Chapter 28

Performance Testing of Hydroconversion Catalysts

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Performance testing of hydroconversion catalysts is reviewed, with the emphasis on the use in catalyst development. This necessitates application of procedures to accelerate reaching a steady state performance, and also to determine long term deactivation. Catalyst deactivation phenomena in hydroconversion, especially in distillate desulfurization, hydrogenation, distillate hydrocracking and residue hydroconversion are discussed in detail. It is argued that at the present state-of-the-art performance testing in small scale equipment under realistic conditions, supported by process modelling, is the most effective approach. Examples are given, and areas for further study identified.

1. Introduction

Catalyst deactivation has been extensively studied, and excellently reviewed in many places, for example by Butt and Petersen (1). Much attention has been given to the area of hydroconversion (particularly residue hydroprocessing) (2). In general, however, these reviews have focussed on the description and understanding of deactivation, with little consideration to the point of view of the process or catalyst developer. In this review the deactivation phenomena in the various areas of hydroconversion and their modelling will be considered. Options for performance testing of catalysts that are meaningful without being excessively lengthy will be derived.

Catalyst performance is determined by activity, selectivity and stability. Whereas activity is indispensable, selectivity is often of prime importance (e.g. lube base oil yield in catalytic dewaxing), particularly if an improved selectivity can break a bottleneck in a unit (e.g. by lower gas makes which break up the gas train bottleneck a in a hydrocracking unit). Catalyst life is determined both by the start of run activity and deactivation rate. With high activity catalysts in low severity duty (e.g. naphtha hydrotreating), catalyst life can be very long (e.g. 5–10 years), and in some cases the

total cycle length is determined by a fouling of a top layer of the catalyst rather than by deactivation. (This fouling can be counteracted by applying dedicated top-bed materials with higher tolerance of foulants, particulates, scale, etc. (3)). Such long catalyst lifecycles may seem desirable, but an earlier catalyst replacement, e.g. in case of deteriorating selectivities, may be attractive. Also, a more severe operation of the catalyst, e.g. by increasing feedstock heaviness (such as can be envisaged in hydrocracking or residue conversion) or by increasing severity/operating tempera-ture (such as by going from VGO HDS to MHC (4)), thereby decreasing feedstock costs or increasing product value, may be economically much more attractive than a longer catalyst life. This is obvious when one considers that most catalysts are regenerable and the availability of presulfurized catalysts and off-site regeneration often allow shorter downtimes of the processing units.

2. Catalyst Poisoning and Catalyst Deactivation

In the following, catalyst poisoning and deactivation through coking and metals deposition will be considered, but not fouling by salt deposition, etc.

a. Reversible Poisoning. In hydroprocessing oil fractions, the feedstocks and products are complex mixtures of hydrocarbon molecules of different molecular weight, shape, aromaticity, and heteroatom (S, N, O, Ni, V, etc.) content. As a re-sult of this vast range of molecular species, a reaction such as hydrodesulfurization is in fact the overall sum of the desulfurization reactions of the different individual sulfur species. Some of these (or other) species will also act as a catalyst poison for the reaction of e.g. lower molecular weight species. Such poisoning effects can be expressed for the example of desulfurization over one type of active site, and neglecting pore diffusion effects, by Equations 1 and 2,

$$r_{\text{HDS}} = -\frac{d[S]}{dt} = k_{\text{emp}} S_f^n \tag{1}$$

$$r_{\text{HDS}} = \frac{\sum_i k_i(T) K_i(T) S_i(\xi) p_{H_2}(\xi)}{1 + \sum_j K_j(T) S_j(\xi) + \sum_k K_k(T) A_k(\xi)} \tag{2}$$
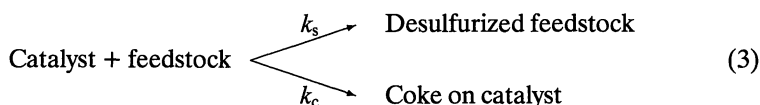
where Equation 1 simply defines the empirical overall rate constant according to a power law with reaction order n. In practice n often equals 2, with the individual components having an order of 1 (as in Equation 2), which is a consequence of multicomponent kinetics (5). Equation 2 expresses in detail that (i) HDS is the sum of many individual reactions (each taken first order in hydrogen partial pressure), which (ii) are poisoned by absorption of S molecules j and other molecules k on the active site, to a degree (iii) that depends on conversion (ξ, location in the reactor) and temperature T, in case of non-isothermal reactors again dependent on ξ.

The importance of such poisoning can be illustrated by, for example, the poisoning of gasoil HDS by addition of N compounds (6), or the reduction in activity for gasoil/thiophene HDS of a catalyst after a short period of processing residual feedstocks (7). As stated earlier by Somorjai (8), catalysis is the science of dirty surfaces.

Poisoning as defined by Equation 2 is due to an equilibrium absorption to active sites, and is in principle completely reversible, as has been shown for instance for nitrogen compounds in gasoil HDS (6). (This is also the basis for the common practice of blocking-in feedstocks/conditions in pilot plant testing). Nevertheless, it may take a long time to achieve total equilibrium adsorption over the entire catalyst bed, because, e.g., the concentration of the poisons in the feedstock is low or the adsorption/desorption processes are slow, especially at low temperatures. An example is the second, cracking stage of hydrocracking unit running under low ammonia/low organic nitrogen levels in the feed ("two stage"), where it may take some 2000 h to reach a stationary state (Figure 1) (9). Slow desorption of adsorbed species is also the basis for the common practice of processing lighter feedstocks before heavier ones in blocked-in pilot plant experiments. In the coke deactivation both catalyst poisoning through adsorption of polyaromatics ("RCT") in the feed and deactivation through condensation reactions can play a role.

Kinetic effects of a different nature occur if the strong catalyst poisons diffuse so slowly that at first only the outer parts of the catalyst particles are poisoned (shrinking-core model, as discussed for dewaxing (10)) or that these poisons are converted in the outer layers of the catalyst, leaving a clean active core (11).

b. Irreversible Deactivation. If the species such as deposited metals, silicon and coke that poison the active sites do not desorb, a different situation exists, and a progressive, irreversible deactivation, as expressed by Equations 3 to 5, will often occur.

$$\text{Catalyst + feedstock} \begin{array}{c} \xrightarrow{k_s} \text{Desulfurized feedstock} \\ \xrightarrow{k_c} \text{Coke on catalyst} \end{array} \tag{3}$$

$$r_{\text{HDS}} = -\frac{d[S]}{dt} = k_s(t, \xi)S^n \tag{4}$$

$$k_s(t, \xi) = k_{s,o} \cdot X(t, \xi) \tag{5}$$

Here the rate constant for HDS becomes time dependent, the degree of deactivation $X(t, \xi)$ also being dependent on the location in the reactor/conversion. X can sometimes be directly correlated to the amount of metals or coke deposited on the catalyst; in other cases a definition has to be based on the total "history" of the catalyst (according to Equations 6 and 7), instead of simply its state.

$$X(t, \xi) = 1 - \int_0^t k_{\text{coking}}(\xi) X(t, \xi)\, dt \tag{6}$$

$$\frac{dk_s}{dt} = -k_{\text{coking}}(\xi)k_s \tag{7}$$

Again, the degree of deactivation can be expected to depend on the temperature and conversion level, as expressed by Equations 4 and 5. Indeed, coke profiles over isothermal laboratory reactors (12) show such differences, primarily due to a reduction in hydrogen partial pressure. Metals deposition over residue catalysts beds show a decrease with conversion simply because of depletion of the reactant (2,13,14).
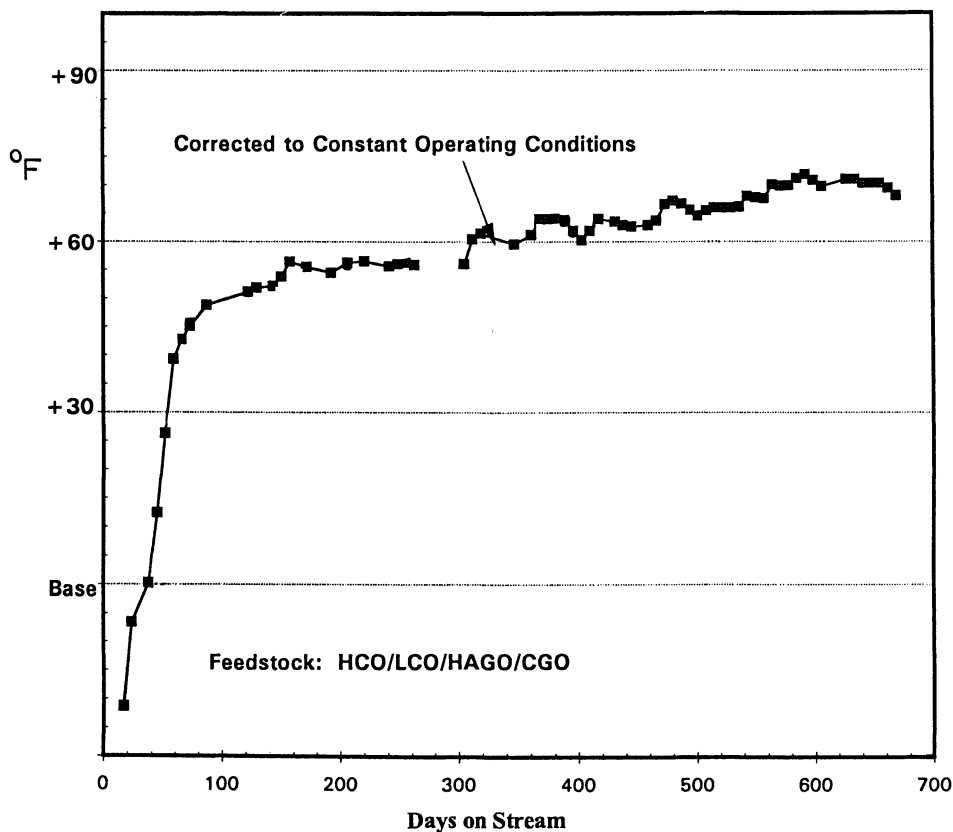
Figure 1. Activity (°F) versus catalyst age for Z 753 in a commercial hydro-cracker. (Reproduced with permission from reference 9. Copyright 1994 Safa George.)

Similar to the situation with poisoning, the permanent deactivation may be non-uniform over the catalyst particle, which can sometimes be used to advantage, as for instance in residue HDS catalysts where the metals are deposited at the periphery of the particles and the core remains "clean" and active for HDS (*15–17*).

Permanent catalyst deactivation effectively leads to a reduction in the number of active sites available for reaction (and poisoning). In commercial practice, catalyst deactivation is generally coped with by increasing the reaction temperature, expressed as degrees Celsius (Fahrenheit) per 1000 run-hours. This experimental measure is related to the fundamental deactivation parameters discussed above through the apparent activation energy. A high activation energy results in a lower temperature increase requirement for a given fractional deactivation X. The strongly poisoned systems often have high apparent activation energies, as follows from Equation 2, since the degree of poisoning decreases with increasing temperature. Thus in a practical application a strongly poisoned system can have excellent long-term stability (although not always good short-term reactor temperature stability).

c. Separation of Reversible and Irreversible Deactivation. Taking together the adjustment of the catalyst to the feedstock, and the irreversible deactivation generally gives a plot as shown in Figure 1 for catalyst activity (expressed as temperature required for a desired conversion) versus runtime. From Figure 1 it can be seen that at times shorter than about 100 days the catalyst is still reaching stationary state. Obviously this separation of these two stages may not always be easy or complete. A catalyst that has not yet been poisoned to its stationary state may, however, be very active for coking, etc. If a catalyst is quickly brought to its stationary operating temperature, it may suffer a higher deactivation than with a more careful start-up. This is possibly the basis for procedures such as "soft start-up" in first-stage hydrocracking (*18*).

The challenge now is to arrive at such an understanding of the processes and the poisoning and deactivation phenomena that the catalyst performance during its entire life, often with a variety of feedstocks and conditions, can be reliably predicted on the basis of short performance tests. Because of the complexities noted above, modelling, as an expression of an understanding of the process, will have to play a major role here. Before discussing the desired rapid performance tests, we will therefore look at the individual process areas separately, and then briefly review modelling.

3. Hydroprocessing

a. Distillate Desulfurization. In HDS of distillates such as naphtha, gasoil, etc., the traditional CoMo on alumina catalysts are used because of their high stability. Alternative catalyst formulations, such as CoMo supported on mixed oxides containing titania, have been studied (*19*), but so far their high initial activity was accompanied by a high deactivation rate. Hence the main emphasis in catalyst development has been a further optimization of the traditional CoMo alumina systems in terms of start-of-run activity. With the tightening sulfur specifications

for gasoline and distillates, deep desulfurization for which alternative catalysts might be developed is now being studied (20).

The current HDS catalysts clearly operate in a state of partial poisoning by reactants, nitrogen compounds, H_2S, etc. These phenomena have been extensively studied (21,22). Fortunately, the steady state is generally reached quickly (see Figure 2), and often reversibly. A deactivated catalyst can have a change in selectivity with respect to one that is fresh: a NiMo alumina catalyst poisoned by nitrogen compounds had increased selectivity to HDS relative to hydrogenation (23), and recently Texaco claimed the use of partially deactivated catalysts for selective processing of naphtha (24). This suggests that at least two types of active sites are present (cf. Section 2), a feature most recently discussed by van Veen et al. (25).

The structure and activity of coked catalysts exposed for a short time to aromatic feedstocks has been studied (26). It was concluded that coke is primarily located on the bare alumina support, and that the Ni(Co)Mo sulfides have a "self-cleaning" capability; with increasing coke content, coke gradually approaches the (active) edges of the NiMoS function. At a coke level of 10%, catalyst activity decreased by some 75%. It has been shown (27) that the nature of the coke not only depends on conditions but also on the type of catalyst.

b. Sulfur-Tolerant Hydrogenation. The hydrogenation of aromatics in middle distillates is done to comply with regulatory specifications on middle distillates as are now established in places such as Sweden and California (28). The mixed sulfides, because of their low activity, can only operate at high temperature, and for thermodynamic reasons require a high hydrogen pressure. The much more active noble metal catalysts that have been equipped with an enhanced resistance to sulfur poisoning are therefore preferred. These catalysts operate in a regime where the large majority of the metal sites are poisoned by S, even when sulfur tolerance has been improved by choosing modern metals and support functions (29). Thus these catalysts are currently used only in situations of relatively low sulfur contents, such as the Shell Middle Distillate Hydrogenation Process (30,31) and the SYNSAT process (32); in both cases the majority of the sulfur compounds have been eliminated by processing over a NiMo catalyst, and the noble metal catalyst operates in a low S/H_2S environment. Noble metal catalysts that can operate in a stacked-bed operation with a NiMo catalyst without intermediate H_2S removal have not yet been reported.

Laboratory tests (Figure 3) (28) and commercial experience (30,31) show that the catalysts need considerable time to reach the stationary state, after which further deactivation is very slow. This is related to the high sensitivity of the catalyst to poisons, and their necessarily low concentration.

c. Hydrocracking. The area of hydrocracking is particularly complex, because it involves both denitrogenation and cracking, because multiple catalyst systems are generally used, because hydrocracking itself is based on bifunctional catalysis, and because product recycle is often applied.

Generally the feedstock is first denitrogenated over NiMo alumina catalysts to reduce the poisoning of the cracking catalyst (33). This step is very similar
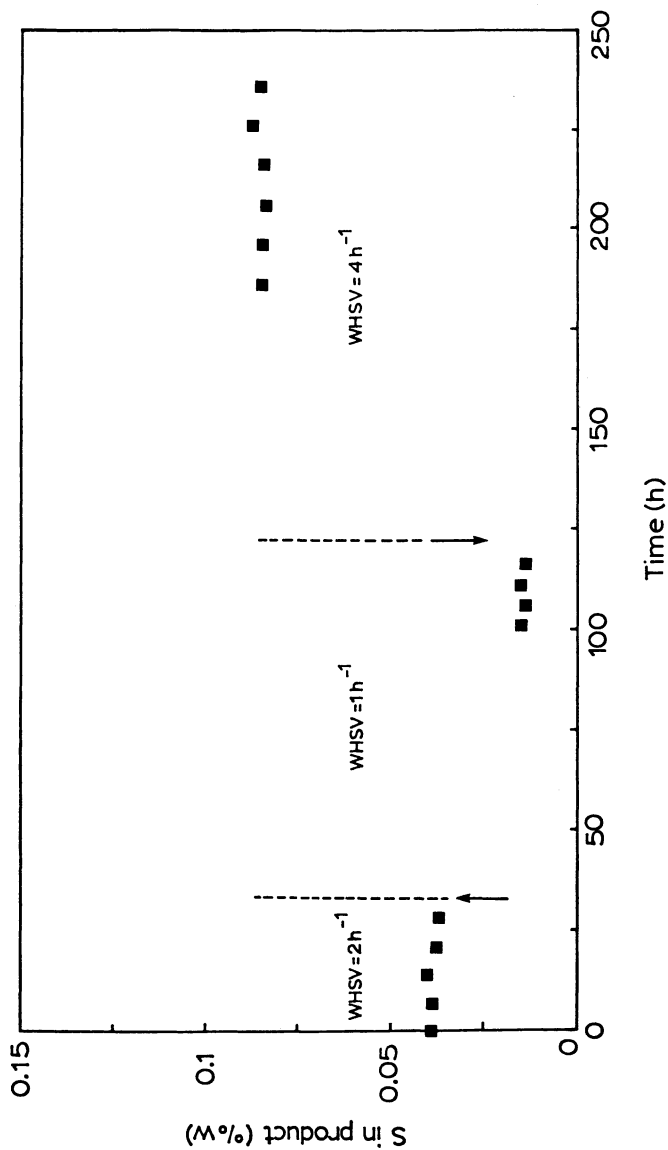
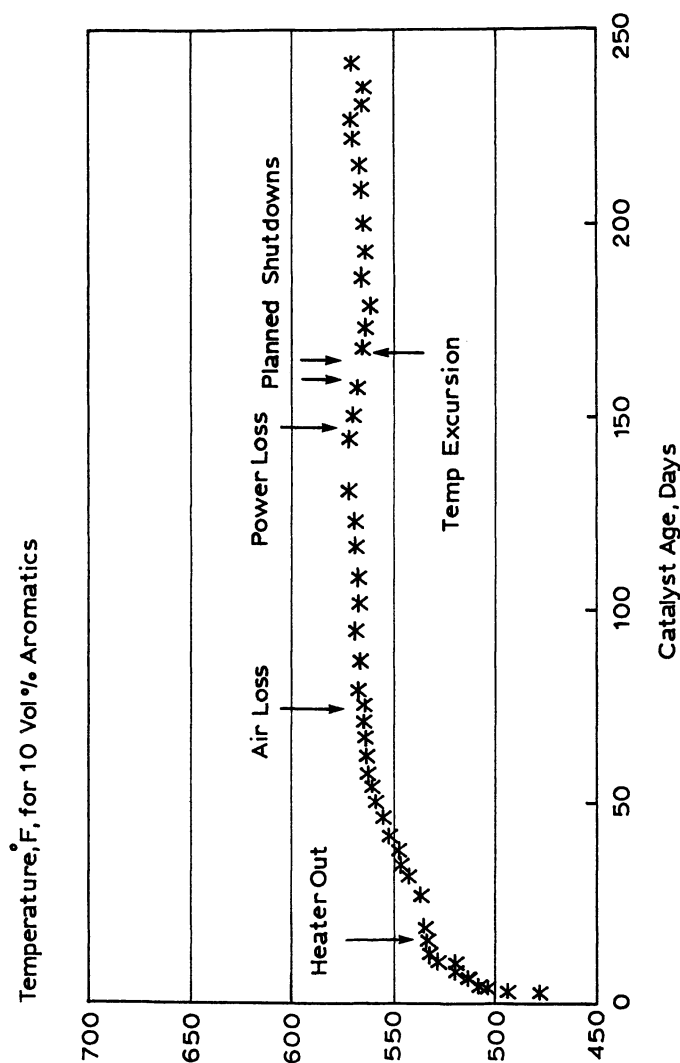Figure 2. Stabilization of a high activity HDS catalyst, DC 130, in HDS of gasoil at 3 space velocities.

Figure 3. 242 Day stability test with hydrotreated West Coast diesel (35.1 vol.% aromatics; 19 ppm N; 156 ppm S; 700 psig; 2.0 LHSV). (Reproduced with permission from reference 28. Copyright 1994 B. D. Murray.)

to distillate HDS, although attaining the stationary state may sometimes take as long as 1000 h depending on feedstock and conditions. Similar to the situation in hydrogenation, equilibrium effects may occur in HDN, with the consequence that increasing temperature above a given value will not be effective in increasing the reaction rate (*34*). Clearly one must not confuse this inherently lower response to temperature increase with a supposedly high rate of deactivation. At least part of the denitrogenation is often also carried out over NiMo(W) catalysts with an acidic support such as amorphous silica alumina (ASA) or a zeolite (*34,35*); these catalysts often have a higher activation energy (*33,34*) that favours stability (see Section 2), as well as a higher cracking activity.

Hydrocracking itself is based on bifunctional catalysis, with a (de)hydrogenation function (mixed sulfides or noble metals) and a cracking function (zeolite, ASA) combined in one catalyst. In the fresh catalyst these have been well balanced for the given duty, as has been described by Ward (*36,37*). A change in stabilization of zeolite Y can markedly affect both selectivity and stability of a hydrocracking catalyst (*38*). Deactivation of the catalyst can affect each function differently, and result in a change in selectivity. Butt and coworkers (*39*) have studied in detail a series of commercially deactivated catalysts consisting of CoMo/ASA/Ultra Stable Y sieve supplied by Amoco. The activities of both functions were studied separately using several methods, and it was established that both deactivated during commercial operation, with the acidic function more affected. A catalyst cannot be expected to operate constantly in terms of product yields and properties during its lifetime, which is in agreement with observations (*40*) (see however Refs. (*9,35*) where selectivity is very constant).

In two-stage operation, where in the second (hydrocracking) stage the denitrogenated feed (from the first stage) is cracked at low ammonia partial pressure and at low temperature, it takes a very long time to reach the stationary state, as is illustrated in Figure 1 (*9*). In series-flow operation, where the first-stage effluent is cracked at high ammonia partial pressures and high temperatures, steady state is reached much faster. Obviously the poisoning by ammonia has major consequences (*41*): higher temperature requirements and different selectivities such as a higher middle distillate selectivity. These effects are related to a changed ratio in hydrogenation over cracking activity, and to an enhanced evaporation of cracked products at higher temperatures (*42*).

Hydrocracking is special in that often a recycle of unconverted feedstock is applied. Since hydrocracking catalysts generally do not convert all compounds with the same activity, e.g. due to the size exclusion effects occurring with zeolites such recycles can easily lead to the build-up of "inert" species, the nature of which depends on the catalyst used (Figure 4) (*43*). Sometimes such species can even be further generated (*44*). These recycle effects were studied in detail by Yan (*45–47*) who concluded that addition of a NiWASA catalyst, either separately in the recycle stream or in a ASA/zeolite composite catalyst (*35*), could reduce or eliminate the recycle effects which otherwise occur when processing cycle oils (end point 450°C; see Figure 5). It is interesting to note that a later publication reports that a (noble) metal REX catalyst instead of its Ni/W analogue does not lead to build-up effects, which is attributed to the much smaller volume taken up by the noble metals than the mixed sulfide, thus resulting in higher diffusion coefficients. Whether such
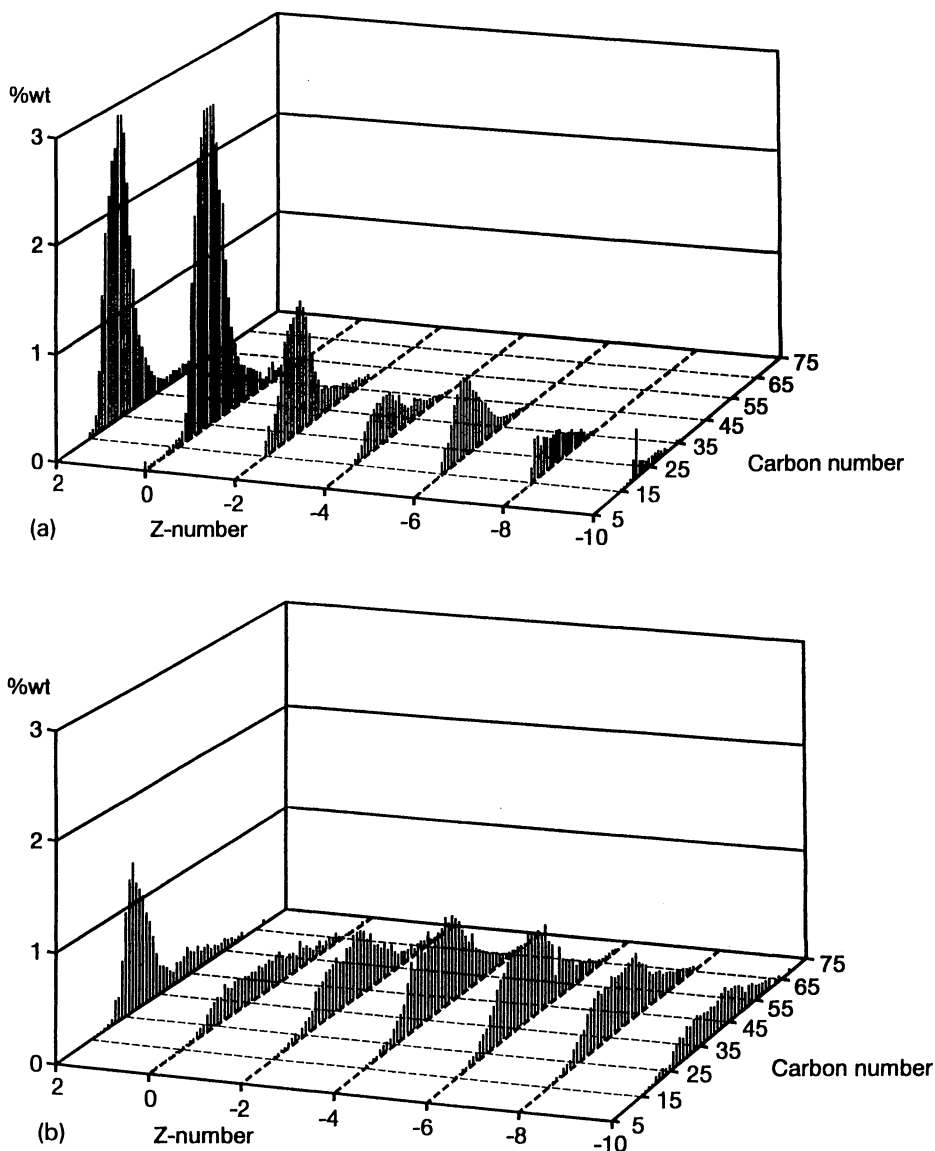
Figure 4. FIMS spectra of the unconverted material after hydrocracking treated VGO over (a) all-amorphous, and (b) all-zeolitic catalysts (two-stage operation), Z indicates the hydrocarbon stoichiometry, C_nH_{2n+z}, i.e. (poly)naphthenes occur for $Z \leq 0$, and aromatics are possible at $Z \leq -4$ (Reproduced with permission from reference 35. Copyright 1994 T. Huizinga.)
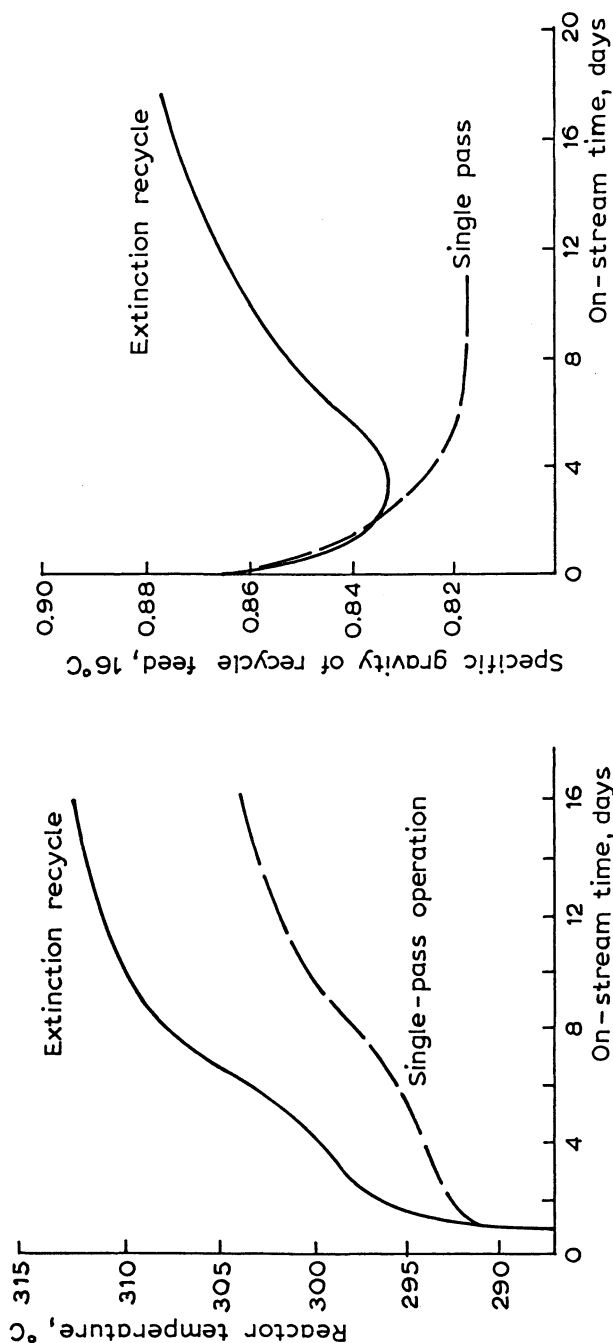
Figure 5. Reactor temperature and specific gravity of the recycle feed as a function of time-on-stream for recycle-to-extinction and single-pass modes of hydrocracking using NiW/RE-X catalyst. (Reproduced from reference 45. Copyright 1983 American Chemical Society.)

catalysts would also be adequate to avoid recycle effects with heavier feedstocks is not known. Abdul Latif (*48*) approached the recycle problem from the point of view of the refiner, showing that in recycle operation the polynuclear aromatics build-up causes catalyst deactivation and heat exchanger fouling ("red death"). PNA removal from the recycle stream leads to a clear increase in catalyst lifetime. Options include a bleed stream, a recycle of unconverted product to the vacuum column, or adsorption to a dedicated guard bed. These findings illustrate the importance of avoiding unrealistically large bleeds (e.g. due to sampling) in small-scale laboratory testing.

d. Fixed-Bed Residue Hydroprocessing. Process-wise fixed-bed residue hydro-processing is relatively simple compared to hydrocracking: it is a once-through operation using a number of multi-bed reactors; in some cases the catalyst can be continuously replaced on-line (*49,50*). Catalyst deactivation is much more pronounced than in the process-wise similar distillate hydrotreating (Figure 6). Fouling by salt, scale, etc., is more pronounced but generally coped with by using (double) desalting (*51*) and special guard beds with high-porosity material (*3*), or by using on-stream catalyst replacement (*49,50*). The presence of asphaltenes and metals (especially Ni and V) in residue leads to severe progressive deactivation, which has been extensively studied primarily by Chevron (Gulf) and Shell, and often reviewed (*2,13,50*): generally coke deactivation rapidly reaches a stationary state (*51,52*), the deactivation becoming more severe with conversion and increasing temperature, while metals deactivation is progressive, through a combination of poisoning of sites active for HDS, and closure of the pore mouth (*1,2,14,50,52*). This pore-mouth plugging model (*14*) was later extended to active site poisoning (*14*), and has been extended by several other groups (*53–55*), which also considered metals poisoning more explicitly (*56*), pore size distribution effects (*57*), bimodal catalysts (*58*), interstitial deposition (*59*), and combined coke and metals deactivation (*60*). The interference between coke deactivation and metals deposition has been noted but is difficult to describe quantitatively.

In general an attempt is made to first remove the larger part of the metals using catalysts with a high metals uptake capacity but low HDS activity — generally wide-pore or bimodal catalysts with a rather low intrinsic activity. After this the demetallized feedstock is processed over dedicated HDS catalysts with smaller pores/higher surface area, where the core is not poisoned by metals (and less by coke), which also have a higher intrinsic activity. If desired this approach can be extended to more than two catalysts. In all cases pore diffusion plays a major role (it has been shown that diffusion coefficients of molecules such as coronene are reduced by a factor of about 500 — depending on pore diameter — in spent residue catalysts, relative to fresh ones (*61*)), and the pore texture is one of the prime characteristics in developing optimized catalysts (*62*). Product properties such as asphaltenes solubility may indirectly be correlated with catalyst stability. Upon residue hydroconversion the solvency of the maltenes for asphaltenes generally decreases, and at a given stage asphaltenes precipitate. This can result in bed plugging, interstitial growth, products with insolubles, indirect deactivation of the catalyst bed, and in general limits attainable conversion both in fixed- and in ebullating-bed operation. Catalysts that allow a higher conversion before

Temperature required (°C) above base

Run time.months
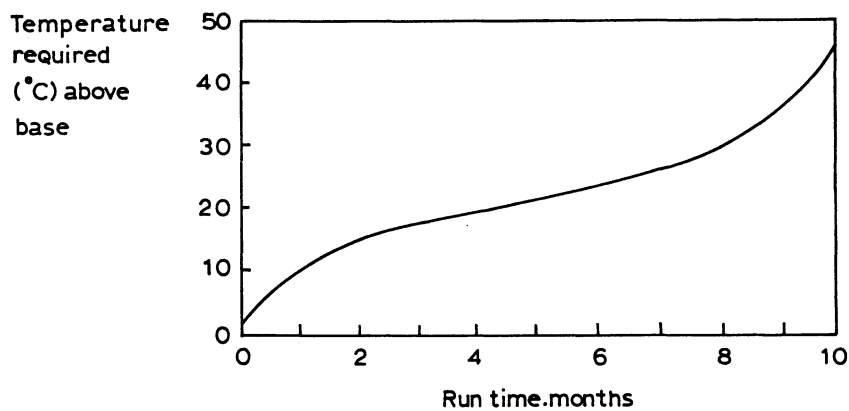
Case: 90°/o HDM: A/B/C catalyst system

Figure 6. Residue test. (Reproduced with permission from reference 50. Copyright 1989 Elsevier.)

asphaltenes precipitation sets in are therefore more stable at the higher conversion level and extremely valuable, as reported in Ref. (63) for ebullating-bed operation.

A more recent development in fixed bed residue processing is the use of zeolitic cracking catalysts. These have been developed primarily in Japan, and are quite stable according to the literature (64).

4. Modelling

In a (rapid) catalyst screening test, conditions will in general be different from those in actual operation, and experience and understanding of the particular process is essential for defining a test that is relevant, and for the translation of its results to the actual operation. The total process "know how" that has been obtained can be captured in an accessible form in a process model. One should not necessarily expect this model to be perfect, however, and extrapolations to conditions, feedstocks and catalysts that are outside the experimental base from which the model was constructed should be made with caution. This does not detract from the fact that, given the proper expertise, process models are extremely useful. In principle, two types of process models can be distinguished. In correlative models the effect of certain process (or catalyst) variables has been incorporated in mathematical formulae, which in themselves may be without physical meaning. They are an abbreviated form of the experimental database, relatively easy to set up, convenient to use, but sometimes difficult to expand. More ambitious, and generally more time-consuming to set up, are the kinetic models, in which the feedstock is split into certain (groups of) components, which then react according to a kinetic scheme for which parameters have been fitted. An example of such an approach for gasoil HDS has been reported (65), where the oil is split into 26 components, which are followed in the reactor, which has been split into 10 segments, on the basis of a detailed analysis. Between all these segments heat effects, evaporation, etc., can be taken into account. A similar approach of segmenting the reactor was described by De Jong et al. (66). This molecular approach can be extended and ultimately used to evaluate entire refining schemes (67).

In general such models focus on the description of the stationary state, predicting reaction rates, product yields, product quality, etc. as a function of feedstock and conditions. Catalyst deactivation usually does not have a prominent place in these models, and is based on a simple description, again because the available database is limited. In the example quoted above (65), however, a dedicated series of experiments on catalyst aging at different conditions was carried out to model the catalyst deactivation.

Ideally one would therefore choose a model, similar to that of described in Ref. (65), in which the reactor is split into a number of sectors, and in which for each the activity of the catalyst is calculated as a function of time. This is essentially what the RESIDS model (14,50) does for residue hydroprocessing: it correlates local catalyst activity/deactivation with local reaction rates for HDM, HDS, etc. Thus, at any time and location in the reactor, the actual state and activity of the catalyst are defined, allowing predictions of complex multi-catalyst/multi-bed systems over a range of feedstocks and conditions. For this the catalyst activity and

deactivation parameters have to be determined in dedicated experiments — see Section 5 — a complex task generally only undertaken by major oil companies. However, once these performance parameters can be correlated with the physical and chemical properties of the catalysts in their fresh (or stationary) state, the way will be open to "catalyst design".

5. Catalyst Performance Testing

An unequivocal determination of catalyst activity and stability is of crucial importance in the design of a new processing unit or sometimes even when introducing a new catalyst package in an existing unit, and to this end often lengthy, dedicated pilot plant tests are carried out before a design is finalized. For catalyst development this is not realistic, and shorter tests, which are still relevant, must be used. Ideally activity and deactivation of catalyst particles should be measured in one well defined, uniform environment. This can be achieved by using a differential reactor (possibly with external recycle), as was done in Shell's work on residue catalyst deactivation by metals (*15*). Even in this extensive study, however, metals deposition on the catalyst was accelerated by using high metals feedstocks at high spatial velocity and temperature, and still necessitated translation to the real conditions (*15,50*).

Often such an extensive effort cannot be justified, and one has to be satisfied with deactivation experiments that measure the average over a catalyst bed where a considerable conversion is achieved, hence where the catalyst is definitely not operating in a uniform environment. Examples are the variations in metals in or over the catalyst bed in residue hydroprocessing, and in organic nitrogen in hydro-cracking; for both cases dedicated top-bed catalysts which are more stable under high concentrations of metals (HDM catalysts, ABC concept (*15,50*)) or nitrogen (Z 763 specifically developed from Z 753 for improved nitrogen tolerance in top-bed duty (*68*)) are used commercially. [In principle the variation in deactivation in the axial direction might be derived from the temperature (heat generation) profiles over the catalyst bed, but this is easier for adiabatic industrial reactors than for the isothermal laboratory scale ones.] The translation to situations with different conversions, etc., will remain difficult, however. Indeed, the definition of a relevant rapid screening test is generally a major task, and many tests in the end give results that are not relevant. When determining catalyst activity and stability, one will want to accelerate both the approach to the stationary state and the (subsequent) long-term deactivation; also it will remain crucial to have a good separation of the two, otherwise too high apparent deactivation rates are reported (see Section 2 and Figure 3).

Thus, when the considerations of the earlier sections are taken into account, the following points can be made on setting up a screening test:

a. Feedstock. Clearly, performance testing should be done using feedstocks that closely resemble the intended one. Use of feedstocks with a different boiling point will influence catalyst activity differences as well as catalyst stability; in addition, cracked feedstocks generally lead to faster catalyst deactivation because of the high aromatics content. In practice, therefore, one generally uses one screening

feedstock for catalyst development, and then assesses the performance of the promising candidates with a range of other feedstocks.

Performance testing in trickle-flow operation invariably takes longer than in gas-phase tests with model compounds. Testing with model compounds such as thiophene can be an effective contribution to fast screening, e.g. for the effectiveness of catalyst functions in a defined context, but should not be taken beyond that.

b. Accelerating the Reaching of the Stationary State. As was discussed in Section 2, the stationary state is reached reasonably quickly in situations where the feedstock contains a high concentration of catalyst poisons, such as in gasoil HDS, first-stage hydrocracking and in residue hydroprocessing. In sulfur-tolerant hydrogenation experiments and in second-stage hydrocracking at low ammonia levels, however, this takes much longer. The poisons in the feed are strongly absorbed at the catalyst, and at the same time converted over it. The "equilibration time" can be shortened by several means, such as blocked-in periods with high feed rates, or with higher contaminant levels, or even a total screening with a feedstock with a higher concentration of poison. These procedures can give a useful ranking test, but the translation to the envisaged application must be confirmed. Too often such a test develops into something which ultimately is merely a complicated titration rather than a determination of catalytic activity.

c. Long-Term Catalyst Deactivation. Obviously here also accelerated tests to measure deactivation by coke and by metals are required in a catalyst screening stage. The accelerated coking is achieved by operation at lower hydrogen partial pressures and/or higher temperatures, as described in Ref. (65).

Accelerated deactivation tests in hydrocracking have been reported (38), where a constant conversion mode was run at much higher space velocity (and hence temperature) than under actual operation conditions. Differences in deactivation were measured that were later substantiated in commercial operation (38). Although all these approaches aim at accelerating the catalyst deactivation reaction in Equation 7, such tests should obviously not be applied to catalyst systems that — at the high space velocity — operate at such high temperatures that very high polyaromatics concentrations prevail.

In residue hydroprocessing, however, coke is often set at a quasi-stationary level dictated by factors such as temperature, so here this approach must be followed with care (51–53,69). Metals deactivation can be accelerated by using a high metals feedstock, higher space velocity (to get a higher overall loading) and higher temperature. This was studied for instance by Altag (69): in a "normal" test, at normal temperature, blocked-in conditions were used with high space velocity, high temperature and high metals feedstock (Hondo, Maya), such that although most of the time the test is run under normal feed/conditions, most of the metals are deposited in the blocked-in periods. The amount of deposition is a good measure of activity/deactivation for HDM, although possible feedstock effects need to be taken into account, Maya AR giving larger than expected deactivation in the quoted reference (attributed to stronger coke make and hence larger diffusion hemming). For HDS the result was different, and the blocked-in experiments always gave lower HDS activity, including the check-back periods. A

fair representation of the deactivation by metals for HDS was obtained by simply impregnating Ni and V onto the catalyst.

d. Modelling. In Section 4 the importance of modelling was stressed. In practical terms the following examples can be quoted: in Ref. (*49*) test results with improved catalysts are given, the new catalyst apparently having a lower start-of-run temperature and stability for HDS. It is only by considering the total dual catalyst system that the advantage of the improved HDM catalyst, emerges (Figure 7); obviously models predict these phenomena far more effectively than experiments. Also, Shell has reported on a dedicated test for residue catalyst screening, where a series of temperatures was applied that is closely linked to their RESIDS model (*14,50*) (Figure 8), also using correlations between metals deactivaton and metals penetration into the catalyst particles. An occasional confirmatory experiment then suffices to validate the results and complete the catalyst development.

e. Recycle Operation. The recycle in hydrocracking poses special problems because it has a clear effect on catalyst performance, dependent on the formulation of the catalyst. The preferred option to cope with this is to carry out recycle tests using small-scale equipment with realistic feeds and conditions (*43*). The deactivation can be accelerated by the usual means, lower gas rates and pressures, higher space velocities and temperatures, and heavier feedstocks. In our experience this is an excellent procedure for catalyst development (*43*). An alternative is to carry out once-through experiments with feedstocks that contain recycle material, obtained either directly from a commercial hydrocracker or by separate blending of first stage effluent and a recycle stream. Obviously this set-up is experimentally easier; at the same time it is less rigorous in that build-up effects with the catalyst under study are not really monitored.

f. Further Development. Clearly the design of accelerated tests hinges on a good understanding of the process. Nevertheless, the slow approach to stationary state in some of the above-mentioned applications would in particular lend itself to modelling. This would lead to generic procedures to shorten such periods that are nevertheless more specific than those quoted earlier. For the acceleration of coking and metals deposition the approach and dangers are clear, and here less basic work is necessary. Modelling will become increasingly more important, but we are still a long way from the stage where deactivation can be predicted theoretically with a reasonable precision. Hence it is necessary to continue to develop and implement cost-effective small-scale equipment to measure catalyst performance, in conjunction with process models for interpretation of the data. A review of reliable small-scale testing methods is presented by S.T. Sie in this symposium (*70*).

6. Conclusions

Performance testing is essential in the development and application of catalysts, and the preferred approach will depend on the target to be reached. Thus for a final process evaluation long and detailed pilot plant tests will be carried out whereas for catalyst development this is not realistic. In the latter process simple
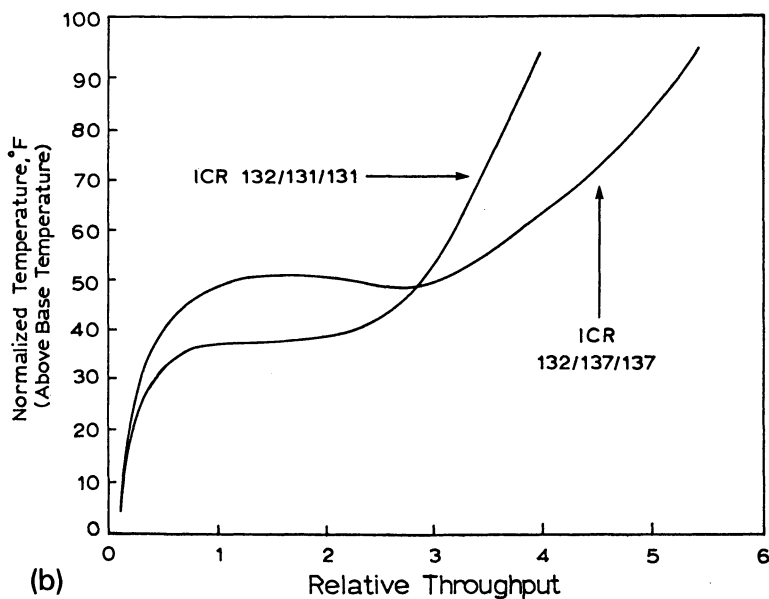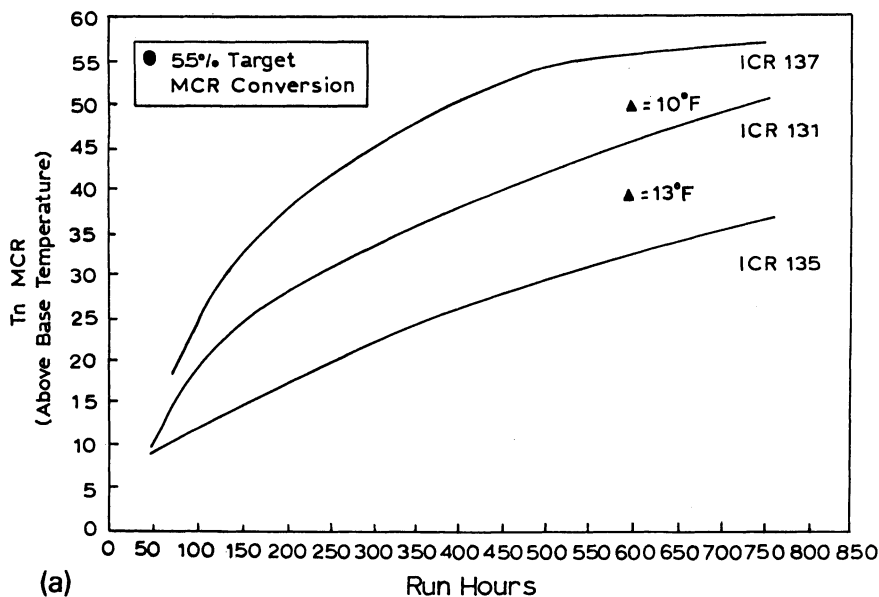
Figure 7. a. MCR Conversion activity for ICR catalysts (Arabian Heavy AR).
b. Normalized temperature for MCR removal (55% conversion target in
whole liquid product). (Reproduced with permission from reference 49.
Copyright 1993 Elsevier.)
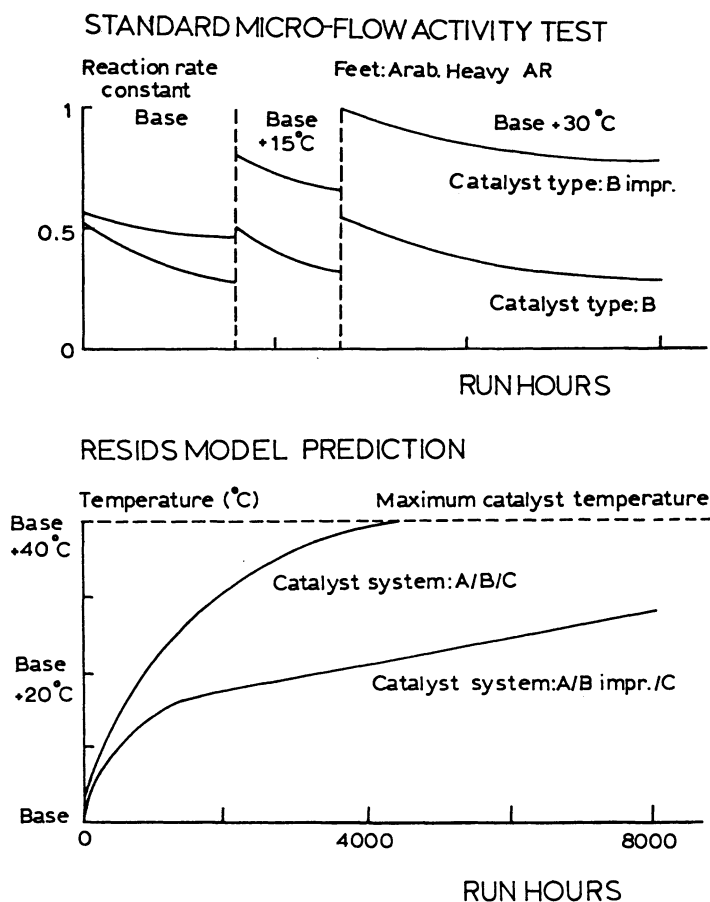
STANDARD MICRO-FLOW ACTIVITY TEST

Figure 8. Testing and prediction of catalyst performance. (Reproduced with permission from reference 50. Copyright 1989 Elsevier.)

screening tests, both for initial performance and for stability, will have to be selected carefully on the basis of an adequate process knowledge, and preferably supported by process models. In this situation the use of small-scale equipment that is nevertheless able to reliably mimic the essential features of the process, including product recycles, is of great value.

Acknowledgments

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