Engineering 30 (2023) 100–109

Contents lists available at ScienceDirect

Engineering

journal homepage: www.elsevier.com/locate/eng

Research
Frontiers of Chemical Engineering—Review

Targeted Catalytic Cracking to Olefins (TCO): Reaction Mechanism, Production Scheme, and Process Perspectives

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ARTICLE INFO

Article history:
Received 15 October 2022
Revised 31 December 2022
Accepted 26 February 2023
Available online 26 July 2023

Keywords:
Light olefins
Steam cracking
Catalytic cracking
TCO process
Oil processing revolution

ABSTRACT

Light olefins are important organic building blocks in the chemicals industry. The main low-carbon olefin production methods, such as catalytic cracking and steam cracking, have considerable room for improvement in their utilization of hydrocarbons. This review provides a thorough overview of recent studies on catalytic cracking, steam cracking, and the conversion of crude oil processes. To maximize the production of light olefins and reduce carbon emissions, the perceived benefits of various technologies are examined. Taking olefin generation and conversion as a link to expand upstream and downstream processes, a targeted catalytic cracking to olefins (TCO) process is proposed to meet current demands for the transformation of oil refining into chemical production. The main innovations of this process include a multiple feedstock supply, the development of medium-sized catalysts, and a diameter-transformed fluidized-bed reactor with different feeding schemes. In combination with other chemical processes, TCO is expected to play a critical role in enabling petroleum refining and chemical processes to achieve low carbon dioxide emissions.

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1. Introduction

Fluid catalytic cracking (FCC) technology has long been at the heart of the oil refining industry. Due to the relentless exploration of several generations of scientists and technicians [1–4], China's FCC technology is currently at a world-leading level. In the 21st century, to enable the upgrading of China's vehicle-use gasoline standards from National I to National VI, unique FCC technology and associated technical routes created for various stages were innovated within a period of only ten years—in comparison with the typical 20–30 years in developed countries—by taking advantage of a unique gasoline quality upgrading solution [5–10].

New and renewable energy sources are gaining attraction, and the rapid growth of electric vehicles is exerting an increasing impact on the refined oil market, with gasoline consumption decreasing and an increasing structural surplus of refining capacity [11–13]. Oil refining must be transformed into chemical production, and the catalytic cracking process, which is mostly used to generate gasoline, is the first to face the brunt of this change. In addition, the FCC unit is responsible for more than 30% of all carbon dioxide (CO_2) emissions from the refinery sector [14,15]. Thus, new technology is required for the transition from refining petroleum to chemical production, in order for the oil industry to cope with the combined challenge of producing more low-carbon olefins and less coke and gasoline.

Ethylene, propylene, and butene are collectively referred to as "light olefins." As monomers, ethylene and propylene can be used to make a variety of fundamental organic materials, including polyethylene, styrene, polypropylene, propylene oxide, and many more. More than 75% of petrochemical products are ethylene-based, and the light-olefin industry plays a significant role in the national economy. In terms of overall production, propylene is the second-most produced raw chemical material after ethylene, and the demand for propylene is expected to increase in the coming years.

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https://doi.org/10.1016/j.eng.2023.02.018
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It is expected that ethylene demand will also continue to rise steadily over the next few years, with the compound annual growth rate of ethylene demand in the market remaining positive, while growth rate of propylene capacity will grow faster than that of propylene demand. The difference between supply and demand in the light olefins market is directly related to the available production process. Low-carbon olefins are mostly produced via oil-based processes, such as naphtha steam cracking (NSC), which produces ethylene [16], and FCC, which produces propylene (Fig. 1). Non-petroleum processes, such as coal-based methanol to olefins (MTO), have a smaller market share. Due to technical restrictions, none of the NSC, FCC, or MTO processes can switch flexibly between the production of various types of light olefins.

In line with China's policy of achieving a carbon peak and carbon neutrality, the high-consumption petrochemical industry is likely to be subjected to carbon taxation in the future. Carbon emissions will progressively become a major factor in the technical and economic evaluation of light-olefins production processes, and the coal-based MTO process cannot be used to resolve this issue quickly. Intensive competition between various light-olefins production processes is inevitable until one of them can dominate the market.

There are still a number of challenging scientific problems related to the current technologies for producing light olefins that need to be solved. One problem is how to precisely break C–C bonds and increase carbon efficiency while adapting to changing olefin production schemes. Another issue is how to optimize the catalytic and thermal reactions in the reaction–regeneration process to significantly lower the selectivity of dry gas, particularly methane. Carbon–carbon bond cleavage in current NSC and catalytic cracking technologies is far from ideal, and the utilization of raw-material hydrocarbons still has a great deal of room for improvement. It is expected that, in the future development of light-olefins production, attention will be paid not only to olefin selectivity but also to methane. In addition, it has not yet been determined how to build a production plan from a technological standpoint to meet the need for light olefins and thereby fundamentally resolve the supply-demand imbalance. Based on the key distinctions between NSC and catalytic cracking, the targeted catalytic cracking to olefins (TCO) process [17,18] presents a new reaction pathway for flexible and light olefin cracking on microporous MFI zeolites to produce light olefins. Its use will refresh the refinery process and pave a way to enrich the technology of light-olefins production.

2. Light-olefins synthesis from hydrocarbons

Light olefins can be produced from fossil materials and renewable resources, with fossil feedstocks still occupying a leading position at present. Steam cracking and catalytic cracking are currently the most widely used technologies for the synthesis of light olefins, producing 80%–90% of the world's ethylene and propylene [19–21]. In addition, the direct conversion of crude oil to olefins is considered to be a key technology for transforming petroleum refining into chemical processing, as it can shorten the process and reduce CO_2 emissions [22,23].

2.1. Steam cracking

Steam cracking is a key chemical process for light-olefins production, both at present and in the foreseeable future [24–26]. The feedstocks for steam cracking include light hydrocarbons from ethane to naphtha fractions. The selection of feedstocks is closely related to the distribution of resources. For example, gas-phase feedstocks are mostly used in the United States and the Middle East, while liquid-phase feedstocks are mostly used in Europe [19,25]. The ethylene yield accounts for the highest proportion of products from steam cracking, varying between 25% and 80%, while the composition of the products mainly depends on the feedstocks and reaction conditions [27–29]. The highest ethylene yield can be obtained when ethane is used as the feedstock [28,30], while larger amounts of propylene are produced when longer-chain hydrocarbons are used. The operating conditions are critical factors affecting the selectivity of steam cracking products. The production of propylene and butylene can be carried out at a lower temperature, while the production of ethylene requires a higher reaction temperature [31]. Steam cracking is a non-catalytic process and is a strongly endothermic reaction. It usually needs to be carried out at a very high temperature (> 800 °C) [32]. The main production cost of steam cracking to produce light olefins comes from its energy consumption, which also generates a large amount of greenhouse gases [25,33].

Ethane, liquefied gas, naphtha, light diesel, and gas oil are all used as feedstock for the steam cracking process. More than half of the feedstock is light naphtha, while 25%–30% is ethane. Ethane feedstock predominates in North America and the Middle East, while naphtha feedstock predominates in the Asian–Pacific region.

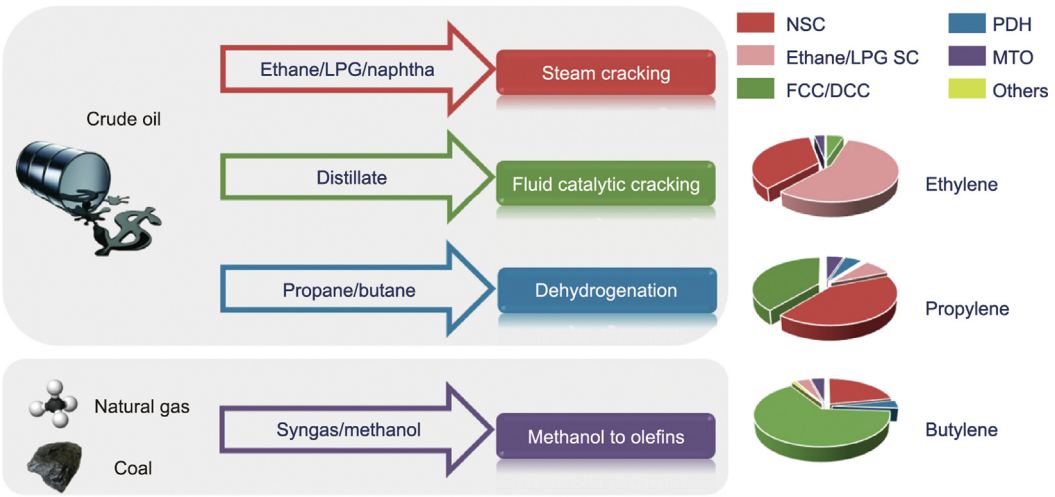

Fig. 1. An illustration of various processes for producing light olefins and their relative capacity. DCC: deep catalytic cracking; LPG: liquefied petroleum gas; MTO: methanol to olefins; PDH: propane dehydrogenation; SC: steam cracking.

Therefore, ethylene production via steam cracking varies substantially with the feedstock. The best feedstock for the steam cracking process is light hydrocarbons, particularly ethane [34,35], which has the highest ethylene output of about 54%. Although low-value propane and butane from liquefied gas can be used to produce ethylene, the ethylene selectivity is much lower than that of ethane. The key to ethylene selectivity when using naphtha feedstocks is the naphtha chain alkane concentration, with paraffin-based straight-run naphtha cracking producing the greatest ethylene yields of up to 35%.

2.2. Catalytic cracking

The development of catalytic cracking technology began in 20th century, when acid clay was first used in catalytic cracking [36]. The process gradually evolved from the initial fixed bed to the fluidized bed. Since the first fluidized catalytic cracking unit was put into operation in 1942, catalytic cracking has developed rapidly, becoming an important process in refineries to produce high-value fuels. Catalytic cracking units mainly produce fuel oil, with their gasoline production accounting for 35%–50% of today's global gasoline production [37,38]. However, with the change in the energy consumption structure and the increasing demand for environmental protection, the byproducts of the catalytic cracking of propylene have become increasingly important. The catalytic cracking unit has gradually become an important alternative technology for light-olefins production due to its higher operational flexibility, feedstock adaptability, and lower CO_2 emissions.

2.2.1. Feedstocks

Heavy hydrocarbons (e.g., vacuum gas oil (VGO) and atmospheric residue (AR)) are the main feedstock for traditional catalytic cracking, which is used to produce fuel oil. However, with the change in market demand, catalytic cracking units are also starting to use light hydrocarbons (e.g., naphtha distillates, olefins) as feedstock in order to produce more light olefins. In response to the limits of the steam cracking process and the demands of the light-olefins industry, scientists and engineers worldwide have focused on developing alternative processes via catalytic reactions in order to improve the yield of light olefins, enhance the adjustability of the propylene/ethylene (P/E) ratio, expand feedstock sources, reduce energy consumption and reaction temperature, and mitigate coking in the process. Research shows that the selectivity of light olefins can be greatly improved when olefins are used as feedstocks [17].

2.2.2. Catalysts

In catalytic cracking, a catalyst is used to reduce the activation energy required to break the C–C bond, making the reaction temperature of catalytic cracking lower than that of steam cracking. Catalytic cracking catalysts include acid catalysts, basic catalysts, and transition metal oxide catalysts, among which acid catalysts are the most widely studied and applied [39]. In the 1950s, foreign oil companies applied X/Y zeolites to catalytic cracking units for the first time, promoting a technical reform of catalytic cracking and opening up a new era of zeolite-based catalytic cracking. The Y zeolites have been used as the active component of catalytic cracking catalysts thus far. ZSM-5 zeolites were applied to catalytic cracking units as a propylene promoter or gasoline octane number promoter in the 1970s. The use of a shape-selective zeolite catalyst can effectively increase olefin selectivity in the catalytic cracking process and reduce the gasoline yield [40]. Shape-selective zeolites have a stronger confinement effect and weaker acidity, which can inhibit the hydrogen-transfer reaction. Thus ZSM-5 zeolites are often used as an active component in catalytic cracking processes aimed at synthesizing light olefins [41,42], whose feedstocks are light hydrocarbons. In 2022, a pure ZSM-5 zeolites catalyst was applied to a heavy hydrocarbon catalytic cracking process for the first time, significantly improving olefin selectivity [43]. The distribution of light-olefin products can be further controlled by changing the pore structure, crystal size, and acid properties of ZSM-5 zeolite. It was found that hierarchical ZSM-5 catalysts with enhanced mesoporosity exhibited higher activity with feedstocks containing large molecules when evaluated in the cracking of hydrocarbons to light olefins; furthermore, their short diffusion length favored the selectivity of propylene and total light olefins [44]. Compared with nano-ZSM-5 zeolites, the yield of olefins on macro-ZSM-5 zeolites is lower [45]. Lin et al. [46,47] found that the P/E ratio and selectivity of olefin cracking products could be adjusted by changing the ratio of the strong/weak acid sites of the zeolites.

2.2.3. Mechanisms of catalytic cracking reactions

The cracking of alkanes requires the formation of carbonium ions (C_x^+, where x indicates the number of carbon atoms and "+" indicates a positive charge), and is thus disadvantageous compared with the cracking of olefins in terms of energy. The functional groups of olefins can be directly activated by protons, making it very easy to activate them using Brønsted acid sites [48,49]. Olefin catalytic cracking mainly occurs at acidic sites, and the operating conditions, feedstock properties, and catalyst properties determine whether the olefin molecules undergo monomolecular cracking or dimerization cracking [50]. In general, the monomolecular cracking of long-chain olefin molecules, such as C_5^+ olefin molecules, on acid zeolite occurs in a higher proportion [51,52]. In terms of operating conditions, a high temperature is more conducive to monomolecular cracking, while olefin molecules are more prone to polymerization cracking at a low temperature [53]. In addition, the nature of the catalysts affects the cracking path. Zeolites with holes that are close to the molecular size of the reactants are more conducive to monomolecular cracking, while molecular sieves with larger pore sizes cause a higher proportion of olefin molecules to undergo polymerization cracking [54,55].

The main reaction in the catalytic cracking of 1-pentene differs significantly from the cracking of other olefins, such as octylene [47,56–59], in that both monomolecular cracking and dimerization cracking reactions can occur [18,60]. The study of these primary and secondary reactions has led to a network of possible reactions for the catalytic cracking of 1-pentene, as shown in Fig. 2. The main

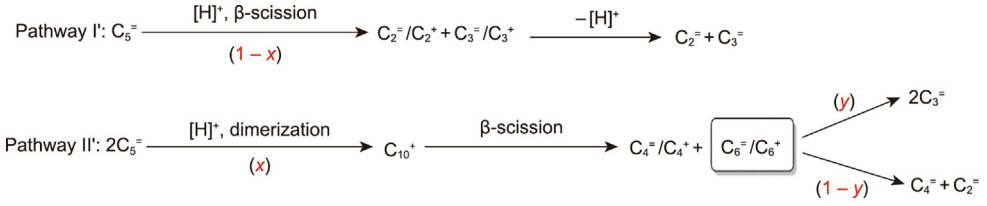

Fig. 2. Reaction pathways of monomolecular cracking and dimerization cracking of 1-pentene. The probability of dimerization cracking ($2C_5 \rightarrow C_{10} \rightarrow C_4 + C_6$) and monomolecule cracking ($C_5 \rightarrow C_2 + C_3$) are x and $1 - x$, respectively, and the probability of C_6 cracking to $2C_3^=$ is y (x, $y \in [0, 1]$).

reaction consists of a single-molecule direct cleavage pathway I′ and a dimerization cracking reaction pathway II′.

Pathway I′: 1-Pentene is protonated under acidic conditions to form C_5^+, which is then directly cleaved to form ethylene and propylene.

Pathway II′: C_5^+ is polymerized with another 1-pentene to form C_{10}^+ [61], which is isomerized and then cleaved to form $C_4^=$ and $C_6^=$, while $C_6^=$ can be further cleaved to form $C_2^=$ and $C_4^=$ (pathway II′-1) or two molecules of $C_3^=$ (pathway II′-2) (where the "=" symbol indicates the presence of a double bond between carbon atoms).

In order to improve the selectivity of propylene, the 1-pentene cleavage reaction requires the inhibition of side reactions (isomerization and aromatization) while controlling the cleavage pathway of the main reaction and promoting pathway II′-2.

The reaction can be divided into types A–F according to the difference in the carbonium ion structure before and after the reaction. The limiting step of olefin cracking is β-scission [52], which affects the distribution of products. As shown in Fig. 3, it is generally believed that there are five main types of β-scission, denoted as A, B, C, D, and E, and type F is newly introduced, which forms methane via methyl carbenium ion as a reactive intermediate. Types E and F β-scission are both disadvantageous in terms of energy and are usually ignored [46]. The high energy barrier of primary carbonium ion involved reaction pathways also explains why the ethylene yield of catalytic cracking is low. Recent research shows that, on ZSM-5 zeolites, with an increase in the reaction temperature, energetically unfavorable β-scission types (e.g., D and E types) will gradually become dominant, producing a large amount of ethylene [55].

To further investigate the mechanism of olefin cracking with zeolite at ultra-high temperatures (> 600 °C), experiments [18] were carried out on ZSM-5 zeolite and SiO_2 at 460–740 °C. With an increase in reaction temperature, methane selectivity improves dramatically in both thermal and catalytic processes, and the increase in methane selectivity on SiO_2 was much greater than that on ZSM-5. At 460–530 °C, the ethylene and methane yielded by the thermal reaction are less than 1%, while they are virtually undetectable in the catalytic process. However, relatively little methane was formed from the catalytic cracking of 1-pentene in the presence of the solid acid catalyst ZSM-5, demonstrating that the presence of acidic sites at high temperatures inhibits the 1-pentene cracking process from proceeding via a radical mechanism. Corresponding to the experimental results for all temperature ranges, the ratio of the B-type β-scission reaction rate constants decreases significantly as the temperature rises, while the rate constants for the C, D, and E types exhibit a volcanic profile. In the experimental temperature range, F-type β-scission does not occur below 670 °C or reach the turning point. This means that the energy barriers for B–F-type β-scission follow the order B < C < D < E < F [62,63]. For the first time, the challenging D, E, and F β-scission types have been demonstrated to dominate the cleavage reactions of carbenium ions under adequate catalytic reaction circumstances, enriching the understanding of carbenium ion β-scission types and providing a theoretical basis for the generation of ethylene.

2.2.4. Operating parameters

The operating conditions of catalytic cracking are highly flexible, and the reaction process can be adjusted through the feedstock properties, reaction temperature, residence time, catalyst-to-oil ratio, or steam-to-hydrocarbon feed ratio to achieve different production goals. Meng et al. [64] showed that the yield of light olefins could be increased by increasing the H/C molar ratio and reducing aromatic carbon in the feedstocks. The cracking temperature is also closely related to product distribution, and light olefins usually need a higher reaction temperature. Wan et al. [65] found that the yield of light olefins from naphtha catalytic cracking at 630 °C was close to that from steam cracking at 880 °C, and that the yield of low olefins could be further increased with the increase of catalytic cracking reaction temperature. When the residence time is too short, the lower conversion depth of the feedstock results in fewer light olefins, while a too-long residence time promotes the secondary reaction and also reduces the yield of light olefins [28]. In general, a higher catalytic cracking catalyst-to-oil ratio can improve ethylene yield, but dry gas will also increase; for propylene, there is an appropriate catalyst-to-oil ratio to maximize its yield [39]. Increasing the amount of steam can improve the yield of light olefins, but an optimal value is required, due to plant scale and economy [28].

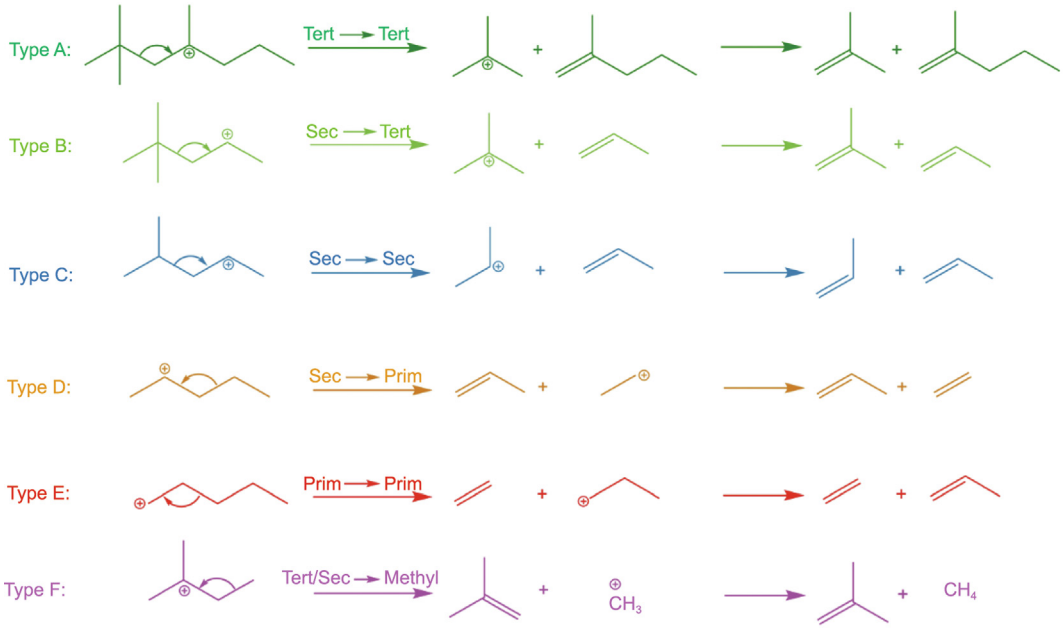

Fig. 3. Typical types of β-scissions in zeolite catalyzed C_5 cracking. Prim: primary; Sec: secondary; Tert: tertiary.

2.2.5. Catalytic cracking process of light-olefin production

Since the mid-1980s, the Sinopec Research Institute of Petroleum Processing (RIPP) has been engaged in research on these topics. In 1994, RIPP developed a deep catalytic cracking (DCC) process to produce light olefins from paraffin-based heavy distillates (i.e., vacuum distillate oil, coked wax oils, residual oils) with a riser and a dense-phase fluidized-bed reactor. The propylene yield from this process exceeds 24%, while the combined yield of ethylene, propylene, and butene is greater than 40%. Following the industrialization of DCC technology, RIPP developed a catalytic pyrolysis process (CPP) for the direct production of ethylene and propylene from heavy oil, with various production options such as maximizing ethylene, maximizing propylene, or maximizing both ethylene and propylene. Compared with the steam cracking process, the CPP broadens the feedstock sources and reduces the reaction temperature, resulting in a significant reduction in energy consumption. Using Daqing atmospheric residual oil as the feedstock, the yield of ethylene and propylene reached 14.84 and 22.21 weight percent (wt%), respectively, and the ratio of aromatics in cracked naphtha reached 82.46 wt% under the maximum ethylene and propylene operation mode.

The catalytic cracking of light oil is primarily a process in which light gasoline or naphtha is used to produce ethylene and propylene in the presence of a catalyst [49,50]. There are two types of naphtha cracking technology: fixed-bed and fluidized-bed catalytic cracking. The representative fixed-bed catalytic cracking was developed by Asahi Kasei Corporation; it uses straight-chain alkanes as feedstock and Mg/ZSM-5 as a catalyst. With a reaction temperature of 680 °C, the yield of ethylene and propylene reaches 43 wt%, and the P/E weight ratio is 0.93. SK Chemical and KBR Engineering have jointly developed the advanced catalytic olefins (ACO) process, which has a reaction temperature of about 650 °C and increases the total ethylene and propylene yield to 65%, with a P/E close to 1.0.

Olefin cracking technologies include the olefin cracking process (OCP) jointly developed by Atofina and Universal Oil Products Company (UOP), the Omega process developed by Asahi Kasei, and the olefins catalytic cracking (OCC) process developed by Sinopec Shanghai Research Institute of Petrochemical Technology. The Omega process can convert C_4–C_8 olefins into propylene, ethylene, and C_5^+ gasoline using a proprietary high-propylene selective ZSM-5 zeolite catalyst. The process is based on the cracking reaction in an adiabatic fixed-bed reactor at 530–600 °C, 0–0.5 MPa, and 3–10 h^{-1} of weight hourly space velocity (WHSV), with no dilute gas present, and has a propylene yield of 40–60 wt%. The OCC process also uses an adiabatic fixed bed as the reactor, pure crystalline ZSM-5 zeolite with a hierarchical pore structure as the catalyst, and a switchable regenerator device for catalyst regeneration. C_4/C_5 olefins are transformed into propylene and ethylene at a temperature of 500–600 °C and pressure of 0.1–0.2 MPa.

2.3. Conversion of crude oil

The direct production of chemicals from crude oil can shorten the original process, reduce costs, and reduce CO_2 emissions; thus, it is expected to become an alternative technology for the future transformation of petroleum refining into chemical processing. However, this technology also requires the reconfiguration of refining technology, optimization of the process, and innovation of the catalyst formula [23]. Regardless of whether the crude oil is converted by catalysis or treated by steam cracking, the coke yield is high. In the steam cracking process, this problem can be solved by first fractionating the crude oil and then injecting the light components into the steam cracking reactor. In the catalytic process, large molecules such as asphaltene can easily be converted into coke. Thus, enhancing the diffusion performance of large molecules is conducive to inhibiting the formation of coke. Catalysts with good selective cracking performance for large molecules, long life, and high selectivity for chemicals are crucial [22]. Alabdullah et al. [66] proposed the new concept of the catalytic reactor, which includes a multi-zone fluidized bed and can perform several refining steps in a single reactor. As a result, this reactor-catalyst combination has shown a stable conversion of untreated Arabian light crude into light olefins with yields per pass of over 30 wt% and a minimum production of dry gas.

2.4. Summary

This section introduced the ethylene-to-methane mass ratio as a key index for evaluating the efficiency of hydrocarbon feedstock utilization for different processes. The main issue with the steam cracking process is the significant yield of low-carbon alkanes such as methane and ethane, which are difficult to recycle and have a low hydrocarbon utilization rate as a result. When ethane is used as the feedstock, the methane yield is low and the ethylene-to-methane mass ratio rises to 17.4; however, when other alkanes are used, the methane yield exceeds 10% (typically around 20%), and the ethylene-to-methane mass ratio is less than 2.0. For isomeric alkanes, the ethylene-to-methane mass ratio is even lower than 1.0. Processing alkanes above C_3—notably isomeric alkanes—causes a severe imbalance in the C–C bond breakage, which significantly reduces the material efficiency. In addition, the high reaction temperature of steam cracking results in the plant consuming significant amounts of energy, and current technology often uses fuel gas as an energy source during real production. The combustion of hydrocarbons in the steam cracking process results in a large amount of carbon emissions, significantly increasing the overall carbon emissions of the plant.

In order to produce light olefins efficiently, steam cracking is preferred for processing ethane, the propane dehydrogenation (PDH) method is ideal for processing propane, and new technologies must be developed in order to produce C_4 alkanes, especially those above C_5. Alkanes can be transformed into aromatics and propane using alkane aromatization technology; propane can then be dehydrogenated to create propylene. Similarly, alkanes can be dehydrogenated to produce hydrogen and olefins, which can then be processed using olefin conversion technology to produce low-carbon olefins. In this way, the methane yield can be considerably reduced and hydrocarbon utilization can be increased.

Fig. 4 summarizes the product distribution with feedstock variation and its hydrocarbon utilization efficiency for the steam cracking, FCC, DCC, CPP, ACO, and two olefin catalytic cracking (OCC and OCP) processes. In order to produce light olefins, an integrated oil–chemical transition has the following requirements: First, methane generation must be controlled. For example, the steam cracking process is highly advantageous for producing light olefins, especially ethylene. However, such thermal cracking is accompanied by the generation of a large amount of fuel gas (i.e., methane). Among all the feedstocks, only ethane, which has a carbon and hydrogen atom utilization of about 80%, is an ideal feedstock for steam cracking processes, as other feedstocks are not high in atom utilization. Second, ethylene selectivity must be effectively increased. When the reaction temperature for FCC is raised from 510 to 550 °C with a similar feedstock composition, the ethylene yield only increases by 2%–3%. When the temperature is raised to 620 °C (CPP), the ethylene yield increases by 9%, while 7%–8% fuel gas (methane) is correspondingly produced. Thus, increasing the temperature in order to produce more light olefins costs too much for reducing carbon dioxide emissions. Third, light olefins must be created through olefin cracking. The current method of producing light olefins from olefin feedstock results in a 30%–70% higher yield of light olefins than distillate catalytic cracking (which is

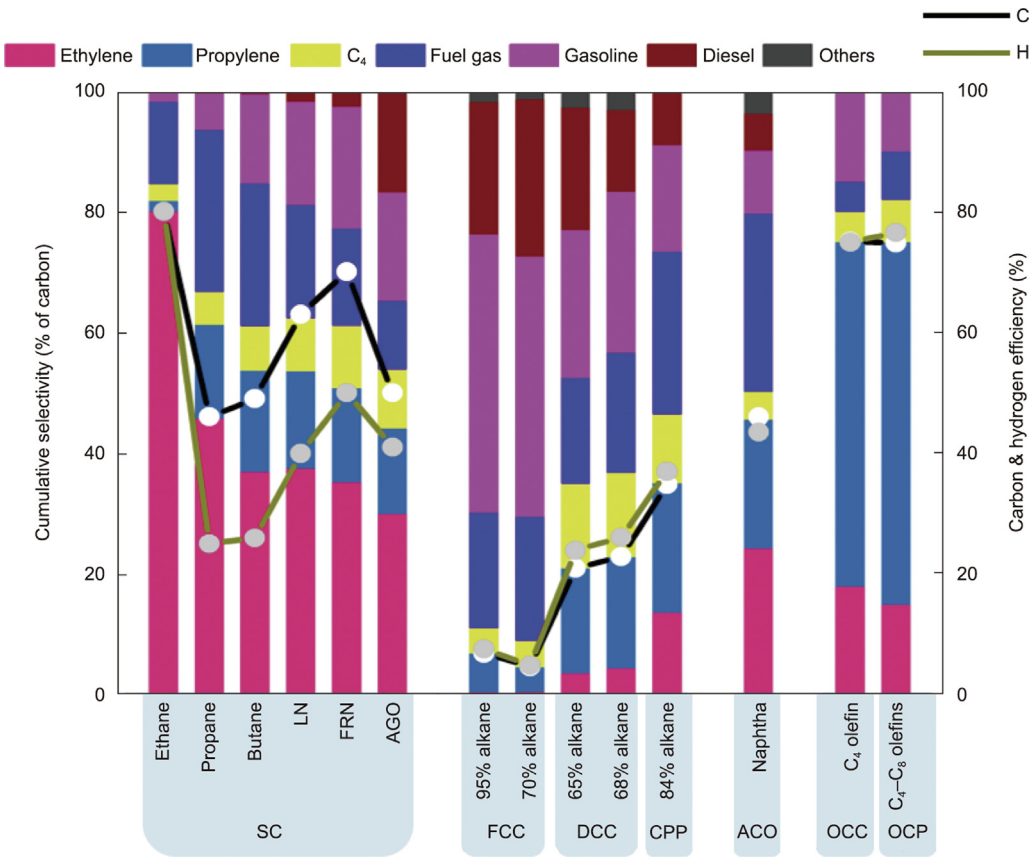

Fig. 4. The distribution of products from various hydrocarbon converting processes and utilization of carbon and hydrogen atoms. AGO: atmospheric gas oil; FRN: full-range naphtha; LN: light naphtha.

practically olefin-free). Olefin catalytic cracking is equivalent to steam cracking in terms of the light-olefins yield, methane yield, and utilization of carbon and hydrogen atoms. The only downside of olefin catalytic cracking is that ethylene selectivity cannot be greatly increased. Unlike the paraffins cracking reaction that involves carbonium ions, the hydrogen in OCC and OCP processes is mainly formed through hydrogen transfer reactions. Compared with normal paraffin cracking, the olefin cracking process using a microporous zeolite with MFI topology increases the aromatics content by 10%–20%. As shown in Fig. 4, others (including coke formation and process losses) are also rather low in the olefin cracking process.

3. Conceptual design of the TCO process

In order to achieve flexible and low-carbon production of light olefins, we propose the TCO process, which is based on the catalytic cracking of olefins and involves innovation in three aspects—namely, feedstock structure, catalyst activity components, and catalytic reaction engineering. By deeply integrating steam cracking, catalytic cracking, and olefin cracking, the TCO process optimizes the hydrocarbon equilibrium in the reaction process and precisely implements C–C bond cracking, which helps to reduce the generation of small-molecule alkanes, especially methane, and improve the utilization efficiency of carbon atoms.

As the first innovation, there are three main sources of feedstock. Naphtha, reforming raffinate, or other light hydrocarbons can be dehydrogenated to produce hydrogen and C_5–C_{12} olefins, which can then be used as high-quality feedstock to produce light olefins. Heavy oil can also be introduced to the heavy hydrocarbon conversion zone in the TCO unit, where the reaction to produce olefins is first carried out as far as possible, and the olefins are then separated from the primary products and returned to the olefin cracking zone of the TCO plant. Methanol or ethanol can also be used as feedstock for the TCO plant and can be injected into the reactor in the appropriate location to produce light olefins.

As the second innovation, full attention is paid to the effectiveness of confinement catalysis in the diffusion process of olefin products. A 10-membered ring zeolite is adopted as the active component in the catalyst design, which completely solves the defect of product olefin saturation caused by the 12-membered ring Y-type zeolite in the currently used catalyst. After systematic research and repeated screening, the catalyst TCC-1 has been developed and prepared for the TCO process. With the excellent performance of TCC-1, the propylene selectivity in the liquefied petroleum gas (LPG) is as high as 48.71%, and the olefin ratio of LPG can reach 89.25%.

As the third innovation, based on the characteristics of the MFI zeolite catalyst, the catalytic reaction and the gas–solid separation in the reactor are balanced and optimized. By integrating the advantages of a riser reactor and a dense-phase fluidized-bed reactor, the newly designed diameter-transformed fluidized-bed reactor takes into account the residence time of the reactants and the gas–solid separation of the products and catalyst.

The flow and feed locations of the TCO process [67,68] in a single reactor are shown in Fig. 5. The ultra-high temperature regenerated catalyst enters the bottom of the reactor and comes into contact with the fresh heavy feedstock at 650 °C or above, which meets the reaction temperature requirements for the cracking of olefin-rich feedstock into ethylene and propylene. After coming into contact with fresh material, the temperature of the reactive

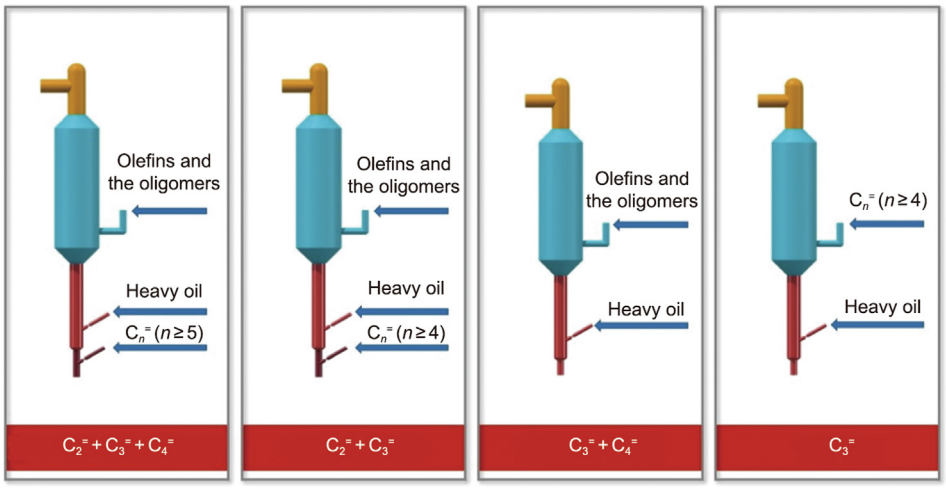

Fig. 5. The single diameter-transformed fluidized bed reactor for the TCO process with different feeding schemes.

flow decreases rapidly. The temperature at the expansion point of the reactor is generally controlled at below 530 °C, which meets the temperature requirements of propylene and butylene production. Based on different feed locations, the TCO process is designed to have four different production modes: producing ethylene, propylene, and butylene; producing ethylene and propylene; producing propylene and butylene; and producing propylene. Based on the changing market demand for light olefins, the feed position of the olefin-rich feedstock can be adjusted for flexible switching between production modes.

The flow and feed locations of the TCO process in a dual reactor are shown in Fig. 6. The heavy and olefin feedstocks are treated separately, with a dedicated olefin conversion reactor. Based on controlled differences in the reaction conditions, olefins can be selectively converted to ethylene, propylene, or butylene in the olefin conversion reactor, thus allowing for a diversity of production modes.

4. The revolution in oil processing

The technology for the direct conversion of crude oil to chemicals (COTC) is the key to achieving the transformation of oil refining into chemical production, which is an obvious trend for the oil industry. UOP's MaxEne technology, which is based on the concept of molecular refining, separates straight-chain alkanes from isoalkanes and cycloalkanes. Isoalkanes and cycloalkanes are used as the feedstocks of the reforming unit to produce more aromatics, while straight-chain alkanes are used as steam cracking feedstocks to produce olefin products, while increasing the yield of olefins and aromatics.

If the refinery does not need aromatics, the isomeric alkanes can be converted into straight-chain alkanes through reverse isomerization, so as to provide more high-quality feedstocks for the steam cracking unit and improve the olefin yield. UOP's COTC technology was formed in this way, and its typical process flow is shown in Fig. 7 [22]. In this process, NSC is still used to produce ethylene, which will inevitably produce methane, while a catalytic cracking process or catalytic cracking technology is used for heavy hydrocarbons, reducing the utilization rate of oil resources.

To maximize the production of chemicals and reduce losses, the future TCO unit will be at the heart of integrated refining and chemical processes, as shown in Fig. 8. Light naphtha and reforming raffinate are transferred directly to the alkane dehydrogenation unit, and the product olefins are used as feedstock for the target catalytic cracking unit. Waxy oil and hydrogenated tail oil are also used directly as feedstock for the target catalytic cracking unit. In the TCO process, waxy oil is a high-quality feedstock with largely saturated hydrocarbons that can be selectively converted into olefins which is the predecessors of light-olefin. Moreover, the saturated hydrocarbons in the hydrogenated tail oil are converted into coke via gums and asphaltenes, providing a sufficient heat source for the targeted catalytic cracking process. In addition to light olefins, the heavy product—the FCC gas oil (FGO) fraction—can be used in low-sulfur marine fuel technology or aromatic controlled condensation technology to produce special oils or feedstock for high-quality carbon materials.

The feedstock of the TCO unit can be expanded to include C_4 or C_5 fractions, which can integrate existing light-olefin production technologies. Furthermore, the TCO unit can be deeply coupled with alkane dehydrogenation, the separation of olefin and alkane, olefin oligomerization, aromatic controlled condensation, and other units, thus shortening the refining and chemical integration process and bridging the refining and chemical production. The first industrialization of the use of only MFI zeolites as an active component was achieved on a catalytic cracking unit [69]. The high propylene selectivity in the products indicates that the core concept of the TCO process has been successfully tested. The remaining technologies for olefin conversion, alkane dehydrogenation, and the separation of alkanes from olefins remain to be industrialized.

5. Prospects and challenges

With the enormous challenges currently faced by domestic petrochemical firms, the question of how to make effective use of existing resources and achieve green and efficient production of low-carbon olefins has become a crucial issue in enterprises'

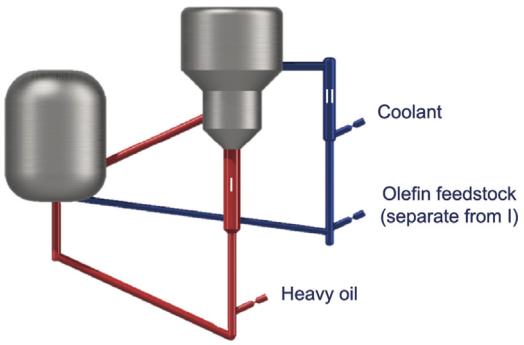

Fig. 6. TCO process flow and feed location in the dual reactor.

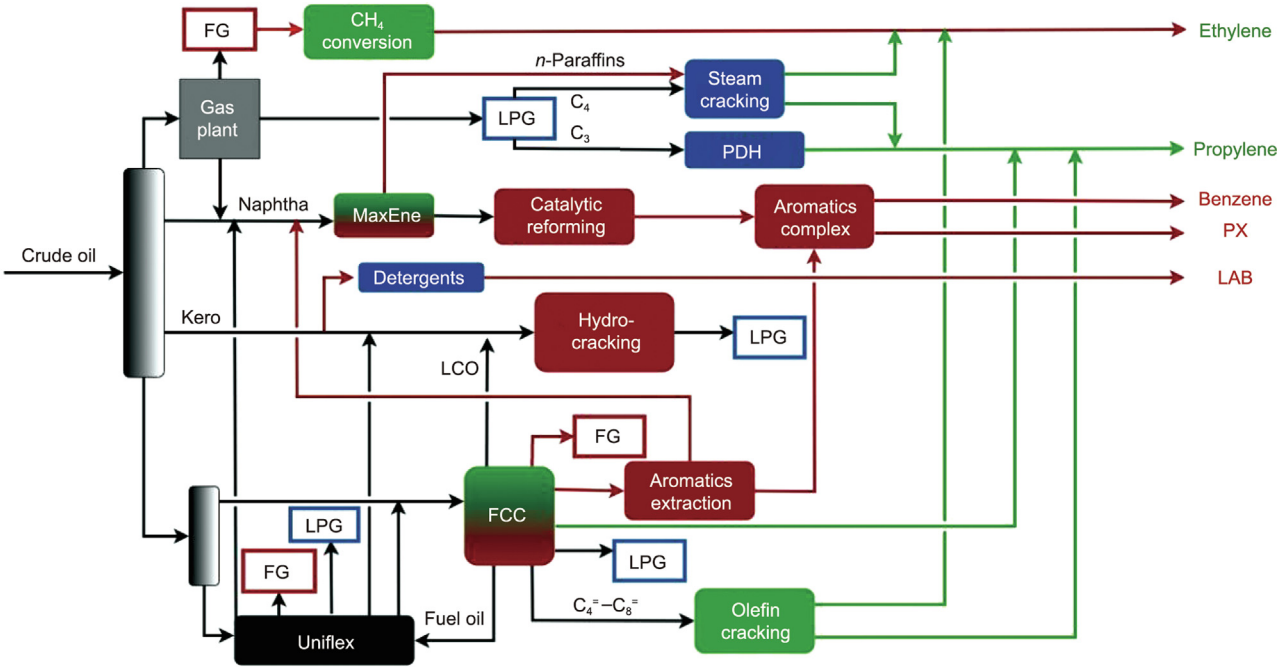

Fig. 7. UOP's COTC (also known as Future Refinery) general processing flow chart. FG: fuel gas; LAB: linear alkylbenzene; LCO: light cycle oil; PX: *para*-xylene. Reproduced from Ref. [22] with permission.

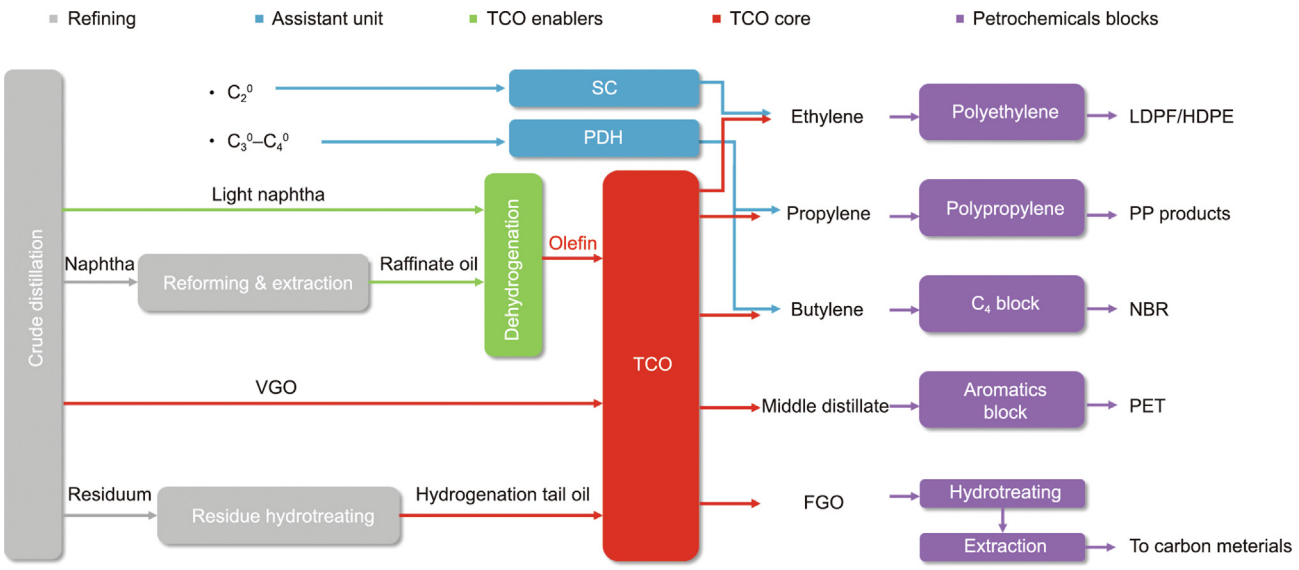

Fig. 8. Role of the TCO unit in the zero-fuels refining and chemical complex. FGO: FCC gas oil; HDPE: high-density polyethylene; LDPF: low-density polyethylene foam; NBR: nitrile rubber; PET: poly(ethylene terephthalate); PP: polypropylene.

efforts to sustain their vitality. Both NSC and catalytic cracking suffer from an imbalance in the breaking of C–C bonds, and there is still room for improvement in their feedstock utilization, in order to align with China's carbon peak and carbon neutrality policy. To achieve the necessary improvement, the mechanism of the olefin catalytic reaction on microporous MFI zeolite has been thoroughly investigated, and the TCO process has been proposed, based on the concept of developing technology for the highly selective conversion of olefins, with advancements in three areas: feedstocks, catalysts, and reaction engineering.

The TCO process uses olefin conversion and generation as a link to expand upstream and downstream processes, improve feedstock supplies, and optimize product output. Moreover, it gives the refinery industry the opportunity to implement the transformation of existing plants, thereby maximizing the use of stock assets already in place, aligning with China's carbon peak and carbon neutrality policy, and offering a progressive path to achieve efficiency and diversity. In the future, the TCO process is expected to reshape the refinery process and lay a solid technical foundation for oil reduction and low-carbon development.

Acknowledgments

This work was financially supported by a research grant from the National Key Research and Development Program of China (2021YFA1501204) and China Petroleum and Chemical Corporation (Sinopec Corp.), China (ST22001).

Compliance with ethics guidelines

Youhao Xu, Yanfen Zuo, Wenjie Yang, Xingtian Shu, Wei Chen, and Anmin Zheng declare that they have no conflict of interest or financial conflicts to disclose.

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