Enhancing the production of light olefins from heavy crude oils: Turning challenges into opportunities

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ABSTRACT

The large reserves of heavy crude oils and the significant demand of light olefins, particularly propylene, have created new opportunities for developing advanced catalyst and process technologies that efficiently upgrade asphaltenes-enriched crudes to high values chemicals. Indeed, many petrochemicals are produced during crude oil refining as side streams, because the primary goal of the crude oil refinery is the production of transportation fuel. This paper attempts to briefly review the properties of heavy crude oils, the major process technologies for the production of light olefins such as steam cracking and fluid catalytic cracking and finally the catalyst technology mainly focused on ZSM-5 and HY zeolites. We include not only the current understanding of the olefin production technologies, but also the challenges involved in the upgrading of unconventional crudes and residue with high content of heteroatoms and unsaturated poly-aggregate asphaltenes. A strategy for processing unconventional oil that involves the utilization of steam (catalytic) cracking process, in a FCC-type configuration, and enhanced cracking catalyst with high hydrothermal stability is also analyzed.

Keywords: Unconventional crude, Ethylene and propylene, Steam (catalytic) cracking, Fluid catalytic cracking, HY and ZSM-5 zeolites

1.0 Introduction

Petroleum oil continues to be major energy source up to 2040. As of 2014, the total primary energy supply was 273.9 million barrels of oil equivalent per day (mboe/d). On a global level, total primary energy demand is forecast to increase by 40% in the period to 2040 to reach 382 (mboe/d) according to OPEC's World Oil Outlook 2016 **[1]**. Due to the limited amount and depletion of traditional light petroleum resources, low quality heavy oils and or residues, which are subsequently obtained by processing heavy crudes, are considered as alternate suitable source for transportation fuels, energy and petrochemicals to fulfil the requirements of rapid population and civilization growth. Moreover, many statistical studies have showed that reservoirs of heavy crude are much larger than those of conventional crude, which made the appropriate deep upgrading of heavy crude, for both, refining and petrochemicals, more interesting and is attracting more and more attention from scientists and engineers **[2,3].**

Heavy oil and residues are viscous with low API gravity ranging from seven up to twenty, and contain very complex molecules and many impurities such as asphaltenes, metals, sulfur, and nitrogen that pose numerous problems during their up gradation processes into high value added products such as light olefins. Principally, ethylene and propylene, which are sometimes called as king and crown of chemicals respectively, are the most important light olefins because they are building blocks for many petrochemicals products, such as polypropylene, polyethylene, propylene oxide, ethylene oxide, acrylo-nitrile, cumene, and acrylic acid. Therefore, many petroleum refineries worldwide are becoming more oriented to produce mainly light olefins (ethylene, propylene, butenes and butadiene) and BTX rather than the production of transportation fuels (gasoline, diesel and kerosene).

Today and for more than half a century light olefins are primarily produced by thermal cracking of hydrocarbons (light naphtha) in the presence of steam (steam cracking) which is a pyrolysis process and the single most energy-consuming process in the chemical industry. Steam cracking alone cannot satisfy the market demand for light olefins and especially propylene. Consequently, there is a need of alternative approaches such as (steam) catalytic cracking to olefins **[4],** synthesis gas to olefins **[5]** and methanol to olefins **[6]** to produce more olefins to bridge the gap between supply and demand. The direct catalytic cracking of low quality grade crude oil to produce basic chemicals, mainly light olefins, using technologies derived from fluid catalytic cracking (FCC), which has been the second major supplier of propylene after steam cracking process, have been intensively investigated **[7,8].**

This paper aims to review the basic aspects, limitations and strategies of the major processing and catalytic technologies for maximizing light olefins production from the upgrading of heavy crude oils and residues. It is proposed an integrated approach that considers not only the process technology, but also the properties of the heavy feedstock and the required functionality of the solid catalyst to maximize the process efficiency based on the production of light olefins. Initially, we describe the properties of the conventional and unconventional crude oils, then it is briefly reviewed the major two processing technologies for producing light olefins (i.e., steam cracking and fluid catalytic cracking) followed by the analysis of the required catalytic properties of efficient cracking catalysts and finally a future perspective and conclusion are given in the last section of this paper.

2.0 Properties and composition of heavy crude oils

Natural gas, crude oils and petroleum cuts all contain a wide variety of chemical compounds (hydrocarbons) made up of two main elements: carbon and hydrogen. Some of these compounds also contain other hetero-elements, which are often considered as impurities: sulfur, nitrogen, oxygen and some metals such as nickel and vanadium. These Petroleum fluid impurities can be classified as follow:

- Major low molecular weight impurities, which include carbon dioxide (CO_2), hydrogen sulfide (H_2S), metal oxides (Al_2O_3, Fe_2O_3, SiO_2, etc.), nitrogen (N_2), oxygen (O_2), salts (NaCl, $CaCO_3$, etc.), sulfur (S) and water (H_2O).
- High molecular weight impurities, which could be present in the petroleum fluids heavy fractions and include asphaltenes, asphaltogenic acids, diamondoids and derivatives, mercaptans, metal carbenes, organometallics, petrole um resins and wax.

However, world demand on lighter fuels such as naphthas and middle distillates of crude oils is on the rise, global crude quality is decreasing and era of easy oil almost over. Therefore, future crudes to be heavy and extra heavy increasingly, so extra heavy crudes and unconventional oils are alternative to conventional and sweeter oils. Future refineries are dealing with conversion of nearly all residues to light and middle distillates through various separations and cracking processes. Optimum operation of such units depends on the knowledge of feedstocks and products physical and chemical properties **[9, 10]**.

2.1. Sources of vacuum residue and heavy oil

Heavy oil, extra-heavy oil and bitumen are found all over the world, and according to the US classification, heavy oil has a density of $934 < \rho < 1000$ kg m^{-3} (20-10°API). In petroleum refining industries, there are two types of residues are generated. Atmospheric residues (AR, boiling point temperature more than 360°C) are generated at the bottom of atmospheric distillation tower. AR is again treated in vacuum distillation tower. Heaviest fractions obtained at the bottom part of the vacuum distillation column tower are called vacuum residues (VR) as illustrated in **Figure 1**, and its atmospheric boiling points are above 550 °C. It is the "non-vaporizable" fraction of the crude oil and made up of very heavy hydrocarbons compounds, which are not vaporized at high temperature and low pressure in the vacuum distillation units. Thus the name vacuum residue or “Bottom of the Barrel” generally synonymous with vacuum residue. The yields of vacuum residues are very variable according to the crude oil used. They are frequently in the region of 20-30% for heavy crude from Middle-east Arabian light and can exceed 50% for heavy crude from Venezuela or from Canada. Their quality, particularly the amount of sulfur, metals impurities and API gravity depend on their origin. For some crude oils, the vacuum residue is an excellent road bitumen without any further processing **[8, 9, 11]**.

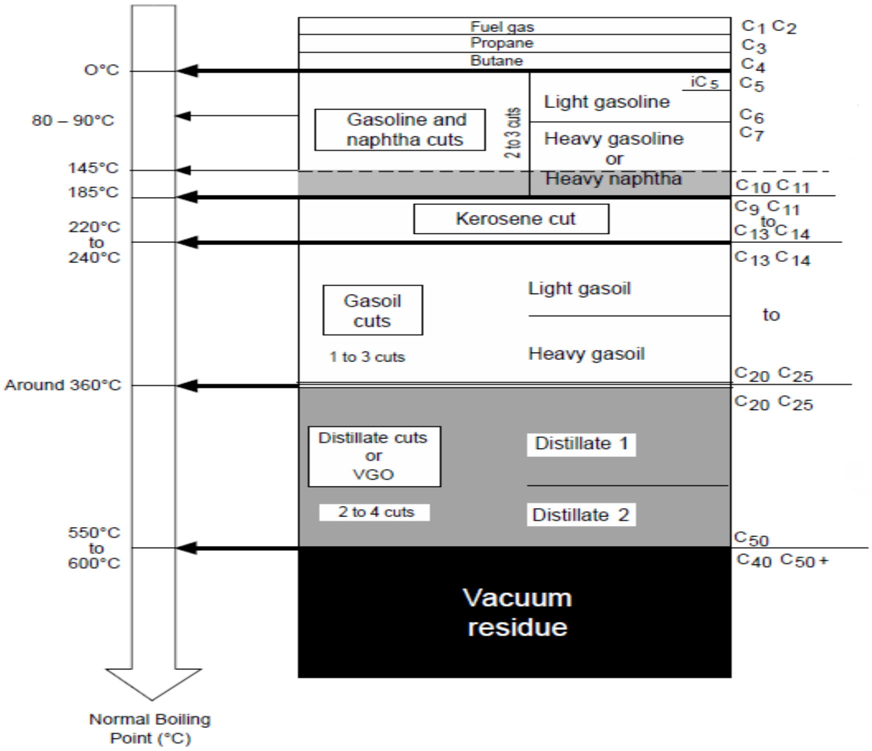

Fig. 1. Trend of different fractions, carbon ranges and boiling points for crude oil

2.2. Properties of vacuum residue and heavy oil feedstock

Vacuum residue physical and chemical properties are wide-ranging according to its original place but it generally is a complex, black in color, highly dense and viscous solid material at room temperature with API gravity ranging between 10 and 20°. Therefore, it must be stored at more than 130 °C for it to be fluid enough to be treated in refinery units. It has also high molecular weight, and low hydrogen to carbon (H/C) ratio. Hence, one of the most important parameter is to convert residue into lighter products by increasing the H/C ratio. These vacuum residues contain impurities such as nickel, vanadium, iron, calcium, silica, compounds of nitrogen, oxygen, and sulfur. **Tables 1,** shows Percentages of impurities (heavy metals, nitrogen, sulfur, etc.) and physical properties of heavy crude oils (source of VR). Moreover, there are main four organic fractions in VR content that can be classified as saturates C_{38-50}, aromatics C_{41-53}, resins, and asphaltenes. **Table 2,** provides the elemental analysis, feed compositions of these various fractions. Depending on the predominant content of saturated (paraffins and naphthenes), cyclic or aromatic compounds, crude and heavy oils are referred to as paraffin-, naphthene- and aromatic-base oils. For example, Venezuelan and West Africa bitumens are known as naphthenic bitumens. Generally, it is found that the vacuum residue and vacuum gas oil consist mainly of resins and asphaltenes. In addition, resins peptize asphaltenes in crude oils and petroleum residues. They maintain them in solution by dispersing them and thus preventing their flocculation (formation of deposits, precipitation). On a microscopic scale, a residue therefore does not have the characteristics of a homogenous solution; it is a colloidal system **[10-12]**.

Table 1. Composition and physical properties of different residues [8]

Crude oil Origin	Gravity (API°)	Ni + V (ppm wt)	S (wt.%)	C-residue (wt.%)	Residue yield (vol.% of crude)	
					AR-343°C	VR-565°C
Saudi Arabian, Safaniya	13.0	125	4.3	12.8	53.8	23.2
North Sea, Ekofisk	20.9	6	0.4	4.3	25.2	13.2
Canada, Athabasca	5.8	374	5.4	15.3	85.3	51.4
Venezuela, Bachaquero	9.4	509	3	14.1	70.2	38.0
Mexico, Maya	7.9	620	4.7	15.3	56.4	31.2

Table 2. Analysis of various crude oil residues [8]

Organic Fraction, wt. %	HC	S	N	V	Ni	AR. 345°C	
						Ni	V
Arabian heavy crude oil							
Saturated	20.1	<1	6.7				
Aromatics	31.0	29.6	8.4	3.4	10.4	5.2	1.6
Resins	31.2	46.3	43.8	25.2	28.2	14.2	11.8
Asphaltenes	12.2	23.9	41.1	71.4	61.8	80.6	86.6
Maya crude oil							
Saturated	20.7	0.9	3.3				
Aromatics	26.5	24.6	8.2	0.4	3.3	2.7	2.7
Resins	29.9	39.0	39.6	17.9	17.7	13.0	13.1
Asphaltenes	20.6	36.3	48.9	81.7	79.0	84.3	85.6
Kern river crude oil							
Saturated	21.8	<1	2.7				
Aromatics	28.7	30.7	4.2	7.5	4.5	1.8	2.7
Resins	37.6	60.3	77.2	52.8	63.0	22.8	16.7
Asphaltenes	5.5	8.8	15.8	39.8	32.5	75.4	80.6

Resins are sticky, viscous and easy vaporized polyaromatic heavy hydrocarbons present in vacuum residue or heavy oils. Structurally, resins consist of (40-53 wt. %) aromatics and naphthenic carbons with long aliphatic side chains and molecular weight of 600-700 unit. Resins may contain sulfur (S), nitrogen (N) and small amounts of metals (Ni and V). **Figure 2** shows two representative structures for petroleum resin molecules belonging to the Athabasca tar sand and crude oil.

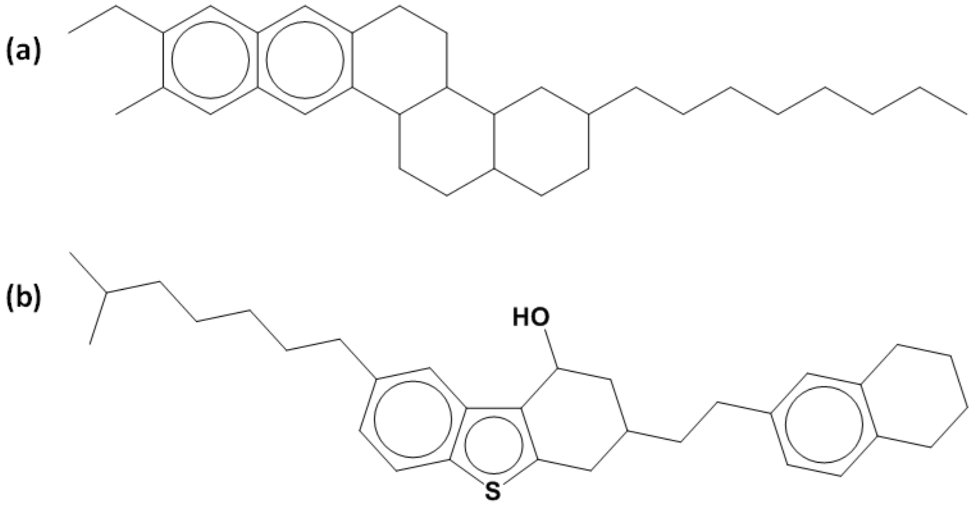

Fig. 2. Structural models for (a) resin fraction of Athabasca tar-sand and (b) resin fraction of Athabasca petroleum [10].

Asphaltenes are said to be the most complex fractions contained in residual petroleum oil, their exact nature is still not very well defined and is very different among crudes from different reservoirs. They are in various color (from brown to black), non-volatile, high molecular weight, amorphous molecules that tend to agglomerate to give rise to micelles or aggregates (colloidal system) that are present in crude oils dispersed through the hydrocarbon mixture. These compounds contain a stack or cluster of naphthenic and aromatic molecules, fused ring aromatic molecules, small aliphatic side chains and polar functional groups, according to the π-π stacking model **(Figure 3a)**. A supramolecular assembly model that combines cooperative binding by Brønsted acid-base interactions, hydrogen bonding, metal coordination complexes, interactions between cylcoalkyl and alkyl groups to form hydrophobic pockets and aromatic π-π stacking interaction was recently proposed by Gray and co-workers **[13] (Figure 3b)**. Most of metals such as nickel and vanadium are concentrated in asphaltenes **[10, 13, 14]**.

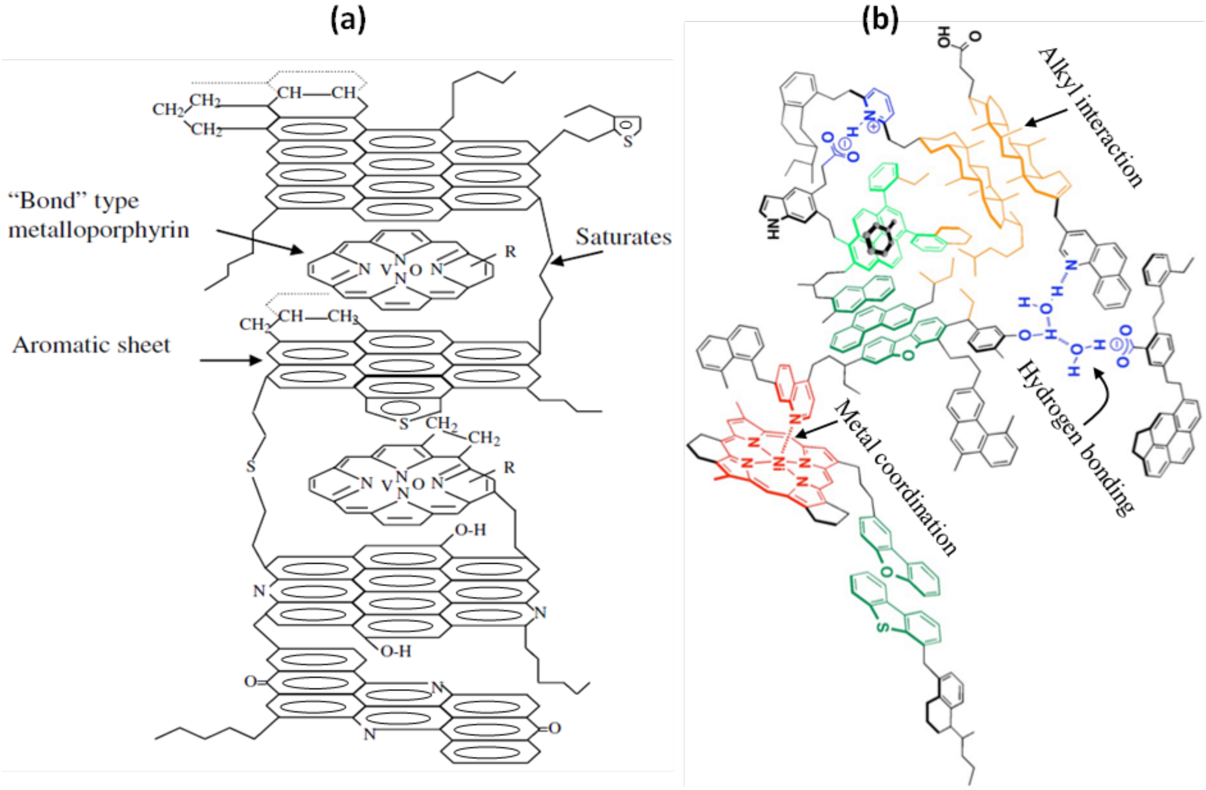

Fig. 3. Pictorial representations of asphaltenes through (a) π-π stacking model, adapted from [10], and (b) supramolecular assembly model, adapted from [13].

Sulfur and nitrogen compounds and metals, especially nickel and vanadium poison the petroleum refining catalysts that are used to transform excess petroleum residues into more valuable light and intermediate cuts for which demand is high. Moreover, asphaltenes, naphthenes and their metal complexes, which are present in significant amounts in heavy feedstock, not only block the catalyst surface but are also deposited on metallic reactor surfaces, thus substantially harming their service performance. Consequently, these impurities are a significant obstacle to the use of petroleum residues.

Because the feedstocks used by refineries are getting heavier, the solvent deasphalting, that is the separation of asphaltenes from the oily medium from heavy vacuum gas oil, atmospheric residue, vacuum residue, or other petroleum based materials to produce valuable deasphalted oil. It is obtained by the injection in the heterogeneous mixture of light liquid hydrocarbons such as propane, butane or pentane, which will mix with the oily medium and consequently modify their physical characteristics and especially the specific gravity. This causes the precipitation of the asphaltenes and even possibly a fraction of the resins. The result, after the separation of the light hydrocarbon, is deasphalted oil (DAO) with much improved properties when compared with the vacuum residue and asphalt concentrating the asphaltenes, which contain a large proportion of the metals. DAO can be used as a high impurity content feedstock to the fluid catalytic cracker, hydrocracker, or other refinery units **[14].**

3. Petroleum refining technologies for light olefins production

The refining or upgrading of unconventional heavy fossil resources such as residue, natural bitumen (tar sand) and extra-heavy crudes have attracted markedly attention from scientists and engineers to produce efficiently fossil fuels and/or petrochemicals in a separated or integrated fashion. The development of advanced, efficient and environmental friendly technologies for upgrading these feedstocks is strongly supported not only by the continues increasing demand of fossil fuels but also by the limited availability of conventional crudes and, of course, the stringent environmental legislations that many countries have adopted to mitigate greenhouse gas emissions.

A straightforward approach to establish the quality and some properties of heavy oils is considering the H/C atomic ratio. Values between 2.2 and 1.9 correspond to high-quality oils; while good-quality feeds have H/C ratio between 1.9 and 1.7; values below 1.6 correspond to low-quality feedstocks as given in **Figure 4**. Obviously, the carbon number, boiling point distribution alongside the API gravity (specific gravity relative to the water at 15.6 ºC) and viscosity among other properties can give further insight into the quality of the feedstock **[15].** For instance, API gravity for median crudes are approximately between 20° and 30°, for heavy oils are between 10° to 20°. The extra-heavy oil and natural bitumen have less than 10°API gravity **[16]**. In fact, the distinction between natural bitumen and extra-heavy oil is a matter of viscosity instead of API gravity or chemical composition. Natural bitumen is more viscous (viscosity above 10,000 cP) and virtually immobile at the reservoir temperature than extra-heavy oil, which has some degree of mobility **[17]**.

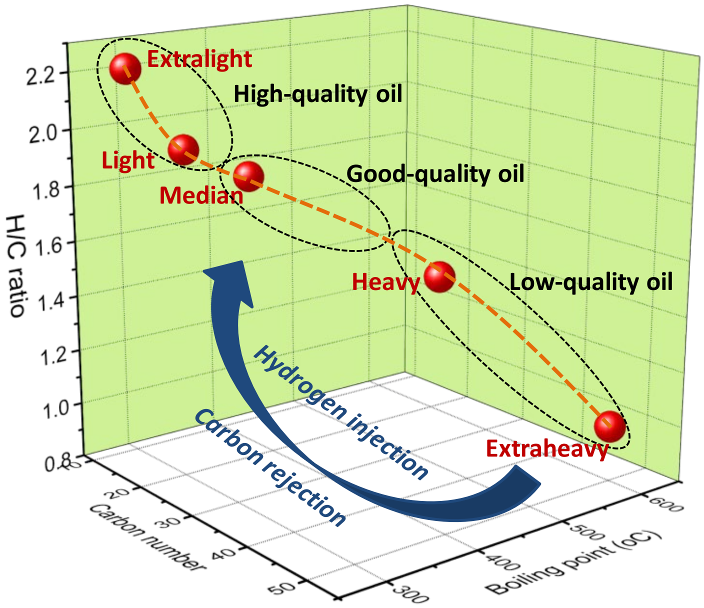

Fig. 4. H/C ratio, carbon number and boiling point distribution for various crude oils. The upgrading of unconventional fossil resources with H/C atomic ratio < 1.5; carbon range number > 40 and normal boiling point range > 550ºC can be achieved by hydrogen injection or carbon rejection processes. Data from reference [15].

The excessive carbon content relative to hydrogen leads to the extra-heavy feature of these resources that is also reflected in the high Conradson carbon (CCR), high microcarbon residue (MCR), high concentrations of heteroatoms (S, N and O), metals (Ni, V, Fe) and high content of asphaltenes. Heavy fossil resources have showed up to 45 wt. % of asphaltenes and 39 wt. % of resins (or maltenes), which are markedly higher than those (i.e., 12 wt. % of asphaltenes and 22 wt. % of resins) found on conventional crude oils **[18]**. Therefore, the upgrading of the unconventional heavy fossil resources entails the increase of the H/C ratio, which can be achieved by either hydrogen injection or by removing certain amount of carbon (carbon rejection). This latter approach decreases the liquid product yield relative to the hydrogen injection process. The processes carried out in the crude oil refinery to produce light olefins are based on carbon rejection technologies: Steam cracking (SC) and fluid catalytic cracking (FCC). Below, we describe these technologies and their capability to deal with heavy crudes to produce efficiently high value chemicals, particular light olefins.

3.1. Steam (catalytic) cracking

The thermal steam cracking of hydrocarbons is a continues process able to produce light olefins with a ethylene to propylene ratio usually below 0.6 at temperatures generally between 750 and 850 °C, steam/oil mass ratio between 0.2 and 1.0 and reaction times usually below one second. The feedstock for the SC process is generally gaseous (e.g., ethane, propane, butane, liquefied petroleum gas) or liquid (e.g. naphtha, gasoil and vacuum gas oils). The selection of the feedstock is a matter of availability and profitability. For instance, gas cracker is convenient when sufficient amounts of the feedstock are available; otherwise, a liquid cracker is more profitable, since gas transportation or gas liquefaction and then transportation are relatively costly **[19]**. The processing of crude oils in steam crackers is further demanding because of coke fouling issues. Several strategies have been identified: (1) steam cracking of crude oils with controlled vaporization; (2) combining pre-treatment of crude, steam cracking and catalytic cracking of the heavy fraction and (3) steam cracking and bottoms upgrading process combination for petrochemical refinery **[2]**.

The steam cracker mainly consists of cracking furnace, quench section and fractionators or separation columns, which are displayed in **Figure 5.** The hydrocarbon feed and the steam are fed into the cracking furnace that contains a tubular reactor with a length between 45 and 90 m and a coil outlet temperature between 700 and 900 °C. The steam-oil mixture flows across the furnace with a residence time usually below 1 second and coil outlet pressure between 0.07 and 0.14 MPa. The stream is rapidly quenched at about 350 °C in the outlet of the cracking furnace to minimise further cracking and potential polymerization reactions. The quenched stream is sent to a primary column or fractionator to be separated into a gas and liquid product streams. The gaseous mixture is then separated into individual gas by compression and high-pressure separation **[20]**. The steam cracker unit is one of the most energy-intensive processes since the steam cracking furnace operates at high temperatures, which can be achieved by combustion of natural gas. Unfortunately, this process produces not only heat but also large amount of greenhouse gas emissions. According to Ren *et al.,*

[21], the combustion section utilizes 65% of the consumed total energy and 75% of the total exergy is lost in the processing of feedstock.

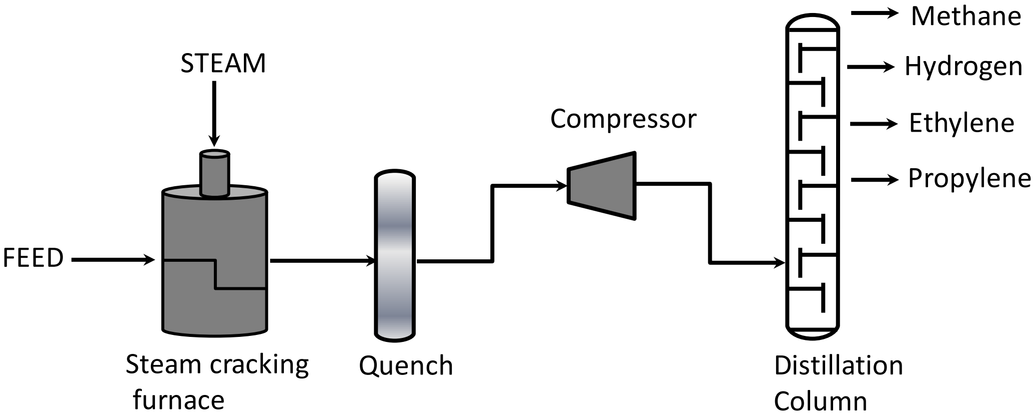

Fig. 5. Main sections of a typical steam cracker diagram, adapted from [22].

The thermal cracking reaction of hydrocarbons proceeds via free-radical intermediates thought the homolytic breaking of C-C bonds to produce alkyl radicals, according to the Rice and Kossiakoff radical theory **[23]**. The radicals subsequently suffer β-scission (cleavage of the C-C bond located in the β position to the carbon lacking a hydrogen atom) to generate a terminal (or alpha) olefin and a primary radical that lacks of one hydrogen atom on a primary carbon atom. The β-scission from a primary radical produces ethene and another primary radical that would produce further ethene in the absence of radical isomerisation reaction. By successive cracking reactions the ultimate methyl and ethyl fragments would react with reactant molecules to produce methane, ethane and new primary radicals that propagate the cracking (chain) reaction [**24]**. The termination of the cracking reaction mechanism can occur by combination and disproportionation of (ultimate) alkyl radicals to produce hydrogen and light alkanes. Several kinetic models have been developed for the thermal cracking of gases and liquid hydrocarbons to light olefins **[25-27].**

The direct processing of light or conventional crude oil into light olefins is rather limited because of fooling issues of coke over the steam cracking unit **[2].** Obviously, the production of petrochemicals from heavy crude oil is even more challenging as a consequence of the high concentrations not only of heteroatoms (S, N and even O), but also micro-aggregates of asphaltenes, resins (or maltenes) and metals (mainly Ni and V). The former can produce a relative high concentration of H_2S in the outlet stream, whilst asphaltenes can speed up the fooling issues of coke.

The catalytic cracking of heavy crude oil is an attractive strategy to produce low cost liquid fuels and petrochemicals. This process can be carried out through either thermal cracking or a combination of simultaneous thermal and catalytic cracking processes. Steam can also be co-fed alongside crude oil in the steam catalytic cracking (SCC) process, which may be the most reliable and efficient process to upgrade heavy crude oil. Indeed, the production of olefins from catalytic cracking of light feeds (i.e., light gases and naphtha) has been intensively studied on pure ZSM-5 and modified ZSM-5 due to its high capability to produce light olefins with higher propene/ethene (P/E) ratio at lower reaction temperature than the steam cracking process **[4].** The catalytic cracking of C_4 olefins to propene and ethene over various ZSM-type zeolites and SAPO-34 has also revealed the superior performance of ZSM-5 relative to other zeolite structures **[28, 29].** However, it was subsequently reported that IM-5 zeolite improves the catalytic activity relative to ZSM-5 zeolite in SCC process of naphtha, without altering the yield to olefins. Unfortunately, both zeolites (i.e., ZSM-5, IM-5) suffer deactivation when increasing time on stream as a consequence of zeolite dealumination during SCC process **[30]**. The incorporation of phosphorous and even La enhances the hydrothermal stability of zeolite **[4, 30].** The (steam) catalytic cracking of crude oil could enhance the production of olefins taking into account the fact that the direct thermal cracking of crude oil can produce only 24 wt. % of C_2-C_4 olefins at operation conditions fairly comparable to the SCC of naphtha (i.e., 640 °C and 2 s residence time) **[31].**

The mechanism of the catalytic cracking of different alkanes has been widely studied **[14, 32]**, as discussed in **Section 4.3**. However, the influence of the steam over the catalytic cracking mechanism over zeolite-type catalysts has been very little investigated, likely due to the severe effect of steam over the zeolite dealumination under SCC operation conditions. The steam catalytic cracking of 2-methylpentane at mild temperatures (400-500 °C) over USY zeolite revealed that steam enhances the reactions of isomerization and hydrogen transfer and also increase the alkane/alkene ratio **[33,34]**. A close inspection of the listed data for propene and ethene also reveals that ethene production is significantly improved as increasing steam/feed ratio, particularly at higher reaction temperatures; see **Figure 6.** Propene content, on the other hand, significantly decreased in presence of steam, at lower reaction temperatures. However, propene molar content shows about 10-fold increase relative to ethene.

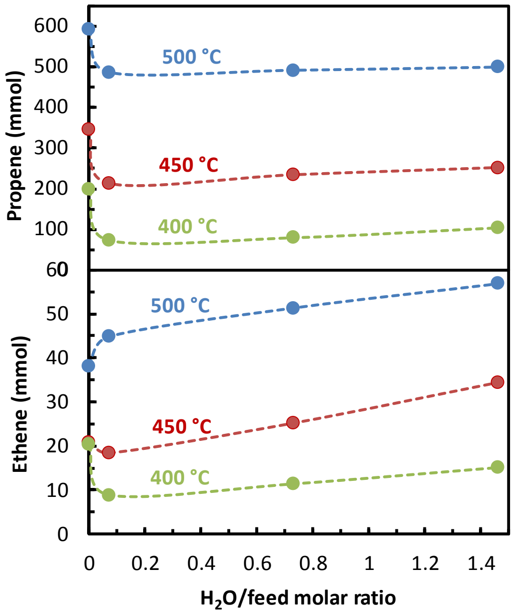

Fig. 6. Influence of the H_2O/feed molar ratio over initial ethane and propene contents in the steam reforming reaction of 2-methylpentane over USY zeolite **[33].**

A potential strategy to maximise the petrochemical production from heavy crude oil (HCO) is illustrated in **Figure 7.** The HCO is initially divided into two fractions through a separation process by either distillation (i.e., difference in the boiling point) or solvent deasphalting (SDA) (i.e., difference in solubility and density). In the SDA process, the heavy feed is mixed with a light and lineal paraffinic hydrocarbon (propane, butane, pentane, or n-heptane) to extract the light oil or deasphalted oil (DAO), whilst the insoluble asphaltenes-enriched pitch remain as heavy fraction **[35, 12]**.

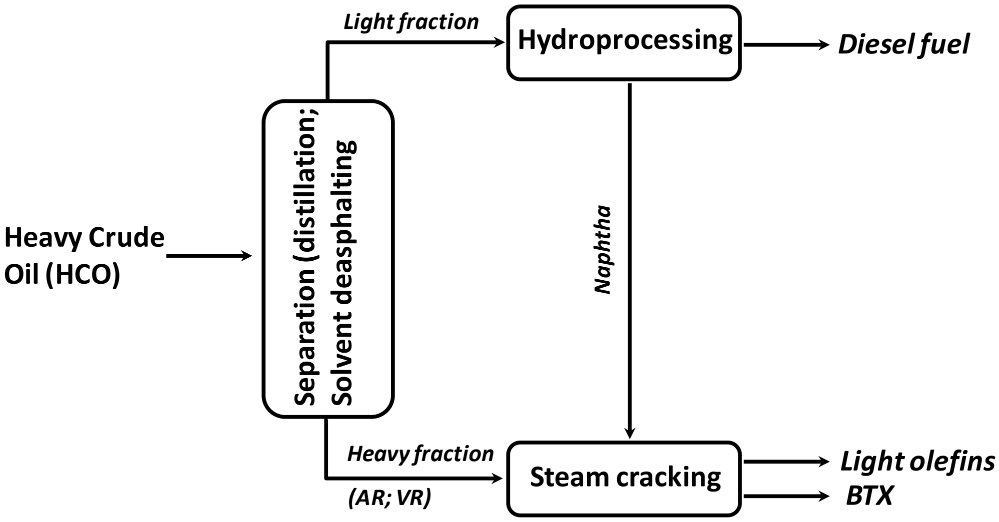

Fig. 7. Steam cracking strategy for upgrading of heavy crude oil. AR, VR and BTX stand for atmospheric residue, vacuum residue and a mixture of benzene, toluene and xylene, respectively.

The selection of the separation process would depend upon the properties of the feedstock, for instance, for extra heavy crude or natural bitumen, the separation process by SDA is convenient because of the high content of asphaltenes and hence relative low amount of DAO (i.e., liquid fraction). It is also viable a combination of both separation processes, in which the atmospheric residue (AR) or vacuum residue (VR) produced after the distillation process, is then treated in a SDA unit to obtain further (light) liquid fraction. Subsequently, the liquid fraction enriched by paraffinic molecules can be hydroprocessed to crack large molecules and remove heteroatoms (S and N) to produce diesel fuels and naphtha **[12, 36, 37]**, which can be treated in the steam cracker to produce further light olefins. On the other hand, the heavy fraction (i.e., asphaltenes-enriched fraction) alongside the cracking catalysts may be pelletized and then treated through a continuous (moving bed) pyrolysis process to produce light olefins (mainly ethylene and propylene) and a BTX-enriched liquid fraction. It is also expected the production of coke as a consequence of the deep dehydrogenation of poly-aromatics and possible condensation of unsaturated molecular fragments. The coke can be processed in a gasification unit to generate heat/power that can fuel the overall process **[38]**.

We have assessed the thermal catalytic cracking of a solid paraffinic feedstock blended with various carbons such as activated carbon (AC), graphite and mesoporous carbon (MC) using microwaves to assist the cracking reactions. Carbon can act as microwaves absorber and also as possible catalyst to speed up the (thermal/catalytic) cracking reactions. The compositions of the gaseous products are listed in **Table 3.** Note that the production of olefins (alkenes) is significantly enhanced with the loading increase of heavy hydrocarbon (i.e., paraffin wax, PW). The highest production of olefins (ca. 43 %) arise from graphite and mesoporous carbon as catalysts, which also showed markedly lower ethylene/propylene ratio (2.2-2.3) and H_2/olefins ratio (0.2-0.4) compared with high loading of PW (50 and 70 wt. %). It indicates that both carbons selectively produce light olefins whilst minimize the deep dehydrogenation reactions, certainly the utilization of acid catalysts would be an interesting alternative option to enhance the production of propylene. This process could be a viable route to make feasible the above-described strategy. Indeed, the microwave-assisted catalytic process was also used to catalyse the deep dehydrogenation of a variety of hydrocarbons to high-purity hydrogen and residual carbon as by-product **[39, 40]**.

Table 3. Gas composition (mol %) from the microwave-assisted catalytic decomposition of PW blended with various carbons.

Sample	H2 (%)	CH4 (%)	C2-C4 (%)	COx (%)	$(C2\text{-}C4)^{=}$ (%)	$(C2/C3)^{=}$	$H2/(C2\text{-}C4)^{=}$
15 % PW @ AC	37.2	21.2	23.7	9.5	8.4	0.9	4.4
33 % PW @ AC	38.5	23.1	18.6	6.1	13.7	1.3	2.8
50 % PW @ AC	33.0	30.4	10.9	2.5	23.2	3.1	1.4
70 % PW @ AC	34.2	22.5	8.4	2.5	32.4	2.9	1.1
49 % PW @ Graphite	9.5	28.1	12.4	6.7	43.3	2.2	0.2
64 % PW @ MC	16.6	30.9	8.9	0.7	42.9	2.3	0.4

3.2. Fluid catalytic cracking (FCC)

Fluid catalytic cracking (FCC) is the second supplier of olefins after steam cracking and nowadays accounts for 30 % worldwide production of propylene. The type of feedstock usually upgraded in a FCC unit is vacuum distillation derivates such as vacuum gas oil (VGO), vacuum residue (VR), atmospheric residue (AR) and even deasphalted oil blended with VGO, see **Figure 8**. Feeds with high contents of asphaltenes and metals are currently addressed by Resid FCC and high-severity fluid catalytic cracking (HS-FCC), whilst lighter feeds can be treated by deep catalytic cracking (DCC) and conventional FCC process **[2, 14, 41, 42]**. Various reactions such as cracking, hydrogen transfer, isomerization and condensation are assisted by an acid zeolite catalyst, whose composition is also described in this review. Catalytic cracking is preferred over thermal cracking to maximise propylene production. Indeed, when the severity of the FCC process is increased by operating at high reaction temperature, short residence time and high catalyst/oil ratio, liquefied petroleum gas (LPG) and olefin production are also increased. To maximise the production of light olefins from extra heavy crude oil and natural bitumen an advanced FCC process and catalyst would be necessary since FCC is a very well-established technology able to deal with a variety of feedstocks. Obviously, a unit of steam cracking to crack lighter fractions into light olefins can complement the conversion unit.

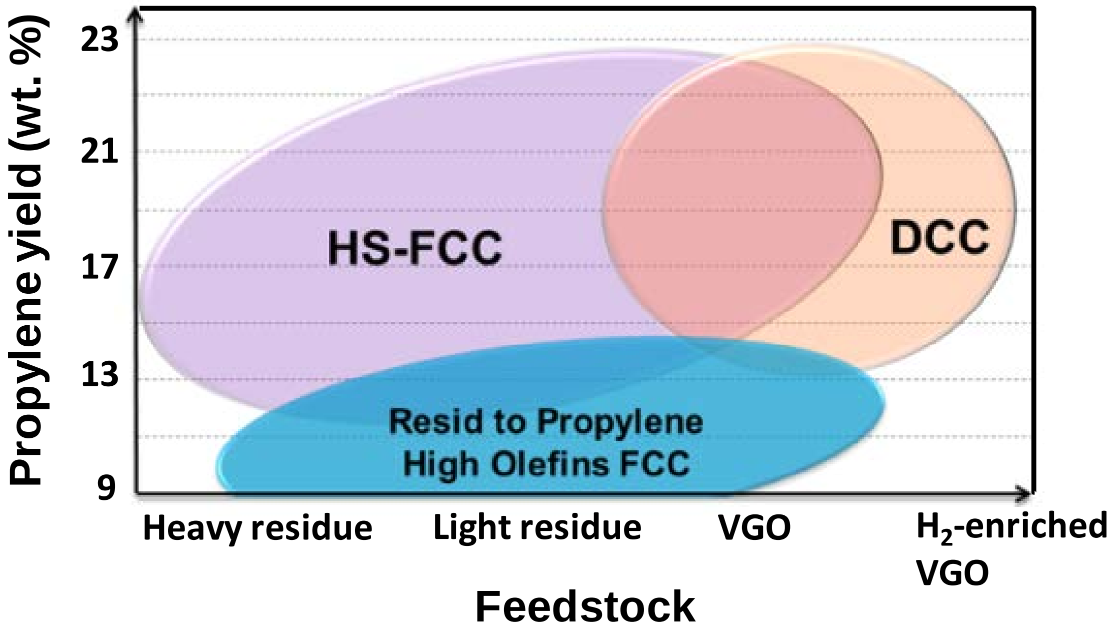

Fig. 8. Technology platform for propylene production from various feeds. Adapted from [41, 43].

A large number of different FCC designs are currently available in the market, nevertheless, three major components such as catalyst regenerator, reactor and the distillation/separation sections are always present in a typical FFC unit, see **Figure 9,** in which the catalyst particles move in an up-flow configuration. The process flows consist on the access of the catalyst at the bottom of the riser at temperatures between 480 and 570 °C, alongside the feed heated at temperatures between 260 and 425 °C. The catalyst/oil mass ratio is above one and usually about 6, whilst the residence time is below one second **[20]**. The catalyst is separated from the product vapours and the oil remaining on the catalyst is tripped by steam treatment. The product stream is taken to a fractionation column for separation into liquid fuels and olefin-enriched gaseous mixture. The spent catalyst with coke content below 5 wt. % is flowed into the regenerator section where the catalyst is reactivated by burning the coke off at maximum temperature of 760 °C under an appropriate oxygen concentration **[14]**.

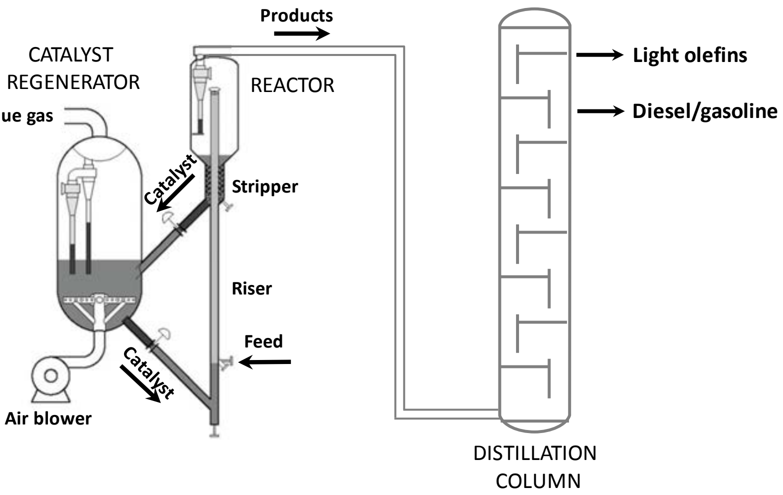

Fig. 9. Schematic representation of the FCC unit with its major components (i.e., catalyst regenerator, reactor and distillation column). Figure adapted from [14].

It is well-established that the FCC process involves a large number of successive reactions, therefore, the production of olefins as desired product can be considered as intermediate products that can be facilitated by minimising back-mixing and improving the distribution of residence time into the reactor using down-flow configuration **[44]**. This strategy is the main core of a new FCC technology (i.e., high-severity fluid catalytic cracking (HS-FCC)) for upgrading of heavy crude oil to olefins developed by Nippon Oil Corporation, King Fahd University of Petroleum & Minerals and Saudi Aramco **[41, 43]**. This technology is currently in the semi-commercial status and is licensing by Axens and Technip Stone & Webster Process Technology **[43]**. The technology advantage is due to the combination of FCCU design, catalyst development and operation conditions, which is based on high reaction temperature, short contact time and high catalyst/oil ratio. This enhances the primary reactions towards olefins, while hindering the unwanted secondary reactions (i.e., hydrogen transfer and thermal degradation) **[7]**.

4.0 FCC Catalysts and production of light olefins

Fluid catalytic cracking (FCC) is one of the most important chemical processes used in petroleum refineries. It is widely used to convert the heavy crude oil to gasoline, olefinic gases, and other valuable products. In the conventional FCC, the hydrocarbons fluidize the catalyst and the mixture flows upward in the riser. Comparing to other processes, the FCC process has many important technical advantages such as continuous operation of the process and heat supply for hydrocarbon cracking. The cracking reactions produce some coke material that deposits on the catalyst surface causing fast catalyst deactivation. The deposited coke can be easily burned off in the regenerator, as was previously discribed, thus the catalyst is continuously reactivated. Furthermore, the combustion of the coke produces a large amount of heat, this heat provide the energy required for vaporization of the feedstock and the endothermic cracking reactions that take place in the reactor **[18, 20]**.

4.1 FCC catalyst composition

The FCC catalysts must possess several chemical and physical properties to be suitable for the FCC process **[7, 14, 45]**:

- The catalyst must compose acid properties to facilitate (C-C) cracking in the large feedstock molecules to the desired products.
- It must have high attrition resistance to the impact of the collision with each other and the unit walls during the fluidization;
- The catalyst must be stable at high temperature and steam partial pressure,
- It must contain large pore sizes to crack larger molecules then, they can get into smaller pores.
- The catalyst must be able to withstand the poisons of the heavy metals and heteroatoms in the heavier feedstock;
- The catalyst components must be available in a form that allows fluidization in the regenerator,
- It must form the minimum amount of coke at the high cracking activity of heavy feedstock so, the catalyst remain active during the reaction.

The first catalyst used for FCC process was clay-based catalyst. In 1940s, SiO_2-Al_2O_3 or SiO_2-MgO-based catalysts were developed and greatly improved over the natural clay catalysts **[14, 46]**. However, the most significant advance was in the beginning of 1960s when the zeolite Y was invented. This catalyst vastly improved gasoline yield and quality. Since then, zeolite Y in various improved forms has been the main cracking component of FCC catalysts and still in use today **[46]**.

As showed in **Figure 10**, the conventional FCC catalyst is composed of an active component (zeolite), a matrix such as amorphous silica-alumina, binder (i.e., bentonite clay) and filler catalyst **[7, 11, 47-49]**. Ultra-stabilized zeolite Y (USY) is used as the main active catalyst for this process. USY zeolite material is composed of spherical particles, suitable for application in a fluidized circulating reactor. The zeolite crystals are dispersed in the active matrix together with clay particles. The spherical particles contain large voids and pores necessary for allowing the mass transport of the heavy feedstock. The matrix catalyst (amorphous SiO_2-Al_2O_3 or SiO_2-MgO) have both physical and catalyst functions **[7]**. It provides particle integrity and attrition resistance, acting as a heat transfer medium, and providing a porous structure to allow diffusion of hydrocarbons into and out of the catalyst microspheres. The matrix provides catalyst sites and can affect reaction activity, catalyst selectivity, product quality and resistance to poisons. Binder (bentonite clay) and filler provide physical strength to the catalyst. They also have high heat capacity, which is important for balancing material in the catalyst and carrying sufficient heat from the regenerator to riser **[7, 47]**. The as-prepared zeolite is not very stable under the hydrothermal conditions. The stability can be improved by the hydrothermal steaming method to obtain ultra-stable Y (USY) form. The other well well-known method is the introduction of rare earth (RE) ions to the Y zeolite. These two methods improve both the activity and the hydrothermal stability of the catalyst **[7, 14]**.

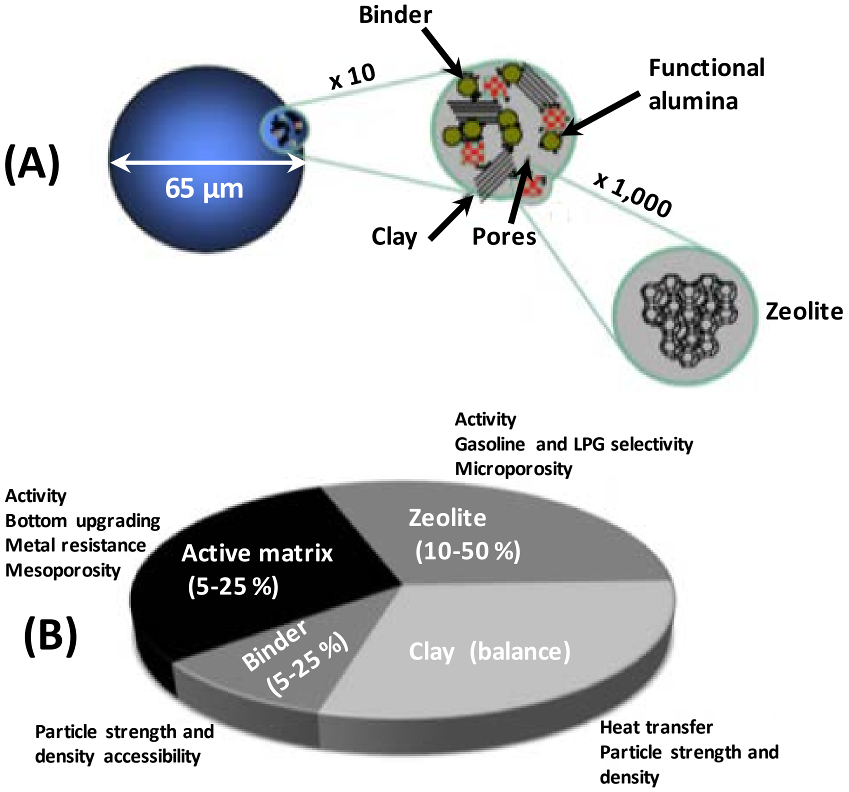

Fig. 10. (A) Schematic representation of FCC catalyst and (B) compositions and functions of the catalyst components, adapted from [46].

4.2. HY zeolite optimizations

In this section, we will focus on the catalysts used to increase light olefins production in the FCC process. Corma et al., **[2]** claim that there are varieties of parameters of the Y zeolite based catalysts can have a direct impact on the ability of the catalyst to produce light olefins during FCC operations. These parameters includes for example rare-earth content, unit cell size, zeolitic compound content, matrix content and activity.

In the conventional FCC unit, it is generally accepted that gasoline, LPG and olefins production are favoured low hydrogen-transfer reaction. Increasing the rate of hydrogen-transfer reaction promotes the hydrogenation of olefins and promotes the formation of coke deposits on the catalyst **[50]**.

The introduction of rare earth (RE) in Y zeolite minimizes the framework dealumination under hydrothermal conditions and leads to enhance the rate of hydrogen transfer reaction **[51]**. Therefore, the optimum content of rare-earth element in Y zeolite based FCC catalyst showed that the utilization of low radius rare-earth cations to stabilize HY zeolite increases the dealumination and produces smaller unit-cell size catalyst **[52]**. At lower FCC catalyst unit cell sizes, the activity of the zeolite is low due to the low concentration of active sites and at higher unit cell sizes hydrogen transfer reactions are favoured due to the rapid increase in the number of paired Al atoms **[2]**. This explains the lower of the light olefins production and the higher coke formation over rare-earth exchanged zeolites **[2, 53]**. In addition, it was found that the ionic radius of the rare earth has a great impact on the acidity of HY zeolite. The density of the Brønsted acid sites is higher with larger ionic radius of the rare-earth atom **[54]**.

Another important parameter which can help to tune the Y zeolite based FCC catalyst to produce more light olefins is the nature of the matrix and the ratio of zeolite-to-matrix. The matrix may be an acidic or non-acidic material, depending on the requirement of the FCC unit operation. A non-acidic matrix usually used when only coke reduction is required. While acidic matrix is recommended for the cracking of large molecules in the residual feed to smaller molecules, which can also diffuse into the pores of the zeolite to be further selectively cracked **[55]**. It has been reported in many cases that the use of acidic matrix helps to increase the olefins yield together with the gasoline and its octane number **[2, 56]**. However, using active matrix may increase the coke formation over catalyst surface **[57]**.

As mentioned above, SiO_2-Al_2O_3 based matrices are commonly used as an active matrix in the FCC process. Other active matrix material were also studied **[58]** such as magnesium silicate, silico-alumino-phosphate and mixed oxides such as SiO_2-ZrO_2, or SiO_2-Al_2O_3-MgO. These components have shown that they can help to vary the overall FCC catalyst selectivity and to increase the olefins production. In commercial FCC catalysts, it is possible to adjust the catalyst activity and selectivity by changing the zeolite-to-active matrix ratio. However, the optimum ratio depends on feedstock composition, process operating conditions and the target products. For example, it is observed that a decrease in zeolite-to-matrix results in an increase of LCO, coke, dry gas yields, and a decrease in bottoms yields. The gasoline octane and olefin/paraffin ratio in LPG also increase under these conditions **[59]**. Furthermore, special attention has been paid on the effect of the mesopores surface area of the FCC catalyst particularly in the case of heavy oil feedstock **[60]**. Highly accessible catalysts will facilitate large molecule diffusion to enhance their cracking as well as diffusion of reaction products outside the catalyst, lowering coke formation and limiting hydrogen transfer reactions that reduce olefins yields **[2]**.

4.3 FCC Reaction

It should be obvious that the large molecules in the heavy oil feedstock cannot enter the pores (about 7.3 Å) of zeolite Y. Therefore, it is clear that the conversion occurs in stages, and gasoline is not the primary reaction product **[61]**. Alternatively, the large molecules are pre-cracked in the matrix on their way to the zeolites **[14]**. The cracking reactions are likely a combination between thermal and catalytic reactions. The catalytic cracking reaction is acid catalyzed. Matrix particles and zeolites both provide the acidity (Brønsted acid sites and Lewis acid sites). Brønsted acidity is generated by the presence of aluminum in the silica framework. While Lewis acidity is formed by the presence of aluminium sites (coordinatively unsaturated) on the silicate surface **[62]**.

The mechanism of the catalyic cracking reaction has been studied and extensively dissscused **[14, 32, 61, 63]**. The reaction network in zeolite-assisted cracking of hydrocarbon is given in **Figure 11**. It involves proton transfer from zeolite Brønsted site to alkane to form carbonium ion (reaction 1), proton transfer from zeolite to alkene to form carbenium ion (reaction 2), hydride transfer from alkane to zeolite to form carbenium ion (reaction 3) and β-scission of a carbenium ion to form a primary carbenium ion and an alkene (reaction 4). The primary carbenium ion abstracts a hydride from a larger alkane molecule to desorb from the acid site as an alkane, or undergoes a β-scission to desorb from the acid site as ethene, leaving a carbenium ion on the zeolite acid site to propagate the reaction. The primary carbenium ion can also transfer a proton back to the zeolite to produce an alpha-alkene and regenerate the Brønsted acid site.

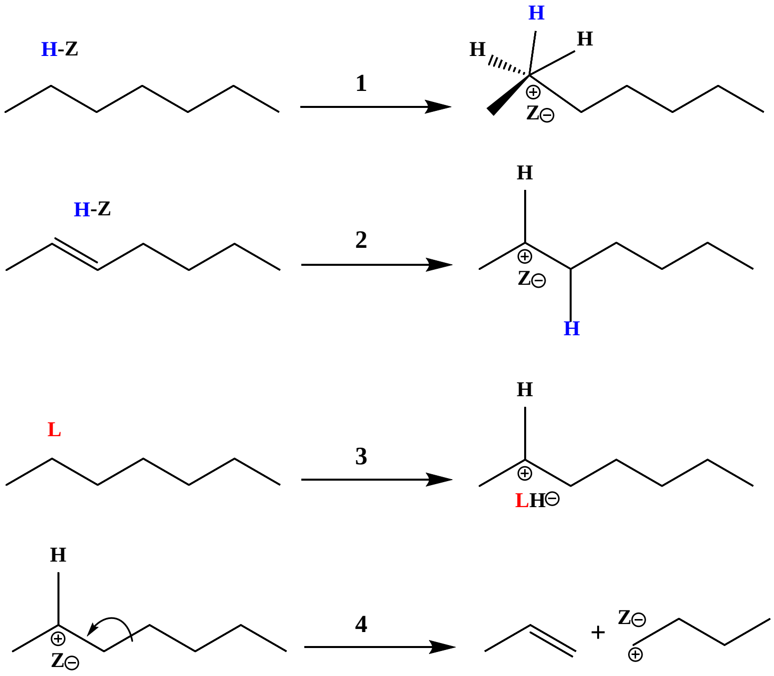

Fig. 11. Reaction pathways for the catalytic cracking of hydrocarbons over zeolite-based acid catalysts involving carbonium formation (reaction 1), carbenium formation through proton and hydride transfers (reactions 2 and 3) and β-scission to form a primary carbenium (reaction 4). H-Z and L stand for Brønsted and Lewis acid sites, respectively. Reaction network adapted from [14].

In general, it is accepted that the catalytic cracking involves the formation of carbenium ions. In summary carbenium ions are formed through the flowing ways:

1) Initially, thermal (radical) cracking formed alkenes and Brønsted acid sites can donates proton to the alkenes.
2) Lewis acid sites and Brønsted acid sites abstract a hydride from an alkane to form dihydrogen.
3) On the other hand, a penta-coordinated carbonium ion can be formed when Brønsted acid site donate a proton to an alkane. An alkane and a carbenium ion remain when the carbonium ion cracks protolytically (Haag-Dessau mechanism) **[14, 32]**.

Smaller alkene and a smaller carbenium ion are formed through β-scission cracking of the larger carbenium ions produced in steps 1-3. When, the larger alkane molecule abstract hydride, the smaller carbenium ion desorb from the acid site as an alkane, leaving a new larger carbenium ion on the zeolite acid site to replicate the reaction. In addition, the carbenium ion can donate the proton back to the acid site, and desorb as an alkene.

4.4 ZSM-5 zeolite based additive

ZSM-5 based additives were firstly commercially used in the FCC process since 1980s in order to improve gasoline octane number. Nowadays, ZSM-5 is used as an efficient additive to increase C_2-C_5 olefins yield. The efficiency of the ZSM-5 based additives to increase gasoline octane and light olefins selectivity have been repeatedly proved in the literatures **[64-66]**. Optimum additive content was claimed to be around 25 wt% of the total FCC catalyst composition **[67]**. Above this value, there is no further improvement in light olefins yield as illustrated in **Figure 12**. ZSM-5 is a high silica pentasil zeolite with intermediate pore size distribution, a preferential cracking selectivity to light olefins (C_2-C_5) in general and to propylene in particular, at the expense mainly of linear and low octane compounds of the gasoline pool. The wide pore system of HY zeolite allows for bimolecular cracking and hydrogen transfer reactions resulting low light olefins yield **[68]**. ZSM-5 cracked essentially gasoline into light olefins, instead of gasoline-range paraffins, through hydrogen transfer reactions on the main cracking catalyst. As a result, the gasoline contained less paraffins and proportionally more aromatics by a concentration effect, improving octane number **[69]**.

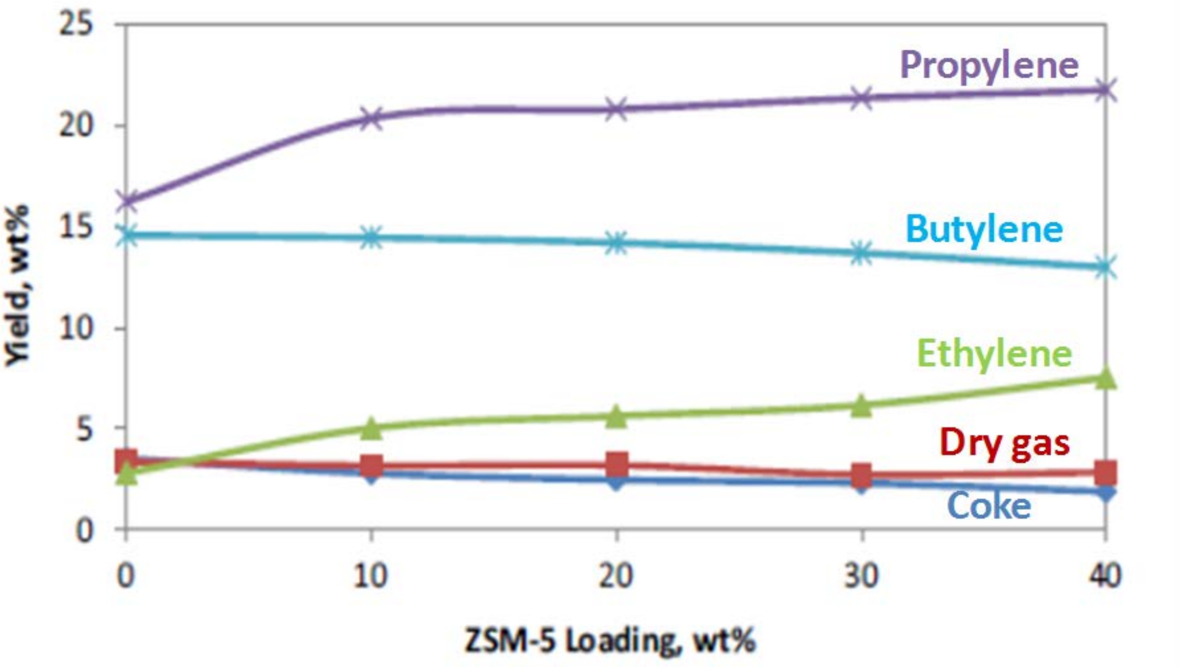

Fig. 12. Effect of ZSM-5 contents on propylene yield, adapted from [7].

4.4.1 ZSM-5 modifications

In this section, we highlight the most important modification methods applied for improving ZSM-5 performance in the FCC process to increase the yield of light olefins. In order to increase the concentration of ZSM-5 in their additives to avoid dilution effects at high levels of additive, hydrothermal deactivation method has been developed **[66]**. It has been claimed that the light olefins increase when using hydrothermally deactivated ZSM-5 combined with USY catalysts **[62, 67, 70, 71]**. This may be due to the selective monomolecular cracking of gasoline pool olefins previously produced by the USY catalyst. The modification of ZSM-5 based additives for maximization of light olefins production should take into account the acidity of the modified catalyst. The changes of the Si/Al ratio in ZSM-5 affect the yield of light olefins **[72, 73]**. Most hydrogen transfer reactions in ZSM-5 occur on the surface of the catalysts and are more pronounced at low Si/Al ratios when the acidity is high. Hydrogen transfer reaction produces more dry gases (i.e. methane and ethane) and less light olefins yield.

Reducing the particle size of the zeolite is an effective method to overcome diffusional limitations. Nano-sized zeolites reduce the diffusion length for reactant/product hydrocarbons **[74-76]**. In general, it is accepted that a smaller crystal size in combination with high Si/Al ratio gives higher light olefins yields due to lower residence time of primary products in the pores of the catalyst in contact with the acid sites **[29, 77]**. It is clear that the *n*-hexane conversion decrease with time on stream over ZSM-5 with large crystal size; see **Figure 13**. While over ZSM-5 with small and medium crystal size, remain high with time on stream.

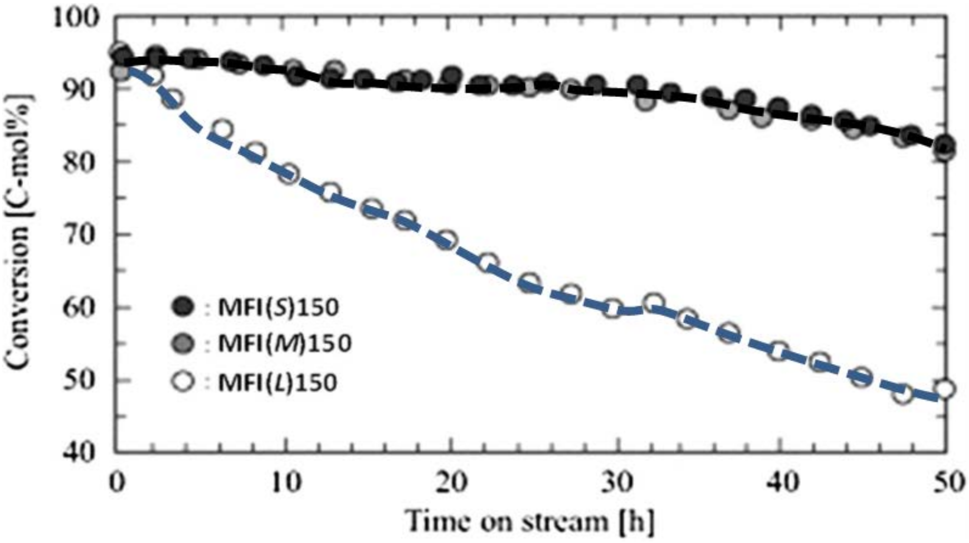

Fig. 13. *n*-Hexane cracking over ZSM-5 zeolite (Si/Al = 150) with different crystal sizes, adapted from [75].

As mentioned in the case of Y zeolite, ZSM-5 with mespores structures will improve the accessibility of the catalyst, lowering undesirable reaction such as hydrogen transfer. Mesoporosity can be introduced by steaming **[78]**, alkaline treatment **[79]** acid leaching **[80]**, and reaction with EDTA or other chelating and secondary templating **[72, 81]**. A hierarchical pore structure, in which mesopores and micropores are connected in zeolites **(Figure 14)**, can be produced using different techniques **[82-84]**. The hierarchical zeolite can be synthesized directly from a silica-alumina gel (bottom up) or when the zeolites are post-treated after synthesis (bottom up) **[82]**.

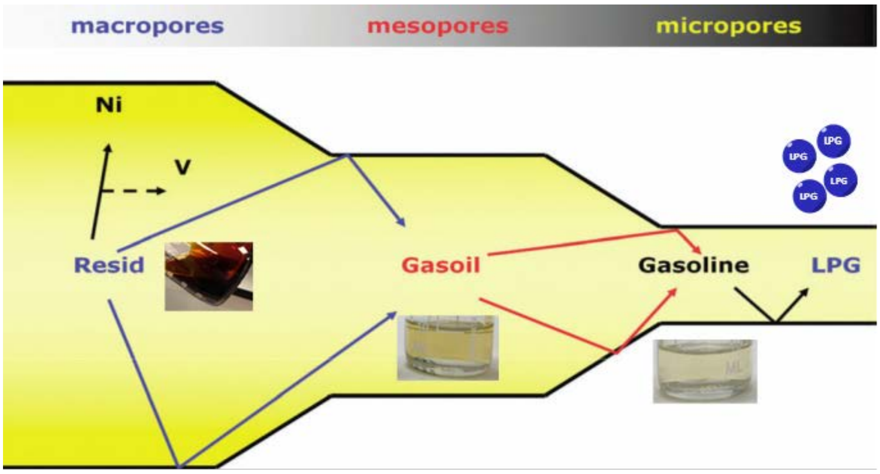

Fig. 14. Schematic representation of the hierarchical pore structure in zeolite, adapted from [72].

Numerous studies compared the performance of the normal ZSM-5 and mesoporous structure ZSM-5 catalyst in the FCC process to increase light olefins production. For instance, higher overall activity, and higher yield of lower olefins such as propylene and butylene was observed over ZSM-5 with hierarchical pore systems compared to normal ZSM-5 in the cracking of gas oil **[85]**. In other study **[72]**, the production of propylene and ethylene were enhanced significantly over mesoporous structure ZSM-5 catalyst compared with the conventional ZSM-5 in the catalytic cracking of the FCC naphtha. The author attributed this enhancement not only to the small crystal of meso-ZSM-5 that suppressed secondary and hydrogen transfer reactions, but also to the mesoporous structure that facilitated the transport and access of the naphtha to the active sites.

The first usual and most widely used modification method applied for improving HZSM-5 zeolites stability and its performance is the treatment with phosphorus **[86]**. The incorporation of phosphorus stabilizes the lattice aluminum ions impeding aluminum from leaving the zeolite framework and prevents structural changes leading to high hydrothermal stability of the ZSM-5 catalyst **[87]**. It is also thought that, phosphorus modified ZSM-5 zeolite retains a larger fraction of the acidity compared to ZSM-5 zeolite when the catalyst is subjected to severe hydrothermal conditions **[65]**. Significant improvements in the light olefins yield (i.e., ethylene and propylene) and the acid stability have been reported over P/ZSM-5 catalysts in the cracking of C_4 olefins and naphtha **[88, 89]**. Using phosphorus modified HZSM-5 catalyst led to increase propylene and butenes selectivity in n-decane catalytic cracking **[87]**.The modification of HZSM-5 zeolite with phosphorus reduces the Brønsted acidity of the ZSM-5 **[90]**. This may provide a pathway for reaction to occur with enhanced light olefin production **[87, 88]**.

On the other hand, it has been proven that the introduction of a rare-earth metal cation (i.e., La, Ce, Sm, etc.) into ZSM-5 zeolites could have a great impact on its acidic properties **[91]**. As the rare earth oxides usually possess some basic character, they modify the basicity of ZSM-5 **[2]**. Therefore, La-loading of ZSM-5 zeolite generates basic sites on the surface of ZSM-5 **[92]**. Over the later catalyst, yields of ethylene plus propylene close to 60 wt. % were reported. In addition, as the amount of La loading increases, the olefin adsorption over La/HZSM-5 zeolites decreases **[93]**. Therefore, the main reason for the higher yield of ethylene and propylene is due to the decrease of the rate of the bimolecular reactions which is negatively affected by the decrease of readsorption of the basic compounds of the cracking products, such as ethylene, propylene and butenes **[2]**.

In addition, the incorporation of alkali metals and/or alkali earth metals modifies the ZSM-5 acid character by weakening acid strength or reducing acid sites and is even able to make basic zeolite. For example, barium as the strongest Lewis base in alkaline earths series resulted in the highest yield of light olefins **[94].** The treatment of ZSM-5 zeolite with alkaline-earth metal controls the ZSM-5 acid character and it may able to limit hydrogen transfer reactions and catalyze dehydrogenative cracking and dehydrogenation activity, resulting an improvement of light olefins yield **[92, 95]**. However, it is worth to note that strong alkali solutions destroy zeolite crystal structure, leading to convert them to amorphous materials with macropores and extremely small acid sites **[96, 97].** While using weak alkali solutions dissolve a small amount of silica and alumina and create mesoporosity.

The incorporation of transition metals produces new Lewis acid sites in ZSM-5 zeolites, leading to interesting bifunctional catalysts. The combination of Lewis sites for the dehydrogenation of the paraffinic feedstock with Brønsted acid sites for the cracking of subsequent higher olefins to light olefins could enhance the yield of light olefins **[98].** For example, the use of Cu-exchanged ZSM-5 with an optimum balance between dehydrogenation activity of the metal and acid function of the shape selective ZSM-5 zeolite seems promising to improve the yield of light olefins **[99].** Meanwhile, the addition of Fe and Cr to ZSM-5 lead to diminution of the total olefins and increase of aromatic hydrocarbon selectivity because of enhancing further oligomerization and cyclization reactions **[100].**

4.5 Other zeolite structures

Besides zeolite Y and ZSM-5, other zeolites have been tested in the FCC process to maximize light olefins production. Although they show interesting reactivity in cracking and light olefins production, stability issues and/or synthesis costs have so far prevented their commercial application. For instance, it is well known that zeolite beta improves butenes yields **[3]** and increasing both diesel and propylene selectivity **[101]**. Zeolite MCM-22, used as an additive, exhibited high selectivity to propylene, but low cracking activity, and stability problems **[102]**. As well as, mixture of ZSM-5 and ferrierite was used as an additive and propylene yield was increased over traditional ZSM-5 addition **[103, 104]**.

ZSM-5 was replaced by IM5 zeolite, which gave a higher activity. The enhancement of IM5 hydrothermal stability by phosphorus leads to improve the catalyst activity and improved ethylene selectivity and aromatics **[30]**.

Many new structures proposed for FCC applications such as ITQ-7 **[105]**, ITQ-13 **[106]**, ITQ-21 **[107]** and ITQ-39 **[108]** exhibit good activity and good light olefins selectivity in FCC reaction but the synthesis costs and the stability constrain their commercial application.

5. Future perspective and conclusions.

The considerable increase of heavy crude oil reserves worldwide alongside the demand of propylene have opened new opportunities for developing advanced catalytic and processing technologies for upgrading demanding unconventional feedstocks. The stream cracking for upgrading of heavy crude oils to olefins may be an effective technology despite its poor capability to produce high propylene/ethylene ratio and its limitation to use asphaltenes-enriched crude because of excessive wall coking. These issues could be overcome with the utilization of acid catalysts with large pore size or hierarchically structured and high hydrothermal stability to resist the severity of the steam catalytic cracking (or thermal and catalytic cracking) operation conditions to maximize the olefin production.

The impressive advances of FCC-based technologies to deal with heavy residue is a consequence of a well-designed and optimised combination of process, catalyst and operation conditions able to maximise the primary reactions towards olefins, while minimising the unwanted secondary reactions such as hydrogen transfer and thermal degradation. Nevertheless, further advances need to be achieved to upgrade unconventional crudes such as extra heavy oil and natural bitumen that have low H/C ratio, high content of asphaltenes, heteroatoms and metals. A combination of high temperatures and advanced acid catalyst may be necessary to operate in a regimen where thermal and catalytic cracking have important contributions.

The characterization of highly demanding feedstock represents an important aspect for developing advanced cracking catalysts since the feed properties affect their catalytic performances. The contents of carbon, hydrogen, heteroatoms (N, O and S) and metals are usually used for indicating the degree of saturation/unsaturation, oxygenated and/or heteroatoms of a determined feedstock. It is also important to determine the density (or specific gravity), viscosity, carbon residue, specific heat, heat of combustion, boiling point distribution, molecular weight distribution among others. It is important to find out the content and aggregation degree of asphaltenes in heavy crude oils, since they require very specific functionalities (e.g., acidity, hydrogenolysis and selective ring opening) from the solid catalysts to minimize the coke formation and hence the catalyst deactivation.

A suitable (steam) catalytic cracking catalyst for heavy crude oil should contain strong acid sites and hierarchically organised pore structures to crack large molecules into small molecular fragments in large pore size and then diffuse into specific pore micro-cavity with strong acid sites to selectively produce light olefins. ZSM-5 zeolite with high Si/Al ratio and modified with phosphorous and La has showed not only high selectivity to light olefins but also high hydrothermal stability for the steam catalytic cracking of naphtha. This catalyst formulation could be properly tailored to produce olefins from the catalytic cracking of heavy crude oil.

It is also generally accepted that olefins production are favoured at low hydrogen-transfer reaction. High rate of hydrogen-transfer reaction promotes the hydrogenation of olefins and promotes the formation of coke deposits on the catalyst, consequently, lead to low olefins production. Therefore, the FCC catalyst based Y zeolite has to be tailored to have as low hydrogen transfer activity as possible. Low content of rare earth increases the stability of Y zeolite under hydrothermal conditions and leads to limit the rate of hydrogen transfer reaction. Furthermore, HY zeolite with mesopores surface area facilitates large molecule diffusion to enhance their cracking as well as diffusion of reaction products outside the catalyst, lowering coke formation and limiting hydrogen transfer reactions that reduce olefins yields.

The most efficient additive to increase light olefins yield in the FCC process is ZSM-5 zeolite. Numbers of modification methods may be used to decrease hydrogen transfer reaction rate while keeping high olefins yield. For instance these methods and parameters include:

- Using ZSM-5 with optimized Si/Al ratios in the range of the hundreds (low acidity),
- Smaller crystal size (nano-size) ZSM-5,
- Hydrothermally deactivated ZSM,
- ZSM-5 with hierarchical pore structure which can be introduced by steaming, alkaline treatment,acid leaching, reaction with EDTA or other chelating and secondary templating,
- Treatment with phosphorus,
- Incorporation of suitable contents of a rare-earth, alkali metals and/or alkali earth metals,
- Incorporation of some transition metals with an optimum balance between dehydrogenation activity of the metal and acid function of the shape selective HZSM-5 zeolite.

Although, the above mentioned optimizations and modification methods would enhance the conversion of conventional crude oil to light olefins, the unconventional crude oil (e.g., extra heavy oil, residues and natural bitumen) will remain a big challenge. The intrinsic properties of these feeds such as the high average molecular weight, low hydrogen to carbon ratio, high contents of metals (or contaminants) and unsaturated poly-aggregate asphaltenes will call for more intensive research to develop catalytic systems with better resistance to contaminants and ultra-low coke production. We obviously envisage that the upgrading of the unconventional crude oil to fuels and petrochemicals, particularly to the maximization of olefins, in the oil refinery industry will generate innovative solutions to turn the current challenges into great opportunities.

Acknowledgments

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