

Catalytic Naphtha Reforming

The distillation of crude oil provides a gasoline fraction of too low a quality to be used directly as automobile fuel. The quality can be improved in the refinery by the catalytic reforming process. This process converts fractions of low octane number (40-60) into fuels of high octane number (95-105). Moreover, the catalytic reforming provides most of the hydrogen used by the hydrotreatments (see CRS 23 of this series) and gives petrochemistry aromatic hydrocarbons.



FIGURE 1.

The fractions treated by this process are mixtures of paraffinic and naphthenic hydrocarbons containing between 6 and 10 carbon atoms. These fractions are characterized by the range of boiling points, the specific gravity, the average molecular weight, the content of impurity (sulfur, nitrogen, metals) and of course the octane number. The high sensitivity of catalyst to impurities requires the feedstock to be thoroughly purified before reforming. The cost of the catalyst amounts to 20-40 \$ per kg and its lifetime is generally 4-5 years or more.

The Reactions

Two principal reactions leading to aromatics formation are essential :

- naphthene dehydrogenation,
- paraffin dehydrocyclization.

However, side reactions of cracking and coking decrease the yields of reformat and hydrogen.

From a thermodynamical point of view, the dehydrogenation of naphthenes and the dehydrocyclization of paraffins are equilibrated, endothermic reactions occurring with an increase of entropy. The side reactions of cracking are exothermic and consumes hydrogen. That is why, thermodynamically, the reactions leading to the formation of aromatics are

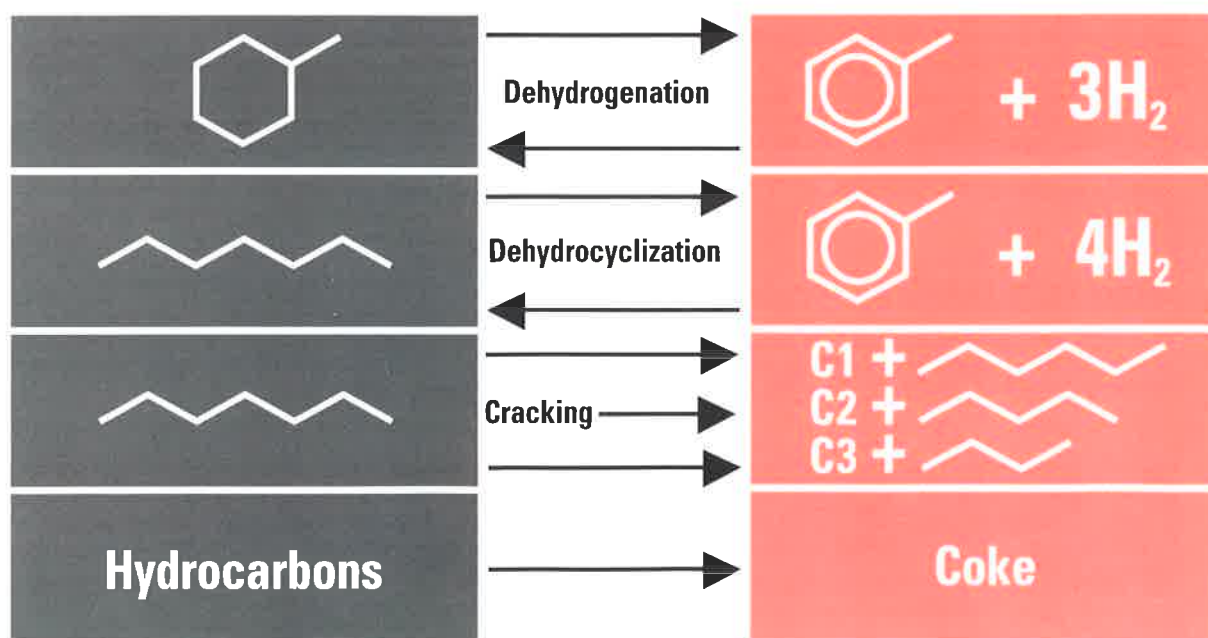


FIGURE 2.

favoured at high temperature and low pressure. Kinetically, naphthene dehydrogenation is the fastest reaction.

The coke formed during the reactions is deposited at the surface of catalyst and provokes deactivation. Fortunately, the coking rate is low compared to that of the other reactions, and the increase of hydrogen partial pressure limits the coke formation. Increasing the operating temperature can compensate for the deactivation caused by coking ; however, as a result, the rate of the side reactions increases faster than that of the desired reactions, which can be limited by the use of bimetallic catalysts.

The Catalysts

The catalysts of the first generation were made of chromium and molybdenum oxides (10 weight %) deposited on an alumina support. At the beginning of the 1950s, a new generation appeared, based on platinum (0.2 to 0.7 weight %) deposited on high surface area alumina (200 m²/g) promoted by chlorine. Nowadays a second metal is added to platinum, generally Ge, In, Ir, Re, or Sn.

Bifunctional catalysts have :

- a hydro-dehydrogenating function provided by the finely dispersed metal, and
- an acidic function provided by the chlorinated alumina, which induces skeletal rearrangement of hydrocarbons.

The metal of the catalyst has a key function because of its role in the formation of unsaturated intermediates and in the dehydrogenation of naphthenic species. The quasi-atomic dispersion of the metal in the form of particles with diameters small than 7Å, assures a maximum dehydrogenation. This high dispersion is obtained by ionic exchange between the PtCl₆²⁻ ion and the hydroxyl groups of the alumina.

Maintaining the correct balance between the two functions of the catalyst is essential to obtain a good activity and high selectivities. Too strong an acidic function results in excessive cracking, whereas a weak function prejudices activity. The continuous control of chlorine content in the catalyst assures this equilibrium on an industrial scale.

Coke deposited at the catalyst surface is eliminated during regeneration by controlled combustion. Any excessive in temperature during regeneration risks damaging irreversibly the catalyst.

Modern reforming catalysts are bimetallics. The second metal stabilizes metal dispersion, limits coke formation and modifies the product selectivities, thus enabling to operate at a lower pressure favouring the formation of aromatics.

The Industrial Processes

The high endothermicity and the differences in the reaction rates require the use of several successive reactors between which are located the furnaces.

The operating pressure is maintained by recycling part of the hydrogen produced by the reaction.

Depending on the nature of catalyst, two types of technology can be employed :

- fixed bed with cyclic catalyst regeneration,
- moving bed with continuous catalyst regeneration.

The operating conditions for both technologies are shown in the *Table*.

In fixed bed processes, only the feedstock is moved through the reactors. The temperature is increased progressively to compensate for the deactivation of the catalyst until a maximum values is attained. At that point, the unit is stopped for regeneration. Fixed bed processes require the use of stable catalysts such as Pt-Re.

The continuous regeneration processes assure the permanent circulation of the catalyst through the different reactors and the regenerator. These processes require the use of bimetallic catalysts such as Pt-Sn which are more selective, allowing to operate at a lower pressure. It is however the higher rate of coking at low pressure which requires continuous regeneration of the catalyst.

TABLE

Processes	Cyclic regeneration	Continuous regeneration
Pressure (bar)	12 to 25	4 to 10
Temperature (°C)	480 to 530	480 to 530
H ₂ /hydrocarbon (mole)	3 to 6	2 to 5
Cycle duration (month)	6 to 12	0.1 to 0.3
Octane number	96 to 102	98 to 105

Conclusion

Up to now, addition of leaded compounds to motor fuel allowed to increase the octane number and to reach European commercial specifications. The application of new environmental regulations, especially the use of automobile catalytic converters requiring unleaded fuel, calls for a significant increase in the octane number. Thus the use of unleaded fuel intensifies the role of the catalytic reforming in refining.

The constant improvements achieved on catalysts formulations have allowed to operate at pressures as low as 5 to 10 bars. Further decrease in operating pressure is limited by the technology. Future progresses will require the development of catalysts and processes which will take into account the present technological constraints.

Recommended Reading

• J.F. Lepage *et al.*, *Catalyse de contact*, Edition Technip, 1976.

• D.M. Little, *Catalytic Reforming*, PennWell Books, 1985.

This Catalysis Reference Sheet (CRS) was prepared with the help of J.M. Deves.