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A TG/DTG KINETIC MODEL AND ITS APPLICATION IN AN IN-SITU COMBUSTION RESERVOIR SIMULATOR *

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ABSTRACT

In-situ combustion is a thermal oil recovery process in which crude oil undergoes a large number of physical and chemical transitions. The chemical reactions involved are to a great extent responsible for the heat generation needed to sustain the combustion front. The kinetic model used to predict the performance of the process needs therefore to be as accurate as possible. To date, all kinetic models used in in-situ combustion simulators have assumed Arrhenius-type reaction rate constants and constant activation energies and heats of reaction.

In this study the TG/DTG curve of the crude oil under study is used to derive a kinetic model suitable for the simulator. The model does not include the assumption that the specific reaction rate constants be of Arrhenius type and thus does not require explicit values of activation energies and frequency factors.

An in-situ combustion tube test was simulated using the present kinetic model and compared with the simulated results obtained by incorporating a commonly used kinetic model. Process variables predicted from the present model were significantly closer to the actual experimental values than those predicted by the old approach. More importantly, to arrive at a reasonable predicted performance for the process using the old technique, the values of activation energies in the kinetic model had to be lowered to unrealistic levels.

INTRODUCTION

Thermal methods such as steam injection, hot water injection and in-situ combustion are used to improve the mobility of crude oil in its reservoir. While steam and hot water injection necessitate external heat input, in-situ combustion produces the necessary heat by burning a small fraction of the crude oil within the reservoir.

In-situ combustion usually starts by injecting an oxygen bearing gas and artificially igniting the crude oil. As air injection is continued, the self sustaining burning front drives the crude oil towards the production wells.

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The heat generated by the process serves to evaporate the crude oil and to promote reactions such as crude oil combustion, crude oil cracking which forms coke-like material, and coke combustion. The great number of reactions which occur in in-situ crude oil combustion makes the kinetic studies very complicated. For this reason, most workers have concentrated on specific reactions. Boussaid and Ramey [1] performed several runs wherein a thin stationary layer of coke in unconsolidated sand was burned isothermally at different temperatures from which an expression for carbon burning rates as a function of carbon concentration, combustion temperature and oxygen concentration was obtained. The authors concluded that the coke burning rate was first order with respect to carbon concentration and oxygen partial pressure, and the reaction rate constant followed the Arrhenius equation for temperature dependency. Activation energies were found to be relatively insensitive to changes in the crude oil gravity, whereas they were shown to decrease by about 20% when 20% clay was added to the sand matrix.

At temperatures lower than 200 ° C, oxidation reactions usually lead to hyperoxides, while complete combustion predominates at higher temperatures. The partial oxidation reactions account for the spontaneous crude oil ignition which is sometimes observed during air injection. Burger and Sahuquet [2] classified the oxidation reactions into seven categories and determined heats of reaction and kinetic equations for low temperature oxidation, heavy oil combustion and cracking, and coke combustion. The authors also determined from differential thermal analysis that both specific area of the host matrix and metallic derivatives promote the oxidation reactions.

Adonyi [3] used thermogravimetric analysis to investigate the evaporation of light pure components as well as light crude oil and concluded that the reaction for this process was of zero order.

Dabbous and Fulton [4,5] studied the kinetics of both low temperature oxidation and high temperature combustion reactions. The reaction order of the low temperature oxidation reactions with respect to oxygen depended on the properties of both the porous medium and crude oil, and that of the high temperature combustion reactions was found to be proportional to both the oxygen partial pressure and the square of the hydrocarbon concentration.

Vossoughi et al. [6] studied the effects of clay on the in-situ combustion process using both tube combustion and thermogravimetric (TG/DTG) and differential scanning calorimetry (DSC) experiments. They observed that coke deposition increased with clay content, activation energies for the combustion/cracking phases were significantly lower for clay/crude oil mixtures than for sand/crude oil mixtures, and addition of clay or silica powder to crude oil shifted the large amounts of heat produced from a higher to a lower temperature range. These phenomena are associated with the large surface area of the clay and its possible catalytic effects.

All the above phenomena render the in-situ combustion process kinetics very complicated, and simple semi-empirical kinetic models cannot accurately describe all phases that the crude oil undergoes. Some of these facts led Vossoughi et al. [7], among other workers [8,9], to develop a kinetic model derived exclusively from TG/DTG and DSC experiments. For the four stages that the oil goes through (distillation, low temperature oxidation, first combustion/cracking and second combustion/cracking reactions), the kinetics of all reactions were expressed in terms of temperature and the fractional weight remaining of the TG/DTG crude oil sample. Later, El-Shoubary [10] used the TG/DSC techniques to develop a more general kinetic model which accounts for the effect of oxygen partial pressure and surface area.

PREVIOUS KINETIC MODELS USED IN IN-SITU COMBUSTION SIMULATION

In-situ combustion is the only thermal recovery method in which a great number of chemical reactions occur. The intensity of the reactions in terms of their heat generation and kinetics determines the success or failure of the process. The kinetic model to be used should then be as consistent as possible with experimental findings.

To the best knowledge of the authors, all kinetic models used in in-situ combustion simulators assumed Arrhenius type reaction rate constants, and constant activation energies and heat of reaction. The models account for (A) light oil combustion, (B) heavy oil combustion (C) heavy oil cracking and (D) coke combustion [11] as follows

$$\phi_3 + A_1\mathrm{O}_2 \xrightarrow{R_\mathrm{A}} A_2\mathrm{CO}_x + A_3\mathrm{H}_2\mathrm{O} \tag{1}$$

$$\phi_4 + A_4\mathrm{O}_2 \xrightarrow{R_\mathrm{B}} A_5\mathrm{CO}_x + A_6\mathrm{H}_2\mathrm{O} \tag{2}$$

$$\phi_4 \xrightarrow{R_\mathrm{C}} A_7\phi_3 + A_8\mathrm{C} + A_9\mathrm{G} \tag{3}$$

$$\mathrm{C} + A_{10}\mathrm{O}_2 \xrightarrow{R_\mathrm{D}} A_{11}\mathrm{CO}_x + A_{12}\mathrm{H}_2\mathrm{O} \tag{4}$$

where ϕ_3 and ϕ_4 designate a light and heavy hydrocarbon pseudo-components representing the light and heavy ends of the crude oil respectively. C denotes the coke and G a noncondensable gas (e.g. CH_4). The A coefficients are determined by stoichiometry. The kinetic rate expressions used are:

$$R_\mathrm{A} = A_\mathrm{A} \exp(-E_\mathrm{A}/RT) y_1 P \phi \rho_\mathrm{O} S_\mathrm{O} X_1 \tag{5}$$

$$R_\mathrm{B} = A_\mathrm{B} \exp(-E_\mathrm{B}/RT) y_1 P \phi \rho_\mathrm{O} S_\mathrm{O} X_2 \tag{6}$$

$$R_\mathrm{C} = A_\mathrm{C} \exp(-E_\mathrm{C}/RT) \phi \rho_\mathrm{O} S_\mathrm{O} X_2 \tag{7}$$

$$R_\mathrm{D} = A_\mathrm{D} \exp(-E_\mathrm{D}/RT) y_1 P n_\mathrm{c} \tag{8}$$

where A_A, A_B, A_C and A_D and E_A, E_B, E_C and E_D are the frequency factors and activation energies of all four reactions respectively. y, P, ϕ, ρ_O, S_O, X_1, X_2 and n_c denote the oxygen mole fraction in the gas phase, pressure, porosity, oil density, oil saturation, light oil mole fraction, heavy oil mole fraction and coke concentration respectively.

First-order dependency of R_A, R_B, R_C and R_D on oxygen partial pressure is in agreement with some experimental findings [1,5] but disagrees with others [10]. Vaporization–condensation of water and oil is governed by a vapor–liquid equilibrium using temperature and pressure dependent equilibrium coefficients. Values of frequency factors and activation energies for all reactions are necessary in order to evaluate the reaction rate constants.

This model assumes that all reactions can occur simultaneously at any given condition of temperature and pressure. Fuel availability and oxygen partial pressure determine whether a reaction takes place or not. This model was incorporated into a one-dimensional in-situ combustion simulator. Simulation results are discussed later in this paper.

TG/DTG KINETIC MODEL DEVELOPMENT

This section briefly outlines the procedure followed in deriving the TG/DTG kinetic model. Detailed analysis of the kinetic model and the simulator can be found elsewhere [12].

Thermal analysis techniques are methods designed to study the physico-chemical changes undergone by a substance subjected to different operating conditions of temperature, pressure and surroundings. A thermogravimetric analyzer constantly measures the weight change and the rate of weight change as a function of temperature, or isothermally as a function of time, in a controlled atmosphere. A differential scanning calorimeter measures the heat per unit time generated by a sample as a function of temperature, or isothermally as a function of time, in a controlled environment.

The complex physico-chemical transitions that a crude oil undergoes in an in-situ combustion process are similar to the ones involved in TG/DTG/DSC runs generated for the crude oil involved in the presence of its native rock. Although these latter runs cannot simulate the dynamics of the in-situ combustion process, they can provide a wealth of information regarding the changes that a crude oil will undergo given certain reservoir conditions of temperature, pressure and oxygen partial pressure. The complex transitions of the crude oil are not simplified as in previous kinetic models but rather, they are included as they appear in the TG/DTG test.

Figures 1 and 2 depict the TG/DTG and DSC curves of Iola, Kansas, crude oil generated in the presence of alumina [10]. These curves were obtained by flowing 120 cm min^{-1} of air at atmospheric pressure through the sample chamber. This air flow rate is deemed appropriate to minimize

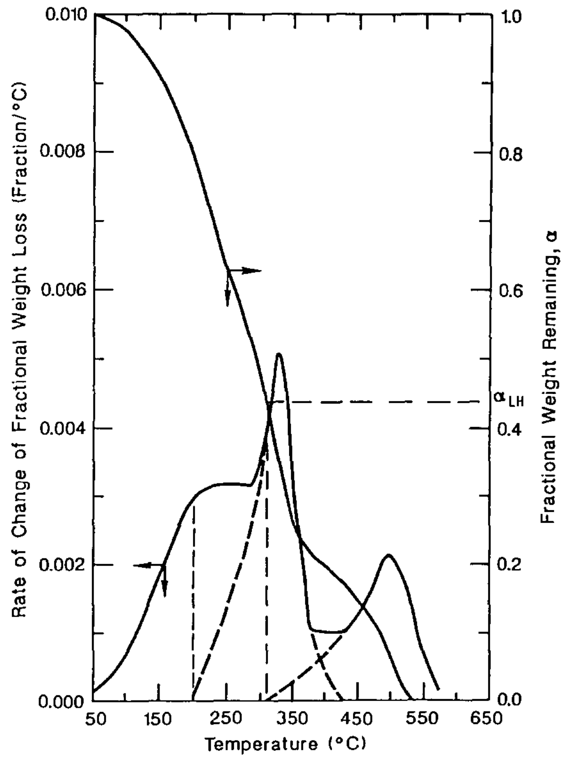

Fig. 1. TG/DTG curves for Iola, Kansas, crude oil in the presence of alumina.

external mass transfer resistance, and to ensure that the sample is always in a fresh air atmosphere. A heating rate of 10 °C $\min^{-1}$ was chosen as this rate is close to the ones recorded in in-situ combustion tube runs [13].

The TG curve (Fig. 1) represents the fractional weight remaining of crude oil sample α, and the DTG curve (Fig. 1) shows the profile of the rate of change of the fractional weight loss $-\mathrm{d}\alpha/\mathrm{d}t$ defined as

$$\alpha = (W - W_f)/(W_i - W_f) \tag{9}$$

$$\mathrm{d}\alpha/\mathrm{d}t = -[1/(W_i - W_f)](\mathrm{d}W/\mathrm{d}t) \tag{10}$$

where W, W_i and W_f are the weight remaining at time t (or temperature T), initial weight, and final weight of the crude oil sample respectively.

The DSC curve in Fig. 2 shows that the heat generation starts at around 200 °C and extends up to about 600 °C. It is thus concluded that crude oil distillation prevails up to 200 ° C, and light oil oxidation starts at around this temperature.

In this in-situ combustion simulator, the crude oil is considered as a mixture of a light and a heavy hydrocarbon pseudo-component representing the light and heavy ends of the crude oil respectively. This assumption did not produce any special incoherence when used in conjunction with the

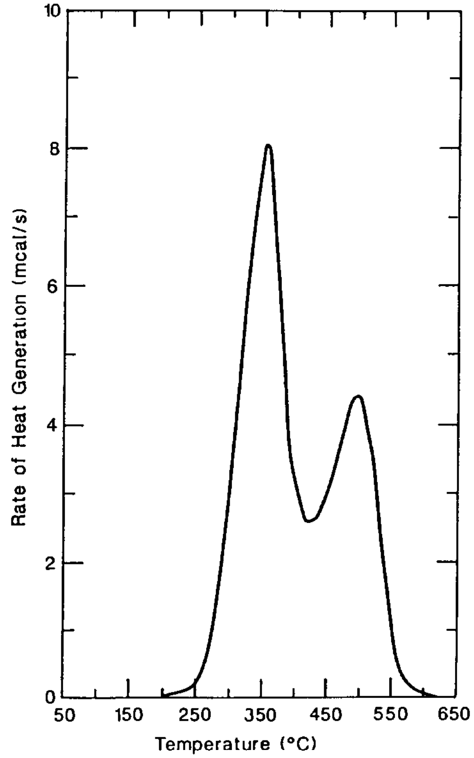

Fig. 2. DSC curve for Iola, Kansas, crude oil in the presence of alumina.

previously described in-situ combustion kinetic model, and should work equally well with the TG/DTG kinetic model.

Vossoughi et al. [7] and El-Shoubary [10] showed that the peak occurring after distillation consists of two low temperature crude oil combustion "reactions" termed as light and heavy oil combustion, and the following peak corresponds to coke combustion. Because light oil combustion, heavy oil combustion and cracking, and coke combustion can all occur simultaneously, it is necessary, for simulation purposes, to sort out the temperatures at which each type of reaction starts and terminates.

The temperatures at which the heavy oil combustion starts and terminates, 200 °C and 425 °C respectively, are determined by extending the left and right branches of the first peak in such a way that this latter is approximately symmetric, as shown in Fig. 1. Light oil combustion occurs in the region above the left branch of the first peak and is seen to start at 200 °C and end at around 312 °C. From these observations we conclude that the boiling point of the light hydrocarbon pseudo-component is in the range 25–312 °C, and that of the heavy hydrocarbon pseudo-component is in the range 200–425 °C. Octane (b.p. 125.7 °C) was selected to represent the light oil and hexadecane (b.p. 287.5 °C) was selected to represent the heavy oil.

The procedure described above applied to the second peak in Fig. 1 shows that coke combustion starts at about 312° C and terminates at a temperature close to 600 ° C. Since Vossoughi et al. [7] have shown that the crude oil can be evaporated completely in a nitrogen atmosphere, we also conclude that initially the crude oil contained virtually no coke, and that the coke combusting in the second peak was formed through cracking of the heavy oil. We assume that the cracking reactions occur simultaneously with the coke combustion reactions.

A reaction rate for the oil reservoir is defined as the product of the instantaneous molar fraction of the oil that undergoes a reaction (R) and the total amount of oil per unit reservoir volume, $\phi\rho_O S_O$, where ϕ is the porosity of the reservoir, ρ_O is the oil density and S_O is the oil saturation. The expressions for R for the four different reactions (light oil combustion, heavy oil combustion, heavy oil cracking and coke combustion) (see ref. 14) can be arrived at using the TG/DTG curves (see ref. 14). The procedure is described for the light oil combustion reaction (reaction A).

At any temperature T in the range 200–312° C, the total number of moles of oil remaining in the TG/DTG sample is given by the sum of the number of moles of light oil and heavy oil remaining at this temperature

$$N_O = N_{LO} + N_{HO} \tag{11}$$

where N_{LO} and N_{HO} are given by

$$N_{LO} = (m_s/M_{LO})\alpha_{LO} \tag{12}$$

$$N_{HO} = (m_s/M_{HO})\alpha_{HO}$$

m_s is the initial mass of the TG/DTG sample, and M_{LO} (M_{HO}) and α_{LO} (α_{HO}) are the light oil (heavy oil) molecular weight and fractional weight remaining respectively. α_{LO} and α_{HO} are identified from the DTG curve as the fractional area remaining above and below the extended left branch of the heavy oil combustion peak respectively. R then becomes

$$R = -[1/(N_O)](\mathrm{d}N_{LO}/\mathrm{d}t) \tag{13}$$

or

$$R = -[M_{HO}/(\alpha_{HO}M_{LO} + \alpha_{LO}M_{HO})](\mathrm{d}\alpha_{LO}/\mathrm{d}t) \tag{14}$$

Note that R is independent of the initial sample mass, and that the time derivative is easily transformed into a temperature derivative since the heating rate in the TG/DTG experiments was kept constant. The derivative is evaluated by numerical differentiation of α_{LO} at various temperatures in the range 200–312° C.

The reaction rates determined from above are not applicable in a reservoir because, contrary to the TG/DTG experiments, the partial pressure of oxygen is not constant and varies widely with location. Since evidence in the literature [2,10] suggests that the light oil combustion reaction rate is proportional to the oxygen partial pressure, the light oil combustion reaction rate becomes

$$R_A = R(\phi \rho_O S_O) P_R / P_G \tag{15}$$

where P_R and P_G are the oxygen partial pressure in the reservoir and oxygen partial pressure in the TG/DTG experiments (0.21 atm) respectively.

The same logic as above was applied to the rest of the reactions in order to determine their kinetics [12,14].

RESULTS AND ANALYSIS

Guvenir [13] constructed an automated in-situ combustion assembly to study the effect of clay on the dry forward in-situ combustion process. He performed experiments on a crude oil from Iola, Kansas. The combustion tube consisted of a well insulated high pressure, 40 in cylinder. The temperature at several equidistant thermocouples placed along the combustion tube, along with the oxygen and CO_2 composition at the production end were recorded. Guvenir's experimental run VI was simulated using both the previously described Crookston's power law kinetic model [11] and the TG/DTG kinetic model. This run was chosen because of the availability of both the TG/DTG curves and the in-situ combustion results of the same crude oil. Physical property data were either taken from Guvenir's dissertation or estimated using appropriate correlations. All parameters used with both simulators are the same except for the kinetic model. A list of these parameters is given in ref. 14, page 179.

SIMULATION OF GUVENIR'S EXPERIMENT USING THE POWER LAW KINETIC MODEL

For simulation purposes, the combustion tube was divided into 10 equal length grid block cells. At each grid block, the simulator solves simulta-

TABLE 1

Activation energies used in the model

Reaction type	A	B	C	D
E used in the model (Btu/lb mol)	30000	30000	30000	15000
Actual E from TG/DSC model [10]	60000	62000	N.A. [a]	53000

[a] N.A., Not available.

neously 8 equations expressing molar balances for light oil, heavy oil, water, oxygen and non-condensable gases, the oil mole fraction constraint (light oil mole fraction + heavy oil mole fraction = 1), and an overall energy balance. Preliminary simulation runs using reasonable values of activation energies failed to produce a self sustaining combustion front. Activation energies, E, of all four reactions were then arbitrarily lowered to unreasonable values, as shown in Table 1, in order to have as good a match with the experimental results as possible.

This type of simulation difficulty was also reported by Rubin and Vinsome [15]. Simulation results are discussed in the following section.

SIMULATION RESULTS USING THE TG/DTG KINETIC MODEL

Figures 3 and 4 depict the temperature profiles at cells 3 and 7 throughout the duration of the process, obtained (1) experimentally, (2) using the previous kinetic model, and (3) using the TG/DTG kinetic model. All three profiles are seen to agree on the steam plateau temperature (160 °C at 200 lbf in^{-2}). As the reactions start taking place (~ 200 °C), sharp increases in temperature are observed in all three profiles. When coke combustion is terminated (330 °C), temperature changes become less pronounced. We

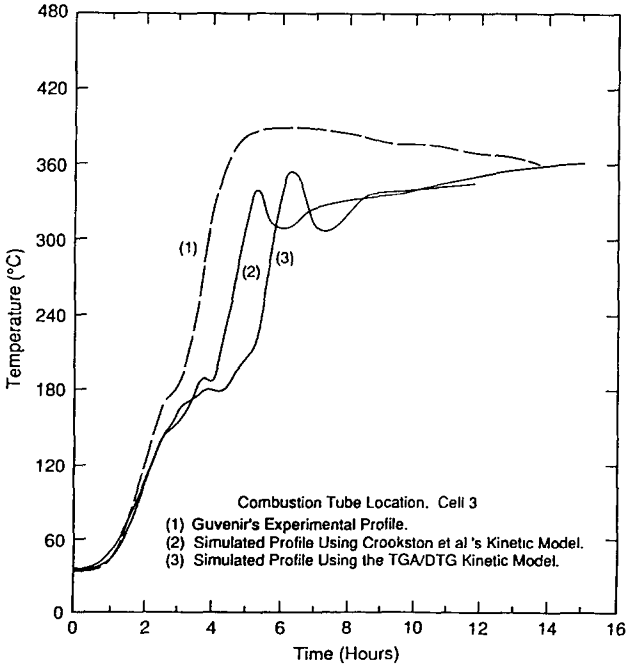

Fig. 3. Temperature profiles at cell 3.

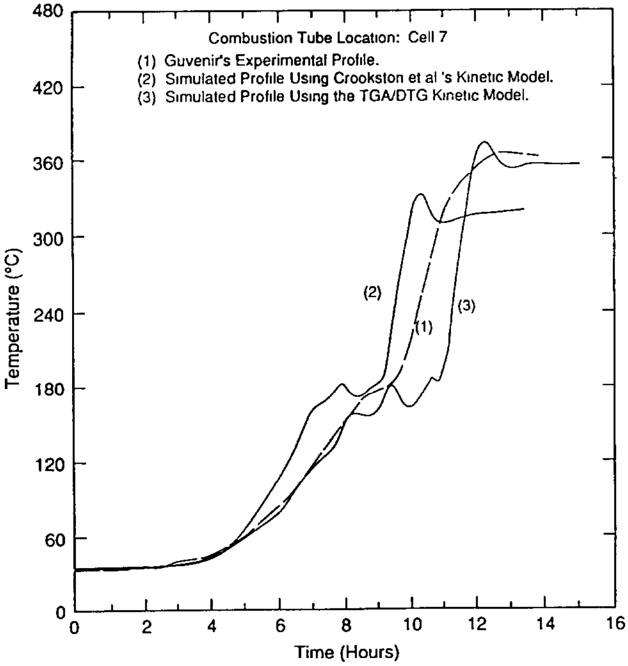

Fig. 4. Temperature profiles at cell 7.

observe that coke combustion terminates at a lower temperature than in the TG/DTG run (600 ° C) owing to the fact that both the total concentration of coke laid down in a combustion cell, as well as the oxygen mole fraction in this cell, which account for the rate of coke combustion, are different from those in a TG/DTG run. A requirement of our model, however, is that coke combustion can not start below a temperature of 312 ° C.

The simulated temperature profile using the power law model of Crookston et al. is seen to start out closer to the experimental profile than the TG/DTG model does, as evidenced by the profile at cell 3 on Fig. 3. However, as the combustion peak proceeds through the combustion tube (cell 7), we observe that the proposed TG/DTG model predicts the experimental temperature profile better than the power law model. The average front temperature between cells 3 and 10 of the experimental run, the simulated run using the TG/DTG kinetic model, and the simulated run using that kinetic model of Crookston et al. are approximately 363, 360 and 332 ° C respectively. Summarized results given in Table 2 also attest the superiority of the TG/DTG model in predicting the experimental run time and carbon combustion rate.

We conclude that, overall, the TG/DTG model approach to determining the kinetics of the in-situ combustion process is superior to the previous semi-empirical approach. More importantly, this new approach necessitates only the TG/DTG curve of the crude oil in question, whereas the Arrhenius

TABLE 2

Comparison of simulated and experimental results

	Average exit O_2 mole fraction	Average front temperature (°C)	Steam plateau temperature (°C)	Average front velocity (in h^{-1})	Carbon combustion rate (g h^{-1})	Run completion time (h)
Guvenir's results [13]	0.0300	363	160	2.35	13.0	17.0
Using model of Crookston et al. [11]	0.0443	360	160	3.0	6.72	13.3
Using the TG/DTG model	0.0580	332	160	2.6	10.2	15.1

type kinetic model requires activation energies and frequency factors that are usually difficult to determine. A new successful approach to in-situ combustion simulation is thus introduced.

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