

Review

A Review on Production of Light Olefins via Fluid Catalytic Cracking

Zahra Gholami ^{1,*}, Fatemeh Gholami ², Zdeněk Tišler ¹, Martin Tomas ² and Mohammadtaghi Vakili ³

¹ ORLEN UniCRE, a.s., Areál Chempark 2838, Záluží 1, 436 70 Litvínov, Czech Republic; Zdenek.Tisler@unicre.cz

² New Technologies—Research Centre, University of West Bohemia, Engineering of Special Materials, 301 00 Plzeň, Czech Republic; gholami@ntc.zcu.cz (F.G.); mtomas@ntc.zcu.cz (M.T.)

³ Green Intelligence Environmental School, Yangtze Normal University, Chongqing 408100, China; mvakili1981@yahoo.com

* Correspondence: Zahra.Gholami@unicre.cz; Tel.: +420-471-122-239

Abstract: The fluid catalytic cracking (FCC) process is an alternative olefin production technology, with lower CO₂ emission and higher energy-saving. This process is used for olefin production by almost 60% of the global feedstocks. Different parameters including the operating conditions, feedstock properties, and type of catalyst can strongly affect the catalytic activity and product distribution. FCC catalysts contain zeolite as an active component, and a matrix, a binder, and a filler to provide the physical strength of the catalyst. Along with the catalyst properties, the FCC unit's performance also depends on the operating conditions, including the feed composition, hydrocarbon partial pressure, temperature, residence time, and the catalyst-to-oil ratio (CTO). This paper provides a summary of the light olefins production via the FCC process and reviews the influences of the catalyst composition and operating conditions on the yield of light olefins.

Keywords: light olefin production; FCC process; catalyst types; operating conditions



Citation: Gholami, Z.; Gholami, F.; Tišler, Z.; Tomas, M.; Vakili, M. A Review on Production of Light Olefins via Fluid Catalytic Cracking. *Energies* **2021**, *14*, 1089. <https://doi.org/10.3390/en14041089>

Academic Editor: Vladislav Sadykov

Received: 23 January 2021

Accepted: 16 February 2021

Published: 19 February 2021

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

Olefins, also known as alkenes, are critical components in the chemical industry. Light olefins are used to produce many different derivatives used in our daily life, such as packaging, solvents, synthetic fibers, construction, and coatings. Olefins are aliphatic hydrocarbons with one or more C=C double bonds, with the general molecular formula of C_nH_{2n}. Alkenes are called unsaturated because the number of hydrogen atoms in alkenes is less than the maximum possible number per carbon atoms [1–4]. Ethene (or ethylene) with the molecular formula of C₂H₄ is the simplest alkene molecule and is followed by propylene (C₃H₆), butene (C₄H₈), pentene (C₅H₁₀), and other homologues.

Olefin production depends on the crude oil fractions or the products of natural gas processing. It is reported that annually 400 million tons of olefins are produced through different routes such as steam cracking (SC), fluid catalytic cracking (FCC), and dehydrogenation using one billion tonnes of hydrocarbon as feedstock. A wide range of products, such as gasoline, kerosene, jet fuel, and diesel, can be produced by cracking the large molecules. Light gases and olefins, liquefied petroleum gas (LPG), and butanes can also be generated via cracking. Heat is required for breaking of the C–C bonds in the cracking process. Thermal cracking processes comprise steam cracking, coking, and visbreaking, and the catalytic processes comprise hydrocracking and fluid catalytic cracking. In the hydrocracking process, due to the heat generation during the hydrogenation of cracked fragments, the net basis hydrocracking is exothermic [1].

Almost 40% of the global feedstocks are used in SC processes, and about 60% in FCC units, where 59% of olefins are produced by FCC process, and about 39% by steam cracking of ethane, LPG, and liquid feeds [5]. Different technologies have been used to produce light

olefins using different feedstocks such as methane and light alkanes, and naphtha (Figure 1). Steam cracking is the well-known conventional leading technology for olefin production, where the hydrocarbons that mainly originated from fossil resources (such as ethane, naphtha, etc.) are cracked in tubular reactors suspended in a gas-fired furnace [4,6–8]. However, the SC process is one of the most energy-intensive processes in the petrochemical industry, but it is clear that this process, with low CO₂ emission, is still the best-performing technology. It seems to be very difficult to replace this well-established technology without significant breakthroughs in process intensification. Due to the high energy consumption, emission of pollutants during olefin production, and more burdensome environmental regulations, many efforts are being made to develop technologies with low CO₂ emissions.

Depending on the feedstock's composition in steam crackers, about 1–1.6 tonne of CO₂ is produced per tonne of ethylene, and in general, more than 300 million tonnes of CO₂ per annum is emitted through the steam cracking process [9]. The CO₂ emission could be caused by the chemical CO₂ produced in the reaction, as well as the energy requirement of the process (i.e., fuel combustion) [9]. It has been reported that steam cracking plants are responsible for around 30% of all pollution from chemical plants, which is mainly due to the NO_x emissions and unburned hydrocarbons in the flame needed for heating of the cracking furnace [10]. Concerning the expected increase in the production rates by increasing the global population and raising the living standards, development and improvements in the olefin production technologies could significantly affect the common challenge for reducing the adverse effect of climate change [9].

Several studies have been done for a considerable increase in ethylene production, and use of biomass and waste stream for olefin production has become more promising and attracted more attention. The processes of catalytic dehydrogenation of light alkanes are another promising technology with high selectivity for olefin production. These processes have low capital investment, and they are independent of the oil price; production of hydrogen as a value-added byproduct is also another advantage of these processes. Due to the endothermic characteristics of these reactions, high temperatures are required to obtain appropriate productivity, and these processes are known as energy-consuming processes. Another problem of the high-temperature reaction is the acceleration of side reactions and reducing the selectivity. Therefore, the catalyst deactivation and energy efficiency need to be considered and improved in this process [11].

Contrasted with direct dehydrogenation oxidative dehydrogenation process is an exothermic reaction. In this process, due to the presence of oxygen, side-reactions result in the formation of oxygen-containing byproducts, decreasing the selectivity. The separation of light olefins from the product mixture increases the process cost; simultaneously, this process generates a large amount of waste gases that reduce its ecological index [11,12].

Abundantly available methane can also be used as feedstock for olefin production. Several methods for this process, including the oxidative coupling of methane (OCM) [13–15], Fischer-Tropsch synthesis (FTS) [16–18], and methanol to olefins (MTO) [19–21], are potential alternatives for SC process. However, MTO and FTS technologies are well-established processes that already have some operational plants globally, but due to the required step of syngas production in both methods, these methods are not very efficient. In addition, in FTS, the light olefins are not the only products, and a considerable amount of fuel-range hydrocarbons are also produced during the reaction. However, increasing the selectivity of target products is possible by improvements of the catalyst design. The OCM process, with a highly exothermic feature, needs more improvement for catalyst design and development of a reactor suitable for this highly exothermic reaction [6]; this process, with the lowest emission of CO₂ energy (CO₂ emission resulting from the energy requirement of the process i.e., fuel combustion), suffers from the relatively low ethylene selectivity and high chemical CO₂ emission which is produced in the reaction. The direct catalytic conversion of CO₂ to value-added chemicals such as light olefins has recently attracted high attention due to its potentially serious effects on climate and environment; therefore, the development of

stable and efficient catalysts for light olefins production with excellent olefin selectivity is highly desirable [22–27].

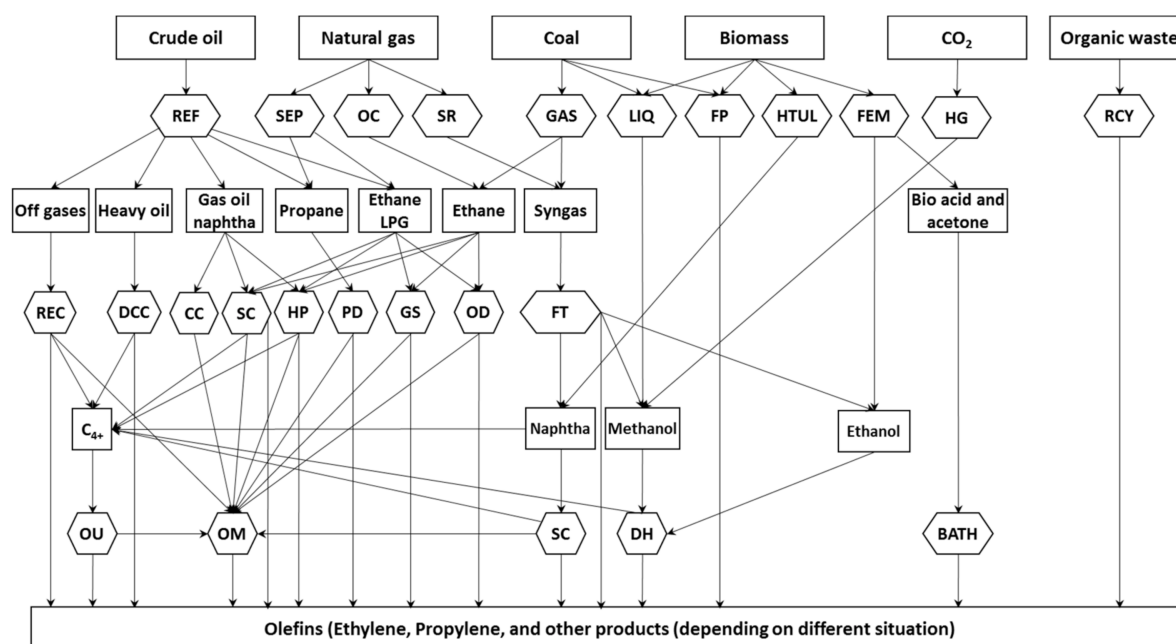


Figure 1. Different technologies for olefins production. BATH: Bio-acid acetone to hydrocarbons; CC: Catalytic Cracking or Catalytic Pyrolysis; DCC: Deep Catalytic Cracking; DH: De-hydration process (e.g., methanol to olefins, methanol to propylene, and ethanol dehydration); FM: Fermentation; FP: Flash Pyrolysis, sometimes in the presence of methane; FT: Fischer-Tropsch synthesis; GAS: Gasification; GS: Gas stream reactor technologies, e.g., shockwave reactors; HG: Hydrogenation; HP: Hydro-Pyrolysis; HTUL: Hydro-Thermal Upgrading Liquefaction which produces naphtha from biomass feedstock; LIQ: liquefaction; OC: Oxidative Coupling of methane via ethane; OD: Oxidative Dehydrogenation of ethane; OM: Olefin Metathesis; OU: Olefins Upgrading (conversion of C_4 – C_{10}) to light olefins; PD: Propane Dehydrogenation; RCY: Re-cycling pyrolysis using organic waste, such as discarded plastics, used rubber; REC: Recovery of refinery off-gases, which contains ethylene, propylene, propane, etc.; REF: Refinery processes. Distillation of crude oil produces naphtha and heavy oil. Catalytic cracking produces off-gases. Cryogenic separation and absorption produce ethane and LPG; SC: Steam cracking (conventional); SEP: Gas separation process produces methane, ethane, and propane; SR: Steam Reforming of natural gas to produce methanol. Reproduced from [28].

Given the importance of olefin production and its rising demand for chemical industries, it is required to use a more sustainable, environmentally friendly, less energy-intensive, and economical process. This review aims to present information about the FCC process for olefin production and provides a summary of different parameters affecting the process, such as the catalyst properties and compositions, and operating parameters, including temperature, residence time, catalyst-to-oil ratio, steam-to-hydrocarbon ratio, and feed properties.

2. Fluid Catalytic Cracking

Catalytic cracking is an olefin production technology, with lower CO_2 emission and higher energy saving. The FCC units were initially developed to convert low-value feedstock into gasoline, but by increasing the demand for some of its byproducts, such as propylene, some modifications have been made to the FCC process and the unit to achieve this aim. Therefore, FCC unit, process, and catalysts were upgraded and redesigned to produce propylene as a co-product instead of the byproduct [29]. The fluid catalytic cracking leads to a much lower operating temperature than conventional steam cracking [8]. Additionally, the control and propylene/ethylene ratios in the olefins produced via steam cracking are limited, while the propylene demand is growing quicker than ethylene. Employing a cata-

lyst in a cracking reaction could also provide the possibility of tuning the product selectivity, such as increasing the propylene selectivity instead of ethylene, and it helps to increase the propylene/ethylene ratios [8,30]. The light olefins production research through the catalytic cracking of hydrocarbons such as naphtha started in the late 1960s [31]. The FCC process used zeolite catalysts implemented by US refineries in 1977 and helped to save about 30 million tonnes of crude oil in the US alone [28]. The FCC process was initially designed to produce gasoline via upgrading low-value feedstocks, such as vacuum gas oil (VGO), and atmospheric residue (AR). The lighter feedstocks such as naphtha need a relatively higher cracking temperature than heavier feedstocks [8]. Owing to the flexibility of the FCC process, the operating conditions, and type of catalysts can be changed according to the type and quality of the feedstock [29]. A schematic of an FCC reactor is shown in Figure 2 [32].

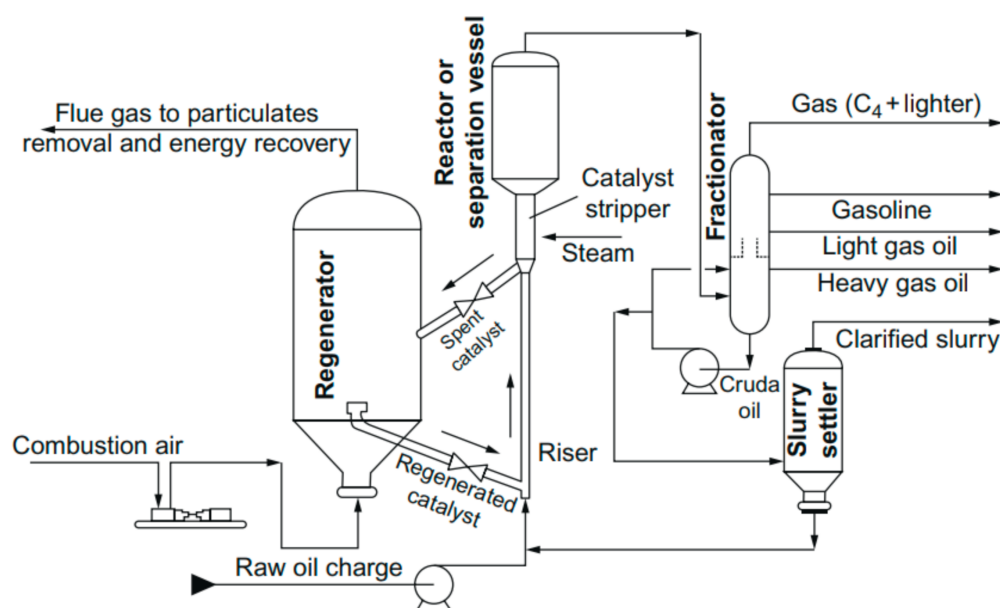


Figure 2. Detailed schematic of a fluid catalytic cracking reactor [32].

In the FCC process, the hot catalyst material is aerated with air or pre-heated feedstock at the bottom of the riser reactor, and the catalyst is moving through pipes. Therefore, a vaporized feedstock and fluidized catalyst simultaneously flow into a reactor chamber where the catalyst forms beds in the reaction chamber, and the cracking reactions occur. The temperature at the bottom of the riser is about 550 °C, whereas the catalyst to oil ratio (CTO) is larger than 1 (typically 5.5). The cracking reaction and formation of gases resulted in the expansion of the reactant mixture, and the mixture of the feedstock and the catalyst is quickly (at the speed of 40 m/s) transported up the riser reactor. The contact time in a riser is in the order of seconds. The temperature at the top of the reactor decreased to about 500 °C due to the endothermic nature of the catalytic cracking process. Cracked vapors go through the cyclone placed at the top of the reaction chamber and the spent catalysts are separated from the cracked vapors using the centrifugal force. Then, the cleaned cracked vapors fractionate into the products such as gasoline and cracked heavy and light gas oils. During the cracking process, the catalysts are contaminated with coke, and the coke deposited on the catalysts is removed by burning in the regenerator. The regenerated catalysts are added to the fresh catalyst to be used again in the FCC process. The temperature in the regenerator can reach 760 °C, and the heat of the catalysts at the entrance of the reaction chamber is high enough for the evaporation of the fresh feed before entering the reactor [32,33].

The high capacities of a cracking unit and its positive effect on the overall refinery economics have made it an essential object for innovation. In order to improve olefin production, researchers have made more effort to redesigning the FCC units [34]. Catalytic

pyrolysis process (CPP) and deep catalytic cracking process (DCC) are technologies developed based on Riser FCC by Sinopec, Research Institute of Petroleum Processing [35]. The first commercial DCC unit has been demonstrated in 1990 and commercialized since 1994, and now, 10 commercial units in operation in China (eight units), Thailand (one unit), and Saudi Arabia (one unit) [36,37]. Later, the CPP process was designed and developed by modification of DCC process to facilitate production of ethylene and propylene [37]. Depending on the type of feedstock, operating conditions, and nature of the catalyst, a low amount of olefins are produced (~1–2 wt.% ethylene and ~3–6 wt.% propylene) in the conventional FCC process, which can be enhanced by choosing a proper catalyst and optimizing the operating conditions. The Indian Oil Corporation's Research and Development Center developed the Indmax fluid catalytic cracking (I-FCC) process for the production of light olefins from heavy feedstocks. This process is able to produce more than 20 wt.% propylene using a wide range of feedstocks including the residues [38,39]. Another process, high-severity down-flow FCC (HS-FCC), developed by an alliance of Saudi Aramco, King Fahd University of Petroleum and Minerals (KFUPM), and JX Nippon Oil & Energy (JX), can produce up to 25 wt.% propylene through the cracking of heavy hydrocarbons at a temperature of 550 °C to 650 °C [40,41].

3. Catalysts

FCC catalysts decrease the activation energy for breaking the C–C bonds; subsequently, the cracking's operating temperature decreases. The cracking temperature of naphtha in the FCC process is in the range between 550 to 650 °C, which is about 200 °C lower than the operating temperature in the steam cracking process. In addition, the selectivity to the desired products improved by using the proper catalyst in the reaction, even at the same operating conditions as those of SC. Regeneration or decoking of catalysts help to remove the coke formed during the cracking process [29]. The FCC unit's design and operation are influenced by the type of catalysts to be used in the process. In general, three different groups of catalysts are available, including acidic catalysts, basic catalysts, and transition metal oxide catalysts. Olefin production via the FCC process is expected to be a more energy-saving process with higher operational flexibility.

It has been reported that the catalytic cracking over the basic catalysts proceeds through a free radical mechanism. The formation of free radicals over the catalyst surface could occur at lower temperatures than steam cracking, but at the same time, some of the formed free radicals are quenched. According to the compositions of olefins produced over the basic catalysts, it was suggested that the radical chain reaction is presented in the furnace tube and in the empty space between the catalyst particles [31]. The catalytic cracking over non-reducible transition metal oxide catalysts under aerobic conditions (oxidative catalytic cracking) follows a free radical mechanism, where activated oxygen species take hydrogen from hydrocarbons and produce radicals. The high yield of ethylene could be obtained by accurate control of the combustion reactions. The oxidative catalytic cracking can shift the equilibrium, and the furnace temperature can also be decreased due to the partial supply of heat by combustion reactions. Another benefit of the naphtha cracking using oxidative catalysts is using the lattice oxygen of the reducible transition metal oxide catalysts [31,42]. Table 1 shows the performances of different cracking catalysts, including acidic, basic, and transition metal oxide catalysts, for the light olefins production [31].

Catalytic cracking of naphtha over α -Al₂O₃ spheres [43] revealed that the yields of ethylene and propylene were 10% and 5% higher than thermal cracking without the catalyst. The coke formation increased with increasing the reaction time and the axial length of the reactor. The KVO₃-impregnated α -Al₂O₃ catalyst was also used for the production of light olefins via naphtha cracking [44], and same as α -Al₂O₃ spheres, compared to the thermal cracking, the KVO₃-impregnated catalyst also showed a 10% increase in the ethylene yield and a 5% in the propylene yield. The coke formation increased along with the axial length of the reactor and with increasing the reaction temperature. The coke deposition on the catalyst surface could be suppressed by addition of KVO₃. The lower coke

deposition of these catalysts attributed to the coke gasification by KVO_3 , and increasing the concentration of CO_x in the gas phase products. Similar results observed by Lee et al. [45], where $\text{KVO}_3\text{--B}_2\text{O}_3$ supported on SA5203 consisting of mainly $\alpha\text{-Al}_2\text{O}_3$ and about 12% glassy silica as a binder, was used as the catalyst. The catalytic cracking of naphtha on calcium aluminate ($12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$) catalysts in a fixed-bed reactor at 760–820 °C and atmospheric pressure was studied by Mjukhopadhyay and Kunzru [46]. The addition of K_2CO_3 significantly decreased the coke formation, and the selectivity to hydrocarbons (such as ethylene, propylene) also decreased over the potassium modified catalyst.

Table 1. Catalytic performances of different groups of catalysts in naphtha cracking to olefins [31].

	Reaction Atmosphere		
	Non-Aerobic	Non-Aerobic	Aerobic/Non-Aerobic
Type of catalysts	Basic catalysts	Acidic catalysts	Transition metal oxides/basic catalysts
Temperature (°C)	750–850	550–650	500–800
Steam/oil ratio (wt. base)	1–2	0–1	0.5–1
Products yield (wt.%)			
Ethylene	30–40	15–27	20–50
Propylene	15–22	15–50	3–10
Aromatics	0	11–34	–
CO, CO ₂	5–20	Neg.	15–30
Example of catalysts	CaO–SrO–Al ₂ O ₃ WO ₃ –K ₂ O–Al ₂ O ₃ KVO ₃ /corundum	AgO–MOR/Al ₂ O ₃ Cu/HZSM-5/P Steamed HZSM-5	Cr ₂ O ₃ /Al ₂ O ₃

The solid proton-donor acids, such as zeolites, are the most active catalysts for the cracking of hydrocarbons. In 1962, zeolite catalysts were used in catalytic cracking of vacuum distillates; and compared with the amorphous silica-alumina catalysts, they showed higher catalytic activity with an improved yield to gasoline. Soon after, all of the catalytic cracking units in Canada and the United States and about 95% of all cracking units in the world were using zeolite catalysts [47]. Zeolite-based catalysts for the olefins production via catalytic cracking of hydrocarbons were investigated by Pop et al. [48] in 1979. The catalysts were bifunctional modified mordenite zeolite with the formula of $(y\text{H.zM.uNa})\text{O}\cdot\text{Al}_2\text{O}_3\cdot n\text{SiO}_2$, wherein M is Cu, Ag, or Co/2, and $u+y+z$ is around 2, and n is a number more than 20. The catalyst with the formulation of $(1.6\text{H}0.3\text{Ag}0.1\text{Na})\text{O}\cdot\text{Al}_2\text{O}_3\cdot 25\text{SiO}_2$ showed the highest propylene yield than those catalysts where M was Cu or Co/2. The yields of 5–42% and 11–17%, for the ethylene and propylene were obtained for the catalytic cracking of n-butane using $(1.6\text{H}0.3\text{Ag}0.1\text{Na})\text{O}\cdot\text{Al}_2\text{O}_3\cdot 25\text{SiO}_2$ catalyst, while the temperature was in the range of 650 °C to 725 °C.

The acidic catalysts showed a higher yields of propylene and aromatics and lower ethylene yield at a temperature of 550–650 °C and under the non-aerobic conditions [31]. Higher yields of light olefins are attainable by minimizing the aromatization reaction which are fast over the FCC catalysts [31]. HZSM-5 zeolites have been widely used to enhance the light olefin production via FCC process. The effect of feed composition on the yield of light olefin in catalytic cracking processes is not as significant as its effect in the steam cracking process. In addition of operation conditions, the production yields and the ration of propylene to ethylene in FCC process could be affected by altering the acid properties (such as type, strength, distribution, i.e., Lewis/Brønsted (L/B) acid sites) [30,49,50].

3.1. Zeolite-Based Catalysts

The FCC catalysts consist of an active component, usually zeolite, a matrix such as amorphous silica-alumina, a binder such as bentonite clay, and a filler to provide a physical strength catalyst [29,51]. A schematic of an FCC catalyst is shown in Figure 3 [51]. The catalyst consists of spherical particles, which are appropriate to be used in a fluidized circulation reactor. The spherical particles contain large pores and voids necessary for the mass trans-

portation of the heavy feedstocks. The matrix assists both catalytic and physical functions. The product quality, catalyst selectivity, and the resistance of the catalyst to poisons can be affected by the matrix. The matrix's physical functions provide a porous structure, which allows the hydrocarbons to diffuse into and out of the catalyst microspheres, acting as a heat transfer medium, providing particle integrity and attrition resistance [29].

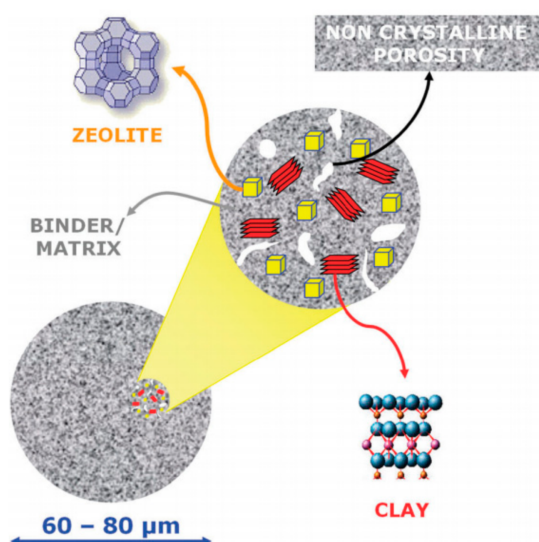


Figure 3. Schematic representation of a FCC catalyst [51].

Zeolite-based materials are widely used in industries for adsorption and catalytic reactions, including petroleum refining, petrochemicals, and pollution control [52]. Zeolitic materials with a special pore structure, shape selectivity, and ion-exchange properties, can be used as active catalysts or supports in different types of reactions such as isomerization, aromatization, alkylation, and cracking of hydrocarbons [53].

The first FCC catalysts were natural occurring clays, with low cracking activity and poor stability. In the 1960s, molecular sieves and then zeolite catalysts were introduced into FCC catalysts, which revealed significantly higher activity and stability and improved selectivity. Some modifications have been made in the catalysts and process hardware to improve the olefin yield from the FCC process. Zeolite Y is capable of cracking the large vacuum gas oil (VGO) molecules to gasoline range molecules. The shape selectivity and high activity of zeolite Y enhance the olefin production, converting the gasoline molecules coming from the primary cracking into light olefins [53,54]. Later, ZSM-5 was added to zeolite Y catalyst to improve the olefin production. The ZSM-5 consumes the carbenium ions generated during the primary cracking immediately after being produced from zeolite Y catalysts. In contrast, in the absence of ZSM-5, these carbenium ions will enter into the hydrogen transfer reaction mechanism; thus, the olefin yield is decreased. Using ZSM-5 type catalysts, the yield of light olefin and gasoline octane levels increase, while the gasoline yield decreases [53,55].

It has been proposed that the cracking reaction could be carried on by transferring a hybrid ion to a surface carbenium ion from another feed molecule; this new parent carbenium ion could release and replace the saturated surface piece and go through a normal cracking via β -scission [56–58]. The catalytic cracking of linear alkane proceeds via protonation of C–C/C–H bonds by the acid sites, converting them to the carbonium ion, as a transition state, which quickly breaks down into a carbenium with smaller alkane or hydrogen molecules. This step is known as “monomolecular protolytic cracking”. Hybrid transfer reactions between the formed carbenium and the feed molecules keep the reaction chain alive. The generated carbenium ions break down into smaller carbenium ions and light alkene molecules via β -scission. Finally, the reaction chain terminates by the deprotonation of carbenium ions and restore the acid sites (Figure 4a) [56,57].

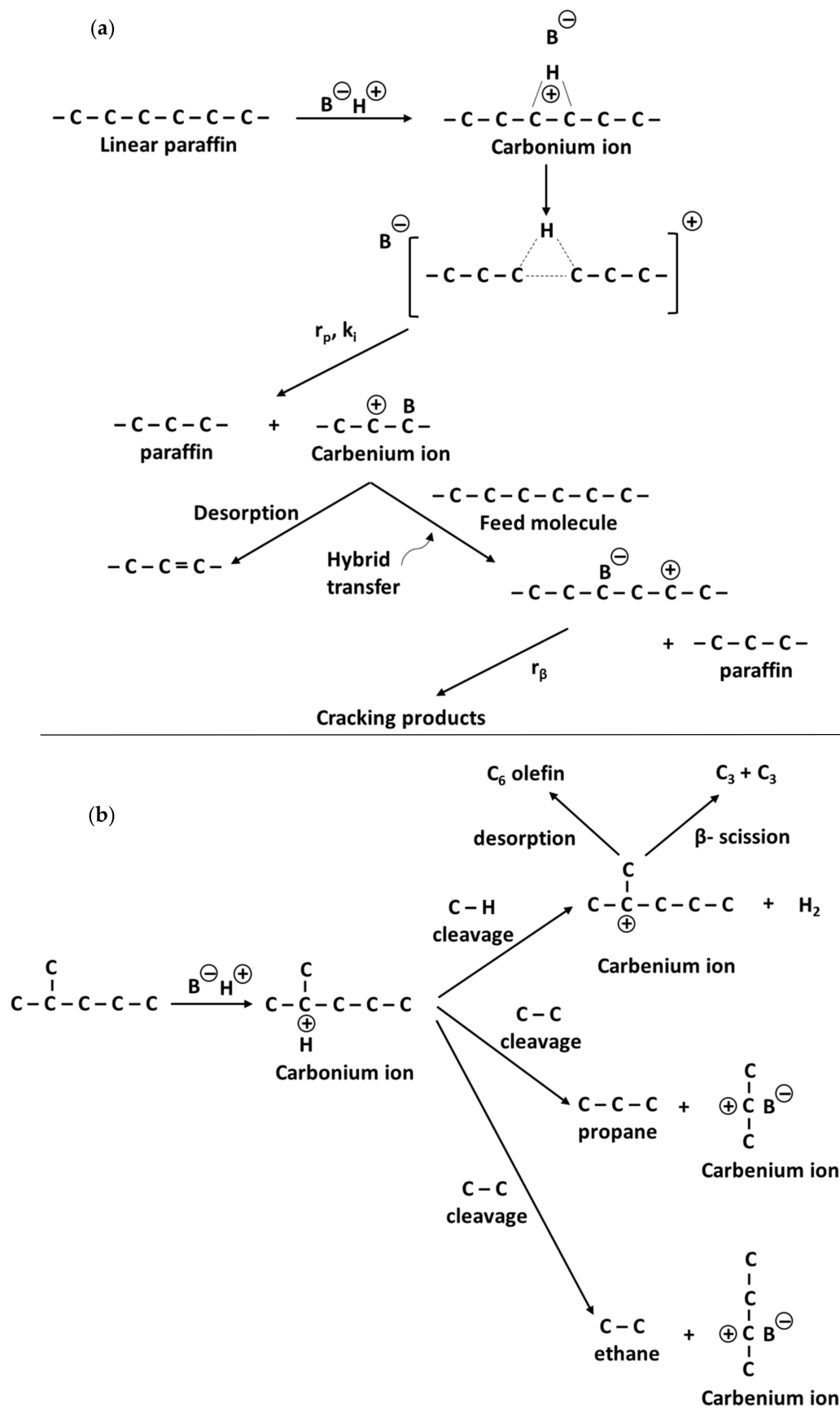


Figure 4. (a) Reaction mechanism for cracking of a linear paraffin on HY zeolite; (b) initiation of cracking for a branched paraffin at a Brønsted site [56].

The molecular hydrogen could be produced during the initial reaction of paraffin on HY zeolite when the molecule contains a hydrogen ion attached to a tertiary carbon atom (Figure 4b). The hydrogen molecule is produced by the interaction of the hydrocarbon with a Brønsted site. The formed carbenium ion can undergo C–C bond cleavage to produce a carbenium ion and ethane or propane, or C–H bond cleavage to produce a carbenium ion and hydrogen. The presence of hydrogen at the beginning of the reaction reveals that both these processes (C–H and C–C bond cleavage) must occur even if initiation of cracking occurs only on the Brønsted site [56,58].

More than 30% of the world's FCC units are using ZSM-5 additives either continuously or intermittently. The addition of 10 wt.% ZSM-5 additive results in the formation of more than 9 wt.% propylene [53]. The addition of a high amount of ZSM-5 is together with the poor “bottom cracking”, results in the high yield of heavy residue. The catalyst improvements could be together with the process modifications to enhance the olefin production. The Propylene Maximization Catalyst (PMC) catalyst series was developed by Grace Davison using a proprietary shape-selective zeolite and matrix technologies, which shows a high propylene yield with low coke formation and bottoms cracking activity. Akzo Co. also developed the Advanced Fuels eXperimental (AFX) series of catalysts as a novel catalytic system containing ZSM-5 crystal, ex situ phosphorus activated. The yield of propylene could be increased up to four times over this series of catalysts. The deep catalytic cracking (DCC) process is the extension of FCC, developed by the Research Institute of Petroleum Processing (RIPP) and Sinopec International, utilizes FCC principles combined with a proprietary catalyst, different operating conditions, and other enhancements for the production of light olefins from VGO [31,53,59].

FCC catalyst with different pore structures (macro-, meso-, and microporous) has a specific role in the catalytic process. As shown in Figure 5, heavy molecules' transformation to gas oil and gasoline as the valuable products occurs in the meso- and micropores. Ultra-stabilized zeolite Y (USY), which comprises different phases, is also used as the conventional FCC catalyst. The micropores of USY could impede the diffusion and consequently hamper the cracking of heavy components of the feedstock. Therefore, mesostructured materials were considered as a proper type of zeolites for the FCC process [51]. Previous studies revealed that using Al-MCM-41 catalyst instead of USY resulted in the selectivity to liquid fuels in the FCC process [60].

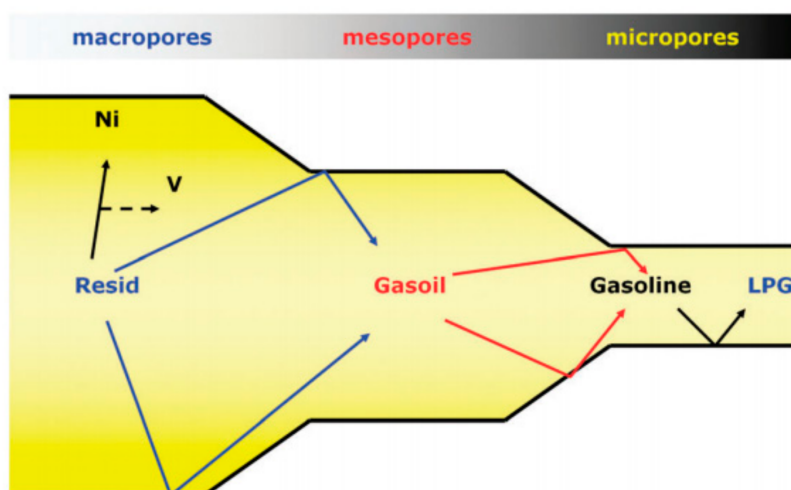


Figure 5. Schematic of the hierarchical pore structure in the catalyst of fluid catalytic cracking [51].

3.2. ZSM-5 Additive in FCC Catalysts

In addition to increasing the reactor temperature and using the zeolite-based catalysts, the catalysts with lower hydrogen transfer can be designed to decrease isobutylene's conversion to isobutane. The C_4 -olefinity of the product also can be increased using the

catalysts with moderate matrix activity [61]. The use of ZSM-5 as an additive in known as a promising method to enhance the light olefins production at the expense of gasoline [30,55,62,63]. It has been reported that the cracking of the feedstock containing VGO and atmospheric distillation residue is significantly affected by the catalyst properties [64]. A physical mixture of a commercial cracking catalyst (supplied by Akzo Nobel) with HZSM-5-based catalyst was prepared and used for the cracking of the mixture of VGO and atmospheric distillation residue [64]. The ability of catalyst for the cracking of HCO fraction of the residue in the feedstock decreased by the addition of about 25 wt.% of HZSM-5 zeolite-based catalyst (acid matrix without macroporous) into the structure of the commercial cracking catalyst.

The cracking reaction results revealed that the hybrid catalysts (physical mixture of the commercial catalyst with the HZSM-5 zeolites-based catalysts) had lower conversion than the commercial catalyst. The catalytic activity is related to the porous structure and acidity of the catalysts. The acidity in the matrix is very important for the cracking of bulky residue components. The presence of HZSM-5 in the hybrid catalyst resulted in a significant increase in the gasoline yield, which might be due to the lower gasoline overcracking and coke formation, whereas the overcracking of gasoline and coke formation are known as unfavorable properties of the base catalyst. The addition of HZSM-5 zeolite could enhance the cracking reaction by the β -scission over hydrogen transfer reactions [64]. The addition of HZSM-5 zeolite increased the content of C₃ and C₄ olefins in the LPG, C₅, and C₆ in the gasoline, and caused a decrease in the content of C₆–C₈ aromatics [64]. The product selectivity also could be controlled to increase the butene to propene ratio by increasing the Si/Al ratio in ZSM-5, however, it can cause a significant decrease in the overall activity. The effects of zeolite-based catalyst compositions, including ZSM-5 content, crystal size, and Si/Al ratio in catalytic performance of FCC units, are discussed in the following section.

3.3. ZSM-5 Content

The type of the feedstock in the FCC unit is related to the crude oil' source, and the mechanical restriction of the reactor could limit the severity of the operating condition; therefore, it is essential to use a proper catalyst to maximize the yield of desired products and enhance the profitability of the unit. As mentioned earlier, the use of a ZSM-5 additive as an active component in FCC catalyst helps in the higher production of propylene and olefins. The maximum propylene selectivity, C₃[−]/C₄[−] ratio, and gasoline octane can be obtained over the proper catalyst, whereas the hydrogen transfer, oligomerization, isomerization, and aromatization reactions are minimized over this catalyst [55,62,64–68].

Aitani et al. [62] reported that the addition of 0–20 wt.% ZSM-5 caused an increase in the olefins yield (propylene and butenes) with a corresponding loss in the gasoline yield. The variations of the light olefins' yields and product distributions as a function of the ZSM-5 concentration are shown in Table 2 and Figure 6a,b. Results revealed that increasing the concentration of ZSM-5 resulted in a significant increase in propylene yield along with a decrease in gasoline yield. In comparison with propylene, the yield of ethylene had only a minor increase by the addition of ZSM-5 up to 20 wt.%. The addition of ZSM-5 did not have a noticeable effect on the dry gas formation (ethane and methane) at both 500 °C and 650 °C. The addition of 5 wt.% ZSM-5 decreased the yields of light cycle oil (LCO), heavy cycle oil (HCO), and coke, while further increases in ZSM-5 content did not make significant changes.

Bulatov and Jirnov [69] have conducted a study to evaluate the performances of the FCC catalysts with different concentrations of ZSM-5. The ZSM-5 concentration was in the range of 0–40 wt.%. The conversion slightly decreased from 61.9 % to 60 % by increasing the ZSM-5 content from 10 % to 40 %. As shown in Figure 6c, the yields of ethylene and propylene increased by adding ZSM-5, while the other products (butylene, dry gas, and coke) had a minor decrease by the addition of ZSM-5 [69]. The ZSM-5 additives are used in more than one-third of the world's FCC units, either continuously or intermediately.

Most of the units are using 2–5 wt.% of the ZSM-5 additives to improve the propylene yield to around 6–7 wt.%. Some units also use 10 wt.% of the additives to increase the propylene yield to more than 9 wt.% [59].

Table 2. Product distribution of vacuum gas oil (VGO) cracking at 500 °C and 650 °C [62].

	ZSM-5 Additive (wt.%)							
	Base 0.0		5.0		10.0		20.0	
	500 °C	650 °C	500 °C	650 °C	500 °C	650 °C	500 °C	650 °C
CTO (g/g)	4.5	2.0	4.5	1.0	4.3	1.2	4.0	3.2
Product yields (wt.%)								
Dry gas	1.1	9.1	+0.7	0.0	+1.3	+0.5	+1.6	+1.1
Propylene	4.5	8.7	+5.2	+7.2	+6.4	+7.8	+6.3	+9.5
Total C ₃ s	5.1	9.7	+6.1	+7.6	+7.7	+8.5	+8.3	+10.1
Butenes	6.3	9.6	+2.8	+3.2	+4.0	+3.0	+3.8	+3.2
Total C ₄ s	11.6	11.0	+5.2	+4.6	+7.2	+4.0	+7.8	+4.1
Gasoline (C ₅ , 221 °C)	51.5	40.0	−12.3	−12.3	−16.3	−13.3	−17.6	−15.6
LCO (221–343 °C)	17.8	14.4	+0.3	−0.6	−0.7	+1.7	−0.9	+0.7
HCO (+343 °C)	11.0	14.5	0.0	+0.2	+1.0	−1.7	+1.2	−0.7
Coke	1.9	1.3	+0.1	+0.6	0.0	+0.1	−0.3	+0.3

(The results obtained at 71 wt.% conversion).

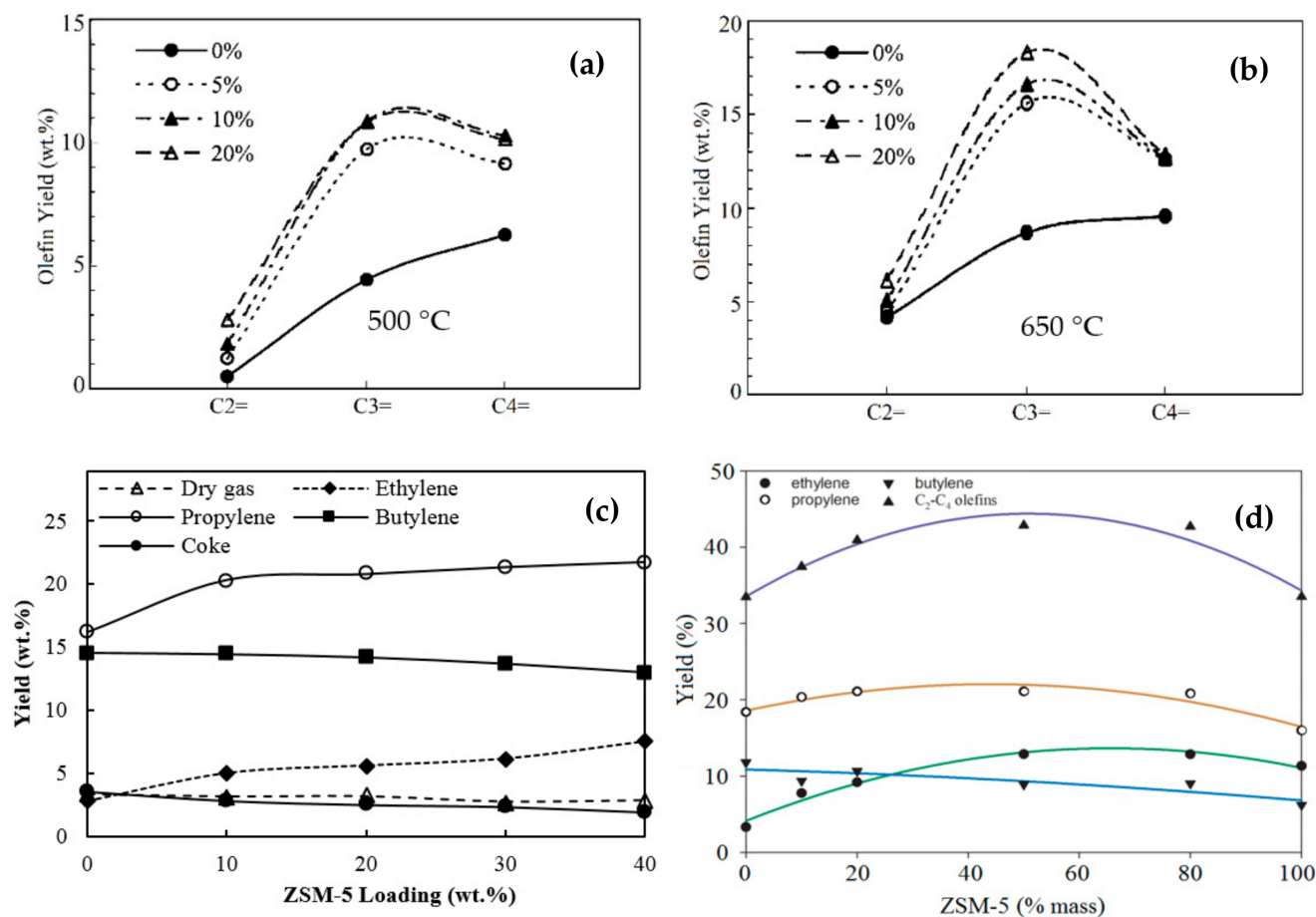


Figure 6. Effect of the ZSM-5 concentration on the yields of light olefins (a) at 500 °C [62], (b) at 650 °C [62], (c) T = 566 °C, riser partial pressure = 0.0793 MPa [69], and (d) T = 650 °C; residence time, 0.1 s; CTO = 4 g/g [70].

Conversion of FT liquids into C₃-C₄ olefins using a commercial Y zeolite-based catalyst was studied by Dement'ev et al. [70]. The effect of ZSM-5 content on the yield of light olefins was evaluated at the reaction temperature of 650 °C, CTO ratio of 4, and the residence time of 0.1 s (Figure 6d). The addition of ZSM-5 increased the ethylene yield, which is similar to the previously reported results [69]. The butylene yield decreased from 11% to 7% by increasing the ZSM-5 content, which could be due to the enhanced cracking of butylene, and also the formation and stabilization of bulk transition states could be impeded by the steric limitations in the narrow pores of the zeolite [70]. Propylene reached a maximum yield (~20%) at the ZSM-5 content of 20% and then decreased gradually. The cracking of linear hydrocarbons could be improved in the presence of acidic zeolites with a highly porous structure, where propylene is the main product, and the cracking of bulk isostructures could occur in the presence of broad porous zeolite Y.

3.4. Crystal Size

The shape selectivity of the zeolites is due to a steric effect, which means that only molecules with a diameter less than the channel's diameter can enter the zeolite pores and react on the active sites, exit them, and recover as the reaction's final product. The effects of the transition state shape selectivity can limit the formation of bulky transition state intermediates inside the pores; additionally, the formation of some undesired products could be avoided [71]. The catalytic active sites are usually located on the external surface and at the zeolite catalyst's pore mouth. These active sites are responsible for the undesired non-selective catalysis for the shape-selective reactions. In order to reduce and avoid the non-selective reactions, the external surface and extra-framework materials could be limited by the production of large well-crystallized zeolite crystals. Lowering the aluminum concentration in the zeolite is known as an option to reduce the extra-framework species [71].

The diffusional limitations could be eliminated using an efficient method to reduce the zeolite particle size. The length of diffusion for reactant/product hydrocarbons could be minimized by deploying the nano-sized zeolites [72,73]. The effect of zeolite crystal size (nano- and macrosizes) on the catalytic cracking of model naphtha in a fixed-bed reactor was studied by Konno et al. [73]. The composition (mol%) of the model naphtha is 20%, 20%, 15%, 10%, 10%, 10%, 5%, 5%, and 5% for n-Hexane, 3-Methylpentane, n-Heptane, n-Octane, Cyclohexane, Methylcyclohexane, Benzene, Toluene, and Xylene, respectively. Different products, including paraffins (CH₄, C₂H₆, C₃H₈, C₄H₁₀), olefins (C₂H₄, C₃H₆, C₄H₈), and aromatics were obtained over this reaction (Figure 7a,b).

Compared with the nano-ZSM-5 zeolite, a lower yield of olefins was obtained over macro-ZSM-5 zeolite. Both reactants and products are adsorbed on the catalyst's pore wall and then diffused inside the zeolite's pore. Generally, in diffusion systems with multi-components, diffusion of the molecules with high diffusivity, including linear alkanes and olefins, is inhibited by the hydrocarbon molecules with low diffusivity (such as naphthenes). Therefore, it could be difficult for the produced olefins to diffuse out of the intracrystalline pores of the macro-ZSM-5 zeolites, resulting in a long residence time of the olefins inside the zeolite pores. A longer residence time enhances the allyl carbenium ions formation by hybrid transfer between the olefin and carbenium ions resulting in the benzene, toluene, and xylene isomers (BTX) and coke formation. Consequently, the gradual catalyst deactivation occurs due to the coke deposition on macro-ZSM-5 zeolite (Figure 7c). On the other hand, nano-ZSM-5 zeolite is more selective for the light olefins production (about 57% C₂= + C₃= + C₄=), and showed higher stability against deactivation than macro-ZSM-5 zeolite, while the activity remained unchanged during the reaction (Figure 7d).

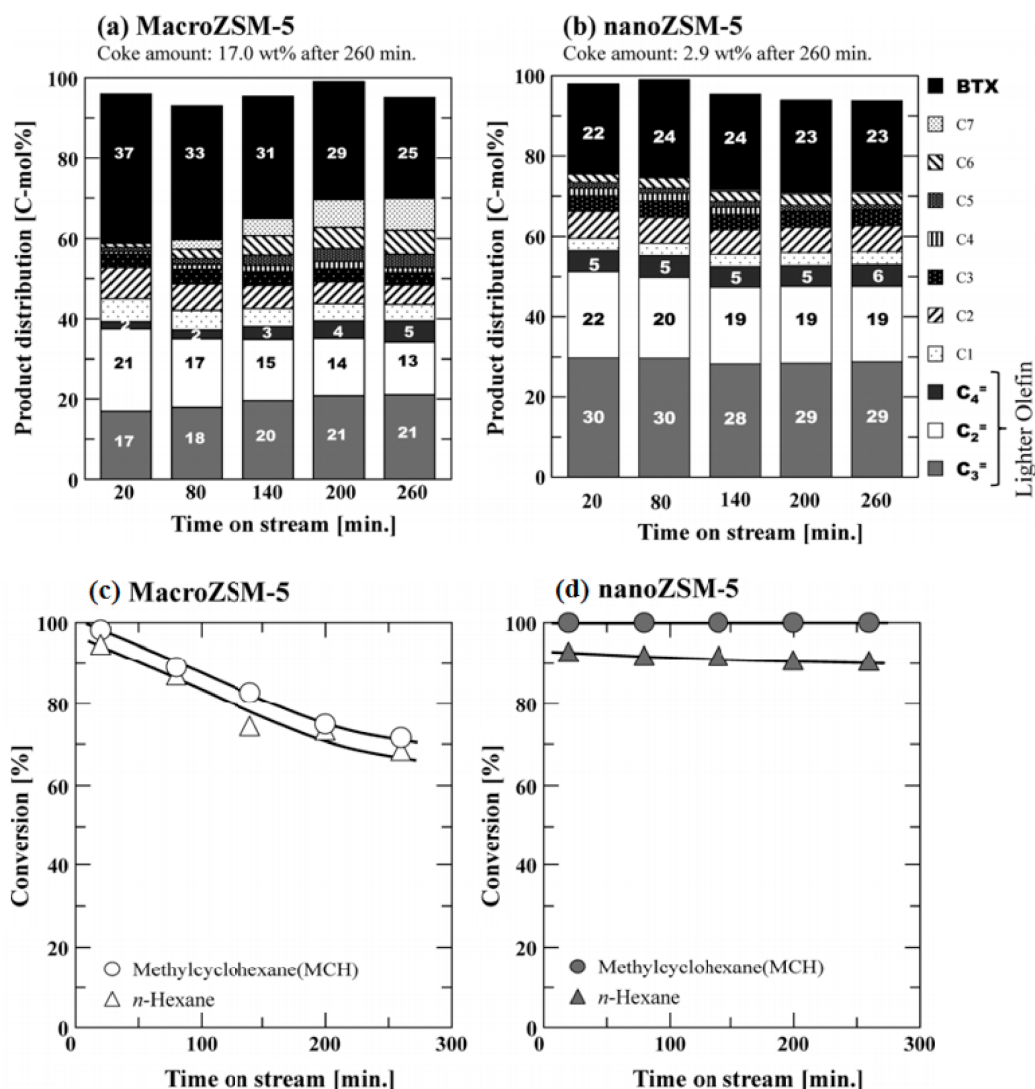


Figure 7. Product distribution during catalytic cracking of model naphtha over (a) macro-ZSM-5, and (b) nano-ZSM-5; conversions of methylcyclohexane and n-hexane over (c) macro-ZSM-5, and (d) nano-ZSM-5. $T = 650\text{ }^{\circ}\text{C}$, $W/F = 0.25\text{ h}$ [73].

The diffusion resistance of the feed components and the products inside the nano-ZSM-5 zeolite was about 400 times lower than that of macro-ZSM-5 zeolite, which clearly affected the product distributions and the catalyst's lifetime [73]. The textural properties of the catalysts are affected by the crystal size of the ZSM-5 zeolite, but the acidic properties of the catalysts remain unchanged by changes in the crystal size [74]. The crystal sizes determine the diffusion resistance; therefore, the rate-limiting step for the cracking is also changed by crystal sizes. The diffusion resistance is reduced by decreasing the crystal sizes of the zeolites, and the reaction occurs under the reaction control conditions. Thus, the products could be quickly diffused out of the micropore channels and avoid the secondary reactions; and in addition to lower coke deposition, the selectivity for the light olefins also improves. The effect of ZSM-5 zeolites' crystal size on the catalytic performance and diffusion properties in the catalytic cracking of n-heptane was investigated by Xu et al. [74]. It was found that the catalytic reaction proceeded under the reaction control condition using zeolites with nanocrystal sizes in the range of 15–30 nm, while the reaction proceeded under transition-limiting conditions over the nanocrystals larger than 50 nm. Therefore, as mentioned earlier, due to the lower diffusion resistance and the shorter diffusion path lengths of smaller ZSM-5 nanocrystals, zeolite with smaller crystal size revealed a higher selectivity to light olefins along with a lower coke formation [74]. Other researchers have

also investigated the effect of crystal size on the product distribution, olefin yield, and catalyst stability and lifetime, and the positive effect of smaller crystal size was reported for the zeolite catalysts [75–79]. Controlling the zeolite framework's active sites might be a core technology to attain the higher selectivity and a longer catalyst lifetime [80]. It can be concluded that the catalytic performance is significantly affected by the crystal size of the zeolites, and using the nano-ZSM-5 for cracking of naphtha could enhance the olefin yield and lifetime of the catalyst.

3.5. Si/Al Ratio

Besides the crystal size and pore structure, the catalyst stability is also affected by the acidity of the zeolites. The catalytic activity of the zeolites is related to two main parameters: (a) shape selectivity effects because of the molecular sieving properties associated with the well-defined crystal pore sizes; and (b) the strong Brønsted acidity of bridging Si–(OH)–Al sites, which has been formed by the presence of aluminum inside the silicate framework [71]. It is known that modification of zeolite's acidity could enhance the light olefins' yield. The acidity of the catalysts can be modified by the variations of the Si/Al ratio in zeolites. Hydrogen transfer reactions within ZSM-5 mainly take place on the catalyst's surface, and the reactions are more evident in high acidity at low Si/Al ratios. The hydrogen transfer reaction results in the production of higher dry gases and lower light olefins [55]. Investigation of the effect of Si/Al ratio on the catalytic performance of HZSM-5 catalyst in naphtha cracking revealed that the HZSM-5 with the high Si/Al ratio of 250 had a lower number of weak and strong acid sites than the HZSM-5 with lower Si/Al ratio of 25 [81]. The strength of weak and strong acid sites was lower in the HZSM-5 with the higher Si/Al ratio [81].

The effect of Si/Al ratio on catalyst properties of the HZSM-5 zeolites, including acidity, crystallinity, textural properties, and their catalytic performances for the production of light olefins via cracking of isobutene was studied by Lu et al. [82]. A series of HZSM-5 zeolites with different Si/Al ratios were used in this research [82]. The crystallinity of HZSM-5 catalysts with different Si/Al ratio is shown in Table 3. The H-ZSM-5(25) was defined as standard with a crystallinity of 100%, and relative values for the crystallinity of other samples were measured by the strongest height of other samples divided by that of HZSM-5(25). The zeolite sample with the lowest Si/Al ratio had the lowest relative crystallinity, affecting its catalytic performance. The acidic properties of fresh HZSM-5 samples, the calcinated HZSM-5 samples (700 °C in the air for 4 h), and also Fe (0.010 mmol/g), and Cr (0.004 mmol/g) impregnated HZSM-5 samples with different Si/Al ratios are shown in Figure 8 [82]. The amount of both weak and strong acid decreased by increasing the Si/Al ratio for all samples. Compared with the fresh HZSM-5, the amount of acid and acid density of the calcined samples were much lower, especially at lower Si/Al ratios. A more significant decrease in the amount of both weak and strong acid sites was observed at lower Si/Al ratios of the samples (25 to 50), while at higher Si/Al ratios (50 to 150), the decrease in the acidic sites were lower. The fresh (uncalcined) zeolites with a low Si/Al ratio have higher acid density and can be easily dehydroxylated at high calcination temperature.

Table 3. Crystallinity of fresh HZSM-5 zeolite samples with different Si/Al ratios [82].

Catalysts	HZSM-5(25)	HZSM-5(38)	HZSM-5(50)	HZSM-5(80)	HZSM-5(150)
Crystallinity (%)	100	132.3	109.0	124.6	136.6

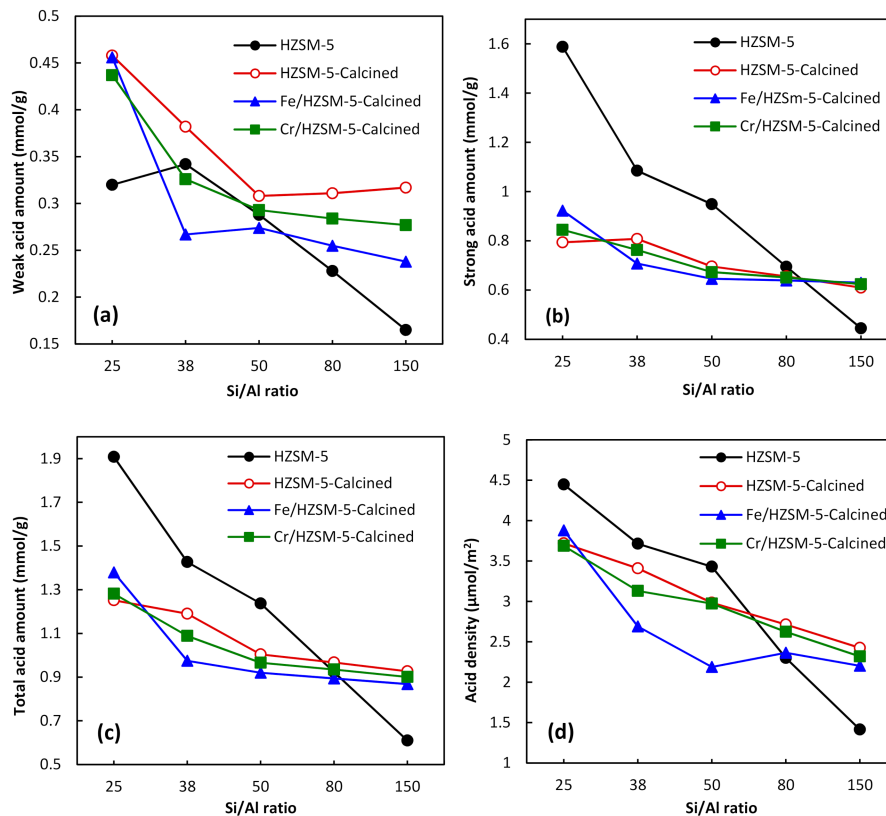


Figure 8. Acidic properties: (a) weak acid amount, (b) strong acid amount, (c) total acid amount, and (d) acid density of the HZSM-5 zeolite catalysts with different Si/Al ratios [82].

Konno et al. [78] studied the effect of the Si/Al ratio of ZSM-5 zeolite on the cracking of *n*-hexane. The dependency of *n*-hexane conversion to the Si/Al ratio indicating the reaction progressed over the zeolite acid sites (Figure 9). As mentioned earlier, zeolites with the lower Si/Al ratios have a higher number of acid sites, enhancing the cracking reaction. The highest yield to light olefins (C_2^- , C_3^- , C_4^-) were obtained over the ZSM-5 with Si/Al ratio of 150. The lower acidity of the catalyst (higher Si/Al ratio) suppressed the excessive reactions such as consumption of light olefins and formation of BTX.

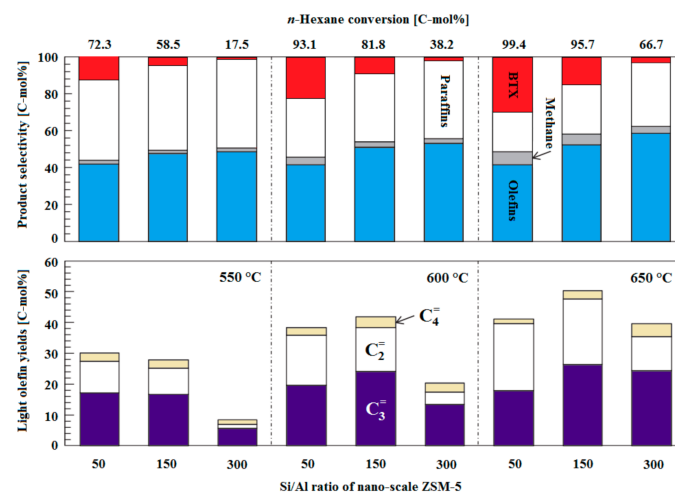


Figure 9. Effect of Si/Al ratio of the non-ZSM-5 zeolites on the product distribution and yields of light olefin through the *n*- C_6H_{14} cracking. $T = 550\text{--}650\text{ }^\circ\text{C}$, $W/F = 0.15\text{ h}$ [78].

The stabilities of different types of zeolites with different pore structure and different Si/Al₂ ratios, including zeolite beta (Si/Al₂ = 27), MCM-22 (Si/Al₂ = 26), ZSM-5 (Si/Al₂ = 50), and ZSM-23 (Si/Al₂ = 106) for the butene cracking process were investigated by Zhu et al. [83]. The characteristics and compositions of these zeolites are listed in Table 4. A higher Si/Al ratio (lower acidity) exhibits a lower coke formation, which extends the catalyst lifetime. The formation and deposition of coke on the catalyst's surface are reliant on hydrogen transfer reaction, which is related to the catalyst's acidity. The lower catalyst acidity leads to the lower coke deposition.

Table 4. Compositions and physical characteristics of zeolites with different structures [83].

Zeolite	Pore Diameter (nm)	Member Ring	Dimensional	Si/Al ₂ Ratio
Beta	0.56 × 0.65 0.56 × 0.75	12	3	27
MCM-22	0.40 × 0.59 0.71 × 0.71 × 1.82	12 10	Multiple	26
ZSM-5	0.51 × 0.55 0.54 × 0.56	10	2	50
ZSM-23	0.45 × 0.52	10	1	106

From Figure 10a, it can be seen that the catalyst activity and stability is in the following order: ZSM-5 (Si/Al₂ = 50) > MCM-22 (Si/Al₂ = 26) > ZSM-23 (Si/Al₂ = 106) > Zeolite Beta (Si/Al₂ = 27) [83]. Results showed that the pore structure's role in the catalyst's stability is more important than the catalyst acidity in butene catalytic cracking. The poor stability of zeolite Beta could be due to their large pores and supercages, which improved the formation of hydrogen-deficient condensed-ring aromatics via consecutive hydrogen transfer reactions. The formed coke could be strongly adsorbed on the catalyst's acid sites of the catalysts and led to the fast catalyst deactivation. The high stability of ZSM-5 is attributed to the particular two-dimensional structure of the zeolite consisting of a 10-membered ring, which, unlike the zeolite Beta, can inhibit the production of hydrogen-deficient condensed-ring aromatics. Due to the inter-crossed connection of the channels, the pore-blocking probability is also low.

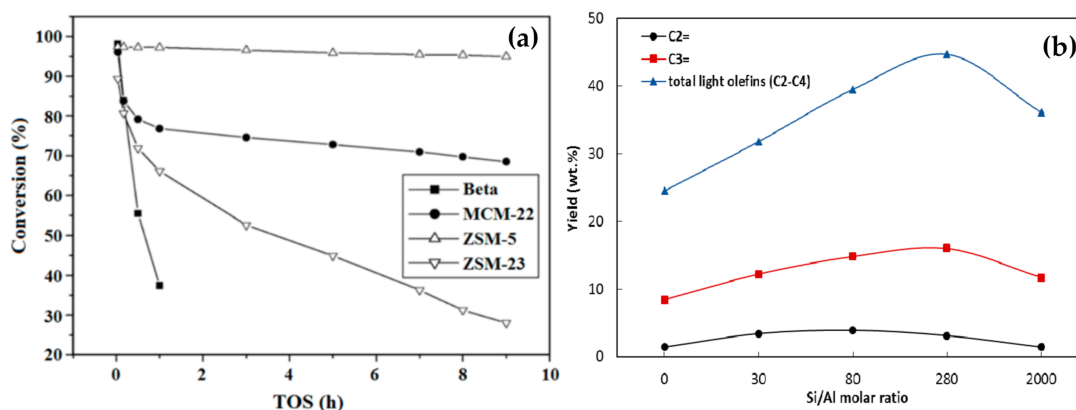


Figure 10. Cont.

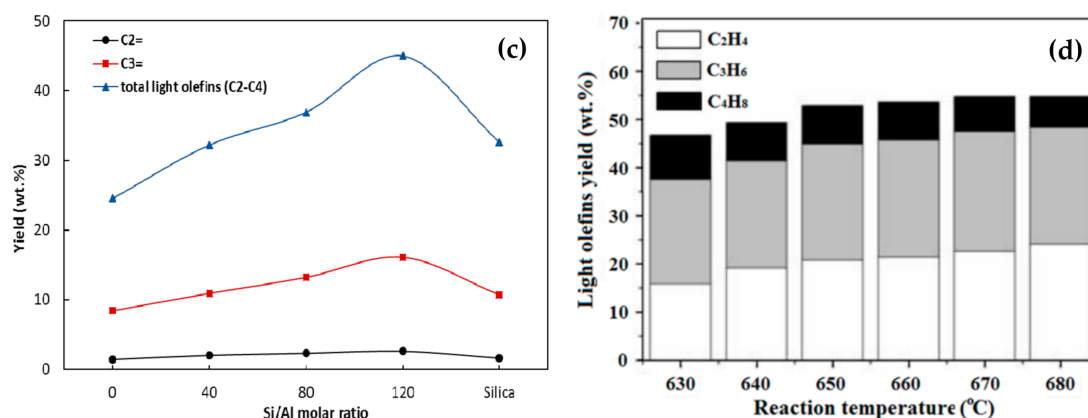


Figure 10. (a) Stability of the zeolites Beta, MCM-22, ZSM-5 and ZSM-23 in butene catalytic cracking [83]; effect of Si/Al ratio on the yields light olefins at 70% conversion over (b) MFI zeolite [84]; (c) -SVR zeolite [84]; (d) the light olefins yield at different temperature in naphtha catalytic cracking over ZSM-5 zeolite ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 25$) [85].

Kukade et al. [86] also reported that increasing the ratio of the Si to Al from 30 to 80 caused a decrease in the formation of dry gas, C_2^- , and C_4^- , while the yield of C_4^- increased at a higher Si/Al ratio. Hussain et al. [84] studied the catalytic cracking of hydrotreated VGO derived from Arabian Light crude oil. Two different medium-pore aluminosilicate zeolites, MFI ($10 \times 10 \times 10$ -ring channels) and -SVR ($10 \times 10 \times 10$ -ring channels), with different Si/Al molar ratio were used in this study. The yield of ethylene, propylene, and light olefins reached a peak at the Si/Al ratio of 280 (MFI) and 120 (-SVR) and then decreased by increasing the Si/Al ratio (Figure 10b,c). The presence of a maximum value for the yield could be due to the over-cracking of gasoline range reactive species in the presence of zeolite catalysts with an appropriate Si/Al ratio; additionally, at this point, the catalyst is able to inhibit the olefin saturation and their conversion into paraffins. It can be concluded that because the primary products in the catalyst pores in contact with the acid sites have lower residence time; the catalyst with a smaller crystal size, smaller pore diameter, along with a high Si/Al ratio, gives a higher conversion rate, higher stability, and a higher olefin yield.

4. Effects of Operating Parameters on Olefin Yields

In addition to the catalyst properties, the FCC unit's performance depends on operating parameters, including the feed composition, temperature, hydrocarbon partial pressure, residence time, and catalyst-to-oil ratio.

4.1. Temperature

The cracking reaction temperature is related to the type of feedstock, catalyst properties, and the expected products. In general, metal oxide catalysts need a higher cracking temperature, while a relatively lower temperature is needed when molecular sieve catalysts are used for the cracking [8]. Many efforts have been made to increase the olefin yield or decrease the deposition of coke on the catalysts and reactor walls to preserve their activity. It has been reported that reducing the secondary reactions (such as hydrogen transfer reactions), which result in the formation of methane and condensation products, could be an efficient method for increasing ethylene and propylene yield at high temperatures [87].

Different types of catalysts which can provide a reaction pathway with a lower activation energy were studied to increase the yield of light olefins, reduce the reaction temperatures, and optimize the economics. Several types of zeolitic materials have been examined to achieve a high yield of light olefins and lower the operating temperature. The catalytic cracking of naphtha in a fluidized-bed reactor for the production of light olefins using a ZSM-5-based catalyst was studied by Wan et al. [85]. The catalytic cracking at 630–680 °C revealed that the catalytic cracking could be more efficient than the steam

cracking. Generally, the yield of light olefins (ethylene and propylene) for the commercial thermal cracking of naphtha at 880 °C can be around 45–47 wt.%, while the catalytic cracking of naphtha using the ZSM-5 catalyst resulted in the production of 47–55 wt.% of olefins (ethylene, propylene, and butenes) at 630–680 °C (Figure 10d). Increasing the temperature from 630 °C to 680 °C results in a gradual increase of the light olefins yield and reached around 55% at 680 °C.

In another study [88], the effect of mild temperatures (500–560 °C) on the catalytic activity of vacuum gas oil (VGO) to propylene using two types of zeolite catalysts (ZSM-5 and USY), at different catalyst-to-oil (CTO) weight ratio, has been investigated. As shown in Figure 11, the propylene yield using both ZSM-5/ Al_2O_3 and USY/ Al_2O_3 significantly increased by raising the temperature; however, the increase of propylene yield over ZSM-5/ Al_2O_3 was higher than USY/ Al_2O_3 catalyst. Generally, the reaction temperature increases by increasing the circulation of the catalyst in commercial units. The higher CTO results in an increase in the reaction rate and the propylene yield of the catalytic cracking. A short contact time is required to control the hydrogen transfer reaction and avoid the secondary reactions. Pyrolysis of Chinese Daqing AR using the commercial FCC catalyst in a confined fluidized bed reactor system has been investigated by Meng et al. [89]. Table 5 shows the yield of products at different reaction temperatures. The higher reaction temperature resulted in the higher yields of hydrogen, methane, ethane, ethylene, and carbon oxides, while the butane yield decreased. The highest yields of butylene and propane was obtained at 630 °C, and the highest yield of propylene and total light olefins was observed at 660 °C.

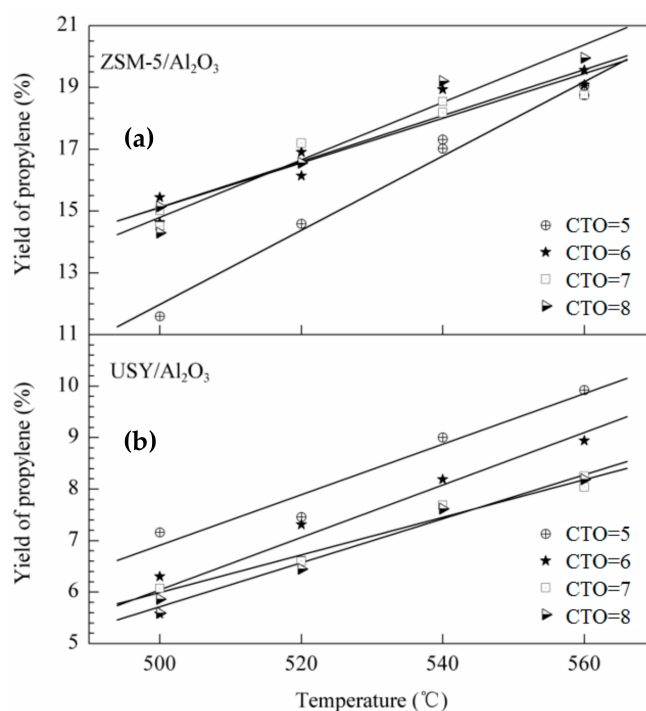


Figure 11. The yield of propylene using (a) ZSM-5/ Al_2O_3 and (b) USY/ Al_2O_3 catalyst at different temperature and CTO ratios [88].

Table 5. Product distribution of the catalytic pyrolysis of Daqing atmospheric residue using the commercial FCC Catalyst [89].

Product (wt.%)	Temperature (°C)			
	600	630	660	700
Ethylene	4.88	7.16	10.79	15.77
Propylene	15.84	16.94	17.47	14.79
Butylene	13.44	14.22	12.97	8.22
Total light olefins	34.16	38.32	41.23	38.77
Carbon oxides	1.43	2.73	2.62	3.52
Hydrogen	0.30	0.59	0.76	1.22
Methane	4.10	7.08	11.29	17.21
Ethane	2.29	3.67	5.01	6.45
Propane	3.25	3.36	2.81	1.78
Butane	6.43	4.60	2.55	0.88

The effect of temperature on the product distribution of the catalytic cracking of Chinese Daqing AR using a zeolite-based catalyst (CEP-1) was also studied earlier by Meng et al. [90]. As mentioned earlier, the higher reaction temperature resulted in a deep pyrolysis extent. Results (Figure 12a) revealed that the yield of coke and dry gas, which are the end products of the reaction, increased by increasing the temperature. The yield of ethylene also increased gradually by rising the temperature, though the yields of propylene, butylene, and total light olefins reached their highest amount at 640–680 °C. Ethylene is mainly generated from thermal cracking reactions following the free radical mechanism, and it is considered as the end product, and most probably, it is not going through the secondary reactions, apart from hydrogenation to ethane [8,90,91].

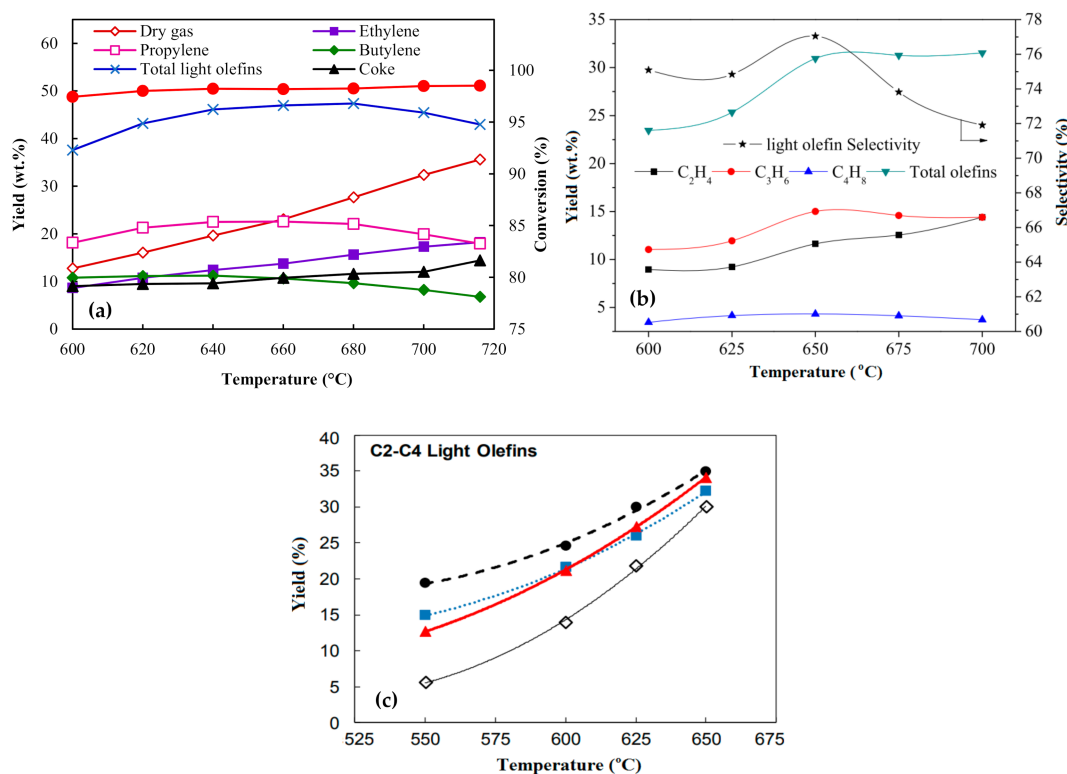


Figure 12. (a) Product distribution at different reaction temperature, residence time = 2.3 s, CTO = 13.5 (g/g), steam-to-oil = 0.70 [90]; (b) Yield and selectivity of light olefins at different reaction temperature [92]; (c) Yield of C₂-C₄ light olefins at different reaction temperature for Arab Super Light (ASL) crude oil cracking in ACE over (■) E-Cat, (●) E-Cat/MFI, (▲) MFI and (◇) no-catalyst [93].

As mentioned in Section 3.1, formation of propylene and butylene via catalytic cracking reactions generally follows the carbenium ion mechanism, and the formed intermediate products can go through secondary reactions such as hydrogen transfer, aromatization, cracking, and polyreactions [90,91]. The catalytic cracking process comprises (a) catalytic cracking reactions on the surface of the catalyst, and (b) thermal cracking reactions on the surface of the catalyst and the interspaces of catalyst particles. By increasing the reaction temperature, the catalytic reactions rate and thermal cracking reactions rate increase, resulting in more pyrolysis, and consequently, the light products yields are increased. By the further increase in the temperature, the thermal cracking reactions surpass the catalytic cracking reactions. Thus, the ethylene yield is close to the propylene yield and exceeds it at a temperature above 716 °C. The secondary reactions of propylene and butylene are accelerated by increasing the reaction temperature, and the yield of propylene and butylene are showing a maximum peak at 640–680 °C. Therefore, to reach the high yield of light olefins, the proper reaction temperature is in the range of 640–680 °C, where the yield of propylene is considerably higher than the yield of ethylene at this condition, and the yield of butylene is less than that of ethylene.

Tian et al. [92] reported that the yield of ethylene increased gradually from 8.96% to 14.40% while temperature increased from 600 °C to 700 °C (Figure 12b). The propylene and butylene showed a maximum value at 650 °C; and then, both slightly decreased by increasing the temperature to 700 °C. The reaction rate of the catalytic cracking could be accelerated at higher reaction temperatures and increase the cracking of gasoline and diesel into lighter hydrocarbons [92,94]. In another study by Al-Khattaf et al. [93], the catalytic cracking of light paraffinic crude oil was evaluated in a fixed fluidized-bed Advanced Cracking Evaluation (ACE) unit, using different catalysts including an equilibrium FCC catalyst (E-Cat), steamed commercial MFI catalyst, and an equal mixture of E-Cat and MFI (E-Cat/MFI). The total yield of C₂–C₄ light olefins increased with increasing temperature over all different catalysts and the thermal cracking without catalyst (Figure 12c). The light olefins yields at 650 °C followed this order: E-Cat/MFI > MFI > E-Cat > thermal cracking. The higher olefin yield at higher temperature could be due to the conversion of reactive isoparaffins and available olefin species in the Arab Super Light (ASL) crude oil.

Xiang-hai et al. [91] studied the catalytic pyrolysis of Daqing AR in a confined fluidized-bed reactor using an LCM-5 catalyst, which is a catalyst for the heavy oil contact cracking process. They found that the ethylene yield increases by increasing the temperature from 660 to 720 °C, while propylene and butylene yields reach a peak at the temperature in the range of 680–700 °C [91]. The residue fluid catalytic cracking (RFCC) for the maximum production of ethylene and propylene also revealed that the light olefins, formed during the cracking of Daqing AR, may go through the hydrogen transfer reaction and convert to alkanes [95].

4.2. Residence Time

In the FCC reaction, the residence time refers to the contact time of oil vapor with the catalyst [91]. The optimum residence time depends on the feedstock nature and the catalytic system used [96]. The effect of residence time on product distribution for catalytic pyrolysis of Chinese Daqing atmospheric residue using CEP-1 catalyst has been studied by Meng et al. [90]. The reaction was evaluated at 650 °C, CTO of 17.6, and the steam/oil ratio of 0.58, while the residence time was in the range of 1.5 s to 4.5 s (Figure 13). The feed conversion is about 98.5% and remains almost constant with residence time. A longer residence time provides more time for the catalytic pyrolysis of the feedstock. The yield of light olefins increased slightly by increasing the residence time from 1.59 to 2.04 s and remaining almost constant by increasing the residence time [90].

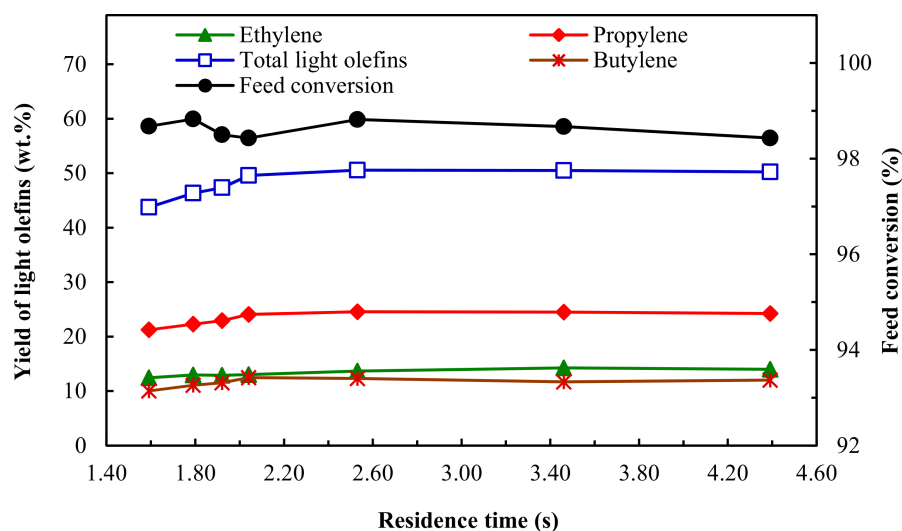


Figure 13. Effect of residence time on the distribution of light olefins [90].

The effect of residence time in the range between 1.0 s to 3.5 s for the catalytic pyrolysis of Daqing AR over an LCM-5 catalyst at 700 °C, CTO of 16, and the steam-to-oil ratio of 0.5 was studied by Xiang-hai et al. [91]. It was observed that the yield of total light olefins decreased gradually from about 52.5 wt.% to 49 wt.% by increasing the residence time, and the same trend was also observed for each light olefin. It is claimed that the yields of light olefins decreased due to the secondary reactions in the prolonged reaction (Figure 14a). The high yield of light olefins could be guaranteed by selecting an optimum residence time [8]. As a result of the lower conversion, a lower yield of olefins could be obtained at a residence time of below the optimum point, while the residence time above the optimum time provides more chances for the secondary reactions, and therefore decreases the yield of light olefins. Sha et al. [97] also reported that the yield of light olefins increased by increasing the residence time up to 2.0 s and then decreased by increasing the residence time. In another study reported by Basu and Kunzru [98], the catalytic pyrolysis of naphtha was studied at 800 °C, with a steam-to-oil ratio of 0.8, over a calcium aluminate ($12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$) catalyst, with the residence time in the range of 0.13 s to 0.3 s. They observed that the yield of propylene slightly increased by increasing the residence time and then decreased gradually by residence time, whereas the yield of butylene decreased with increasing residence time.

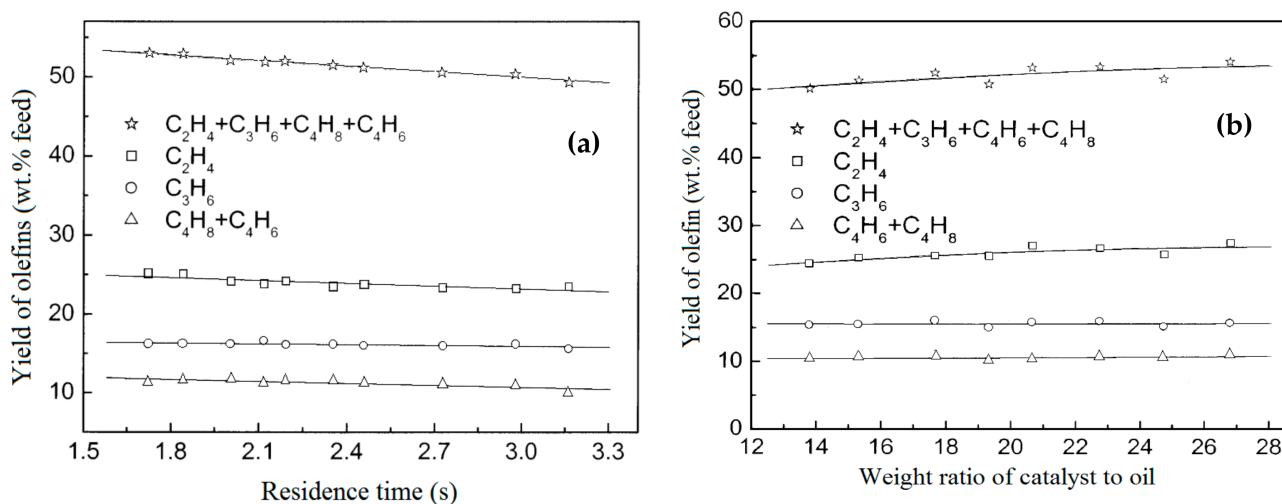


Figure 14. Effect of (a) residence time and (b) weight ratio of catalyst-to-oil on the distribution of light olefins [91].

Since the reaction temperature is usually increased to increase the yield of light olefins, the residence time should be reduced to prevent the excessive thermal cracking reactions [96]. A good choice for shortening of the residence time are downer reactors. In riser reactors, it is necessary to push up the catalyst, and it might be difficult to reduce the residence time to sub-second range, and the catalyst backmixing also does not help. In the downer reactors, it is necessary to ensure sufficient mixing of feedstock and catalyst at the entrance and the quick separation of the products and catalyst at the outlet of the reactor. In addition, downer reactors provide the possibility of working at higher CTO ratios, mitigating at the same time the lower conversion and bottom cracking implied by the use of relatively short residence times [96]. Compared with riser reactors, the plug-flow nature and uniform flow structure in downer reactors ensure better control on reaction extent to increase the selectivity of desired intermediate products. The downer reactors have more tendency for the production of middle distillates and light olefins [99].

4.3. Catalyst-to-Oil Ratio

The number of catalytic active sites in contact with the feed can be affected by the catalyst formula, temperature of the regenerated catalyst, the feedstock's quality and condition, and reactor severity. A higher CTO ratio could increase the feed conversion and light olefins selectivity [8,90,100]. It has been reported that a higher CTO led to a higher yield of ethylene and dry gas, while the yield of propylene reaches a maximum with increasing of CTO and decreased by the further increase in the CTO ratio [97].

The product distributions for the FCC cracking of naphtha using a mixture of two commercial FCC catalysts, containing 95 wt.% Y zeolite-based catalyst, and 5 wt.% ZSM-5 zeolite-based additive, at a reaction temperature of 600 °C, a residence time of 3.0 s, and with different CTO ratios, are shown in Table 6 [101]. Since the catalyst is the main heat source for the FCC process, increasing the CTO ratio results in an increase in the severity of the secondary reactions such as condensation and hydrogenation, resulting in the overcracking and formation of more saturated hydrocarbons. Therefore, more dry gas (mostly methane and ethane) is generated. For the thermal cracking, free radicals are generated via the splitting of H-C, and C-C bonds, which then tend to go through α and β scissions and polymerization to produce H₂, CH₄, C₂H₂, and coke [8,101].

Table 6. Yields of different products for FCC naphtha cracking at different CTO ratios [101].

CTO	10	14	18
Conversion (wt.%)	37.93	45.09	47.27
Dry gas	5.79	6.91	7.14
H ₂ + C ₁	2.15	2.10	1.94
C ₂ ⁼	2.94	3.72	4.05
LPG	30.65	36.58	38.32
C ₃ ⁼	13.99	17.27	18.54
C ₄ ⁼	9.66	10.37	10.59
nC ₄	1.12	1.41	1.45
iC ₄	4.20	5.30	5.51
Gasoline	59.45	52.70	50.55
LCO	2.61	2.21	2.18
Coke	1.49	1.60	1.81
HTC ^a	0.55	0.65	0.66

^a HTC: Hydrogen transfer coefficient = (nC₄ + iC₄)/C₄⁼.

At a higher CTO, due to the higher possibilities of contact between the hydrocarbons in the feedstocks and the active centers of the catalyst, thermal cracking is efficiently inhibited; subsequently, the yields of methane and hydrogen decrease by increasing the CTO. However, smaller pore-zeolites (ZSM-5) at higher CTO are more favorable for the ethane formation; therefore, the amount of ethane in dry gas increased. More contacts between the catalyst's active centers and the feedstock improve the catalytic cracking of hydrocarbons and increase the yield of light olefins even at high temperatures. It is worth

mentioning that the too high CTO (above 14) does not result in a considerable increase of propylene and butylene because of the improved hydrogen transfer reaction stemming from the presence of more Y zeolite-based catalyst [101].

The effect of different CTO on the yield of light olefins in the catalytic pyrolysis of Daqing atmospheric residue over LCM-5 catalyst, at 700 °C, the residence time of about 1.8 s, and the steam-to-oil ratio of 0.63 is shown in Figure 14b [91]. The yield of ethylene and total light olefins increased slightly by increasing the CTO, while the yield of propylene and butylene remained unchanged. The primary function of a catalyst is to provide energy and active centers for the reaction. The thermal pyrolysis reaction follows the free-radical mechanism and produces more ethylene. The catalyst's efficiency will become trivial when the catalyst provides the required energy and active centers for hydrocarbon pyrolysis. Increasing the CTO means high reaction consistency and a high degree of pyrolysis, and the yield of ethylene as an end product slightly increases.

Al-Absi and Al-Khattaf [97] studied Arabian light crude oil's pyrolysis to light olefins over two different catalysts in a fixed bed Micro-Activity Test (MAT) unit. The catalysts used in this study were named M-cat and E-cat. M-cat was a fresh MFI (ZSM-5) zeolite additive supported on a matrix, and E-cat was an equilibrium FCC USY catalyst. Before the pyrolysis reaction, M-cat was subjected to steam in a fixed-bed steamer at 810 °C for 6 h, while E-cat was calcined at 650 °C, with a heating rate of 5 °C/min for 3 h. The effect of the CTO variations on the crude oil conversion and the product distribution was investigated for both catalysts at the reaction temperature of 650 °C (Figure 15a,b). The conversion of crude oil increased by increasing the CTO ratio. It can be seen that at lower CTO (1 to 3), M-cat is more active, which could be as a result of its acidity and shape selectivity, and it can crack the naphtha fraction of oil to produce LPG and dry gas. At higher CTO (>3), E-cat shows more capability to crack heavier fractions (HCO and LCO) and has a higher conversion. It was found that the yield of ethylene, propylene, LPG, dry gas, and coke increased by increasing the CTO for both catalysts, whereas the yield of ethylene + propylene over the M-cat was higher than that of E-cat throughout the whole CTO range [102]. It has been reported that in the entrance section of a downer reactor, the conversion is relatively low because the solids are not held up in the reactor as much as they are in a riser reactor [96]. Therefore, a higher reaction temperature, higher CTO, and/or a higher catalyst activity will be required for the lower residence time and lower catalyst holdup to retain a sufficient conversion level. Downer reactors allow working with higher CTO because lifting of catalyst by vaporized feeds and steam is not a restrictive parameter in these reactors [96,103]. The plug flow would be ensured without backmixing in the down-flow reaction. As is known, the FCC process comprises successive reactions, and the preferred products such as gasoline and olefins are considered intermediate products, and suppression of backmixing could increase the yield of these intermediate products [103].

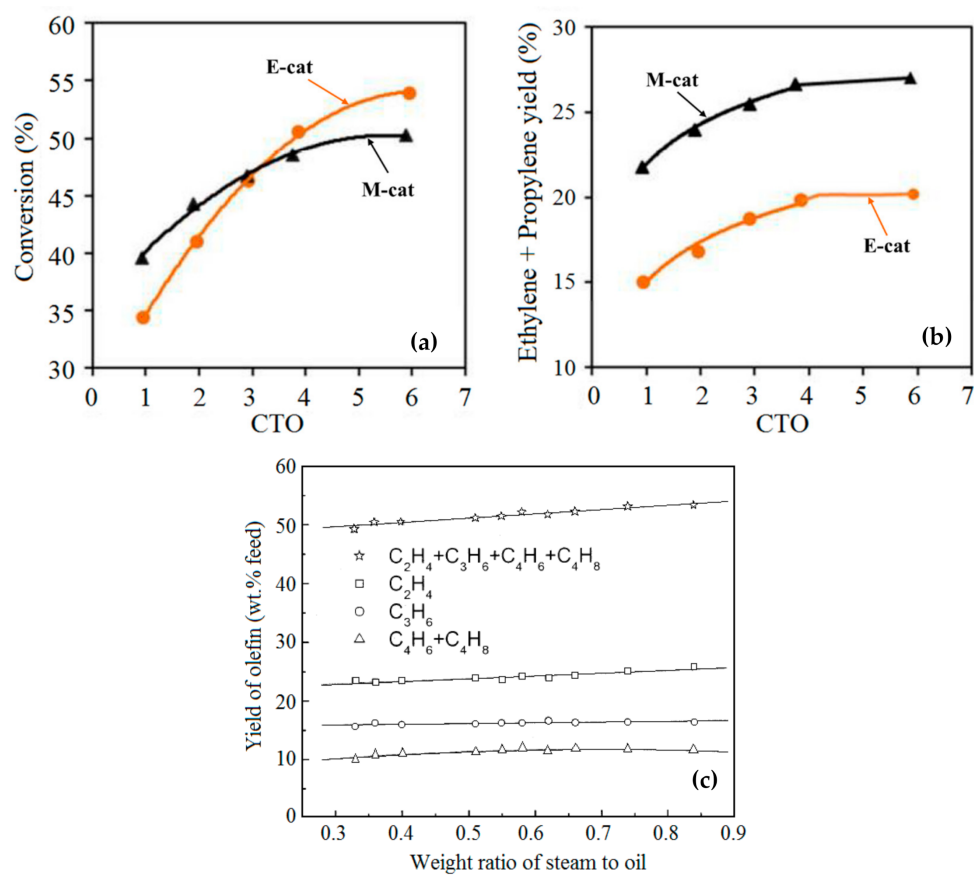


Figure 15. (a) Effect of CTO ratio on (a) conversion and (b) yields of ethylene + propylene for the catalytic cracking of AL crude oil [102]; (c) Effect of the steam-to-oil ratio on the yields of light olefins [91].

4.4. Steam-to-Hydrocarbon Feed Ratio

Steam is a low-cost diluent in the FCC process to reduce the coke deposition on the catalyst. The amount of steam and the steam-to-oil ratio could affect the light olefin products [8]. The effect of steam-to-hydrocarbon ratio, in the range of 0.2–1.6, for the catalytic pyrolysis of Chinese Daqing atmospheric residue at the reaction temperature of 650 °C, the residence time of 2.7 s, and CTO of 15.5 investigated by Meng et al. [90]. The results are shown in Table 7. By increasing the steam-to-oil ratio, the yields of dry gas, ethylene, propylene, and total light olefins gradually increased; yields of diesel, gasoline, and coke decreased slightly, while the changes in the feed conversion and the LPG yield were negligible. The partial pressure of the hydrocarbons in the feedstock could be reduced by increasing the steam-to-feed ratio, enhancing the cracking of hydrocarbons into the products with low molecular weight. Moreover, the high average catalyst activity could be preserved due to the lower coke deposition in the presence of steam. However, the results prove that the higher steam-to-feed ratio is beneficial to the light olefin production, but due to the restrictions such as the disposal capacity of the unit and the economic benefits, the steam-to-oil ratio cannot be increased unlimitedly.

In the industrial FCC units, steam and hydrocarbon feed are injected into the riser reactor at the same time. In addition to the feed dilution, injection of steam have some mechanical reasons. The steam injected at the base of the riser for the catalyst fluidization and transportation coming from the regenerator. Injection of steam into the feed nozzles also improves the dispersion and vaporization of the feedstock. The use of the especially designed nozzles, together with the feed and steam's potential energy, results in the breaking and dispersion of the feed into the mist size droplets and allowing a rapid vaporization of feed when in contact with the hot catalyst. The amount of injected steam is between 2–6 wt.% referred to the feedstock, corresponding to a dilution ratio of 0.42–1.2 [104].

Table 7. Effect of steam-to-hydrocarbon weight ratio [90].

	Steam-to-Hydrocarbon Feed Weight Ratio						
	0.21	0.39	0.66	0.84	1.08	1.23	1.58
Yields of products (wt.%)							
Dry gas	21.45	21.83	22.74	22.71	23.79	23.94	24.68
LPG	44.24	43.09	43.28	43.57	44.84	44.71	44.95
Gasoline	18.27	18.42	17.71	17.60	16.46	16.31	16.10
Diesel oil	3.87	4.31	3.52	3.54	3.70	3.93	3.15
Heavy oil	1.73	1.90	1.16	1.30	1.18	1.25	1.30
Coke	10.44	10.44	11.59	11.29	10.03	9.87	9.83
Feed conversion (%)	98.27	98.10	98.84	98.70	98.82	98.75	98.70
Yields of light olefins (wt.%)							
Ethylene	12.45	12.98	13.72	13.87	14.93	15.17	15.63
Propylene	22.60	22.95	24.04	23.96	26.11	26.70	27.04
Butylene	11.81	11.76	11.92	11.79	11.81	11.94	12.33
Total light olefins	46.87	47.69	49.67	49.62	52.86	53.82	55.01
Selectivity (%)	47.69	48.62	50.26	50.27	53.49	54.49	55.73

Xiang-Hai et al. [91] reported the same trend for the changes of olefins yield with the steam-to-oil ratio. The catalytic cracking of Daqing oil over an LCM-5 catalyst at 700 °C, a CTO of 16, a residence time of 1.9 s, and a steam-to-feed ratio in the range of 0.2–1.0 (Figure 15c) revealed that the yield of total light olefins increased gradually with increasing the steam-to-oil ratio. The lower coke deposition on catalyst at a higher steam-to-oil ratio enhanced the pyrolysis reactions of hydrocarbons, and therefore, the yields of light olefins increase at higher ratios of steam-to-oil. Different researchers studied the effect of steam-to-feed ratio, and they observed the same trends for the yields olefin with steam-to-feed ratio [104–106]. Evaluation of different FCC process parameters revealed that the reaction temperature is the crucial factor of the operating conditions. Therefore, the optimum conditions could be selected for obtaining the maximum production of light olefins.

4.5. Feed Properties

The property of the feedstock is also another parameter affecting the product distribution and yield of light olefins. During the past decades, the FCC feed mostly consists of heavier hydrocarbons with a growing tendency to incorporate residue. These feeds with more aromatic contents, are difficult to convert to light olefins. However, using a proper catalyst system with high resistance to deactivation by coke and metals could overcome the problem of using heavier feedstocks, such as residue, to produce light olefins. Recently, tight oils with a paraffinic nature also have entered the market as an interesting feedstock for the olefin production. Generally, tight oils are relatively light, and contain low amounts of nitrogen, sulfur, nickel, and vanadium [33]. In addition to the traditional oil-based stocks, there are also other stocks which are of interest for olefin production. For example, Fischer-Tropsch waxes with high paraffinic, produced from the biomass gasification or ethane reforming, would be a good candidate for this purpose [107]. Hydrotreated pyrolysis oils were also reported as another feedstock in FCC, with low selectivity to light olefins [108].

The hydrogen content is associated with the maximum reachable olefins yield in the unit and depends on the feedstock's paraffins amount. In addition, maximization of the propylene yield needs a proper process and catalyst system to avoid the hydrogen transfer reactions, which reduces the yield of light olefins. Without the proper process and catalyst system, the use of highly paraffinic feedstock will not have any benefits for maximizing propylene yield [96]. The feedstock with higher hydrogen content (more paraffinic) could yield higher propylene than the feedstock with lower hydrogen content (more aromatic). Thus, it may be helpful if the refineries go through severe hydrotreating of the feed to be cracked. Therefore, the hydrogen content in the feedstock can curb the potential of producing light olefins.

As mentioned above, the feed properties could affect the production of the light olefins. The catalytic pyrolysis of different types of heavy oils at 660 °C, a residence time of 2.2 s, a CTO of 15.5, and a steam-to-oil ratio of 0.75, over a CEP-1 catalyst was investigated by Meng et al. [90]. The main properties of each type of feedstocks are given in Table 8. The obtained results of the catalytic cracking of these different types of feedstocks are shown in Table 9. The feed conversion for all feedstocks was more than 98%. It can be seen that the yield of light olefins increased by increasing the H/C mol ratio and decreasing aromatic carbon. The feedstocks with higher aromatics content produce less olefin precursors in the gasoline boiling range, leading to a lower yield of light olefins.

Table 8. Pyrolysis feedstocks properties [90].

	Feedstocks			
	Daqing AR	Daqing VR	Daqing VGO	Huabei AR
Density (20 °C) g/cm ³	0.9069	0.9221	0.8011	0.9162
Viscosity (100 °C) mm ² /s	28.9	106	7.2	43.3
Carbon residue (wt%)	4.3	8.8	0.05	8.9
Molecular weight	577	895	426	608
Hydrogen (wt%)	13.11	12.78	13.58	12.87
Carbon (wt%)	86.52	86.93	86.36	86.51
H/C mol ratio	1.82	1.76	1.89	1.79
Aromatic carbon (wt%)	10.90	13.76	6.84	13.00
Group analysis (wt%)				
Saturates	57.08	42.91	85.39	56.80
Aromatics	27.61	34.53	11.98	22.65
Resin and asphaltene	15.31	22.56	2.63	20.55

Table 9. Product distribution with different types of feedstocks [90].

	Feedstock			
	Daqing VGO	Daqing AR	Huabei AR	Daqing VR
H/C mol ratio	1.89	1.82	1.79	1.76
Aromatic carbon (wt%)	6.84	10.90	13.00	13.76
Yields of products (wt%)				
Dry gas	26.31	24.06	28.22	27.36
LPG	41.68	42.17	37.13	35.18
Gasoline	16.28	16.86	14.92	16.51
Diesel oil	3.53	4.31	4.51	4.61
Heavy oil	0.99	0.82	0.88	1.56
Coke	11.22	11.78	14.33	14.78
Feed conversion (%)	99.01	98.18	99.12	98.44
Yields of light olefins (wt.%)				
Ethylene	13.53	13.75	12.21	12.14
Propylene	22.60	22.58	19.27	19.93
Butylene	11.94	10.65	10.43	8.41
Total light olefins	48.07	46.98	41.92	40.48
Selectivity (%)	48.55	47.86	42.29	41.12

Meng et al. [90] also studied the effect of temperature on these different feedstocks, and their results revealed that the yield of ethylene increased by temperature for all types of feedstocks, while the yields of propylene and total light olefins reached a peak and then decreased by increasing temperature. Compared with the yields of total light olefins and propylene obtained from the catalytic cracking of Huabei AR and Daqing VR, the higher yields obtained when Daqing VGO and Daqing AR were used as the feedstock.

This behavior is attributed to the higher H/C molar ratios and lower aromatic content of the Daqing AR and VGO. Compared to the yields of propylene and total light olefins, the yield of ethylene did not significantly change with the type of feedstocks [90].

The aromaticity, or C/H ratio, of the feedstock, can be measured using the Bureau of Mines Correlation Index (BMCI) [109,110]. BMCI is determined from the parameters, including the average boiling point of a distillation fraction and its specific or API (American Petroleum Institute) gravity, according to the following equivalent formulas in Equations (1)–(3) [110]:

$$\text{BMCI} = 473.7 \left(d_{60}^{60} \right) - 456.8 + \frac{48460}{^{\circ}\text{C} + 273} \quad (1)$$

$$\text{BMCI} = 473.7 \left(d_{60}^{60} \right) - 456.8 + \frac{87552}{^{\circ}\text{F} + 460} \quad (2)$$

$$\text{BMCI} = \frac{67030}{\text{API} + 131.5} - 456.8 + \frac{87552}{^{\circ}\text{F} + 460} \quad (3)$$

where $^{\circ}\text{C}$ is the average boiling point of the fraction, d_{60}^{60} is the liquid specific gravity of the fraction at 60°F , and API is the API gravity at 60°F .

The BMCI value in the range of 0–15 shows the paraffinic oils, and values higher than 50 indicate the aromatic oils [109]. The lower the BMCI, the higher the yields of light olefins. As mentioned earlier the feedstocks with the higher content of paraffins and long-chain alkyl cyclic lead to a good performance in light olefins production. The catalytic cracking of naphtha fractions for the production of light olefins was studied by Akah et al. [111]. The composition of different naphtha fractions existing at Saudi Aramco Refineries, including heavy cracked naphtha (HCN), heavy straight run naphtha (HSRN), light straight-run naphtha (LSRN), and light cracked naphtha (LCN) are shown in Table 10. The results for the cracking of different fractions of naphtha (Table 11) at 650°C , and a CTO of 6 revealed that the lowest conversion and yield of light olefins belonged to the HCN fraction with the highest aromaticity, while this fraction had the highest coke formation [111].

Further investigations showed that the conversion and also yield of propylene increased by increasing the temperature; however, at different temperatures, they follow the same trend for both conversion and yield of propylene (LCN > HSRN > LRSN > HCN) (Figure 16a,b) [111]. The higher conversion of HSRN than LSRN could be due to its lower thermal stability. The higher increase in the conversion of LSRN by increasing the temperature from 625°C to 650°C might be due to the further cracking of hydrocarbon molecules at higher temperatures. For both LSRN and HSRN, the yield of propylene followed the same trend as the conversion. The HSRN fraction, which comprises the molecules with longer chains and higher activity than those found in LSRN, leads to a higher propylene yield than LSRN fraction. LCN was found to be the most reactive feedstock with the highest conversion and yield to light olefins. The presence of high content of olefins in the LCN fraction (28.5 wt.%) can act as an intermediate and increase the yield of light olefins.

Table 10. Composition of different naphtha fractions [111].

	Component (wt.%)	n-Paraffins	Iso Paraffins	Olefins	Naphthalenes	Aromatics	Total
LSRN	C-5	29.8	8.2	-	2.2	-	40.3
	C-6	26.9	28.5	-	3.7	-	59.1
	C-7	-	0.6	-	-	-	0.6
	total	57.3	36.7	-	6.0	-	100.0

Table 10. Cont.

	Component (wt.%)	n-Paraffins	Iso Paraffins	Olefins	Naphthalenes	Aromatics	Total
HSRN	C-6	4.8	1.5	-	2.2	0.3	8.7
	C-7	11.4	8.5	-	5.5	2.5	27.9
	C-8	10.0	9.4	-	3.3	6.4	29.1
	C-9	7.0	8.6	-	2.7	5.0	23.2
	C-10	2.8	3.6	-	0.6	1.3	8.4
	C-11	0.9	1.1	-	0.1	0.1	2.3
	C-12	0.2	0.1	-	-	-	0.3
	total	37.0	32.9	-	14.4	15.7	100.0
LCN	C-4	-	-	0.6	-	-	0.6
	C-5	4.5	24.7	22.2	1.6	-	53.1
	C-6	1.5	9.4	4.2	3.5	11.8	30.4
	C-7	0.8	2.9	0.9	3.7	6.7	14.9
	C-8	-	0.5	0.3	0.18	-	1.0
	total	6.8	37.5	28.2	9.0	18.5	100.0
HCN	C-5	0.2	1.5	1.1	0.1	-	2.9
	C-6	0.1	0.4	0.5	0.2	-	1.2
	C-7	-	-	-	0.1	20.7	20.8
	C-8	0.3	1.0	1.3	0.6	33.0	36.2
	C-9	0.3	1.5	0.3	0.6	23.4	26.0
	C-10	0.3	2.1	0.1	0.2	6.0	8.6
	C-11	0.2	2.1	-	0.1	1.6	3.9
	C-12	-	0.2	-	-	-	0.2
	total	1.4	8.8	3.3	1.9	84.6	100.0

Table 11. Comparison of the products of naphtha cracking at 650 °C [111].

	Feedstock			
	HCN	LCN	HSRN	LSRN
CTO	5.98	6.04	5.71	5.95
Conversion (%)	14.71	40.07	34.79	26.55
Yields (wt.%)				
Methane	0.85	2.81	1.81	2.33
Ethylene (C ₂ ⁻)	4.75	9.14	5.45	4.79
Propylene (C ₃ ⁻)	5.78	17.75	12.94	10.12
Coke	0.79	0.07	0.66	0.70
Groups				
H ₂ – C ₂ (Dry gas) incl C ₂ ⁻	6.60	13.48	9.04	9.78
All C ₃ – C ₄ (LPG)	7.32	26.53	25.09	16.08
C ₂ ⁻ – C ₄ ⁻ (total light olefins)	11.23	33.63	25.79	18.46
C ₃ ⁻ + C ₄ ⁻ (LPG olefins)	6.48	24.49	20.34	13.66
C ₄ ⁻ (Butenes)	1.70	6.74	7.40	3.54
Selectivities				
Dry gas	44.86	33.63	25.98	36.82
Propylene	32.49	44.28	37.19	38.12
Coke	5.36	0.16	1.89	2.64

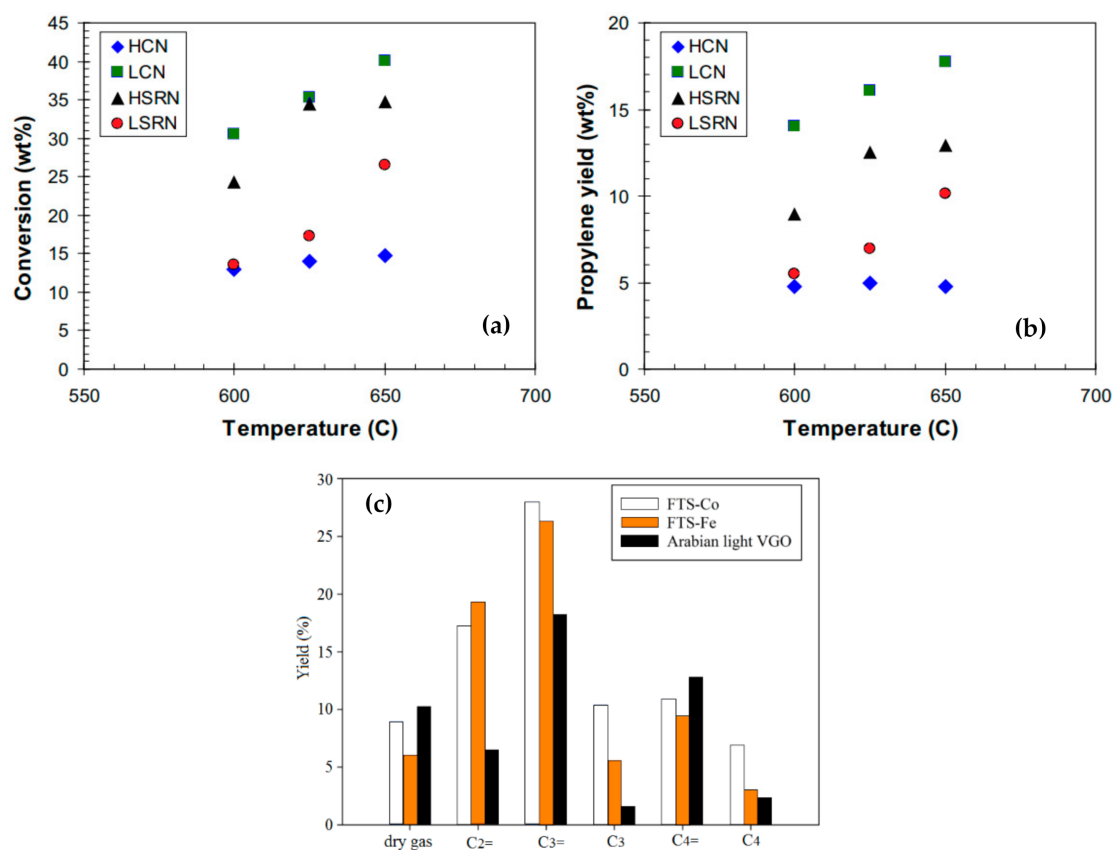


Figure 16. (a) Effect of temperature on (a) the conversion, (b) the propylene yield of catalytic cracking of various naphtha fraction cracking at CTO of 6 [111], (c) the gas product yields from catalytic cracking of FTS-Co, FTS-Fe, and Arabian light VGO [70].

Recently, the impact of feed composition on the yield of light olefins was studied by Dement'ev et al. [70]. They used a series of FT products, including the FT products over a Co catalyst (FTS-Co) and also over a Fe catalyst (FTS-Fe), as feedstock, and compared them with the results reported for Arabian light VGO [62] as feedstock (Figure 16c). Compared with FTS-Fe, FTS-Co feedstock generated more dry gas, while more ethylene was produced using the FTS-Fe feedstock. A higher formation of propylene and butylene was also observed using the FTS-Co feedstock. The results obtained for the FTS-type feedstocks compared with that of Arabian VGO, and as can be seen, the yield of ethylene and propylene using FTS-type feedstocks were obviously higher than Arabian VGO, while the yield of dry gas and butylene was higher for the Arabian VGO. The higher yields of ethylene and propylene for FTS-type feedstocks could be due to the much higher reactivity of linear alkanes and alkenes in these feedstocks than VGO.

5. Concluding Remarks

Olefins, as the critical components in chemical industries, are produced using different technologies. According to the types of feedstocks, such as methane and light alkanes, and naphtha, different processes such as steam cracking, Fluid catalytic cracking (FCC), oxidative coupling of methane (OCM), Fischer-Tropsch synthesis (FTS), and methanol to olefins can be used for the olefin production. Almost 59% of olefins are produced by FCC process, and about 39% by steam cracking of ethane, LPG, and liquid feeds. FCC as an energy-saving process with high flexibility for the operating conditions is the second major process for olefin production.

The acidic catalysts such as zeolites are the most active catalysts for hydrocarbon cracking. Reducing the aromatization reaction in the FCC process increases the light olefins yield. The FCC catalysts usually contain an active component (zeolite), a matrix (e.g.,

silica-alumina), a binder (e.g., bentonite), and a filler to provide high physical strength. The FCC catalyst can be appropriately designed for the production of desired products. Several parameters, including the ZSM-5 content, crystal size, and Si/Al ratio of the zeolite-based catalysts, are discussed in this review. The cracking of linear hydrocarbons improves using the highly porous zeolite structure with high acidity and increases the ethylene and propylene yields. Generally, the addition of ZSM-5 in the catalyst structure increases the yield of light olefins, mainly propylene, reaching a maximum and then decreasing by a further increase of the ZSM-5 content. By increasing the ZSM-5 content as the main active component of the FCC catalyst, an increase in the propylene yield at the expense of gasoline was reported. ZSM-5 cracks the olefins before they go through hydrogen transfer reactions; therefore, the yield of butylene could be slightly decreased due to the intensification of butylene cracking and the steric restrictions in the narrow pores of zeolite, which inhibits the formation and stabilization of bulk transition states.

The effect of shape selectivity limits the formation of intermediates inside the catalyst's pores. The active catalytic sites on the external surface and the zeolite crystals' pore mouth are responsible for the undesired reactions. These non-selective and undesired reactions could be controlled and limited by tuning the crystal sizes; the lower the particle size, the lower the diffusional limitations. The diffusing out of the products from the microporous channels avoids the secondary reactions, reduces the coke formation, and improves the light olefins yield.

Besides the parameters mentioned above, the light olefins yield is also affected by the zeolite's acidity. The strong Brønsted acidity of bridging Si-(OH)-Al sites are formed by the presence of aluminum inside the silicate framework. The acidity of the catalyst can be adjusted by altering the Si/Al ratio in the zeolites. The zeolitic catalysts with a lower Si/Al ratio have a higher number of acid sites, improving the cracking reaction. Hydrogen transfer reactions mostly occur on the catalyst's surface, and they are more evident at lower Si/Al ratios (higher acidity). The hydrogen transfer reactions result in higher production of dry gas and lower production of light olefins. Increasing the Si/Al ratio and hindering the hydrogen transfer reactions improves the yield of light olefins. Due to the catalysts ability for over-cracking of gasoline range reactive species to the light olefins and preserving their saturation into paraffins, the yields of light olefins ($C_2^=$, $C_3^=$, $C_4^=$) increase by increasing the Si/Al ratio.

In addition to the catalyst properties, the performance of FCC units also depends on the operating parameters, including temperature, hydrocarbon partial pressure, residence time, catalyst-to-oil ratio, and feed composition. The rate of catalytic and thermal cracking reactions increases at higher reaction temperatures, thus achieving more thorough pyrolysis and yielding higher light products. The higher reaction temperatures accelerate the reaction rate of the catalytic cracking and increase the cracking of gasoline range hydrocarbons into lighter hydrocarbons. Ethylene is mainly produced from thermal cracking reactions, and as the end product, it is improbable to go through secondary reactions, apart from hydrogenation to ethane. Usually, propylene and butylene are produced from the catalytic cracking reactions, and as intermediate products, they can undergo secondary reactions (e.g., hydrogen transfer, aromatization), which are more pronounced at higher temperatures.

The optimum residence time is related to the catalyst and feedstock compositions. The longer residence time increases the feedstock's catalytic pyrolysis, and yields of light olefins decrease due to the secondary reactions in the prolonged reaction and higher residence time. The yields of light olefins increase slightly by increasing the residence time to the optimum point and then decrease by increasing the residence time.

Due to the higher possibilities of the contact between the feedstock and the catalyst's active sites at the higher CTO, the feed conversion and the light olefins yields increase by increasing the catalyst-to-oil ratio, and thermal cracking is efficiently prohibited. However, similar to the reaction temperature and the residence time, the yields of propylene and total light olefins reach a peak and then decrease slightly by increasing the CTO.

Steam is generally used as an inexpensive diluent in the FCC process to reduce the coke deposition on the catalyst. Yields of ethylene, propylene, and total light olefins gradually increased by increasing the steam-to-oil ratio. At a higher steam-to-oil ratio, the partial pressure of hydrocarbons in the feedstock reduces and improves hydrocarbons' cracking into the low molecular weight products. As a result of lower coke deposition, the average catalyst's activity preserves for a longer time.

The feedstocks with a higher hydrogen content (more paraffinic) result in higher light olefins, such as propylene, than the feedstocks with lower hydrogen content (more aromatic); therefore, using the feedstocks with severe hydrotreatment could improve the performance of the FCC unit.

Author Contributions: Conceptualization, Z.G.; writing—original draft preparation, Z.G. and F.G.; writing—review and editing, Z.G., F.G., Z.T., M.T. and M.V. All authors have read and agreed to the published version of the manuscript.

Funding: This publication is a result of the project CATAMARAN, Reg. No. CZ.02.1.01/0.0/0.0/16_013/0001801, which has been co-financed by European Union from the European Regional Development Fund through the Operational Programme Research, Development and Education. This project has also been financially supported by the Ministry of Industry and Trade of the Czech Republic which has been providing institutional support for long-term conceptual development of research organisation. The result was achieved using the infrastructure of the project Efficient Use of Energy Resources Using Catalytic Processes (LM2018119) which has been financially supported by MEYS within the targeted support of large infrastructures.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

Abbreviations

The following abbreviations are used in this manuscript:

ACE	Advanced Cracking Evaluation
AFX	Advanced Fuels eXperimental
API	American Petroleum Institute
AR	atmospheric residue
ASL	Arab Super Light
BATH	Bio-acid acetone to hydrocarbons
BMCI	Bureau of Mines Correlation Index
BTX	benzene, toluene, and the isomers of xylene
CC	Catalytic Cracking
CPP	catalytic pyrolysis process
CTO	Catalyst-to-oil ratio
DCC	Deep Catalytic Cracking
DCC	deep catalytic cracking process
DH	De-hydration process
FCC	Fluid catalytic cracking
FM	Fermentation
FP	Flash Pyrolysis
FTS	Fischer-Tropsch synthesis
GAS	Gasification
GS	Gas stream reactor technologies
HCN	heavy cracked naphtha
HCO	heavy cycle oil
HG	Hydrogenation
HP	Hydro-Pyrolysis
HSRN	heavy straight run naphtha
HTUL	Hydro-Thermal Upgrading Liquefaction
KFUPM	King Fahd University of Petroleum and Minerals

LCN	light cracked naphtha
LCO	light cycle oil
LIQ	liquefaction
LPG	liquefied petroleum gas
LSRN	light straight run naphtha
MAT	Micro-Activity Test
MTO	methanol to olefins
OC	Oxidative Coupling
OCM	oxidative coupling of methane
OD	Oxidative Dehydrogenation
OM	Olefin Metathesis
OU	Olefins Upgrading
PD	Propane Dehydrogenation
PMC	Propylene Maximization Catalyst
RCY	Re-cycling pyrolysis
REC	Recovery of refinery off-gases
REF	Refinery processes
RIPP	Research Institute of Petroleum Processing
SC	steam cracking
SEP	Gas separation process
SR	Steam Reforming
USY	Ultra-stabilized zeolite Y
VGO	vacuum gas oil

References

- Hsu, C.S.; Robinson, P.R. *Petroleum Science and Technology*; Springer: Cham, Switzerland, 2019.
- Speight, J.G. Organic chemistry. In *Environmental Organic Chemistry for Engineers*; Elsevier BV: Cambridge, MA, USA, 2017; pp. 43–86.
- Stauffer, E.; Dolan, J.A.; Newman, R. Chapter 3—Review of Basic Organic Chemistry. In *Fire Debris Analysis*; Stauffer, E., Dolan, J.A., Newman, R., Eds.; Academic Press: Burlington, VT, USA, 2008; pp. 49–83.
- Fakhroleslam, M.; Sadrameli, S.M. Thermal cracking of hydrocarbons for the production of light olefins; A review on optimal process design, operation, and control. *Ind. Eng. Chem. Res.* **2020**, *59*, 12288–12303. [[CrossRef](#)]
- Zacharopoulou, V.; Lemonidou, A.A. Olefins from biomass intermediates: A review. *Catalysts* **2017**, *8*, 2. [[CrossRef](#)]
- Amghizar, I.; Vandewalle, L.A.; Van Geem, K.M.; Marin, G.B. New trends in olefin production. *Engineering* **2017**, *3*, 171–178. [[CrossRef](#)]
- Sadeghbeigi, R. *Fluid Catalytic Cracking Handbook: An Expert Guide to the Practical Operation, Design, and Optimization of FCC Units*; Elsevier Science: Waltham, MA, USA, 2020.
- Akah, A.; Williams, J.; Ghrami, M. An overview of light olefins production via steam enhanced catalytic cracking. *Catal. Surv. Asia* **2019**, *23*, 265–276. [[CrossRef](#)]
- Amghizar, I.; Dedeyne, J.N.; Brown, D.J.; Marin, G.B.; Van Geem, K.M. Sustainable innovations in steam cracking: CO₂ neutral olefin production. *React. Chem. Eng.* **2020**, *5*, 239–257. [[CrossRef](#)]
- Subramanian, R.; Schmidt, L.D. Renewable olefins from biodiesel by autothermal reforming. *Angew. Chem. Int. Ed.* **2005**, *44*, 302–305. [[CrossRef](#)]
- Shelepova, E.V.; Vedyagin, A.A. Intensification of the dehydrogenation process of different hydrocarbons in a catalytic membrane reactor. *Chem. Eng. Process. Process Intensif.* **2020**, *155*, 108072. [[CrossRef](#)]
- Wu, T.; Yu, Q.; Roghair, I.; Wang, K.; Annaland, M.V.S. Chemical looping oxidative dehydrogenation of propane: A comparative study of Ga-based, Mo-based, V-based oxygen carriers. *Chem. Eng. Process. Process Intensif.* **2020**, *157*, 108137. [[CrossRef](#)]
- Lima, D.S.; Perez-Lopez, O.W. Oxidative coupling of methane to light olefins using waste eggshell as catalyst. *Inorg. Chem. Commun.* **2020**, *116*, 107928. [[CrossRef](#)]
- Luo, L.; You, R.; Liu, Y.; Yang, J.; Zhu, Y.; Wen, W.; Pan, Y.; Qi, F.; Huang, W. Gas-phase reaction network of Li/MgO-catalyzed oxidative coupling of methane and oxidative dehydrogenation of ethane. *ACS Catal.* **2019**, *9*, 2514–2520. [[CrossRef](#)]
- Wang, P.; Zhang, X.; Zhao, G.; Liu, Y.; Lu, Y. Oxidative coupling of methane: MO_x-modified (M = Ti, Mg, Ga, Zr) Mn₂O₃-Na₂WO₄/SiO₂ catalysts and effect of MO_x modification. *Chin. J. Catal.* **2018**, *39*, 1395–1402. [[CrossRef](#)]
- Pedersen, E.Ø.; Svenum, I.-H.; Blekkan, A. Mn promoted Co catalysts for Fischer-Tropsch production of light olefins—An experimental and theoretical study. *J. Catal.* **2018**, *361*, 23–32. [[CrossRef](#)]
- Tian, Z.; Wang, C.; Yue, J.; Zhang, X.; Ma, L. Effect of a potassium promoter on the Fischer-Tropsch synthesis of light olefins over iron carbide catalysts encapsulated in graphene-like carbon. *Catal. Sci. Technol.* **2019**, *9*, 2728–2741. [[CrossRef](#)]

18. Di, Z.; Zhao, T.; Feng, X.; Luo, M. A newly designed core-shell-like zeolite capsule catalyst for synthesis of light olefins from syngas via Fischer–Tropsch synthesis reaction. *Catal. Lett.* **2019**, *149*, 441–448. [[CrossRef](#)]
19. Yang, M.; Fan, D.; Wei, Y.; Tian, P.; Liu, Z. Recent progress in methanol-to-olefins (MTO) catalysts. *Adv. Mater.* **2019**, *31*, e1902181. [[CrossRef](#)] [[PubMed](#)]
20. Hua, J.; Dong, X.; Wang, J.; Chen, C.; Shi, Z.; Liu, Z.; Han, Y. Methanol-to-olefin conversion over small-pore DDR zeolites: Tuning the propylene selectivity via the olefin-based catalytic cycle. *ACS Catal.* **2020**, *10*, 3009–3017. [[CrossRef](#)]
21. Kang, J.H.; Alshafei, F.H.; Zones, S.I.; Davis, M.E. Cage-defining ring: A molecular sieve structural indicator for light olefin product distribution from the methanol-to-olefins reaction. *ACS Catal.* **2019**, *9*, 6012–6019. [[CrossRef](#)]
22. Ding, J.; Huang, L.; Gong, W.; Fan, M.; Zhong, Q.; Russell, A.G.; Gu, H.; Zhang, H.; Zhang, Y.; Ye, R.-P. CO₂ hydrogenation to light olefins with high-performance Fe_{0.30}Co_{0.15}Zr_{0.45}K_{0.10}O_{1.63}. *J. Catal.* **2019**, *377*, 224–232. [[CrossRef](#)]
23. Goud, D.; Gupta, R.; Maligal-Ganesh, R.; Peter, S.C. Review of catalyst design and mechanistic studies for the production of olefins from anthropogenic CO₂. *ACS Catal.* **2020**, *10*, 14258–14282. [[CrossRef](#)]
24. Ye, R.-P.; Ding, J.; Gong, W.; Argyle, M.D.; Zhong, Q.; Wang, Y.; Russell, C.K.; Xu, Z.; Russell, A.G.; Li, Q.; et al. CO₂ hydrogenation to high-value products via heterogeneous catalysis. *Nat. Commun.* **2019**, *10*, 5698. [[CrossRef](#)]
25. Numpilai, T.; Wattanakit, C.; Chareonpanich, M.; Limtrakul, J.; Witoon, T. Optimization of synthesis condition for CO₂ hydrogenation to light olefins over In₂O₃ admixed with SAPO-34. *Energy Convers. Manag.* **2019**, *180*, 511–523. [[CrossRef](#)]
26. Wang, X.; Wu, D.; Zhang, J.; Gao, X.; Ma, Q.; Fan, S.; Zhao, T.-S. Highly selective conversion of CO₂ to light olefins via Fischer-Tropsch synthesis over stable layered K–Fe–Ti catalysts. *Appl. Catal. A Gen.* **2019**, *573*, 32–40. [[CrossRef](#)]
27. Wu, T.; Lin, J.; Cheng, Y.; Tian, J.; Wang, S.; Xie, S.; Pei, Y.; Yan, S.; Qiao, M.; Xu, H.; et al. Porous Graphene-Confined Fe–K as highly efficient catalyst for CO₂ direct hydrogenation to light olefins. *ACS Appl. Mater. Interfaces* **2018**, *10*, 23439–23443. [[CrossRef](#)]
28. Ren, T.; Patel, M.K.; Blok, K. Olefins from conventional and heavy feedstocks: Energy use in steam cracking and alternative processes. *Energy* **2006**, *31*, 425–451. [[CrossRef](#)]
29. Akah, A.; Al-Ghrami, M. Maximizing propylene production via FCC technology. *Appl. Petrochem. Res.* **2015**, *5*, 377–392. [[CrossRef](#)]
30. Rahimi, N.; Karimzadeh, R. Catalytic cracking of hydrocarbons over modified ZSM-5 zeolites to produce light olefins: A review. *Appl. Catal. A Gen.* **2011**, *398*, 1–17. [[CrossRef](#)]
31. Yoshimura, Y.; Kijima, N.; Hayakawa, T.; Murata, K.; Suzuki, K.; Mizukami, F.; Matano, K.; Konishi, T.; Oikawa, T.; Saito, M.; et al. Catalytic cracking of naphtha to light olefins. *Catal. Surv. Jpn.* **2001**, *4*, 157–167. [[CrossRef](#)]
32. Speight, J.G. Chapter 11—Fouling during catalytic cracking. In *Fouling in Refineries*; Speight, J.G., Ed.; Gulf Professional Publishing: Boston, MA, USA, 2015; pp. 271–302.
33. Vogt, E.T.C.; Weckhuysen, B.M. Fluid catalytic cracking: Recent developments on the grand old lady of zeolite catalysis. *Chem. Soc. Rev.* **2015**, *44*, 7342–7370. [[CrossRef](#)]
34. Maadhah, A.G.; Fujiyama, Y.; Redhwi, H.; Abul-Hamayel, M.; Aitani, A.; Saeed, M.; Dean, C. A new catalytic cracking process to maximize refinery propylene. *Arab. J. Sci. Eng.* **2008**, *33*, 17–28.
35. Zhu, G.; Xie, C.; Li, Z.; Wang, X. Catalytic processes for light olefin production. In *Springer Handbook of Nanotechnology*; Springer: Cham, Switzerland, 2017; pp. 1063–1079.
36. Yujian, L.; Jun, L.; Huiping, T.; Yun, X.; Liuzhou, Z. Advances in DCC process and catalyst for propylene production from heavy oils. *China Pet. Process. Petrochem. Technol.* **2011**, *13*, 1–5.
37. Genquan, Z.; Chaogang, X. Research and commercial application of CPP technology for producing light olefins from heavy oil. *China Pet. Process. Petrochem. Technol.* **2013**, *15*, 7–12.
38. Soni, D.S.; Shorey, S.; Rao, M.R. Maximizing propylene through catalytic cracking: Indmax fluid catalytic cracking (I-FCC) process. In Proceedings of the 2008 AIChE Spring National Meeting, New Orleans, LA, USA, 6–10 April 2008.
39. Banjare, M.; Pal, M.P.; Nanacharaiyah, C.; Desai, V.S.; Guria, S.; Vardhan, H.; Mondal, B.C. Use of phased array ultrasonic testing for sizing of hydrogen blisters in LPG wash water vessel in INDMAX unit. *Int. J. Mech. Ind. Eng.* **2012**, *1*, 203–207. [[CrossRef](#)]
40. Fujiyama, Y.; Al-Tayyar, M.H.; Dean, C.F.; Aitani, A.; Redhwi, H.H. Chapter 1 Development of high-severity FCC process: An overview. In *Studies in Surface Science and Catalysis*; Ocelli, M.L., Ed.; Elsevier: Amsterdam, The Netherlands, 2007; Volume 166, pp. 1–12.
41. Parthasarathi, R.S.; Alabduljabbar, S.S. HS-FCC high-severity fluidized catalytic cracking: A newcomer to the FCC family. *Appl. Petrochem. Res.* **2014**, *4*, 441–444. [[CrossRef](#)]
42. Haribal, V.P.; Chen, Y.; Neal, L.; Li, F. Intensification of ethylene production from naphtha via a redox oxy-cracking scheme: Process simulations and analysis. *Engineering* **2018**, *4*, 714–721. [[CrossRef](#)]
43. Jeong, S.M.; Byun, Y.C.; Chae, J.H.; Lee, W.-H. Coke formation on the surface of α -Al₂O₃ in the catalytic pyrolysis of naphtha. *Korean J. Chem. Eng.* **2001**, *18*, 842–847. [[CrossRef](#)]
44. Jeong, S.M.; Chae, J.H.; Lee, W.-H. Study on the catalytic pyrolysis of naphtha over a KVO₃/ α -Al₂O₃ catalyst for production of light olefins. *Ind. Eng. Chem. Res.* **2001**, *40*, 6081–6086. [[CrossRef](#)]
45. Lee, W.-H.; Jeong, S.M.; Chae, J.H.; Kang, J.-H.; Lee, W.-J. Coke formation on KVO₃–B₂O₃/SA5203 catalysts in the catalytic pyrolysis of naphtha. *Ind. Eng. Chem. Res.* **2004**, *43*, 1820–1826. [[CrossRef](#)]
46. Mukhopadhyay, R.; Kunzru, D. Catalytic pyrolysis of naphtha on calcium aluminate catalysts. Effect of potassium carbonate impregnation. *Ind. Eng. Chem. Res.* **1993**, *32*, 1914–1920. [[CrossRef](#)]

47. Oudejans, J.C. Zeolite Catalysts in Some Organic Reactions. Ph.D. Thesis, Delft University of Technology, Delft, The Netherlands, 1984.
48. Pop, G.; Ivanus, G.; Boteanu, S.; Tomi, P.; Pop, E. Catalytic Process for Preparing Olefins by Hydrocarbon Pyrolysis. U.S. Patent 4172816, 30 October 1979.
49. Zhao, Y.; Liu, J.; Xiong, G.; Guo, H. Enhancing hydrothermal stability of nano-sized HZSM-5 zeolite by phosphorus modification for olefin catalytic cracking of full-range FCC gasoline. *Chin. J. Catal.* **2017**, *38*, 138–145. [[CrossRef](#)]
50. He, Z.; Jiao, Q.; Fang, Z.; Li, T.; Feng, C.; Li, H.; Zhao, Y. Light olefin production from catalytic pyrolysis of waste tires using nano-HZSM-5/ γ -Al₂O₃ catalysts. *J. Anal. Appl. Pyrolysis* **2018**, *129*, 66–71. [[CrossRef](#)]
51. Perego, C.; Millini, R. Porous materials in catalysis: Challenges for mesoporous materials. *Chem. Soc. Rev.* **2013**, *42*, 3956–3976. [[CrossRef](#)] [[PubMed](#)]
52. Marcilly, C. Evolution of refining and petrochemicals. What is the place of zeolites. In *Studies in Surface Science and Catalysis*; Galarneau, A., Fajula, F., Di Renzo, F., Vedrine, J., Eds.; Elsevier: Amsterdam, The Netherlands, 2001; Volume 135, pp. 37–60.
53. Bellussi, G.; Pollesel, P. Industrial applications of zeolite catalysis: Production and uses of light olefins. In *Studies in Surface Science and Catalysis*; Elsevier: Amsterdam, The Netherlands, 2005; Volume 158, pp. 1201–1212.
54. Alotaibi, F.M.; González-Cortés, S.; Alotibi, M.F.; Xiao, T.; Al-Megren, H.; Yang, G.; Edwards, P.P. Enhancing the production of light olefins from heavy crude oils: Turning challenges into opportunities. *Catal. Today* **2018**, *317*, 86–98. [[CrossRef](#)]
55. Alotibi, M.F.; Alshammari, B.A.; Alotaibi, M.H.; Alotaibi, F.M.; Alshihri, S.; Navarro, R.M.; Fierro, J.L.G. ZSM-5 zeolite based additive in FCC process: A review on modifications for improving propylene production. *Catal. Surv. Asia* **2020**, *24*, 1–10. [[CrossRef](#)]
56. Abbot, J. The mechanism of paraffin reactions on HY zeolite. *J. Catal.* **1989**, *115*, 1–15. [[CrossRef](#)]
57. Hou, X.; Ni, N.; Wang, Y.; Zhu, W.; Qiu, Y.; Diao, Z.; Liu, G.; Zhang, X. Roles of the free radical and carbenium ion mechanisms in pentane cracking to produce light olefins. *J. Anal. Appl. Pyrolysis* **2019**, *138*, 270–280. [[CrossRef](#)]
58. Corma, A.; Orchillés, A. Current views on the mechanism of catalytic cracking. *Microporous Mesoporous Mater.* **2000**, *35*, 21–30. [[CrossRef](#)]
59. The changing dynamics of olefin supply/demand. *Catal. Today* **2005**, *106*, 10–14. [[CrossRef](#)]
60. Aufdembrink, B.A.; Chester, A.W.; Herbst, J.A.; Kresge, C.T. Ultra Large Pore Cracking Catalyst and Process for Catalytic Cracking. U.S. Patent 5258114, 2 November 1993.
61. Harding, R.; Peters, A.; Nee, J. New developments in FCC catalyst technology. *Appl. Catal. A Gen.* **2001**, *221*, 389–396. [[CrossRef](#)]
62. Aitani, A. Maximization of FCC light olefins by high severity operation and ZSM-5 addition. *Catal. Today* **2000**, *60*, 111–117. [[CrossRef](#)]
63. Čejka, J.; Morris, R.E.; Nachtigall, P. (Eds.) *Zeolites in Catalysis: Properties and Applications*; Royal Society of Chemistry: London, UK, 2017.
64. Arandes, J.M.; Torre, I.; Azkoiti, M.J.; Ereña, J.; Olazar, M.; Bilbao, J. HZSM-5 Zeolite As Catalyst Additive for Residue Cracking under FCC Conditions. *Energy Fuels* **2009**, *23*, 4215–4223. [[CrossRef](#)]
65. Buchanan, J. The chemistry of olefins production by ZSM-5 addition to catalytic cracking units. *Catal. Today* **2000**, *55*, 207–212. [[CrossRef](#)]
66. Degnan, T.; Chitnis, G.; Schipper, P. History of ZSM-5 fluid catalytic cracking additive development at Mobil. *Microporous Mesoporous Mater.* **2000**, *35*, 245–252. [[CrossRef](#)]
67. Zhao, X.; Roberie, T.G. ZSM-5 additive in fluid catalytic cracking. Effect of additive level and temperature on light olefins and gasoline olefins. *Ind. Eng. Chem. Res.* **1999**, *38*, 3847–3853. [[CrossRef](#)]
68. Bastiani, R.; Lau, L.Y.; Pinho, A.D.R.; Wasserman, R.; do Espirito Santo, I.B. Additives for Maximizing Light Olefins in Fluid Catalytic Cracking and Process Units. U.S. Patents US20150094511A1, 3 March 2018.
69. Bulatov, R.; Jirnov, B. FCC process of heavy feed stock with improved yield of light olefins. *Electron. Sci. J. Oil Gas Bus.* **2009**, 1–10.
70. Dement'Ev, K.I.; Sagaradze, A.D.; Kuznetsov, P.S.; Palankoev, T.A.; Maximov, A.L. Selective production of light olefins from Fischer–Tropsch synthetic oil by catalytic cracking. *Ind. Eng. Chem. Res.* **2020**, *59*, 15875–15883. [[CrossRef](#)]
71. Armaroli, T.; Simon, L.; Digne, M.; Montanari, T.; Bevilacqua, M.; Valtchev, V.; Patarin, J.; Busca, G. Effects of crystal size and Si/Al ratio on the surface properties of H-ZSM-5 zeolites. *Appl. Catal. A Gen.* **2006**, *306*, 78–84. [[CrossRef](#)]
72. Schneider, D.; Mehlhorn, D.; Zeigermann, P.; Kärger, J.; Valiullin, R. Transport properties of hierarchical micro–mesoporous materials. *Chem. Soc. Rev.* **2016**, *45*, 3439–3467. [[CrossRef](#)]
73. Konno, H.; Ohnaka, R.; Nishimura, J.-I.; Tago, T.; Nakasaka, Y.; Masuda, T. Kinetics of the catalytic cracking of naphtha over ZSM-5 zeolite: Effect of reduced crystal size on the reaction of naphthenes. *Catal. Sci. Technol.* **2014**, *4*, 4265–4273. [[CrossRef](#)]
74. Xu, S.; Zhang, X.; Cheng, D.-G.; Chen, F.; Ren, X. Effect of hierarchical ZSM-5 zeolite crystal size on diffusion and catalytic performance of n-heptane cracking. *Front. Chem. Sci. Eng.* **2018**, *12*, 780–789. [[CrossRef](#)]
75. Mochizuki, H.; Yokoi, T.; Imai, H.; Watanabe, R.; Namba, S.; Kondo, J.N.; Tatsumi, T. Facile control of crystallite size of ZSM-5 catalyst for cracking of hexane. *Microporous Mesoporous Mater.* **2011**, *145*, 165–171. [[CrossRef](#)]
76. Konno, H.; Okamura, T.; Kawahara, T.; Nakasaka, Y.; Tago, T.; Masuda, T. Kinetics of n-hexane cracking over ZSM-5 zeolites—Effect of crystal size on effectiveness factor and catalyst lifetime. *Chem. Eng. J.* **2012**, *207*, 490–496. [[CrossRef](#)]
77. Rownaghi, A.A.; Rezaei, F.; Hedlund, J. Selective formation of light olefin by n-hexane cracking over HZSM-5: Influence of crystal size and acid sites of nano- and micrometer-sized crystals. *Chem. Eng. J.* **2012**, *191*, 528–533. [[CrossRef](#)]

78. Konno, H.; Tago, T.; Nakasaka, Y.; Ohnaka, R.; Nishimura, J.-I.; Masuda, T. Effectiveness of nano-scale ZSM-5 zeolite and its deactivation mechanism on catalytic cracking of representative hydrocarbons of naphtha. *Microporous Mesoporous Mater.* **2013**, *175*, 25–33. [[CrossRef](#)]
79. Alipour, S.M. Recent advances in naphtha catalytic cracking by nano ZSM-5: A review. *Chin. J. Catal.* **2016**, *37*, 671–680. [[CrossRef](#)]
80. Blay, V.; Louis, B.; Miravalles, R.; Yokoi, T.; Peccatiello, K.A.; Clough, M.; Yilmaz, B. Engineering zeolites for catalytic cracking to light olefins. *ACS Catal.* **2017**, *7*, 6542–6566. [[CrossRef](#)]
81. Sendesi, S.M.T.; Towfighi, J.; Keyvanloo, K. The effect of Fe, P and Si/Al molar ratio on stability of HZSM-5 catalyst in naphtha thermal-catalytic cracking to light olefins. *Catal. Commun.* **2012**, *27*, 114–118. [[CrossRef](#)]
82. Lu, J.; Zhao, Z.; Xu, C.; Duan, A.; Wang, X.; Zhang, P. Catalytic cracking of isobutane over HZSM-5, FeHZSM-5 and CrHZSM-5 catalysts with different SiO₂/Al₂O₃ ratios. *J. Porous Mater.* **2007**, *15*, 213–220. [[CrossRef](#)]
83. Zhu, X.; Liu, S.; Song, Y.; Xu, L. Catalytic cracking of C₄ alkenes to propene and ethene: Influences of zeolites pore structures and Si/Al₂ ratios. *Appl. Catal. A Gen.* **2005**, *288*, 134–142. [[CrossRef](#)]
84. Hussain, A.I.; Palani, A.; Aitani, A.M.; Čejka, J.; Shamzhy, M.; Kubů, M.; Al-Khattaf, S.S. Catalytic cracking of vacuum gasoil over -SVR, ITH, and MFI zeolites as FCC catalyst additives. *Fuel Process. Technol.* **2017**, *161*, 23–32. [[CrossRef](#)]
85. Wan, J.; Wei, Y.; Liu, Z.; Li, B.; Qi, Y.; Li, M.; Xie, P.; Meng, S.; He, Y.; Chang, F. A ZSM-5-based catalyst for efficient production of light olefins and aromatics from fluidized-bed naphtha catalytic cracking. *Catal. Lett.* **2008**, *124*, 150–156. [[CrossRef](#)]
86. Kukade, S.; Kumar, P.; Peddy, V.C.R.; Gandham, S. Fluid Catalytic Cracking (FCC) Process and Apparatus for Production of Light Olefins. U.S. Patent WO2010067379A8, 20 February 2020.
87. Adel'Son, S.V.; Rudyk, E.M.; Smirnov, A.P.; Gurevich, V.I.; Pavlyukhin, V.N. Catalytic pyrolysis of kerosine and gas oil cuts. *Chem. Technol. Fuels Oils* **1975**, *11*, 583–585. [[CrossRef](#)]
88. Li, X.; Li, C.; Zhang, J.; Yang, C.; Shan, H. Effects of temperature and catalyst to oil weight ratio on the catalytic conversion of heavy oil to propylene using ZSM-5 and USY catalysts. *J. Nat. Gas Chem.* **2007**, *16*, 92–99. [[CrossRef](#)]
89. Meng, X.; Xu, C.; Gao, J.; Li, L.; Liu, Z. Catalytic and thermal pyrolysis of atmospheric residue. *Energy Fuels* **2009**, *23*, 65–69. [[CrossRef](#)]
90. Meng, X.; Xu, C.; Gao, J.; Li, L. Studies on catalytic pyrolysis of heavy oils: Reaction behaviors and mechanistic pathways. *Appl. Catal. A Gen.* **2005**, *294*, 168–176. [[CrossRef](#)]
91. Meng, X.-H.; Xu, C.-M.; Li, L.; Gao, J.-S. Studies on the kinetics of heavy oil catalytic pyrolysis. *Ind. Eng. Chem. Res.* **2003**, *42*, 6012–6019. [[CrossRef](#)]
92. Tian, Y.; Che, Y.; Chen, M.; Feng, W.; Zhang, J.; Qiao, Y. Catalytic upgrading of vacuum residue-derived cracking gas-oil for maximum light olefin production in a combination of a fluidized bed and fixed bed reactor. *Energy Fuels* **2019**, *33*, 7297–7304. [[CrossRef](#)]
93. Al-Khattaf, S.S.F.; Saeed, M.R.; Aitani, A.; Klein, M.T. Catalytic cracking of light crude oil to light olefins and naphtha over E-Cat and MFI: Microactivity test versus advanced cracking evaluation and the effect of high reaction temperature. *Energy Fuels* **2018**, *32*, 6189–6199. [[CrossRef](#)]
94. Yang, M.; Shao, J.; Yang, H.; Chen, Y.; Bai, X.; Zhang, S.; Chen, H. Catalytic pyrolysis of hemicellulose for the production of light olefins and aromatics over Fe modified ZSM-5 catalysts. *Cellulose* **2019**, *26*, 8489–8500. [[CrossRef](#)]
95. Zhu, X.; Jiang, S.; Li, C.; Chen, X.; Yang, C. Residue catalytic cracking process for maximum ethylene and propylene production. *Ind. Eng. Chem. Res.* **2013**, *52*, 14366–14375. [[CrossRef](#)]
96. Corma, A.; Corresa, E.; Mathieu, Y.; Sauvanaud, L.; Al-Bogami, S.; Al-Ghrami, M.S.; Bourane, A. Crude oil to chemicals: Light olefins from crude oil. *Catal. Sci. Technol.* **2016**, *7*, 12–46. [[CrossRef](#)]
97. Sha, Y.; Cui, Z.; Wang, M.; Wang, G.; Zhang, J. Olefin production by heavy-oil contact cracking. *Pet. Technol.* **1999**, *28*, 618–621.
98. Basu, B.; Kunzru, D. Catalytic pyrolysis of naphtha. *Ind. Eng. Chem. Res.* **1992**, *31*, 146–155. [[CrossRef](#)]
99. Wu, C.; Cheng, Y.; Jin, Y. Understanding riser and downer based fluid catalytic cracking processes by a comprehensive two-dimensional reactor model. *Ind. Eng. Chem. Res.* **2009**, *48*, 12–26. [[CrossRef](#)]
100. Siddiqui, M.; Aitani, A.; Saeed, M.; Al-Yassir, N.; Al-Khattaf, S. Enhancing propylene production from catalytic cracking of Arabian light VGO over novel zeolites as FCC catalyst additives. *Fuel* **2011**, *90*, 459–466. [[CrossRef](#)]
101. Wang, G.; Xu, C.; Gao, J. Study of cracking FCC naphtha in a secondary riser of the FCC unit for maximum propylene production. *Fuel Process. Technol.* **2008**, *89*, 864–873. [[CrossRef](#)]
102. Al-Absi, A.A.; Al-Khattaf, S.S.F. Conversion of Arabian light crude oil to light olefins via catalytic and thermal cracking. *Energy Fuels* **2018**, *32*, 8705–8714. [[CrossRef](#)]
103. Farshi, A. An experimental study to investigate propylene increasing in the FCC process by high-severity condition. *Pet. Sci. Technol.* **2011**, *29*, 2113–2122. [[CrossRef](#)]
104. Corma, A.; Bermúdez, O.; Martínez, C.; Ortega, F. Dilution effect of the feed on yield of olefins during catalytic cracking of vacuum gas oil. *Appl. Catal. A Gen.* **2002**, *230*, 111–125. [[CrossRef](#)]
105. Forissier, M.; Formenti, M.; Bernard, J. Effect of the total pressure on catalytic cracking reactions. *Catal. Today* **1991**, *11*, 73–83. [[CrossRef](#)]
106. Hu, R.; Weatherbee, G.; Ma, H.; Roberie, T.; Cheng, W.-C. Effect of hydrocarbon partial pressure on FCC propylene. *Pet. Technol. Q.* **2008**, *13*, 37–44.

-
107. Dupain, X.; Krul, R.A.; Makkee, M.; Moulijn, J.A. Are Fischer–Tropsch waxes good feedstocks for fluid catalytic cracking units? *Catal. Today* **2005**, *106*, 288–292. [[CrossRef](#)]
 108. Fogassy, G.; Thegarid, N.; Schuurman, Y.; Mirodatos, C. The fate of bio-carbon in FCC co-processing products. *Green Chem.* **2012**, *14*, 1367–1371. [[CrossRef](#)]
 109. Scherzer, J.; Gruia, A. *Hydrocracking Science and Technology*; Marcel Dekker: New York, NY, USA, 1996.
 110. McKetta, J.J. *Encyclopedia of Chemical Processing and Design: Volume 6—Calcination Equipment to Catalysis*; Marcel Dekker: New York, NY, USA, 1978.
 111. Akah, A.; Al-Ghrami, M.; Saeed, M.; Siddiqui, M.A.B. Reactivity of naphtha fractions for light olefins production. *Int. J. Ind. Chem.* **2016**, *8*, 221–233. [[CrossRef](#)]