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# Is it economically feasible to use heterogeneous catalysts for VOC control in regenerative oxidizers?

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## Abstract

A method of VOC control based on the use of reverse-flow operation in a fixed catalyst bed is compared with high temperature regenerative incineration. The selection of the optimal VOC control system is discussed.

*Keywords*: VOC control; Regenerative oxidizers

## 1. Introduction

The use of a reverse-flow operation in fixed bed catalytic reactors is gaining broad interest [1–5] as an efficient method for VOC control. Reverse-flow regenerative catalytic oxidizer (RCO) includes fixed bed of catalyst placed between two beds of ceramic packing. This technology may be considered as an attractive alternative to high temperature regenerative thermal oxidizers (RTO) [6], which are widely applied for VOC abatement. RTOs employ homogeneous oxidation of volatile organic compounds in gaseous phase. These systems preheat process gas stream in two or more ceramic packed beds. These beds act as regenerative heat exchangers and are typically followed by a combustion chamber where one or several burners are located (Fig. 1b). The burners are required to maintain the high temperatures necessary to promote the oxidation of VOCs.

RCO also uses ceramic beds as regenerative heat exchangers but includes a catalyst bed in lieu of the combustion chamber to accelerate oxidation. At very low VOCs concentration a burner or electric heater can be installed in the reactor center (Fig. 1a). The principal difference between these two processes of VOC control is the required oxidation temperature. The objective of this report is to present a short comparison of RTO and RCO technologies. The analysis will focus on the nature of each process and an economical evaluation of the systems.

## 2. Mathematical modeling

Developed up to date procedure of mathematical modeling allows for a basic design of such complex reaction systems as reverse-flow catalytic and thermal reactors. Our study uses one-dimensional model [2] of unsteady-state

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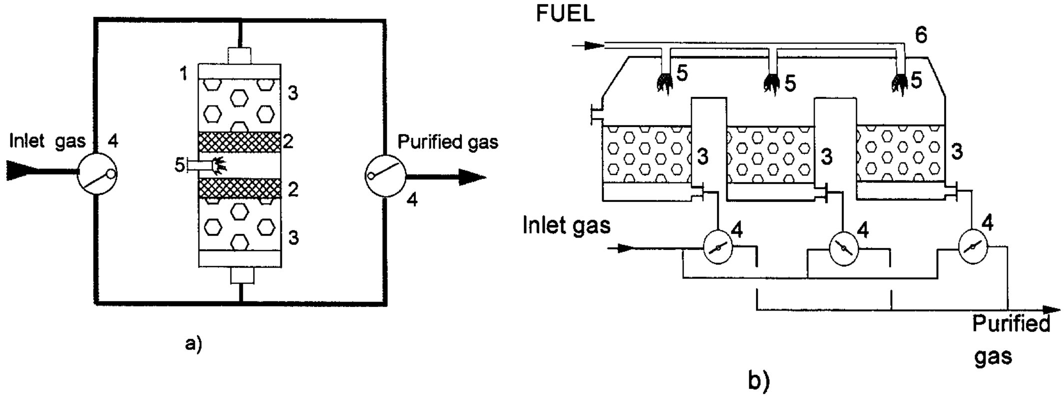
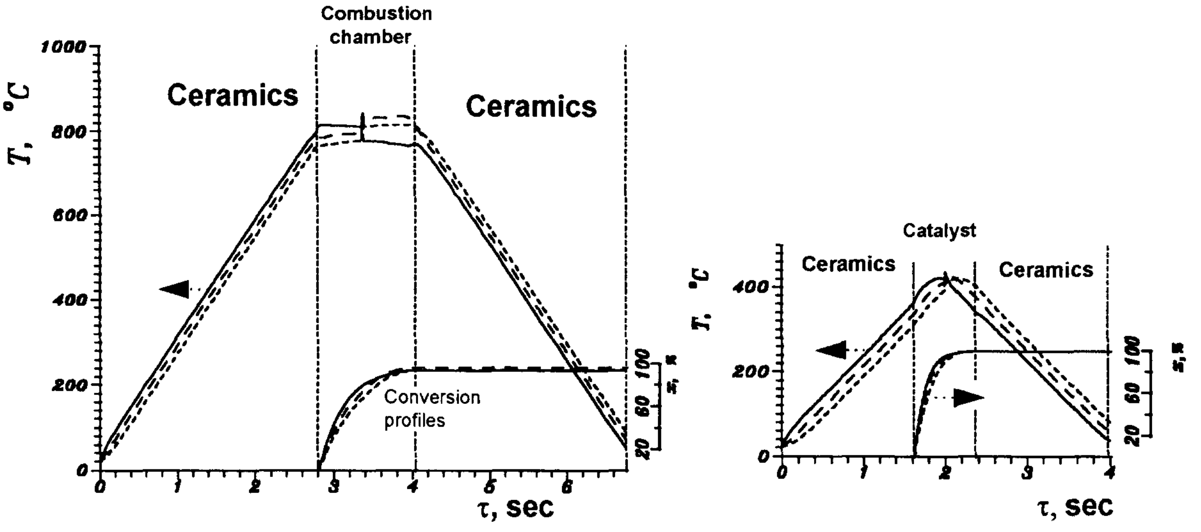


Fig. 1. Principle flow-diagrams of a reverse-flow catalytic reactor (a) and regenerative thermal oxidizer (b). 1:reactor, 2: catalyst bed, 3: ceramic packing, 4: switching valves; 5: burner, 6: combustion chamber.

processes in a packed catalyst bed that considers the following components: the chemical reaction, intraparticle mass transfer, heat transfer between the surface of solid particles and the bulk of the gas phase. This model has been presented in detail in several works on theory and mathematical simulation of RCO reactors (see for example Refs. [2,4,5,7]). In the modeling, the most important dynamic factor to be considered is the heat capacity of the solid phase that determines the time scale of reactor dynamics. Temperature in the gas flow phase and gas composition is assumed to be in quasi-steady state in relation to the temperature field in the solid. At commonly used linear velocities, higher than 0.3–0.5 m/s, the effect of packed bed heat conductivity is secondary to the influence of interphase heat transfer. For typical VOCs concentrations, in a range less than 5 $g/m^3$, catalyst or ceramic particles are nearly isothermal. Influence of intraparticle diffusion limitation is described by an effectiveness factor. For VOC oxidation modeling a first order reaction rate equation is assumed. This form of reaction kinetics is typically observed for oxidation of low-concentrated VOC in the mixture with air. Gas-phase reaction in the void fraction of ceramic packing is assumed to be negligible. The combustion chamber is described as a plug flow reactor. The model of the entire reactor also accounts for the adiabatic mixing of the purified gas and flue gas generated by a fuel burner. The average difference between inlet and outlet gas temperatures due to supplemental heating ($\Delta T_f$) is also determined from the calculation.

By application of the model we are able to clearly demonstrate the differences between RTO and RCO technologies. Fig. 2 shows examples of calculated temperature and conversion profiles for comparison of RTO (a) and RCO (b) processes. Horizontal coordinate in Fig. 2a and Fig. 2b corresponds to the space time of gas flow in an oxidizer ($\tau$) that is proportional to the packed beds length divided by the linear velocity of the gas mixture at normal temperature and pressure. For these examples, the heat- and mass-transfer coefficients were computed from experimental correlations [8] at specified linear velocity, surface, and porosity of packed bed. For catalytic reaction the kinetic parameters were: $k_{RCO} = 4\ s^{-1}$ and $E_{RCO} = 6.5$ kcal/mol, where $E_{RCO}$ and $k_{RCO}$ are activation energy of catalytic reaction and reaction rate constant, respectively. These parameters correspond to the estimates of oxidation rate of light alcohols and ketones over a metal oxide catalyst. For homogeneous oxidation, the kinetic parameters were determined as $k_{RTO} = 0.015\ s^{-1}$ and $E_{RTO} = 15$ kcal/mol. Reaction rate constants ($k_{RCO}$ and $k_{RTO}$) were given at 300°C.

The model considers start-up of catalytic oxidizer by preliminary preheating of the catalyst bed. In actual applications this preheating can be accomplished with the aid of a fuel burner or electric heater installed in the center of the reactor (Fig. 1a). For RTO the model also assumes pre-



(a)

(b)

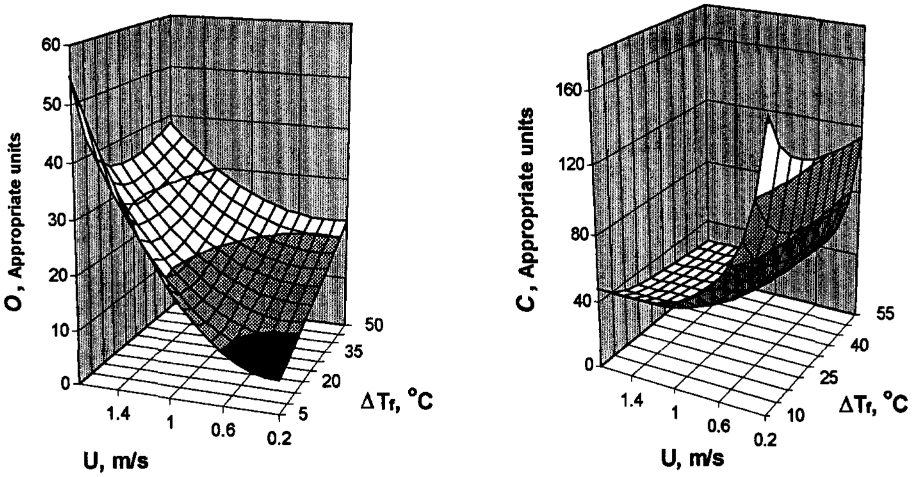
Fig. 2. Temperature ($T$) and conversion ($x$) profiles in regenerative thermal oxidizer (a) and reverse flow catalytic reactor (b). Solid, dashed and dotted lines represent the profiles at the beginning, middle and end of the period between flow reversals for stabilized operation.

heating of the upper fraction of ceramic beds adjacent to combustion chamber. The preheating of the oxidizers is accelerated with periodic flow reversals. After a number of flow reversals, high temperature is achieved in the catalyst bed for the RCO process and in the combustion chamber for RTO process. At these conditions, moving temperature and conversion profiles acquire periodically repeated shapes. The balance between inlet and outlet streams of energy is equilibrated during a cycle. Examples of such continual operation are shown in Fig. 2.

RTO systems typically operate at high reversal frequencies. This provides minimum heat losses with the effluent air and increases thermal efficiency in the oxidizer. Cycle time ($t_c$) for the given example (Fig. 2a) is equal to 3 min, while for the RCO process (Fig. 2b) this parameter is specified to be twice as long. At such short cycles the axial temperature profiles in ceramic beds are almost linear. Changes in the profiles during each cycle are very small. The temperature peaks in the oxidizers centers (at $\tau = 3.4$ s, Fig. 1a and at $\tau = 2$ s, Fig. 1b) are the result of supplemental fuel burning. The adiabatic temperature rise for VOC oxidation ($\Delta T_{\mathrm{VOC}}$) in both RCO and RTO is specified to be 8°C. The additional heat required for the RTO to maintain necessary oxidation temperature is 30°C, while for the RCO, it is only 15°C. The lower process temperature required in the RCO system allows for a substantial decrease in ceramics bed length when compared to the RTO (about 40%) as shown in Fig. 2. As a result the pressure drop for the RCO using the same sizes and shape of ceramic packing and catalyst is about two times less than for the RTO.

## 3. Optimal parameters

To compare economics for both the RTO and RCO processes, we must consider both capital costs and ongoing operating costs elements. For the common case of a low VOC concentration, the operating costs for the RCO includes the costs of electricity for a process blower, the costs of fuel for a supplemental heat burner, and the costs of catalyst which will slowly deactivate over time. Fuel costs is proportional to that portion of the temperature rise of the purified gas ($\Delta T_f$) which results from supplemental fuel burning (as opposed to burning of the VOC). Electricity costs



(a) (b)

Fig. 3. Annual operating (a) and capital (b) costs versus fuel consumption ($\Delta T_f$) and linear velocity ($U$).

is proportional to reactor pressure drop. Capital costs consist of the price of equipment, including the reactor vessel with insulation, valves, connecting ducts, the costs of the catalyst and ceramics packings, as well as installation labor.

Fig. 3a and Fig. 3b show examples of operating ($O$) and capital ($C$) costs calculated for RCO. The costs dependencies are constructed in 3D spaces versus linear velocity $U$ and temperature rise $\Delta T_f$. The velocity $U$ is specified at normal condition, so it is the reciprocal of the area of oxidizer cross-section. Gas flow rate is specified to be equal to $1.3 \times 10^5$ $m^3/h$. All design variables of the system, necessary for creating the surfaces $O(\Delta T_f, U)$ and $C(\Delta T_f, U)$ were specified except for the length of the ceramic beds. This length was calculated to achieve a 95% degree of conversion for each variant of the reactor design. Explicit functional forms for both capital and operating costs were determined from the results of reactor modeling using known utility and material prices. The dimension of the costs in Fig. 3 corresponds to a monetary unit which irrelevant to our goal of demonstrating general features for the process economies.

As one can see from Fig. 3a and Fig. 3b, changes of operating and capital costs have opposite tendencies. High linear velocity produces economy in capital costs but results in higher operating costs due to an increase in pressure drop. Higher supplemental heat requirements ($\Delta T_f$) result in decrease in the ceramic bed length and pressure drop, but also result in an increase in fuel consumption. Generally, an increase in fuel consumption produces higher operating costs (Fig. 3a) and lower capital costs (Fig. 3b). The influence of fuel consumption on capital costs is not as high as that of linear velocity.

We can estimate the domain of the optimal process parameters by defining an integral criterion ($J$), combining two separate costs categories in the same format. This combination is obtained by converting the capital costs into an annual depreciation value ($\Psi$, $\text{year}^{-1}$) and adding it to the annual operating costs ($J = O + \Psi C$). Factor $\Psi$ will vary in practical cases from 0.2 to 1 $\text{year}^{-1}$ according to the time value of money for each unique application.

Fig. 4. shows an example of the calculation the criterion $J$ using the values of operating and capital costs in Fig. 3.

The observed shape of the surface $J$ in Fig. 4 is directly dependent upon both capital and operating costs. An optimal system design becomes possible to accomplish when the user can choose the preferable relation between the value of one time capital costs versus the value of ongoing operating costs. However, the smooth shape of the minimum

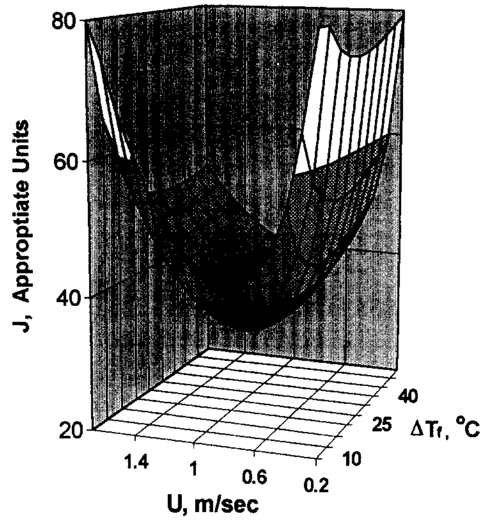


Fig. 4. Combined annual costs $J = O + \Psi C$ versus fuel consumption $(\Delta T_f)$ and linear velocity in reactor $(U)$. $\Psi = 0.5 (\text{year})^{-1}$.

shown in Fig. 4, in the domain of linear velocity between 0.6 and 1 m/s and $\Delta T_f$ between 15 and 50°C, suggests that this domain of parameters contains the preferred economic choice for typical treatment of high flow rate and low concentrated VOC gases. Additional calculations have shown that the position of the minimum for criterion $J$, in the plane $< \Delta T_f, U >$ is not changed strongly with variation the parameter $\Psi$ within the practically important interval $(0.2 < \Psi < 1 \text{ year}^{-1})$.

## 4. RCO versus RTO. Economic comparison

When comparing the economics of the two methods of VOC control, the parameters of thermal and catalytic oxidizers were taken at minimal value of criterion $J$. We define a profitability for the RCO process as a relative difference between the minimum values of criterion $J$ for two types of VOC control systems:

$$\text{Profitability} = \frac{(J_{\min})_{\text{RTO}} - (J_{\min})_{\text{RCO}}}{(J_{\min})_{\text{RTO}}} \times 100\%$$

Fig. 5 shows typical results of such a comparison.

The relative economic efficiency of RCO vs RTO was computed in Fig. 5 at various adiabatic temperature rises of VOC oxidation and various degrees of conversion of volatile organic compound. The first parameter $(\Delta T_{\text{VOC}})$ is in a direct proportion with inlet VOC concentration. The second parameter, VOC conversion, is typically specified by the user.

The criteria $(J_{\min})_{\text{RTO}}$ and $(J_{\min})_{\text{RCO}}$ for computing the profitability in Fig. 5 were calculated at a gas flow rate of $1.3 \times 10^5$ m$^3$/h and an inlet temperature of purified gas of 20°C. Kinetic parameters are close to those for Fig. 2. It was assumed that RTO design includes only two beds of ceramic packing with a burner installed between these two beds. Capital costs required for the construction of a separate combustion chamber were not considered.

As one can see from Fig. 5, the economic efficiency of catalytic reactor is higher than that of thermal oxidizer in a broad domain of low adiabatic temperature rises $(\Delta T_{\text{VOC}})$. This domain of $\Delta T_{\text{VOC}}$ corresponds with a majority of practical applications. At these conditions, the additional costs of the catalyst replacement is lower than the costs of electricity and supplemental fuel necessary to maintain the temperature in the combustion chamber. RTO is more profitable compared to RCO only at adiabatic temperature rises higher than approximately 95°C (shadow part of surface

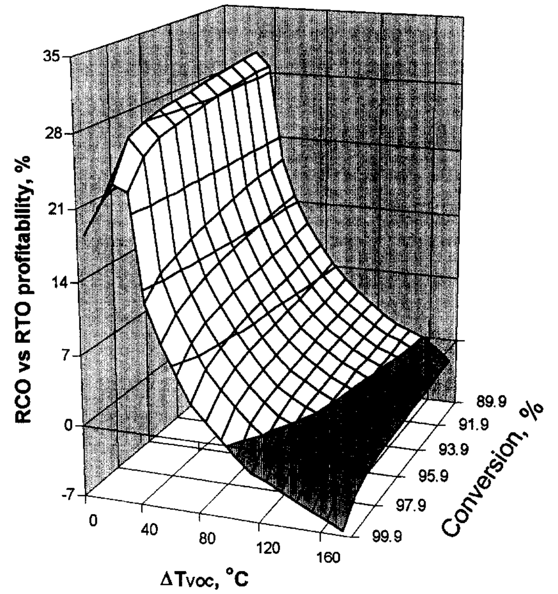


Fig. 5. Comparison between RTO and RCO economics at various VOC conversion and $\Delta T_{\text{VOC}}$. Vertical axis corresponds to the relative deference between minimum cost criterion $(J_{\min})$ for RTO and RCO.

Table 1
Economics characteristics RTO and RCO technologies

| Economics index | RTO | RCO | Difference (%) |
|---|---|---|---|
| *Annual operation costs (US \$/($m^3$/h))* | | | |
| Electricity | 0.82 | 0.53 | |
| Fuel | 0.82 | 0.26 | |
| Catalyst | 0.00 | 0.31 | |
| Total | 1.64 | 1.10 | 33 |
| *Capital cost of oxidizer (arbitrary units)* | | | |
| Ceramics | 1.00 | 0.50 | |
| Catalyst | 0.00 | 2.10 | |
| Reactor vessel, including insulation | 6.50 | 3.40 | |
| Total | 7.50 | 6.00 | 20 |

in Fig. 5). For normal hydrocarbons this limit corresponds to VOC concentrations 3 g/m$^3$.

The relative economic efficiency of RCO vs. RTO has a maximum at $\Delta T_{VOC}$ about 10–15°C (Fig. 5). This feature conforms to the increase in fuel consumption at low VOC concentrations. Note, that this extremum of relative economic efficiency does not take place when comparing absolute values of the annual costs. With this form of comparison, the maximum profitability of catalytic process corresponds to lowest VOC concentration (when $\Delta T_{VOC} \to 0$). Note, also, that the relative efficiency of RCO slightly decreases at higher requirement to VOC conversion (Fig. 5). This is determined by the higher activation energy of homogeneous combustion against heterogeneous catalytic oxidation. However, even at 99.9% conversion, the use of catalyst has a significant effect (Fig. 5).

An example, shown in Table 1, compares the operating and capital costs for a specific plant purifying 100 000 m$^3$/h air contaminated by 0.5 g/m$^3$ of VOCs (specifically, styrene).

The advantages of the RCO system demonstrated by a decrease in operating costs of about 30% and 20% decrease in capital costs. This is also in agreement with the data given in Fig. 5.

The economic efficiency of the regenerative catalytic oxidizer results from the inherent features of the reverse-flow catalytic process.

Autothermal or self-sustained operation in RCO may be obtained even at very low VOC concentrations. This operation can be achieved for adiabatic temperature rise $(\Delta T_{VOC})_{min}$ of about 15°C. In a typical case of hydrocarbons oxidation, this would be equivalent to VOC concentration about 0.5 g/m$^3$. For commercial RTOs, having thermal efficiency between 92%–95%, the minimum temperature rise required for autothermal operation is between 45 and 70°C, this is equivalent to a hydrocarbons concentration between 1.5–2.5 g/m$^3$. Consequently, the RCO, for autothermal operation, will require 3–5 times less fuel than the RTO.

Under identical conditions of purified gas, the volume of packing in the RTO is 2–3 times higher than in the RCO at comparable velocities, cycle times, and otherwise constant conditions. The RCO operates at a much lower average temperature than the RTO (Fig. 2) which results in a dramatic decrease in the pressure drop ($\Delta P$) for the RCO. For example, if all input and internal hydrodynamic conditions for RCO and RTO are equivalent, $(\Delta P_{RTO})/(\Delta P_{RCO}) = $ ca. 1.5.

Substantial savings in capital investments can be achieved with RCO in comparison with the RTO if the catalyst costs is reasonable. This is due to the smaller size of regenerative beds and the lower operating temperature, which allows smaller reactor size and the use of less expensive steel and insulation.

We should also note there are some distinct advantages of RCO which do not directly influence on the process economy but are important in final decision of technology selection.

1. Long characteristic cooling time and short characteristic heating time for RCO ensure the stable autothermal operation even though inlet parameters fluctuate greatly [4]. This includes fluctuations in concentrations up to tenfold, changes in the type of VOC, flow rate fluctuations (up to threefold), and temperature changes (practically, without limits). For the reasons discussed, temporary shutdowns in the gas-flow rate or zero input VOC concentrations during relatively long periods do not cause disruptions in the operation of the RCO unit. Often RCO installations can be placed to operation after a weekend shutdown

without preheating. Note also that heterogeneous VOC oxidation on the surface of catalyst is inherently more stable than homogeneous combustion in hollow space.

2. Heat losses in the RCO system are lower compared to RTO because of the lower temperatures and smaller size of the RCO system.

3. Fast start-up of RCO is possible because the catalyst temperature does not need to exceed 250–350°C. This procedure requires only 1 to 3 h even when the catalyst bed is cold [4].

4. The relatively low temperature in the RCO reaction zone minimizes production of thermal-$NO_x$. In contrast, the temperature is 800°C or higher in the RTO combustion chamber and higher than 1500°C in the fuel burner installed into the chamber. Under these conditions, thermal-$NO_x$ is formed.

5. The RCO purification unit can be used as a source of secondary high-potential energy (steam, hot water, hot gas, etc.) when the VOC content in the gas mixture is higher than 2.5–3 g/m$^3$. For these conditions, the released heat can be removed from the hottest area of the packed bed. In some cases, this actually makes the process of gas purification profitable.

Monsanto Enviro Chem Systems, Inc. of St. Louis, MO, USA offers a range of regenerative catalytic systems from 2500 to 170 000 m$^3$/h in size. The US trademark for this technology is DynaCycle.

In 1993, Monsanto Enviro Chem built a mobile unit to demonstrate their 'DynaCycle' process utilizing the RCO concept for catalytic purification of industrial off-gases containing VOC. The unit has capacity about 500 m$^3$/h of gas and was designed on the basis of mathematical simulation results. An example of DynaCycle operating test results has been recently discussed [9].

An industrial system for purifying exhaust gases after asphalt-bitumen plant has been in operation for over 2 years. Industrial plants ranging in size from 17 000 to 40 000 m$^3$/h of exhaust gases are currently under construction.

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