



Full Length Article

Fundamental study of hierarchical millisecond gas-phase catalytic cracking process for enhancing the production of light olefins from vacuum residue

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ABSTRACT

In order to enhance the production of light olefins from vacuum residue (VR), a novel hierarchical millisecond gas-phase catalytic cracking (HM-GCC) process was proposed. The process integrated the pyrolysis of VR and the catalytic cracking of the pyrolysis oil in the gas phase. Firstly, the effects of reaction temperature on the millisecond pyrolysis behavior of VR were investigated, and the results showed that the increase of C₂–C₄ hydrocarbons content was not obvious when increasing the temperature from 600 to 750 °C. However, the thermal cracking as a pretreatment process converted the VR macromolecule into the low molecular pyrolysis oil. After that, five different catalysts calcium aluminate, FCC catalyst, and ZSM-5 zeolites (Z-40, Z-80, and Z-200) were investigated to evaluate their activities in catalytic cracking of pyrolysis oil, and among them Z-40 showed the highest selectivity for C₂–C₄ hydrocarbons and BTX. For further study, the relative contents of C₂–C₄ hydrocarbons were higher for the combination of calcium aluminate and Z-40 (Z + C-cat) than that of the pure Z-40 catalyst. This result was attributed to the fact that Z + C-cat facilitated the cracking of macromolecules and inhibited hydrogen transfer reactions. Finally, the conversion of VR and pyrolysis oil was studied in the bench scales with calcium aluminate and Z-40 catalyst. The yield of ethylene, propylene and butenes increased by 4.69, 7.87 and 3.37 wt% respectively in the presence of Z-40.

1. Introduction

With the development of stored energy battery and the strict requirements of the environmental regulations, the electric vehicle has emerged with the advantages of near-zero pollution and energy saving. Replacement of fuel vehicles with electric vehicles has become an irreversible trend, which will follow by a sharp drop in transportation fuel consumption. Thus, petroleum refineries worldwide should be transformed from the production of transportation fuel (gasoline and diesel) to light olefins (ethylene, propylene and butenes) and BTX (benzene, toluene and xylene).

Light olefins and BTX are very important basic chemical raw materials. Particularly, ethylene and propylene are the most important light olefins because they are used to produce many petrochemicals products, such as polypropylene, polyethylene, propylene oxide, ethylene oxide, acrylonitrile, and acrylic acid. At present, about 95% of ethylene and 60% of propylene in the world are produced using light raw materials (natural gas, naphtha or light diesel oil) by steam thermal cracking process [1]. However, due to the depletion of traditional light petroleum resources [2,3], the very limited flexibility of steam cracking

(in particular, the low propylene to ethylene ratio and the difficulties to use heavy oil [4]) indicates that it is unappeasable for the market demand. Therefore, to directly produce light olefins through the catalytic cracking process using heavy oil appears to be a very attractive strategy to solve this problem [5].

To increase the yield of light olefins, refiners and researchers have paid more attention to redesigning FCC unit processes in the last few decades; such as the Indmax process developed by Indian Oil Corporation [6]; the PetroFCC process licensed by UOP [7]; the deep catalytic cracking process (DCC) and catalytic pyrolysis process (CPP) licensed by Sinopec, Research Institute of Petroleum Processing [8,9]; the high severity fluid catalytic cracking process (HS-FCC) developed by Nippon Oil Corporation [10,11]; and the two-stage riser catalytic cracking of heavy oil for maximizing propylene yield (TMP) process proposed by China University of Petroleum [12]. Compared with steam cracking, these processes have the advantages of wider range of raw materials, low reaction temperature, and adjustable product distribution. However, these processes still have some trouble such as the poison of catalysts, poor atomization, and low conversion etc. when processing the inferior feedstocks.

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ZSM-5 zeolite has been widely used in the catalytic cracking process for enhancing the yield of light olefins due to its shape-selectivity [13,14]. However, ZSM-5 zeolite mainly contains micropores, which are not large enough to contain larger molecules to allow the fast diffusion of substances. In addition, the heavy oil macromolecules accumulated on the surface of the zeolite are easy to form coke, thereby blocking the catalyst pores.

Furthermore, because the distillation range of VR is mainly above 500 °C, hydrocarbons mainly undergo liquid phase reaction in the existing process. The free radicals which split from hydrocarbon can disperse quickly in the gas phase whereas they are surrounded by surrounding molecules like a “cage” in the liquid phase. Thus, to disperse the formed free radicals, it is necessary to overcome the extra energy barriers spread out from the “cage” in the liquid phase. This is the so-called “radical cage effect” [15,16]. Therefore, how to improve the gas-phase reaction ratio and suppress the liquid-phase reaction will become the key problem for the next generation of heavy oil processing technology.

To solve the problems mentioned above, the author proposes the hierarchical millisecond gas-phase catalytic cracking (HM-GCC) process. As shown in Fig. 1, the heavy oil is sprayed into the downer-type reactor through a high-efficiency nozzle and quickly contacts with high temperature regenerated alkaline catalyst. After millisecond pyrolysis reaction, the produced oil-gas and coked catalyst are separated by a horizontal cyclone separator at the bottom of the downer reactor. The high temperature gas oil contacts and mixes with the regenerated catalyst in another downer-type reactor directly, and takes place millisecond catalytic cracking without condensate separation. The coked catalyst enters a riser-type gasifier for combustion and regeneration; and then returns to the downer reactor for recycling. The products are piped to a fractionation tower and cut into dry gas, light olefins, BTX, and fuel oil. The major advantages of this process are as follows: fully use the heat of pyrolysis gas-oil; overcome the “cage effect” of the liquid phase reaction, and maximize the light olefins yield.

Via this HM-GCC process, the VR is mainly converted into light olefins and BTX. The process is essentially a hierarchical conversion of the inferior heavy oil. Fig. 2 clarifies that the VR macromolecule can be pyrolyzed to produce gas-oil which has lower molecules; the gasoil is further catalytically cracked into light olefins. Besides, to improve catalytic performance in the gas-phase cracking gasoil, catalyst with micro-mesoporous hierarchical structure is needed [17–19]. Thus, the catalyst should have the hierarchical porosity of the pore and the ability to easier transport and access to the active sites [3].

The purpose of this work is to investigate the fundamental characteristics of the HM-GCC process using an analytical Py-GC/MS and a

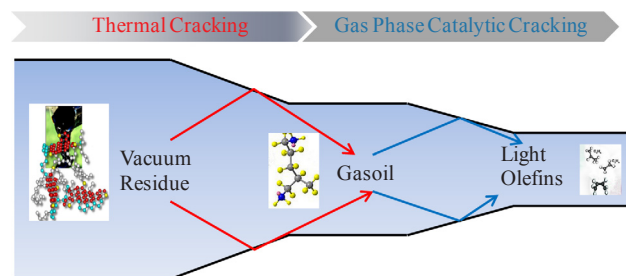


Fig. 2. Schematic representation of the hierarchical conversion of VR.

bench-scale fluidized bed-fixed bed dual-reactor. The effects of temperature on the thermal behavior of VR millisecond pyrolysis were investigated firstly. Then five catalysts including calcium aluminate catalyst, FCC catalyst, and ZSM-5 zeolites with the silica-alumina ratios of 40, 80 and 200 were used to study the product distribution (especially the yield of C₂-C₄ hydrocarbons and BTX) of the gas-phase catalytic cracking of pyrolysis oil. The combination of ZSM-5 and calcium aluminate catalysts was tested for optimizing catalyst in terms of high C₂-C₄ hydrocarbons selectivity. Finally, the analysis of the yields and compositions of the gas and liquid products obtained by a larger scale experiment provided an insight into the potential application of VR to chemicals.

2. Experimental section

2.1. Feedstock and catalyst

The heavy feedstock was the vacuum residue (VR) provided by Shida Changsheng Energy Technology Co., Ltd. (Shandong Province, China) and its properties were shown in Table 1. The density, viscosity, and Conradson carbon residue (CCR) of the VR were 1020 kg/m³, 3985 mm²/s, and 22.38 wt%, respectively.

The FCC catalysts, ZSM-5 zeolites with different silica-alumina ratios of 40, 80, and 200 (Z-40, Z-80, and Z-200), and calcium aluminate catalysts were used in the experiments and their properties were shown in Section 3.2.1. The Z-40 and calcium aluminate were physically mixed to prepare the Z + C-cat catalyst. The catalysts were formed by tablet machine after fully grinding and blending. And the particle sizes of the catalysts distributed between 0.075 and 0.090 mm.

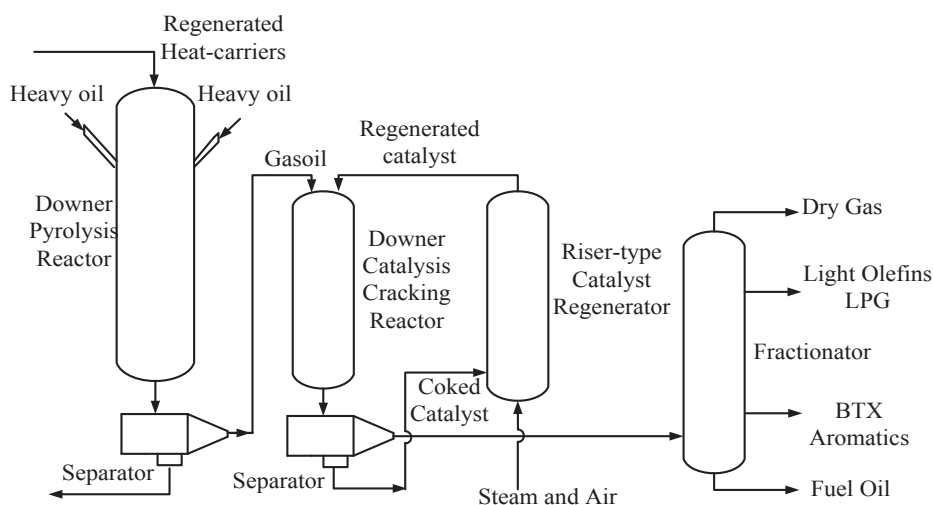


Fig. 1. Schematic diagram of the HM-GCC process.

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