ELSEVIER

Catalysis Today 39 (1997) 69–75

CATALYSIS TODAY

Deep hydrodesulfurization process for diesel oil

Toru Takatsuka*, Shin-ichi Inoue, Yukitaka Wada

Environmental Technology Center, Chiyoda Corporation, 3-13 Moriya-cho, Kanagawa-ku, Yokohama 221, Japan

Abstract

In Japan, in late 1989, the Environmental Agency's Central Council for Environmental Pollution Control instituted an exhaust gas control program for diesel vehicles, setting forth the permissible emission levels. The program not only imposes a substantial curb on NO_x emissions but also calls for the reduction of black soot exhaust gas, which is peculiar to diesel vehicles, and restricts it in terms of the particulate matter (PM) emission level.

Oil companies, on the other hand, have been required to reduce diesel oil's sulfur content, which corrodes the equipment and piping tubes and causes deterioration of the catalyst, from 0.4% (or 0.5% under the Japanese Industrial Standards) to 0.2% by 1993 and further to 0.05% by 1997.

The overall performance of the deep hydrodesulfurization (HDS) process for diesel oil is advancing with both improvements in catalysis and developments in process design. The item most focused on in the process development is how to control the color of product diesel oil. Japanese consumers of diesel oil tend to object to the current color on grounds that it reminds them of erstwhile inferior-quality products. This market inclination has become an essential point of quality control. Some problems are also discussed concerning a scale up of reactor, reactor efficiency, reaction kinetics, catalyst life and hydrogen consumption. © 1997 Elsevier Science B.V.

Keywords: Diesel oil; Hydrodesulfurization

1. Environmental issues involving diesel-powered vehicles

During the second half of the 1980s, the environmental impact of emissions from diesel-powered vehicles, which had not been adequately addressed, received renewed attention in Japan, US and the industrial countries in Europe. A global net of environmental controls was placed on these vehicles. In response, vehicle manufacturers demanded improvement in the quality of diesel oil, the fuel for diesel vehicles. In Japan, they wanted the sulfur content of diesel oil, which was then 0.5%, to be reduced to 0.2% by 1992 and 0.05% by 1997. Though schedules for the tightening of diesel vehicle emission standards differ from country to country, the demanded quality standard of diesel oil is substantially the same. The tightened standard was made law, and work has begun in Japan to develop high-performance desulfurization catalysts and processes. As the target desulfurization rate is higher than for earlier processes, the intended process is known as the deep hydrodesulfurization

---

*Corresponding author. Tel.: +81 45 441 1269; fax: +81 45 441 1299; e-mail: ttakatsuka@ykh.chiyoda.co.jp

PII S0920-5861(97)00089-8

process for diesel oil, or simply the deep HDS process.

In Japan, motor vehicle manufacturers and oil companies worked together to achieve lead-free gasoline engines in the 1970s. Since then, mainly through improvements on the automobile side, including the installation of the exhaust gas recirculation system (EGR) and the use of exhaust gas cleaning catalysts, nitrogen oxide (NO_x), carbon monoxide (CO) and hydrocarbon (HC) emissions have been successfully reduced, to the benefit of the environment. As a result, gasoline-powered cars in Japan have a reputation for having exhaust emission levels among the lowest in the world.

On the other hand, diesel-powered vehicles, whose exhaust is technically more difficult to clean through improvements to the engine, lag far behind in environmental friendliness, and Japan's experience is typical in this respect. In many parts of the country, it is reported that there are days when the NO_x content in the atmosphere surpasses the reference level, and this is mainly blamed on exhaust gas from diesel vehicles, whose number has quickly increased over the last few years. This exhaust gas poses problems in two respects: NO_x and black soot (containing particulate matter (PM)).

Generally, there is the dilemma that measures to reduce NO_x tend to deteriorate fuel efficiency and increase black soot. NO_x often arouses concern in winter, but the observed low level of NO_x in summer is merely a result of the photochemical reaction that takes place in the strong summer sun between NO_x and HCs, which briskly transpire into the atmosphere when the temperature is high. It has to be kept well in mind that ozone (an oxidant), which is even more harmful to humans, is instead generated at ground level.

In Japan, in late 1989, the Environmental Agency's Central Council for Environmental Pollution Control instituted an exhaust gas control program for diesel vehicles, setting forth the permissible emission levels. The program not only imposes a substantial curb on NO_x emissions but also calls for the reduction of black soot exhaust gas, which is peculiar to diesel vehicles, and restricts it in terms of the PM emission level. Studies are underway to mainly use an EGR system to control NO_x and, against black soot, to equip new vehicles with a trap oxidizer which arrests particulate matter with a filter and at the same time burns it with an oxidation catalyst.

Oil companies, on the other hand, have been required to reduce diesel oil's sulfur content, which corrodes the equipment and piping tubes and causes deterioration of the catalyst, from 0.4% (or 0.5% under the Japanese Industrial Standards) to 0.2% by 1993 and further to 0.05% by 1997.

2. Advances in catalyst performance

The overall performance of the deep HDS process for diesel oil is advancing. Regarding the activity of catalysts for this process, as shown in Fig. 1, their specific activity in 1994 was about 1.2 times higher than was achieved in the reference year 1992, and catalysts 1.5 times more active are likely to emerge soon. This outlook is very encouraging to process designers.

Catalysts widely used in the deep HDS process, like those employed in HDS processes for other oil fractions, are prepared by dispersing molybdenum over a porous alumina carrier. To further raise the desulfurizing activity of this molybdenum, it is general practice to add nickel or cobalt as a promoter. These metals are used in a sulfided state.

Although there is nothing new about HDS catalysts themselves, which have been in use for a long time, there are many unknown points about their catalytic actions. Their manufacture has been indeed more an art than a science, but now many aspects are being understood.

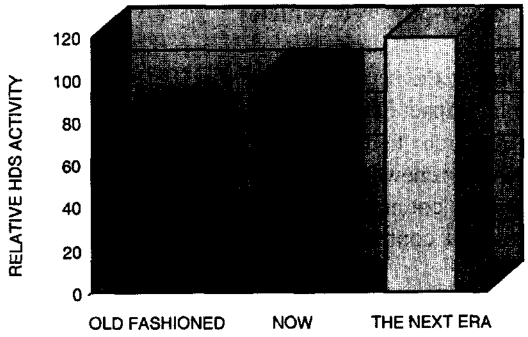


Fig. 1. An improvement of industrial HDS catalyst performance.

3. Development of the deep HDS process

3.1. *Scaling up from experimental to commercial systems*

Commercial and experimental systems vastly differ in the feedstock oil throughput they can treat. Commercial systems can handle four million times as much throughput as experimental systems, which have a daily capacity of only 1 l/day. On a superficial, liquid-linear-velocity basis, the capacity of a commercial system is 100 times as great. As activity testing equipment now in use generally has a treating capacity of 30 cm^3/h, the scaling up to a commercial system is even more extreme. Therefore, a key question is how accurately the performance of a commercial system can be predicted from the laboratory level.

Whether on a laboratory level or a commercial scale, the commonly used HDS reactor for diesel oil is equipped with a trickle bed in which the feedstock oil, accompanied by hydrogen, is supplied in a downflow to a fixed-bed reactor packed with a catalyst. Accordingly, an uneven flow of the liquid in the catalyst layer poses a problem. If this problem is solved and an even flow can be maintained in both experimental and commercial systems, as shown in Fig. 2, a satisfactory relationship of one-to-one correspondence will be achieved between them.

3.2. *Enhancing reactor efficiency*

In a downflow trickle bed reactor, the flow of the reaction liquid deviates from the ideal pattern according to the degree of catalyst wetting or the channeling of liquid flow. In many existing diesel oil HDS units, if the reactor efficiency is measured from the apparent desulfurization rate, the catalyst exhibits no more than one-third to one-half of its true activity, as shown in Fig. 3 [1]. This flow problem explains the puzzling phenomenon, observed in conventional equipment, in which the desulfurization rate rises, when the throughput is increased, instead of falling as it should.

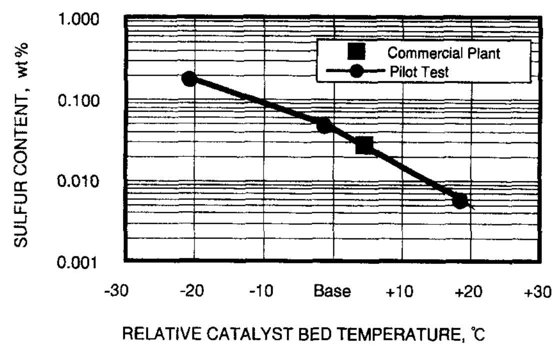


Fig. 2. Comparison of performances between commercial plant and pilot plant.

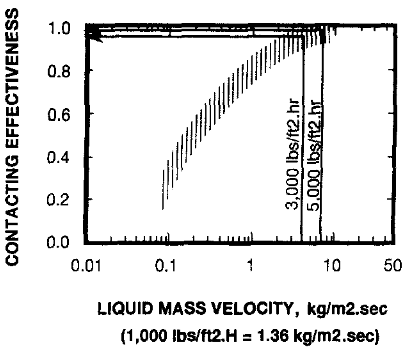


Fig. 3. Contacting effectiveness as a function of liquid mass velocity in trickle bed.

Catalyst loading is one of the important items to attain the full activity of the catalyst. When a catalyst is not packed uniformly, with an uneven void fraction in the reactor, a maldistribution of liquid flow progresses. A bad example is shown in Fig. 4, where catalyst is loaded by different methods but with a result of an uneven void fraction in the radiant position of the reactor bed. A poor distribution of liquid flow across the catalyst bed is predicted from the simple pressure drop calculation throughout the bed. In this

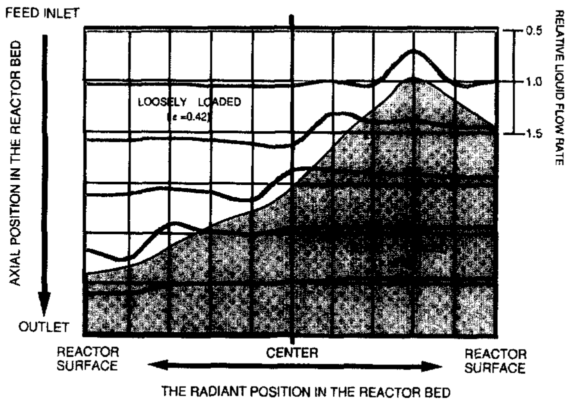


Fig. 4. The effect of catalyst loading on the liquid flow distribution in the HDS reactor bed.

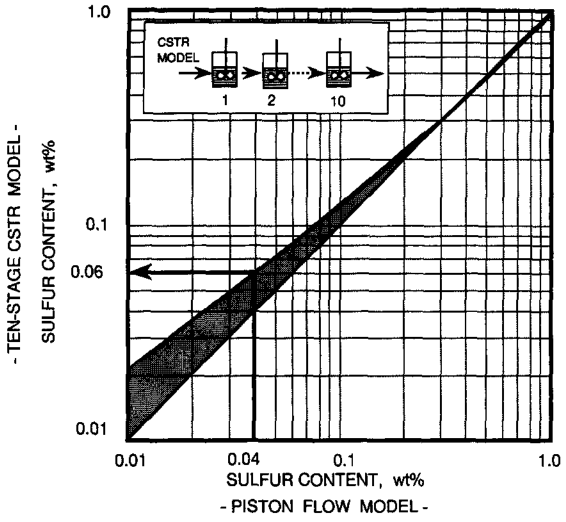


Fig. 5. Effect of backmixing on product sulfur content.

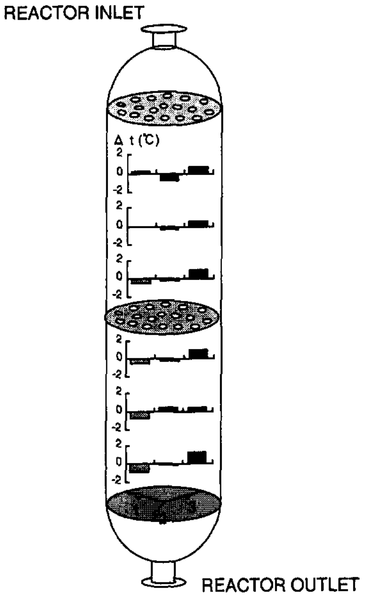


Fig. 6. Radial temperature profile in the reactor with a uniform liquid flow.

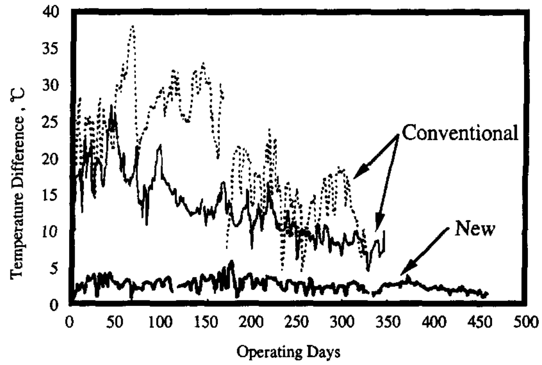


Fig. 7. Improved performance of catalyst loading system.

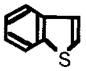
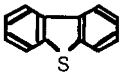
case the boundary surface of the beds with different void fractions should be horizontally flat.

An important point to be noted is that, even if this problem is not observed as a noticeable phenomenon when the desulfurization rate is low, the deviation from the ideal flow increases when the desulfurization rate is high, as it is in the deep HDS process, greatly affecting the properties of the product. This can be confirmed by calculations using a multi-stage complete stirred tank reactor (CSTR) model, as shown in Fig. 5 [2]. A 10-stage CSTR model is assumed. Accordingly, as the deviation from the ideal flow is negligible, there is very little problem at a low desulfurization rate. But the chart shows that in the domain of high desulfurization rates even a little disturbance of the flow can greatly affect the end result.

Therefore, with the deep HDS process, where the desulfurization rate is high, in order to bring the flow as close as possible to its ideal pattern, it is necessary to secure a flow rate and pressure drop that are higher than certain levels and at the same time to improve the internal equipment of the reactor, such as the liquid distributor.

In actual operation, the unevenness of the liquid flow in the reactor can be observed as a radial temperature difference within the reactor. An example is illustrated in Fig. 6. In this case, the temperature difference in the radial direction is no more than 1°C at any place in the reactor, indicating that the aforementioned improvements and precautions are functioning adequately.

Recently, various catalyst loading systems are proposed to achieve a more uniform and dense catalyst packing. Fig. 7 shows the example that the system attained an excellent temperature profile across the radial direction of the reactor bed [3]. The data also implie that an ideal flow brings about more room for increasing reaction temperature to compensate for the loss of catalyst activity or to expect more conversion, as well as increasing catalyst efficiency.

TYPE OF SULFUR COMPOUNDS			%	RELATIVE REACTIVITIES
NON THIOPHENE		RSR, RSSR	23	>>1
THIOPHENES				
	1R		1	1
	2R		35	1/2
	3R		37	1/10
	>4R		4	1/100

$$dc/dt = \Sigma - k_i C_i \fallingdotseq - k C^{1.7}$$

Fig. 8. Relative reactivities of sulfur compounds in gas oil fraction.

3.3. *Handling the HDS reaction*

In the reaction of a petroleum product, different types of sulfur compounds are usually present in the feedstock oil [4], and consequently a number of reactions occur in parallel at different rates. In the case of the HDS of diesel oil, components such as those shown in Fig. 8 take part in the reaction.

In the HDS reaction of a mixture of components with greatly differing reaction rates, it is common practice to treat the sum total of the reaction volumes as representing an apparent reaction against the entire sulfur concentration. In the HDS of a diesel oil fraction, this sum total is treated as a reaction in the order of 1.5–1.7 [5].

Even if such a model is used, there will be no problem if the user is well aware of the limits of its application. But if we set our sights on the ultra-deep HDS being required in the future and even the hydrogenation of aromatics in diesel oil, we need a new model regarding the reaction rate. As it is now possible to directly analyze quantitative data on sulfur-containing components by gas chromatography, as illustrated in Fig. 9 and, moreover, now that more advanced computers are available, we can carry out simulations based on precise reaction calculations.

3.4. *Estimating hydrogen consumption*

The volume of hydrogen consumed in a HDS process is an essential factor in process design and economy, and its accurate estimation can be a vital element in the choice of a process.

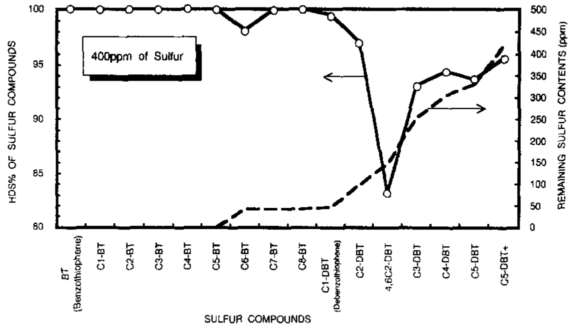


Fig. 9. Refractory sulfur compounds to be removed.

In the deep HDS of diesel oil, even though the consumption of hydrogen is greater than with earlier processes, it is relatively low, no more than tens of Nm^3/kl, a region where precise measurement is difficult. On account of this difficulty, it was necessary to develop a method by which the total volume of hydrogen chemically consumed is determined from the analytical results of the hydrogen-to-carbon ratios of the feedstock oil, product oil and product gas, a method that can calculate the hydrogen consumption on that basis without being affected by changes in the flow rate. It is necessary, in designing the process, to estimate the chemical consumption of hydrogen from the reaction conditions and the properties of the feedstock, but as shown in Fig. 10, accurate data have now

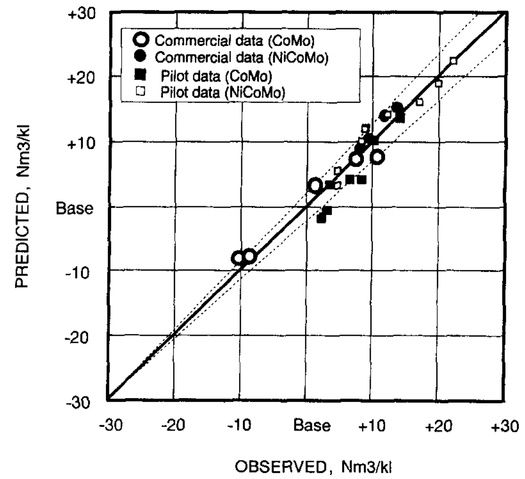


Fig. 10. Chemical hydrogen consumption.

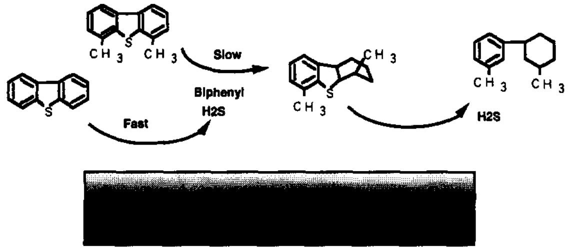


Fig. 11. Schematic model for HDS reactions of steric hindrance.

been accumulated, allowing estimates with a high level of precision.

In the deep desulfurization domain, components with steric hindrance must be desulfurized in a catalytic reaction, as seen in the reactions of alkyl-dibenzothiophene shown in Fig. 11. So the hydrogenation of aromatics precedes the desulfurization reaction. It is necessary, therefore, to analyze changes in the number of rings of the aromatics, and to handle at the same time the hydrogenation reaction of these compounds as shown in Fig. 12.

3.5. *Estimating catalyst life*

One of the most essential points of process design is to estimate the useful life of the catalyst [6].

Fig. 13 illustrates the results of long-term catalyst life tests conducted at different temperatures on a laboratory scale and of data fitting using a catalyst deactivation model. It can be seen that the catalyst deactivation model covers a wide range of conditions from relatively low temperatures and low liquid hourly space velocity (LHSV) to high temperatures and high LHSV. Many models for estimating catalyst life are proposed. Here the deactivation of catalyst is modeled by calculating the rate of the accumulation of coke on the catalyst and taking account of the effects of this coke as it covers the metallic surface of the catalyst and inhibits the diffusion of molecules in diesel oil into the catalyst. Without such a model, many time-consuming experiments would have been necessary, such as those referred to above, and the development of the process would have taken much longer.

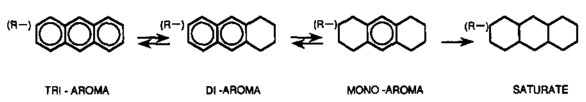


Fig. 12. Aromatics saturation model.

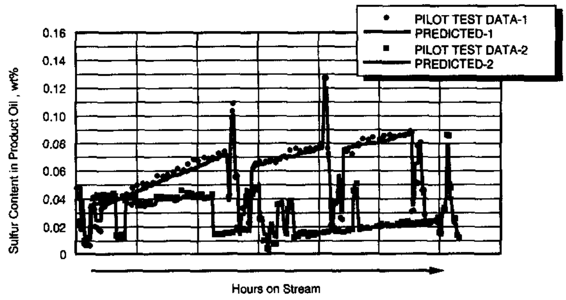


Fig. 13. Degradation of catalyst activity for HDS.

3.6. *Predicting the color of product diesel oil*

In the Japanese market, the requirement for the color of product diesel oil is more stringent than in other countries. There nevertheless is no definite reference color scale for product diesel oil in the domestic market, and oil companies carry out quality control in accordance with their own reference scales under ASTM or APHA or in reference to the Saybolt color standard [5,6].

In the HDS of straight-run diesel oil, the faintly yellow diesel oil feedstock is decolored with the progress of desulfurization, as shown in Fig. 14, and becomes colorless and transparent when a certain rate of desulfurization has been reached. However, if desulfurization proceeds beyond that rate, the diesel oil again takes on color, becoming fluorescent yellowish green. Japanese consumers of diesel oil tend to

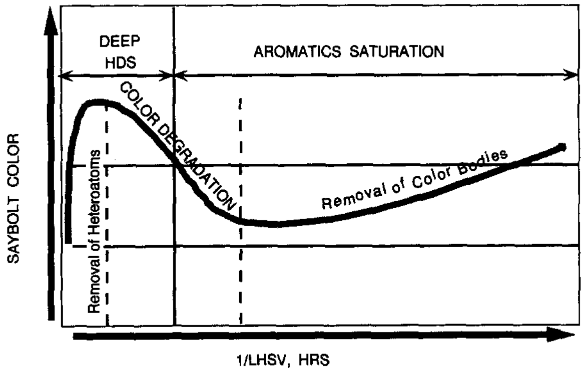


Fig. 14. Color degradation in deep HDS of diesel oil.

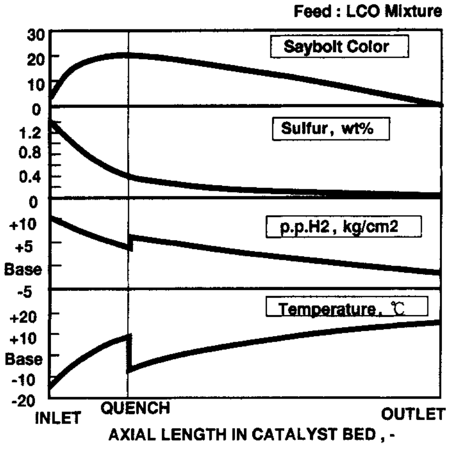


Fig. 15. Deep HDS of diesel oil in the reactor.

object to this color on grounds that it reminds them of erstwhile inferior-quality products. This market inclination has become an essential point of quality control.

Whereas data available on the laboratory level represent the results of isothermal reactions, in a commercial unit a temperature rise of 10–30°C occurs at the reactor inlet and outlet, as shown in Fig. 15. Accordingly, there is the problem of how to match the coloring temperature condition obtained on the laboratory level with a commercial system. It is safer to assume that the coloring temperature is the maximum temperature in the reactor, i.e. the temperature at the reactor outlet.

However, if this assumption is followed, the permissible average temperature must be kept low. This results in an over-design of the size of the reactor that is really needed. However, before the study to develop a deep HDS process began, the reaction which accounts for this color was unknown. In the progress of study it was found that, after the desulfurization of alkyl-dibenzothiophenes, the desulfurized part failed to undergo rapid hydrogenation, leaving radicals behind and, as illustrated in Fig. 16, resulting in the generation of polycyclic aromatic molecules, which were found to be the source of the fluorescent coloring.

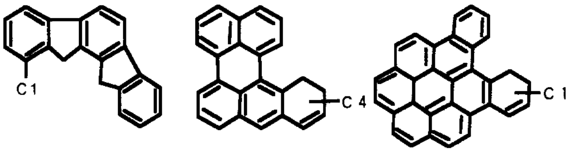


Fig. 16. The color bodies derived from desulfurized aromatic compounds.

In view of this discovery, the reaction process was modeled to take into account the generation of color that accompanies the desulfurization of diesel oil as an intermediate product of the reaction. A high hydrogen pressure serves to accelerate the hydrogenation of radicals and consequently suppresses coloring, while a high reaction temperature conversely retards hydrogenation and facilitates coloring. The model expressed these phenomena, making it possible to treat the reaction as a matter of kinetics. Rational process design has thus become possible.

References

[1] C.N. Satterfield, AIChE J. 21 (1979) 209.
[2] T. Takatsuka, Y. Wada, PETROTECH 13 (1990) 418.
[3] S. Okubo, Haikan Gijutsu 1997 Zoukan-gou, February, 1997, p. 70.
[4] A. Fushiyama, PETROTECH 1 (1978) 705.
[5] T. Takatsuka, Y. Wada, H. Suzuki, S. Komatsu, Y. Morimura, J. Jpn. Petrol. Inst. 35 (1992) 179.
[6] T. Takatsuka, Y. Wada, S. Inoue, Deactivation and testing of hydrocarbon-processing catalysts, ACS Symposium Series, Vol. 634, 1996, p. 414.