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MODELLING OF OPTIMUM CASCADE OF IDEAL MIXING REACTORS

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A b s t r a c t

It is discussed the using of dynamic programming method to optimize the parameters of the cascade of ideal mixing reactors, which is held isothermal first order reaction. It is found, that the minimum volume of the cascade of reactors corresponds to the minimum residence time of substance in this cascade. The optimum value of residence time for all reactors are equal and all ratio of input and output concentrations are equal, hence, and all volumes of reactors are also equal. A total volume of the cascade of reactors is less than the amount single. Application of the method of dynamic programming is illustrated with an example of the calculation of the polymerization in a cascade of four reactors according to the literature experimental data.

Nomenclature

G – mass, mole
i – index of component
k – reaction rate constant, h^{-1} l $mole^{-1}$
N – number of reactors
r – reaction rate, h^{-1}
u – control action
V – volume, l
v – volumetric flow, h^{-1}
x – concentration, mole l^{-1}
τ – residence time, h

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Introduction

Mixing of single and multiphase fluids in stirred tanks is a common operation in chemical process industries. Proper knowledge of fluid flow is essential for scale-up, equipment design, process control, and economic factors. The cascade of mixing reactors is used in various chemical industries (BOYARINOV, KAFAROV 1975, EFREMOV 2001, 2016, LEVENSPIEL 1965, *Handbook of Industrial Mixing: Science and Practice* 2004, BRAYNES 1976, ARIS 1976, KRAMERS, WESTERTERP 1963, HARRIOTT 2003, COKER 2001, KOROBOV, OCHKOV 2011). In such devices, due to the intense mixing, there is no temperature and concentration gradients (HARRIOTT 2003). It is shown (COKER 2001) that the reactors of continuous mixing action are preferable to the batch reactors and the total volume of the cascade of reactors is less than the amount single. If the reaction can result in only one product, the mixing and mass transfer can influence only the reaction rate. If more than one product is possible, contacting can influence the product distribution as well. For the solution of tasks of modeling and optimization of multi-stage processes have been developed and successfully applied the method of dynamic programming (KRAMERS, WESTERTERP 1963, EFREMOV 2016).

At the modeling as a stage of processes the one of elements is accepted, on which it is possible to divide the process parameters, as in time, and as in space. Stage in this case represent a sequence of the same type of equipment (reactors, agitators), in which the flow of raw materials undergoes sequential processing.

The status of the individual stages of the process is described by a set of input and output parameters *h*i. The output of each stage serves as input to the subsequent stage.

In addition to the input and output variables at each stage it is necessary to select a group of control actions *ui* (Fig. 1).

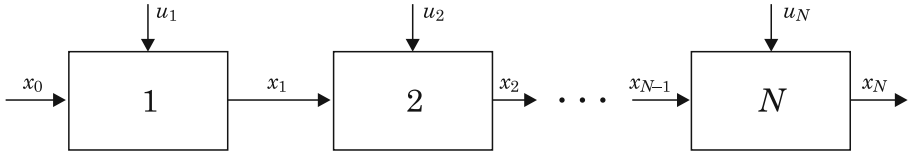

Fig. 1. Diagram of the multistage process

The principle of optimality in dynamic programming allows optimization starting from the last stage, through the selection of control parameters for this stage. Then consider the last two stages, the last three stages etc., reaching

the first one. It should be noted that dynamic programming allows to replace a complicated task by the more simple for the next individual stages.

In this paper it is considered the application of dynamic programming method to optimize the parameters of the cascade of reactors of ideal mixing, which is held isothermal first order reaction. The purpose of the calculation is to find the minimum total volume of the reactor system at a given initial concentration and to obtain the given final concentration of the original substance.

Theoretical analysis

The purpose of the calculation is to find the minimum residence time of the reaction mixture in the system of reactors of ideal mixing for the given initial concentration of x_0 to obtain the desired final concentration of the initial substance.

Considering the model of ideal mixing of volume V, introducing the value of the volumetric flow $v = V/\Delta\tau$ to mass of substance $G_i = Vx_i$ at the input is equal

$$\frac{G_i^0}{\Delta\tau} = \frac{Vx_i^0}{\Delta\tau} = vx_i^0 \tag{1}$$

Accordingly, the mass flow at the output is equal to

$$\frac{G_i}{\Delta\tau} = \frac{Vx_i}{\Delta\tau} = vx_i \tag{2}$$

Given (1) and (2) a change of mass flow in the apparatus is

$$\frac{\mathrm{d}(Vx_i)}{\mathrm{d}\tau} = v(x_i^0 - x_i) \tag{3}$$

Considering isothermal chemical reactions (rate of reaction r_i), at stationary regime the equation (3) is

$$v(x_i^0 - x_i) + Vr_i = 0 \tag{4}$$

Below it is considered the cascade of three reactors for a given initial concentration $x_0 = 1\%$ and at a given final concentration of the initial

substance x_3, equal to 10%. The rate constant of the chemical reaction is $k = 1\ \text{h}^{-1}(\text{mol/l})^{-1}$.

Using for the cascade the concentration of the initial substance on the entrance to each unit and on the exit from it as x_{i-1} and x_i, given the rate of reaction of the first order

$$r_i = kx_i \tag{5}$$

denoting the residence time of the substance $\tau_i = V_i/v$, taking into account equations (4) and (5), it may be obtained, respectively, for each of the three reactors (BOYARINOV, KAFAROV 1975, EFREMOV 2001, 2016, LEVENSPIEL 1965, *Handbook of Industrial Mixing: Science and Practice* 2004, BRAYNES 1976, ARIS 1976, KRAMERS, WESTERTERP 1963):

$$\frac{x_1}{x_0} = \frac{1}{1 + k\tau_1}; \quad \frac{x_2}{x_1} = \frac{1}{1 + k\tau_2}; \quad \frac{x_3}{x_2} = \frac{1}{1 + k\tau_3}; \tag{6}$$

The start of the optimization is from the last reactor. Thus, taking into account the initial data of (6), the process time is

$$\tau_3 = \frac{1}{k}\left(\frac{x_2}{x_3} - 1\right) \tag{7}$$

The dependence of τ_3 on x_2, according to (7), is a straight line. Thus, to minimize τ_3 is necessary to select the concentration of x_2.

Similarly, the process time for the second reactor is

$$\tau_2 = \frac{1}{k}\left(\frac{x_1}{x_2} - 1\right) \tag{8}$$

The formula (8) is built in MathCAD in the coordinates of τ_2, x_2 for different values of x_1 (0.1, 0.3, 0.5, 0.7, 0.9) and shown in Figure 2.

For the last two reactors, the total residence time $\tau_2 + \tau_3$ is a function of the concentration of the substance entering to the second reactor x_1

$$\tau_2 + \tau_3 = \frac{1}{k}\left(\frac{x_1}{x_2} + \frac{x_2}{x_3} - 2\right) \tag{9}$$

$$i = 1...5$$

$$\frac{1}{k} \cdot \left(\frac{x_1^i}{x_2} - 1\right)$$

$$x_1^i = \begin{pmatrix} 0.1 \\ 0.3 \\ 0.5 \\ 0.7 \\ 0.9 \end{pmatrix}$$

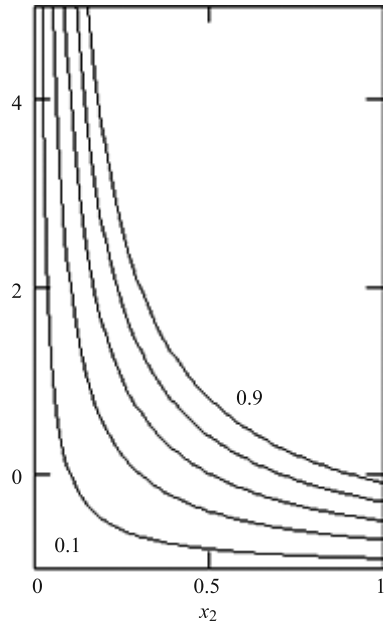

Fig. 2. Dependence of the residence time in the 1st reactor vs. the concentration in the 2nd reactor

The dependence (9) can be also presented in the system MathCAD as function ($\tau_2 + \tau_3$) vs. x_2 for different values of x_1 (Fig. 3).

$$i = 1...5$$

$$\frac{1}{k} \cdot \frac{x_1^i}{x_2} + \frac{x_2}{x_3} - 2$$

$$x_1^i = \begin{pmatrix} 0.1 \\ 0.3 \\ 0.5 \\ 0.7 \\ 0.9 \end{pmatrix}$$

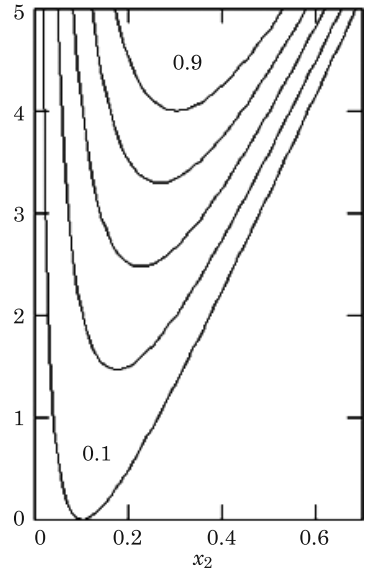

Fig. 3. Dependence of the total residence time in the 2-nd and 3-rd reactors vs. concentration in the 2-nd reactor

For the optimization it is necessary to find the minimum value of $(\tau_2 + \tau_3)$ and the optimal value of x_{2opt} for the adopted above values of x_1. To do this, it is necessary to find the derivative of the function (9) by x_2 and to equate it to zero. As the result, the next dependence appears

$$x_{2opt} = \sqrt{x_1 x_3} \tag{10}$$

Substituting the values of x_{2opt} from the equation (10), the minimum value of the sum $(\tau_2 + \tau_3)_{min}$ as a function of x_1 can be calculated

$$(\tau_2 + \tau_3)_{min} = \frac{1}{k}\left(2\sqrt{\frac{x_1}{x_3}} - 2\right) \tag{11}$$

The equation (11), as a function of x_1 is a power-law dependence in the form

$$(\tau_2 + \tau_3)_{min} = A \cdot \left(\frac{x_1}{x_3}\right)^n - B \tag{12}$$

From equations (11) and (12) it follows that the minimum of $(\tau_2 + \tau_3)$ is dependent on the concentration in the first reactor x_1.

With the found values of the coefficients A, B and n the graph, according to the equation (11) in the coordinates $(\tau_2 + \tau_3)_{min}$ vs. x_1 is shown on Figure 4. In this graph, marked also adopted higher values of x_1. As can be seen from Figure 4 good agreement with the calculation by equation (11) is obtained.

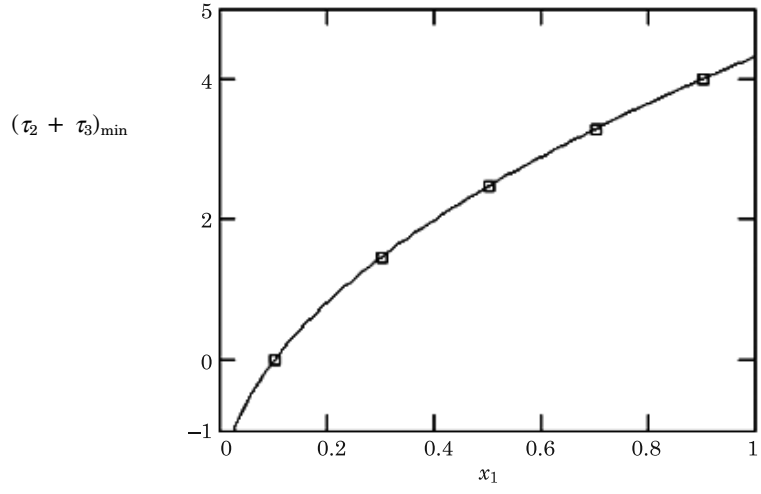

Fig. 4. Dependence of total time in 2-nd and 3-rd reactors vs. concentration in 1-st reactor

Next, the addition of the process time dependence for the first reactor

$$\tau_1 = \frac{1}{k}\left(\frac{x_0}{x_1} - 1\right) \tag{13}$$

in the equation (11) gives by result

$$\tau_1 + \tau_2 + \tau_3 = \frac{1}{k}\left(2\sqrt{\frac{x_1}{x_3}} + \frac{x_0}{x_1} - 3\right) \tag{14}$$

The diagram of dependence $(\tau_2 + \tau_3 + \tau_1)$ vs. x_1 is submitted in a Figure 5.

For finding of a minimum of function $(\tau_2 + \tau_3 + \tau_1)_{\min}$ it is necessary to equate to zero the derivative of function (14) on x_1. This value at the accepted above parameters makes 0.4642. This value $x_{1\text{opt}}$ is shown by a dotted line on the diagram (Fig. 5). Substituting the found value in the equation (13), the appropriate value of time $\tau_1 = 1.1542/k$ may be finding.

Further at optimum value of $x_{1\text{opt}}$ from the equation (14) the value $(\tau_1 + \tau_2 + \tau_3)_{\min} = 3.4633/k$ and from the equation (11) the value $(\tau_1 + \tau_2)_{\min} = 2.3087/k$ may be calculated. From equation (10) the optimum value of $x_{2\text{opt}} = 0.2155$.

Knowing the optimum values of all concentration, the ratio of entrance and outlet concentrations for all reactors is.

$$\frac{x_0}{x_1} = \frac{x_1}{x_2} = \frac{x_2}{x_3} = 2.1542$$

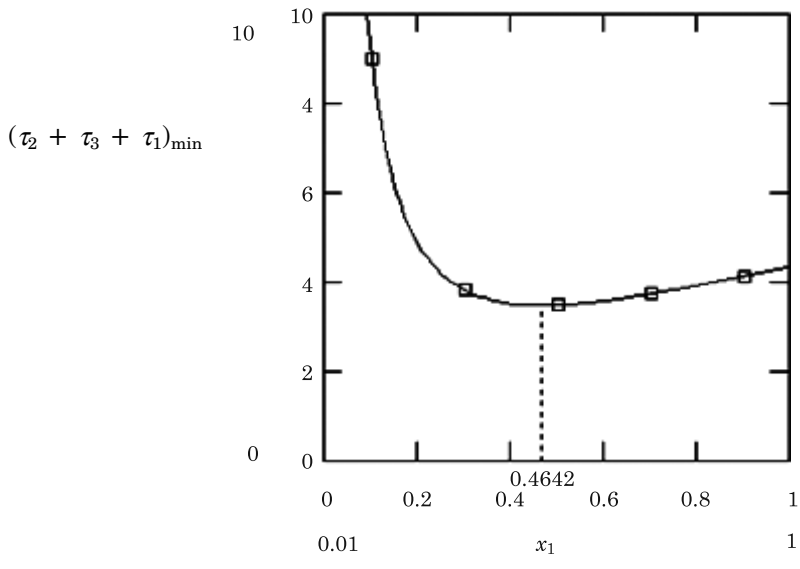

Fig. 5. Dependence of total time in 3 reactors vs. concentration in the 1-st reactor

It is obtained the same ratio of the input and output concentrations for all reactors and, according to equations (7), (8) and (13) the residence times are

$$\tau_1 = \tau_2 = \tau_3 = 1.1542/k.$$

All calculations and graphics are realized in MathCAD.

For optimization, in the general case, N series of the cascade of isothermal ideal mixing reactors it is necessary to find the minimum of the sum of the residence time in all reactors

$$\Sigma\tau = \frac{1}{k}\sum_{i=0}^{N}\left(\frac{x_i}{x_{i+1}} - 1\right) \tag{15}$$

under the condition of positivity of the values of all concentrations. Since the residence time in the reactor is equal to τ_i, the ratio of the output and input concentrations of the cascade of N reactors with (6) can be calculated as

$$\frac{x_N}{x_0} = \frac{1}{(1 + k\tau_i)^N} \tag{16}$$

Minimizing of the residence time in the cascade of isothermal ideal mixing reactors can be realized in MathCAD or Excel (add-in "solver"). Such calculations for given initial concentrations were performed for cascades of 2 to 7 reactors. The results are shown in the Table 1.

Table 1

The parameters of the cascades of isothermal ideal mixing reactors

Number of reactors, N	$k\ \Sigma\tau_{\min}$	x_i/x_{i+1}	$\tau_i\ k$
2	4.3246	3.163	2.163
3	3.4633	2.154	1.154
4	3.1131	1.778	0.778
5	2.9264	1.585	0.585
6	2.8106	1.468	0.468
7	2.7943	1.399	0.399

The results of calculations show that the optimal values of residence time of the reactors within each of the cascades are equal, the ratio of input and output concentrations are equal also, therefore, all the volumes of the reactors are equal for each cascade.

In literature (EFREMOV 2001) it is observed that the concentrations in the cascade of reactors of ideal mixing can be represented graphically. Each reactor of the cascade is one-step concentration change as the concentration changes abruptly. The line connecting the top of each step of the reactor cascade corresponds to the same curve of the ideal isothermal plug flow reactor. The graphic for the cascade of five reactors (Table 1) is shown in Figure 6 in the coordinates of the concentration – residence time. The curve connecting the top of the steps of the reactors of the cascade, is built on the equation of isothermal ideal plug flow reactor (KRAMERS, WESTERTERP 1963, EFREMOV 2016).

$$x/x_0 = \exp(-k\ \tau) \tag{17}$$

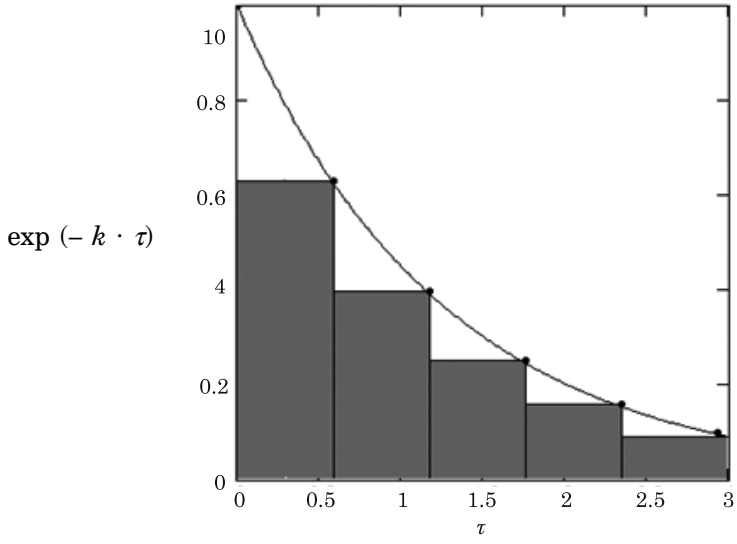

Fig. 6. Dependence of the concentration x from the residence time p for the cascade of five reactors

Experimental part

As an example of the using of the dynamic programming PC method, the design optimization of a polymerization process in the four ideal mixing reactors cascade is considered. The experimental data are used from (HARRIOTT 2003). The reaction of polymerization is the first order. The degree of conversion is 95%, i.e. the concentration at the outlet of the last reactor $x_4 = 0.05$. Calculation of reaction rate constants is made according to the experiment in a single reactor, where the residence time to reach a given

degree of conversion amounted to $\tau = 6$ h. The constant for the rate of the first order chemical reaction was calculated according to the equation

$$k = \frac{1}{\tau} \ln\left(\frac{1}{x_4}\right) \tag{18}$$

In Figure 7 the calculation in MathCAD the optimal parameters of the polymerization process (HARRIOTT 2003) in the cascade of four ideal mixing reactors is shown. Calculation of reaction rate constant according to equation (18) yields the value $k = 0.499$ h^{-1}(mole/l)$^{-1}$.

The residence time in the each reactor (Fig. 7) is written similarly to equations (7), (8), (13).

Optimization function $f(x_1, x_2, x_3)$ is the total residence time in all reactors. Unknown values are the concentrations at the outlet of the first three reactors: x_1, x_2, x_3. When calculating the specified initial approximation for these positive values of concentrations, then by the code word "Given" a program to find the minimum value of the total residence time in the cascade of reactors starts:

$$P = \text{minimize } (f, x_1, x_2, x_3).$$

The calculation results are obtained in the concentration of $x_1 = 0.4728$ h^{-1} l mole^{-1}, $x_2 = 0.2236$ h^{-1} l mole^{-1} and $x_3 = 0.1057$ h^{-1} l mole^{-1}. The minimum value of the total residence time is 8.928 h, and the residence time in each reactor is 2.235 h. The value of the ratio of output and input concentrations in each reactor is 0.473.

Conclusion

The modeling and optimization of multi-stage processes in cascade of consecutive ideal mixing isothermal reactors by the method of dynamic programming are considered. It is found, that the minimum volume of the cascade of reactors for isothermal reaction of the first order corresponds to the minimum residence time of substance in this cascade. In this case, the optimum meanings of residence time for all reactors are equal and all ratio of input and output concentration are equal. Hence, and all volumes of reactors are also equal.

The modeling and optimization of N consistently connected isothermal reactors can be similarly executed, that also gives result in equality of volumes of reactors and equality of residence time of the reactive mixture in each reactor.

Initial data: $x_4 = 0.05$ outlet concentration for 4-th reactor, mole/l
$\tau = 6$ residence time for single reactor, h
$x_0 = 1$ inlet concentration for first reactor, mole/l

Chemical rate constant: $k = \dfrac{\ln\left(\dfrac{1}{x_4}\right)}{\tau}$ $k = 0.499$ h^{-1}

Residence time for 4-th reactor: $\tau_4 = \dfrac{1}{k}\left(\dfrac{x_3}{x_4} - 1\right)$

Residence time for 3-rd reactor: $\tau_3 = \dfrac{1}{k}\left(\dfrac{x_2}{x_3} - 1\right)$

Residence time for 2-nd reactor: $\tau_2 = \dfrac{1}{k}\left(\dfrac{x_1}{x_2} - 1\right)$

Residence time for 1-st reactor: $\tau_1 = \dfrac{1}{k}\left(\dfrac{x_0}{x_1} - 1\right)$

Find concentrations x_1, x_2 and x_3

Residence time for 4 reactors: $\tau_1 + \tau_2 + \tau_3 + \tau_4 = \dfrac{1}{k}\left(\dfrac{x_0}{x_1} + \dfrac{x_1}{x_2} + \dfrac{x_2}{x_3} + \dfrac{x_3}{x_4} - 4\right)$

Calculation of x_1, x_2 and x_3

Optimization function: $f(x_1 + x_2 + x_3) = \dfrac{1}{k}\left(\dfrac{x_0}{x_1} + \dfrac{x_2}{x_3} + \dfrac{x_1}{x_2} + \dfrac{x_3}{x_4} - 4\right)$

$x_1 = 1$ $x_2 = 1$ $x_3 = 1$ Given $x_1 \geq 0 x_2 \geq 0$ $x_3 \geq 0$

$P = \text{Minimize}(f, x_1, x_2, x_3)$ $P = \begin{pmatrix} 0.4728 \\ 0.2236 \\ 0.1057 \end{pmatrix}$ $f(P_0, P_1, P_2) = 8.9306$

$(\tau_1 + \tau_2 + \tau_3 + \tau_4)_{\min} = 8.9358$ $x_1 = 0.4728$ $x_2 = 0.2236$ and $x_3 = 0.1057$

Residence time for each reactor:		Ratio of output and input concentrations:	
$\tau_1 = \dfrac{1}{k}\left(\dfrac{x_0}{x_1} - 1\right)$	$\tau_1 = 2.233$	$\dfrac{x_1}{x_0} = 0.473$	$\dfrac{x_0}{x_1} = 2.115$
$\tau_2 = \dfrac{1}{k}\left(\dfrac{x_1}{x_2} - 1\right)$	$\tau_2 = 2.232$	$\dfrac{x_2}{x_1} = 0.473$	$\dfrac{x_1}{x_2} = 2.114$
$\tau_3 = \dfrac{1}{k}\left(\dfrac{x_2}{x_3} - 1\right)$	$\tau_3 = 2.234$	$\dfrac{x_3}{x_2} = 0.473$	$\dfrac{x_2}{x_3} = 2.115$
$\tau_4 = \dfrac{1}{k}\left(\dfrac{x_3}{x_4} - 1\right)$	$\tau_4 = 2.231$	$\dfrac{x_4}{x_3} = 0.473$	$\dfrac{x_3}{x_4} = 2.114$

Total residence time for cascad of 4 reactors: $42.232 = 8.928$ h

Fig. 7. Calculation in MathCAD of optimal parameters for polymerization process (HARRIOTT 2003) in the cascade of four ideal mixing reactors

Permission

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