

Conversion of heavy aromatic hydrocarbons to valuable synthetic feed for steam-crackers

Alberto Cesana, Leonardo Dalloro, Franco Rivetti, Roberto Buzzoni, Renzo Bignazzi
ENI S.p.A. Refining & Marketing Division - Via G. Fauser, 4 28100 Novara (Italy)

The scope of the present study was upgrading a set of heavy aromatic hydrocarbons mixtures whose commercial value ranks close to fuel oil and should become even lower in the next future because of the introduction of more stringent regulations on fuels, through hydro-conversion to a synthetic feed for steam-cracking.

The resulting process provides an opportunity to improve the economic return of a steam-cracking plant, offering the chance of converting low-value mixtures produced by the plant itself, such as fuel oil of cracking (FOK), saving an equivalent amount of naphtha. The method can also be used for converting pyrolysis gasoline (pygas). Although pygas has at present a fair commercial value, it could suffer a significant penalization in the future due to further limitations on total aromatic content in gasoline. Pygas hydro-conversion to a synthetic steam-cracking feedstock has been recently reported ¹.

Fractions from refinery, such as heavy distillates (e.g. Heavy Vacuum Gas Oil, VGO), deasphalted resids (DAO), or some FCC streams (e.g. LCO) resulted suitable and very attractive mixtures to be treated as well. No more than deasphalting was required as pretreatment of the feed mixture and only when the asphalts were >2%. Hetero-elements are often present in such kind of feeds at quite high concentrations, but no problems were observed due to the presence of sulphur and nitrogen, respectively, up to 15000 and 5500 ppm.

The process essentially consists in a severe hydrocracking of these mixtures into paraffinic hydrocarbons with <6 carbon atoms, particularly into C2÷C4 molecules. A low yield to C1 and C5 (respectively <10% and < 5%) leads to a maximum yield to linear paraffins, allowing the best economic return in terms of ethylene and propylene production in the steam-cracker and a value upgrading of +5 ÷ +8% compared with that of a standard naphtha.

The reaction is carried out employing bifunctional hydrogenating / acidic catalysts. The hydrogenating components are mainly NiMo and ZnMo combinations and the acidic component is Ultra Stable Y zeolite, having a SiO₂/Al₂O₃ ratio of 5. The process is carried out in a series of fixed-bed reactors with intermediate cooling, owing to the large enthalpic heat of the hydro-conversion. The whole hydrogen and oil amount may be fed at the first bed or, preferably, splitted in different ways at the beds. Following H₂S / NH₃ removal and H₂ separation, the resulting mixture of light paraffins can be fed to the steam-cracker.

Operative conditions and performances are mainly depending on N concentration in the mixtures. With N <1000 ppm (pygas, LCO, FOK, straight run VGO) the reaction temperature is 450÷470°C, while with N >1000 ppm (DAO, VGO) it must be increased up to 490÷510°C. Pressure is 60 bar, H₂/oil ratio 2000÷8000 NI/l, highly depending on the reactor design. Most part of unconverted H₂ is recycled.

Tuning the reaction temperature to the N content of the feed allows to maintain 100% conversion, but the distribution of products changes. With feeds having N <1000 ppm the yield to n-paraffins C2÷C5 is ≥ 80%, to i-paraffins ~10% and to CH₄ ≤10%, whereas with a higher N content the yield to n-paraffins C2÷C5 is slightly lower (≥ 70%), and a small amounts of BTX is formed (~10%). It is preferable not to push excessively the conversion of residual BTX in order to maintain an acceptable selectivity (low CH₄ yield) and H₂ consumption.

¹ ★ C. Ringelhan, G. Burgfels, J.G. Neumayr, W. Seuffert, J. Klose, V. Kurth, "Conversion of naphthenes to a high value steamcracker feedstock using H-ZSM-5 based catalysts in the second step of the ARINO1-process", *Catalysis Today*, 97 (2004) 277–282

★ A. De Angelis, C. Flego, P. Pollesel, M. Tagliabue, "Molecular sieves: from basic research to industrial applications" - *Studies In Surface Science And Catalysis*, 158 Part A-B (2005) 1701-1708