

Experimental and Modeling Studies of Self-Sustaining Reactions Between Nanopowders

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Introduction

During the past several years, a significant effort has been on investigation of reaction front propagation and the rate of energy release in heterogeneous systems consisting of nanopowder reactants^{1,2}. Substantial size reduction of each reactant powder (e.g. from micro- to nano-size) leads to increase of reaction front propagation in some systems under unconfined conditions by approximately two to three order of magnitude³. This is accomplished when nano-sized fuel and oxidizer particles are mixed. The scaling of these reactants to the nano-scale has allowed for several capabilities and applications that were not previously possible with conventional micro-sized thermite mixtures. A significant size reduction of reactant powders allows more intimate contact. As a consequence of this significant reduction of size, new issues such as dispersion and mixing of reactants, safety, and surface functionalization of fuel particles in order to minimize potential undesired reaction with oxygen and water vapor must be addressed.⁴ Contemporary work in this area primarily revolves around experimental effort; therefore, there is a need to develop reliable models describing propagation of reaction fronts which are accompanied by gas expansion in different geometric configurations. Prior modeling studies involving strongly exothermic heterogeneous reactions focused primarily on two general types of systems. The first considers “gasless” conductively driven combustion fronts whereas the second describes combustion fronts propagated by exothermic reaction a solid reactant and gas which is transported to the reaction zone through the porous structure (filtered combustion).^{5,6}

This contribution focuses on both experimental and modeling studies of reaction front propagation in cylindrical tubes. Different cylindrical setups with one or both ends open are considered. Experimental results have revealed that the combustion front velocity in “almost” gasless reacting system consisting of aluminum and iron oxide nanopowders is very sensitive to the place of reaction initiation within the cylindrical tube and configuration setup. In addition, another reacting system consisting of aluminum and copper oxide nano-reactants, which is characterized by partial vaporization of reaction products, was investigated using similar geometric configurations. Experimental determination of kinetic constants for both heterogeneous reacting systems was done using differential scanning calorimetry. Utilizing this data, mathematical models describing reaction front propagation in cylindrical tubes in the presence of gas expansion were developed. The effect of pressure generation due to inert gas expansion in porous matrix and/or partial product vaporization as well as reactant

composition, porosity, and geometric setup on dynamic characteristics, such as temperature, pressure, conversion, reaction zone dimension, and gas velocity will be discussed.

Dynamics of aluminum-metal oxide systems reacting in small diameter tubes

Conventional thermite systems, comprised of micron scale particles, are much slower reacting systems than their nanoscale counterparts. The primary mechanism responsible for combustion front propagation and heat transfer through such systems is conduction. The reactions tend to not produce gaseous products or react quickly enough to cause fast expansion of gas throughout the system. As the particle size is decreased to the nanoscale level (~100 nm and below), pressure generation in the reacting system due to gasification of products and fast expansion of gas due to heating. This effect needs to be taken into consideration when modeling the combustion front propagation in these nanothermite systems as the mechanism for reaction propagation transitions to a convectively driven one. Typically, reactions in unconfined loose powder mixtures of energetic materials are difficult to predict and model as the pressure release and convective movement of hot gases can occur in any direction, resulting in an undefined combustion front. The inclusion of these energetic materials in a tube configuration allows for various types of confinement and control of the pressure release in the system. The combustion front propagation can also then be modeled as one-dimensional.

The scope of this research was to determine the effect of pressure generation in slower burning nanothermite systems and how that pressure effect changes during the transition to ultra-fast reacting systems. In the slower reacting systems, where the combustion front propagation is on the order of tens of meters per second, it is possible for the pressure generated due to fast gas expansion to move forward through the unreacted powder ahead of the combustion front and eventually displace the unreacted powder. In faster reacting systems, where pressure is generated by both gasification of products and fast expansion of hot gases, it is possible for the combustion front propagation velocities to reach the order of hundreds of meters per second, faster than the speed of sound in air. In such cases, the combustion front and pressure front move through the unreacted material more like a shock wave. This does not allow pressure build-up ahead of the front and unreacted materials should not be displaced prior to ignition. The systems investigated to characterize these two different types of propagation were Al-Fe₂O₃ which is a slower reacting system that creates pressure only by fast expansion of gas and has a combustion front propagation velocity on the order of tens of meters per second and Al-CuO that propagates on the order of hundreds of meters per second and generates much high pressures at the combustion front boundary.

It was previously demonstrated that when both ends of the tube are left open to the atmosphere, the combustion front will accelerate in the direction of propagation as the pressure builds up behind the combustion front and drives the convective wave ahead of the reaction zone, preheating unreacted material. When the end of the tube opposite ignition is sealed shut, the pressure cannot drive the hot gases forward and the reaction propagates with a constant velocity profile. This was found to be true in the slower reacting Al-Fe₂O₃ system. Since then, faster high-speed imaging equipment was

purchased, allowing for more detailed experiments to be performed in order to understand the reaction mechanisms necessary to include in modeling such systems.

One important factor that needed to be investigated was whether or not the reactants actually did remain stationary prior to and during reaction. Factors that will affect this include the pressure generated by the system and the size of the particles ahead of the combustion front. Both were investigated in these studies. Previous experiments involving the system comprised of Nanotechnologies 50 nm aluminum and Nanophase Fe₂O₃ showed that when both tube ends were kept open, the combustion front accelerated in the direction of propagation and unreacted material was possibly ejected from the end of the tube. To investigate this effect further, a configuration was used in which the tube was half filled with the Al-Fe₂O₃ nano-mixture and the remaining half was filled with only nanoscale aluminum. Since the rate of combustion of aluminum powder is controlled by the rate at which oxygen can diffuse to the surface of the particles, it should burn much slower than the metal-metal oxide nanosystem. If the particles remain in place prior to reaction and during reaction, the combustion front should slow down significantly at the interface between the Al-Fe₂O₃ mixture and the nanoscale aluminum. High speed imaging, shown in Figure 1 does not confirm this occurrence.

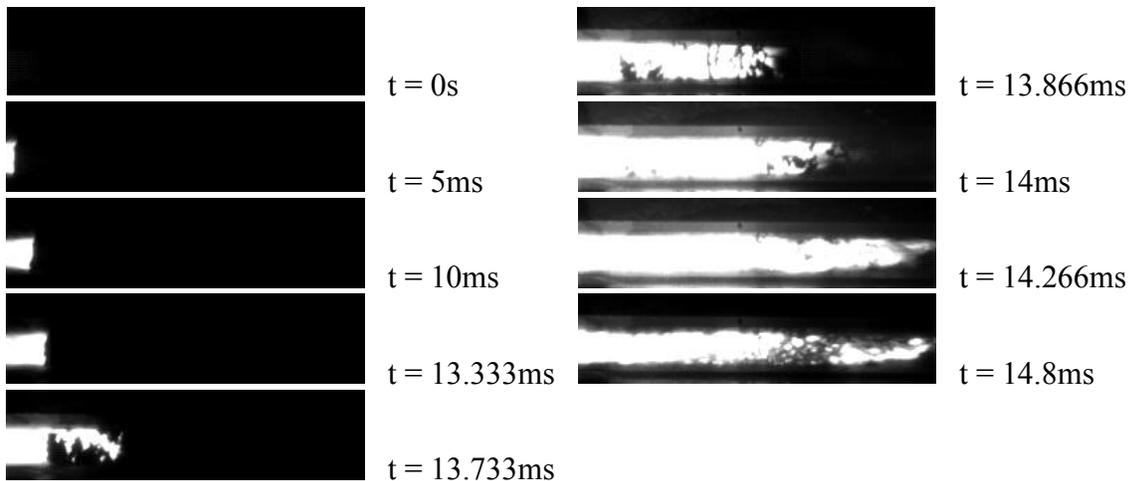


Figure 1. High speed imaging of combustion front propagation in a small diameter tube containing Al-Fe₂O₃ nanoenergetic mixture in the left half and nanoscale aluminum powder in the right half.

After the material is ignited, it appears to propagate at a relatively constant rate for approximately 3/16 of an inch. As pressure begins to build up, however, hot gases are pushed forward at a rate much faster than that of combustion propagation and eventually the reaction front accelerates in an almost shock-like manner. The interface between the two different materials does not appear to slow down the reaction as the pressure generated due to gas expansion becomes great enough to expel the material forward before and during reaction.

For comparison, a slower system that would generate less pressure due to expansion of gas was investigated. This system was comprised of Valimet 2 μm aluminum and Nanophase Fe_2O_3 . The first configuration tested using this system involved no other components. The entire tube was filled with the reactant mixture to observe whether or not the combustion front would accelerate. Figure 2 shows that like the system comprised of nanoscale components, the combustion front eventually accelerated and appeared to eject unreacted material from the tube. The onset of this occurrence, however, did not occur until the reaction front had proceeded a further length down the tube, allowing for pressure to buildup great enough to drive the hot gases ahead of the combustion front.

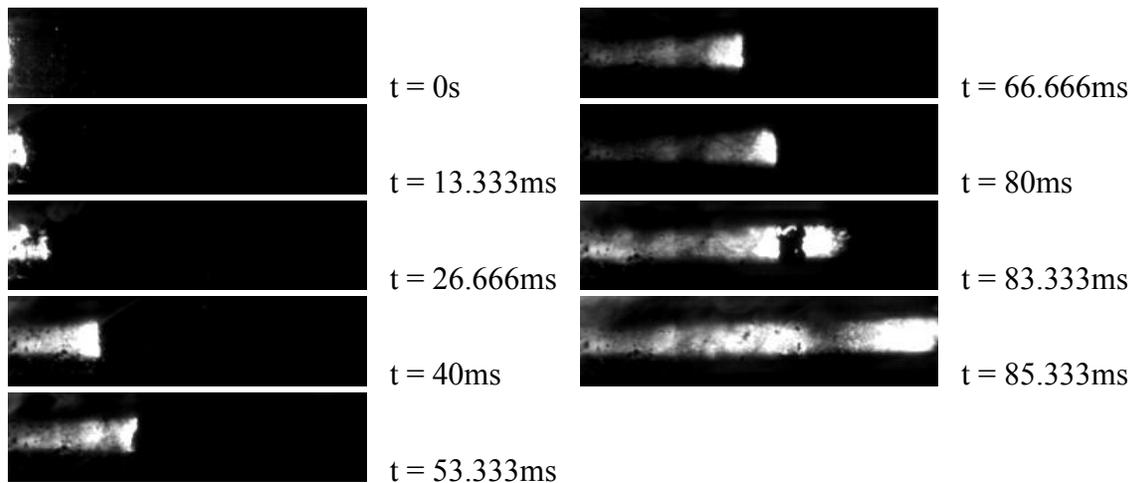


Figure 2. High speed imaging of combustion front propagation in a small diameter tube containing a mixture of micron Al and nanoscale Fe_2O_3 .

As with the faster nanoscale system, a configuration was investigated that replaced the right half of the tube mixture with nanoscale aluminum to create an interface that should slow down or stop the combustion front. High speed imaging of this reaction showed that not enough energetic material was combusted to generate the pressure needed to eject the aluminum material from the end of the tube, resulting in the extinguishing of the combustion front at the interface between the two .

To investigate the effect of particle size on particle movement ahead of the combustion front, a different setup was used. In this case, a section of inert micron sized Al_2O_3 powder was placed in the center of the tube between to sections of Al- Fe_2O_3 nanoenergetic mixture. The first section of energetic material is greater than what was needed to cause combustion front acceleration and eventual ejection of material in the system containing half aluminum powder. The second section of energetic material was placed at the end of the tube to observe if pressure driven hot gases would ignite the material. Results showed a relatively steady rate of combustion as the Al_2O_3 particles are too large to be moved by the amount of pressure generated by the reaction, therefore hindering the transfer of energy in the form of hot gases across the inert material. The second section of energetic material is never ignited.

Although these Al-Fe₂O₃ mixtures generate enough pressure to expel hot gases forward, the amount of pressure generated is only due to expansion of gas due to heating and is not great enough to give significant readings on our piezoelectric pressure transducers. Another nanoenergetic system, Al-CuO that generates gaseous products as well as pressure due to gas expansion was investigated using the equipment. If the combustion front velocity and pressure profile travels like a shock wave, however, the material should react with a constant velocity profile regardless of configuration and pressure will not displace any unreacted material from the tube.

To verify these predictions, a nanoscale system of Al-CuO was added to two different tube configurations for reaction. The first system was set up so both ends of the tube were kept open to the atmosphere and the second setup involved keeping the end opposite the ignition end sealed. This would prevent any pressure generation ahead of the combustion front from escaping the tube. If pressure generation occurred ahead of the combustion front, it would affect the combustion front velocity of the system as in the Al-Fe₂O₃ system.

Both tubes were filled with approximately 115mg of energetic material. Combustion front propagation in each system was monitored using high-speed video recording at a rate of 100,000 frames per second. Figure 3 shows video stills of combustion front propagation in the setup where both ends of the tube were left open to the atmosphere. Unlike in the same setup using the Al-Fe₂O₃ nanoenergetic mixture, the Al-CuO system propagates with a constant velocity profile at a rate of 635 m/s.

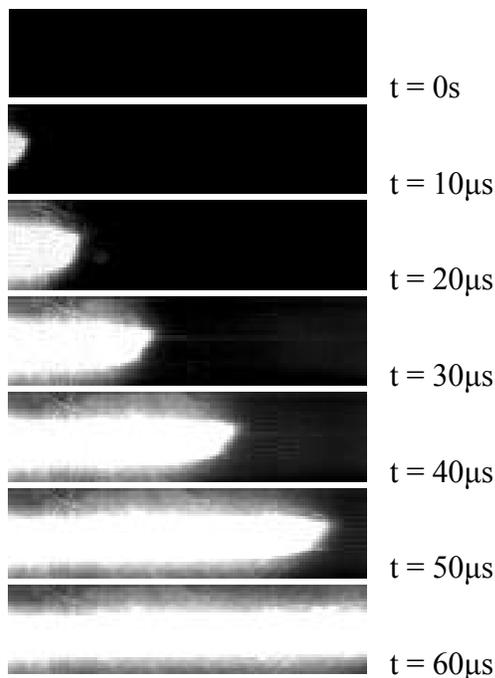


Figure 3. High speed imaging of combustion front propagation in a small diameter tube containing Al-CuO nanoenergetic mixture. Both ends of tube open to atmosphere.

Testing of the second tube configuration to prevent any possible pressure release in the direction of the propagation proved that the combustion front does propagate in a shock-like manner as the front traveled at the same constant velocity of 635 m/s as the first tube configuration. In the Al-Fe₂O₃ system, no such shock was present and the pressure was allowed to buildup ahead of the combustion front in the setup with both ends open and the preheating of the reactants accelerated the reaction. Another noticed effect in the Al-CuO system with the end opposite from ignition sealed shut was a reflection of the shock wave after reaction that ejected the tube from the apparatus as seen in Figure 4.

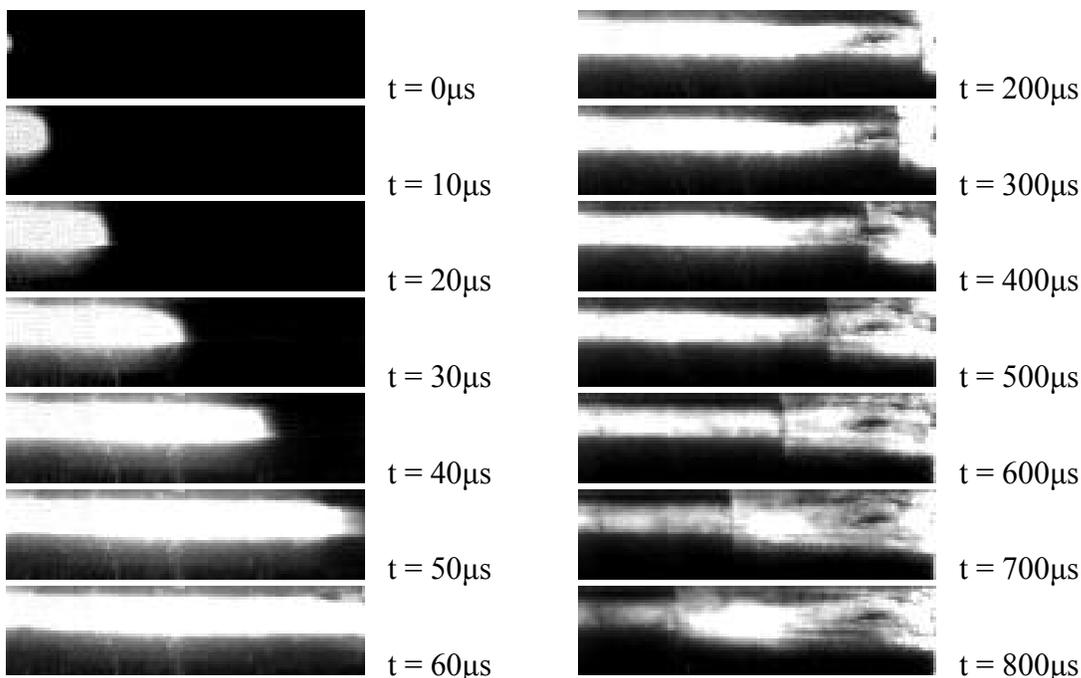


Figure 4. High speed imaging of combustion front propagation and shock-wave reflection in a small diameter tube containing Al-CuO nanoenergetic mixture. Right side of the apparatus sealed shut to prevent pressure release. Left side open to atmosphere.

These results confirm the theory that ultrafast nanoenergetic reactions (on the order of hundreds of meters per second) behave in a shock-like manner while the slower reactions (tens of meters per second and slower) depend more on the direction of pressure release.

Modeling of Combustion Front Velocities

With respect to the modeling study, preliminary work considered the “gasless” conductively driven combustion front. This model qualitatively simulated that observed experimentally, in particular the relatively slow and constant combustion front propagation through the tube. However, this model did not take into account observed phenomena related to reactions in which gas generation was more significant and the combustion front was observed to accelerate through the chamber. Observed solids migration and theorizing ignition by convected gases and pressure shock, a natural progression for the model was treat the reaction as a two-phase mixture of interacting continua incorporating reacting solid and gaseous combustion products. The fundamental model used for this study was that proposed by Baer and Nunziato (BN) with

modification⁷. Other contemporary work deemed relevant includes Kapila et.al⁸, J. B. Bdzil et. Al^{9,10}, and Powers, Stewart and Krier^{11,12}, and Powers¹³.

The BN model consists of a system of partial differential equations which incorporates the two continuity, two momentum, and two energy equations, one associated with each phase. An underlying assumption is that each phase is in local thermodynamic equilibrium and interactions between phases are consequences of drag, compaction, heat transfer and the combustion reaction. The relationships which describe the interaction between the phases (mass, momentum and energy exchange) are typically formulated via simplification of the model and experimental data. Source terms are typically introduced to represent exchange of mass, momentum, and energy across the interfaces separating the phases. In general, the BN model is hyperbolic with solutions exhibiting a complex wave structure. The numerical discretization of the non-conservative terms is difficult and the theory of numerical methods for such non-conservative systems is relatively absent. Numerical results of the 1D tube geometry are qualitatively compared to experimentally observed phenomena and the relevance of this model as it applies to self-sustaining reactions of nanopowders is discussed.

Following the BN model, the physical system is postulated as follows:

For each phase, gas (subscript g) and solid (subscript s) the following variables were postulated and subsequently assigned:

ρ_s, ρ_g	- densities
v_s, v_g	- specific volumes
u_s, u_g	- particle velocities
e_s, e_g	- specific internal energies
T_s, T_g	- temperatures
ϕ_s, ϕ_g	- volume fractions
P_s, P_g	- pressures
η_s, η_g	- specific entropies
E_s, E_g	- $E_i = e_i + \frac{1}{2}u_i^2$ is total specific energy (associated with phase $i = g$ or s)

1. The assumption these variables represent an average of the microscopic phase variables is presumed. Also assumed is the existence of no void space, thus the saturation condition, $\phi_s + \phi_g = 1$, holds.

The mass fraction will be denoted by $\lambda_g = \frac{\phi_g \rho_g}{\phi_g \rho_g + \phi_s \rho_s}$ and $\lambda_s = \frac{\phi_s \rho_s}{\phi_g \rho_g + \phi_s \rho_s}$

for the gas and solid phase respectively.

2. The material-specific variables for each phase is also assumed to be dependent upon the independent variables associated with that particular phase.
3. The weighted sums of the properties of the constituents represent the properties of the mixture, m . For example:

$$\begin{aligned}\rho_m &= \phi_s \rho_s + \phi_g \rho_g \\ P_m &= \phi_s P_s + \phi_g P_g \\ e_m &= \lambda_s e_s + \lambda_g e_g \\ u_m &= \lambda_s u_s + \lambda_g u_g \\ (u\rho)_m &= \phi_s (u_s \rho_s) + \phi_g (u_g \rho_g)\end{aligned}$$

4. The PDE's and constitutive functions which represent the model are assumed to be independent of the observer (Galilean invariance).
5. The mass, momentum, and energy balances that describe the motion for single-phase materials will adequately represent the motion of each constituent. These "laws" are viewed as evolution equations for the local, phase-averaged density, momentum, and energy of each phase. [Drew and Passman, 1999]
6. The volume fraction, ϕ_s , is carried with the solid phase; thus it follows that the porosity, $\phi_g = 1 - \phi_s$, also advects in conjunction with the solids.

The Governing Equations

Mass Balance

$$\frac{\partial}{\partial t}(\phi_s \rho_s) + \frac{\partial}{\partial x}(\phi_s \rho_s u_s) = C$$

$$\frac{\partial}{\partial t}(\phi_g \rho_g) + \frac{\partial}{\partial x}(\phi_g \rho_g u_g) = -C$$

Momentum Balance

$$\frac{\partial}{\partial t}(\phi_s \rho_s u_s) + \frac{\partial}{\partial x}(\phi_s \rho_s u_s^2 + \phi_s P_s) = \mathcal{M}$$

$$\frac{\partial}{\partial t}(\phi_g \rho_g u_g) + \frac{\partial}{\partial x}(\phi_g \rho_g u_g^2 + \phi_g P_g) = -\mathcal{M}$$

Energy Balance

$$\frac{\partial}{\partial t}(\phi_s \rho_s E_s) + \frac{\partial}{\partial x}[\phi_s u_s (\rho_s E_s + P_s)] = \mathcal{E}$$

$$\frac{\partial}{\partial t}(\phi_g \rho_g E_g) + \frac{\partial}{\partial x}[\phi_g u_g (\rho_g E_g + P_g)] = -E$$

Compaction dynamics

$$\frac{\partial \rho_s}{\partial t} + \frac{\partial}{\partial x}(\rho_s u_s) = -\frac{\rho_s}{\phi_s} F$$

The right-hand sides are source terms that characterize phase interaction and correspond to mass (C), momentum (M), and energy (E) respectively. The total mass, total momentum and total energy are all conserved as the source terms for the gas and solid phases sum to zero. Using the BN model, combustion front propagation in the Al-MoO₃ systems was calculated as it relates to temperature and conversion as shown in Figure 5.

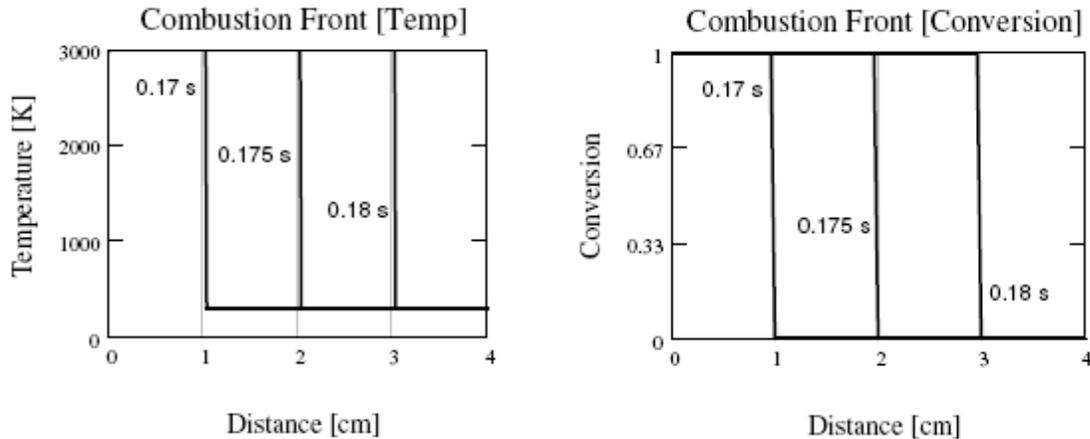


Figure 5 . Temperature and conversion transient profiles during the combustion front propagation in pressed pellet made from Al and MoO₃ nanopowders – unconfined conditions.

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