Experimental Study of Particle to Gas Heat Transfer in Fixed-Bed Reactors

Particle to gas heat transfer studies were carried out for the exothermic benzene hydrogenation and endothermic cyclohexane dehydrogenation reactions on the same catalyst bed. A recirculation type reactor and eggshell type commercial platinum on alumina catalyst were used. When the thermodynamic value for the heat of reaction is used for both reactions in the steady-state energy balance, local J_H factors for the exothermic reaction were found to be, in general, higher than those for the endothermic reaction. This was attributed to product molecules leaving the catalyst surface with excess vibrational energy, which implies that the actual heat of reaction would be different than the thermodynamic value used in the J_H factor calculations. The study also indicated significant variations in the local J_H factors; these were attributed to variations in the linear velocity in the radial direction.

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Introduction

In the design of packed-bed catalytic reactors it may be necessary to account for the temperature difference between the bulk gas and the catalyst surface if the mass velocities are low and heat of reaction is high. This is typically done by employing correlations for particle to gas heat transfer. A comprehensive review of particle to gas heat transfer correlations can be found in the work of Barker (1965) and Balakrishnan and Pei (1974). Recently Rao and Toor (1984) addressed the problem of the continuity assumption during heat transfer between particles of relatively large sizes.

Correlations for particles to gas heat transfer have been based on experiments where there is no chemical reaction, with the understanding that they will also hold for packed-bed reactors where chemical reaction takes place on the surface of the catalyst. In our previous study (Pathangey and Kovenklioglu, 1985), J_H factors for particle to gas heat transfer were obtained in a packed-bed system with endothermic cyclohexane dehydrogenation reaction taking place on a commercial platinum on alumina catalyst. The J_H factors were found to be on the lower side of those previously reported for unreactive systems. The question was then raised as to whether the endothermic chemical reaction was somehow responsible for the low J_H factors. Earlier, Gabrielson (1956) had carried out a series of heat transfer experiments with a platinum wire that was electrically heated. It was found that for some exothermic reactions, heat transfer coefficients calculated on the basis of using the thermodynamic value for the heat of reaction in the steady-state energy balance were higher than in the nonreactive case. Higher values calculated for the heat transfer coefficients were attributed to having used the thermodynamic heat of reaction in the steady-state energy balance instead of the actual heat of reaction, which would be lower if the product molecules left the catalyst surface with excess vibrational energy. Gabrielson (1956) gives an extensive discussion of the plausibility of speculating that product molecules can indeed leave the catalyst surface without coming into thermal equilibrium with the solid. When the thermodynamic value for the heat of reaction is employed in the steady-state energy balance for the catalyst particle, it is assumed that the product molecules have thermally equilibrated with the catalyst surface.

For an endothermic reaction the implication of product molecules not reaching thermodynamic equilibrium before leaving the catalyst surface would be higher heat of reaction than the thermodynamic value. This would result in lower heat transfer coefficients calculated by using the thermodynamic value of the heat of reaction in the steady-state energy balance. On the basis of this background we speculated that the low J_H factors we calculated for the endothermic cyclohexane dehydrogenation reaction (Pathangey and Kovenklioglu, 1985) may be attributable to product molecules not reaching thermodynamic equilibrium before leaving the catalyst surface. However, the wide variation in the J_H factors reported in the literature (DeAcetis and Thodos, 1960; Wilke and Hougen, 1945; Gamson et al., 1943; Satterfield

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and Resnick, 1954; Glaser and Thodos, 1958) made it difficult to make a definitive statement based on a comparison of our results with those of other investigators. We have pursued this problem further by conducting experiments for the exothermic benzene hydrogenation ($C_6H_6 + 3H_2 = C_6H_{12}$) and the endothermic cyclohexane dehydrogenation ($C_6H_{12} = C_6H_6 + 3H_2$) reactions on the same catalyst bed, thereby ensuring that the packed-bed configuration would be the same for both reactions. We have here, as before, presented our results in terms of the J_H factors (calculated on the basis of using the thermodynamic value for the heat of reaction in the steady-state energy balance) as a function of the Reynolds number.

Experimental System

In the experiments a 0.076 m dia. Berty internal recirculation reactor and commercial platinum on alumina catalyst were used. $Pt\text{-}Al_2O_3$ catalyst is effective in catalyzing both the endothermic and the exothermic reactions. Unlike our previous work, where catalyst surface temperature was evaluated based on an extrapolation technique, we have here imbedded microthermocouples into the catalyst. Another improvement is the use of eggshell type catalyst (Engelhard D286) in which the active outside layer is only 0.1 mm thick. A thin catalyst layer decreases the diffusion path and hence the number of collisions with the walls as the product molecules diffuse out. This would make it more likely for the product molecules to leave the catalyst surface with excess vibrational energy.

Open-junction, 0.5 mm dia. microthermocouples were calibrated at the freezing and boiling points of water and melting points of tin and aluminum. 4.75 mm dia. cylindrical catalyst particles were drilled by hand with a very fine drill bit and the hole filled with a binder solution. The junctions of the microthermocouples were coated with a high-temperature cement powder and inserted into the holes extending into the inert core of the catalyst pellet. The system was cured in an oven and subsequently tested and found to exhibit strong adhesion of the pellet to the thermocouple.

Figure 1 illustrates the loading of the catalyst bed. Note that six pellets are placed among 6 mm dia. glass beads at the same axial location and radial distance, which is midway between the center and the wall. This was done to ensure that all catalyst particles were at the same temperature. Two catalyst temperatures and two bulk gas temperatures were monitored, with the gas temperature being measured at approximately 1 mm from the surface of the catalyst pellet. When the bed was heated with an inert gas all thermocouples indicated the same temperature.

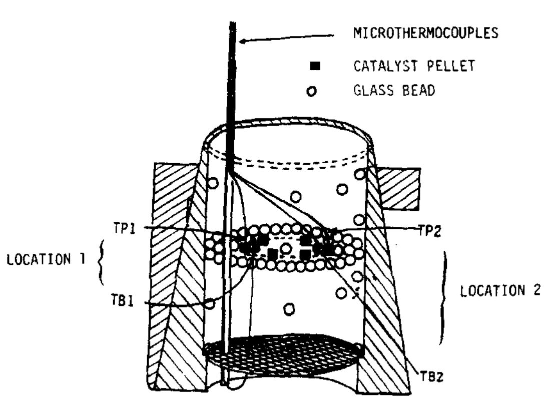

Figure 1. Reactor configuration, all pellets at same axial and radial location.

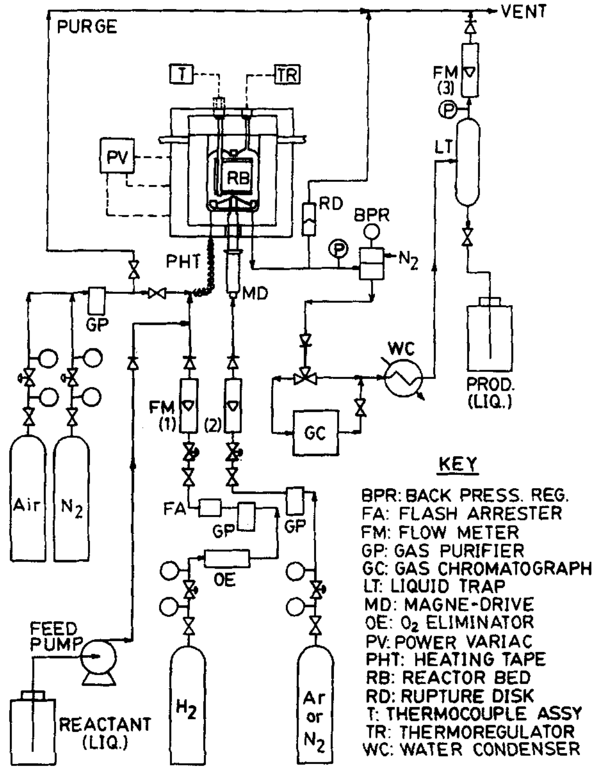

Figure 2. Flow diagram.

The flow diagram describing the experimental system, which is a modified version of the one used in the previous experiments, is given in Figure 2. Some aspects of the experimental procedure have already been outlined in previous work (Pathangey and Kovenklioglu, 1985). Calibration of various instruments, determination of linear velocity as a function of the impeller speed, the gas analysis technique, catalyst conditioning, and the reduction and regeneration procedures, are detailed elsewhere (Pathangey, 1987). Catalyst regeneration was necessary due to the formation of carbonaceous deposits on the catalyst surface. Excess oxygen in the regeneration process would result in a rapid temperature rise and would sinter the catalyst. The ability to monitor the catalyst temperature enabled us to carry out catalyst regeneration in an optimal manner by varying the composition of the nitrogen and air mixture admitted to the reactor from mostly nitrogen in the beginning to all air at the end of the regeneration process.

Experimental Data

All the experiments were carried out at steady state. Catalyst and gas temperatures, reactor pressure, reactor impeller speed, inlet flow rates, and benzene and cyclohexane area percentages as calculated by the gas chromatograph were recorded. The temperature difference between the catalyst surface and the gas varied in the 10–30°C range. For the endothermic reaction the pressure and temperature ranges were 200–700 kPa and 340–430°C, whereas for the exothermic reaction these ranges were 400–800 kPa and 210–260°C. Conversions ranged up to 70%. J_H

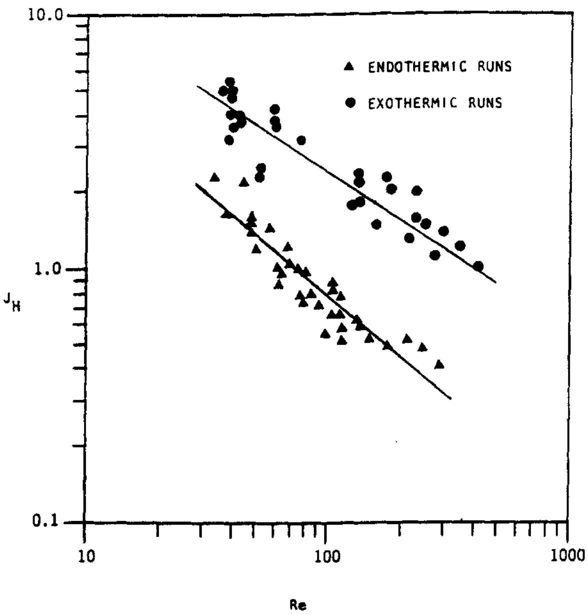

Figure 3. J_H vs. *Re*, location 1.

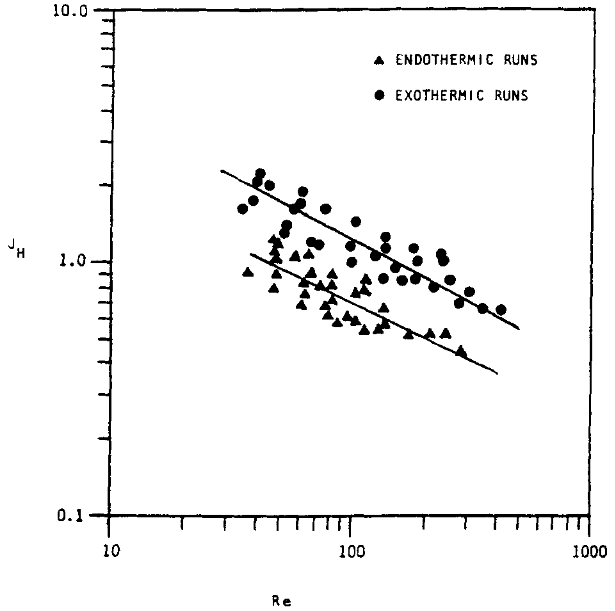

Figure 4. J_H vs. *Re*, location 2.

factors, calculated on the basis of such data, are plotted vs. Reynolds number in Figures 3 and 4.

High reaction rates are desirable from the viewpoint of achieving high interphase temperature differences in order to minimize the error in calculating the J_H factors. In general, for specified inlet gas composition, space velocity, and pressure, reaction rate can be increased by increasing the temperature. However, this was found not to be the case for the benzene hydrogenation reaction. Under conditions far from equilibrium, we have observed a maximum in reaction rate with temperature, as illustrated in Figure 5. This result is consistent with the benzene hydrogenation studies of previous investigators (van Meerteen and Coenen, 1975). The circumstances under which heterogenous catalytic reaction rates can exhibit maximum with temperature have been illustrated by Satterfield (1980).

Analysis of Data and Discussion

J_H factors were calculated from the following equations

$$J_H = \frac{h}{C_pG}(Pr)^{2/3} = f(Re) \qquad (1)$$

$$ha_m(T_B - T_P) = R_o\Delta H \qquad (2)$$

$$R_o = \frac{F}{W_c}X \qquad (3)$$

As is evident from these equations, for a specified mass flow rate and gas mixture properties one would expect that h would be the same regardless of whether the reaction is endothermic or exothermic. However, since the thermodynamic value for the heat of reaction is being employed in the J_H factor calculations, to the extent that the actual heat of reaction may be different from the thermodynamic value, calculated h values will be different. One could perhaps argue that pedagogically it would be more sound to place the emphasis in this study on illustrating the variation of the actual heat of reaction from the thermodynamic value. Calculating h values by employing the thermodynamic value for the heat of reaction would in effect indirectly show this when J_H factors for the endothermic and exothermic reaction are compared. The results here were presented in the form of J_H factors vs. the Reynolds number in order to conform to previous literature.

The physical properties for the gas mixture in Eq. 1 were evaluated at each conversion level at the corresponding composition and the average film temperature. The temperature dependence of the heat of reaction was taken into account by means of the

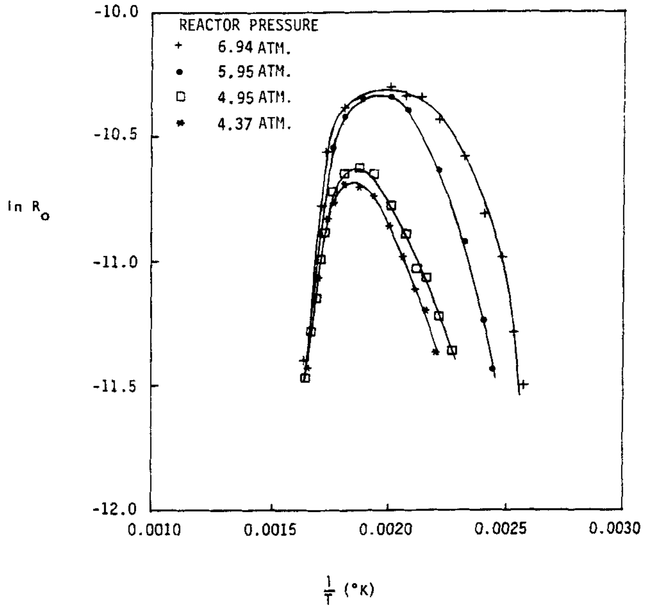

Figure 5. Maximum rate with respect to temperature—benzene hydrogenation.

van't Hoff equation. The Reynolds number is based on equivalent catalyst diameter, $d_P = 6\ (V_P/A_x)$. Reynolds numbers at different impeller speeds were calculated based on the empirical relationship between the impeller speed and the linear velocity, which was found to be independent of system pressure. The variation in the impeller speed alone does not provide a sufficiently broad range of Reynolds numbers unless the gas density is increased, which was achieved by increasing the reactor pressure. Conversion calculations for the exothermic and the endothermic reactions were based on the reactant hydrocarbon and evaluated as the ratio of the product hydrocarbon area percentage to the sum of reactant and product hydrocarbon area percentages.

Figures 3 and 4 show that the J_H factors for the exothermic reaction are higher than for the endothermic reaction. The J_H factors calculated on the basis of the temperature measurements at location 1 are somewhat higher than at location 2, particularly for the exothermic reaction (approximately 20%). Bearing in mind that the film model is an approximation in which all the thermal resistance is lumped into a very thin film adjacent to the particle surface, it is possible that the discrepancy is due to the bulk gas thermocouple being closer to the catalyst surface at location 1 than at location 2. Consequently, the temperature difference at location 1 would be less, resulting in higher values for the calculated heat transfer coefficients. However, we are unable to explain why this effect should be more prominent for the exothermic reaction.

Another rather unexpected result is that the J_H factors in Figures 3 and 4 are about an order of magnitude higher than those in previous work (Gamson et al., 1943; Glaser and Thodos, 1958; Pathangey and Kovenklioglu, 1985). Although the measured gas-solid temperature differences in these experiments are probably less than expected on the basis of the film model, this would not explain such a large discrepancy. Another consideration is that for the configuration in Figure 1, the stagnant pockets of gas in the vicinity of points of contact may be less than what is typical for a packed bed as reflected in previous J_H correlations. This would result in higher heat transfer coefficients calculated for the bed configuration in Figure 1. However, it may be that the dominant factor which affects the J_H factors in the present work is the velocity variations in the radial direction in the packed bed. McGreavy et al. (1986) who used laser doppler anemometry technique to study local velocity variations in a packed bed observed a pair of maximum and minimum velocities in between the particles; the highest velocity appeared near the wall and the lowest near the center. If the local velocity for the radial location shown in Figure 1 is higher than the radial average velocity, this would explain the high J_H factors found here. One way of testing this hypothesis without directly making velocity measurements would be to configure the bed as in Figure 1 but place the pellets at a different radial location in the packed bed. Before collecting data with the configuration in Figure 1, we had already collected data with a configuration illustrated in Figure 6. Here the catalyst particles are not placed at the same radial and axial locations and thus the radial and axial temperature variations in the bed would result in the local variation in reaction rate from one pellet to another. Consequently, application of Eq. 2 based on one pair of catalyst and bulk gas temperature readings would be an approximation because the rate on the righthand side of Eq. 2 reflects the contribution of all pellets. (This in fact was the reason for choosing the configuration in Figure 1.) Although Figure 6 is not the ideal configuration for testing our hypothesis, it should still be adequate, since based on temperature measurements at different radial and axial locations, the local variation in reaction rate from one pellet to another is estimated to be only about 15%. Consequently, the J_H factors displayed in Figure 7, which are based on temperature readings at the center of the bed in Figure 6 (*TP*1 and *TB*1), can be used to assess to what extent the J_H factors depend on the radial position of the thermocouples. Indeed the J_H factors presented in Figure 7 are significantly lower than those in Figures 3 and 4 and fall within the range of the J_H factors obtained in previous work. This implies that the local velocity at the center of the bed is lower than at the radial location midway between the center and the wall. The J_H factors presented here therefore should be viewed as local.

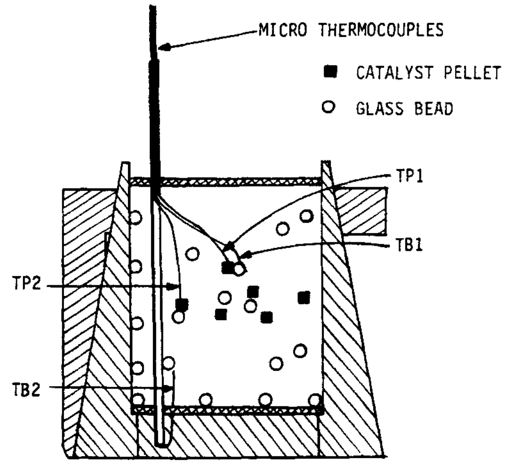

Figure 6. Reactor configuration, pellets randomly distributed.

One also observes that at higher Reynolds numbers J_H factors for the exothermic reaction in Figure 7 are again distinctly

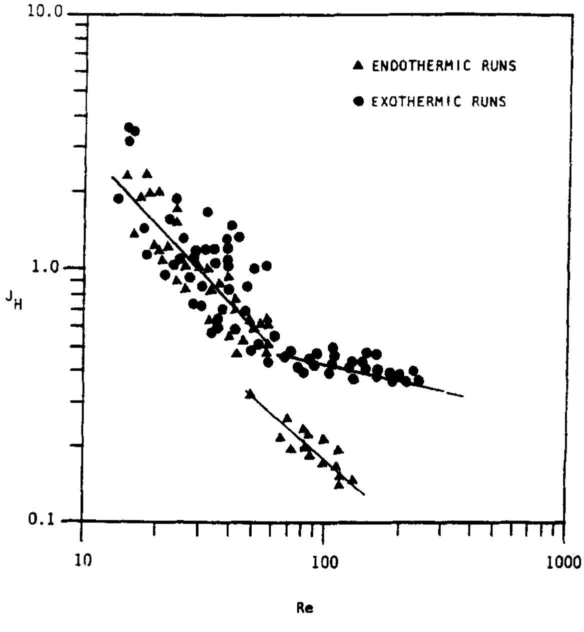

Figure 7. J_H vs. *Re* for configuration in Figure 6.

higher than those for the endothermic reaction. For $Re < 50$ there is considerable scatter in the data due to the small temperature difference between the catalyst and the bulk gas (less than 5°C). In this region, the reaction rate is lower. Lower reaction rates would allow more time for the product molecules to thermally equilibrate with the catalyst surface; however, it is not clear whether this factor alone is responsible for the apparent indistinguishability between the J_H factors for the endothermic and the exothermic reaction. Nevertheless, the general trend in the local J_H factors presented in Figures 3, 4, and 7 appears to confirm our speculation that the local heat transfer coefficients for the exothermic reaction are indeed higher than for the reverse endothermic reaction. If this is due to product molecules leaving the catalyst surface with excess vibrational energy, one may inquire as to whether it is possible for a molecule not to lose all its excess vibrational energy in collisions with the pore walls as it is transported to the surface of the catalyst.

For the shell-type catalyst employed here the thickness of the active layer on the outside is about 0.1 mm. For a product molecule such as cyclohexane or benzene which desorbs from the inside layer of the active shell, the diffusion time will be in the order of 10^{-3} s. Gabrielson (1953) reports that for a CO_2 molecule with excess vibrational energy, depending on the type of molecule the CO_2 collides with, it may take anywhere from 10^{-6} to 10^{-1} s to reach thermal equilibrium. Comparison with our situation is difficult because we are unable to estimate relaxation times for cyclohexane and benzene. (Relaxation time is defined as the period during which the product molecules lose 46% of their excess vibrational energy.) Moreover, the collision process, which is predominantly with the pore walls in our case, is different from molecular collisions on which the CO_2 calculations were based. Nevertheless, a rough comparison with CO_2 would indicate that one could not rule out the possibility that the hydrocarbon molecules desorbing from any site in the active catalytic layer can leave the catalyst surface with excess vibrational energy, which gives rise to the deviation in the calculated heat transfer coefficients as compared to a nonreactive situation.

It is not possible for us to make generalizations for other reactions on the basis of the results presented here. Even for a given reaction, it is possible that the actual heat of reaction may deviate from the thermodynamic heat of reaction only for a certain range of reaction conditions. Perhaps the best we can do is to point out the possibility of such an occurrence and the direction of such deviations.

We have also observed that the slow deactivation process does not affect the calculated J_H factors. With activity loss, all other parameters remaining the same, reaction rate decreases, but so does the temperature difference between the bulk gas and the catalyst. Consequently, the heat transfer coefficient calculated from Eq. 2 would not be affected as long as the deactivation process is slow relative to the data collection time.

We expect that the temperature readings from thermocouples inserted into the inert core of the pellet are very close approximations to the surface temperature. This is because at steady state the inert core is isothermal and the active layer, which is only 0.1 mm thick, can be considered to be nearly isothermal.

Finally, in calculating heat transfer coefficients from Eq. 2 the radiation contribution was neglected. This was based on the estimate that the ratio of the radiative heat transfer to convective heat transfer would be at most 0.03 (Pathangey, 1987).

Acknowledgment

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Notation

a_m = external surface area of catalyst pellet per unit mass
A_x = external surface area of catalyst pellet
C_p = specific heat of reaction mixture
d_p = equivalent catalyst pellet diameter
F = molar flow rate of cyclohexane or benzene
G = mass flow rate of reaction mixture over packed bed, based on superficial velocity
h = particle-to-gas heat transfer coefficient
ΔH = heat of reaction
J_H = J factor to heat transfer
Pr = Prandtl number
Re = Reynolds number defined as Gd_p/μ
R_o = observed reaction rate per unit mass catalyst
T_B = gas phase temperature
$TB1$, $TB2$ = gas phase temperature readings at locations 1 and 2
T_P = catalyst temperature
$TP1$, $TP2$ = catalyst temperature readings at locations 1 and 2
V_p = apparent catalyst pellet volume
W_c = catalyst weight
X = cyclohexane or benzene conversion

Greek letters

ϵ = bed porosity
μ = viscosity of reaction mixture

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