One Step Conversion of Crude Oil to Light Olefins using a Multi-Zone Reactor

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With demand for gasoline and diesel expected to decline in the near future, crude-to-chemicals technologies have the potential to become the most important processes in the petrochemical industry. This trend has triggered intense research into the optimization of current refining processes to maximize the production of light olefins and aromatics at the expense of fuels. Although attractive, this approach has shown certain limitations and calls for disruptive processes able to directly transform crude to chemicals in a more efficient and environmentally friendly way. Here we propose a new reactor concept consisting of a multi-zone fluidized bed (MZFB) along with a new catalyst formulation able to perform several refining steps in one single reactor vessel. The MZFB configuration allows for in situ catalyst stripping and regeneration, while the incorporation of silicon carbide during catalyst shaping via spray drying confers this new catalyst formulation with improved physical, mechanical and heat transport properties. As a result, we demonstrate that, using this reactor-catalyst combination, it is possible to achieve stable direct

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conversion of untreated Arabian Light (AL) crude oil to light olefins with yields per pass over a 30 wt.% with a minimum production of dry gas.

Introduction

Fluid catalytic cracking (FCC) is the primary conversion unit in most petroleum refineries.¹ The FCC technology consists of a pipe coil reactor (usually a riser), where the cracking reaction takes place, and a regenerator where the catalyst is continuously regenerated by combustion. Since the first commercial unit in 1942,² FCC processes have produced most of the consumed gasoline in the world. However, the alarming CO₂ concentrations in the atmosphere, a profound change in the energy landscape and the development of electric, fuel cell-based and hybrid automobiles forecast a mid-term plateau and a long-term decrease in the demand for transportation fuels.³ On the other hand, the demand for traditionally oil-manufactured base chemicals is expected to keep rising in the foreseeable future.^{4,5} The mismatch between current oil refining schemes and future demand for oil-based products is stirring intense research into the development of technologies that maximize the production of chemicals over that of fuels, giving rise to multi-billion investments in different oil-to-chemicals (OTC) projects (some of these technologies have been summarized in the Supporting Information). At present, the main approach in OTC is to combine technologically mature technologies (*i.e.* high severity FCC units and naphtha crackers) to maximize the production of ethylene, propylene, and aromatics. Although economically attractive, this approach still requires the use of oil pretreatment processes (*i.e.* hydrotreating), energy-intensive distillation units for the separation of the different fractions of which oil is composed and of the primary products of FCC, and the use of other highly energy-intensive (and highly polluting) units such as steam crackers.⁶⁻
⁸ Ideally, the development of on-purpose technologies that would allow, in one or a few steps, the direct conversion of untreated crude oil to chemicals, is expected to be as disruptive for the oil industry as the development of FCC was one century ago.

The challenge at hand is not trivial: what we know as oil consists of a mixture of thousands of components with boiling points that vary between 25 and 700 °C along with the

presence of contaminants such as S and N heterocycles and metals. From the process design point of view, it would strike as suicidal to think of a single process unit that may, in one step, be able to co-process such a complex mixture of reactants. This is indeed the reason why, in traditional refineries, oil is thoroughly pretreated and separated prior to any conversion unit.

Current riser reactors can convert large quantities of feedstock in few seconds. Zeolite-based FCC catalysts allow short contact times with an optimal yield, selectivity and coke resistance, but continuous regeneration is required. In an FCC unit, the catalyst and a portion of the feedstock are burned in a second vessel to produce the necessary heat for cracking.⁹ Despite the vast number of proposals to improve their capacity for chemicals production,¹⁰⁻¹³ this configuration represents a drawback since the catalyst shows a different catalytic behavior along the riser due to coking (deactivation) and temperature gradients. On the other hand, there is very little control over residence time (RT) and therefore not much flexibility in terms of feedstock, the reason why heavy oils are still preferred by most refineries.

To date, different technologies have been proposed for the one-step conversion of crude oil. In 1965, BASF developed an uncatalyzed process consisting of a single fluidized bed filled with coke particles, intermediate crude feeding and bottom regeneration with air. In such a way, the necessary heat to carry out the highly endothermic cracking is provided by burning coke in the same reactor vessel. However, the high temperatures needed to maintain operation and the absence of catalyst leads to a typical thermal cracking product distribution, with ethylene and dry gas as main products.^{5,14,15} More recently, in 2010, Sinopec patented a steam-cracker riser reactor with two reaction zones at different temperatures reporting a yield of light olefins and aromatics around 55 and 25 wt.%, respectively.¹⁶ In 2014, ExxonMobil launched in Jurong (Singapore) a steam cracking technology that allows the direct conversion of pre-treated light crude oil into valuable products, targeting 40-50% yield to chemicals and reporting 1 Mtpy of ethylene production. In this case, crude is evaporated in a flash separator in such a way that only vaporized hydrocarbons are processed, thus avoiding coke fouling issues.^{6,17}

Here, we present an alternative one step catalytic approach consisting of a multi-zone reactor where catalyst particles undergo cycles of deactivation, stripping, and regeneration in separate zones of the same fluidized bed vessel (Fig. 1a). The reactor concept is based on the so-called two-zone fluidized bed reactor, first reported in 1979 by Hupp *et al.* for the oxidative coupling of toluene,¹⁸ and later by several authors in the dehydrogenation of light paraffins.¹⁹⁻²¹ Multi-feeding points for crude oil and regenerative streams generate different reaction zones in the reactor vessel that can be fine-tuned to achieve different environments and residence times with continuous operation of the catalyst.²²

Results and discussion

In the MZFB reactor here presented (Fig. 1a), crude oil is evaporated and fed through a gas distributor located on the top of the reaction zone. The catalyst is fluidized from the bottom with an up-flow regenerative mixture. In steady fluidized conditions, catalyst particles are subjected to reaction-stripping-regeneration cycles in few seconds; however this rate can be adjusted by varying the flows fed to each reactor zone.²³ Hence, this configuration is composed of (i) a vaporization zone where the crude/water emulsion is vaporized (200-

Fig. 1 Representation of a Multi-Zone Fluidized Bed (MZFB) reactor (a), comparison of catalytic performance in terms of total gas yield between MZFB and FB modes (b), and temperature (c)* and residence time (d)** effect in catalytic cracking of Arabian Light over E-Cat in MZFB mode.*Average values during 1st hour on stream using 30 g of E-Cat.**Average values during 1st hour on stream at 510 °C. Error bars indicate the standard deviation (2 σ) of duplicate experiments.

500 °C); (ii) two feeding points, one situated at the beginning of the reaction zone, where the vaporized mixture is fed, and another one at the bottom of the catalyst bed for the regenerative stream ($O_2:N_2$); (iii) a reaction zone for the cracking of hydrocarbons (510-700 °C) situated on the top of the catalyst bed; (iv) a regeneration/stripping zone covering 80-85% of the catalyst bed at 750 °C; and (v) a condensation zone to recycle the unreacted heavier hydrocarbons towards the reaction zone. As mentioned above, crude oil consists of a mixture of thousands of components with boiling points that range between 25 and 700 °C (see simulated distillation curve of the AL crude used for this study in Fig. S1).²⁴ We, therefore, speculated that the use of a multi-zone bed where temperature can be controlled at different lengths of the reactor would help adjust residence times for the individual components of oil based on their boiling points. In this regard, backmixing (with reference to the generated gaseous products) is a common pitfall of the principles on which fluidized bed reactors operate. The constantly changing balance of drag *versus* centrifugal forces on the solids, which thereby interact with the flowing gases, result into a residence time of products dominated by a tailing behaviour (i.e. high species backmixing), with strong influence on product distribution.^{5,25} In contrast, CFD-based residence time distribution (RTD) analysis (included in the Supporting Information) reveals a similar performance of the single/multiphase flows in an MZFB reactor to that of a plug flow reactor. By definition, an ideal plug flow reactor displays no back-mixing in the axial direction, meaning there is no transfer between the immediate axial packets of fluid. Therefore, the CFD simulated RTD performance of MFZB reactor in this work is testimonial to the fact that there is very little or no species back-mixing for this reactor configuration as opposed to a typical fluidized bed reactor.

To evaluate the potential application of this new reactor concept, a series of AL catalytic cracking tests were performed over an equilibrium commercial FCC catalyst (E-Cat). Table 1 summarizes the most important reaction parameters and experimental results.

Table 1 Catalytic cracking of Arabian Light indicators over commercial E-Cat using a liquid feed flow of 0.5 mL·min⁻¹ of oil:water [50:50, vol/vol] and an up-flow stream of 400 mL·min⁻¹ of N₂, at different temperatures, residence times and reaction modes.

Temperature / °C	Residence time ^a / ms	Reaction mode	C ₃ ⁼ /C ₂ ⁼	C ₂ ⁼ /C ₂	C ₃ ⁼ /C ₃	C ₄ ⁼ /C ₄	Total gas yield / wt.%	olefins / paraffins	HTC ^b
510	153	FB	11.2	2.8	10.5	2.3	11.5	3.4	0.43
510	130	MZFB	3.7	4.2	2.9	1.1	24.0	1.5	0.92
510	180	MZFB	3.3	4.2	2.8	0.6	38.6	1.1	1.78
510	153	MZFB	3.4	4.9	3.4	0.7	28.5	1.4	1.44
570	146	MZFB	2.7	4.1	3.9	1.3	32.4	1.9	0.75
700	130	MZFB	1.0	3.2	12.5	34.6	39.2	2.1	0.03

^aBased in CFD simulations (see details in *Materials and methods* section and ESI). ^bHTC: hydrogen transfer coefficient (HTC=(nC₄ + iC₄)/C₄=).

Fig. 1b shows a comparison in catalytic performance between experiments performed at 510 °C in a MZFB with in situ stripping (occurring in the bottom zone of the reactor) and similar experiments performed in a classical fixed bed (FB) configuration. As it can be observed, the MZFB leads to a 30 wt.% yield to C₁-C₄ hydrocarbons accompanied by a slow deactivation of the catalyst, whereas experiments performed under similar conditions in FB result in yields or circa a 12 wt.% and a more pronounced catalyst deactivation. Considering that in both cases residence times are similar, the best performance of the MZFB reactor could be explained as a consequence of (i) the recirculation of middle distillates on the condensation zone of the reactor, thus increasing the conversion of the heavier fractions of the feedstock and (ii) stripping of bigger hydrocarbons (which act as coke precursors) adsorbed on the catalyst surface in the regeneration zone of the MZFB, which partially prevents coke formation (Fig. 2a).

Interestingly, catalyst deactivation is much less pronounced when working in MZFB mode after 3 hours on stream, as shown in Fig. 1b. While 20% of activity loss is observed for the MZFB, half of the activity is lost in FB mode after a similar reaction time. In line with this, the lower olefin/paraffin ratios obtained in the MZFB can also be explained as a consequence of catalyst stripping, which maintains a higher activity, hence favoring both cracking and hydrogen transfer reactions of intermediate products like aromatics and

olefins.^{5,26} Complementary AL catalytic cracking experiments on a micro-fixed bed reactor and subsequent DTG-TPO studies of the spent catalysts (Fig. S2) demonstrate that in the initial stages of the reaction (0-60 min) coke builds up in the catalyst following a linear trend (Fig. S2a), and increasing in about $10 \text{ mg}_{\text{coke}} \cdot \text{g}_{\text{cat}}^{-1}$ every 15 minutes. This justifies the progressive activity loss observed in Fig. 1b.

The influence of temperature and residence time on reactor performance was studied in the 510 to 700 °C range (Fig. 1c and 1d). At 700 °C the contribution of thermal cracking is more pronounced, fostering the production of dry gas (C_2 and lighters) as well as coke (see TGA analysis on Fig. 2c). C_4 paraffin yield dramatically decreases at high temperature, probably due to enhanced cracking reactions leading to lighter products and also to a low degree of hydrogen-transfer reactions which can be evaluated by the hydrogen transfer coefficient ($\text{HTC} = (\text{nC}_4 + \text{iC}_4)/\text{C}_4$)^{27,28} which decreases quickly with temperature. At milder reaction conditions (510-570 °C), a slight temperature increase results in a higher olefin/paraffin ratio and hence higher ethylene and propylene yields, with a $\text{C}_3^-/\text{C}_2^- > 2.5$ which decays below 1 at 700 °C, when thermal cracking becomes dominant. The overall heavier nature of the products as well as the decreasing relevance of hydrogen transfer reactions upon increasing temperature, lead not only to enhanced total (hard) coke deposition but also to a coke with a higher structural order, heavier and more condensed in nature, as deduced from the DTG-TPOs in Fig. S2b, where the maximum rate of coke combustion slightly shifts towards higher temperatures.

On the other hand, longer residence times give way to a linear increase of C_2^- and C_3^- (Fig. 1d). Indeed, propylene yield increases from 5.5% to 10.7% when increasing the residence time from 130 to 180 ms. These results are associated with the HTC that also follows the same trends ($\text{HTC} = 0.9, 1.2$ and 1.8 at $\text{RT} = 130, 153$ and 180 ms, respectively) and indicate a higher bimolecular hydrogen-transfer rate.

As mentioned earlier, operation in MZFB and FB modes results in essential differences in catalytic cracking performance, especially in terms of stability, as illustrated in Fig. 1b, which is known to be associated with catalyst deactivation due to coke formation. Analysis of the spent catalyst enables us to quantify and to identify the type of coke and may

provide information about the deactivation process. For this purpose, it is convenient to distinguish between (i) coke precursors, generally lighter in nature adsorbed on the catalyst, which can be quantitatively estimated by TGA as the hydrocarbon species desorbed in inert atmosphere during a heating treatment of the spent catalyst in the range of 200-800 °C; and (ii) hard coke, remnant deposits of highly unsaturated species removed by combustion at 800 °C (Fig. S3).²⁹ In FCC like processes, the presence of both, thermal (hard) coke associated to the Conradson carbon residue (CCR) of the feedstock and adsorbed species (coke precursors) are expected.³⁰ As shown in Fig. 2a, the MZFB reactor produces a lower amount of precursors and hard coke than FB mode which could be explained as a result of the stripping effect over the catalyst that allows adsorbed heavier hydrocarbons to be later cracked, then avoiding high-molecular-weight components to condense into polynuclear aromatic coke.^{31,32}

Fig. 2 Coke quantification by thermo-gravimetric analysis (TGA) of the spent catalyst: effect of reactor operation mode (a), steam (b) and temperature (c). *Experimental conditions in ESI. Error bars indicate the standard deviation (2σ) of duplicate experiments.

To shed light on this effect, and specifically about structural information of trapped-organics as well as the nature of coke species responsible for catalyst deactivation, advanced magic angle spinning (MAS) solid-state NMR (ssNMR) spectroscopy was performed on the spent catalyst (Fig. 3 and Fig. S4). For this purpose, two samples were

selected: spent E-Cat after the catalytic cracking of AL at 510 °C on a fixed bed (FB_510) and a multi-zone fluidized bed (MZFB_510) (see Materials and methods section-MAS ssNMR).

In the 1D $^1\text{H} \rightarrow ^{13}\text{C}$ cross-polarization (CP) spectra (Fig. 3a), primarily two features were detected: (i) 10-35 ppm saturated (like aliphatics), and (ii) 115-140 ppm unsaturated (like olefinics/aromatics) hydrocarbon groups.³³ In general, all spectra appeared to be broad in nature, which could be attributed primarily to the utilization of naturally abundant crude oil as the reactant. Since we have relied upon $^1\text{H} \rightarrow ^{13}\text{C}$ CP transfer only to increase the sensitivity of the residual coke species, it also primarily highlights the rigid/immobilized zeolite-trapped organics (*i.e.*, so-called “hard coke”).³⁴ Although $^1\text{H} \rightarrow ^{13}\text{C}$ CP transfer is not very reliable to provide a detailed insight into the hydrogen-deficient organics, it also has

Fig. 3 1D ^1H - ^{13}C cross-polarization MAS solid-state NMR spectra of identified post-reacted hybrid-zeolite trapped molecular scaffolds materials FB_510 (blue), MZFB_510 (red), FB_570 (green) and FB_570_w/o water (violet) to illustrate the effect of reactor and water, respectively (a). 1D ^2H NMR spectra of identified post-reacted hybrid-zeolite trapped molecular scaffolds materials after co-feeding experiment with deuterium oxide (D_2O) instead of water on FB_570 (green) to track down the effect of water during the reaction (MAS= magic angle spinning=13kHz, FB=fixed bed, MZFB=multi-zone fluidized bed) (b).

its own advantages. Since the hard-coke materials were typically envisioned as “highly unsaturated” and “hydrogen deficient”, it would give a lower sensitive response in the corresponding $^1\text{H} \rightarrow ^{13}\text{C}$ CP spectrum. Hence, it is feasible to correlate the sensitivity/intensity of $^1\text{H} \rightarrow ^{13}\text{C}$ CP NMR spectrum with the thermo-gravimetric coke analysis, as the $^1\text{H} \rightarrow ^{13}\text{C}$ CP intensity should be inversely proportional to the hard coke content.

In Fig. 3a, an identical spectral profile was observed in both operation modes (FB vs. MZFB) in terms of the nature of trapped organics. However, a lot less response for the aromatic species was recorded on the post-reacted fixed-bed sample. This is well in line with thermo-gravimetric coke analysis, which suggested the presence of less coke on the MZFB_510 sample (8.8% coke on FB_510 sample vs. 4.2% coke on MZFB_510 sample), and hence, delivered a better $^1\text{H} \rightarrow ^{13}\text{C}$ CP response due to its relatively more hydrogen-rich nature. However, we observed a different feature on the effect of water (Fig. 3a: FB_570 vs. FB_570_w/o water). No noticeable aliphatic moieties were detected in the absence of water on FB_570_w/o while displaying almost a similar intensity from the aromatic species from both samples. Again, the thermo-gravimetric coke analysis corroborates this observation (5.8% coke on FB_570 vs. 3.7% coke on FB_570_w/o water) besides showing a higher extent of coke precursors in the absence of steam (Fig. 2b). Guozhen *et al.*³⁵ noted a similar effect in acid-catalyzed methanol conversion to light olefins over SAPO-34. It could essentially mean that the presence of water not only promotes hydrogen-transfer reactions on the acid sites of the zeolite but also slows catalyst deactivation due to water steam stripping of coke precursors, hence prolonging the lifetime of the catalyst.³⁶ Coke quantification through DTG-TPO analyses of spent samples in a micro-fixed bed reactor (Fig. S2a) showed that after 30 min of reaction, co-feeding of water could prevent coke deposition by 25% ($18.0 \text{ mg}_{\text{coke}} \text{ g}_{\text{cat}}^{-1}$ vs $23.8 \text{ mg}_{\text{coke}} \text{ g}_{\text{cat}}^{-1}$ with and without water, respectively). In this line, Corma *et al.*³⁷ have related the presence of water with the suppression of bimolecular reactions (responsible for coke formation) during the catalytic cracking of VGO which is attributed to better dispersion and contact between the feedstock and the catalyst. To illuminate the effect of water in

the present case, one control experiment was performed, where deuterium oxide (D_2O) was co-fed instead of water. The corresponding 2H NMR spectrum (Fig. 3b) shows two primary peaks at around 2.0 and 7.8 ppm, *i.e.*, originated from aliphatic and aromatic moieties, respectively. Interestingly, the contribution from the aliphatic part is much higher than that of the aromatic, which indeed suggests that water is promoting hydrogen transfer reactions on the zeolitic Brønsted acid sites to inhibit the deactivation of the catalyst.

Next, 2D 1H - ^{13}C CP-HETCOR (HETCOR: HETeronuclear CORrelation spectroscopy) was performed for 1H - ^{13}C correlations on all four post-reacted materials to illuminate the nature of zeolite-trapped organics in more detail (Fig. 3b). In general, 2D correlation spectra were consistent with their corresponding 1D counterparts. In addition, Fig. S4 elegantly demonstrates a few interesting features on the nature of residual coke species. For instance, the correlations between ~ 7.7 ppm (1H)/ ~ 128 ppm (^{13}C) and ~ 7 ppm (1H)/ ~ 120 ppm (^{13}C) were clearly visible on all 2D correlation spectra, which could be assigned to the aromatic and aliphatic counterpart of the unsaturated coke species, respectively.³³ Simultaneously, at elevated temperatures (both in the presence (green) and in the absence of water (violet)) an additional correlation, ~ 8 ppm (1H)/ ~ 134 ppm (^{13}C), was detected as well due to the polyaromatic part of coke species. Hence, 2D 1H - ^{13}C CP-HETCOR measurements clearly (but qualitatively) distinguish among four different classes of hybrid-zeolite-trapped organic/coke species on the post-reacted materials: aliphatic, olefinic, aromatic, and poly-aromatics.

Overall, the in-depth ssNMR characterization confirms that co-feeding of water results in a slower formation of coke due to the adsorption of more aliphatic than aromatics species. In the same line, the absence of stripping in the case of FB results in more unsaturated coke species (more harmful) accompanied by a higher total amount of both hard coke and coke precursors. It is worth to mention that while FB experiments are time-limited as a consequence of catalyst bed plugging, the fluidized mode permitted much longer experiments. Finally, an increase of the reaction temperature resulted in the formation of

polyaromatic coke species (ssNMR) which correlates well with the higher accumulation of hard coke over the catalyst as quantified by thermo-gravimetric analysis.

A novel catalyst formulation for MZFB processes

Several challenges are associated with the new reactor system for the catalytic cracking of crude oil. Among other aspects, the catalyst formulation needs to be adapted for continuous operation in the static fluidized bed. One of the main drawbacks of this approach is catalyst loss due to the vigorous fluidization to which the bed is subjected, thus requiring denser catalyst particles to avoid undesired fragmentation. An upgrade on the catalyst formulation, typically comprising low-density components (*i.e.* zeolite and clay), by adding dense and inert additive such of silicon carbide, could not only increase the density of the catalyst but also act as a heat carrier. Besides, the low thermal expansion of silicon carbide reduces the formation of undesirable fine particles as a result of lower catalyst attrition. Surprisingly, to the best of our knowledge, SiC has never been proposed as an additive during catalyst formulation for FCC or analogous processes.

Therefore, we explored our homemade catalyst formulation (further denoted as ACM-101) containing 20 wt.% ZSM-5 (SAR 23), 20 wt.% zeolite HY (SAR 30), 20 wt.% kaolin clay, 20 wt.% aluminum chlorhydrate (as a binder) and 20 wt.% of nanometer-sized (*ca.* 800 nm) silicon carbide (detailed in Supporting Information), optimized for light olefins production in the catalytic cracking of Arabian Light crude. For more details on the experimental setup and spraying procedure, the reader is referred to our recent publication on the topic.³⁸ The catalytic performance of the equilibrated ACM-101 catalyst (Fig. 4a) reveals higher activity compared to the commercial E-cat at analogous conditions (570 °C, see Fig. 1c-blue), showing a total gas yield above 40 wt.% with a light olefins fraction of *ca.* 30 wt.%. Moreover, the O/P ratio of 2.7 (see Table 2) exceeds in almost two units the value obtained when using the commercial catalyst. The higher C₃/C₄ ratio achieved on ACM-101 formulation is a consequence of an optimal combination of

ultrastable zeolite Y and ZSM-5, as evidenced from the higher olefinicity ratios ($C_3^=/C_3$ and $C_4^=/C_4$) at similar gas yields.³⁹⁻⁴² However, the high yield to gaseous products is only maintained during the first stage of the reaction after which the catalytic activity starts to decrease dramatically. Indeed, the higher activity of the catalyst leads to a faster coke deposition.

Fig. 4 Catalytic performance of ACM-101 in the cracking of Arabian Light at 570 °C using an up-flow stream of nitrogen (a) and a 0.6:0.4 N₂:O₂ mixture (b), products distribution (c)*, and coke analysis of the spent catalyst by TGA (d). *Average after 2 hours of reaction. Error bars indicate the standard deviation (2σ) of duplicate experiments.

Since coke preferably deposits on Brønsted acid sites, on which the cracking reaction proceeds following a bimolecular reaction mechanism,⁴³ the hydrogen transfer reaction rate wanes quickly and serves as an indicator of catalyst deactivation. The hydrogen transfer rate of ACM-101 expressed in terms of HTC declines from 0.79 to 0.36 after 150 minutes at 570 °C. To address this obstacle beyond the stripping effect of nitrogen and water described above, we show below that the addition of a regenerative mixture of N₂ and O₂ [0.6:0.4 vol:vol] to the regeneration/stripping zone of the reactor allows for in situ coke removal.

Table 2 Catalytic cracking of Arabian Light indicators over ACM-101 catalyst in presence and absence of O₂.

Temperature / °C	Regenerative stream	$C_3^= / C_2^=$	$C_2^= / C_2$	$C_3^= / C_3$	$C_4^= / C_4$	Total gas yield / wt. %	olefins / paraffins	HTC ^a
570	N ₂	2.73	3.32	5.38	2.96	25.8	2.74	0.36
570	40% O ₂ : 60% N ₂	2.94	5.65	6.58	1.85	32.4	3.00	0.54

^aHTC: hydrogen transfer coefficient ($HTC = (nC_4 + iC_4) / C_4 =$).

Prior to performing experiments under oxidizing conditions, safe operating regimes were established to avoid auto-ignition of the fuel/oxidizer mixture. Detailed chemical kinetic modelling simulations were performed for the most reactive paraffinic fraction of AL crude, as described in the Supporting Information, to determine its auto-ignition limits. The reactive mixture comprises fuel (AL crude), water, N₂, and O₂. While fuel/O₂ mixtures are prone to auto-ignition within a few milliseconds of contact time at 450-650 °C, the addition of water serves as a quenching agent. Furthermore, simulations demonstrate that the AL crude:O₂ mixture fraction, as in Fig. 4, is beyond the rich ignition limit. Even in the absence of water vapor, the mixture would not auto-ignite because there is too much AL crude present to ignite a hot flame. However, if the O₂ concentration is increased or the total AL crude concentration is decreased, then the mixture may enter an auto-ignition regime (Supporting Information). Therefore, safe startup of the reactor should involve first introducing AL crude followed by O₂; and safe shutdown should turn off the O₂ flow first to avoid entering auto-ignition regimes.

The catalytic behavior under these oxidizing reaction conditions is shown in Fig. 4b. A stable catalyst performance with gas yield values wobbling around 30 wt.% and circa 25 wt.% of light olefins can be reached. Remarkably, the presence of oxygen on the stream does not substantially perturb the distribution of products (see Fig. 4c), however it increases the O/P ratio from 2.73 to 3.00 at the same time that hydrogen transfer coefficient (HTC) remains stable during the whole process at 0.52 ± 0.03 (see Table 2). Indeed, GC analysis demonstrates that O_2 is consumed before reaching the reaction zone. Furthermore, the analysis by TGA of coked ACM-101 catalyst (Fig. 4d) shows great differences when the material has been exposed to the oxidative stream, exhibiting a three times lower amount of coke, including coke precursors, and especially hard coke deposits, that decrease from 3.7 to 1.0 wt.% in the presence of oxygen.

The simulated distillation results of the liquid fraction collected during these experiments is shown in Fig. 5a and highlights the significantly lighter nature of the liquid products obtained from the reaction feeding the regenerative $N_2:O_2$ mixture. Up to 80% of the liquid has a boiling point below 250 °C, while this fraction remains below 50% in the case of the liquid from the reaction feeding only N_2 . In line with the aforementioned, FT-ICR analysis (Fig. 5b) of the liquid reactions products showed molecular weight distributions with decreasing average mass/charge (m/z) ratios of ca. 450, 390, and 300 for the Arabian Light crude, and the liquid products feeding only N_2 and the $N_2:O_2$ mixture, respectively. The data in Table 3, as obtained from complementary GC-MS measurements, show that paraffins were the mainly cracked chemical group in the Arabian Light, leading to the formation of predominant amounts of total aromatics (A1+A2, 55.6-59.5 wt.%) in the liquid products, with smaller amounts of paraffins. Specifically, due to the higher cracking activity maintained by the catalyst regenerated with the oxidative stream, a higher amount of total paraffins (41.8 wt.%) was quantified in its derived liquid products in contrast to the O_2 -free approach (39.0 wt.%). It is noteworthy that the GC chromatograms of both liquid products are analogue (Fig. S11). It should also be noted that, in the GC-detectable fraction, A2 aromatics consist solely of naphthalene.

Fig. 5 Simulated distillation curve (SIMDIS) (a) and FTICR-MS spectra (b) of the Arabian Light crude oil feedstock and collected liquid fraction after catalytic cracking of AL in presence and absence of O₂.

Table 3 Chemical composition of the Arabian Light crude and the liquid products after the catalytic cracking reaction in presence and absence of O₂.

	AL	MZFB, N ₂	MZFB, N ₂ + O ₂
n-Paraffins	40.4	27.1	24.0
i-Paraffins	23.8	11.9	17.8
Naphthenes	7.4	0.4	1.0
Aromatics A1	11.4	48.8	48.2
Aromatics A2	-	10.7	7.4
Others	17.0	1.1	1.6

Conclusions

In summary, our results demonstrate that the direct transformation of crude oil to chemicals in a one step process is possible when the right catalyst and reactor configuration are selected. In situ catalyst stripping, regeneration and the addition of the appropriate amount of steam in a Multizone Fluidized Bed Reactor allow for the transformation of Arabian Light crude to valuable olefins in yields much higher than what most state of the art refining processes are able to deliver. Further optimization in catalyst

formulation demonstrates that a large room for improvement in terms of performance is still possible. The addition of silicon carbide during spray drying is shown to improve not only heat transport, but also to decrease the potential for catalyst fragmentation further improving stability. Moreover, the addition of a regenerative stream rich in oxygen improved the stability of the reaction in long term by preventing the accumulation of harsh coke over the catalyst at the same time that it provides extra-heat to the highly endothermic cracking process.

Alltogether, our results demonstrate that new reactor engineering concepts, when accompanied by complementary catalyst development, offer great opportunities for process intensification and will be key in the modernisation of the oil industry.

Materials and methods

Feedstock characterization: Arabian Light crude oil (AL) from a domestic oil field was used in all catalytic experiments. The main properties are summarized in Table 4. Its density was measured using an Anton Paar DMATM 35 equipment at 15 °C. Chemical analysis by CHN and ICP-OES (S, Ni, V) was carried out using a Flash 2000 Elemental Analyzer (Thermo Fisher) and Agilent 5100, respectively. Simulated distillation (SIMDIS) of the feedstock was carried out by using the ASTM D2887 protocol to measure the boiling range distribution of crude oil. GC-MS analysis was performed in an Agilent 7890A apparatus with split flame ionization detector (FID) and a mass spectrometer detector (5975C MS, Agilent Technologies).

Table 4 Physico-chemical properties of Arabian Light crude oil

Density at 15 °C / kg·m ⁻³	Gravity / °API	CHN / wt.%			ICP-OES / ppm		
		C	H	N	S	Ni	V
846	35.8	79.3	10.7	0.1	17330	6	14

Catalysts: An equilibrium FCC catalyst (E-Cat) received from a domestic refinery and thermally pre-treated under air at 800 °C for 10 h. Our formulated catalyst, further denoted as ACM-101, was composed of kaolin clay (Sigma-Aldrich), $\text{Al}_2\text{Cl}(\text{OH})_5$ binder (Spectrum), ZSM-5 with $\text{SiO}_2:\text{Al}_2\text{O}_3$ molar ratio (SAR) of 23 and FAU zeolite with SAR 30 (Zeolyst), SiC powder with size 800 nm (US Research Nanomaterials), admixed at 20:20:20:20:20 wt.% proportion, respectively. Prior to the shaping, the composite slurry was homogenized applying ball milling pretreatment at 350 rpm for 30 min. Fluidizable fraction of the catalyst comprising 38 – 100 μm spherical particles was produced spray-drying (Lab-scale mini Spray Dryer Buchi B-290) the formulation slurry at optimized conditions: nozzle diameter = 2.0 mm, $T_{\text{inlet}} = 220\text{ }^\circ\text{C}$, $T_{\text{outlet}} = 130\text{ }^\circ\text{C}$, air and feed flow of $35\text{ m}^3\cdot\text{h}^{-1}$ and $15\text{ mL}\cdot\text{min}^{-1}$, respectively. Finally, the catalyst was calcined at 700 °C for 7 hours ($5\text{ }^\circ\text{C}\cdot\text{min}^{-1}$) in air.

Catalytic Cracking tests: The catalytic cracking of AL over E-Cat and ACM-101 was conducted in a multi-zone fluidized bed (MZFB) reactor, as that in Fig. 1a, heated by a tubular oven. An AL/water emulsion was feed by using two different Gilson HPLC 307 Pumps and mixing inside an ultrasonic bath at 40 °C. Gas carrier flow (N_2/He) was controlled by mass flow controllers (Bronkhorst). Reaction products were passed through a system of three condensers in series maintained at 70, 25 and 10 °C, respectively, where the liquid fraction was collected for further analysis.

Meanwhile, gas products were analyzed online by gas chromatography conducted on a Trace 1310 gas chromatograph (Thermo Scientific) with a MolSieve analytical column and TCD for the analysis of He (internal standard) and H_2 , and an Alumina Plot column and FID for the separation analysis of $\text{C}_2\text{-C}_5$ hydrocarbons. GC-MS analysis was performed in an Agilent 7890A apparatus with split flame ionization detector (FID) and a mass spectrometer detector (5975C MS, Agilent Technologies). FT-ICR MS measurements with atmospheric photo ionization (APPI) source were conducted in a Bruker Solarix XR 9.4 Tesla instrument, and the spectrum were further treated by the Bruker DataAnalysis V4.5 software. The chemical formula assignment was performed by Composer software (Sierra Analytics). Fixed bed (FB) experiments were carried out by using the same MZFB reactor

but in a top-bottom configuration adapted for that purpose. Mass balances, in all cases found to be higher than 85%, were estimated from the combination of gas products yield (GC), recovered mass of liquid oil products and solid residues over the catalyst determined by thermogravimetric analysis. All calculations are described in the ESI.

Temperature programmed oxidation (TPO) and Thermo-gravimetric analysis (TGA): Coke analysis of the spent catalysts was carried out by using a TGA/DSC1 STAR-e system apparatus (Mettler Toledo). Prior to TPO experiments, the catalyst was subjected to stripping under N₂ stream (50 mL·min⁻¹) up to the reaction temperature using a heating ramp of 10 °C·min⁻¹. After that, the sample was cooled down and stabilized at 100 °C. For the coke combustion step, the temperature was increased up to 800 °C using a heating ramp of 5 °C·min⁻¹ under an airflow of 50 mL·min⁻¹ and kept at 800 °C for 20 minutes so ensure the total coke combustion.

For TGA analysis, the spent catalyst was heated from 40 to 800 °C, using a heating ramp of 10 °C·min⁻¹, under a nitrogen flow of 25 mL·min⁻¹, to remove all so-called “coke precursors”. After half an hour at 800 °C in this inert atmosphere, and maintaining the same temperature, the catalyst was submitted to an air flow of 25 mL·min⁻¹, burning in this way the remaining “hard coke”. Details about coke amount estimation are included in the ESI.

Solid-state Nuclear magnetic resonance (ssNMR) measurements: the magic angle spinning (MAS) ssNMR spectroscopic experiments were performed on Bruker AVANCE III spectrometers operating at 400 MHz frequency for ¹H using a conventional double-resonance 4 mm CPMAS probe (CP: Cross-polarization). NMR chemical shifts are reported with respect to the external references adamantane. For 1D ¹H-¹³C CP experiments, the following sequence was used: 90° pulse on the proton (pulse length 2.4 s), then a CP step with the contact time of typically 2 ms, and finally the acquisition of the ¹³C NMR signal under high-power proton decoupling. The delay between the scans was set to 4 s to allow the complete relaxation of the ¹H nuclei. The number of scans (NS) was as follows (Fig. 3: FB_510 (blue, NS=6k) and MZFB_510 (red, NS=14k) and (b) FB_570 (green, NS=15k) and FB_570_w/o water (violet, NS=6k). Fig. 3 is represented in a normalized manner keeping into account of respect number of scans. An exponential apodization

function corresponding to a line broadening of 80 Hz was applied prior to Fourier transformation. The 2D ^1H - ^{13}C heteronuclear correlation (HETCOR) solid state NMR spectroscopy experiments were performed according to the following scheme: 90° proton pulse, t_1 evolution period, CP to ^{13}C , and detection of the ^{13}C magnetization under TPPM (*i.e.*, a two-pulse phase modulation) decoupling. For the CP step, a ramped radio frequency (RF) field centered at 75 kHz was applied to the protons, while the ^{13}C channel RF field was matched to obtain an optimal signal. Using a short contact time (0.2 ms) for the CP step, the polarization transfer in the dipolar correlation experiment was verified to be selective for the first coordination sphere to lead to correlations only between pairs of attached ^1H - ^{13}C spins (C-H directly bonded). The total number of scans (NS) and the size of fid (TD) were 2.5K and 2048(F2)/24 (F1), respectively. Both ^1H and ^{13}C chemical shifts were externally referenced to adamantane. In all cases, other relevant acquisition parameters were described in figure captions. All NMR spectra were processed and analyzed by Bruker TopSpin 3.6.0.

Powder X-ray diffraction (PXRD): diffraction patterns for ACM-101 were recorded on Bruker D8 Advance operated at 30 kV and 30 mA using monochromatic Cu-K α radiation ($\lambda = 1.5418 \text{ \AA}$), a scan speed of 0.5 s per step, and a step size of 0.2° in the 2θ range of $5\text{--}90^\circ$. The crystalline phases were identified using PDF-4+ (2019) crystal database.

Nitrogen physisorption measurements: N_2 adsorption/desorption isotherms of fresh/spent catalysts were obtained using a Micromeritics ASAP 2040 instrument at 77 K. Prior to the measurements, the samples were outgassed at 300°C for 8 h under a dry N_2 flow. Specific surface areas were estimated according to the BET method in the relative pressure range of 0.05-0.25. Total pore volume was estimated from a single point adsorption measurement at $P/P_0 = 0.94$, for pore sizes below 35 nm, disregarding macropores. Micropore volume was estimated from the T-plot approximation.

Scanning electron microscopy (SEM): The catalysts were evaluated by SEM technique using a scanning electron FEI TENE0 VS microscope. Micrographs were obtained with the electron energy of 2 kV and 5 mm working distance.

Residence Time Distribution in a Multi-zone Fluidized Bed reactor via CFD Simulations: Non-reactive CFD simulations over a 2D domain of the reactor were used to evaluate the gas-phase

residence time distribution (RTD) in a Multi-zone Fluidized Bed (MFZB) reactor. The computational domain follows the same principles as that of the experimental reactor with the regeneration stream inlet being at the bottom of the reactor and liquid inlet located on the top left hand side of the reactor geometry. The single, common outlet of the reactor is located on the top right side. The choice for the 2D computational domain, as is common for many intricate reactor designs operating with complex chemical kinetics, comes from the point of view of reducing the complexity of the actual design; thereby speeding up the desired simulations without affecting the accuracy of the results obtained. A mesh with ca. 18000 cells is chosen for the further calculations based on the mesh independency study performed on multiple meshes of this reactor geometry. More details about RTD studies are included in ESI.

Conflicts of interest

There are no conflicts to declare.

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