



Methanol to gasoline (MTG): Parametric study and validation of the process in a two-zone fluidized bed reactor (TZFBR)



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ABSTRACT

Methanol to Gasoline (MTG) process transforms methanol to hydrocarbons within the boiling point range of gasoline. The result is a wide spectrum of products (olefins, paraffins, aromatics and naphthenics, among others), with the total conversion of methanol to hydrocarbons and water. Catalyst deactivation by coke is a main problem in this process. This work aims to determine the feasibility of carrying out the production of gasoline from methanol in a two-zone fluidized bed reactor (TZFBR). The hypothesis is that the formation of carbonaceous deposits (coke) on the catalyst particles can be counteracted by its combustion in the regeneration zone that this novel reactor presents, thus achieving stable and continuous operation. In this way, both processes (reaction and regeneration) would be being carried out simultaneously in the same reactor (process intensification). The comparison of results between a conventional fluidized bed reactor and a TZFBR shows that the second one actually provides a better stability over time.

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Introduction

Methanol to Gasoline (MTG) chemistry was discovered by ExxonMobil scientists in the 1970s [1]. This process selectively transforms methanol into hydrocarbons in the gasoline range through the catalytic action of a ZSM-5 type zeolite. The mechanism on which this process is based consists of a first dehydration of methanol to an equilibrium mixture of methanol, di-methyl ether (DME), and water. Subsequently, methanol and DME are completely dehydrated by a HZSM-5 based catalyst forming light olefins and water. At the MTG reactor conditions, light olefins oligomerize into higher olefins, which combine through various reaction paths into paraffins, naphthenes, and methylated aromatics. The shape-selective MTG catalyst limits the hydrocarbon synthesis reactions to about C₁₁ [2–4].

The MTG process is commercially attractive because hydrocarbons are produced in a specific composition range. In addition, high methanol conversion, high selectivity to isoparaffins and high octane aromatics are achieved. ExxonMobil commercialized the first MTG plant in New Zealand in 1985. This plant produced 14,500 BPD (Barrels Per Day) of gasoline. In 1995, the gasoline production section was closed due to the decline in the price of gasoline. Currently, Jincheng Antracite Mining Group (JAMG) has two

MTG units with a production capacity of 2,500 and 12,500, respectively [5]. One of the greatest difficulties of the MTG process resides in the control of the temperature, given the strongly exothermic nature of the overall reaction, $\Delta H_r^0 = -1.74$ MJ/kg (methanol) [6]. It has been shown that the use of a fluidized bed reactor (FBR) reduces the amount of coke formed on the catalyst with respect to a fixed bed one: the characteristic mixing regime of FBR favours the contact of all the catalyst with the water vapour generated and, consequently, the coke removal by stripping [7]. The use of a FBR coupled with another regeneration unit was proposed for greater process stability [8]. The simulation results were validated experimentally, although a third vessel was required for stabilization of the deactivated catalyst. Constant addition of fresh catalyst was also necessary due to attrition losses. In the last decade, the use of a pilot plant operation of a FBR working in alternative reaction-regeneration cycles was published [9]. It was found that the yield to gasoline initially increased by increasing the temperature in the range of 380–460 °C, although deactivation by coke formation was also favoured, which caused the yield to decrease above 410 °C. Regeneration was carried out in the same reactor by combustion of the generated coke at temperatures between 500–600 °C.

An alternative that allows reaction and regeneration to be carried out in the same reactor, and thus obtain continuous operation, is the two-zone fluidized bed reactor (TZFBR). This novel reactor represents a useful system to be applied for such heterogeneous

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catalytic processes where the catalyst is deactivated by coke deposition or even for a red-ox process. The reactor configuration consists of two gas feed points that generate two different atmospheres inside the reactor (Fig. 1). A reactive agent, e.g. methanol, is fed at an intermediate point of a fluidized bed (through a gas distribution rod), creating the reaction zone in the upper part of the bed. Simultaneously an oxidant agent, e.g. diluted oxygen, is fed at the bottom of the bed, creating the regeneration zone. The characteristic bubbling regime in fluidized bed reactors provides the catalyst circulation between both zones. Therefore, the catalyst, which is deactivated by coke deposition in the reaction zone, flows down to the regeneration zone where coke combustion takes place. Due to the bed fluidization, the regenerated catalyst comes up to the reaction zone and it may react again with the same activity, resulting in a steady state system in only one unit (process intensification concept).

In our research group, TZFBR was initially used to carry out a selective catalytic oxidation such as the oxidative coupling of methane [10], thus verifying its viability in red-ox reactions. Subsequently, it was used for oxidative dehydrogenation reactions of alkanes, specifically butane and propane [11,12], seeing how the selectivity to butadiene increased substantially. Selective oxidation reactions of n-butane to maleic anhydride on a VPO catalyst were also carried out successfully [13]. Improvements in the TZFBR were disclosed in a patent in 2008 [14]. Its application was found advantageous in many other reactions, such as methane aromatization [15], methane steam reforming [16] or dry reforming of methane [17]. It can also be combined with a selective membrane, providing

further process intensification [18,19]. A review has discussed the advances and trends in two-zone fluidized bed reactors [20]. Recent papers have shown the application of this TZFBR in the direct transformation of oil to chemicals [21].

The objective of this work is to compare the stability over time of the production of gasoline from methanol (MTG process), both in a fluidized bed reactor (FBR) and in a two-zone fluidized bed reactor (TZFBR). In addition, the influence of temperature and relative velocity to the minimum fluidization (u_r) in FBR configuration has been determined. The starting hypothesis is that the formation of carbonaceous deposits (coke) on the catalyst particles can be counteracted by its combustion in the regeneration zone that this novel reactor presents, thus achieving stable and continuous operation.

Experimental

Catalyst

Catalyst was prepared from commercial zeolite (molar ratio $\text{SiO}_2/\text{Al}_2\text{O}_3 = 30$) supplied by Zeolyst International in its ammonium form, boehmite (Sasol Germany) and an aqueous dispersion of colloidal alumina (Alfa Aesar, 20 wt%, 50 nm particle size, approx.). The preparation procedure of the catalyst can be summarized in two stages: i) calcination of the zeolite ZSM-5, and ii) agglomeration of the zeolite HZSM-5 with the boehmite (binder) and the colloidal alumina (inert filler).

The first stage was carried out by calcining the zeolite in a muffle (Nabertherm, model B180). This allowed the zeolite to change from ammonium ($\text{NH}_4\text{ZSM-5}$) to protonic form (HZSM-5), which is catalytically active in the MTG process. After the conditioning step, the zeolite HZSM-5, boehmite, colloidal alumina and distilled water was vigorously stirred for 2 h at room temperature. The catalyst particles were obtained by the wet extrusion method. The extrudates were dried overnight at room temperature and then in an oven at 110 °C. Once dry, it was ground and sieved (160–315 μm) and calcined in muffle furnace (575 °C for 2 h, with a heating rate of 1 °C/min) in order to fix the structure of the synthesized catalyst.

The catalyst characterization, as well as its catalytic validity in the MTG process in FBR, has been recently reported [22].

Experimental system

The experimental system used during the laboratory tests has three differentiated zones (feeding, reaction and analysis) (Fig. 2).

Different gaseous species were available in the feeding zone: nitrogen (Alphagaz N1 $\geq 99.999\%$, Air Liquide España), oxygen (Alphagaz N1 $\geq 99.995\%$, Air Liquide España) and carbon dioxide (Alphagaz N38 $\geq 99.98\%$, Air Liquide España). All of them stored in commercial cylinders and fed through mass flow controllers: nitrogen (Alicat Scientific, model MC-500SCCM-D, range 0–500 mL/min), oxygen (Alicat Scientific, model MC-50SCCM-D/5M, range 0–50 mL/min) and carbon dioxide (Alicat Scientific, model MC-100SCCM-D/5M, range 0–100 mL/min). On the other hand, an HPLC pump (Shimadzu, model LC-10AT VP) was used to feed liquid methanol (Ultrapure, HPLC grade $\geq 99.8\%$, Alfa Aesar). An evaporator located after the pump vaporized the methanol (operating temperature of 250 °C, approx.) to be fed in gas phase to the reactor. This evaporator consists of a container with a silicon carbide bath, heated by a heating plate, through which the methanol feed pipe is passed. The network of pipes that runs from the vaporizer outlet to the reactor feed were traced with electrical resistances (Omega, model FG-100) to avoid methanol condensation. A power regulator kept the temperature outside the pipes

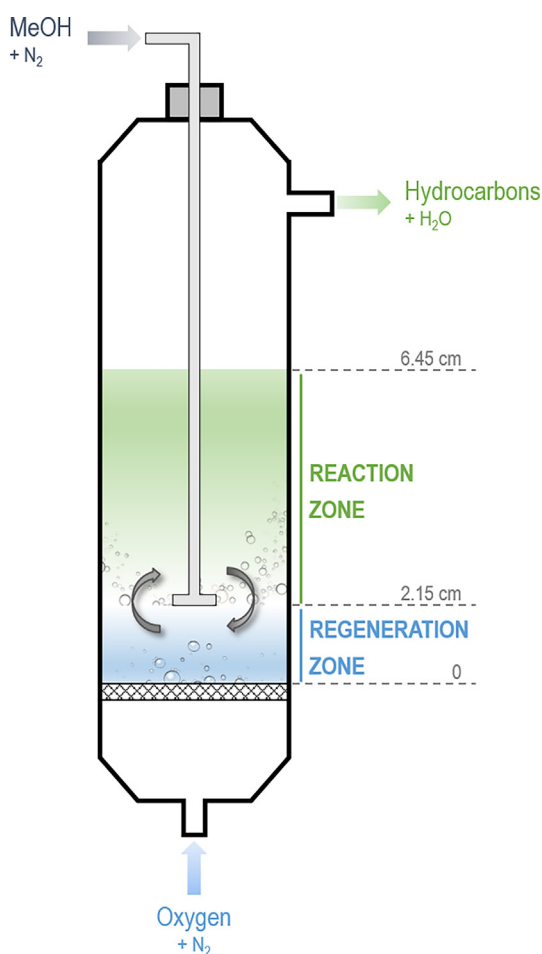


Fig. 1. Scheme of a two-zone fluidized bed reactor (TZFBR).

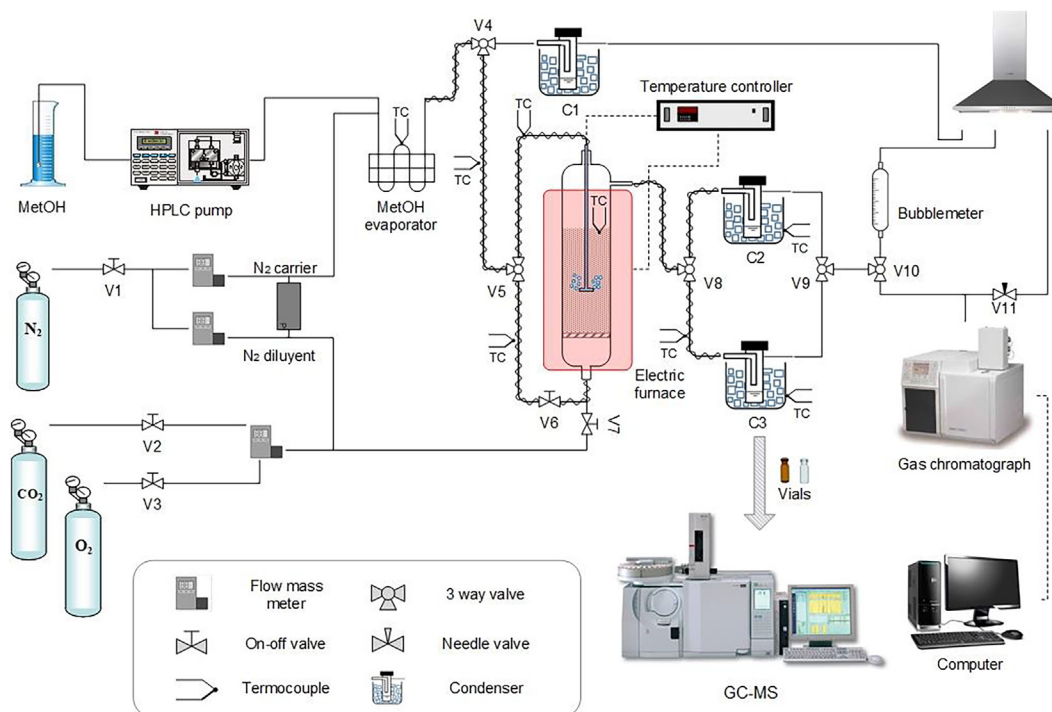


Fig. 2. Scheme of the experimental plant.

over 150 °C. In addition, the pipes were coated with glass wool (insulating element) and aluminium foil (homogenizing element). Nitrogen was used both as a carrier gas for the vaporized methanol and as a diluent gas. A period of stabilization of the vaporized methanol flow was maintained before starting the reaction. During this time, valve V4 was bypassed towards the extractor hood, after passing through condenser C1.

In the reaction zone, the reactor was the main element. It was made of quartz 2.8 cm diameter and 30 cm length, and it had a porous sintered quartz plate (pores smaller than 90 μm) that supported the catalyst bed and allowed the flow of gases. The design of the plant allows working with two configurations: as a fluidized bed reactor (FBR) or as a two-zone fluidized bed reactor (TZFBR). In TZFBR configuration, there were two feed points (Fig. 1). The methanol (and N_2 carrier) was introduced through the quartz rod at a distributor plate height of 2.15 cm. The regenerating agent was fed at the bottom of the reactor. From the analysis of the previous results [22], it is justified to work with synthetic cylinder air (20 vol.% O_2 –balance N_2 –) as a regenerating agent. Specifically, the O_2 volumetric flow that was required by stoichiometry to burn the coke required this configuration to be able to operate within the working limits of the gas-mass flow controller. A K-type thermocouple inside the catalyst bed connected to the PID control (Eurotherm, model Controller 3116) of the electric furnace controlled the temperature. The total mass of catalyst was determined so that the amount in the reaction zone (upper zone of the TZFBR according to Fig. 1) remained constant in relation to the experiments in FBR (15 g). The same with the reference temperature (450 °C). Another parameter that was conserved (with respect to the experiments in FBR with $u_r = 2$), was the total flow rate of methanol fed or, in other words, the total millimoles of carbon introduced into the reactant system. In this way, we wanted to evaluate the effectiveness of the in-situ regeneration of the catalyst, characteristic of the TZFBR proposed in this work. The reaction products (composed of light vapor fraction and a condensable fraction at room temperature), left the reactor and were conducted through a heat-insulated metal pipe to the condensation system. It was a system

composed of two condensers arranged in parallel, where valves V8 and V9 regulated the passage of the fluid. In this way, it was possible to work continuously, with an alternative sampling of liquids in vials every 20 min, approximately. Condenser operating temperatures were below -6 °C. These temperatures were achieved by a bath with a mixture of ice, NaCl and ethanol. In this way, heavier hydrocarbons, water and possible traces of unreacted methanol remained as a liquid fraction in the condenser.

Finally, in the analysis zone, the fraction of non-condensable vapours (permanent gases and light hydrocarbons) could be directed towards a bubble flow meter or towards a gas chromatograph (Varian CP3800, equipped with a thermal conductivity detector –TCD–, and with a flame ionization detector –FID–). The column used in the TCD was MolSieve 13X (Agilent Technologies, model CP-81071) and in the FID it was Capillary column (FactorFour, model VF-624 ms). The analysis of the liquid fraction was carried out in discrete samples (1 μL) by means of a gas chromatography-mass spectrometry (Shimadzu, model GCMS-QP2010).

The catalyst was regenerated after each reaction experiment and the analysis of the CO_x gases during the regeneration was employed to calculate the amount of carbon deposited. All regenerations were carried out at 550 °C with a total flow of 250 mL (STP) $\cdot \text{min}^{-1}$ and 2 vol.% O_2 composition (N_2 balance).

Results and discussion

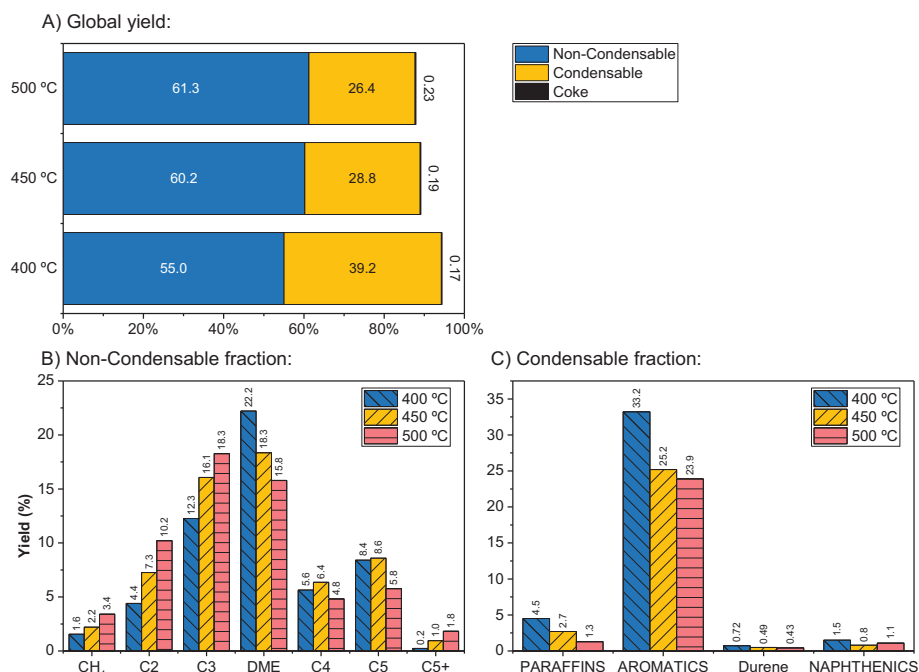
In order to analyse the optimal working range in FBR, a study of the variables ‘temperature’ and ‘relative velocity to the minimum fluidization’ (u_r , where $u_r = u_0 / u_{mf}$), was carried out. The operating conditions used in the different experiments of this work are shown in Table 1:

Effect of temperature in FBR

Fig. 3A shows the distribution of products broken down by phases: gas, liquid and solid (coke), for the three temperatures

Table 1
Experimental conditions.

| Parameter | Units | Zone | Reference value | Range |
|-----------------|-------|--------------|-----------------|------------------|
| FBR | | | | |
| Temperature | °C | – | 450 | 400, 450 and 500 |
| Catalyst weight | g | – | 15 | |
| u_r | – | – | 2 | 2 and 4 |
| MeOH | vol.% | – | 90 | |
| TZFBR | | | | |
| Temperature | °C | Both | 450 | – |
| Catalyst weight | g | Reaction | 15 | – |
| | | Regeneration | 7.5 | – |
| u_r | – | Reaction | 2.4 | – |
| | | Regeneration | 1.6 | – |
| MeOH | vol.% | Reaction | 45.2 | – |
| O ₂ | vol.% | Regeneration | 0.001 | – |

**Fig. 3.** Distribution of products with FBR for the three temperatures tested. Values calculated as an average of the complete TOS of each experiment. Operating conditions: $W/F_{AO} = 11.3 \text{ g}_{\text{cat}} \text{ h mol}_{\text{MeOH}}^{-1}$ at 400 and 450 °C and $11.5 \text{ g}_{\text{cat}} \text{ h mol}_{\text{MeOH}}^{-1}$ at 500 °C.

studied (400, 450 and 500 °C). These phases are obtained respectively as: non-condensable fraction (light hydrocarbons), condensable fraction (gasoline) and fraction of carbon attributable to coke deposited on the catalyst during the experiment (205 min), according to the CO_x gases obtained in the regeneration (all referred to the total of C fed). Fig. 3B and C show the contribution of the different groups of compounds in the gas and liquid phase, respectively, expressed as carbon-based yield.

Regarding the distribution of gaseous products, the yield to light hydrocarbons increased as with the operating temperature increases (Fig. 3A). The most abundant are hydrocarbons with three carbon atoms, apart from DME since it is considered an intermediate product of the transformation of gasoline. Breaking down C₂ and C₃, the yield to olefins (ethylene and propylene) was always higher than that of paraffins (ethane and propane). With respect to the yield to dimethyl ether, it fell as the temperature was increased, an aspect that, based on the previous discussion, is advantageous.

The net formation of coke increased with temperature, which is an expected and common trend in this type of process, even though it remains at surprisingly low values. At the highest tem-

perature (500 °C), the carbon formed, measured by analysing CO_x in the regeneration gases as, was only 0.23% with respect to the total carbon fed. In this regard, the literature also reports low rates of coke formation in the MTG process on HZSM-5 under similar operating conditions [23].

The opposite effect to that previously mentioned with gases occurred with liquid products (gasoline). An increase in temperature translated into a decrease in its production (Fig. 3C). The set of aromatics only represented 83.8 wt% of the liquid fraction, with p-xylene (21.2%) as the major contributor (values taken as a reference at 400 °C).

The results of post-reaction regeneration of the catalytic bed reflect that the net formation of coke increases with temperature, which is an expected and common trend in this type of process. Even keeping the temperature at high values, 500 °C in most cases, the carbon collected in the regeneration gases as CO_x represents a contribution of 0.23% with respect to the total carbon fed.

The stability of the process at different temperatures is analysed in Fig. 4, showing the effect of the variable time-on-stream (TOS) on the yield to BTX and light olefins. It is interesting to see how, for higher temperatures, the BTX yield progressively decreased

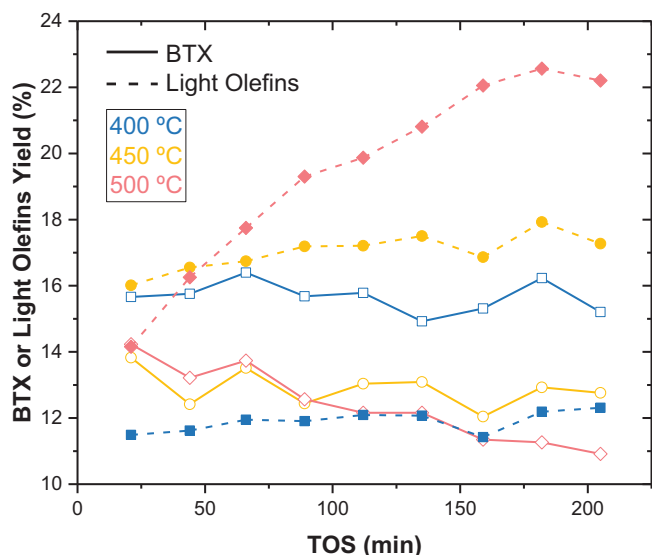


Fig. 4. Temporal evolution of yield to BTX (solid lines) and light olefins (dashed lines) at different temperatures with FBR configuration.

while that of light olefins increased. This increase in the yield to intermediate products is an indicator of catalyst deactivation. This is consistent with what is reported in the literature. Aguayo et al. [7], pointing out that as a consequence of deactivation the gasoline yield decreased and the production of light olefins increased.

The TZFBR configuration involves the removal of the coke deposited on the catalyst in the same vessel in which the reaction of methanol to gasoline takes place. For this reason, the selected temperature was 450 °C. Although the ratio 'yield to liquids vs. gases' is higher at 400 °C than at 450 °C (0.71 vs. 0.48, respectively and according to Fig. 3A), 400 °C is considered insufficient for in-situ catalyst regeneration [7].

Effect of u_r in FBR

The yields to the different phases are presented in Fig. 5A for two different space velocities (u_r) in a FBR. Globally, the yield to both light hydrocarbons (non-condensable phase) and gasoline (condensable phase) is greater at high reduced velocity. Going into detail (Fig. 2), increasing the feed flow translates into two aspects. The first, a slight decrease in the conversion of methanol. Until now, this conversion had been maintained at values greater than 99.99%. For $u_r = 4$, its value is reduced to 98.4%. The second, an increase in the yield of DME (intermediate product in the transformation of methanol to light olefins). Taking into account these two aspects, both of them a consequence of the lower space time in the catalytic bed, the global yield to the species of interest, non-condensable fraction (excluding DME) and condensable fraction, was very similar.

The contribution of the coke deposited on the catalyst also deserves special mention. Despite feeding practically twice the flow rate of methanol, the lower production of coke in the experiment at $u_r = 4$ has to be related to that shorter residence time of the species in the bed. Apparently, when $u_r = 2$ the carbon deposits become more stable due to a greater graphitic character, that is, lower H/C ratios in their composition. This implies a higher accumulation rate throughout the operating time. Previous works [24], report a first phase of coke formation in MTG with zeolites that begins relatively slowly and then accelerates by direct reaction of methanol with coke [25] and a second phase that is favoured at lower residence times. In addition, a direct relationship between methane yield and the extent of coke formation was also established [26], which is also perceived in these experiments.

Considering the distribution of products in both phases (Fig. 5B and C), the same aforementioned trend was observed. In general, the yield to CH_4 , C_2 and C_3 is greater with $u_r = 2$, while the opposite happens for yields to C_5 and liquid paraffins. Regarding the formation of durene, it doubles with the reduced velocity but always remains below the desirable limit of 2 wt% [1].

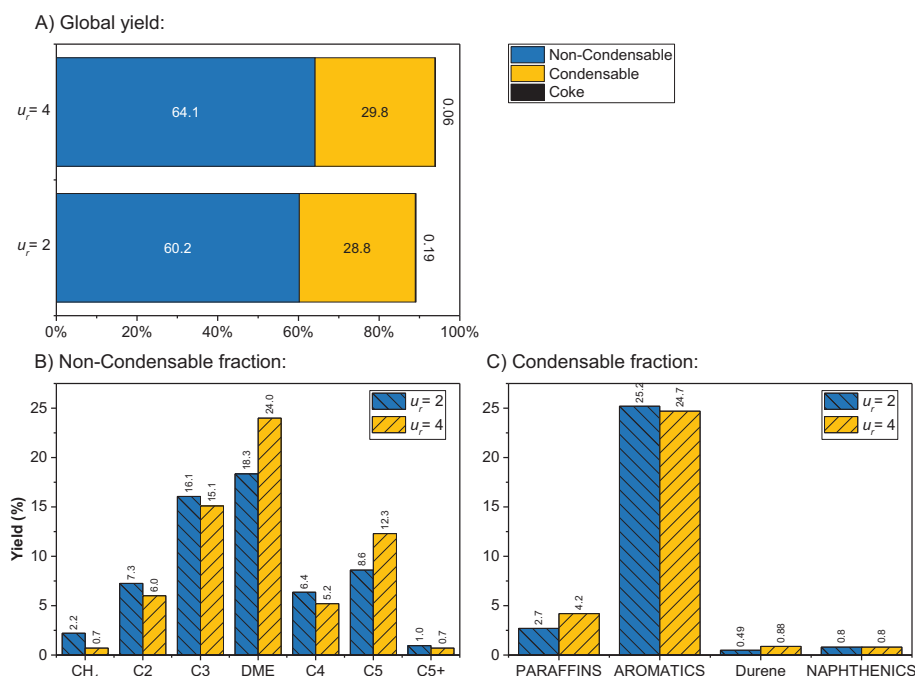


Fig. 5. Distribution of products with FBR for the two reduced velocities (u_r) tested. Values calculated as an average of the complete TOS of each experiment. Operating conditions: $W/F_{A0} = 11.3 \text{ g}_{\text{cat}} \text{ h mol}_{\text{MeOH}}^{-1}$ at $u_r = 2$ and $5.7 \text{ g}_{\text{cat}} \text{ h mol}_{\text{MeOH}}^{-1}$ at $u_r = 4$; $T = 450 \text{ °C}$.

The effect of the time-on-stream on the yield to BTX and light olefins (ethylene and propylene) is represented in Fig. 6. These results confirm two previously commented aspects. On the one hand, and referring to the study of the reduced velocity, the yield to light olefins always was higher with $u_r = 2$ than with $u_r = 4$. On the other hand, and with respect to the stability of the system, the indicator of catalyst deactivation introduced in the previous section (i.e., the temporary increase in selectivity to light olefins and decrease in that of BTX), was attenuated with high reduced velocity. For example, for $u_r = 4$ the slope in the temporary increase of yield to light olefins is clearly lower (Fig. 6).

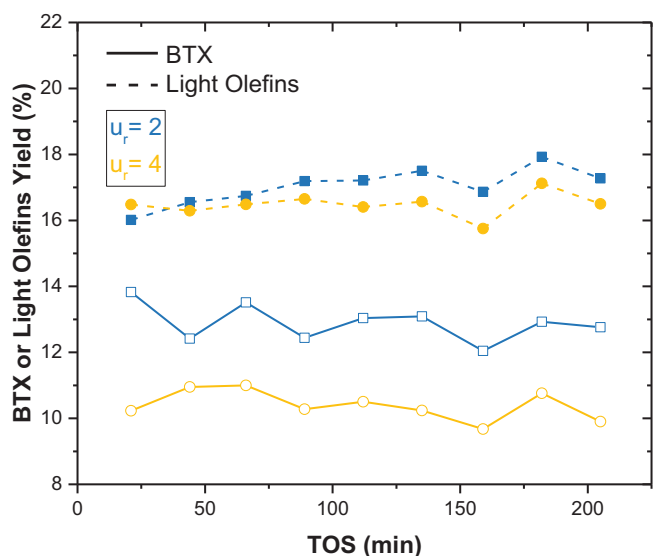


Fig. 6. Temporal evolution of yield to BTX (solid lines) and light olefins (dashed lines) at different reduced velocities with FBR configuration.

FBR vs. TZFBR

Fig. 7A shows the distribution of carbon-based yield to gaseous, liquid and solid products (coke) for the two reactor configurations studied. The degree of similarity between the two was very great. Both the yield to light hydrocarbons (non-condensable fraction) and to liquid hydrocarbons (condensable fraction) was very similar. The final amount of coke obtained was greater in the TZFBR than in the FBR configuration. Although part of the catalyst is being regenerated during reaction in the TZFBR, it accumulates more coke because the total amount of catalyst is 1.5 times greater than in the experiment in FBR. In other words, the results are consistent with an effective regeneration area of lesser height than initially proposed (26%, approx.). The rest (74%, above the first and below the reaction zone) would have continued to accumulate coke. This should be corrected in the future with an increase in the proportion of oxygen supplied, an increase in temperature, or a change in the relative volume of the regeneration zone.

The specific distribution of products, both for the non-condensable and for the condensable fraction, is represented in Fig. 7B and C. An interesting aspect is the decrease in methane yield with the TZFBR configuration, which, as has been seen, is related to lower deactivation by coke [25].

The similarity observed in the distribution of global yields also appeared in the detailed distribution of products. More DME was formed in the TZFBR, which may be explained by the fact that, although the space velocity (W/F_{A0} , ratio of catalyst weight to molar flow of methanol in the feed) in the reaction zone was the same in both configurations, the residence time was smaller. Due to the characteristic of TZFBR (regeneration of the catalyst in-situ in the reactor itself), the total volumetric flow rate in the reaction zone includes the contribution of the gas coming from the regeneration zone. Therefore, there is a shorter residence time in TZFBR than in FBR, and a lower molar fraction of methanol (45%, approx.) due to dilution, with said lower stream. All this changes resulted in lower DME conversion. The same reasoning explains the slight decrease in methanol conversion observed in TZFBR, which was

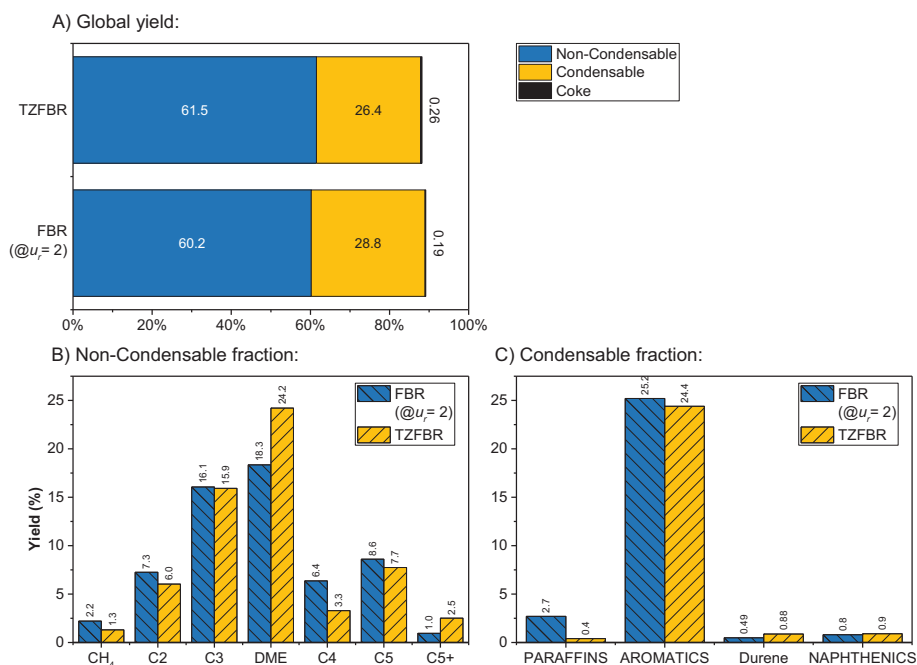


Fig. 7. Distribution of products for the two reactor configurations used. Values calculated as an average of the complete TOS of each experiment. Operating conditions: $W/F_{A0} = 11.3 \text{ g}_{\text{cat}} \text{ h mol}_{\text{MeOH}}^{-1}$; $T = 450 \text{ }^\circ\text{C}$.

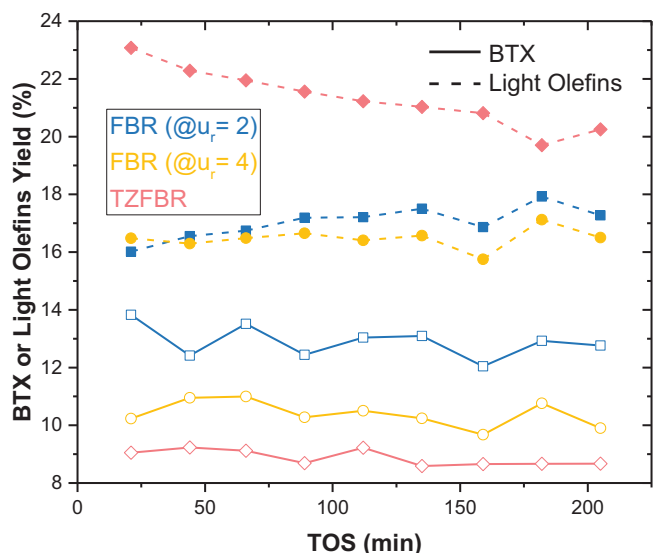


Fig. 8. Temporal evolution of yield to BTX (solid lines) and light olefins (dashed lines) at different reactor configurations (FBR and TZFBR).

approximately 99%, while in FBR conversion was almost complete. On the other hand, it is interesting to note that in the TZFBR configuration, the C_3 hydrocarbons were only propylene and propane was not formed. The yield to durene increased in TZFBR (staying within the set operating limit of 2%) compared with the FBR, while the yield to paraffins decreased (Fig. 7C).

The stability of the process in the two reactor configurations is analysed in Fig. 8:

The yield to olefins was higher in TZFBR than in FBR. Taking into account that the yield to ethylene is similar in both cases, the fact that in TZFBR the contribution to C_3 is exclusively from propylene and not from the propylene and propane group, justifies this increase. Regarding the temporal evolution of the yields, the stability of the process improved with the TZFBR. The evolution of yield to BTX remains constant at a value of around 8 wt%. Unlike the FBR operation with the same W/F_{AO} ($u_r = 2$), the yield to BTX does not decrease. Same stability was observed with half of W/F_{AO} ($u_r = 4$). On the other hand, the yield to light olefins in TZFBR decreased over time, modifying the upward trend that had been obtained so far in FBR. Although the presence of steam can cause deactivation by dealumination of the catalyst, no changes were observed in this study. These results demonstrate the feasibility of TZFBR as a tool to correct the original trend of loss of activity observed in FBR.

An interesting perspective opens up for the use of the TZFBR reactor in the MTG reaction, seeking to achieve a stable process. Additional optimization of operating conditions will be required, to that maximize the gasoline yield.

Conclusions

The present work compares the production of gasoline from methanol (MTG process) in two different fluidized bed reactor configurations: conventional (FBR) and two-zone (TZFBR). Initially, a parametric study has been carried out to determine the effect of temperature and residence time (modified by variation of the reduced velocity or relative velocity to the minimum fluidization).

Referring to the study of the process variables in FBR, an increase in temperature translates into an increase in the yield to light hydrocarbons and coke (the opposite to gasoline). The stability study shows that, when the temperature increases, the BTX yield decreases progressively with time-on-stream, while the light olefins yield increases. This behaviour is considered as an indicator

of non-stability (catalyst deactivation). Decreasing the residence time of the reactants in the FBR (i.e., increasing the reduced velocity from 2 to 4), decreases the coke yield. A longer residence time translates into a more stable coke (low H/C ratios) and a self-accelerating effect on its formation. The hydrocarbon distribution varied little, but the stability of the system improved with higher reduced velocity.

In TZFBR, the yield to the different phases (non-condensable, condensable and coke) is similar to that obtained with the conventional configuration (FBR). However, it is interesting to note that in TZFBR the contribution of C_3 hydrocarbons is only olefinic (propylene) since there is no propane formation. Another aspect to highlight is the positive effect on stability along time-on-stream provided by this alternative configuration. In this sense, the viability of the MTG process in TZFBR is confirmed. Further analysis and optimization of the operating variables in the TZFBR can lead to maximizing gasoline yield with stable operation.

Declaration of Competing Interest

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

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