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Multifunctional Two-Stage Riser Catalytic Cracking of Heavy Oil

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S *Supporting Information*

ABSTRACT: The continuous deterioration of feedstocks, the increasing demand of diesel, and the increasingly strict environmental regulations on gasoline call for the development of fluid catalytic cracking (FCC) technology. To increase the feed conversion and the diesel yield as well as produce low-olefin gasoline, the multifunctional two-stage riser (MFT) FCC process was proposed. Experiments were carried out in a pilot-scale riser FCC apparatus. Results show that a higher reaction temperature is appropriate for heavy cycle oil (HCO) conversion, and the semispent catalyst can also be used to upgrade light FCC gasoline (LCG). The synergistic process of cracking HCO and upgrading LCG in the second-stage riser can significantly enhance the conversion of HCO while reducing the olefin content of gasoline at less expense of gasoline yield. Furthermore, the novel structure riser reactor can increase the conversion of olefins in gasoline. Because of the significant increase of HCO conversion, the fresh feedstock can be cracked under mild conditions for producing more diesel without negative effects on the feed conversion. Compared with the TSR FCC process, in the MFT FCC process, the increased feed conversion, diesel and light oil yields can be achieved, at the same time, the olefin content of gasoline decreased by approximately 17 wt %.

1. INTRODUCTION

Fluid catalytic cracking (FCC) units, as the heart of refineries, are used for converting gas oils and residues into high octane gasoline and diesel. In China, approximately 80% of gasoline and 30−40% of diesel comes from FCC products.[1,2] However, as the crudes are getting heavier and the demand for high value petroleum products is increasing, the FCC units are facing many new challenges. The major challenge is to adapt to inferior feedstocks, such as residues which have higher metal contents and coking tendency,[3] or coker gas oil (CGO) with higher nitrogen content and aromatic content which would poison the catalyst and retard the cracking of hydrocarbons.[4−6]

In order to enhance the conversion of heavy oil, the common way is to increase the operating severity, however, which may lead to the overcracking of diesel [also commonly referred as light cycle oil (LCO)] and the increase of olefin content in gasoline.[7] When the inferior feedstocks are added into the conventional FCC feeds, the properties of catalysts should also be improved.[8−10] Besides the catalyst, the FCC technology also plays a crucial role. To minimize nonselective post riser cracking, UOP developed a millisecond catalytic cracking (MSCC) process.[11] In China, Shan et al.[12−14] researched a two-stage riser (TSR) FCC technology where the traditional riser reactor was divided into two stages. In this technology, the fresh feedstock, which is easy to be cracked but difficult to be vaporized, diffused, and adsorbed on the active centers is injected into the first-stage riser, while the heavy cycle oil (HCO) which has the opposite adsorption and reaction properties is injected into the second-stage riser. Therefore, the fresh feedstock and HCO can be upgraded under proper reaction conditions, respectively. The TSR FCC technology which can improve light oil yield and reduce dry gas and coke yield has been applied in more than 10 commercial units.

On the basis of the fact that increasing the catalyst-to-oil ratio (CTO) without raising the reaction temperature can improve the product distribution, UOP developed an RxCat technology which mixes spent and regenerated catalyst in a blending vessel located at the bottom of the riser.[15,16] Thus the CTO can be increased due to the decrease of the catalyst-temperature. However, the activity of the mixed-catalyst decreased at the same time, which is unfavorable for converting residues. To increase the activity of the mixed-catalyst, Wang et al.[17] proposed a dual-reactions mutual control (DMC) process where the spent catalyst is from the subsidiary riser for gasoline reformation, which still retains an inherently high level of activity. Even though these processes can improve the conversion of heavy oil to some extent, the blending ratio of inferior feedstocks is still limited; therefore, the study of novel FCC processes need continue.

Another challenge is that the increasingly strict environmental regulations on transportation fuels and the market demand for clean fuels leaves the refiners no option but to improve the qualities of gasoline and diesel. Besides, the blending of heavy oil will lead to the increase of olefin content in gasoline.[18] Although olefins can be removed by hydrotreating, this will also lead to octane loss due to the high octane aromatics and olefins being converted into low octane *n*-paraffins and naphthenes.[19,20] Moreover, the saturation of olefins will consume a lot of hydrogen which is an expensive material. Therefore, if the olefins can be reduced in the FCC process, it might be profitable. Additionally, because of the decrease of olefin content, the upgraded FCC gasoline becomes more resistant to octane loss in the hydrodesulfurization process.[21] Much work has been done on both FCC catalysts and technology. Catalysts have been designed to reduce the olefin content while maintaining the RON of gasoline,[8,22] but the effects are limited. Simultaneously, several FCC processes

have been developed in China to reduce the olefin content of gasoline, such as the maximizing iso-paraffins (MIP) process,[23] the flexible dual-fluid catalytic cracking (FDFCC) process,[24] the subsidiary riser FCC (SRFCC) process,[25] the DMC process,[17] and the TSR FCC process.[13] Reprocessing FCC gasoline in the FCC process is relatively inexpensive but the yield loss of gasoline cannot be neglected. Hence, more work should be focused on reducing the gasoline loss as well.

The third challenge is the fast-growing demand of diesel, at least in China and Europe.[2,26] In China, the diesel to gasoline consumption ratio had increased to 2.04 in 2009.[2] Compared with the ratio is only around 0.5 in conventional FCC units, to increase diesel to gasoline ratio is also a main task for refineries. However, the key problem is that the yield of diesel oil always reaches the peak under moderate operating conditions while the feed conversion is very low.[27] In the conventional FCC processes, the contradiction of diesel yield and feed conversion is difficult to be resolved, especially when processing inferior feedstocks. Adding the bottom cracking additive (BCA) to the USY catalyst can slightly increase the diesel yield, but due to the less catalytic activity of BCA, more dry gas and coke are generated while gasoline selectivity is negatively affected.[26]

The purpose of this paper is to propose a novel FCC process to process heavy oil and produce gasoline with less olefin content and, furthermore, increase the yield of diesel oil without negatively affecting the feed conversion. In the first work, the operating conditions in the first stage riser for converting fresh feed into more diesel were studied. Then the appropriate conditions for further cracking HCO in the second stage riser were investigated. On the basis of the experimental results, the synergistic process for converting HCO and upgrading LCG was proposed and its performance was analyzed. Finally, the comprehensive evaluation of the MFT FCC process was discussed.

2. EXPERIMENTAL SECTION

2.1. MFT FCC Process. The multifunctional two-stage riser (MFT) FCC process was proposed based on the following.

In order to obtain more diesel under higher selectivity, the operating conditions of the first stage riser should be moderate (low reaction and catalyst temperature, short residence time, and small catalyst-to-oil ratio),[27] but this would lead to the increase of the HCO yield. If the HCO could be converted efficiently, the purpose could be achieved without negatively affecting the feed conversion. Because of the inferior feedstocks being more difficult to convert, the crackability of the HCO would be poorer, hence in order to obtain a higher feed conversion the HCO should be cracked under higher severity. However, in the commercial TSRFCC unit, the two stage risers share one disengager, if the reaction temperature of the second stage riser is much higher than the first one, the product distribution might be aggravated because of the overcracking of light oil in the disengager. Therefore, the operating severity should be increased without rising the outlet temperature of the riser.

In the TSR FCC process, little work has been done on efficiently upgrading the gasoline which is one of the major improvements of the MFT FCC process. In order to increase the gasoline reformation efficiency, two objectives should be achieved.

The first one is to reduce the cracking loss of gasoline, which could be done from three aspects. First, recycling the light cracking gasoline (LCG) selectively is conducive to efficiently

upgrade the gasoline. Researchers found that gasoline components with a carbon number of seven or higher are easier to crack even with a short reaction time, while pentene and hexene are difficult to be cracked under conventional FCC operating conditions.[28−31] Moreover, the majority of olefins are in the light fraction gasoline, and the increase of the concentration of reactant is beneficial to the upgrading reactions. In addition, it can reduce the load of the fractionation system and energy consumption due to the light gasoline only accounting for approximately half of the full range gasoline. Second, Wang et al.[17] suggested that decreasing the temperature difference between FCC gasoline and regenerated catalysts could restrain the thermal cracking and improve product distribution of gasoline reformation. This can be conducted by cooling the regenerated catalyst and preheating the gasoline feed. Third, partial-coked catalyst could be used to further reduce the cracking loss of gasoline. Corma et al.[32] found that despite a coke-on-catalyst content of 1.2 wt %, the Y zeolite still has enough activity for transforming olefins into paraffins through hydrogen-transfer reactions. However, the coke may reduce the site density, which will decrease the reaction rate for bimolecular hydrogen transfer reactions,[33] thus the coke content on the catalyst should not be too high for further upgrading gasoline. Zhang et al.[34] and Yuan et al.[35] found that little coke on catalyst (no more than 0.5 wt %) could increase the gasoline yield as well as reduce the dry gas and coke yields during the process of upgrading FCC gasoline, while only little influence on olefin reduction was observed.

The other objective is to increase the conversion of olefins. If the olefins cannot be converted by cracking, then they can only be converted via hydrogen transfer, isomerization, and aromatization reactions which are the desired secondary reactions for gasoline reformation. Hydrogen transfer, being a bimolecular reaction, is favored by a higher acid density,[36] which could be achieved by increasing the catalyst-to-oil ratio (CTO) or the density of catalyst in the riser when the catalyst is determinate. Wang et al.[37] and Lu et al.[38] studied the gas−solids flow patterns in the MIP reactor by cold model and computational fluid dynamics (CFD) simulation and found that with an enlarged section the solid density can have a significant increase. Therefore, changing the structure of the reactor is a useful way to further increase the catalyst density in the reactor. Because the hydrogen transfer and isomerization are exothermic reactions with slower reaction rates; they will benefit from a relatively lower reaction temperature[33] and longer residence time.[39]

As both of the two processes (cracking HCO and upgrading LCG) are difficult to be separately operated at proper conditions analyzed above, a more convenient way is to develop a synergistic process for converting HCO and upgrading LCG in the second riser where split feed injection mode could be used. However, previous research always focused on recycling low-value hydrocarbon cuts[40−42] or FCC gasoline[14,32,43] from the bottom of the riser to increase light olefins yields and the gasoline octane, which seems unsuitable in our work. Considering the inferior crackability of HCO and our goal of reducing the cracking loss of gasoline, a more suitable mode is recycling the LCG from the upper position of the riser and recycling the HCO from the lower position. As once the LCG is injected, more heat should be provided by the catalyst, according to the heat balance, it requires a larger catalyst circulation. The higher the catalyst circulation is, the larger the CTO is, and the higher severity in the HCO reaction
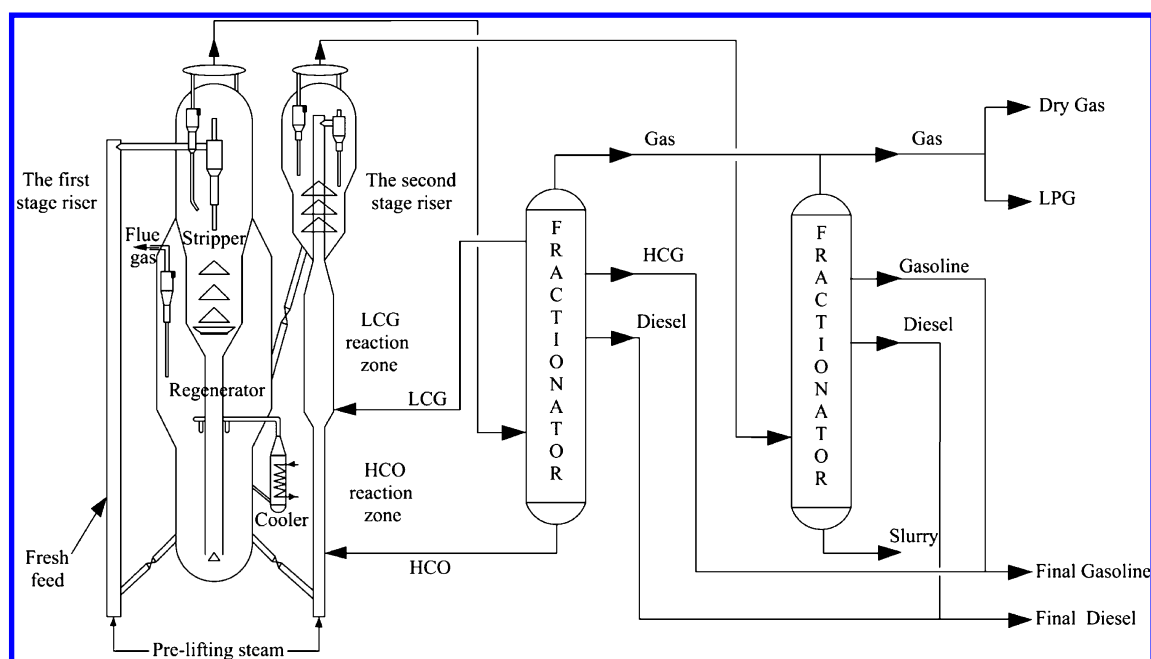
Figure 1. Schematic of the MFT FCC process.

Table 1. PIONA Compositions of Daqing FCC Light Gasoline

	n-paraffins	iso-paraffins	naphthenes	aromatics	olefins	total (wt %)
C_4	0.00	0.00	0.00		0.95	0.95
C_5	1.40	5.80	0.18		34.82	42.20
C_6	0.87	5.30	1.21	0.56	20.94	28.32
C_7	1.37	1.70	1.25	3.19	4.83	12.36
C_8	0.81	0.70	0.00	4.20	2.45	8.70
C_9	0.33	0.18	0.24	3.95	0.00	4.70
C_{10}	0.28	0.35	0.00	1.28	0.00	1.91
C_{11}	0.22	0.25	0.21	0.18	0.00	0.86
total (wt %)	5.28	14.28	3.09	13.36	63.99	100.00

Table 2. PIONA Compositions of Hengyuan FCC Light Gasoline

	n-paraffins	iso-paraffins	naphthenes	aromatics	olefins	total (wt %)
C_4	0.05	0.00	0.00		0.35	0.40
C_5	6.46	35.31	0.18		57.38	99.33
C_6	0.00	0.23	0.00	0.00	0.04	0.27
total (wt %)	6.51	35.54	0.18	0.00	57.77	100.00

zone will be. Therefore, the HCO could be converted at a higher severity without raising the outlet-temperature of the riser, while the LCG could be upgraded at a lower severity where the catalyst is temperature-lowered and partially coked.

All these have led to the development of a new FCC process for efficiently converting heavy oil into low-olefin gasoline and diesel oil. The operating scheme of the MFT process in a pilot scale FCC unit is shown in Figure 1. The fresh feedstock is converted at moderate operating conditions to generate more diesel oil in the first stage riser. Then the oil gas is piped to the fractionator and cut into dry gas, LPG, light cracking gasoline (LCG), heavy cracking gasoline (HCG), diesel, and heavy cycle oil (HCO). The HCO is recycled to the bottom of the second stage riser while the LCG is injected to the fast bed. The final gasoline product is the mixture of the HCG from the first fractionator and the full-range gasoline from the second fractionator. It should be noted that this process is designed for experimental research because in the pilot-scale unit, the

two stage riser cannot run simultaneously. In commercial units, the two risers can share a disengager and fractionator. (The comparison schematic of the TSR and MFT processes can be seen in Figure S1 in the Supporting Information).

2.2. Feedstock and Catalyst. Five kinds of heavy oil were used in the study and their properties are shown in Table S1 (see the Supporting Information). QL-CGO, HR-CGO, and HY-CGO-2 were chosen as the comparative heavy oil with different crackability, mainly due to their different hydrogen and nitrogen content and the group composition. HY-CGO is the main feedstock in the study, which was obtained from Hengyuan refinery. CQ-HCO was provided by Changqing refinery, which was the feedstock of the second stage riser in the commercial TSR FCC unit.

Two kinds of FCC light gasoline were used as the experimental feeds. One is Daqing LCG produced from the Daqing atmospheric residue and its final boiling point is 150 °C; the other one is Hengyuan LCG provided by Hengyuan

Table 3. Properties of Catalyst

				particle size distribution (vol %)			
microactivity	surface area (m^2/g)	pore volume (cm^3/g)	packing density (kg/m^3)	0−40 μm	40−80 μm	80−110 μm	>110 μm
72	153	0.16	980	12.0	45.8	23.0	19.2

refinery and its final boiling point is 70 °C. The detailed PIONA analyses of the two LCG are listed in Tables 1 and 2, respectively.

The catalyst used in the experiments was a commercial Y zeolite based equilibrium FCC catalyst supplied by Changqing refinery, which is specially designed for cracking heavy oil. The properties of the catalyst are given in Table 3.

2.3. Experimental Apparatus and Product Analysis. The experiments were carried out in a pilot-scale riser FCC apparatus. The pilot plant unit is comprised of a feed and steam injection system, a reaction/regeneration system (shown in Figure 2), a product condensing and measurement system, a
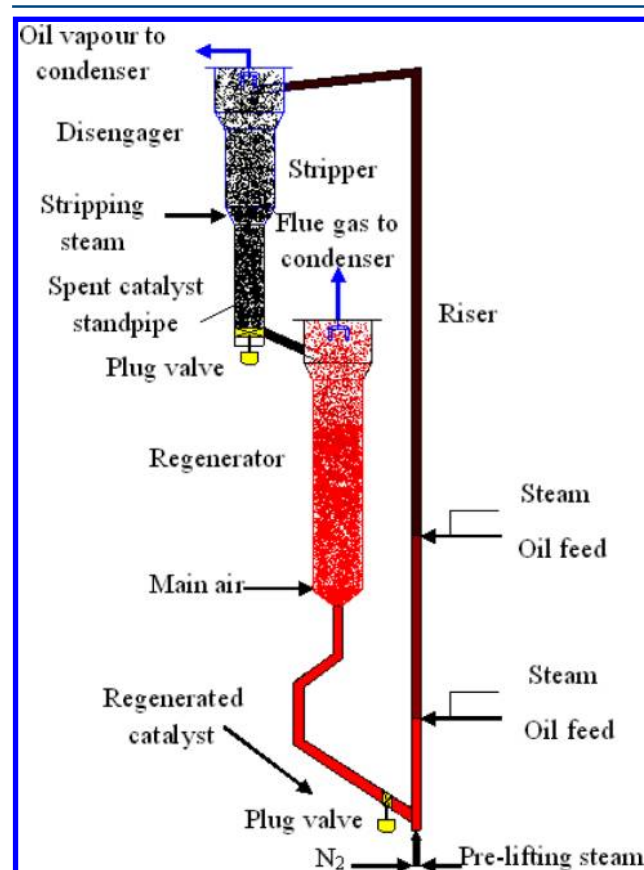

Figure 2. Schematic of the pilot-scale riser FCC apparatus.

pneumatic control system, and a computer control system (which shows the main operation parameters and can be used to adjust the unit conveniently). The apparatus can be operated continuously similar to the commercial FCC units.

Along the riser reactor, there are two feed nozzles at different heights, so the reaction time can be adjusted in a wider range. In the conventional experiments, only one feed injection point is used, while in the synergistic process both of them are used, the lower one is for HCO injection and the upper one for LCG injection. When carrying out the MFT process, the traditional riser can be replaced by another novel configuration-changed riser reactor.

In the study, the conversion was defined as the total-yield of dry gas, liquefied petroleum gas (LPG), gasoline, diesel, and coke. In addition, the light oil referred to the sum of gasoline and diesel yields, and the liquid products were the yields of LPG and light oil. The selectivity was defined as the product yield divided by conversion.

The compositions of cracking gas and flue gas were analyzed by a Varian CP-3800 gas chromatograph (GC), while the liquid products collected were first weighed then analyzed for the simulated distillation by another Varian CP-3800 GC according to the ASTM-2887-D procedure. The cut points were set at 204 °C for gasoline, 350 °C for diesel, and higher than 350 °C for HCO or slurry. Thus, the product distribution can be computed. The liquid products collected is then fractionated by the true boiling point distillation to separate the LCG, HCG, diesel, and heavy oil fractions, and then their properties can be tested. PIONA analyses for both gaseous and liquid products were carried out using a third Varian CP-3800 GC equipped with a CP-Sil PONA CB silica column connected to a FID detector.

2.4. Characterization of the Catalyst Samples. Nitrogen adsorption and desorption isotherms were performed at −196 °C on a Micromeritics ASAP 2020 volumetric adsorption system. The pore size distribution and pore volume were deduced from the adsorption isotherms using the Barrett−Joyner−Halenda (BJH) method, while BET method and the t-plot method were used to calculate the BET surface area, micropore area, and external surface area. The relative acid strength and acid amount of catalysts were measured by the NH$_3$-TPD. The microactivity of catalysts was evaluated on a MRCS-8010 unit, according to the ASTM 2292 method.

3. RESULTS AND DISCUSSION

3.1. Operating Conditions for Fresh Feedstock. Even though the properties of the feedstocks have significant influence on the product distribution, the maximal diesel yield always exists under a lower conversion rooted in the fact that catalytic cracking is a parallel-series reaction[44] and the diesel fraction is more susceptible to serial cracking reactions than gasoline fractions.[27] Nevertheless, in the studies of Wang et al.,[27] the residence time was always as long as approximately 3 s, which is different from the operating concept of our work. Therefore, three different CGO, which is a main feedstock of FCC units but has inferior crackability, were studied under a short residence time. The results (Figure 3) show that the maximal diesel yield can be obtained at a certain conversion, instead of monotone decreasing which was shown in the work of Wang. From his research, it can be inferred that in the conventional one-stage riser FCC process it is difficult to maximize the diesel yield due to the low feed conversion. However, in the MFT FCC process, it can be achieved as the heavy cycle oil can be further converted in the second-stage riser.

On the basis of the above analysis, three operating severities were chosen for converting HY-CGO in the first-stage riser. The experimental results presented in Table S2 in the Supporting Information indicate that the crackability of HY-
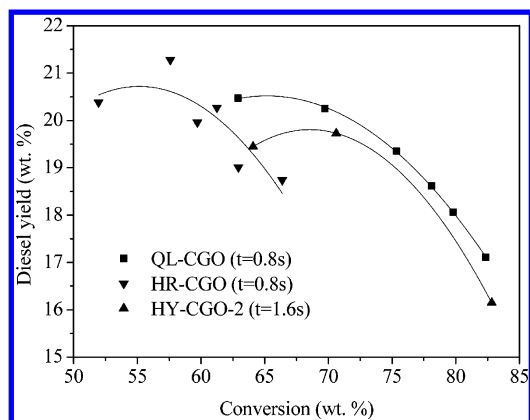
Figure 3. Relationship of conversion and the diesel yield.

CGO is better than the QL-CGO, HR-CGO, and HY-CGO-2. When the operating conditions were 480 °C of the reaction temperature, 6 of the CTO, and 1.3 s for the residence time, the most diesel oil was obtained as well as the highest selectivity for diesel and light oil could be achieved. On the other hand, the yield of HCO reached up to about 25 wt %, which meant that the operating severity could not be further lowered as the recycling process would increase energy consumption. Therefore, the operating conditions in the first stage riser depend on the properties of the feedstock, while a shorter residence time is always supported.

3.2. Operating Conditions for Heavy Cycle Oil. In order to convert heavy oil into lighter hydrocarbons as completely as possible, the conversion of heavy cycle oil in the second-stage

riser is still critical as in the MFT process and it accounts for approximately one-fourth of the fresh feed. However, little work has been done on studying the cracking behavior of FCC HCO. Thus, this study was designed to investigate the catalytic cracking behavior of HCO and then to determine the appropriate operating conditions to convert HCO in the second-stage riser. Here, the CQ-HCO was used, which was obtained from the TSR FCC unit of the Changqing refinery.

HCO has a distillation range similar to the fresh feed. However, its aromatic content is much higher than the fresh feedstock, often in excess of 40 wt %. Because of the strong adsorption ability and low reaction rate of aromatics,[45] in the conventional one-stage riser FCC process, when the HCO is recycled to the same riser or blended with the fresh feedstock, the cracking performance of the fresh feedstock would be retarded.[46] A good way to resolve this problem is recycling HCO to a second riser reactor where it can be cracked by regenerated catalysts.[12]

For enhancing the conversion of HCO, a higher operating severity should be chosen. This is because a relatively higher mixing temperature is beneficial to the vaporization of heavy oil and the cracking of macromolecules. Considering the reaction dynamics, the activation energy of heavy oil cracking is larger than that of gasoline cracking and coking. Therefore, by increasing the reaction temperature within the proper range, more desired products could be obtained. In commercial FCC units, when increasing the reaction temperature, the CTO would rise at the same time, so they should change together. Therefore, in this work, we fixed the temperature of the regenerated catalyst at 690 °C and set the reaction temperatures at 500, 540, 555, 570, and 580 °C, respectively. On the
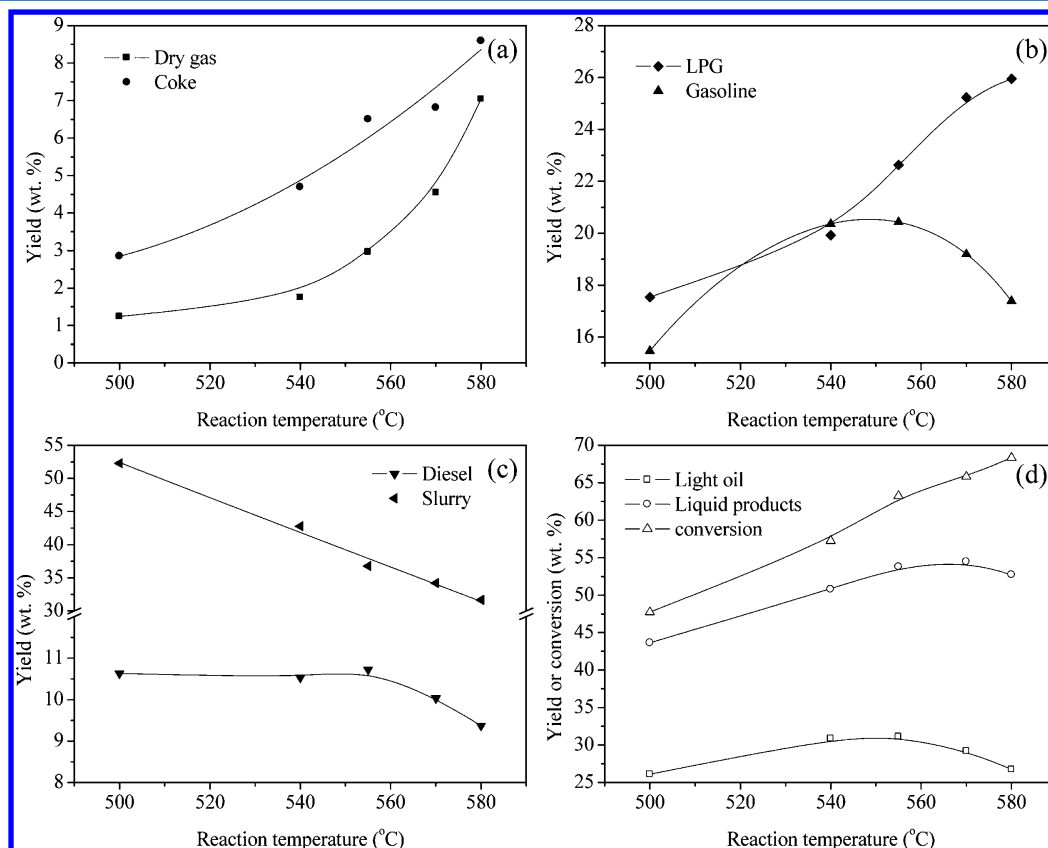

Figure 4. Effect of reaction temperature on the product distribution.

basis of the hypothesis that no reactions take place at the moment of catalyst contacting with oil,[27] the CTO values can be calculated by a local heat balance, which were 5, 8, 9, 11, and 13, respectively. The residence time was fixed at 1.5 s. In Figure 4 the product distribution is shown. At the conventional FCC operating temperature (500 °C), the conversion of HCO was only 47.7 wt %, which reflects that the HCO is harder to crack than the fresh feedstock. A conspicuous monotonic increase could be found in the influence of reaction temperature on the conversion, which increased to 68.3 wt % at 580 °C. However, the yields of undesired products (dry gas and coke) had a significant increase as well. When the reaction temperature was 555 °C, the yield of light oil reached the top of about 31 wt %. As the H/C ratio of the HCO is only 1.41, the light oil yield of cracking HCO is much lower than that of cracking fresh feedstock. This problem also exists in the cracking of FCC slurry.[47] To further investigate the effect of reaction temperature and CTO on the reaction routes of HCO cracking, three parameters are introduced, thermal cracking index (TCI), dehydrogenation index (DHI), and cracking mechanism ratio (CMR), which are shown in Figure 5.
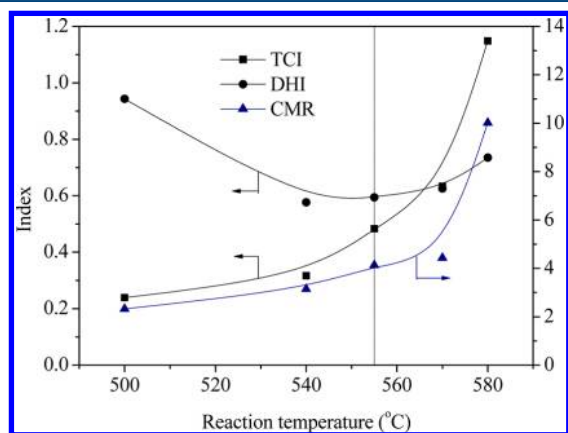

Figure 5. Three indexes as a function of reaction temperature.

The characteristic products, under classical β-scission route, are C_3 and C_4, especially isobutane and isobutene, while the typical products of thermal cracking are methane, ethane, and ethene.[48] Therefore, TCI is defined as the weight ratio of the sum of C_1 and C_2 yields to the sum of isobutane and isobutene yields $\{(C_1 + C_2)/(i\text{-}C_4 + i\text{-}C_4^=)\}$,[27,45] the higher of the value means the ratio of thermal cracking is larger. When the value of TCI is lower than 0.6 it means that catalytic cracking is the main reaction, while when it is above 1.2 it means that thermal cracking is serious.[45] As can be seen from Figure 5, thermal cracking becomes more prominent with increasing reaction temperatures. This is because thermal cracking, which has much higher activation energy than catalytic cracking, is favored by higher temperature. Specifically, the value of TCI slowly increased to 0.48 before 555 °C but soared to 1.15 after that. The variation trend is similar to that of dry gas, which means that the generation of dry gas is closely related to thermal cracking reactions. In addition, this also due to HCO having more aromatics with short side chains, which can be cracked under higher severity and then C_1 and C_2 hydrocarbons are produced. Dry gas is a hydrogen-rich component which should be kept as low as possible. Thus in order to decrease the yield of dry gas, the reaction temperature should not above 555 °C.

On the other hand, a relative high temperature could significantly enhance the conversion of HCO.

DHI which is defined as the volume ratio of H_2 to the sum of C_1 and C_2 yields $\{H_2/(C_1 + C_2)\}$, always be used to reflect the poisoning degree of heavy metals (Ni and V) on the catalyst.[45] On the basis of the hypothesis that H_2, CH_4, and C_2 hydrocarbons are generated at random during thermal cracking and hydrogen is mainly produced by thermal cracking and dehydrogenation reactions, Wang et al.[49] used it to describe the degree of dehydrogenation. However, we found that the influence of protolytic cracking could not be neglected in our studies. According to the studies of Haag and Dessau,[50] H_2, CH_4. and C_2 hydrocarbons also could be created by protolytic cracking, which is favored by higher temperatures. Ye et al.[51] studied the effects of thermal cracking and catalytic cracking on the cracking of heavy FCC gasoline and found that the volume fraction of H_2 in the dry gas decreased with increasing temperature. This would be the main reason that caused the decline of the DHI value before 555 °C. However, when the reaction temperatures are higher than 555 °C, the increase of DHI value can be attributed to the enhanced dehydrogenation and condensation reactions, which is proven by the sharp increase in the yield of coke. Therefore, the reaction temperature significantly affects the relative contribution of different cracking pathways. Additionally, a lower proportion of hydrogen in the dry gas could reduce the load of gas compressors. The DHI data reflect that the percentage of hydrogen in the dry gas reached the bottom when the reaction temperature was 555 °C.

Wielers et al.[52] proposed the CMR index to describe the relative contribution of the monomolecular protolytic pathway and the classical β-scission route, which is defined as the volume ratio of the sum of the C_1 and C_2 yields to isobutane yield $\{(C_1 + C_2)/i\text{-}C_4^°\}$. Figure 5 shows that protolytic cracking becomes more prominent with increasing temperature, especially after 555 °C, which further proved that in high temperature operations, the protolytic cracking could not be neglected.

On the basis of the above research, it can be concluded that the appropriate reaction temperature for HCO conversion is 555 °C, which could enhance the conversion of HCO without leading to the sharp increase of undesired reactions, hence more light oil could be obtained.

3.3. Synergistic Process in the Second-Stage Riser. In the MFT FCC process, the second-stage riser combines the two processes of cracking HCO and upgrading the light FCC gasoline (LCG). The catalyst, in contact with the LCG, is partially coked, which is different from the regenerated catalyst or spent catalyst, and we call it "semispent" catalyst. In this work, the semispent catalyst was characterized first, and then the synergistic process was carried out in a pilot-scale riser FCC apparatus.

3.3.1. Characterizations of the Semispent Catalyst. In order to investigate the characterizations of the semispent catalyst from the HCO reaction zone, the N_2 adsorption, NH_3-TPD, and microactivity analysis were used. The semispent catalysts were obtained under the reaction conditions of reaction temperature 555 °C, CTO = 9, and residence time 1.5 s, with a coke load of 0.48 wt %.

Figure 6 shows the N_2 adsorption−desorption isotherms of regenerated and semispent catalysts. The high adsorption isotherm exhibited at a low relative pressure indicates the existing of micropores.[53] At high relative pressures, the curve
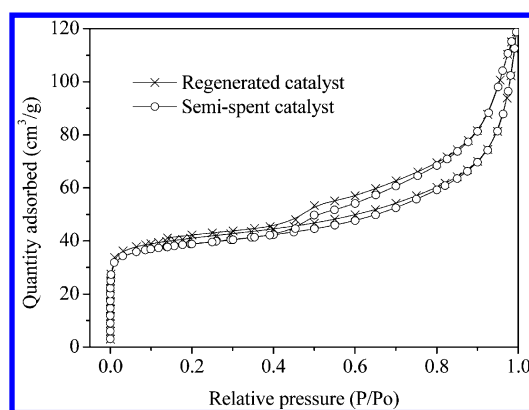
Figure 6. N$_2$ adsorption−desorption isotherms for catalysts.

exhibits a hysteresis loop which was caused by the effect of capillary condensation due to the existence of mesopores.[54,55] These are the typical characteristics of zeolites.[55] The figure also shows that the quantity of N$_2$ adsorbed by semispent catalysts decreased due to the pore blockage,[56] which conforms with the studies of Wang et al.[49] However, the degree of reduction in our results is much lower, which means the degree of pore blockage in the semispent catalyst is lower than that in the spent catalyst. The BET isotherms of the semispent catalysts are almost same as that of the regenerated catalysts, which indicates that no or only slight changes in the pore structure of the catalysts took place after the coke deposition.

Table 4 shows the comparison of the structural characteristics of these two catalysts. Most of the coke deposited is a flat

Table 4. Structural Characteristics of the Regenerated and Semispent Catalyst

items	regenerated catalyst	semispent catalyst	
		residual value	loss rate[a] (%)
BET surface area (m^2/g)	153	131	14.2
micropore surface area (m^2/g)	108	88	18.6
external surface area (m^2/g)	45	43	3.6
micropore volume (cm^3/g)	0.045	0.040	11.1
pore volume (cm^3/g)	0.160	0.153	4.4

[a]Loss rate = (initial value − residual value) × 100/initial value.

epitaxial and layered structure and the surface area of the coke is smaller than that of the catalyst.[57] Thus, the change of the surface area can reflect the position that the coke deposited on. As can be seen from Table 4, the reduction in micropore surface area is more serious than the external surface area. It was suggested that during HCO cracking more coke deposited on the micropores. Comparing the spent catalyst,[49] it is apparent that the pore blockage in the semispent catalyst after HCO reaction is not very serious. Thus it can be further used for LCG reformation.

The microactivity (MA) of both the regenerated and semispent catalysts were evaluated under the standard ASTM 2292 method. The results show that the MA of catalysts decreased from 72 to 52 after partially coking, the activity loss of the semispent catalyst is approximately 27.8% compared with the regenerated catalyst. However, in the MA tests, the reactant is diesel which is much larger in molecular size than light gasoline. Thus it cannot reflect the real activity of the semispent

catalyst for light gasoline. To further investigate the change of acid distribution of the semispent catalyst, the NH$_3$-TPD method was used.

The TPD curves given in Figure 7 show that there are three main peaks for the regenerated catalyst. One low-temperature
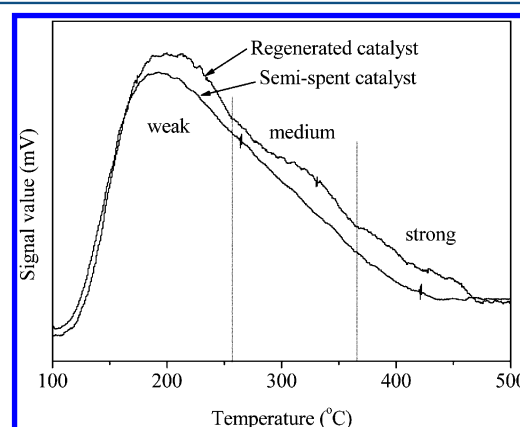

Figure 7. TPD of NH$_3$ curves of the catalysts.

peak from 100 to 255 °C, one medium peak between 255 and 365 °C, and one high-temperature peak in the range of 365−500 °C corresponding to the desorption of ammonia from the weak, medium, and strong acid sites, respectively. It can be seen that the depositing of cokes on catalyst changed the acid strength distribution, where more strong acid sites associated with dry gas or coke formation were covered by cokes compared with weak ones.[58] Therefore, the acid strength distribution of semispent catalysts might be more beneficial for preventing gasoline from being cracked. From calculating the area of the peaks, the relative acid amount of catalysts can be obtained. The result shows that there is only a reduction of 19% present, which is much lower than the reduction of microactivity. This further supports our previous opinion that more light gasoline than diesel can enter into the partly blocked pores then react over the inner acid sites.

3.3.2. Performance of the Synergistic Process. In this experiment, the CQ-HCO and DQ-LCG were used. When the LCG recycle ratio (relative to the feed rate of HCO) is approximately 50 wt %, the reaction temperature of HCO is around 555 °C (detected by thermalcouple in the experiment). In this work, the performance of the synergistic process was evaluated from four perspectives: the increasing conversion of HCO, the reduction of olefin content in gasoline, the loss rate of gasoline, and the reforming efficiency of gasoline.

According to our previous studies and the research by Wang et al.,[17] in the process of gasoline reformation, no heavy oil would be generated. Therefore, the yield of slurry for HCO ($Y_{s,\,HCO}$) can be calculated by

$$Y_{s,HCO} = Y_{s,total} \cdot F_{total}/F_{HCO} \tag{1}$$

where $Y_{s,\,total}$ is the yield of slurry for total feeds, F_{total} is the total feed rate, and F_{CGO} is the feed rate of HCO. Thus, the conversion for HCO can be calculated, which was shown in Table 5. A significant increase (about 13 wt %) of conversion can be seen after recycling 50.1 wt % of LCG.

In the synergistic process, two parts of gasoline are upgraded, one is the recycling light gasoline and the other is that generated by HCO cracking. However, the yield of gasoline created by HCO cannot be directly obtained, but the

Table 5. Effect of Recycling LCG on the Product Distribution

recycle ratio of LCG[a] (wt %)	0	50.1
temp. of riser outlet (°C)	500	500
reaction temp. of HCO (°C)		555
CTO (HCO/LCG) (kg/kg)	5	9/18
Res-time (HCO/LCG) (s)	1.5	0.5/1.6
Product Distribution (wt %)		
dry gas	1.24	1.39
LPG	17.54	14.71
gasoline	15.47	43.96
diesel	10.63	8.83
slurry	52.27	26.18
slurry for HCO[b]		39.30
coke	2.85	4.93
conversion	47.73	
conversion for HCO		60.70

[a]The recycle ratio of LCG is with respect to the CGO feed. [b]Deducting the influence of recycled LCG.

approximate value can be obtained from the separate cracking of HCO. Since the olefin content of gasoline can be obtained by the combination of true boiling point distillation and PIONA analysis, the olefin content of the mixing gasoline before reformation (O_M) can be calculated by

$$O_M = O_{HCO,g} \cdot Y_{HCO,g} / (Y_{HCO,g} + R_{LCG}) + O_{LCG}$$
$$\cdot R_{LCG} / (Y_{HCO,g} + R_{LCG}) \qquad (2)$$

where $O_{HCO,g}$ is the olefin content of gasoline generated by HCO (41.97 wt %), $Y_{HCO,g}$ is the yield of gasoline generated by HCO cracking under 555 °C (20.43 wt %), R_{LCG} is the recycle ratio of LCG (50.1 wt %), and O_{LCG} is the olefin content of light gasoline (63.99 wt %). Further, the reduction of gasoline-olefins before and after reformation can be calculated ($O_R = 57.61 - 34.36 = 21.27$ wt %).

The loss of gasoline was estimated based on the hypotheses that the gasoline yields generated by HCO in the synergistic process were similar to that in the separate process at similar reaction conditions. Thus, the quantity of gasoline ($F_{HCO,g}$) generated by HCO cracking can be calculated by

$$F_{HCO,g} = F_{HCO} \cdot Y_{HCO,g} \qquad (3)$$

where F_{HCO} is the feed rate of HCO. Then the total gasoline loss ($L_{total,g}$) can be estimated by

$$L_{total,g} = F_{HCO,g} + F_{LCG} - F_{total} \cdot Y_{total,g} \qquad (4)$$

where F_{LCG} is the feed rate of LCG, F_{total} is the total feed rate of CGO and LCG, and $Y_{total,g}$ is the yield of gasoline in the synergistic process. On the basis of the hypotheses in the reformation process, the loss rates of gasoline and light gasoline are equal,[25] and the loss rate of gasoline (R_{loss}) can be calculated by

$$R_{loss} = L_{total,g} / (F_{HCO,g} + F_{LCG}) \qquad (5)$$

The calculated result is 6.48 wt %, which is much lower than that reported in the literature (more than 17 wt %).[17]

In order to describe the efficiency of gasoline reformation, we defined the reforming efficiency (e), which refers to the ratio of the olefin reduction to the gasoline loss rate ($e = O_R/R_{loss}$), a higher value means the gasoline can be upgraded at a less expense of the gasoline yield. It can be calculated, and the

reforming efficiency of gasoline was 3.28 in the synergistic process, which is almost 2 times higher than that reported in the literature (between 1.6 and 1.7).[17] It can be expected, upgrading gasoline in the MFT process, at least half of the gasoline loss can be prevented.

Therefore, on the basis of the analysis of the experimental results mentioned above, the synergistic process in the second-stage riser can significantly enhance the conversion of HCO and upgrade gasoline at a less expense of gasoline yield.

3.4. Heavy Oil Catalytic Cracking by the MFT FCC Process. To evaluate the performance of the MFT FCC process, the HY-CGO was chosen as the representative of heavy oil due to its inferior crackability. Because in the pilot-scale unit, most of LCG fractions exist in the cracking gas, the LCG cannot be obtained from the cracking gasoline of the first-stage riser. Therefore, the LCG used in the experiment was taken from the FCC commercial unit of the Hengyuan refinery, and the PIONA compositions was listed in Table 2. However, the HCO used in the second stage riser was obtained from the liquid products of the first-stage riser by true boiling point distillation. In this work, the calculation method of the product distribution of the MFT process was presented and then the processing of HY-CGO by different processes, the conventional FCC process, the TSR process, and the MFT process, were compared.

3.4.1. Results of Multifunctional Two-Stage Riser Catalytic Cracking. In the simulated experiments, the recycle ratios of HCO and LCG are determined by the product distribution of the first-stage riser (the yields of distillation ranges that are higher than 350 °C and lower than 70 °C). The results of the two-stage riser catalytic cracking are calculated according to the following equations. For the yield of gasoline,

$$Y_{t,gasoline} = Y_{f,gasoline} + Y_{s,gasoline} \times (Y_{f,LCG} + Y_{f,HCO})$$
$$- Y_{f,LCG} \qquad (6)$$

where t, f, and s refer to two stages, first stage, and second stage, respectively. For the yield of slurry,

$$Y_{t,slurry} = Y_{s,slurry} \times (Y_{f,LCG} + Y_{f,HCO}) \qquad (7)$$

For the yield of other products,

$$Y_{t,i} = Y_{f,i} + Y_{s,i} \times (Y_{f,LCG} + Y_{f,HCO}) \qquad (8)$$

where i refers to dry gas, LPG, diesel, or coke. According to the product distribution, the blending ratio of gasoline from the first stage (heavy gasoline) and second stage (full range gasoline) are 94:100, thus the group composition of final gasoline can be calculated. The calculated results are shown in Table S3 in the Supporting Information.

From the product distribution of the second stage riser, it can be found that with the help of the configuration-changed riser reactor, the olefin content of LCG decreased from 57.8 wt % to 22.7 wt %. Without considering the gasoline created by HCO cracking, the olefin conversion of LCG has reached approximately 61%, while in the conventional riser reactor it is below 40%. The results further demostrate that increasing the density of catalyst in the LCG reaction zone can make up the loss of acid sites which are covered by cokes and can increase the contact opportunities between oil vapor and catalytic active centers. Therefore, the conversion of olefins in gasoline was enhanced. Because of the inferior crackability of the CGO, only about 65 wt % of the HCO can be further cracked. However,

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dx.doi.org/10.1021/ie302650t | Ind. Eng. Chem. Res. 2013, 52, 658–668

the final conversion still can reach 91 wt %, which is attributed to the advantages of the novel FCC process. Because about half of the olefins in the gasoline of the first-stage riser were recycled to the second stage riser, the olefin content of the remaining heavy gasoline was only 19.5 wt %. A desired group composition can be seen in the final gasoline, where more than 16 wt % of olefins were converted into high-octane iso-paraffins and aromatics and the olefin content of the final gasoline was only 21 wt %, which is much lower than that produced by the conventional FCC process.

3.4.2. Comparison of Different FCC Process. In order to describe the advantages and disadvantages of the MFT FCC process, the conventional FCC and TSR FCC processes were used as comparative tests. The advantages of the TSR technology have been reported previously,[12,13] thus there is no focus on them in this work.

As shown in Table S4 in the Supporting Information, due to the inferior crackability of CGO, the conventional FCC process cannot convert it effectively. Despite the feed conversion being low, the diesel-to-gasoline ratio is still only 0.73, moreover the olefin content of gasoline is as high as 42.4 wt %. When the CGO was processed by the TSR FCC process, a significant increase in the feed conversion can be seen, while the selectivity of dry gas and coke decreased, and the olefin content decreased to 38 wt %, which still cannot meet the gasoline regulations. Although both the riser outlet temperatures of two stages in the MFT FCC process were lower than that in the TSR FCC process, a higher once-through conversion still can be seen, which is beneficial for processing heavy oil. This is because in the MFT process, the synergistic process was used in the second-stage riser, indeed, the HCO was cracked in a higher severity (555 °C reaction temperature and 8 CTO). Even though the high temperature and large CTO operation would lead to the increase of dry gas and coke yields, it is an effective method to enhance the conversion of HCO. When the synergistic process was used in the second stage riser, where a short residence time in the HCO reaction zone was controlled, more light oil still can be obtained. Because of the improved performance in the second stage riser, lower operating severity can be carried out in the first stage riser; therefore, more diesel oil can be obtained. Compared with the TSR process, in the MFT process the feed conversion, light oil yield and diesel yield increased 2.2 wt %, 2.0 wt %, and 3.3 wt %, respectively, as well as the diesel-to-gasoline ratio increased from 0.84 to approximately 1. Nevertheless, the yields of dry gas and coke also increased 1.3 wt %.

It should be noted that the gasoline reformation process also contributes to the increase of dry gas and coke yield. But from comparing the product distributions in the TSR and MFT processes, it can be inferred that it accounts for less than 1%, which is much lower than other gasoline reformation FCC processes.[17,23−25] Nevertheless, the gasoline-recycling option significantly improves the quality of FCC gasoline. Approximately 17 wt % of olefins were converted into iso-paraffins and aromatics while maintaining the octane number. This is attributed to several measures which have been described previously, including the selective recycling of LCG, the synergistic process in the second stage riser, and the design of a novel configuration-changed riser reactor. The increase of octane number is due to the isomerization, hydrogen-transfer, and aromatization reactions. In the process of LCG reformation, the proportion of the aromatization reaction is less than the other two reactions, but aromatics have higher

MON (almost higher than 100). Compared with the hydrotreating process, the greatest advantage of the MFT process is that the 1-pentene (MON = 77), *cis*-2-pentene, and *trans*-2-pentene (MON = 80), which accounts for 40 wt % in the olefins (or 23 wt % in the LCG) are converted into isopentane (MON = 90) but not *n*-pentane (MON = 62). Moreover, the operating cost of the FCC process is much lower than the hydrotreating process. Therefore, from the viewpoint of LCG reformation, the MFT FCC process is better than the hydrotreating process. However, the hydrotreating units are essential for removing sulfur from FCC gasoline.

4. CONCLUSIONS

To convert heavy oil into more diesel and low-olefin gasoline, based on the TSR FCC process, the multifunctional two-stage riser (MFT) FCC process was proposed and then experimented with using a pilot-scale riser FCC apparatus.

In the first stage riser, decreasing the operating severity is beneficial to increase diesel yield but the conversion should also be considered. Because of the inferior crackability of HCO, increasing the reaction temperature and CTO is an effective method to enhance the conversion of HCO. However, it would also lead to the increase of dry gas and coke yields, due to the enhanced thermal cracking, dehydrogenation, condensation, and protolytic cracking reactions. In our research the appropriate reaction temperature is 555 °C, which could enhance the conversion of HCO without leading to the sharp increase of undesired reactions, hence more light oil could be obtained.

The semispent catalyst after HCO reaction still has enough activity for upgrading light gasoline. Because of more strong acid sites associated with dry gas and coke formation being covered by cokes, the semispent catalyst has better acid strength distribution than regenerated catalyst, which is beneficial for preventing gasoline from being cracked. Then a synergistic process was proposed, where the LCG was selectively recycled from the upper position of the riser reactor, thus the high-severity reaction zone for HCO cracking and the low-severity reaction zone for gasoline upgrading were provided. A significant increase in conversion can be achieved as well as the LCG can be efficiently upgraded. In addition, changing the structure of riser reactor can further increase the olefin conversion of LCG. Comparing with the TSR FCC process, the MFT FCC process increased feed conversion and diesel yield with 2.2 wt % and 3.3 wt %, respectively, as well as the olefin content of gasoline decreased approximately 17 wt %.

In China, because of the lack of hydrotreating, catalytic reforming, alkylation, and MTBE units, the gasoline quality improvement faces a great challenge. If the novel FCC process can be applied to improve the quality of FCC gasoline at the source, both refineries and individuals would benefit from it. Besides, it can help to secure diesel supplies.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Properties of heavy feedstocks, product distribution of HY-CGO cracked under different operating conditions, product distribution of multifunctional two-stage riser catalytic cracking of HY-CGO, comparison of different processing schemes of HY-CGO on product distribution and gasoline composition, and comparison schematic of the TSR and MFT processes. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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