



Original Paper

Fischer-Tropsch wax catalytic cracking for the production of low olefin and high octane number gasoline: Process optimization and heat effect calculation

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ABSTRACT

To produce low olefin gasoline with high octane number by Fischer-Tropsch (F-T) wax fluid catalytic cracking (FCC) process, operating conditions optimization were carried out in the pilot-scale riser and turbulent fluidized bed (TFB) FCC unit. The experimental results in the riser indicated that under the condition of low reaction temperature and regenerated catalyst temperature, large catalyst-to-oil weight ratio (C/O) and long reaction time, the gasoline olefin content could be reduced to 20.28 wt%, but there is large octane number loss owing to a great loss in high octane number olefin. Therefore, a novel FCC process using the TFB reactor was proposed to strengthen the aromatization reaction. The reaction performance of TFB reactor were investigated. The result demonstrated that the TFB reactor has more significant effect in reducing olefins and improving aromatics. At the expense of certain gasoline yield, the gasoline olefin content reduced to 23.70 wt%, aromatics content could increase to 26.79 wt% and the RON was up to 91.0. The comparison of reactor structure and fluidization demonstrated that the TFB reactor has higher catalyst bed density. The reaction heat and coke combustion heat was calculated indicating the feasibility of its industrial application of the TFB process.

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1. Introduction

With the first resource distribution characteristics of “rich coal, poor oil, and low gas”, China has committed to make full use of coal liquefaction technology to alleviate the dependence on petroleum resources (Liu et al., 2010). The low temperature Fischer-Tropsch (F-T) synthesis process in coal indirect liquefaction technology in China would produce almost 50 wt% of F-T wax (Dry, 2002). Compared with the production of refined F-T wax and lubricant base oil, the production of clean fuels from F-T wax has a greater market demand. The current F-T wax process technology for light fuel oil includes hydrocracking and fluid catalytic cracking (FCC) processes. The hydrocracking process has high hydrogen consumption and high plant energy consumption (Leckel, 2005). Diesel as the main hydrocracking product has higher cetane number but worse low temperature properties, besides the diesel market

demand has been saturated in China (Šimáček et al., 2013; Hodala et al., 2016; Li et al., 2020). The FCC process with high operational flexibility could produce high value-added gasoline fraction. Therefore, the F-T wax FCC process could better meet the market demand and obtain greater economic benefits.

The FCC performance of F-T wax had been investigated, studies have shown that F-T wax is easy to crack and has a high gasoline yield. But the FCC gasoline contains high olefin content and low aromatic content (Dupain et al., 2006; Kubička and Černý, 2012; Malleswara et al., 2012). Nowadays, the worldwide has higher quality standards for the vehicle gasoline, in which China requires further reduction of olefin content in gasoline (Hajbabaie et al., 2013; He et al., 2021). Considering the high proportion of FCC gasoline in the gasoline blending pool in China (Fang et al., 2019), the F-T wax FCC faces a great challenge to in situ reduce gasoline olefin.

In the past decades, diverse FCC processes had been developed to reduce gasoline olefin including maximizing i-paraffin (MIP) process (Xu et al., 2001; Liu et al., 2017), flexible dual-riser FCC (DFCC) process (Meng et al., 2004), two-stage riser FCC (TSR FCC)

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process (Shan et al., 2001), and subsidiary riser FCC (SRFCC) process (Bai et al., 2004; Gao et al., 2005). These processes had the same characteristics of two reaction zones with different reaction conditions for cracking heavy oil and upgrading gasoline simultaneously. The different feature is that the two reaction zones are in the one reactor or two reactors. Dupain et al., (2006) demonstrated that a highly paraffinic feedstock is more prone to crack than conventional feedstock, as well as its gasoline was inclined to overcrack (Fonseca et al., 2012). Therefore, the long process route of two reaction reactors maybe inevitably results a great loss of gasoline yield for F-T wax FCC. Thence, only one reactor was considered to process F-T wax both for cracking of feedstock and upgrading of gasoline with proper reaction conditions. Studies have shown that optimizing reaction conditions is conducive to olefin degradation (Wang et al., 2008a, b; Ouyang et al., 2009).

Apart from reaction conditions, the reactor type also influences gasoline olefin reduction process. Different reactors, such as riser, fast bed and riser + turbulent fluidized bed (TFB) reactors were used in the second reaction zone of these olefin-reduction FCC processes. Moreover, the study showed that the cracking performance of F-T fraction diverse along with a fixed fluidized bed (Yang et al., 2011; Fan et al., 2014), fixed bed reactor (Komvokis et al., 2012) and a riser reactor (Lappas et al., 2011). Different reactors with various characteristics could promote different reactions, the comparison hadn't done in the previous literature.

The heat balance of FCC unit mainly included reaction heat, coke combustion heat, feedstock vaporization heat, oxygen heating heat, water vaporization heat and cooling and condensation heat (Pekediz et al., 1997). The coke combustion heat is used as the heating source. The F-T wax FCC yielded little coke, and then little heat was generated in regenerator. During the process optimization, operation conditions, product distribution and composition changed dramatically and resulted in significant variation in reaction heat of FCC reactor. If the F-T wax has a high degree of cracking and calls for more heat, the heat balance of FCC unit will be destroyed. Therefore, the reaction heat plays an important role in determining the heat balancing of FCC unit, and should be taken into consideration while optimizing the process.

In this work, faced with the high olefin content in the gasoline, operating conditions were firstly optimized on the pilot-scale riser reactor to explore the relationship of octane number loss and olefins content reduction. Afterward, a novel process for the production of low olefin and high octane number gasoline by F-T wax catalytic cracking was developed. The existing riser device was modified into TFB device. The reaction conditions of the TFB reactor were optimized. And the flow regimes, reactor structure and reaction performance of TFB reactor and riser reactors were compared. Finally, reaction heat and coke combustion heat of the TFB reactor were calculated.

2. Experimental

2.1. Feedstock and catalyst

The feedstock (F-T wax) used in the experiments came from the low-temperature F-T synthesis process of Shenhua Group Corporation Limited. The F-T wax is composed of 64.54 wt% n-paraffin, 14.16 wt% i-paraffin and 21.30 wt% olefin. The carbon number distribution of F-T wax is C₁₅–C₈₉. The main properties of F-T wax are shown in Table 1. As a comparison, the properties of Daqing vacuum gas oil (VGO) (Chen and Xu, 2004), a conventional petroleum-based paraffinic FCC raw material, are also listed in Table 1. The comparison shows that the F-T wax has high hydrogen element content. The hydrogen element content is an important indicator to evaluate the cracking performance and conversion of the feedstock. For

Table 1
Main properties of F-T wax and Daqing VGO.

Property	F-T wax	Daqing VGO
Density (20 °C), g·cm ⁻³	0.8873	0.8597
Pour point, °C	84	44
Refractive index n _D ²⁰	1.4638	1.4616
Element, wt%		
C	85.26	85.63
H	14.54	13.45
O	0.2	–
S/N	–/–	0.077/0.058
Boiling range, °C		
Initial boiling point	232	316
10%	320	357
30%	381	390
50%	445	419
70%	521	454
90%	623	508
Dry point	709	537

Note: Oxygen element content in Daqing VGO was not mentioned in the reference.

example, for high paraffin-based raw materials, such as Daqing VGO, the conversion could increase by 8.6% for each 1 wt% increase in hydrogen element content (Chen and Xu, 2004). Besides, the F-T wax has a wide distillation range distribution and heavier fraction, resulting the higher density of F-T wax. As the molecular weight increases, the molecular chain length increases and the cracking performance of the molecule increase obviously (Corma et al., 1994). Therefore, the F-T wax could be expected to have good cracking performance and higher conversion than that of conventional paraffin-based raw materials. Compared with the Daqing VGO, the F-T wax does not contain sulfur and nitrogen elements, and it could directly produce clean fuel oil without desulfurization and denitrogenation processes.

The catalyst used in the experiments was an equilibrium FCC catalyst with appropriate cracking activity and high hydrogen transfer activity. The transition metal elements for dehydrogenation, such as Zn, Ni, M1 and M2 from the periodic table were used to modify HY and ZSM-5 zeolites to strengthen the aromatization activity. The same catalyst was used for two processes, so the specific properties of catalyst was not discussed in this paper, and the main properties are shown in Table 2.

2.2. Experimental equipment and operating procedure

2.2.1. Pilot-scale riser experimental unit

The investigation of F-T wax FCC performance was conducted on a continuous reaction-regeneration pilot-scale riser FCC unit (Gao et al., 2012; Sheng et al., 2018). The operation procedure was divided into several steps: (1) at the bottom of the riser, the pre-heated feedstock reacted with the regenerated catalyst and were lifted to the settler; (2) in the settler, oil vapor and spent catalyst were separated, the oil vapor went to the condensation system, the spent catalyst was stripped and then went to the regenerator; (3)

Table 2
Characteristics of catalyst for FCC.

Property	Value	Property	Value
Pore volume, cm ³ /g	0.24	M2 content, wt%	0.1–3.0
Surface area, m ² /g	96	Particle size distribution, wt%	
Micro-reactivity index	57	20–40, μm	12
Bulk density, g/cm ³	0.84	40–80, μm	54
Zinc content, wt%	0.1–3.0	80–105, μm	22
Ni content, wt%	0.1–3.0	> 105, μm	12
M1 content, wt%	0.1–3.0	–	–

the coke on the spent catalyst were burnt, the regenerated catalyst could go to the bottom of the riser for the next reaction. In this paper, the mass balances of the experiments were all between 97 and 100 wt%.

2.2.2. Structure comparison of the riser and TFB reactors

In this work, the influence of reactor types on the F-T wax FCC performance was discussed. Thus the pilot-scale riser reactor was modified to realize the transformation from the riser reactor to the TFB reactor. The structure comparison of the riser and TFB reactors was shown in Fig. 1.

As shown in Fig. 1, modification of the TFB reactor was based on the available riser FCC unit. The distribution plate and feedstock nozzle were added to the bottom of the fluidized bed. The operating process of the TFB is shown below. The catalysts were lifted by water vapor through the riser and then reached the settler. Amount of catalysts were accumulated on the distribution plate to form catalysts stack. The feedstock vapor flow upward through the feedstock nozzle and drove the catalyst to flow upward. Meanwhile catalyst could drop off from the sidewall. Thus, the TFB reactor was formed and fluidized. The reaction zone of the riser is a long riser, and the reaction zone of the TFB reactor is the grey area inside the settler as seen in Fig. 1.

After modification, the reactor size and gas velocity of both two reactors were compared. The diameter of the riser reactor is 18 mm and the height is 5.5 m. The gas velocity in the riser reactor is about 0.78–4.24 m/s. While the diameter of the TFB reactor is 49 mm and the height is 0.65 m. The gas velocity in the TFB reactor is about 0.16–0.20 m/s.

2.3. Product analytical methods

The volume of the cracked gas is measured by a flow meter. The components of the cracked gas are analyzed by GC 9790 II gas chromatography with dual detectors. The TCD detector detects H₂, O₂, N₂, CO and CO₂ components, and the FID detector detects gas hydrocarbons. Finally, the volume fraction of each component is

converted into mass fraction through the ideal gas state equation. The gas components will contain a certain amount of C₅⁺ components, which are usually counted into gasoline fraction.

The weight of the liquid product is obtained by weighing. The distillation range distribution and mass yield of the liquid product are analyzed by Agilent 6890N gas chromatography using ASTM D2887 method. The liquid product could be divided into gasoline (IBP ~ 200 °C) and diesel (200–350 °C) according to boiling point. The ASTM D5134 method is used to analyze the gasoline components in the liquid product, and the research octane number (RON) of the gasoline is calculated according to the mass content and the RON of a single hydrocarbon.

The volume of smoke gas from the regenerator is measured by a flow meter, and the volume fraction of CO₂ and CO in the smoke gas is analyzed by an infrared online analyzer. The volume content of CO₂ and CO is converted into mass content through the ideal gas state equation to obtain the mass content of coke.

A/H index is defined as in Eq. (1) to express the ratio of the aromatics generation reactions to hydrogen transfer reactions, in which $m_{\text{aromatics}}$, $m_{\text{n-paraffin}}$, and $m_{\text{i-paraffin}}$ represent the mass percentage of aromatics, n-paraffin and i-paraffin in gasoline, respectively.

$$A/H = \frac{m_{\text{aromatics}}}{m_{\text{(n-paraffin+i-paraffin)}}} \quad (1)$$

2.4. Heat effect calculation method

2.4.1. Heat of the individual reaction

The standard molar formation enthalpy of individual hydrocarbon is calculated by an empirical Eq. (2), in which a_1 , b_1 and c_1 are obtained from handbook (Wang, 2002). The reaction enthalpy change of each reaction is calculated by Eq. (3), where μ is the stoichiometric coefficient of each substance in the chemical reaction formula.

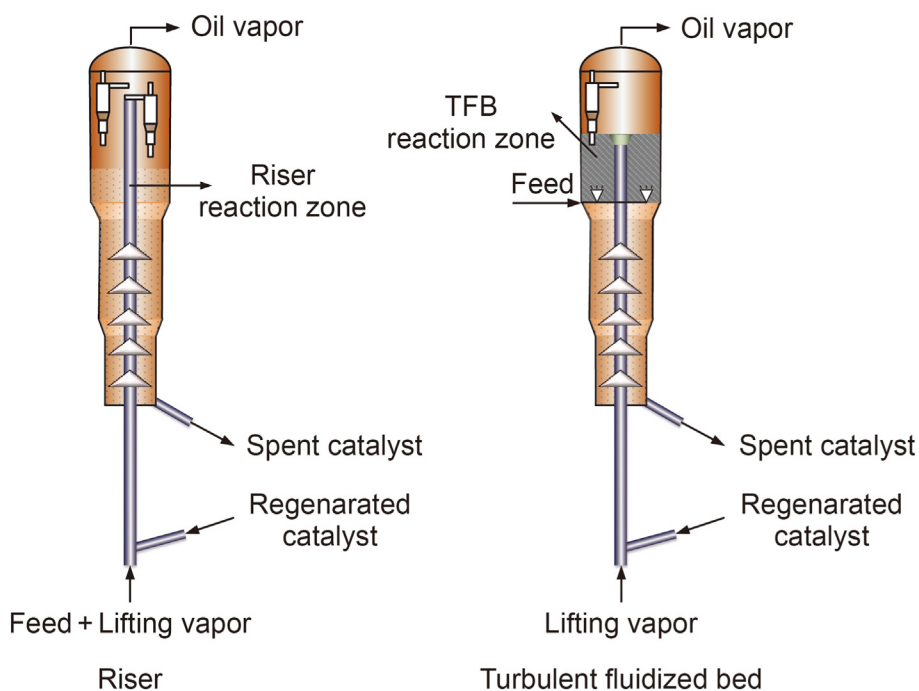


Fig. 1. Schematic diagram comparison of riser and TFB reactor.

$$\Delta H_f^\ominus = a_1 + b_1 T + c_1 T^2 \quad (2)$$

$$\Delta_r H_T = \sum \mu \Delta H_f^\ominus \quad (3)$$

2.4.2. Heat of the reaction system

For the F-T wax FCC process, the conversion of feedstock is high, and the products are mainly light hydrocarbons such as liquefied petroleum gas (LPG) and gasoline, and more accurate composition analysis data could be obtained. Therefore, the product analysis method was adopted for the reaction heat calculation. The principle of this method is to use the difference of the formation enthalpy between the product and the reactant, as shown in Eq. (4) (Pekediz et al., 1997). In Eq. (4), Q_R is the reaction heat of the system, kJ/kg; $\Delta_r H_{Pi}$ is the formation enthalpy of the i component in the product, kJ/kg; $\Delta_r H_F$ is the formation enthalpy of the feedstock, kJ/kg; x_i is the mass fraction of the i component in the product.

$$Q_R = \sum x_i \Delta_r H_{Pi} - \Delta_r H_F \quad (4)$$

C_5 and above components in gas product are included in the gasoline fraction. The gasoline fraction is lumped based on same carbon number and hydrocarbon composition according to PIONA data. For example, 2-methylpentane is selected to represent C_6 i-paraffin, and 1-hexene is selected to represent n- C_6 olefins. The gas chromatography-mass spectrometer analysis of diesel demonstrated that it mainly contained paraffin, naphthene, monocyclic aromatics and polycyclic aromatics. Therefore, n-hexadecane, decylcyclohexane, hexyltetrahydronaphthalene and 1-pentyl-naphthalene were selected to simulate the diesel fraction, respectively. Considering a small amount of heavy oil and coke are produced, formation enthalpies of anthracene and pyrene are used to replace the formation enthalpy of heavy oil and coke.

3. Results and discussion

3.1. FCC performance of the F-T wax in the riser reactor

The high proportion of high boiling point components and higher density of F-T wax indicated that the F-T wax contains a lot of long chain hydrocarbons. Generally, the longer the chain length, the higher the activity. Therefore, this work firstly investigated the feasibility of F-T wax to produce low olefin and high octane number gasoline on a pilot-scale riser reactor.

3.1.1. FCC performance of the F-T wax

The effect of reaction conditions on product distribution and product quality has been discussed in the previous literature (Wang et al., 2009; Jarullah et al., 2017; Miao et al., 2021). According to the literature, low reaction temperature and regenerated catalyst temperature were beneficial to reduce the over-cracking of gasoline. High catalyst-to-oil weight ratio (C/O) with more acid sites and long reaction time could better promote the deep conversion of gasoline olefin. The main intent here is to change the reaction

conditions to produce more low olefin and high octane number gasoline. Therefore, the effect of single variable of reaction conditions on the performance of F-T wax catalytic cracking has not been explored in detail. The specific reaction conditions of the pilot-scale riser reactor are shown in Table 3.

The product distribution, gasoline composition, A/H index and RON of the F-T wax catalytic cracking in the pilot-scale riser reactor under different conditions are shown in Fig. 2. It could be found that the dry gas yield is lower in the F-T wax FCC process compared with the dry gas yield of 3.5–4.5 wt% of paraffinic-base VGO catalytic cracking (Wang et al., 2013). That indicated the rare occurrence of thermal cracking reaction and protolytic cracking reaction. The olefin from feedstock would preferentially be adsorbed by Brønsted acid sites to form carbenium ions and undergo β -scission route. The n-paraffin and i-paraffin in the feedstock were mainly be initiated through chain transfer (Mehla et al., 2019). As in the literature (Malleswara et al., 2012), high LPG and gasoline yields could be obtained under all experimental conditions indicating that F-T wax is easy to crack. In Test 1, under the conditions of reaction temperature 490–500 °C, reaction time 2.5–3.0 s, C/O 4.0–4.5 and regenerated catalyst temperature 690–700 °C, the conversion could reach 95.85%. The cracking reaction was dominant reaction in the F-T wax FCC process under this condition. The yields of gasoline and LPG could reach 50.40 wt% and 42.94 wt%, respectively. Compared with heavy oil FCC, there was little tendency to form coke during the F-T wax FCC reaction process. And only 1.30 wt% coke was yielded. The olefin content in the gasoline was as high as 58.39 wt%. As the F-T wax didn't not contain cyclic structures, any cyclic hydrocarbons were formed through secondary reactions. Under this reaction conditions, secondary reactions were less occurred. The A/H index was 0.283. The aromatics content in the gasoline was only 8.61 wt%. Due to the large amount of high octane number olefins, the RON is as high as 92.0.

The subsequent tests gradually lowered the reaction temperature and the regenerated catalyst temperature. In Test 2, due to the shortened reaction time, second cracking reactions were largely reduced. Therefore, LPG was only 26.92 wt%, and the gasoline was largely maintained with a yield up to 61.89 wt%. But the gasoline olefin content was still very high. Test 3 and Test 4 significantly increased the reaction time and C/O, and had a good effect on improving the gasoline hydrocarbon composition, especially Test 4. In Test 4, the yield of LPG decreased to 27.54 wt%, and the gasoline yield increased to 60.14 wt%. Due to the increase of reaction time and C/O, the secondary reactions were further promoted in which the hydrogen transfer reactions increased prominently. Compared with Test 1, the coke yield increased from 1.30 wt% to 4.28 wt%. The gasoline olefins were reduced from 58.39 wt% to 20.28 wt%, and the aromatics content increased from 8.61 wt% to 13.58 wt%. Olefins could mainly convert to i-paraffin at this condition and the i-paraffin content increased to 56.26 wt%. Since the growth rate of aromatics content is much lower than that of i-paraffin content, the A/H index was finally decreased to 0.217. And the RON was further reduced to 79.1.

In general, the experiments demonstrated that reaction conditions optimization has a good effect on the improvement of gasoline yield and the reduction of gasoline olefin. Besides gasoline RON

Table 3
Reaction conditions of the F-T wax FCC in the riser reactor.

Project	Test 1	Test 2	Test 3	Test 4
Reaction temperature, °C	490–500	470–480	420–430	400–410
Reaction time, s	2.5–3.0	1.3–1.5	6.0–7.0	6.0–7.0
C/O, kg/kg	4.0–4.5	4.5–5.0	9.0–10.0	15.0–16.0
Regenerated catalyst temperature, °C	690–700	680–690	550–560	430–440

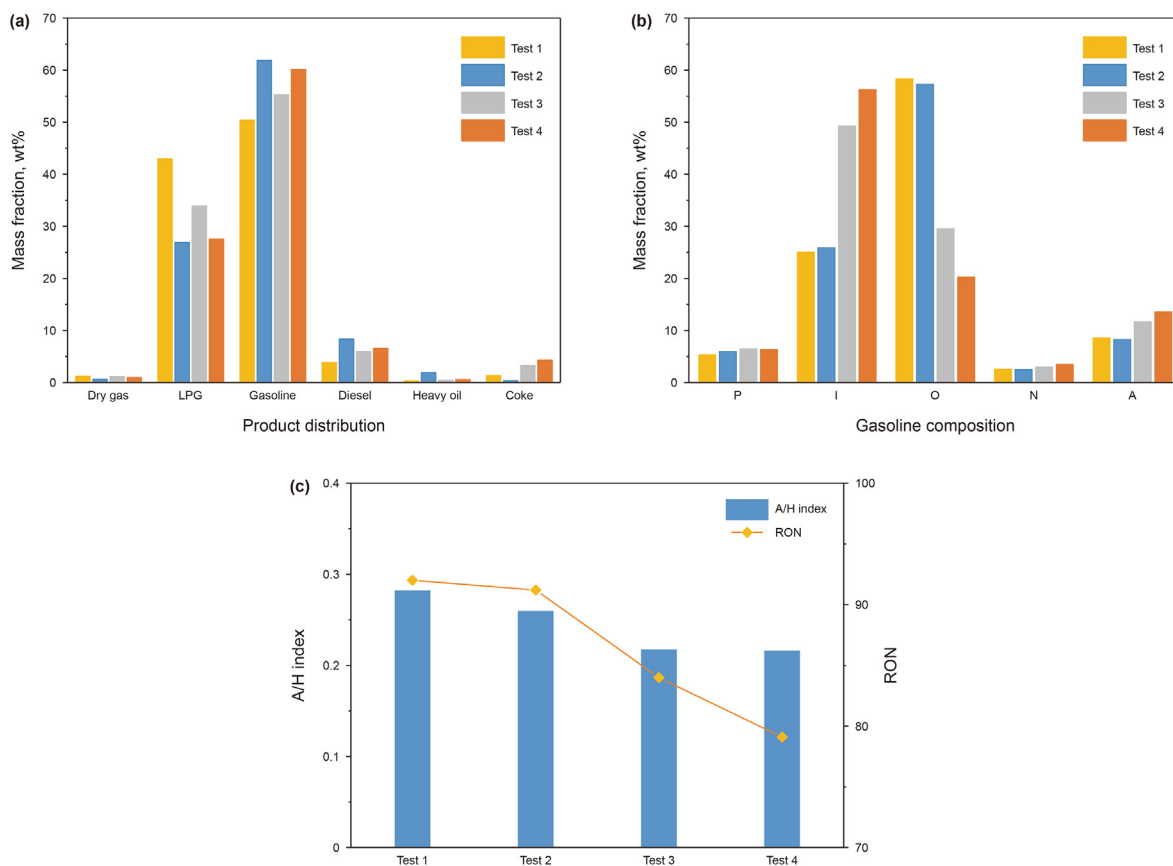


Fig. 2. F-T wax catalytic cracking in the riser reactor: (a) product distribution; (b) gasoline composition; (c) A/H index and RON.

and gasoline olefin are greatly related. The reduction of gasoline olefin will result in the decrease of gasoline RON.

3.1.2. Analysis of the olefin conversion route and difficulty of the production of low olefin and high octane number gasoline

Higher gasoline yield and lower gasoline olefin content could be obtained by optimizing riser reaction conditions. But the RON decreased a lot. That's related to the olefin conversion route and the difference of hydrocarbons octane number (Ouyang et al., 2009; Liu et al., 2016). The gasoline olefin carbon number distribution and olefin hydrocarbon composition in the Tests 1–4 of the riser reactor

were studied as shown in Fig. 3. As shown in Fig. 3(a), the gasoline olefins are mainly composed of C₅, C₆ and C₇ hydrocarbons, and the sum of C₅–C₇ olefins in Test 1–4 accounting for 89.69 wt%, 89.50 wt%, 87.36 wt% and 82.53 wt% of gasoline olefins, respectively. And it could be seen from Fig. 3(b) that gasoline olefin hydrocarbon composition was mainly consisted of i-olefin and n-olefin. Therefore, n-olefins and terminal monomethyl i-olefins of C₅ and C₆ could be chosen to study the olefin conversion route and product octane number variation as shown in Fig. 4 (Chica and Corma, 1999).

It could be seen from Fig. 4 that the contribution to the RON of

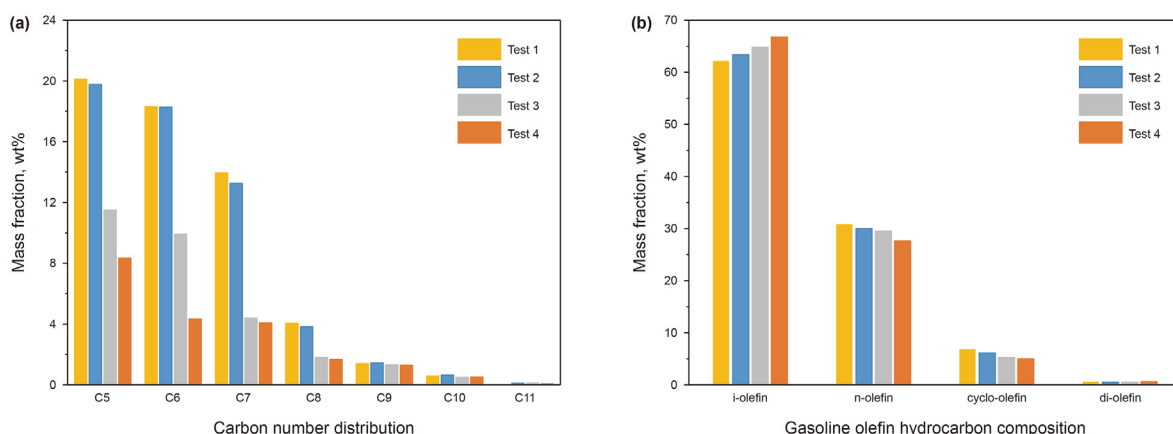


Fig. 3. Gasoline olefin: (a) carbon number distribution; (b) hydrocarbon composition.

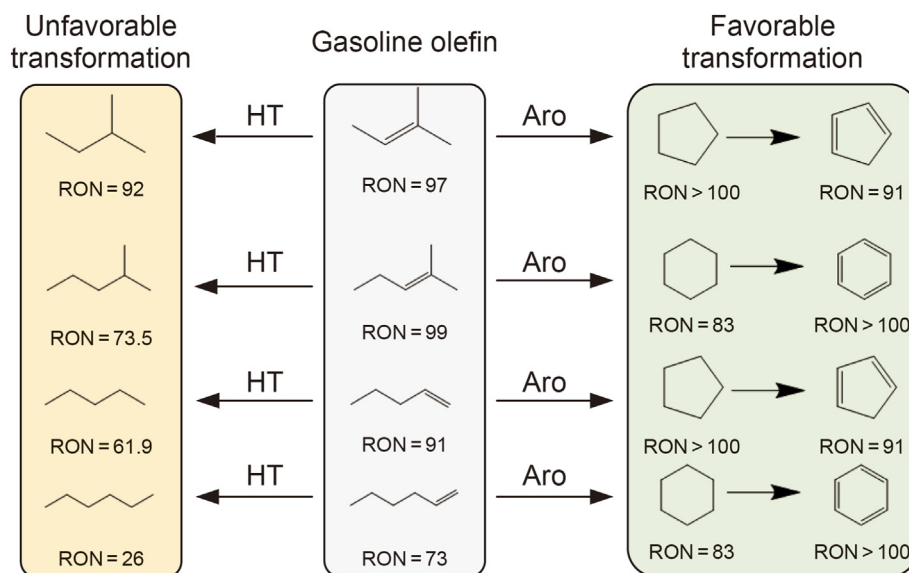


Fig. 4. Gasoline olefin conversion route and octane number variation.

various hydrocarbons in gasoline is obviously different. With the gasoline composition changed, the gasoline RON changed a lot. According to the products octane number, olefin conversion could be divided into favorable and unfavorable reactions route. Hydrogen transfer reaction is unfavorable reaction for gasoline octane number and will produce a lot of saturated hydrocarbons with low octane number. While the aromatization reactions are more favorable to the gasoline octane number. Therefore, not only the extent of olefin conversion, but also the direction of olefin conversion that affect the production of low olefin and high octane number gasoline. In this work, it is necessary to strengthen aromatization reactions.

The olefin production and conversion reactions were studied from the perspective of thermodynamics. The reaction enthalpy change of typical reactions were calculated as shown in Table 4. The results showed that these reactions had diverse heat effect. The strong endothermicity of aromatization reactions and strong exothermicity of hydrogen transfer reactions made it difficult to optimize temperature. The experimental data and calculated results in this research demonstrated that low temperature was only beneficial to hydrogen transfer and isomerization reaction. Thus a lot of *i*-paraffin were produced. The increase of high octane number aromatics was little. The thermodynamic calculation results and previous studies (Sharma et al., 1984) demonstrated that more aromatics are formed at high temperature.

The formation of aromatics would undergo continuous dehydrogenation steps. Higher temperature and longer reaction time are conducive to the aromatization reaction while also promoting the cracking reaction. Studies showed that the strength of acidity

for cracking reactions are higher than secondary reactions (Xu et al., 2018). Considering the good cracking performance of the F-T wax, it's necessary to reduce the strong acid sites to intensify the secondary reactions. Wang et al. (2008a) demonstrated that the spent catalyst in the FCC gasoline reformation were deactivated selectively and the strong acid sites would be firstly covered by coke. The acid density of the coke deposit catalyst is reduced, and the hydrogen transfer is restricted. Reducing the average activity of the catalyst can be achieved not only through the pre-coking process, but also through the back-mixing of the catalyst in the reactor. Lu et al. (2007) demonstrated that the reactor with enlarged sized has the apparent characteristic of high solid density, low gas velocity and catalyst back-mixing. Therefore, further study was performed in the TFB reactor.

3.2. A novel FCC process of the F-T wax

The core of the FCC process is the reactor. The reactor type with different gas-solid contacting characteristics could directly affect the product distribution and quality. Here, the optimization of reactor type and reaction conditions had been implemented to intensify olefins conversion to high octane number components.

3.2.1. FCC performance of the F-T wax in the TFB reactor

Here, the reaction temperature, C/O, weight hourly space velocity (WHSV) and the regenerated catalyst temperature were optimized to improve gasoline yield and composition. The experimental conditions were shown in Table 5.

The product distribution, gasoline composition, A/H index and

Table 4

The reaction enthalpy change of different reactions in FCC process.

Reaction	Reaction heat, kJ·mol ⁻¹			
	500 °C	480 °C	420 °C	400 °C
$n\text{-C}_{13}\text{H}_{26}$ (1-Tridecene) \rightarrow $n\text{-C}_6\text{H}_{12}$ (1-Hexene)+ $n\text{-C}_7\text{H}_{14}$ (1-Heptene)	78.18	78.37	78.94	79.12
$n\text{-C}_7\text{H}_{14}$ (1-Heptene) \rightarrow C_3H_6 + $n\text{-C}_4\text{H}_8$ (1-Butene)	78.34	78.55	79.17	79.37
$n\text{-C}_7\text{H}_{14}$ (1-Heptene) \rightarrow $c\text{-C}_7\text{H}_{14}$ (Methylcyclohexane)	-92.64	-92.90	-93.55	-93.71
$3\text{C}_3\text{H}_6$ + $n\text{-C}_7\text{H}_{14}$ (1-Heptene) \rightarrow $3\text{C}_3\text{H}_8$ + C_7H_8 (Toluene)	-171.20	-170.97	-170.35	-170.16
$n\text{-C}_7\text{H}_{14}$ (1-Heptene) \rightarrow C_7H_8 (Toluene)+ 3H_2	216.46	216.45	216.17	215.99
$n\text{-C}_4\text{H}_8$ (1-Butene) \rightarrow $i\text{-C}_4\text{H}_8$ (Isobutene)	-16.09	-16.10	-16.13	-16.14

Table 5
Reaction conditions of F-T wax FCC in the TFB reactor.

Project	Test 5	Test 6	Test 7	Test 8
Reaction temperature, °C	480–500	460–480	450–475	430–450
WHSV, h ⁻¹	9.0–10.0	1.5–3.0	3.0–4.0	2.0–3.0
C/O	6.0–7.0	8.0–9.0	9.0–11.0	10.0–12.0
Regenerated catalyst temperature, °C	680–690	590–610	600–620	520–540

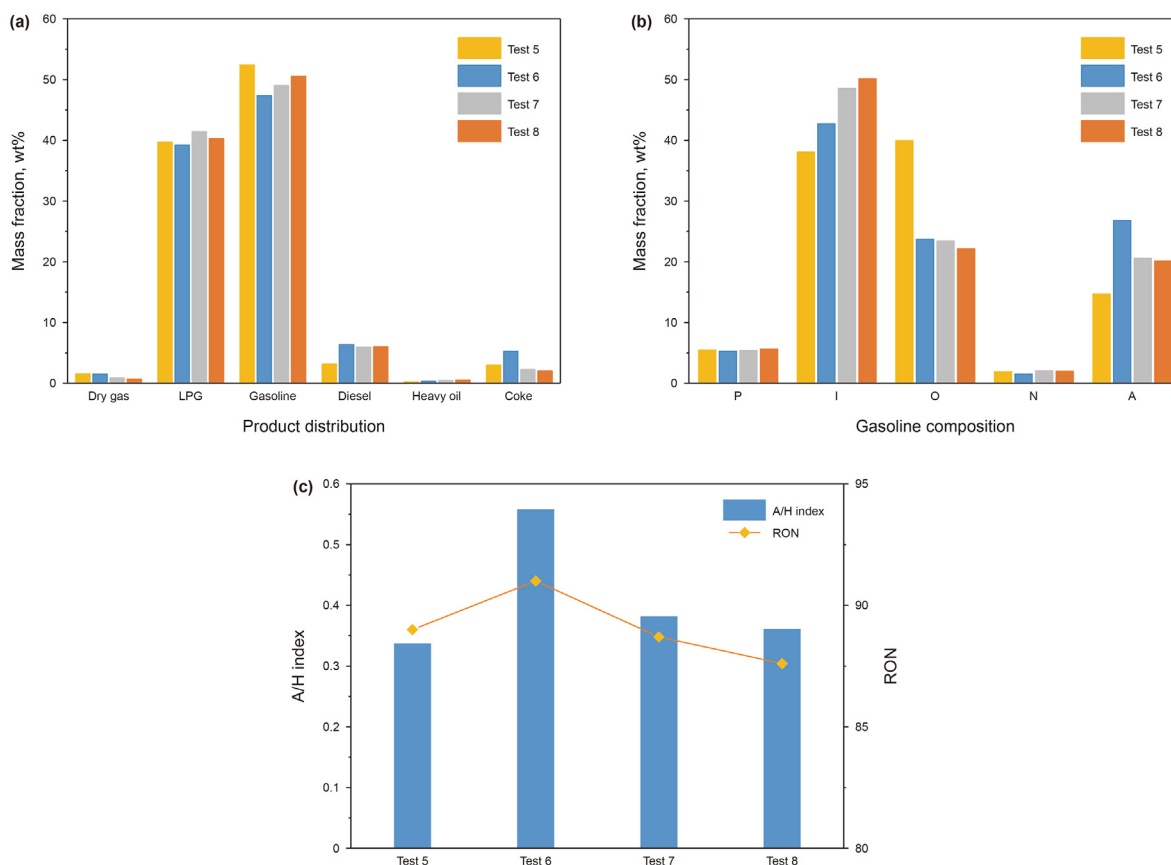


Fig. 5. F-T wax FCC in the TFB reactor: (a) product distribution; (b) gasoline composition; (c) A/H index and RON.

RON under the optimized conditions of the TFB reactor were shown in Fig. 5. It could be discovered that with the optimization of gasoline composition, the gasoline yield decreased to various degrees. In Test 5, under the conditions of reaction temperature 480–500 °C, WHSV 9.0–10.0 h⁻¹, C/O 6.0–7.0 and regenerated catalyst temperature 680–690 °C, the conversion could reach 96.61%. The yield of gasoline and LPG could reach 52.41 wt% and 39.69 wt%, respectively. The olefin content in the gasoline was 39.91 wt%. The A/H index was 0.337. The aromatics content in the gasoline was 14.68 wt%. In Test 6, the WHSV was reduced from 9.0–10.0 h⁻¹ to 1.5–3.0 h⁻¹, and the temperature of the regenerated catalyst was reduced from 680–690 °C to 590–610 °C. The reaction depth increased, the gasoline components transformed into heavier components. The gasoline yield reduced from 52.41 wt% to 47.35 wt%, and the coke yield increased from 2.96 wt% to 5.23 wt%. In Test 6, gasoline olefins reduced by nearly 16 wt%, and mainly converted into high octane number aromatic components. The A/H index increased from 0.337 to 0.558. Therefore, the gasoline RON of Test 6 was 91.0. Based on Test 6, Test 7 reduced the reaction temperature, and increased the regenerated catalyst temperature, WHSV and the C/O. The gasoline yield increased by 1.69 wt%. The reaction

conditions of Test 7 are also beneficial to promote the olefin conversion, but most olefins converted to i-paraffin. The A/H index decreased to 0.382, and the RON of Test 7 reduced to 88.7. Based on Test 7, Test 8 lowered the temperature and increased the C/O. The gasoline yield increased by 1.51 wt%, the LPG yield decreased by 1.18 wt%. The A/H index decreased to 0.361. And the RON of Test 4 was 87.6.

In summary, the TFB reactor has excellent performance in promoting the olefin conversion, especially the conversion to aromatics. Under the conditions of Test 6, low olefin and high octane number gasoline could be obtained at the expense of certain gasoline yield.

3.2.2. F-T wax FCC performance comparison of the riser and TFB reactors

In Test 4, olefins were preferentially transformed into i-paraffin in the riser reactor, while in Test 6, olefins were preferentially transformed into aromatics in the TFB reactor. To investigate the influence of the riser and TFB reactors on F-T wax FCC reaction performance, the carbon number distribution of olefin, i-paraffin and aromatics of Test 4 and Test 6 were compared, as shown in

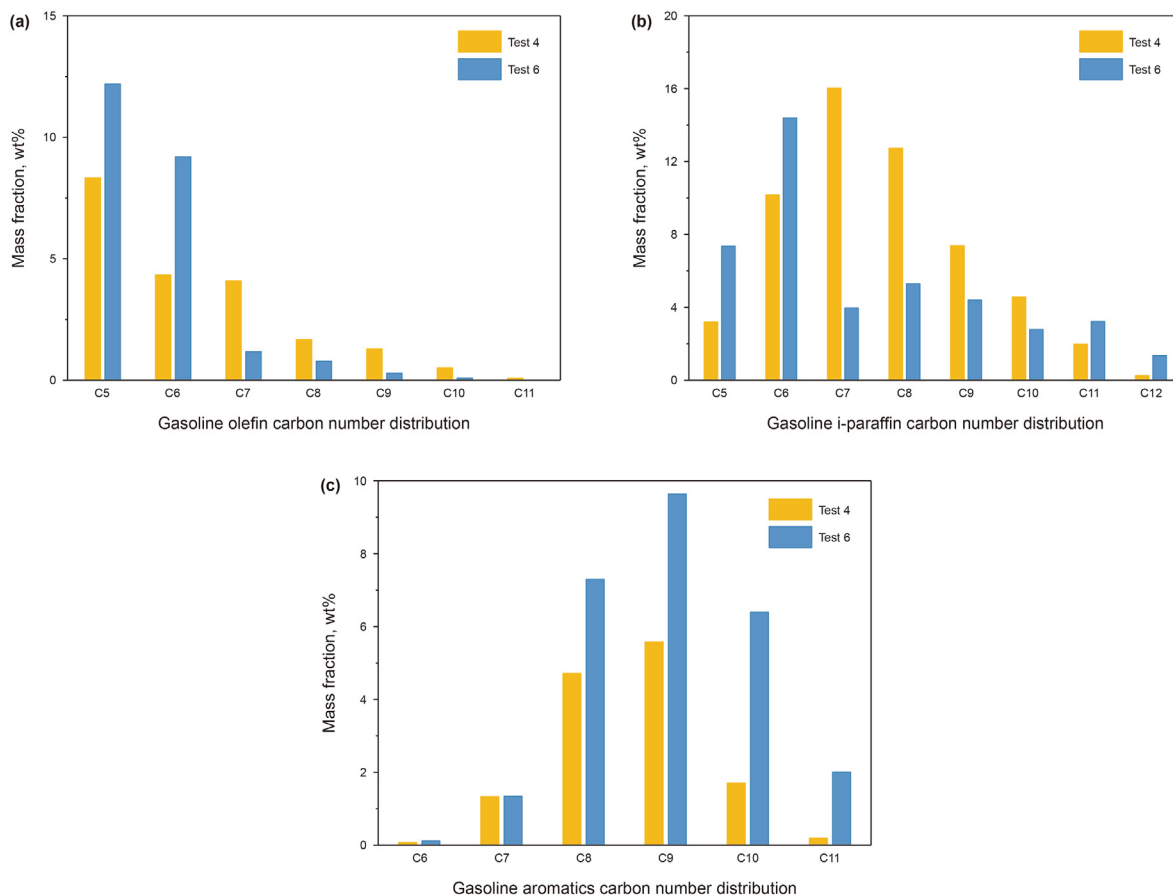


Fig. 6. Comparison of the carbon number distribution of gasoline in riser reactor and TFB reactor: (a) olefin; (b) i-paraffin; (c) aromatics.

Fig. 6.

It could be seen that the gasoline olefins both in riser reactor and TFB reactor are mainly concentrated on C₅ and C₆, respectively. The C₅ and C₆ i-paraffin in the TFB reactor were higher than that in the riser reactor, but the i-paraffin of C₇ and above in the TFB reactor all decreased. The formation of low carbon number i-paraffin is beneficial to increase the gasoline octane number. And the content of aromatics of each carbon number in the TFB reactor is higher than that in the riser reactor, especially the high carbon number aromatics, such as C₈, C₉, and above.

This is because the reactions in the TFB reactor were more sufficient, especially the secondary reaction of high carbon number olefins. The long chain olefins would undergo cracking reactions, polymerization reaction, cyclization reactions, cyclization-dehydrogenation reactions. The sufficient secondary reactions in the TFB reactor promoted a distinct change in gasoline hydrocarbon composition.

3.2.3. Fluidization comparison of the riser and TFB reactors

Some researchers explored the hydrodynamic characteristics of the riser and the TFB reactors. The detailed properties were compared as shown in Table 6 (Zhu and Zhu, 2008; Qi et al., 2009; Zhu, 2010). As we could see, the riser and the TFB reactors belonged to different fluidizations. The two fluidization states are not completely independent. The gas velocity is the fundamental factor to determine the fluidization, and the increase of gas velocity could result the transition from turbulent fluidization to pneumatic transport. The gas velocity is lower in the TFB reactors. Besides it was found that the size of two reactors varied greatly which has a great influence on the catalyst concentration distribution and feedstock handling capacity. The larger the bed diameter, the more uniform the radial distribution of solid holdup, and the greater the capacity of the reactor at the same gas velocity. The axial distribution of solids holdup and radial distribution of local voidage in the riser and TFB reactors from the references (Chen and Xu, 2004; Grace et al., 2010) were compared in Fig. 7.

Table 6 Comparison of riser and fluidized bed reactor.

Project	TFB	Riser
Fluidization	Turbulent fluidization	Pneumatic transport
Back-mixing	More	Less
Temperature gradients	Evenly	Have
Product selectivity	Worse	Good
Operation flexibility	Worse	Good
Apparent catalyst density, kg/m ³	250–400	30–60
Catalyst inventory, ton	10–15	Approximately 1

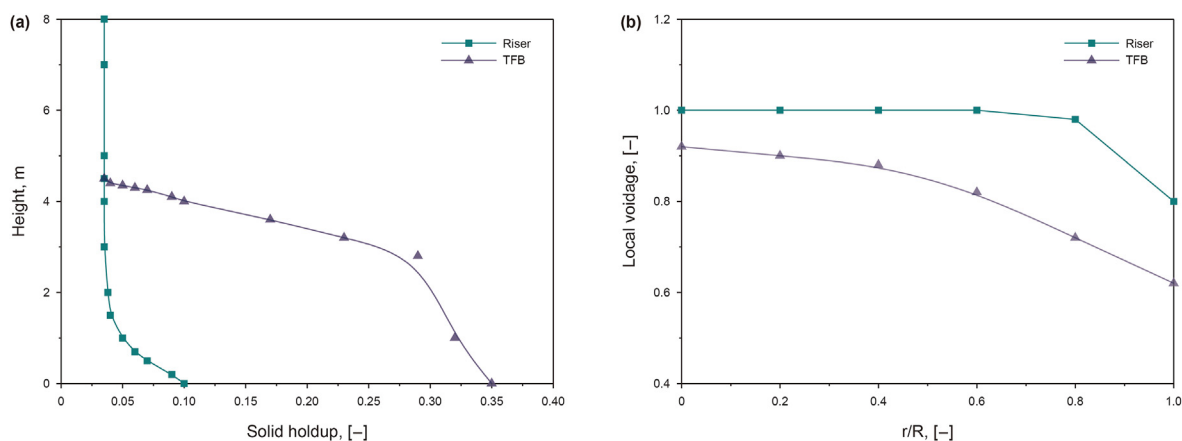


Fig. 7. Difference between riser and TFB in (a) axial distribution of solids holdup (b) radial distribution of local voidage.

It could be found that the axial solids holdup in the riser is limited to 0.1, however the axial solids holdup in the TFB reactor could reach to 0.35. At the same time, the local voidage in the riser reactor is higher than that in the TFB reactor. These demonstrated that the TFB reactor has a larger catalyst bed density than riser reactor in axial and radial distribution. This phenomenon was consistent with the high apparent catalyst density and catalyst inventory in the TFB reactor. Actually, catalyst bed density is the most influential parameter to determine mass and heat transfer efficiency. High solids holdup increase the gas-particle interaction and could reach an ideal reaction intensity. It explained that why the TFB reactor has a good performance in promoting the olefins conversion and aromatics generation.

In industrial application, the advantages of the reactor are utilized maximally to match the reaction characteristics. For example, the heavy oil FCC process takes advantage of the greater flexibility and less back-mixing of the riser reactor. The coke combustion reaction utilizes the characteristic of uniform bed reaction temperature of the TFB reactor. Therefore, the TFB reactor with the characteristics of high bed density and good mass transfer efficiency may better match the F-T wax FCC reaction.

3.2.4. Heat balance of the TFB process

The detailed product yield and reaction heat of individual hydrocarbon of TFB reactor are listed in Table S1. And coke combustion heat calculation is listed in Table S2. Fig. 8 shows the calculation results of reaction heat and coke combustion heat in the TFB reactors of Test 6. It could be seen that in Fig. 8(a), the heat for

gas production is the highest, followed by gasoline and heavy oil + coke. That's because the generation of gas involves more cracking reactions and requires more heat. Meanwhile, the formation of heavy components especially coke is through condensation reactions, which is an endothermic reaction. Cracking from the middle of long chain hydrocarbons requires the lowest energy, so the reaction heat of gasoline is relatively low. The coke combustion heat in the regenerator was calculated and compared with the total reaction heat in Fig. 8(b). The total reaction heat of the system in TFB reactor is lower than the coke combustion heat in the regenerator, accounting for about nearly 37%. Generally, in the heat balance of the FCC unit, the reaction heat accounts for 15%–40% of the coke combustion heat (Pekediz et al., 1997). This shows that F-T wax FCC process could achieve heat balance in the TFB reactor.

4. Conclusion

The F-T wax FCC performance under various conditions was investigated in the pilot-scale riser reactor. Low reaction temperature and regenerated catalyst temperature, large C/O and long reaction time will promote the reduction of gasoline olefin content. But the RON faced a great loss. A novel process with TFB reactor for the production of low olefin and high octane number gasoline by F-T wax FCC was proposed. The experimental results showed that the TFB reactor could better promote the conversion of olefins to aromatics. At the expense of certain gasoline yield, the gasoline aromatics could be obtained with gasoline olefin 23.70 wt% and gasoline aromatics content 26.79 wt%. The gasoline yield was

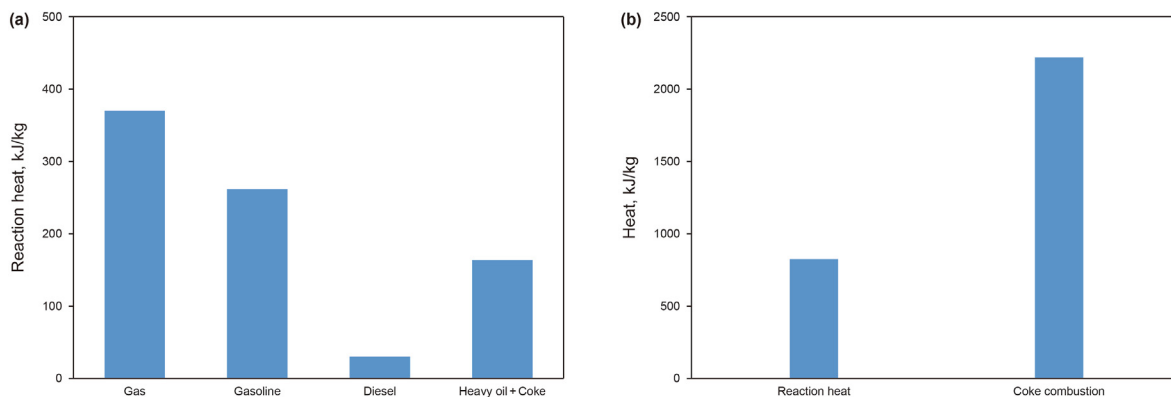


Fig. 8. Comparison of (a) reaction heat of lumped products distribution (b) total reaction heat and coke combustion heat.

47.35 wt% and the RON was 91.0. The fluidization and reactor structure comparison demonstrated that TFB reactor has a higher catalyst bed density. The calculated reaction heat accounted for nearly 37% of the coke combustion heat, which proves that the TFB process could maintain heat balance.

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Nomenclature

Symbol

M1	Transition metal element
M2	Transition metal element
P	Paraffin in gasoline
I	I-paraffin in gasoline
O	Olefin in gasoline
N	Naphthenic in gasoline
A	Aromatics in gasoline
HT	Hydrogen transfer reaction
Aro	Aromatization reaction

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.petsci.2022.08.019>.

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