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# Fundamentals of Petroleum Residue Cracking Gasification for Coproduction of Oil and Syngas

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**ABSTRACT:** Vacuum residue (VR) was stepwise converted via catalytic cracking for liquid and coke gasification for hydrogen-rich syngas in a fluidized bed reactor. Silica sand and spent equilibrium FCC (E-FCC) catalyst were used as the catalysts for VR cracking. The liquid yield was about 89 wt % at 568 °C using silica sand as catalyst and the conversion ratio of heavy fractions was only 55%. About 60 wt % VR was converted into gas and coke over the E-FCC catalyst at 480 °C, showing that the catalyst had too strong acidity for VR cracking. The E-FCC catalyst was thus modified (aged) with both hydrothermal treatment and impregnation of alkali and alkaline-earth metals (K and Mg) to weaken its acidity and facilitate the liquid oil production. The aged FCC (A-FCC) catalyst exhibited appropriate cracking activity to allow both the expected liquid yield of about 80 wt % and heavy fraction conversion ratio of up to 98 wt %. Steam gasification of the deposited coke on the surface of the A-FCC catalyst resulted in the production of syngas containing CO and H<sub>2</sub> content to be about 45 and 42 vol %, respectively.

## 1. INTRODUCTION

Petroleum residues refer usually to the heavy fractions generated in petroleum refining, including atmosphere residue (AR), vacuum residue (VR), and deoiled asphalt. The newly exploited heavy crudes, such as natural bitumen and shale oil, also have properties similar to such petroleum residues. Thus, the terminology of heavy oil or heavy residue can be also used to indicate all such heavy petroleum oils. Worldwide the dependence on heavy oil is increasing because of the extinction of conventional oil feed. The International Energy Agency (IEA) estimated that there will be 6 trillion barrels of heavy oil into market globally, which is more than twice the amount of the normal oil resources.<sup>1</sup> The heavy petroleum residues have the characteristics of high boiling point, high Conradson carbon residue (CCR), and high contents of heavy metals (i.e., Ni and V), sulfur, and nitrogen. Thus, there is a great technology need for deep conversion of these heavy petroleum residues into light and middle distillates that can be further refined to vehicle fuels and raw chemical materials.

Generally, there are two typical technical ways to process heavy oil (heavy residue) based on carbon rejection and hydrogen addition, respectively.<sup>2,3</sup> The former is associated with thermal or catalytic thermal treatment, which includes mainly the visbreaking,<sup>4,5</sup> residue fluid catalytic cracking (RFCC),<sup>6–8</sup> and coking represented by the delayed coking and fluid/flexi coking.<sup>9–11</sup> As a mild thermal treatment technology, visbreaking is usually used to reduce the viscosity of heavy fractions for the downstream units.<sup>4</sup> For RFCC, the metal and sulfur in the heavy feedstock would cause great damage to the textural properties of the catalyst and lead to catalyst deactivation, thus causing the technology to be not applicable for the direct processing of the degraded residue.<sup>6</sup> Fluid/flexi coking has been used commercially for several decades, but is not as popular as delayed coking because of its

high capital investment and technical difficulty. By far, delayed coking has been widely used in refineries because of its wide feed adaptation, low investment, and easy operation.<sup>9</sup> Nonetheless, the delayed coking has often low liquid yield and produces high-sulfur petroleum coke. Essentially, the reactions occurring in any of such carbon rejection processes are to redistribute hydrogen among gas, liquid, and solid products.<sup>12</sup> When gas and liquid with high H/C ratio were produced, the production of coke was inevitable.

The hydrogenation process works to improve the H/C ratio by hydrotreating or hydrocracking the feedstock, which reduces the coke yield through facilitating the reactions between carbon and hydrogen and meanwhile produces more low-sulfur gasoline and diesel.<sup>13–16</sup> It requires, however, high capital investment and high operation cost because the hydrogenation of heavy residues has to be under some demanding conditions such as high pressure and H<sub>2</sub>-rich atmosphere. The hydrogen requirement is also a critical issue for the hydrotreating process.<sup>17</sup> Hydrogen production in the refinery mainly relies on catalytic reforming of naphtha and hydrogen recovery from H<sub>2</sub>-rich off-gases such as LPG and dry gas. When processing heavy crude, however, the supply of hydrogen by such methods is usually insufficient. Thus, for a long time refiners have worked on converting heavy liquid, such as bottom crude or petroleum coke, into hydrogen to meet the growing hydrogen need in the petroleum processing industry.

Recently, the so-called coal pyrolysis gasification process has been tested to extract first the liquid oil as well as gas from coal by pyrolysis at high efficiency and in turn to produce syngas via

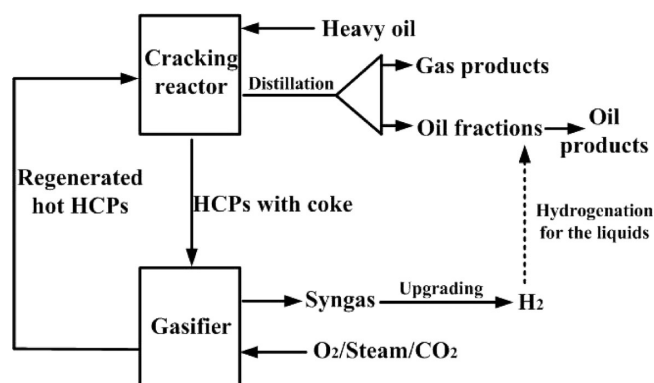
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gasifying the pyrolysis-generated char.<sup>18,19</sup> Applying the principle of this process to heavy oil including petroleum residues, the cracking gasification (RCG) process can thus be devised to crack first the heavy feedstock for liquid and then to gasify its resulting coke for the production of syngas that can be easily transformed into  $H_2$ . The process diagram is conceptualized in Figure 1. To maximize the yield of light liquid,



**Figure 1.** Conceptual diagram of the petroleum residue cracking gasification (RCG) process.

the cracking of the heavy feedstock should be in a catalyst bed for such a RCG process. The catalysts or heat carrier particles (HCPs) are circulated between the catalytic cracking and coke gasification reactors so that the catalyst provides not only catalytic activity but also the endothermic heat needed for the cracking reactions. The catalyst has to maintain its steady activity for oil cracking during circulation, raising thus some critical technical requirements for the integrated coke gasification reaction. For example, the gasification temperature must be appropriately low in terms of preventing the activity loss of the catalyst.

In comparison with delayed coking, the RCG process can be designed to maximize the liquid yield, for example, using steam fluidized bed to speed up the stripping of light volatiles and also optimizing the catalyst to allow the desired moderate conversion ratio. From the sense of the latter aspect, some accessible materials such as natural minerals (kaolin and smectite clay) and the spent commercial FCC catalyst can thus be used as the cracking catalyst for residues. In the RCG process, the coke is formed on the surface of the catalyst and then gasified in the gasifier to produce the hydrogen-rich syngas. From the viewpoint of syngas generation, the RCG process is very like the dual flexi-coking process in which the produced hydrogen via gasification is twice the amount needed for upgrading its extracted liquid.<sup>20</sup>

The objective of the present study is to investigate the fundamentals about the residue cracking and its generated coke gasification in a fluidized bed reactor by targeting the development of the RCG process. The cracking performance variation with the catalyst properties and operation parameters was studied over both silica sand and spent equilibrium FCC (E-FCC) catalysts. The E-FCC catalyst was also treated with the steam aging and alkaline metal impregnation to optimize its liquid yield and heavy component conversion ratio. The cracking-generated coke on the surface of FCC catalyst was gasified to clarify the characteristics of syngas production. Heavy residue cracking over the regenerated FCC catalyst by

gasification was conducted to identify the possibility of catalyst circulation in the RCG process.

## 2. EXPERIMENTAL SECTION

**2.1. Catalyst and Residue Oil.** Silica sand and spent equilibrium FCC (E-FCC) catalyst were chosen to be the catalysts in this study. The sand was first acid-treated, washed, and calcined at 800 °C to remove the impurities. As an inert catalyst, its use was to investigate the thermal cracking behavior of the heavy residue.

The spent E-FCC catalyst was from SinoPec Corporation. The acidity of the E-FCC catalyst was adjusted by doping alkaline salt (Mg and K carbonates)<sup>21</sup> and hydrothermal treatment in steam at 800 °C. It was reported that alkaline-metal additive, especially the potassium-base additive, could not only weaken the acidity of the catalyst but also accelerate the gasification of deposited coke.<sup>22,23</sup> The spent E-FCC catalyst was first immersed into a solution of an alkaline carbonate (Mg or K), and the formed slurry was continuously stirred in a water-bath of 50 °C for about 300 min. The wet catalyst from filtration was in turn dried at 105 °C for 5 h and finally calcined at 600 °C for 4 h. In the prepared catalyst the content of alkaline metal, either Mg or K, was found to be 1 mmol cations/g, and herein the names Mg-FCC and K-FCC are used to indicate the spent E-FCC impregnated with Mg and K, respectively. The aged FCC (A-FCC) shown herein was made by steam deactivation of the spent E-FCC at 800 °C for 17 h. Table 1 shows the properties of these catalysts. The silica sand,

**Table 1.** Properties of the Catalysts Employed in this Study<sup>a</sup>

property parameter	silica sand	E-FCC	A-FCC	K-FCC	Mg-FCC
particle density ( $\text{g}\cdot\text{cm}^{-3}$ )	2800	1480	1480	1480	1480
Sauter mean diameter ( $\mu\text{m}$ )	95	62	61	62	62
surface area ( $\text{m}^2\cdot\text{g}^{-1}$ )		235.2	67.3	182.52	199.94
pore volume ( $\text{cm}^3\cdot\text{g}^{-1}$ )		0.13	0.17	0.13	0.16
average pore diameter ( $\text{\AA}$ )		48.67	83.23	51.63	59.31
XRF analysis of the E-FCC catalyst (wt %)					
type of zeolite		$\text{Al}_2\text{O}_3$	$\text{SiO}_2$	$\text{Na}_2\text{O}$	$\text{Re}_2\text{O}_3$
ultrastable Y-zeolite (USY)		57.88	30.74	0.11	8.21

<sup>a</sup>E-FCC: Equilibrium FCC; A-FCC: aged FCC; K-FCC and Mg-FCC: FCC impregnated with K and Mg, respectively.

potassium carbonate ( $\text{K}_2\text{CO}_3$ ), and magnesium carbonate ( $4\text{MgCO}_3\cdot\text{Mg}(\text{OH})_2\cdot 5\text{H}_2\text{O}$ ) referred to above were all obtained from the commercial market.

A vacuum residue (VR) provided by Changqing oil field (Shaanxi Province, China) was used as the heavy feedstock and its properties were summarized in Table 2. The VR is of high density and high viscosity, as indicated by its high CCR and boiling point. The VR is of paraffinic-base and has thus relatively low asphaltene content but high hydrogen content.

**2.2. Apparatus and Operation.** The fluidized bed (FB) reactor system is shown schematically in Figure 2, which consisted mainly of the parts for oil feeding, gas supplying, reaction (i.e., reactor), and product collection and analysis. The FB was made of stainless steel and had an inner diameter of 60 mm. Its total length was 1000 mm but with a 200-mm long expanded freeboard section of 120 mm in diameter. A porous stainless distributor was mounted at the middle level of the reactor to divide the reactor into a preheating section and a

**Table 2.** Properties of the Tested Changqing Vacuum Residue

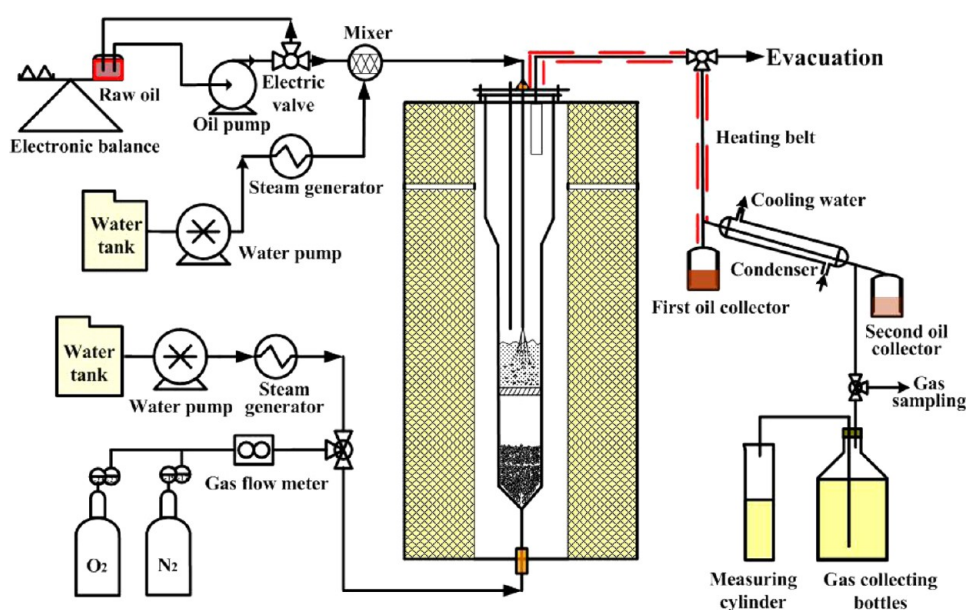
density (20 °C, g·cm <sup>-3</sup> )	0.921
viscosity (80 °C, mm <sup>2</sup> ·s <sup>-1</sup> )	155.6
Conradson carbon residue (wt %)	10.4
molecular weight	690
element analysis (wt %)	
C	86.80
H	12.12
S	0.17
N	0.48
O	0.43
group analysis (wt %)	
saturates	49.8
aromatics	28.7
resin	19.6
asphaltenes	1.9
boiling point range (°C)	
5%	435
10%	475
20%	514
30%	542
40%	569
50%	594
60%	623
70%	654
80%	712
90%	721

reaction section. The temperature of the reactor could be detected via changing the measuring point inside the thermocouple well, which was vertically parallel with feeding pipe. It is found that the temperature inside the reactor was almost axially uniform in about 300 mm above the gas distributor. The heavy oil was preheated and continuously fed into the fluidized hot particles above the gas distributor with a dual-plunger oil pump. Steam generated in an oven of 300 °C was used to atomize the heavy feedstock during feeding and

also to purge the remaining oil in the feeding pipe after stopping the oil supply. Another steam generator was installed in the gas feeding line to provide fluidizing and stripping gas for VR cracking. This steam, by mixing a specified amount of oxygen, was also the reagent for catalyst regeneration in coke gasification. Nitrogen was the purging gas in each experiment.

The test was started with loading a given amount of catalyst into the FB reactor and heating the particle bed to the designated temperature. A designed amount of bottom steam was introduced into the bed to fluidize the catalyst particles. When the bed temperature reached its preset value, heavy oil preheated at 95 °C and mixed with steam of about 300 °C was injected downward into the inside of the fluidized particles through a nozzle. Caught by hot catalyst particles, the tiny oil-steam droplets vaporized and cracked in the bed through interacting with the catalyst. The formed light fraction was quickly stripped and carried by the upward fluidizing steam. To reduce the elutriation of fine particles with the gas product, there was a steel filter sintered with 25- $\mu$ m steel powders on the top of the reactor. The coke formed in the VR cracking was deposited on the surface of catalyst particles, which was in turn put into gasification through the following operations. The bottom steam was switched to nitrogen to purge the entire system and meanwhile the temperature setting of the reactor was raised to the value for gasification. When the bed temperature reached the preset value, the N<sub>2</sub> into the bed bottom was switched to the gasification reagent gas of either pure steam or steam–oxygen mixture. The composition of the produced gas was monitored until no further gas was generated. When coke gasification was not conducted, we could alternatively measure the carbon content of the catalyst after the end of VR cracking and further obtain the coke yield. Surely, the preceding test cycle of VR cracking and coke gasification can be repeated to evaluate the activity variation of catalyst during its circulation in the cracking gasification process.

All gas streams were controlled with mass flow meters, and the gas product of VR cracking was cooled in the downstream of the reactor to collect the condensable liquid (oil). The

**Figure 2.** Schematic diagram of the experimental setup for testing residue cracking gasification.



heavier fraction was first collected at 110 °C by electrically heating the pipelines to the collector with heating belts, and the light oil was then collected by condensing the gas with cooling water at 0.2 °C. The collected liquid was finally mixed and centrifuged to remove water and weighed to determine the liquid or oil yield. The noncondensable gas was volumetrically measured through replacing salted water, giving thus the time-series gas production characteristics by measuring the volume variation of the replaced water with time. In this study, each experiment was reproduced at least twice, and the mass balance was found to be over 95% so that the relative error of the measurement was below 5%.

**2.3. Analysis and Characterization.** The noncondensable gas product of VR cracking was analyzed with a multichannel gas chromatograph (GC, BEIFEN 3420A) that had both hydrogen flame ionization and thermal conductivity detectors. The gas components detectable by the GC are H<sub>2</sub>, CO, CO<sub>2</sub>, and hydrocarbons C1–C6, and these components were divided into two groups: dry gas consisting of H<sub>2</sub>, CO, CO<sub>2</sub>, and C1–C2 hydrocarbons, and liquefied petroleum gas (LPG) of C3–C5 hydrocarbons. The total gas yield was the sum of the LPG and dry gas component. The mass yield for each gas component was calculated from the total gas product volume and gas composition following the ideal gas law. The so-called simulated distillation GC (Agilent 7890A) was used to characterize the liquid or oil product in terms of the distillation fractions for different ranges of boiling points. The fractions distinguished in this article include gasoline in IBP–180 °C, diesel in 180–350 °C, vacuum gas oil (VGO) in 350–500 °C, and heavy oil over 500 °C. The heavy oil fraction was treated as the unconverted part in cracking, thus having the conversion ratio Rc as

$$\text{Rc} = 100\% - \text{liquid yield (wt \%)} \\ \times \text{heavy oil fraction (wt \%)}$$

To determine the coke yield, the carbon deposited on the catalyst was measured with a coke analyzer (CS-344, LECO). The catalyst sample was burnt in pure oxygen and its generated gas was analyzed with a GC for the content of CO<sub>2</sub>.

The used catalyst was characterized using N<sub>2</sub> adsorption at 77 K and in turn outgassed in vacuum at 300 °C for 24 h in an automatic BET analyzer (Autosorb-1, Quantachrome) to determine the specific surface area and pore volume. The catalyst acidity was measured with the temperature-programmed ammonia desorption (NH<sub>3</sub>-TPD, Quantachrome) method. For this, a catalyst sample (0.05 g) was loaded into a U-tube quartz reactor and heated to 200 °C in helium to remove its impurities in advance. Then, the temperature was lowered to 150 °C and the helium stream was changed to an ammonia stream to perform the NH<sub>3</sub> adsorption for about 120 min. After the adsorption, helium was fed again to purge the BET analyzer until the baseline of the analyzer was stable. In turn, the NH<sub>3</sub> desorption was tested by heating the catalyst sample to 900 °C at a rate of 10 °C/min, and mass spectrometry (PROLINE, AMETEK) was taken to monitor the variations in the desorbed ammonia and helium amounts. The X-ray diffraction analyzer (XRD, X'Pert MPD Pro, Panalytical) was equipped with a 1.5408 Å ( $\lambda$ ) Cu K $\alpha$  radiator working at 40 kV and 20 mA, and the adopted scanning rate was 4°/min in the range of 5°–90°. This study also used scanning electron microscopy (SEM, JSM-6700F JEOL) for observing the surface morphology of the fresh and reacted

catalyst. Its accelerating voltage was 20 kV and 20 mm of working distance, and its aluminum stub was 10 mm in diameter.

### 3. RESULTS AND DISCUSSION

**3.1. VR Cracking.** **3.1.1. Condition Determination.** The operating conditions for the catalytic cracking tests are summarized in Table 3. To have the optimal operating

**Table 3. Operating Conditions for the Residue Cracking Tests**

item	value
reaction temperature (°C)	480–600
steam generator temperature (°C)	300
water inflow rate (mL/min)	2–10
oil inflow rate (mL/min)	6
fluidization number against U <sub>mf</sub> (-)	5–20
catalyst-to-oil weight ratio (-)	4–12
steam-to-oil weight ratio (-)	0.3–1.6

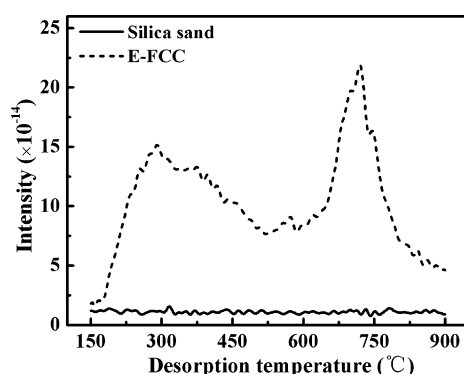
conditions for cracking experiments, some preliminary tests were conducted to understand the effects of reaction temperature, fluidization number against U<sub>mf</sub> for the catalyst particles (related to residence time), catalyst-to-oil weight ratio, and steam-to-oil weight ratio. The VR feeding rate and superficial gas velocity were found to be of great importance in determining the cracking performance for VR. Nonetheless, the maximal VR feeding rate is limited by the so-called bogging phenomenon. If the VR injection rate exceeded the vaporization rate, the bed would lose its fluidity in turn causing quick agglomeration of particles.<sup>11</sup> Our tests found that the required superficial gas (steam) velocity should be 10 times U<sub>mf</sub> to avoid the particle agglomeration in our facility. Based on this value, the steam feeding rates both for the bed bottom and oil injection were appropriately decided. The oil feeding rate was about 6 g/min and lasted for about 4 min. The catalyst-to-oil weight ratio was varied within 4–12 by changing the catalyst amount loaded into the reactor. Experimental results demonstrated that increasing the catalyst-to-oil weight ratio caused slightly higher heavy oil conversion ratio but relatively lower liquid yield. The catalyst-to-oil weight ratio of about 6.3 was thus chosen for the tests of this study, and this ratio was in fact similar to that applied for industrial FCC processes. The detailed operating parameters included a VR feeding amount of about 24 g, 150 g of catalyst in the FB reactor, a steam-to-oil ratio of about 0.6, and a bottom fluidizing steam leading to a superficial gas velocity of about 10 U<sub>mf</sub> of the tested FCC catalyst and silica sand particles. The reaction temperature was varied within 480–600 °C to study its effect on the feedstock conversion, product distribution, and liquid features under various conditions including catalysts.

**3.1.2. Over Silica Sand and E-FCC Catalyst.** Table 4 summarizes the VR cracking performances varying with reaction temperature using silica sand and commercial equilibrium FCC (E-FCC) catalyst. Via contacting with catalyst particles in the fluidized bed, the dispersed VR droplets were first vaporized and in turn converted into light distillates through thermal cracking and cleavage of the C–C, C–H, and C–heteroatom bonds present in the molecular structure of VR.<sup>24</sup> When using silica sand for VR cracking, the realized liquid yield was about 89 wt % but its conversion ratio was limited to 55% at temperatures of up to 568 °C. The major

Table 4. Product Distribution of VR Cracking over Silica Sand and E-FCC at Different Temperatures

	silica sand					E-FCC		
temperature (°C)	502	540	568	600	480	503	517	537
gas yield (wt %)	2.33	3.40	5.53	11.40	37.46	39.59	42.69	45.58
liquid yield (wt %)	92.63	91.44	88.87	82.46	40.90	38.65	35.26	31.56
coke (wt %)	5.05	5.16	5.60	6.14	21.64	21.76	22.05	22.85
dry gas (vol %)	75.69	73.45	72.37	70.42	25.61	30.19	32.55	35.83
fractional distribution of the produced liquid								
gasoline (wt %)	1.29	2.99	4.85	6.31	53.26	53.3	56.74	59.47
diesel (wt %)	6.50	11.08	13.35	18.19	44.9	45.79	42.47	39.92
VGO (wt %)	21.21	28.55	30.88	34.47	1.84	0.91	0.79	0.61
heavy oil (wt %)	71.01	57.38	50.93	41.0	0	0	0	0
conversion (%)	34.23	47.53	54.74	66.17	100.0	100.0	100.0	100.0

fractions in liquid had boiling points above 343 °C (representing VGO and heavy oil fractions). The surface area of the adopted silica sand was quite small, and its NH<sub>3</sub>-TPD diagram in Figure 3 reveals that there was hardly any acidic site

Figure 3. NH<sub>3</sub>-TPD analysis of silica sand and E-FCC catalyst.

on the surface. Thermal cracking is thus the major way to convert VR over silica sand, making more than 70% of the generated cracking gas to be dry gas.<sup>25</sup> The conversion ratio was low as 66% at 600 °C, indicating that thermal cracking only was insufficient to obtain the expected deep conversion of VR.

Over the E-FCC catalyst, VR was completely converted at the tested temperatures, but with more than 60 wt % of the VR into gas and coke so that the liquid yield was low. For example, the gas yield was up to 38 wt % even at 480 °C, meaning that the acidity of the E-FCC catalyst was too strong for VR cracking. The performance of catalytic cracking was subject to both acidity and textural properties of the catalyst.<sup>26</sup> Figure 3 compares the NH<sub>3</sub>-TPD diagrams for silica sand and the E-FCC catalyst (its USY zeolite content was high), revealing that the NH<sub>3</sub> desorption occurred at all the tested temperatures above 150 °C for the E-FCC catalyst but no obvious NH<sub>3</sub> desorption was detected for silica sand. This shows the strong acidity of the E-FCC catalyst, especially at 700–800 °C. The BET analysis showed large surface area (235.2 m<sup>2</sup>·g<sup>-1</sup>) and pore volume (0.13 cm<sup>3</sup>·g<sup>-1</sup>), while the slow oil feeding rate (about 0.1 g/s) guaranteed further the oil droplets to have enough opportunity to interact with acidity sites or to diffuse in pore channels. All of these factors thus facilitated the excessive conversion of VR into gas.

The majority of the liquid generated over the E-FCC catalyst was the fractions with boiling points below 343 °C (i.e., the gasoline and diesel fractions). About 30% of the generated gas was dry gas, much lower than that over silica sand. Thus, the

mechanism of VR cracking over the E-FCC catalyst was different from that over silica sand. While the former was mainly catalytic cracking, the latter was thermal cracking.<sup>27</sup> In fact, it is the acidic sites on the surface of the E-FCC catalyst that work as H<sup>+</sup> donators in the C–C bond cleavage involved in the VR conversion. There were also more LPG components in the cracking gas (than dry gas) over the E-FCC catalyst than that over silica sand because thermal cracking formed mainly dry gas by deep molecule cracking. As anticipated, raising temperature increased the dry gas yield due to the gradually deep cracking at higher temperatures.

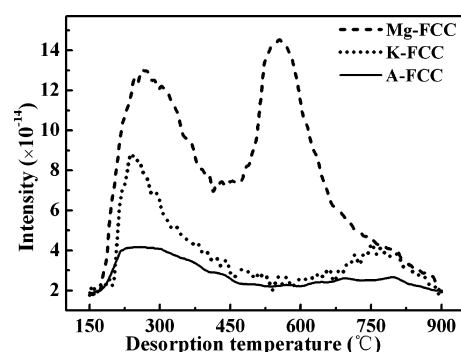
**3.1.3. Catalyst Optimization.** The E-FCC catalyst was further treated according to the method shown in Section 2.1 to reduce its acidity. Table 5 summarizes the product

Table 5. Product Distribution of VR Cracking over Modified FCC Catalysts at Different Temperatures

	Mg-FCC	K-FCC	A-FCC			
catalyst used	510 °C	507 °C	480 °C	503 °C	517 °C	537 °C
gas yield (wt %)	42.38	27.20	7.61	10.27	12.91	16.02
liquid yield (wt %)	38.04	56.03	84.90	82.39	79.61	76.76
coke (wt %)	19.58	16.77	7.49	7.34	7.48	7.23
Dry gas per. (vol %)	29.21	25.56	30.21	36.04	41.29	42.66
fractional distribution of the produced liquid						
gasoline (wt %)	82.34	73.49	36.58	38.5	39.57	42.13
diesel (wt %)	17.66	26.51	43.46	42.28	41.58	39.85
VGO (wt %)	0	0	18.1	17.61	17.3	16.77
heavy oil (wt %)	0	0	1.86	1.61	1.55	1.25
conversion (%)	100.00	100.00	98.42	98.67	98.77	99.04

distribution over the treated FCC catalysts including Mg-FCC, K-FCC, and A-FCC. The impregnation of alkaline metals appeared insufficient to weaken the surface acidity so that the gas yield was still high and liquid product was low for both Mg-FCC and K-FCC catalysts. Figure 4 shows in fact that the Mg-FCC catalyst still has very high acidic density, which is even equivalent to that of the E-FCC catalyst characterized in Figure 3. The liquid yield for K-FCC catalyst was about 10 wt % higher than that of Mg-FCC catalyst, complying with its weaker acidity than Mg-FCC shown in Figure 4. However, the acidic sites in the K-FCC catalyst were still too high to realize a satisfactory liquid yield for VR cracking.

The acidity of the A-FCC catalyst was effectively reduced via hydrothermal treatment at 800 °C with pure steam, as indicated

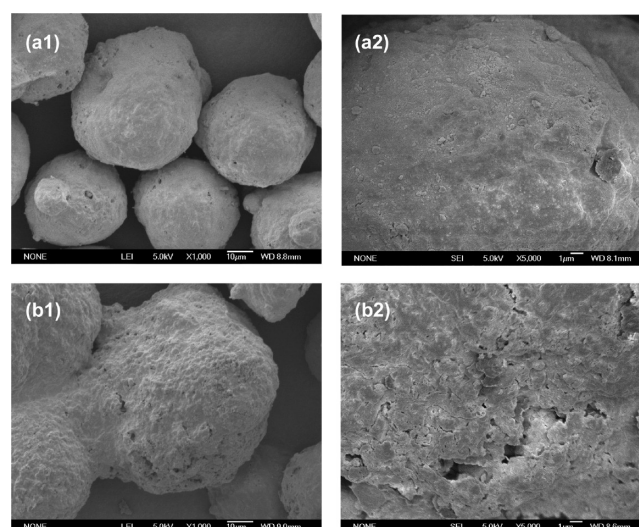


**Figure 4.**  $\text{NH}_3$ -TPD analysis of the A-FCC, K-FCC, and Mg-FCC catalysts.

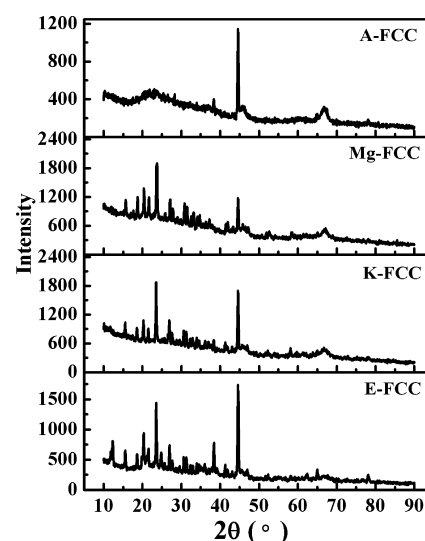
by the disappearance of its strong acidity peaks. As a result, the liquid yield of the A-FCC catalyst greatly enhanced to about 80 wt % at 480–537 °C, and the corresponding conversion ratio of heavy fraction was over 98%. The first reason for the high liquid yield was that the mild acidity of the A-FCC catalyst could avoid the overcracking of VR. Second, the steam-oil droplets were finally presented as a thin surface layer on the catalyst, thus much facilitating the mass transfer to prevent the overcracking as well. Gray et al.<sup>28</sup> found that with the reduction of film's thickness, the coke yield decreased and the yield of distillate products (boiling point <524 °C) increased because of the more effective transport of the products from the liquid phase. Moreover, the volatiles deposited on the surface of catalyst are prone to be stripped out of the high-temperature fluidized bed zone by the upward fluidization steam. This avoided further the secondary cracking of the oil fractions and inhibited the coke formation. As for the delayed coking process, the liquid phase tended to combine into a carbonaceous mesophase because of the limited mass transfer, thus leading to high coke yield.<sup>29</sup> This mechanism has been justified by the high liquid yield for the fluid coking than for the delayed coking.<sup>11</sup> Our data showed that the coke yield in this study was about 0.7–0.8 times of the CCR value, much lower than that of the delayed coking process.

The BET analysis in Table 1 clarified that the textural properties of catalyst were changed by the hydrothermal treatment. Figure 5 verifies this by more large pores in SEM images for the catalyst after hydrothermal treatment. The macropores present in the catalyst provided more reaction sites for the gas–liquid phase and thereby enhanced the gas–liquid mass transfer. In VR cracking, the formed coke would gradually block the pores and eventually deactivate the catalyst. The more and larger pores implied higher resistance to coke plug. Consequently, the improved textural properties and reduced acidity for the A-FCC catalyst both contributed to its high liquid yield and high heavy fraction conversion ratio, while the fluidized cracking itself suppressed as well the secondary cracking.

Figure 6 shows the XRD spectra of all the tested catalysts. Little change in the crystal structure can be found for the FCC catalyst impregnated with alkaline metals. This may also interpret the reason that the alkaline-loaded catalysts had cracking performance similar to that of E-FCC catalyst. Nonetheless, a big difference in the XRD intensity was identified between A-FCC catalyst with steam aging and the original E-FCC catalyst, especially for those characteristic peaks representing zeolite in  $2\theta$  of 10° to 40°. The alumina framework of zeolite would be partially removed in the high-



**Figure 5.** Micrographs of E-FCC catalyst (a1, a2) and aged FCC catalyst (b1, b2) Magnification:  $\times 1000$  for a1 and b1,  $\times 5000$  for a2 and b2.



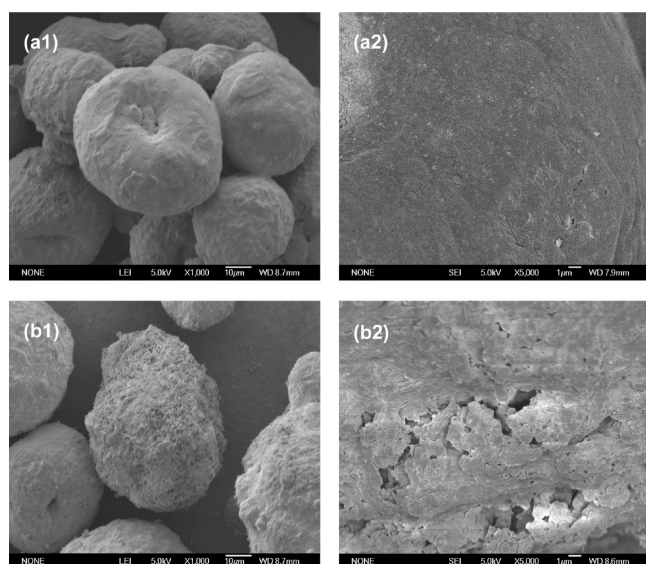
**Figure 6.** XRD spectra of the original and thermally treated FCC catalysts.

temperature steaming process, thus there having much weak peaks in XRD for zeolite and indicating the dealumination effect and the loss of the strong acidity for the zeolite. Figure 6 shows that the A-FCC catalyst still possessed the characteristic peaks of alumina (i.e., 45° and 67°), showing little change in the main skeleton of the catalyst during hydrothermal treatment. The degree of framework change depended on the treatment method and severity upon the E-FCC catalyst.

**3.2. Coke Gasification.** The nascent coke on the surface of the cracking catalyst may have higher reactivity than the densified cold petroleum coke generated in the delayed coking process. The fluid coking process of heavy oil has verified also that the newly deposited nascent coke on the surface of coke particles can be efficiently converted into gas but retaining the original core coke particles. This means that the reaction activity of a coke sample varies greatly with its textural structure.<sup>11</sup> In addition, the metal species (i.e., Fe, Na, and K etc.) in the catalyst and residues may have some promotional effects to accelerate the gasification reaction.



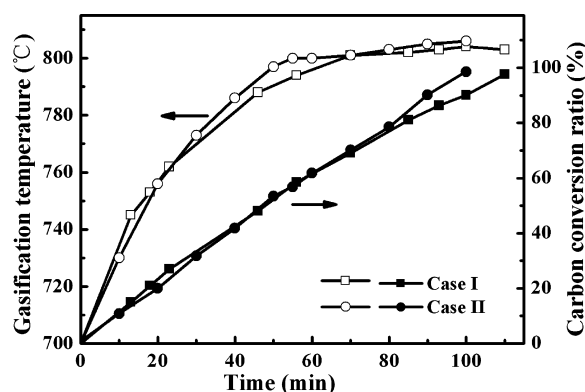
On the other hand, the coke deposited on the surface of catalyst should not only deactivate the catalyst via blocking its pores but also decrease the fluidization propensity because of the increased adherence of particles.<sup>31</sup> Figure 7 shows a dense



**Figure 7.** Micrographs of FCC catalyst coated with coke (a1, a2) and regenerated with gasification (b1, b2) Magnification:  $\times 1000$  for a1 and b1,  $\times 5000$  for a2 and b2.

layer of coke formed on the surface of the coked catalyst particle, which blocked the pore structure and made also several particles tend to be piled up together. The coke layer was removed by steam gasification and the regenerated catalyst (G-FCC) had surface morphology similar to the original aged FCC catalyst pictured in Figure 5. It was reported that the poisoning effect of heavy metals and carbon content in the catalyst could be simultaneously diminished in carbon gasification so that the catalytic activity can be regained.<sup>32</sup> Meanwhile, hydrogen-rich syngas was formed in the process of catalyst regeneration to produce  $H_2$  for liquid upgrading as the dual flexi-coking technology did.<sup>20</sup>

Figure 8 shows the time-series temperature and the corresponding carbon conversion of coke gasification for the tested two cases. Either pure steam (Case I) or a mixture of 95 vol % steam plus 5 vol % oxygen (Case II) was used as the



**Figure 8.** Time-series temperature rise and carbon conversion ratio of coke gasification (Case I: pure steam; Case II: steam with 5 vol % oxygen).

gasification reagent. It was found that before 700 °C the coke gasification reaction was very slow. So the gasification was initiated with feeding steam into the reactor at about 700 °C (thus Figure 8 starts from this point) and ended when no C-containing gas was generated from the reactor. The final gasification temperature was 800 °C for the deposited coke on the FCC catalyst. The temperature-rising stage, that is, from the initial temperature (700 °C) to the desired coke gasification conditions (about 800 °C), was necessary because of the batch operation of the experimental setup. As shown in Figure 8, the reaction lasted for about 100 min, and about 60% of the coke was converted within about 45 min (i.e., the temperature-rising period). This result shows in fact that the coke deposited on the catalyst particles, say, about 0.01–0.02 g coke/g catalyst, has relatively good reactivity for steam gasification. It may be related to the factors that the coke is highly reactive hot coke and the deposited layer on the catalyst surface is very thin, while the cracking catalyst may catalyze as well the coke gasification reaction. However, the reaction rate at the low temperature range might be low because of the limited chemical reaction kinetics. When reaching the designated temperature, there was little carbon left for conversion. This might be the reason for the relatively long time for carbon conversion. In the industrial operation, the regeneration time for catalyst would be greatly shortened because of the absence of a temperature rising period. Introducing oxygen into the reaction slightly shortened the reaction time, but the promotion effect was not very distinctive. It shows again that the deposited hot coke has certainly good steam gasification reactivity and using only steam can realize its full conversion.

Table 6 shows the composition of the produced gas corresponding to the coke gasification tests plotted in Figure

**Table 6. Composition of Syngas from Coke Gasification under Different Conditions<sup>a</sup>**

gas species	case I	case II
$H_2$ (vol %)	42.54	35.48
CO (vol %)	44.93	45.40
$CH_4$ (vol %)	4.81	3.71
$CO_2$ (vol %)	7.07	14.62
C2 hydrocarbons (vol %)	0.66	0.78
carbon conversion (%)	97.60	98.20

<sup>a</sup>Case I: pure steam; Case II: steam with 5 vol % oxygen.

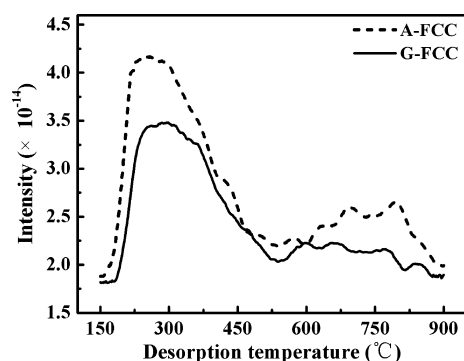
8. The total amount of  $H_2$  and CO was up to 87 vol % of the produced gas for Case I. Considering the practical applications, certain oxygen has to be introduced into the coke gasification in order to keep the reaction temperature and also to promote the reaction. Thus, in Table 6 the  $CO_2$  concentration was doubled for Case II with certain  $O_2$  in the gasification reagent comparing with Case I, and the  $H_2$  concentration in the produced gas was obviously decreased in Case II due to its partial combustion via  $O_2$ .

**3.3. Cracking Gasification.** VR cracking was further tested over the gasification-regenerated catalyst (i.e., G-FCC) depicted above to clarify the possibility of circulating the catalyst in the petroleum residue cracking gasification (RCG) process. Table 7 compares the product distributions obtained over the A-FCC and G-FCC catalysts, showing that there was little difference between the two cases. While this indicates the possibility to circulate the A-FCC catalyst, the  $NH_3$ -TPD diagram in Figure 9 demonstrated a slight decrease in the surface acidity for the G-



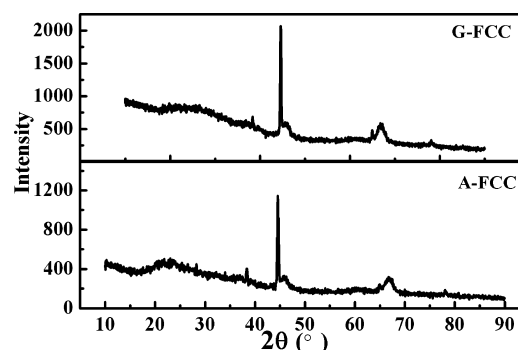
**Table 7. Product Distribution of VR Cracking over A-FCC and Regenerated FCC Catalysts**

	A-FCC	G-FCC
temp. (°C)	517	517
gas yield (wt %)	12.91	10.88
liquid yield (wt %)	79.61	81.76
coke (wt %)	7.48	7.37
dry gas (vol %)	41.29	45.98
fractional distribution of the produced liquid		
gasoline (wt %)	39.57	38.03
diesel (wt %)	41.58	41.01
VGO (wt %)	17.3	18.76
heavy oil (wt %)	1.55	2.2
conversion ratio (%)	98.77	98.20

**Figure 9.** NH<sub>3</sub>-TPD analysis of aged (A-FCC) and regenerated (G-FCC) catalysts.

FCC in comparison with the A-FCC catalyst. And this should be the reason for the slightly lower gas yield, higher liquid production, and also lower heavy fraction conversion ratio over the G-FCC catalyst shown in Table 7. The cause for lowering the acidity and reactivity was that certain carbon should remain still in the catalyst after gasification and this carbon may cover the acidic sites of the catalyst. In practical processes, it is expected that the remaining carbon should change little after a few cycles of circulation so that the G-FCC catalyst can have finally a lower but stable activity. Meanwhile, certain fresh catalysts could be added to compensate the reduced activity in catalyst recirculation and regeneration. With all of these conditions, the studied RCG process should have its justified technology feasibility for converting petroleum residues.

Figure 10 shows the XRD spectra of the A-FCC and G-FCC catalysts. It is true that little change was identified in the crystalline peaks, and this means that the crystal structure of the catalyst remained during the coke gasification. In fact, the gasification circumstance is quite like the aging conditions (here, at 800 °C for 17 h in steam) applied to the E-FCC catalyst. Thus, it is plausible that the G-FCC catalyst kept the characteristics of the A-FCC catalyst. As for the test shown in Figure 8, a temperature rise period was required, which made the catalyst regeneration take much longer time than in an actual industrial process. There, the time for catalyst regeneration (coke gasification) should be much shortened because of the absence of the temperature rise period and the continuous flow of catalyst particles. Thus, the regenerated catalyst may have higher catalytic activity than that demonstrated in Table 7 and Figure 8. This will be further corroborated in a pilot test of the RCG process in the near

**Figure 10.** XRD spectra of aged (A-FCC) and regenerated (G-FCC) catalysts.

future. Notwithstanding, for the RCG process it is ideal to develop the catalyst that has moderate cracking activity for heavy residues or heavy oils but meanwhile good activity for catalyzing the deposited coke gasification so that the gasification can be at reasonably low temperatures to maintain the catalytic activity for cracking heavy fractions.

#### 4. CONCLUSIONS

Vacuum residue (VR) was hierarchically converted via the residue cracking gasification (RCG) process, first by stepwise residue cracking and followed by coke gasification in a fluidized bed reactor. When silica sand was used as the cracking catalyst, very high liquid yields were obtained but the conversion ratio for heavy fraction was very low. When the equilibrium FCC (E-FCC) catalyst was used, the VR was completely converted at the tested temperatures but most of the products were gas and coke due to the strong acidity of the catalyst that made the catalyst too active for VR cracking.

Neutralizing acidic sites with alkaline metal oxides and hydrothermal treatment with steam was conducted to adjust the catalyst activity and optimize the liquid production over the E-FCC catalyst. The aged FCC (A-FCC) catalyst was found to be the best, and it manifested rational cracking acidity and cracking activity, which enabled liquid yields over 80 wt % and heavy fraction conversion ratios of up to 98%.

The deposited coke on the catalyst during VR cracking was well gasified with pure steam and a mixture of 95% steam and 5% oxygen at 800 °C to produce H<sub>2</sub>-rich syngas. When the carbon conversion ratio in cracking was 98%, H<sub>2</sub> and CO in the produced gas was up to 80 vol % of the gas. The possibility to recirculate the catalyst was investigated by showing the equivalently same acidity and cracking activity of the catalyst regenerated via steam gasification of the deposited carbon on the spent catalyst (G-FCC). This was verified also by almost the same XRD spectra for the original and regenerated catalysts. As a consequence, the petroleum residue cracking gasification is shown to be technically feasible and represents an effective process for utilizing petroleum residues at high value and high efficiency.

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##### Notes

The authors declare no competing financial interest.

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