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Infrared Radiometric Observations of Surface Temperatures During Hydrogenation of Ethylene on Commercial Nickel–Kieselguhr

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Steady-state and transient surface temperatures were studied on commercial nickel-on-Kieselguhr in a packed-bed environment using an infrared radiometric microscope. Large gradients between the bulk gas and the catalyst surface were observed and high gradients during the transient period between surface and center of the catalyst were deduced. Existing postulates for steady-state temperature gradients in catalyst pellets appear to be confirmed. Applications related to the observed temperature behavior are suggested for successful experimental and commercial operation.

Although methods for calculating surface and interior temperatures of catalyst particles during reaction have been examined in great detail (*1–9*), confirming experimental evidence is sparse. Most of the reported measurements of surface and interior temperatures are based on the use of thermocouples imbedded in the catalyst particle. The use of thermocouples, however, introduces uncertainties in measurements and slow response times which can mask temperature changes in interesting unsteady-state operating modes. Even with the thinest possible wire, errors will be introduced which are difficult to evaluate. Surface temperature measurement is a particular problem, for the thermocouple on the surface drastically changes the character of the surface in that area. By contrast, infrared radiometry provides an accurate, nondestructive method which requires no contact with the catalyst surface. The rapid response of the detector to the natural infrared energy radiated by the particle makes it possible to record important temperature changes during unsteady-state periods.

Accordingly, we have used a commercial infrared radiometric microscope to study surface temperature behavior on a commercial nickel–Kieselguhr catalyst pellet during the hydrogenation of ethylene. This highly active catalyst and very rapid exothermic reaction afforded the opportunity to confirm certain temperature characteristics previously suggested by theory. Other facets of catalyst temperature behavior were observed which, though intuitively satisfying, have been largely unexplored.

The first study employing radiometric techniques on a catalytic solid was reported by Low and Cusumano (*16*). They followed the surface temperature of reduced nickel-on-silica during chemisorption of oxygen. The catalyst was prepared in the form of a single wafer (1 in. diam) and tested under vacuum where conduction within the sample was negligible. This rapid reaction produced a temperature rise of 200°C in 8–12 sec and a rate of rise from 100 to 300°C/sec at the time of 100 msec. The present work adds data on the reaction surface characteristics of a similar nickel catalyst in a commercial pellet form and under operating conditions related to actual use in fixed-bed hydrogenation.

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WHAT THEORY SUGGESTS

Although theory and more specifically models of nonisothermal catalysts systems have been numerous, the major operative conclusions are small in number. These have been summarized in several recent publications:

1. The value of the modified Nusselt number (hD_p/λ_e)* is less than 10 for most practical systems, and the major temperature gradient occurs across the fluid film. The catalyst is essentially isothermal. Rapid exothermic reactions which cause a high ΔT across the fluid are effectively confined to the exterior layers of the catalyst particle. The remainder of unused particle rises in temperature and upon reaching the steady state has essentially the same temperature as the exterior *(7–9)*.

2. At the steady state the maximum possible ΔT within the catalyst has been estimated from mass and energy balances over the particle. For most systems this ΔT is small *(3, 5)*.

3. Based on assumed constant surface conditions of C_s and T_s, possible transient temperature gradients within the particle have been evaluated mathematically *(5)*. It is possible for these gradients to exceed the steady-state gradient of item 2. The early portion of the transient period is more likely, however, to involve a changing surface condition.

SCOPE OF EXPERIMENTS

The goal of the present study was to observe surface temperatures of reacting catalyst during both the steady-state and transient period. Comparison of such data with existing models and estimating procedures should be enlightening. A differential reactor was operated so that the results might simulate behavior of the first layer of a bed catalyst in a commercial reactor.

EXPERIMENTAL PROCEDURES AND EQUIPMENT

Catalyst

Harshaw Ni-0104T nickel-on-Kieselguhr catalyst was used in the form of ¼ × ¼ in. cylindrical pellets (see Table 1). This catalyst is a stabilized, partially reduced material. It was more completely reduced in a separate reactor for 3–4 hr at 450–650°F to produce uniformly active samples. These were transferred as needed to the test reactor in an inert atmosphere. Inert Kieselguhr extrudates of ⅛ × ⅛ in. in size were used in some tests to surround the single active particle.

TABLE I
PHYSICAL PROPERTIES OF HARSHAW-KIESELGUHR INERT PELLETS

Effective diameter (in.)	0.190
Bulk density (lb/cu. ft)	32.9
Particle density (lb/cu. ft)	52.0
True density (lb/cu. ft)	148.8
External void fraction (porosity)	0.367
Internal void fraction	0.650

Reaction

The reactor, which was constructed of brass, is shown in Fig. 1. A clip is located within the reactor so that the catalyst particle could be held in position for viewing. The ir window was fabricated and coated by the Optical Coating Laboratories in Santa Rosa, CA. The coating was designed to achieve higher than 95% transmissivity in the 1.8–5.5 μ spectral range of the detector.

Radiometric Microscope

A Barnes Model RM-2A Infrared Radiometric Microscope, Barnes Engineering Company (Stanford, CT), was used for detecting the surface temperature. The microscope combines an optical system

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* Nomenclature used: a = radius of spherical particle (or equivalent sphere); C_B = concentration in bulk gas; C_p = heat capacity; C_s = concentration at catalyst surface; $(-\Delta H)$ = heat of reaction; j_D = j-factor for diffusion; j_H = j-factor for heat transfer; r = radial distance; t = time; ΔT = temperature difference between catalyst exterior surface and bulk gas; ΔT_t = temperature at time t minus initial temperature; κ = thermal diffusivity $\lambda/\rho C_p$; λ = effective thermal conductivity of solid; ρ = density of solid.

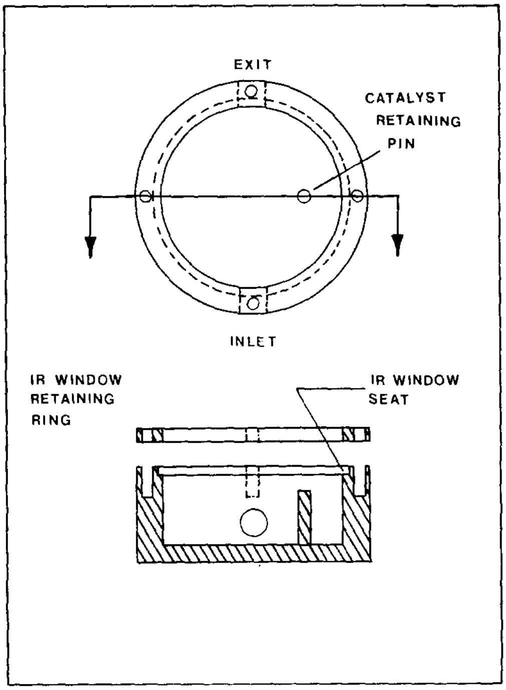

FIG. 1. Viewing reactor.

with a magnification of 150 × and a resolution of 0.0014 in. with an infrared detecting system. The optical microscope was used to locate precisely areas of the surface to be measured. This orientation had to be done prior to closing the reactor because the catalyst was not visible through the coated window. The x–y verniers on the microscope provided the means for directing the instrument to any desired point on the catalyst.

The infrared detector system consists of a liquid nitrogen-cooled, indium–antimonide phovoltaic unit. An internal reference is constantly compared with the specimen under view for maximum accuracy. The ultimate electrical signal is indicated as a temperature on an associated control unit or may be recorded on a suitable recording device. The maximum observable temperature was 355°C with ±2° accuracy throughout the range studied.

Temperatures measured by the detector on the system studied are believed to be within 1–2% of the true temperature, and the observed temperature increases are precise. The air gap between the detector and the reactor window, 0.95 in., was small enough to eliminate any transmission problems in the atmosphere, and the absorption bands of the reactants also introduce no problems. The reported temperatures are based on an assumed emissity of unity which is reasonable for a massive porous body such as a nickel–Kieselguhr, catalyst pellet containing highly dispersed nickel and nickel oxide (*17*).

Recorder

A Sanborn Series 8803A amplifier and Sanborn Series 7700 recorder were used to record transient periods. Linearity: >0.1% full scale (5 V); chart speed: 10 mm/sec.

Chromatograph

Products were analyzed using a Perkin–Elmer Model 154D vapor fractometer and a Type J, silica gel column, 2 m in length, operating at 60°C and 10 psig. Samples were obtained automatically every 7 min and results automatically recorded.

Flow System

Ethylene, hydrogen and nitrogen were metered using ⅛ in. Tri-Flat Fischer–Porter rotameters. Hydrogen was initially passed through a Deoxo unit and an alumina dryer for removing oxygen and water. Gases were combined in a mixing tee, and a three-way valve permitted directing the gases to the reactor or to vent. Nitrogen was used as an inert purge and as a diluent in some runs.

Run Procedure

After an initial warmup period for the instruments during which the reactor system was being purged with nitrogen, the desired reactant gas flow rates were established and then directed into the reactor. This point was designated time zero for transient studies. Surface temperature measurements were automatically recorded during the run for transient studies. During steady-state runs the detector was moved to different predetermined positions using the x–y verniers, and the temperatures were observed.

STEADY-STATE SURFACE TEMPERATURES

Effects of the surrounding environment and mass flow rates on catalyst surface temperature were observed at the steady state for single particles. In all cases the conversion was small enough (<4% for single active pellet) so that the reactor was operated as a differential reactor in the usual context of that experimental technique.

Single Particle Surrounded by Inerts

A single catalyst particle was observed while surrounded by inert ⅛ in. extrudates of the same composition as the catalyst support. In order to maintain an unobstructed view of the catalyst top surface, inert particles were filled to a depth about 1 mm below the top of the catalyst. Temperature traverses were made as shown in Fig. 2. The effect of mass velocity on surface temperature was also measured and compared with predicted values (Fig. 3) based on the method of Hougen (*1*) but applying the more recent transfer data of Thodos *et al.* (*18*, *19*).

The temperature traverses indicate that, within the resolution of the system (0.026 mm), relatively uniform surface temperature existed. Nickel in fresh catalyst of the type tested is known to be well dispersed. It is quite possible, however, that homogeneity of active nickel and, thus, temperature does not exist in the molecular size range. If traverses were possible at much higher resolution, sharp temperature differences between very small agglomerates of nickel could exist particularly during the transient startup period as suggested by Wei (*5*).

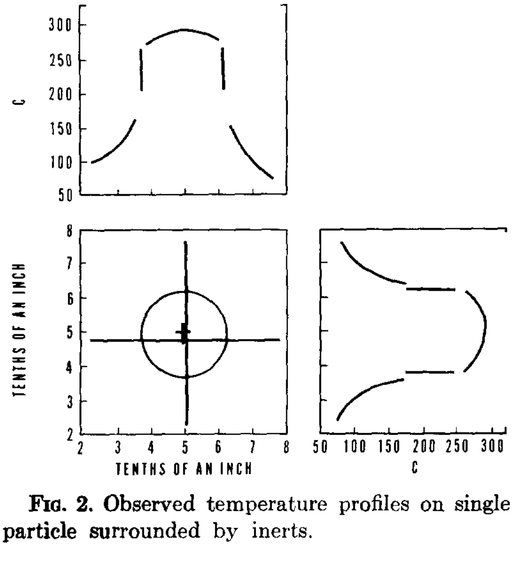

FIG. 2. Observed temperature profiles on single particle surrounded by inerts.

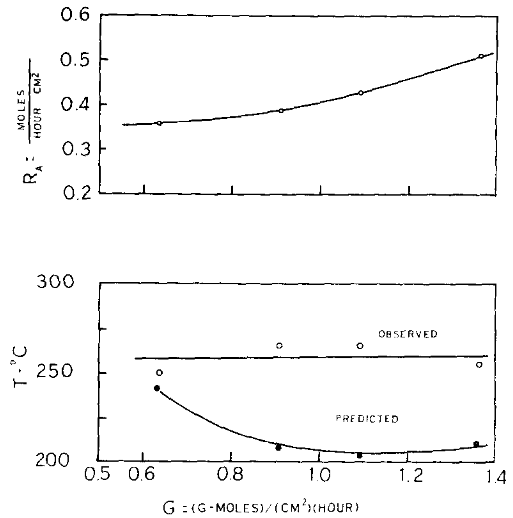

FIG. 3. Reaction rate and temperature gradient versus flow rate.

The gradient from the center toward the two edges shown in Fig. 2 is expected since the sides of the catalyst are in contact at many points with inert particles which appreciably add to the heat losses from the cylindrical surfaces of the inert particles. One can infer from the temperatures observed close to the edge of the catalyst that the surface temperature when completely surrounded by inert particles would be approximately 20–30°C less than the maximum temperature observed. This difference suggests qualitatively, the ability of even low conductivity inerts to reduce catalyst temperature. This contribution could be greatly increased by utilizing high conductivity materials.

It is interesting to compare the calculated surface temperatures with those observed as shown in Fig. 3. Implicit in the calculation is the assumption that the heat transfer correlations for solid-to-bulk fluid in packed beds is applicable to the last layer of particles which were exposed to gas only. The agreement is surprisingly good and within the accuracy of the correlation for heat transfer. The actual surface temperature did not vary within the range of mass velocities tested, indicating that the reactor was operating in the mass transfer-controlled regime such that the fractional concentration gradient between the bulk phase and the surface, $(C_B - C_S)/C_B$ is close to unity.

$$\Delta T = (j_D/j_H)(\mathrm{Pr}/\mathrm{Sc})^{2/3}[(-\Delta H)C_B/\rho C_p] \times [(C_B - C_S)/C_B] \quad (1)$$

In this case ΔT is constant since j_D and j_H vary equally with Reynolds number. The maximum surface temperature occurs when C_S is zero and was calculated from Eq. 1 to be 725°C.

Single Particle Surrounded by other Active Particles

In a second series of runs the specimen pellet was surrounded by several other active catalyst pellets, and the remainder of the reactor was filled with inerts. In this manner the behavior of an actual bed is more closely simulated without producing high total conversions and correspondingly high reaction temperatures beyond the range of the instrumental system. The surface temperature at these conditions was 40°C higher than that observed when a single particle was in contact with only inert pellets. In an actual bed each catalyst pellet is surrounded by other catalyst pellets at essentially the same temperature, and heat loss must occur primarily by convection rather than conduction. Conduction, though reduced in magnitude, continued to be a factor in this test since the walls of reactor were cooler than the bed.

A more nearly adiabatic case was observed by a severe measure that employed a single particle surrounded only by reactants now flowing at much lower velocities. In this case, the catalyst temperature soared far beyond the range of the instrument because of the poor heat transfer. Clearly, the same high ΔT could occur at higher flow rates with a proportionally more active catalyst. High temperature differences such as this which approach or equal the maximum predicted value from Eq. 1 are certainly possible, particularly during periods of low flow rate or in relatively stagnant regions of a bed in which the flow is poorly distributed.

Interior Temperature Profile

Unfortunately, infrared techniques cannot directly probe internal temperatures. Instead, an indirect approach had to be used which nonetheless seemed to confirm the isothermal character of catalyst particles in a reaction system. The exterior surface of the top of one pellet was coated with a high temperature epoxy cement which had previously been shown not to exhibit catalytic activity. The coating rendered the top surface inaccessible to reactants, but all other surfaces were active. In a prior test a similarly coated particle was placed along side an uncoated particle on a hot plate. The temperatures detected by the infrared technique were identical indicating that neither the emissivity nor the heat conducting properties of the coated particle had been altered.

Next the particle coated on its top side was placed near a particle coated on the bottom side, but uncoated on the top side. Both were surrounded by inerts. These two particles were scanned during a reaction period. The uncoated particle showed a profile typical of that in Fig. 2 with an average temperature of 297°C. The temperature of the coated particle declined precipitously toward the center as shown in Fig. 4.

Since it has already been established that heat is conducted effectively through the nonreacting coating, the only feasible explanation for the observed negative profile is the lack of any reaction within the major core of the catalyst as has been postulated by McGreavy and Thornton (*6*). The high temperature on the edge corresponds to the surface temperature of the uncoated edges. If profiles along the same longitudinal line were measurable, these would flatten out at increasing depths within the catalyst. Since no heat is being gen-

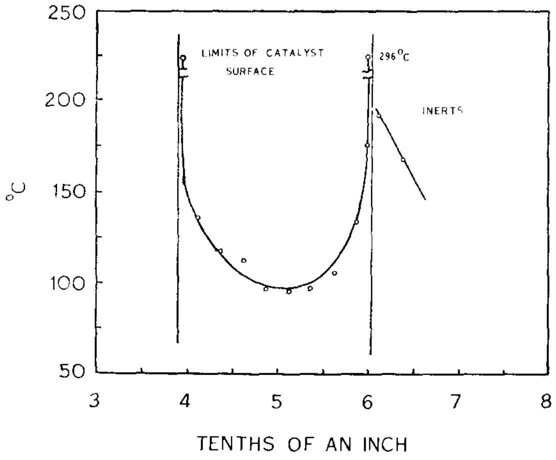

FIG. 4. Observed temperature profile for coated pellet.

erated on the top surface because of the coating, the adiabatic character of the interior at this end is lost. Heat is transferred from the interior of the catalyst through the coated surface.

TRANSIENT STUDY

The transient period, defined as the time reactants were first introduced until the steady state was reached, was observed using a high-speed recorder. Figure 5 summarizes the results of one such study which illustrates the well-known higher activity of fresh catalyst. The curve labeled 1 is for fresh catalyst. Those labeled 2 and 3 are subsequent tests of the same particle after purging with inerts. Even this brief use of the catalyst caused a decline in activity. With a more active catalyst the initial startup can cause even more rapid temperature rise on the surface.

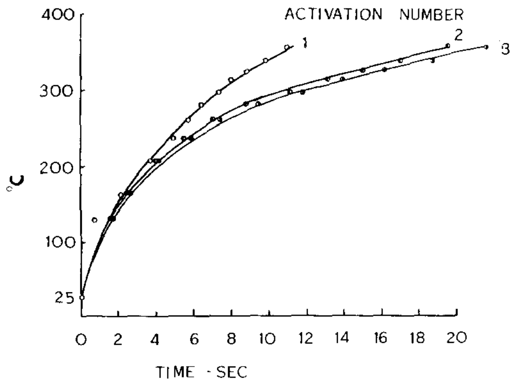

FIG. 5. Thermal transients for $H_2:C_2H_6 = 3.0$; gas temp. = 35°C.

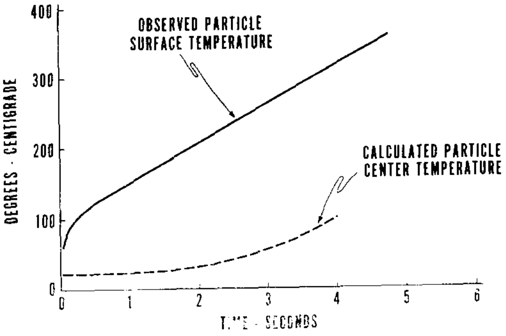

FIG. 6. Thermal transients $H_2:C_2H_6 = 1.25$ gas; temp. = 35°C.

A typical example is shown in Fig. 6 for the same reaction system but a lower ratio of $H_2:C_2H_6$ which produces higher surface temperatures. The temperature increased in the first four seconds at the rate of 85°C per second for the fresh catalyst. During this time and in the steady state that followed the bulk fluid remained in the temperature range of 35°C.

The linear character of this curve makes it possible to estimate the temperature at the particle center as a function of time using an existing equation (*20*) and assuming that the reaction is confined to the exterior of the catalyst.

$$\Delta T_t = m\left[t - \frac{a^2 - r^2}{6\kappa}\right] - \frac{2ma^3}{\kappa\pi^3 r}\sum_{n=1}^{\infty}\frac{(-1)^n}{n^3} \exp(-\kappa n^2\pi^2 t/a^2)\sin\frac{n\pi r}{a} \quad (2)$$

where m = slope of surface temperature curve, $T_s = mt$ and ΔT_t = temperature at time t minus initial temperature.

An effective thermal diffusivity for the particle of 5×10^{-3} cm^2 sec^{-1} was selected as a conservative value (*21*), and the dashed line is the calculated particle center temperature during the initial portion of the transient period. It is seen that the temperature difference between the exterior surface and the center can be substantial. As the steady state is reached and the exterior surface temperature becomes constant, the interior temperature will rapidly approach that of the exterior.

It is possible that the difference between surface temperature and interior temperature in the transient period may be greater than that indicated. Harrington (*22*) has postulated a mechanism that is effective in reducing the normal conductivity or thermal diffusivity in the surface region by large factors. He observed that samples heated by radiative transport reached 2000°C in <0.01 sec though calculations based on the same theory of conduction used here would predict 2.5 sec because of conduction within the solid.

Reactions, in which large ΔT gradients between the fluid and catalyst surface develop, operate in the heat transfer-controlled regime. The high temperature developed at the surface causes the reactants to be consumed before they penetrate very far into the pellet, even though effective diffusivity in the particle is greater than thermal diffusivity. It is not unreasonable to assume that a similar explanation holds for the transient period. For an active catalyst under the conditions tested the reactant will be consumed in the outer layers as well, particularly as the temperature is elevated. During the short period of rapid temperature rise at the surface, diffusion into the particle would even be negligible based on the familiar steady-state analysis involving constant surface concentration (*23*). Beyond this time the surface temperature increases to a point where the chances for reactant penetration become even less.

It would appear, based on this analysis, that during the first few seconds on stream that large temperature gradients within the catalyst are possible if the ΔT between the fluid and catalyst surface is high. A more rapid surface temperature rise than shown is possible for a more active catalyst or a higher fluid temperature. Resulting thermal stresses could shatter the catalyst particle. One such event apparently occurred in this study.

A single particle was fixed in the test reactor, but was not surrounded by inerts, creating a more inefficient heat transfer system and making possible higher and faster temperature increases. Upon admitting reactants to this setup, the temperature instantly exceeded the range of the instrument and upon opening the reactor the catalyst was found to have shattered.

CONCLUSIONS

In addition to confirming existing hypotheses concerning temperature gradients within particles and across the fluid film, this study has produced insights concerning the transient period along with experimental data on fluid–particle surface ΔT both of which relate to operating problems associated with experimental and commercial reactors.

The low Reynold's numbers imposed by the experimental equipment for this work are typical of those necessary for any small-scale experimental system. It should be clear as has been emphasized by theoretical arguments (*1*, *24*) that intrinsic chemical rate data for rapid reactions is impossible to obtain directly in a packed bed. The transport gradients are so large between the fluid and catalyst surface even at low conversion that raw data would have to be corrected using empirical correlations of uncertain accuracy. Further, accurate measurement of reaction (catalyst–surface) temperature is impossible using thermocouples. Certainly, this is not the ideal experimental environment.

Fluidized-bed differential reactors originally described by Pozzi (*23*) appear to be the only reasonable means for overcoming these difficulties. The good solids mixing and high exterior surface area assure uniform temperature throughout the bed. Rapid impact of solids on a properly designed thermocouple will also assure more accurate temperature measurement. Although the fluid flow patterns in a fluidized bed are complex and difficult to analyze, they are not an issue if the reactor is operated differentially.

Basic studies involving catalytic parameters of potentially highly active systems can, at times, be studied in a packed bed if the catalyst can be prepared in a low-activity form such as on a low-area support. This procedure, though eliminating gradients, may not always be consistent with research goals.

Commercial reactors operate at much higher Reynold's numbers than used in this work, but the experimental results described here simulate problems that can occur. At the higher temperatures developed in commercial beds, gradients can be high even at high Reynold's number for very rapid reactions such as must be conducted in nonadiabatic, heat-transfer reactors. Even in well-designed adiabatic reactors high gradients can develop during startup or regeneration if flow rates are not maintained at design levels or if flow distribution is poor. In the latter case, low flow rates will occur in parts of the bed causing high gradients. It is particularly important to operate at design flow rates at all times. Lower reactant concentration during the initial high-activity phase is recommended and possible by use of inerts in the feed.

Plant operating personnel are keenly aware of the difficulties associated with preserving catalyst activity during the transient period of startup and regeneration. It is during this time when gradients within the particle and between the particle and the fluid can be extremely high. Catalyst damage, such as sintering and shattering, can occur with total loss of reactor efficiency. Traditional process thermometry is usually inadequate to detect rapid temperature excursions in time to prevent catalyst damage. Instruments must be selected and operated with some relation to the rapidity and exothermicity of the reaction being controlled with special reference to the transient periods of startup and regeneration.

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