COPRODUCTION OF LIQUIDS AND SYNGAS VIA RESIDUE OIL CRACKING-COKE GASIFICATION (RCCG) PROCESS

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Due to the extinction of conventional oil resources, large portions of heavy oil will be exploited and processed in the refinery, thus in-return generating more degraded residue oil. Fluid catalytic cracking (FCC) process is unable to treat such kind of residue oil because of rapid catalyst deactivation and excessive coke deposition. Delayed coking, featured with wide feed adaptation and low investment, has been widely used for treating petroleum residues in China. Nonetheless, delayed coking has low liquid yield and produces low-value petroleum coke. As a result, a so-called residue cracking–coke gasification (RCCG) process was proposed to realize the hierarchical conversion and value-added utilization of petroleum residues. Heavy oil was first cracked in a fluidized bed reactor via contacting with the catalyst particles to maximize the liquid yield. Coke deposited on the surface of catalysts was gasified and/or combusted for catalyst regeneration. Simultaneously, high-quality syngas could be produced via coke gasification and further used as the hydrogen source for liquid oil upgrading. The regenerated hot catalysts circulated back to the cracking reactor, providing heat and also catalytic activity for heavy oil conversion.

Cracking behaviors of Venezuela vacuum residue were studied in a self-designed fluidized bed reactor (Fig. 1) with spent FCC catalyst to optimize operation parameters for high liquid yield and conversion of heavy fractions. The results showed that the hydrothermal-treated FCC catalyst (A-FCC) showed reasonable activity for residue oil cracking to ensure the acceptable liquid yield and low coke formation. The residue oil conversion above 90% and liquid yield over 75 wt.% were obtained under the operation conditions of 520°C, catalyst-to-oil mass ratio of 6.17 and steam-to-oil mass ratio of 0.6 using A-FCC catalyst. Two methods of catalyst regeneration were used in batch operation, i.e., steam gasification and gasification coupled with combustion of the deposited coke on the catalyst. Steam gasification of the deposited coke was performed at 800°C for the catalyst regeneration, and the total volume fraction of CO and H2 was up to 86 vol.%. In comparison with coke gasification, catalyst regeneration via gasification-combustion was shown to be able to shorten the required reaction time by about 40% (see Fig. 2), while the regenerated A-FCC catalyst manifested the catalytic activity similar to that of the original A-FCC catalyst. RCCG process is characterized with higher liquid yield and lower coke production than that of delayed coking, and also could process heavy feed oil and produce syngas comparing with FCC process, thus justified its technology advantages.
Fig. 1 Schematic diagram of the experimental setup for residue oil cracking combined coke gasification (RCCG)

Fig. 2 Time-series temperature and carbon conversion on spent catalyst via (a) coke gasification and (b) coke gasification coupled combustion