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# Industrial relevance of coking

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## Abstract

The paper gives a general overview of characteristics of coking in industrial catalytic processes. Although there may be similarities in coking mechanism, the big differences in deactivation rates result in different operational strategies and reactor systems.

*Keywords:* Coking; Carbon formation; Catalyst regeneration; Reforming; Cracking; Alkylation; Dehydrogenation; MTG

## 1. Introduction

Coking or the formation of carbonaceous deposits is an important side reaction in many industrial processes. Very often, measures to eliminate or depress coke formation are more decisive for the process lay-out than for instance the activity of the catalyst [1]. As chemical plants have become larger and more sophisticated in their integrated design, the on-stream factor has become one of the most important parameters for the operation. A few days down-time can have a detrimental effect on the plant economy. A high degree of integration means that the weakest part of the chain may determine the performance of the entire plant. Therefore, it is a challenge to the catalyst development to make more coke resistant catalysts available and to process engineering to optimize reactor design and equipment as well as procedures for catalyst regeneration to ensure smooth operation.

This paper is no review. It illustrates general characteristics of coking problems in industrial processes without going into catalytic details.

## 2. Coking mechanisms

A number of phenomena are lumped into the concept of coking without stating how the coke is formed and what is the composition. Most of the coking literature has dealt with the problems of catalytic cracking [2]. The acid sites active for the cracking reactions are blocked by carbonaceous deposits formed via chain growing reactions from olefin intermediates. The catalyst deactivation has usually been described by the empirical Vorhies equation:

$$C = k \cdot t^n \quad (n < 1). \qquad (1)$$

More sophisticated models have been established relating the deactivation to the amount of coke on the catalyst and also considering the impact of pore diffusion on coke deposition profiles [3]. Still, the Vorhies equation appears to be used in practice [4].

In general [4–7], many hydrocarbon reactions suffer from formation of coke being formed by oligorimerization of olefins, poly-alkylation of aromatics and

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condensation of aromatics. This is representative for reactions where olefins or aromatics are intermediates or products (cracking, dehydrogenation, methanol to olefins etc), or where olefins or aromatics are present in the feed (isomerization, alkylation, selective hydrogenation of acetylene in ethylene plants, etc). These catalysts may be complex in composition.

Another general route to coke is catalysed by metals. Some metal catalysts (nickel, cobalt and iron) may form whisker carbon in a process where the hydrocarbon or carbon monoxide is dissociated into carbon atoms on one side of the metal crystal and a carbon fibre (whisker) nucleates from the opposite side [8–10]. This means that the carbon whisker can grow without deactivation of the active site in contrast to the acid site mechanism following the Vorhies equation. The accumulation of whisker carbon may result in a break-down of the catalyst particle (tubular steam reforming) [8].

Metal catalysts may at other conditions form carbonaceous deposits encapsulating the metal particle with a resulting deactivation (low temperature steam reforming (prereforming methanation). At first, a film of paraffinic $-CH_2-$ chains is formed, which is then slowly transformed into less reactive polyaromatic deposits [8,11,12].

Bi-functional catalysts as used for catalytic reforming have acidic sites as well as active metals, which complicates the deactivation mechanism [5,13]. The acidic sites alone form coke rapidly while the metal sites are active in hydrogenating the coke precursors [13]. Again a wide spectrum of coke is found on the catalyst surface.

The catalytic reactions can be accompanied by coke formation from pyrolysis of the hydrocarbons if the temperature is above approx. 650°C. This form of coke is a problem in steam cracking units in ethylene plants [14,15]. It results in dense poly-aromatic deposits on the tube walls which results in poor heat transfer. It is diminished by using residence times approaching milliseconds. Pyrolytic coke may be formed in tubular reformers if poor catalyst activity results in high concentrations of higher hydrocarbons at high temperatures [8]. Even preheaters to steam reformers and other process units may work as a cracking units for producing coke precursors (ethylene) if the coil temperature is too high.

For hydrotreating catalysts, the coking tendency depends on the intrinsic acidic properties of the catalyst, and the loss of catalytic activity may be related to the deactivation of the active sites as well as the physical blockage of the pore mouth [16]. The coke build-up is a result of strong adsorption on the alumina support of poly-aromatics in the feedstock which condense to large aromatic clusters. At high coke contents (>approx. 5%), the deactivation is caused mainly by pore blockage [17]. The deactivation from coking will be overlapped by deactivation caused by deposition of metals when dealing with hydrotreating of non-distillates [16]. The effects which may be difficult to distinguish may lead to inter-particle depositions and hence to increased pressure drop. Catalyst rings with high void fraction will extend the operation of the catalyst bed [18].

The catalyst performance may also be related to the formation of bulk phase carbides. This is essential for the iron-based Fischer–Tropsch (FT) catalyst for the Synthol process [19]. Iron reacts with carbon monoxide forming Hägg carbide ($Fe_5C_2$), which is the active phase for the FT reaction. For the same reason, the carbide phase should be eliminated in the iron-based high temperature shift catalysts to avoid the formation of hydrocarbons [12,20].

Carbon formation may also have an effect on construction materials. Pyrolytic coke deposited on the tube walls may lead to harmful carburization of the high alloy steel tubes [14,15]. A critical phenomenon is metal dusting corrosion which may take place if a CO-containing process gas is cooled below the equilibrium temperature of the CO-decomposition reaction [21,22]. The resulting carbon will typically react with the steel forming iron carbide which will decompose and fall off leaving the construction material with heavy pitting.

## 3. Process parameters and catalysts

The reduction or elimination of coke formation often results in constraints on the operating conditions to be applied. It is difficult to quantify the added costs because the process scheme is often a result of a complex optimization involving several parameters.

Steam and hydrogen are the most important retarding reactants. In steam reformers [8,23], carbon will be formed below a certain steam to carbon ratio which means that in many cases the steam reformer has to operate with a surplus of steam and, hence that a larger reformer is required. When using a catalyst with enhanced steam adsorption, the critical steam to carbon ratio can be reduced. This can be obtained by adding alkali to the catalyst or during active magnesia as support. In this way, operation can also be made possible with liquid hydrocarbons [8]. Carbon-free $CO_2$-reforming can be achieved in spite of thermodynamics on noble metal catalysts [24] or by ensemble control on a partly sulphur poisoned nickel catalyst on which the large sites for the demanding reaction for carbon formation are blocked leaving sites for the reforming reaction [25].

Hydrogen is an important coke retarding reactant in several hydrocarbon conversion processes such as FCC, hydrotreating, hydrocracking, catalytic reforming and prereforming, in essence by reducing the formation of olefin intermediates. In catalytic reforming, there is a balance between the coke retarding effect of hydrogen and the increased rate for hydrocracking with low molecular hydrocarbon products as a result of a high hydrogen partial pressure. The development of bi-metallic catalysts [13] having less selectivity for the hydrocracking reaction has allowed operation at higher severity at given hydrogen pressure.

The rate of coking on acidic catalysts can be diminished by reducing the strength of the acidic sites [5] or even neutralize them by addition of alkali. Another approach is to utilize the shape selectivity of zeolites such as ZSM-5 for the MTG process [26]. In small and medium pore zeolites, deposition of pseudo-aromatic coke cannot take place inside the zeolite, but still coke may be found via linear oligomers if the temperature is too low for cracking [6]. The advantages of zeolite for FCC over amorphous silica alumina catalyst at the same coke yield are reflected by a substantial increase in the yield of gasoline [27].

It is through detailed understanding of the mechanism of coke formation that new catalysts can be developed with minimum coke formation, which allows operation at more economic process conditions.

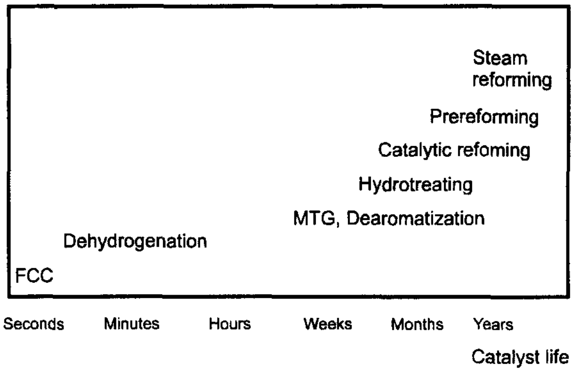

Fig. 1. Coking and catalyst lifetimes.

## 4. Reactor design and operational strategy

The optimum process lay-out depends strongly on rates of carbon build-up which may vary from years (steam reforming) to seconds (FCC), as illustrated in Fig. 1.

In tubular reforming, no carbon is accepted because the break-down of the catalyst will result in build-up of pressure drop with uneven flow distribution and hot spots, etc. [8]. In case of steam reforming of methane, a safe conservative design principle is simply to require that there should be no affinity for methane decomposition reaction at any position in the catalyst bed [8,23].

$$CH_4 + * \rightarrow C\text{-}* \begin{cases} \rightleftarrows \text{gas} \\ \rightleftarrows \text{carbon} \end{cases} \qquad (2)$$

With higher hydrocarbons as feedstock, the reactions are irreversible and whether carbon-free operation is possible, it is a question of steady state carbon activity on the catalyst which can be influenced by the formulation of the catalyst [8].

Reactions with slow build-up, carbonaceous deposits can be carried out in a simple fixed-bed reactor. As long as the deposits are inside the particles and not inter-particle, operation can continue as long as non-deactivated catalyst is available. This performance is practised in prereforming of higher hydrocarbons for manufacture of hydrogen or syngas [11], high temperature methanation for SNG [12], and in the fixed-bed MTG process [26].

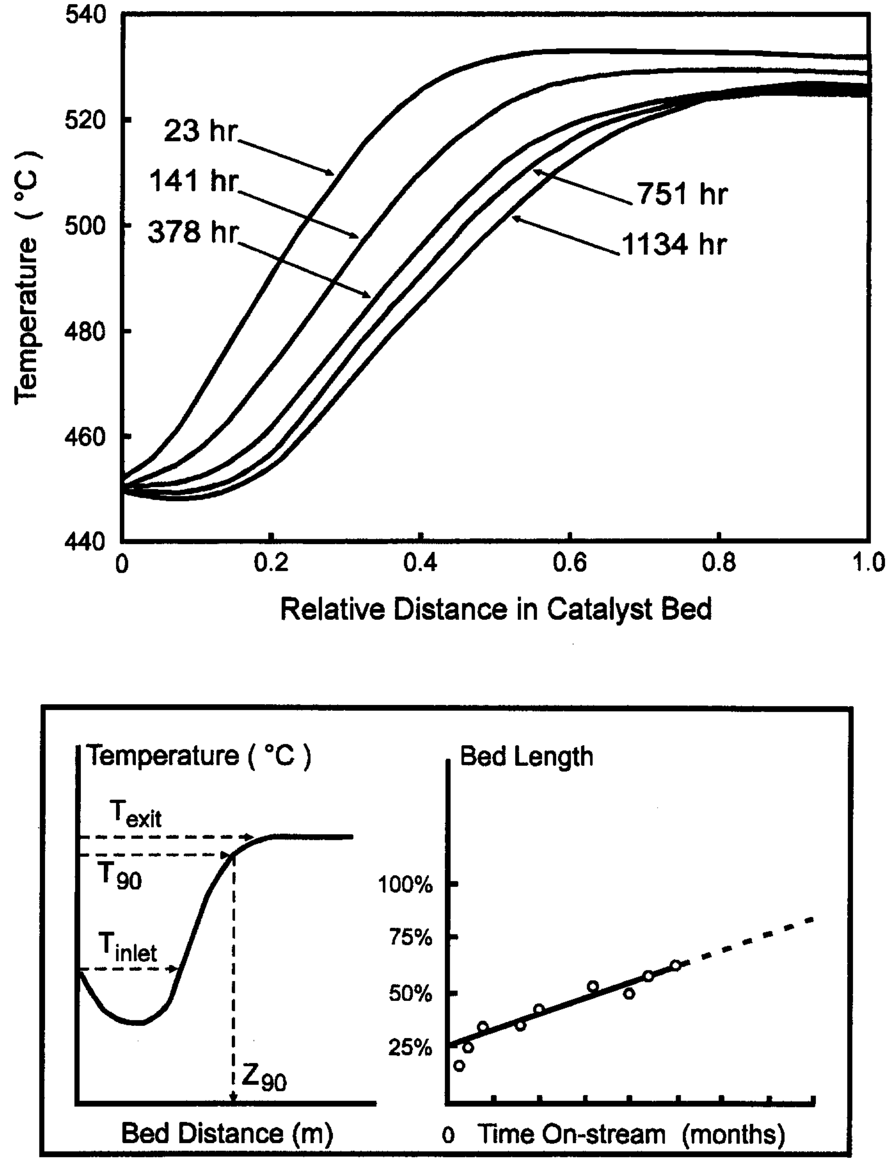

Fig. 2. Temperature profiles in prereforming of naphtha (adapted from Ref. [11]).

The operation time is typical several months to a year. The progressive deactivation can be followed from the movement of temperature profile as shown in Fig. 2(a). There is very little change in the shape of the profile, which reflects that coking is restricted to the reaction zone. The deactivation can be monitored simply by the bed length required to achieve for instance 90% of the adiabatic temperature increase, Fig. 2(b). A plot of $Z_{90}$ versus processed feed usually results in a straight line which reflects a sharp deactivation profile from the slope, a resistance number, $R$ (kg feed/g catalyst deactivated) can be estimated [28]. With typical space velocities, $R$ should be in a size of order of 10 kg/g or above to ensure reasonable catalyst life without regeneration.

In fixed-bed hydrotreating reactors, the deactivation is compensated for by a gradual temperature increase [16] in order to maintain the conversion level. A

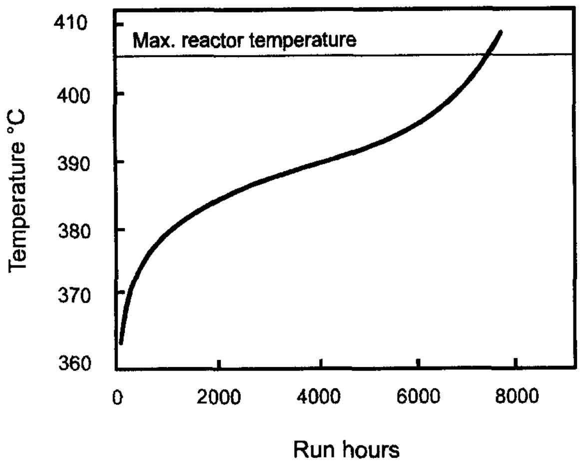

Fig. 3. Hydrotreating; typical run plot.

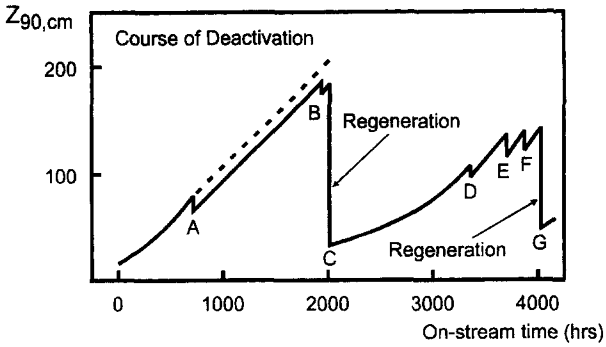

Fig. 4. Regeneration with hydrogen of high temperature methanator [30].

typical plot shown in Fig. 3 illustrates that the deactivation is not linear. It represents an overlap of site poisoning and pore blockage.

A similar strategy is applied in fixed-bed reactors for catalytic reforming [13] in which loss in octane number is compensated for by increase of temperature. There is a limit to this approach because hydrocracking to light products is enhanced by high temperatures. Eventually, the plant must be shut down for regeneration of catalyst.

When the coking rates result in catalyst life less than 1–2 years, regeneration systems should be considered. One example is the Mobil fixed-bed MTG process in which the zeolite catalyst is regenerated several times a year [26,29].

Regeneration of coke deposits can be carried out in various ways depending on the reactivity of the "coke". The encapsulating deposits which cause deactivation of the nickel based catalysts for prereforming and in high temperature methanation can often be removed by treatment in hydrogen at 500°C depending on the age of the carbon [12,30] as illustrated in Fig. 4. Newly formed carbon in tubular steam reformers can be removed by increasing the steam to carbon ratio or by steaming of the catalyst [8].

However, aged coke deposits require regeneration by means of air [31]. At sufficiently high temperatures (typically above 500°C), the regeneration process becomes limited by the diffusion of oxygen through the carbon-free pores as the burn-off progresses after a core/shell mechanism. If the carbon is highly reactive, the regeneration may easily become heat transfer limited meaning that the temperature of the catalyst pellet may be heated up to a temperature corresponding to the adiabatic temperature increase of the combustion reaction. If so, the regeneration can be a delicate process because many catalysts will suffer from sintering by the overheating from the combustion process.

In the case of a metal catalyst, the metallic phase will also be oxidized. Therefore, in many cases it is necessary to carry out the regeneration with controlled addition of air to nitrogen or steam.

Fig. 5 shows a regeneration loop for a fixed-bed process [29]. A typical regeneration procedure will involve the purge of the hydrocarbon reactants by means of nitrogen and heating to the right regeneration temperature, a controlled addition, i.e., 1–5% of air to the nitrogen loop. The regeneration can be followed by the temperature profile in the reactor or by the $CO_2$-content in the exit gas [8]. After completion, the reactor has to be purged for air and in case of a metallic catalyst, the catalyst should be heated to the activation temperature and reduced in for instance hydrogen after which the process conditions can be reestablished. This procedure may take a couple of days and therefore this type of regeneration can hardly be allowed more than once a year (at the annual plant overhaul) if parallel reactors are not installed. Furthermore, the installation of the regeneration system is expensive involving compressors and heaters as illustrated in Fig. 5.

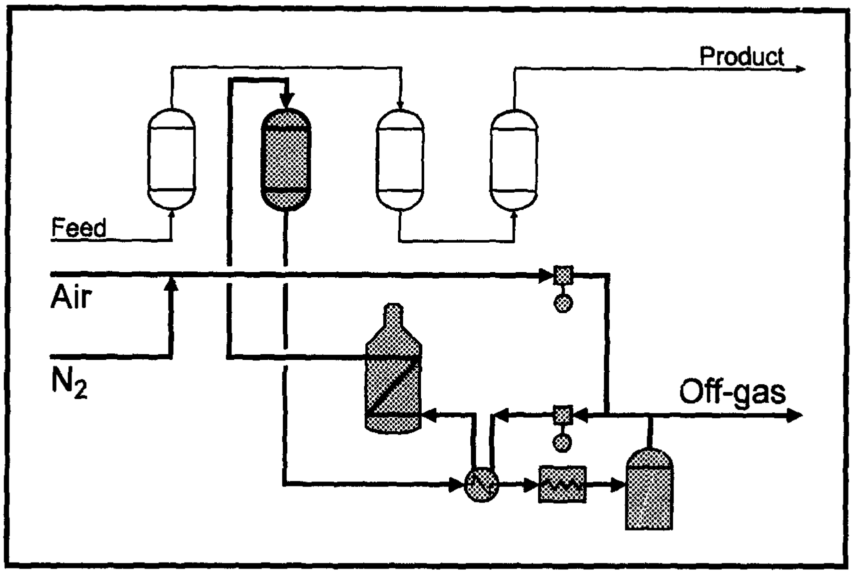

Fig. 5. Regeneration unit (adapted from Ref. [29]).

Hydrotreating catalysts are usually not regenerated in situ, but in special regeneration units on site or typically in special off-site regeneration plants [32]. This allows a better control and flexibility of the regeneration conditions.

It is evident that a regeneration system cannot be applied for a fixed-bed process if the catalyst suffers from rapid deactivation. This appears to be a major problem in the attempts using solid state catalyst for alkylation [33]. Catalytic materials are available with the acidity required for the reaction, but unfortunately the active site is rapidly deactivated in the competition between hydrogen transfer reactions and oligomerization on the surface. The feasibility of frequent regeneration will also suffer from the big temperature difference between the operating and regeneration conditions. A solution to this problem has been to use a supported liquid phase catalyst in which the catalyst is distributed within the pore system of the support [1,34]. It means that the acid surface is renewing itself. Also, because of the reaction mechanism involving an intermediate slightly soluble in the hydrocarbon phase, it means that the acid is moving slowly from pellet to pellet in the bed. This gives the opportunity to constantly withdraw deactivated acid to a regeneration unit.

In general, the regeneration unit can be integrated in different ways with the reactor system as illustrated in Fig. 6. Endothermic processes may take advantage of the combustion heat from the burn-off of coke by using the heat created as heat source for the reaction. This is done in the Catofine process for dehydrogenation of isobutane in a swing-bed system in which the fixed-bed reactors cycles from oxidative mode to a process mode with a typical cycle within approx. 20 min. [7].

An alternative is to continuously remove the catalyst for regeneration thus avoiding the "swing-bed" system. This has been the development in catalytic reforming as practised in the UOP, CCR platforming process [7]. The catalyst moves through the reactor system and is collected at the bottom and lifted in portions to a regenerator section (Fig. 6). With continuous catalyst regeneration, it is possible to operate at more severe reforming conditions whereas the swing-bed process has to compensate for deactivation of the catalyst. The continuous catalyst regeneration system is also used for dehydrogenation of propane and isobutane [35] as well as the Cyclar process for converting LPG into aromatics [36].

Moving-bed reactors are also used in hydrotreating and hydrocracking operations and in the H-oil and LC

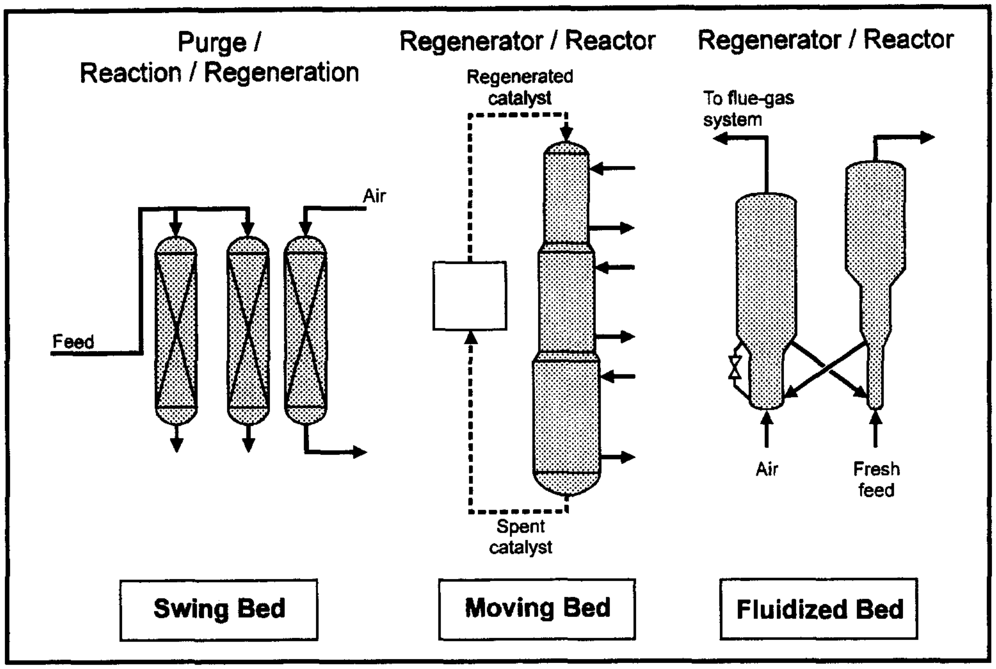

Fig. 6. Integration modes of regeneration and reactor units.

hydrocracking processes, the catalyst is continuously withdrawn from a slurry-bed reactor and replaced [16].

An elegant solution for short-life catalyst for gas phase reactions is the use of a fluidized bed from which the deactivated catalyst is continuously removed to the regenerator and replaced by fresh catalyst (Fig. 6). The heat of combustion heated in the regenerator is balanced with the heat required by the process. This technology was developed in the FCC where the residence time of the catalyst in the reaction zone may be a few seconds [27]. The design of the regenerator is as demanding as that of the reactor system itself, and part of the catalyst optimization is related to its properties for coke burn-off. Fluidized bed technology with continuous regeneration is used for other endothermic reactions as well such as dehydrogenation of isobutane and propane in the Snamprogetti FDH process [37]. The catalyst recirculation is dictated from the heat requirement of dehydrogenation reaction. The rate of coke formation is much slower than in FCC, which means that the heat created by burning the coke is not sufficient and that it is necessary to burn additional fuel in the regenerator [37].

The Mobil MTO processes [38] and the Hydro UOP process [39] for converting methanol into olefins which are slightly exothermic, but apply a similar fluid bed/regenerator system. The rate of coke formation is slower than in the cracking and dehydrogenation reactions and the fluid-bed concept is used to achieve better temperature control and continuous operation.

## 5. Conclusions

The examples have shown that coking is a problem in a number of important catalytic processes. Very often, it determines the process lay-out and the optimum process conditions to be applied. Coking rates, regeneration chemistry and heat supply, etc. are important parameters in determining what is the optimum reactor system and this still represents a challenge to reactor engineering. The understanding of the mechanism for coke formation provides the key to development of more coke resistant catalysts.

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