

Efficient production of propylene and gasoline from methanol in multi-regime riser

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Abstract—High gas-solid contact efficiency and low solid back-mixing are necessary to both promote methanol conversion and inhibit side reactions. Thus, a novel multi-regime reactor with dense-phase reaction section and dilute-phase conveying region was designed. The reactor promoted stable reaction activity during a 300 h pilot-scale evaluation with high yields of propylene and gasoline. A process for maximum propylene and gasoline production from methanol (PGFM) characterized by moderate operating severity, application of ZSM-11 catalyst and novel reactor, and stratified reprocessing or etherification of light gasoline and C₄ olefins was proposed. The PGFM process can be implemented in the existing FCC process and is considered to be more economic and flexible.

Keywords: Gasoline, Methanol, Multi-regime Reactor, PGFM Process, Propylene

INTRODUCTION

Olefin and liquid fuel products are essential for satisfying global material and energy demands. Efforts to achieve independence from current crude oil supplies have made the methanol conversion process more competitive than conventional oil-based routes, typically the steam cracking and fluid catalytic cracking (FCC) processes [1].

Methanol conversion may target toward propylene (MTP), light olefins (MTO), or gasoline (MTG) as the preferential products through appropriate selection of the catalyst used and operating conditions. The molecular sieves industrially applied in this process are ZSM-5 and SAPO-34. SAPO-34, which has a chabazite structure, is recognized as a valuable catalyst for generating high selectivity toward light olefins because of its moderate acid strength and small pore openings [2]. However, SAPO-34 is known to suffer rapid deactivation by coking through the formation of polycyclic arenes in its spacious cavities [3-5]. By contrast, ZSM-5 catalyst is highly coking resistant, which is attributed to the formation of coke on the external surface [6-8], and has been proven to be more promising for the MTP process. Our research group has synthesized a hierarchical ZSM-11 zeolite through a simple and low-cost method; the material features intercrystalline mesopores and rod-like crystal intergrowth morphology [9,10]. This zeolite has been successfully produced on an industrial scale and its derivatives displayed excellent activity in methanol and glycerol conversion reactions [11,12]. HZSM-11 zeolite has an MEL pore topology with a pore diameter of 0.54×0.56 nm and is suitable for the production of gasoline-range hydrocarbons. Moreover, alkene methylation and cracking reactions have been observed to dominate product formation on this zeolite [13]. ZSM-11 zeolite, with a diameter of the maximum

included sphere in the framework of 7.6 Å, can accommodate an estimated pore volume of 180-230 Å³, which is similar to the molecular volumes of olefins with 5-10 carbon atoms and/or their carbenium cations, and therefore can enhance the selectivity of propylene [14]. In addition, the nano-structure, mesopores, and low sinusosity make ZSM-11 favorable for facile diffusion of primary products and coke precursors; thus, it can reduce secondary reactions and prolong the catalyst lifetime [15]. In the previous study, ZSM-11 catalyst indeed promoted the production of propylene and gasoline in methanol conversion [16].

Two types of reactors have been developed for industrial-scale methanol conversion processes: fixed-bed and fluidized-bed. Lurgi adopted a multiple-stage adiabatic fixed-bed reactor system to perform a proprietary MTP process [17]. The complicated reactor system is not economic, and the larger particles used are kinetically less efficient due to the intra-particle mass transfer restriction, causing incomplete utilization of the catalyst and consequently low productivity of the reactor system. In contrast, a fluidized-bed reactor was pursued by UOP and Norsk Hydro in their UOP/HYDRO MTO process [18]. This reactor offers better heat removal properties, fast regeneration of catalyst, and constant activity due to freely moving micron-sized particles of catalyst. In general, the fluidized-bed reactor provides excellent operating flexibility and high throughput per cross-sectional area [19].

In MTO reactors, especially fluidized-bed reactors, high gas-solid contact in the reaction section and relative low solid back-mixing after the reaction are crucial to promote methanol conversion and olefin selectivity [20-22]. The circulating fluidized-bed reactors proposed by previous researchers generally feature a rapid separation between products and catalysts, and therefore increase the yield of light olefins by changing the diameter in the section after reaction [23-25]. However, the complicated structures restrict its practical applications. As a typical process in circulating fluidized beds, the use of FCC equipment offers a potential and feasi-

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ble route to converting methanol. The conventional riser reactor widely used in the FCC process is limited to extremely non-uniform gas-solid suspension flow characterized by a core-annulus flow pattern and solid back-mixing near the wall coupled with low solid concentration. These phenomena result in the segregation of gas-solid phases and low gas-solid contact efficiency [26,27]. High density circulating fluidized-bed (HDCFB) and high flux circulating fluidized-bed (HFCFB) designs have been proposed to inhibit solid back-mixing effectively but also feature gas-bypassing and low gas-solid contact quality [28]. Risers with a diameter-enlarged section or coupled with a draft tube generating internal solid circulation [29], circulating turbulent fluidized-bed (CFB) integrated with circulating and turbulent fluidized-bed [22], and tapered risers possessing high operating flexibility have been put forward to improve the hydrodynamics and intensify the interaction between gas and solid phases [30]. In particular, risers equipped with top/bottom-enlarged sections have been widely used for different processing purposes in China due to relatively simple technical applications and unit upgrades. Thus, it is challenging to combine methanol conversion with the improved FCC equipment.

In the present study, methanol conversion was carried out in a conventional circulating fluidized-bed riser and bubbling-bed reactor. Considering the effect of flow behavior, a novel reactor integrated with an enlarged bottom section was proposed without disturbing upper flow behavior of the riser to produce light olefins (especially propylene) and gasoline [16]. Compared with the non-uniform radial profiles of solid concentration and particle velocity presented by the high-density bottom region of a conventional riser, more uniform solids distribution and better gas-solids contact have been achieved in the diameter-enlarged bottom section of the multi-regime riser [31]. The novel reactor with a dense-phase bottom section (operated in bubbling or turbulent fluidization mode) and a dilute upper region (operated in fast fluidization or pneumatic transportation mode) can enhance overall solids concentration, improve local flow patterns, intensify gas-solid contact, and realize rapid separation of products, as reflected by high methanol conversion and olefins selectivity. A process for maximum propylene and gasoline production from methanol (PGFM) over ZSM-11 catalyst was proposed. This process can be implemented in existing FCC equipment and is of great interest to engineers in practical industries.

Table 1. Properties of ZSM-11 catalyst

Item	ZSM-11 catalyst
S_{BET} (m^2/g)	120.9
V_{total} (cm^3/g)	0.13
Packing density (kg/m^3)	760
Average particle diam (μm)	70
Attrition index	1.70
Particle size distribution (wt%)	
0-20 μm	0.00
20-40 μm	2.78
40-80 μm	46.56
80-160 μm	49.16

EXPERIMENTAL

1. Feedstock and Catalyst

ZSM-11 catalyst was prepared by spray granulation according to a patent [32]. The main properties are given in Table 1.

Because it is impossible to recover gas phase products in the pilot unit, a mixture of C_4 components provided by Sinopec Qilu Petrochemical Co. was used to substitute for that generated from the process investigated. The mixture of C_4 components, with its detailed composition listed in Table 2, was composed of 91.3 wt% butylenes and 7.7 wt% butanes.

2. Catalyst Characterization

Textural parameters of the catalyst were determined by nitrogen adsorption isotherms, which were recorded at $-196^\circ C$ using a Quantachrome Autosorb iQ apparatus. The total surface (S_{BET}) was calculated according to the Brunauer-Emmet-Teller (BET) isothermal equation, and the total volume (V_{total}) was determined from the nitrogen adsorbed nitrogen volume at $P/P_0=0.990$. Average particle diameter was measured with a laser particle analyzer

Table 2. Composition of the mixture of C_4 components

Item	Content (wt%)
Butane	7.7
Iso-butane	3.7
n-Butane	4.0
Butylene	91.3
trans-2-Butylene	39.0
1-Butylene	22.6
Isobutylene	0.1
cis-2-Butylene	29.6
Others	1.0

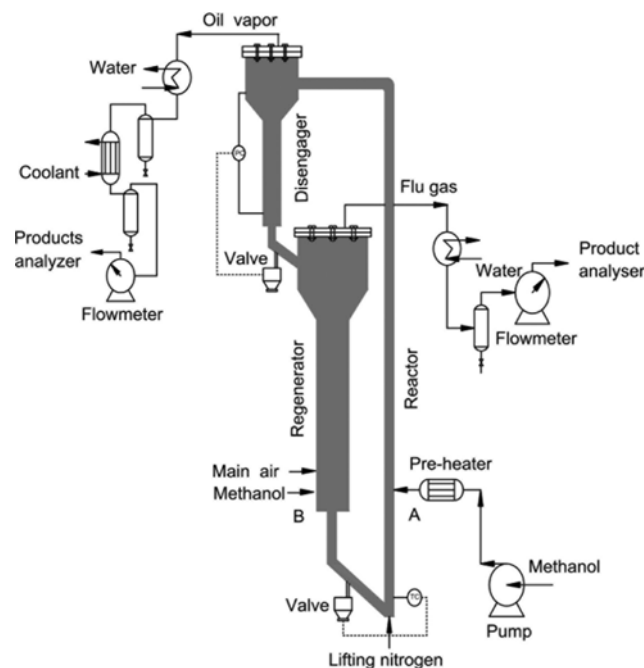


Fig. 1. Schematic diagram of the pilot-scale CFB unit.

(BT-2003). The particles were about 73 μm in diameter. As shown in Table 1, the physical properties of the ZSM-11 catalyst are similar to those of FCC catalyst, and the resultant catalyst belongs to the A-particles classified by Geldart [33].

3. Experimental Apparatus

The pilot-scale CFB unit, presented in Fig. 1, mainly consists of a reactor (with a length of 1 m and an inner diameter of 92 mm) coupled with a disengager, a regenerator, and a delivering riser, as well as product recovery systems. During the tests, methanol was introduced into the bottom of the reactor through a pump at a certain flow rate, flowing upward with nitrogen (320 L/h) and contacting the catalyst (mean diameter of 73 μm) under atmospheric pressure. After reaction, the mixture of products and catalyst was separated in the disengager, where the gaseous products were collected. The spent catalyst was transferred into the regenerator through the delivering riser to burn off the coke in air at 650 $^{\circ}\text{C}$, and the flow rate of the main air was 550 L/h.

4. Product Analysis

The composition of gaseous products was analyzed by using a Bruker 450-GC gas chromatograph (GC) with a TCD detector to analyze the content of hydrogen, nitrogen, and carbon oxide, and an FID detector to determine the composition of hydrocarbons. The gasoline was analyzed on a Perkin Elmer Clarus 580 gas chromatograph (GC). Liquid products were analyzed on an Agilent 6820 gas chromatograph (GC) equipped with an HP-INNOWAX capillary column (30 m \times 0.32 mm \times 0.25 μm) and a flame ionization detector (FID) using ethanol as internal standard.

The methanol conversion and product yield were calculated by applying the mass balance between the inlet and outlet of the reactor as in Eq. (1) and Eq. (2), respectively.

$$\text{Methanol Conversion} = \left(1 - \frac{m_{\text{MEOH}}^{\text{o}} + m_{\text{DME}}^{\text{o}}}{m_{\text{MEOH}}^{\text{i}}} \right) \times 100 \quad (1)$$

$$\text{Product Yield} = \left(\frac{m_{\text{CxHy}}^{\text{o}}}{m_{\text{MEOH}}^{\text{i}}} \right) \times 100 \quad (2)$$

Superscript i refers to the components at the inlet of reactor, and superscript o refers to the components at the reactor outlet; subscript x refers to the number of carbon atoms.

RESULTS AND DISCUSSION

1. Operating Conditions for Maximum Propylene and Gasoline Production

The methanol conversion depends on many parameters. In addition to catalyst composition, the operating conditions, including reaction temperature, catalyst-to-methanol ratio, coke content, residence time, and the reactor structure have significant effects on product distribution.

1-1. Effect of Reaction Severity

Increasing reaction severity is a simple method of enhancing feed conversion and enhancing light olefin production; therefore, the effect of reaction severity on methanol conversion was studied first. Experiments were carried out with a catalyst regenerated at 650 $^{\circ}\text{C}$ and residence time of 5.5 s, while the reaction temperature was elevated from 350 to 550 $^{\circ}\text{C}$ and the catalyst-to-methanol ratio increased from 2.5 to 3.5 (calculated from the local heat balance). Methanol was fed through the bottom of the regenerator (location B in Fig. 1). The results are presented in Fig. 2.

Under the operating conditions investigated, methanol conversion was constantly higher than 90.0 wt%, indicating that ZSM-11 catalyst has an excellent methanol converting ability. High reaction temperature promoted methanol activation and high catalyst-to-methanol ratio increased contact opportunities between catalyst active sites and methanol molecules. Thus, an 8.0 wt% increase in methanol conversion within the reaction severity range tested

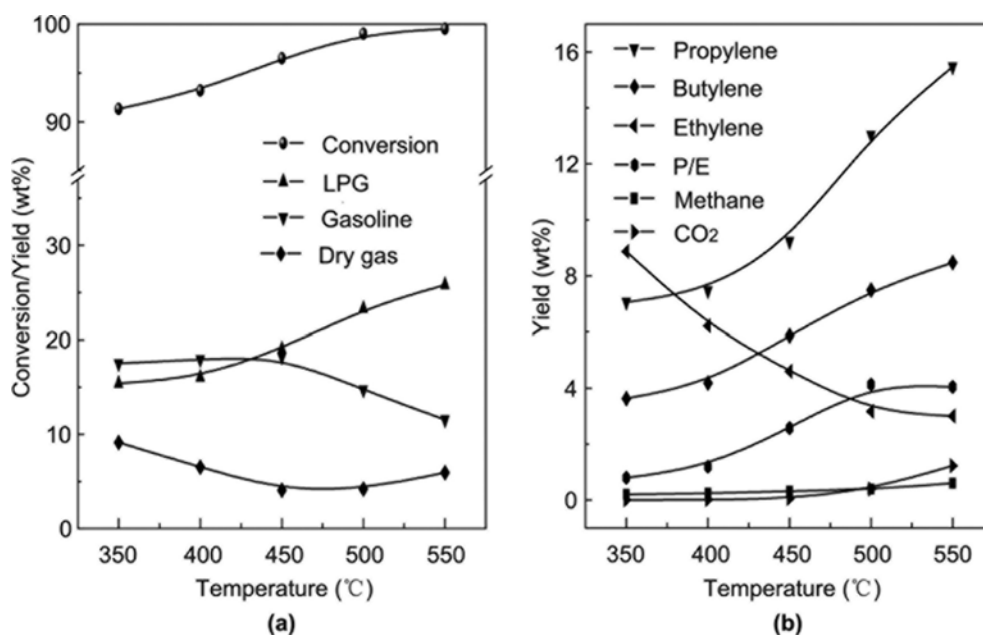


Fig. 2. Effect of reaction severity on methanol conversion over ZSM-11 catalyst: (a) Product distribution and conversion; (b) main products and P/E.

was observed. Propylene, ethylene, and butylene were the main products. At the expense of light oil production, yields of propylene and butylene increased with reaction severity, while that of ethylene decreased, causing a substantial increase in the propylene to ethylene (P/E) ratio [34], indicating that regulating reaction severity is an effective approach for controlling P/E ratio.

Thermal cracking tended to dominate at much higher reaction severity, consequently producing more dry gas and CO_x . High catalyst-to-methanol ratio offered a high catalyst density and low gas velocity, which easily caused channeling. The bad gas-solid contact and high reaction temperature deepened the thermal cracking of methanol.

Results thus far have indicated that propylene and gasoline yields could be kept at high levels and regulated by operating conditions. Equivalent yields for the sum of propylene and gasoline were reached at 450 and 500 °C. Considering the market demands and prices, production of propylene is slightly more preferred, thus, a moderate reaction severity (reaction temperature of 500 °C) is appropriate for the production of gasoline and propylene. However, the yields of by-products (such as alkanes, dry gas, and CO_x) were relatively higher under these conditions, and therefore it was necessary to adjust the other reaction conditions and design a feasible reactor to further enhance the selectivity of olefins.

1-2. Effect of Residence Time

Besides reaction severity, residence time also exerted a significant impact on product distribution. With a regeneration temperature of 650 °C, reaction temperature of 500 °C, and catalyst-to-methanol ratio of 3.2, the effect of residence time in the range of 5.4–7.9 s on methanol conversion was evaluated. Methanol was fed through the bottom of the regenerator (location B in Fig. 1). Relevant results are shown in Fig. 3.

With a residence time of 5.4 s, methanol conversion reached 98.5 wt%. Longer residence time meant longer contact time for cata-

lyst and methanol; thus, methanol converted completely when the residence time was increased to 7.9 s. Meanwhile, subsequent serious secondary reactions, such as polymerization, aromatization, and hydrogen transfer occurred and ethylene, propylene, and butylene yields decreased slightly, leading to a decline of propylene content in LPG. Ethylene dominated the dry gas composition at this temperature and its content almost stayed constant. Within the residence time range studied, which was limited by the experimental facilities, methanol was almost converted completely; thus, the results could not reflect the whole effect of residence time on product distribution. According to the experimental results and considering both methanol conversion and light olefins selectivity, the residence time should be relatively short.

Based on the above analysis, a moderate reaction severity and sufficient residence time are needed for the production of gasoline and propylene. However, the residence time was only varied within the range of 5.4–7.9 s in the present study, during which the high catalyst density was responsible for the high methanol conversion, even at a residence time of 5.4 s. Further reductions in residence time could easily cause channeling and were thus restricted in our experiment. Modification and improvement of the existing unit might further decrease the yield of by-products.

1-3. Effect of Flow Behavior

Solid concentration and gas velocity in the bed are important factors to determine methanol conversion and product distribution. Here, the effect of flow behavior in a gas-solid fluidized-bed for methanol conversion was investigated under a regeneration temperature of 650 °C, reaction temperature of 500 °C, and the same feeding rate. The difference in the gas velocity was obtained through the adjustment of the flow of nitrogen and change of the diameter.

The effects of flow behavior at the gas velocity of 5.9 and 0.4 m/s were compared (see Fig. 4), which according to Lim [35] were in the category of conveying and bubbling bed, respectively. The dif-

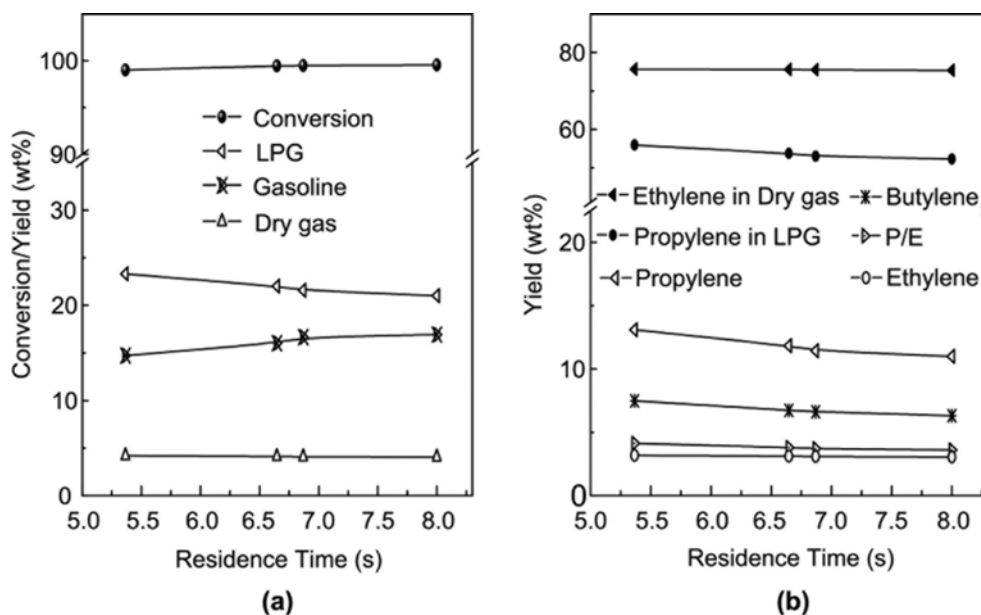


Fig. 3. Effect of residence time on methanol conversion over ZSM-11 catalyst, reaction temperature 500 °C: (a) Product distribution and conversion; (b) main products yields and P/E.

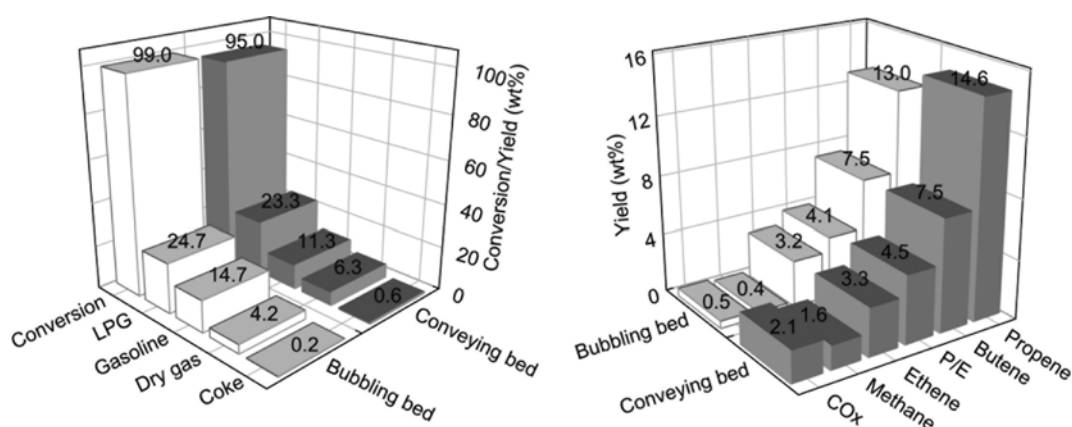


Fig. 4. Effect of flow behavior on methanol conversion and product distribution over ZSM-11 catalyst, reaction temperature 500 °C.

ferent gas velocities were obtained by changing the feeding location marked as A and B in Fig. 1, while keeping the methanol partial pressure constant. The results revealed that the methanol conversion and product distribution were significantly influenced by the flow behavior. In the bubbling bed unit, the particle concentration was high, and thereby the contact between methanol and active sites of catalyst was sufficient, reflected by the high methanol conversion and lower production of thermal reaction products, such as methane and CO_x (0.4 and 0.5 wt% in the bubbling bed and 1.6 and 2.1 wt% in the conveying bed). However, long residence time caused strong solid back-mixing, leading to severe secondary reactions (mainly hydrogen transfer for olefins). Olefin yields tended to be lower in the bubbling bed than in the conveying bed, which featured low particle concentration and non-uniform gas-solid suspension flow. The flow pattern in the riser was not favorable for methanol and catalyst contact, as evidenced by a low methanol

conversion and severe thermal cracking of methanol. The low particle density restrained further reactions of light olefins. As such, propylene yield was higher in the conveying bed (13.0 wt% in the bubbling bed and 14.6 wt% in the conveying bed).

The results showed that the flow behavior in the bubbling and conveying bed reactors did not correspond well with the reaction features of methanol. Methanol conversion and selectivity to olefins and gasoline could not be balanced. The structure of the reactor should be optimized to meet our requirements.

2. Design of a Multi-regime Reactor

The aforementioned results showed that high methanol conversion and low alkanes selectivity are crucial for maximizing propylene and gasoline production and must be taken into consideration when designing reactors. In the reaction zone of a novel reactor, the gas-solid contact efficiency between methanol molecules and catalyst should guarantee high methanol conversion. After reac-

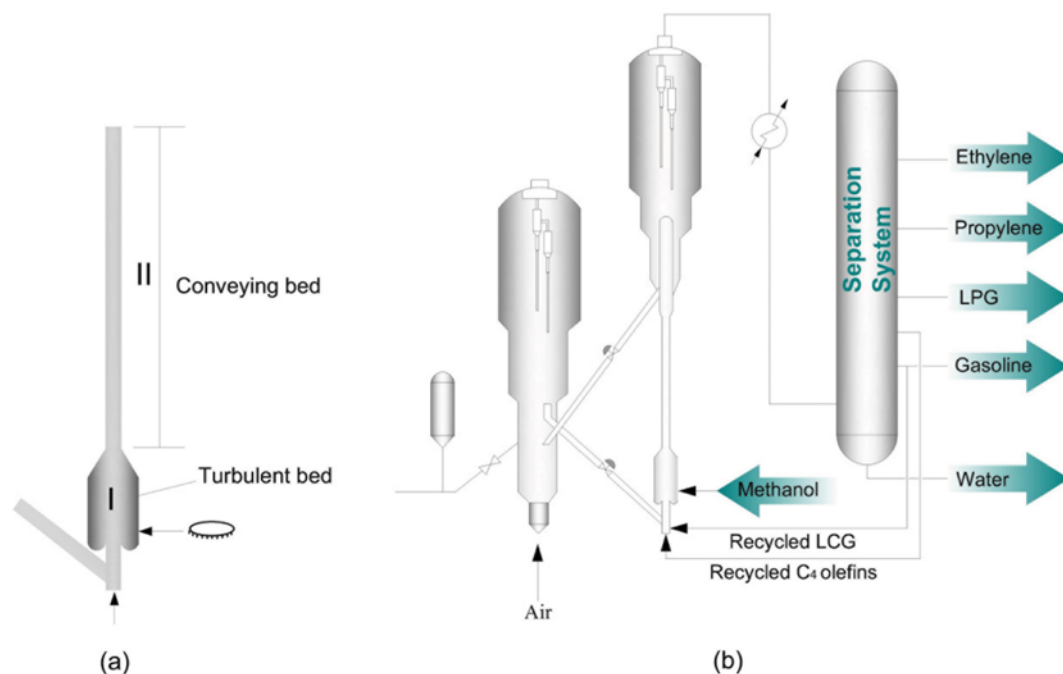


Fig. 5. Schematic diagram of (a) the novel multi-regime reactor, and (b) the PGFM process with light gasoline and C₄ olefins reprocessing.

tion, gas products and catalysts must be separated immediately. At this point, low particle concentrations must be preserved to minimize secondary reactions of olefins, i.e., strong solid back-mixing must be inhibited extensively. The structure of the novel reactor patented by our research group is shown in Fig. 5(a).

The novel reactor mainly consists of two sections: the lower section is the dense-phase fluidized-bed (zone I), and the upper section is the dilute-phase bed (zone II). In addition to high solid density, the gas-solid contact efficiency in zone I is also promoted by improving the feeding methods and reactor structure to relieve the channeling phenomenon. A loop gas distributor is installed in this section to achieve solid internal circulation of the solid. Methanol is fed through a loop with a feed nozzle directed downward, which improves contact between methanol and catalyst. Moreover, the outlet of the riser must be higher than the outlet of the nozzle at the highest point of the loop to ensure that the catalyst is steadily fluidized. The gas velocity in zone I should be controlled within the operating conditions of a bubbling or turbulent fluidization bed. The top of this bed is linked to a fast fluidization or conveying bed by reducing the diameter of the reactor. Consequently, the gas velocity in zone II is much larger and the residence time is much shorter. The low solid concentration can also contribute to reducing the content of oxy-compounds in the resultant gasoline. The designed reactor meets the theoretical requirement for methanol conversion and product distribution.

3. Reaction Performance in the Multi-regime Reactor

This section characterizes the methanol conversion and product distribution over the ZSM-11 catalyst in the novel reactor unit.

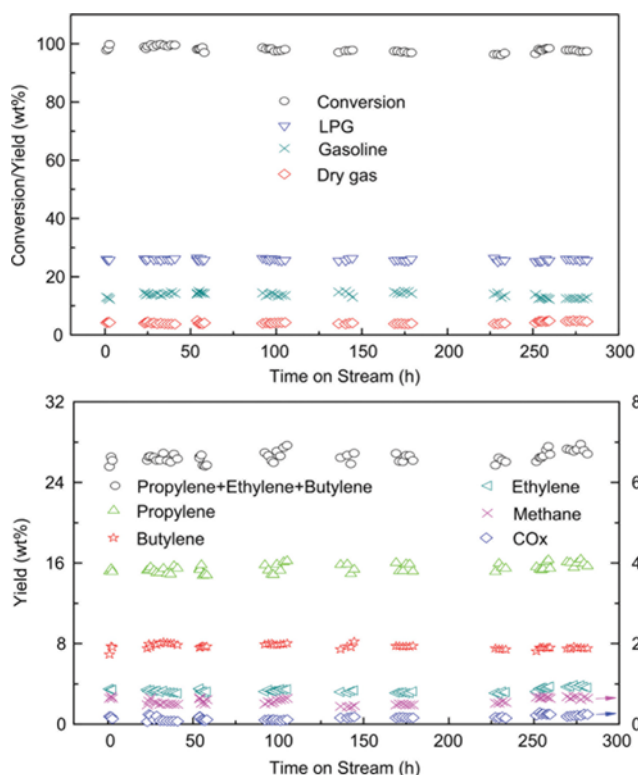


Fig. 6. Methanol conversion and product distribution vs. time over ZSM-11 catalyst in the novel multi-regime reactor.

Experiments were carried out with a catalyst regenerated at 650 °C and at a reaction temperature of 500 °C for 300 h; relevant results are presented in Fig. 6.

Under the experimental conditions, the average gas velocity in zone I was 0.8 m/s and the flow behavior was that of a turbulent dense bed [35]. Moderate gas velocity ensured adequate contact opportunities between methanol molecules and catalyst active sites, as reflected by the high levels of methanol conversion in Fig. 6, varying slightly from 96.1 wt% to 99.9 wt% over a 300 h test. After reaction, gas products and part of the catalyst entered zone II. The decrease in reactor diameter led to an increase in gas velocity in this zone (8.5 m/s). The flow behavior here was that of a conveying bed. High gas velocity and short residence time in zone II lessened secondary reactions, thereby achieving higher propylene, butylene, and ethylene yields than those observed in the bubbling bed described before. Hydrogen transfer in this zone was inhibited by the low density of the catalyst and weak adsorption ability of light olefins. Overall, the propylene, ethylene, butylene, and gasoline yields fluctuated steadily and remained relatively constant at about 15.5, 3.4, 7.8, and 13.8 wt%, respectively; the yields of methane and CO_x were relatively low. These results demonstrated the outstanding potential of the reactor and catalyst for commercial applications.

4. Proposed Novel PGFM Process

Utilizing the concept and experimental results obtained from the novel reactor, a PGFM process was proposed for maximizing propylene and gasoline production. In the process, high gas-solid contact in the reaction zone between methanol and catalyst, rapid transfer of gas products, and low catalyst density after reaction are achieved.

Compared with the Lurgi MTP process and UOP/HYDRO MTO process, the separation of products in our process avoids the complicated separation system in the processes described before and can make full use of the absorption-stabilization system of the FCC process. Moreover, because of the high dry gas yield and energy consumption for cryogenic separation of ethylene in Lurgi's MTP process, in the PGFM process, the dry gas does not need to be separated and can directly be used for producing styrene.

In the conventional Mobile MTG process [36], the content of paraffins, naphthenes, aromatics, and olefins in gasoline is 53.0, 9.0, 26.0, and 12.0 wt% (see Table 3), respectively; thus it is challenging to increase the octane number of the gasoline or obtain a good additive for gasoline. Compared with the gasoline composition of the MTG process, the product of the PGFM process contains a large amount of light olefins, which cannot meet environmental requirements and current standard specification. An option is to transfer the olefins in gasoline and C₄ olefins to the value-added products through etherification. For instance, isopentene (20.2 wt% in gasoline), which dominated in the C₅ olefins, is an excellent feedstock for producing tert amyl methyl ether (TAME) - a good additive for gasoline with high octane number. In addition, reprocessing gasoline and/or C₄ olefins for further cracking is also a possible alternative to reduce the olefin content in gasoline and utilize C₄ olefins to produce light olefins [37,38]. Compared with reprocessing the whole gasoline fraction, reprocessing is performed only on the fraction rich in short olefins, which is more energy efficient

Table 3. The Composition of Gasoline in PGFM and MTG processes

Carbon number ^a	PGFM								Mobile MTG
	5	6	7	8	9	10	11	Σ	
Paraffin	10.22	8.72	3.05	0.3	0.17	0.07	0.05	22.7	53.0
Naphthene	0.80	2.11	0.28	0.14	0.09	0.00	0.02	3.4	9.0
Aromatic	-	0.88	1.09	7.01	4.47	0.98	0.48	14.9	26.0
Olefin	33.52	20.57	3.20	1.52	0.14	0.01	0.00	59.0	12.0

^aThe contents of C₁₁ are less than 0.1 wt% that are not shown in the table

[39]. The heavy gasoline fraction with concentrated aromatics can be retained in the product to maintain a high octane number for further application. Etherification or reprocessing of the gasoline depends on the current situation of the plant, which makes the process more flexible.

In sum, our PGFM process can be implemented easily in the FCC process. It successfully solves the problems of high alkane content in LPG and low octane number of gasoline in the MTG process and of complicated reaction-regeneration-separation systems in Lurgi's MTP process. The ratio of propylene and gasoline can be regulated through operating conditions in the novel reactor, depending on the market demand and price of the two products.

5. PGFM Process Development

5-1. Evaluation of the Reprocessing of C₄ Olefins

To evaluate the promoting effect of the reprocessing of higher alkenes on propylene and gasoline production, an experiment of butylene reprocessing and comprehensive comparison with a routine process was conducted. Typical product distribution in the novel reactor showed that C₄ olefins yields approached 8.0 wt%. Thus, in the experiment of co-feeding methanol and C₄ olefins, the content of C₄ olefins was about 8.0 wt%. The experimental conditions were the same as that in the multi-regime reactor.

After co-feeding with C₄ olefins, methanol conversion was maintained at levels similar to those in the routine process (see Table 4). Increased yields of propylene and gasoline might be primarily attributed to C₄ olefins reprocessing. After reprocessing of C₄ olefins in the riser bottom, methanol was injected and methylated with butylenes, which consequently promoted the production of gasoline. C₄ olefins could also be cracked following a dimerization-cracking mechanism [40]; i.e., catalyzed by acid sites, two C₄⁺ mol-

ecules first dimerize to a C₈ species and then crack to a C₃⁺ and a C₅⁺ molecule or to two C₃⁺ molecules and a C₂⁺ molecule. The results showed that the deep cracking of a C₈ molecule to two C₃⁺ molecules and a C₂⁺ molecule was inhibited in our study. Thus, propylene yield during the reprocessing of C₄ olefins was further increased (from 15.5 wt% to 16.6 wt%), and C₄ olefins are an excellent feedstock for converting methanol into propylene and gasoline [41]. When applied in the industrial equipment, C₄ olefins could be separated from oil vapor through a fractionation system and be recycled into the riser bottom.

5-2. PGFM Process with the Reprocessing of Light Gasoline and C₄ Olefins

C₄-C₆ olefins may be regarded as an excellent feedstock for producing propylene and gasoline [40,42]. Thus, light gasoline and C₄ olefins from the fractionation system can be recycled into the riser. The MTO reaction is exothermic; thus, the regenerated catalyst must be cooled through extra cooling sections. Because the oligomerization and cracking reactions for olefins are endothermic, the recycled light gasoline and C₄ olefins can cool the regenerated catalyst first and should be fed before methanol injection to avoid the adsorption competition. C₄ olefins are suggested to be recycled even before light cycle gasoline (LCG) injection and substitute for partial lifting steam, thereby reducing thermal load and operating costs. A scheme of the PGFM process with light gasoline and C₄ olefins reprocessing is shown in Fig. 5(b).

All of the findings thus far support the development of a PGFM process for maximizing propylene and clean gasoline production. Compared with the routine MTP and MTG processes, the PGFM process development involves production of propylene and clean gasoline. Light gasoline and C₄ olefins produced can be well utilized through etherification or reprocessing.

CONCLUSIONS

Methanol conversion over a hierarchical ZSM-11 catalyst demonstrated that operating conditions and flow behavior determined the methanol conversion and the selectivity of olefins. Thus, high gas-solid contact efficiency and low solid back-mixing were necessary. Based on the reaction features of methanol, a novel multi-regime reactor with a dense-phase fluidized turbulent/bubbling bed and a dilute-phase conveying/fast fluidization bed reactor was designed. This reactor significantly enhanced the gas-solid contact and separation of products and catalyst, demonstrating great potential for commercial applications. A novel PGFM process in which light gasoline and C₄ olefins were reprocessed or etherified was also

Table 4. Product distribution of methanol and co-feeding of methanol and C₄ olefins in the novel reactor

Item	Methanol	Co-feeding
Conversion	99.5	99.4
Product yield (wt%)		
CH ₄	0.6	0.5
CO _x	0.2	0.1
Ethylene	3.4	3.4
Propylene	15.5	16.6
Butylenes	7.8	7.7
Alkanes	2.7	0.6
Gasoline	13.2	14.2

proposed for maximizing propylene or clean gasoline production.

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