Rapid analysis of heavy oil catalytic cracking products using pyrolysis GC

(1) Rapid evaluation of catalytic cracking of long-chain hydrocarbons (C16-C56)

[Background] Catalytic cracking of heavy oil is an important process in oil refinery, and a rapid analytical method is therefore of interest. In this report, a pyrolysis (Py)-GC/FID system is used to evaluate the catalytic cracking of long-chain hydrocarbons (C16 to C56) when the mixing ratio of the equilibrium catalyst and heavy oil is varied.

[Experimental] A solution prepared by dissolving direct-desulfurized heavy oil in toluene was used as a sample, and an equilibrium catalyst commonly used in industry because of its stable activity was used. For the measurement, a Py-GC/FID system with a Multi-Shot Pyrolyzer (EGA/PY-3030D, Frontier Labs) directly interfaced to GC injector was used (Fig. 1). Varying amounts of the equilibrium catalyst was placed in a quartz surface-treated glass sample cup (Eco-Cup GQ), then a given amount of heavy oil sample was added to each sample cup. Then toluene was evaporated off and the sample cup was placed into the pyrolyzer. The mixing ratio of catalyst/heavy oil was varied as 3/1, 8/1, 13/1, 18/1, and 23/1.

[Results] The chromatograms of the heavy oil alone and of the mixtures of catalyst and heavy oil are shown in Fig. 2. In the presence of the catalyst, most of the long-chain hydrocarbons were decomposed into low boiling point compounds, but the decomposition is varied with catalyst/heavy oil mixing ratios. Each chromatogram is divided into three carbon number zones (C16-20, C21-C30, and C31-56) as in Fig. 2. The peak area ratio for each zone is calculated and plotted against the catalyst/heavy oil ratio (Fig. 3). It is found that cracking efficiency is high when the mixing ratio of catalyst/heavy oil is larger than 18/1.

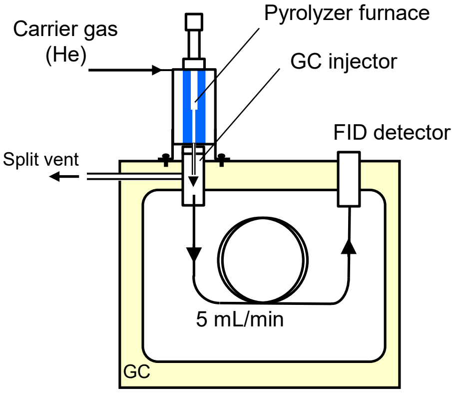

Fig. 1 Schematic illustration of Py-GC/FID

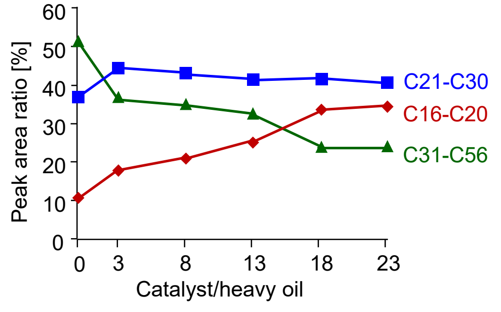

Fig. 3 Peak area ratio versus catalyst/heavy oil mixing ratio

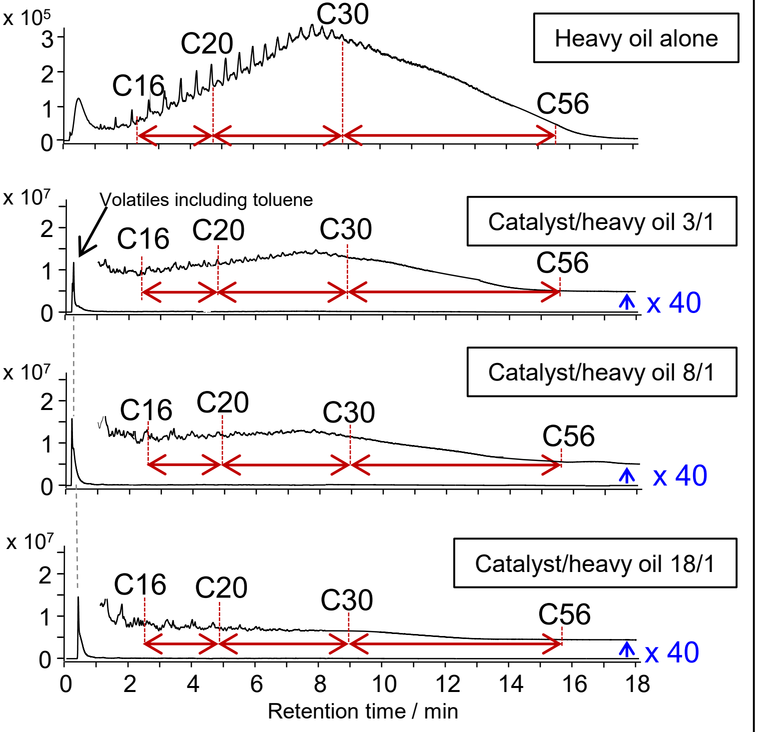

Fig. 2 Chromatograms of heavy oil with/without catalytic reactions

Pyrolyzer furnace temp.: 500 ºC, GC injector temp.: 340 ºC
GC oven temp.: 60 - 400 ºC (20 ºC/min, 3 min hold),
Separation column: UA-SIMDIS(HT) (dimethylpolysiloxane)
L=5 m, i.d.=0.53 mm, df=0.1 μm
Column flow rate: 5 mL/min (He) , Split ratio: 1/10, FID detector temp.: 400 ºC

Keywords : Heavy oil, Catalytic cracking, Catalytic reaction, Py-GC/FID

Products used : Multi-functional pyrolyzer, UA-SIMDIS(HT), Eco-Cup GQ

Applications : Oil refining, Catalyst evaluation

Related technical notes : PYA1-105E

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