic aromatic hydrocarbons with hydrogen transfer reaction,” *Fuel*, vol. 161, pp. 207–214.
- [26] E. Alonso et al., “Evaluating rare earth element availability: a case with revolutionary demand from clean technologies,” *Env. Sci. Technol.*, vol. 46, no. 6, pp. 3406–3414.
- [27] G.P. Hatch, “Dynamics in the global market for Rare earths,” *Elements*, vol. 8, no. 5, pp. 341–346.
- [28] M. Hunger, G. Engelhardt, and J. Weitkamp, “Solid-state ^{23}Na , ^{139}La , ^{27}Al and ^{29}Si nuclear magnetic resonance spectroscopic investigations of cation location and migration in zeolites LaNaY ,” *Micropor. Mater.*, vol. 3, no. 4, pp. 497–510.
- [29] F.E. Trigueiro, D.F.J. Monteiro, F.M.Z. Zotin, and E.F. Sousa-Aguiar, “Thermal stability of Y zeolites containing different rare earth cations,” *J. Alloys. Compd.*, vol. 344, no. 1–2, pp. 337–341.
- [30] B. Qu et al., “Pyrolysis-catalysis of waste tire to enhance the aromatics selectivity via metal-modified ZSM-5 catalysts,” *Process. Saf. Environ. Prot.*, vol. 190, pp. 138–148.
- [31] B. Qu, T. Wang, X. Ji, T. Qin, Y.S. Zhang, and G. Ji, “Effect of reduction temperatures of Ni-modified zeolites on the product distribution, catalyst deactivation, and reaction mechanism during polypropylene pyrolysis,” *Fuel*, vol. 384, p. 133947.
- [32] Y. Zhang et al., “In-situ catalytic pyrolysis of polyethylene to co-produce BTX aromatics and H_2 by Ni/ZSM-5 in the rotary reactor with solid heat carriers,” *Fuel*, vol. 371, p. 131950.
- [33] X. Meng, C. Xu, J. Gao, L. Li, Studies on catalytic pyrolysis of heavy oils: reaction behaviors and mechanistic pathways, *Appl. Catal. Gen.* 294 (2) (2005) 168–176.
- [34] X. Meng, C. Xu, J. Gao, L. Li, Catalytic pyrolysis of heavy oils: 8-lump kinetic model, *Appl. Catal. Gen.* 301 (1) (2006) 32–38.
- [35] X. Meng, C. Xu, J. Gao, L. Li, Seven-lump kinetic model for catalytic pyrolysis of heavy oil, *Catal. Commun.* 8 (8) (2007) 1197–1201.
- [36] X. Meng, C. Xu, J. Gao, Q. Zhang, Effect of catalyst to oil weight ratio on gaseous product distribution during heavy oil catalytic pyrolysis, *Chem. Eng. Process.: Process Intensif.* 43 (8) (2004) 965–970.
- [37] M. Alabdullah, et al., Composition-performance relationships in catalysts for the direct conversion of crude oil to chemicals, *ChemCatChem* 13 (7) (2021) 1806–1813.
- [38] X. He, Y. Tian, L. Guo, C. Qiao, G. Liu, Fabrication of extra-framework Al in ZSM-5 to enhance light olefins production in catalytic cracking of n-pentane, *J. Anal. Appl. Pyrolysis* 165 (2022) 105550.
- [39] E.N. Al-Shafei, Z. Qureshi, M.Z. Albahar, A. Alasseel, S. Asaoka, A. Aitani, Hierarchical ZSM-5@ SiO₂ catalysts: a novel approach to optimizing olefin yield from heavy atmospheric gas oil, *J. Phys. Chem. C* 128 (25) (2024) 10440–10449.
- [40] S.M. Sadrameli, Thermal/catalytic cracking of liquid hydrocarbons for the production of olefins: a state-of-the-art review II: catalytic cracking review, *Fuel* 173 (2016) 285–297.
- [41] Y. Sun, et al., Synthesis of hierarchical MFI zeolite by interzeolite conversion of spent FAU zeolite for the methanol-to-olefins reaction, *Sustain. Energy Fuels* 8 (3) (2024) 641–648.
- [42] Y. Tao, H. Kanoh, L. Abrams, K. Kaneko, Mesopore-modified zeolites: preparation, characterization, and applications, *Chem. Rev.* 106 (3) (2006) 896–910.
- [43] H. Konno, T. Tago, Y. Nakasaka, R. Ohnaka, J. Nishimura, T. Masuda, Effectiveness of nano-scale ZSM-5 zeolite and its deactivation mechanism on catalytic cracking of representative hydrocarbons of naphtha, *Micropor. Mater.* 175 (2013) 25–33.
- [44] S. Mi, et al., Catalytic function of boron to creating interconnected mesoporosity in microporous Y zeolites and its high performance in hydrocarbon cracking, *J. Catal.* 347 (2017) 116–126.
- [45] P. Dong, et al., Dealumination of Y zeolite through an economic and eco-friendly defect-engineering strategy, *AIChE J.* 69 (9) (2023) e18183.
- [46] D.K. Jambhulkar, R.P. Ugwekar, B.A. Bhanvase, D.P. Barai, A review on solid base heterogeneous catalysts: preparation, characterization and applications, *Chem. Eng. Commun.* 209 (4) (2022) 433–484.
- [47] V.P. Doronin, P.V. Lipin, O.V. Potapenko, V.V. Vysotskii, T.I. Gulyaeva, T. P. Sorokin, Modifying zeolite ZSM-5 to increase the yield of light olefins in cracking feedstocks of petroleum and vegetable origin, *Catal. Ind.* 10 (2018) 335–343.
- [48] S. Singh, J. Mart\`inez-Ortigosa, N. Ortu\`no, V. Polshettiwar, J. Garc\`ia-Mart\`inez, Enhanced efficiency in plastic waste upcycling: the role of mesoporosity and acidity in zeolites, *Chem. Sci.* (2024).
- [49] W. Peng, et al., Properties analysis of catalyst particles during stripper distributor fault in industrial fluid catalytic cracking unit, *Fuel* 381 (2025) 133279.
- [50] F. Zaera, Shape-controlled nanostructures in heterogeneous catalysis, *ChemSusChem* 6 (10) (2013) 1797–1820.
- [51] Q. Wu, Acidic and basic catalytic cracking technologies and its development prospects for crude oil to chemicals, *Fuel* 332 (2023) 126132.
- [52] A. Corma, J. Mengual, P.J. Miguel, Steam catalytic cracking of naphtha over ZSM-5 zeolite for production of propene and ethene: micro and macroscopic implications of the presence of steam, *Appl. Catal. Gen.* 417 (2012) 220–235.
- [53] A. Corma, F.X. Llabr\`es i Xamena, C. Prestipino, M. Renz, S. Valencia, Water resistant, catalytically active Nb and Ta isolated Lewis Acid sites, homogeneously distributed by direct synthesis in a beta zeolite, *J. Phys. Chem. C* 113 (2009) 11306.
- [54] M. Alabdullah, et al., One-step conversion of crude oil to light olefins using a multi-zone reactor, *Nat. Catal.* 4 (3) (2021) 233–241.
- [55] X. Meng, C. Xu, J. Gao, Effect of steam on heavy oil catalytic pyrolysis, *Pet. Chem.* 47 (2007) 83–86.
- [56] J. Meusinger, A. Corma, Activation of hydrogen on zeolites: kinetics and mechanism of n-heptane cracking on H-ZSM-5 zeolites under high hydrogen pressure, *J. Catal.* 152 (1) (1995) 189–197.
- [57] Q. Liu, et al., Hydrothermally Ce modified HZSM-5 zeolite enhancing its strong acidity and Brønsted/Lewis acid ratio: stably boosting ethylene/propylene ratio for cracking n-heptane, *Fuel* 368 (2024) 131632.
- [58] C. Chizallet, C. Bouchy, K. Larmier, G. Pirngruber, Molecular views on mechanisms of brønsted acid-catalyzed reactions in zeolites, *Chem. Rev.* 123 (9) (2023) 6107–6196.
- [59] A. Corma, F. Melo, L. Sauvanaud, F.J. Ortega, Different process schemes for converting light straight run and fluid catalytic cracking naphthas in a FCC unit for maximum propylene production, *Appl. Catal. Gen.* 265 (2) (2004) 195–206.
- [60] B. Basu, D. Kunzru, Catalytic pyrolysis of naphtha, *Ind. Eng. Chem. Res.* 31 (1) (1992) 146–155.
- [61] A. Corma, State of the art and future challenges of zeolites as catalysts, *J. Catal.* 216 (1–2) (2003) 298–312.
- [62] F.M.B. Kontchouo, Y. Shao, S. Zhang, M. Gholizadeh, X. Hu, Steam reforming of ethanol, acetaldehyde, acetone and acetic acid: understanding the reaction intermediates and nature of coke, *Chem. Eng. Sci.* 265 (2023) 118257.
- [63] Q. Xu, et al., Kinetic study of crude oil-to-chemicals via steam-enhanced catalytic cracking in a fixed-bed reactor, *Can. J. Chem. Eng.* 101 (7) (2023) 4042–4053.
- [64] L. Li*, J. Gao, X. Meng, The influencing factors of the catalytic pyrolysis processes and their product distribution, *Pet. Sci. Technol.* 23 (3–4) (2005) 243–255.
- [65] Y. Yue, et al., Regulation of acidity properties of ZSM-5 and proximity between metal oxide and zeolite on bifunctional catalysts for enhanced CO₂ hydrogenation to aromatics, *Appl. Catal. B* 355 (2024) 124158.