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## Determination of Heat of Biomass Pyrolysis and Particle Residence Time under Isothermal and Non-Isothermal Heating Conditions

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### ABSTRACT

The experimental investigations for determination of heat of pyrolysis have given quite different results due to the influence of the experimental conditions on the measured heat of pyrolysis of biomass. Consequently, a theoretical investigation into the process is required. Therefore, this paper presents analytical model for the determination of heat of biomass pyrolysis and particle residence time under isothermal and non-isothermal heating conditions. The developed analytical solutions are used to investigate the effects of heating conditions on the heat of biomass pyrolysis and particle residence time. From study, it is established that the heat of the pyrolysis first showed endothermic peaks and followed by exothermic peaks at different temperatures for the different heating rates. Also, as the heating rate increases, the particle residence time in the reactor decreases and high heating rates favoured the production of tar and gas. The length of heating and its intensity affect the rate, extent and sequence of pyrolysis reactions, and composition of the resultant products.

**Keywords:** Biomass particle; Heat of Pyrolysis; Isothermal temperature; Non- Isothermal heating rates; Residence time

### 1. INTRODUCTION

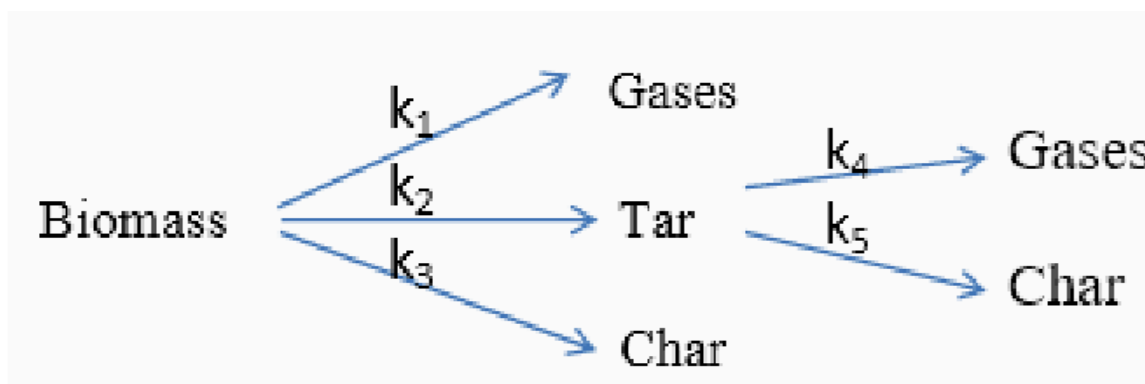
The quest for an improved efficiency of thermomechanical conversion processes of biomass pyrolysis and gasification technologies require detailed knowledge and proper

understanding of biomass thermochemical conversion processes. Indisputably, the required improved efficiency of the conversion processes can be achieved through a detailed analysis of the processes [1-3]. Obviously, in such analysis, the determination of the heat of biomass pyrolysis which has significant effects on the thermal conversion and the final products is a very important. Consequently, various experimental investigations have been carried out to determine heat of biomass pyrolysis [4-9].

However, different results of heat of biomass pyrolysis have been recorded from endothermic to large values of exothermic reactions. This might be due to the secondary pyrolysis reaction between the volatiles and the primary char as well as autocatalytic effects (as a result of impurities). Moreover, quite different results were obtained in this kind of experiments due to the influence of the experimental conditions on the measured heat of pyrolysis of biomass [1]. Consequently, a theoretical investigation into the process is required. To the best of authors' knowledge, a study in open literature on the theoretical determination of the heat of biomass pyrolysis is very scarce. Therefore, this work presents the development of analytical models for the determination of heat of biomass pyrolysis and particle residence time under isothermal and non-isothermal heating conditions. Effects of heating conditions on the heat of biomass pyrolysis and particle residence time are investigated and discussed.

## 2. MODEL DEVELOPMENT FOR THE BIOMASS PYROLYSIS PROCESS

The kinetic scheme that describes the processes of primary and secondary pyrolysis is shown in Fig. 1. The primary pyrolysis process involves thermal decomposition of biomass into gases, tar (liquid product of biomass pyrolysis, known as bio-oil or pyrolysis oil) and char (charcoal, the solid product) while in the secondary pyrolysis, the tar further decomposes into char and gases. This is a two-stage parallel reaction that has previously been used by other researchers [10-16]. According to Prakash and Karunanithi [9], the two stage model is the most classical models for wood pyrolysis. The mathematical model describing this type of reaction is given in Eqs. (1a-1d)



**Fig. 1.** Two-stage parallel reaction model of biomass pyrolysis

The kinetic equations of pyrolysis are given as

$$\frac{\partial C_B}{\partial t} = -(k_1 + k_2 + k_3)C_B \quad (1a)$$

$$\frac{\partial C_T}{\partial t} = k_2 C_B - \varepsilon(k_4 + k_5)C_T \quad (1b)$$

$$\frac{\partial C_C}{\partial t} = k_3 C_B + \varepsilon k_5 C_T \quad (1c)$$

$$\frac{\partial C_G}{\partial t} = k_1 C_B + \varepsilon k_4 C_T \quad (1d)$$

where:

$$k_i = A_i \exp\left[\left(\frac{-E_i}{RT}\right)\right] \quad i = 1-5$$

The above kinetics models show that when the biomass was heated, it decomposes into gases, tar and char. The decomposition equation which is a result of the primary pyrolysis is shown in Eq. (1a). The tar further decomposes into char and gases where the decomposition equation is shown in Eq. (1b). This is a result of the secondary pyrolysis. The formations of char and gas from the primary and secondary reactions are shown in Eq. (1c) and (1d).

The initial conditions are:

$$t = 0, C_B = C_{B0}, \quad C_C = C_G = C_T = 0 \quad (2)$$

The above initial conditions depict that before the thermal decomposition, there is no formation of char, tar and gas. However, the concentration of the biomass is  $C_{B0}$  at the commencement of the pyrolysis.

For the Isothermal condition,  $T = T_o$

$$k_i = A_i \exp\left[\left(\frac{-E_i}{RT_o}\right)\right] \quad i = 1-5 \quad (3)$$

There exists a linear relationship between the temperature and time under the non-isothermal heating condition. Therefore, we have

$$T = T_p + \beta t \quad (4)$$

where:  $T_p$  is the initial/pre-heating temperature in  $K$ ,  $\beta$  is the heating rate in  $K/s$  (change in temperature to change in time) and  $t$  is the time in  $s$ .

For the non-isothermal process, we have

$$k_i = A_i \exp\left[\left(\frac{-E_i}{R(T_p + \beta t)}\right)\right] \quad i = 1-5 \quad (5)$$

The above kinetic models are non-dimensionalized as using the following dimensionless parameters;

$$\begin{aligned} \bar{C}_B &= \frac{C_B}{C_{Bo}} & \bar{C}_{G1} &= \frac{C_{G1}}{C_{Bo}} & \bar{C}_{C1} &= \frac{C_{C1}}{C_{Bo}} \\ \bar{C}_{G2} &= \frac{C_{G2}}{C_{Bo}} & \bar{C}_{C2} &= \frac{C_{C2}}{C_{Bo}} & C_{C2} &= \frac{\bar{C}_{C2}}{C_{Bo}} \end{aligned} \tag{6}$$

The dimensionless forms of Eqs. (1a-1d) are the same as the dimensional forms in Eq. (1a-1d) when the bar on the dimensionless forms are removed for the sake of cleanliness. In order to avoid repetition or writing seemingly similar equations, the non-dimensional forms of Eqs. (1a-1d) are not written out in this work.

The heat of biomass pyrolysis could be modeled as

$$Q_{reaction} = \sum_{i=1}^3 k_i C_B \Delta h_i + \sum_{i=4}^5 k_i C_T \Delta h_i \tag{7}$$

### 3. ANALYTICAL SOLUTIONS TO THE KINETICS MODELS

The exact analytical solutions using Laplace transform have been developed for Eqs. (1a)-(1d) subject to isothermal condition as:

$$C_B = C_{Bo} e^{-((k_1+k_2+k_3)t)} \tag{8a}$$

$$C_T = \frac{k_2 C_{Bo} \left[ e^{-((k_1+k_2+k_3)t)} - e^{-\varepsilon(k_4+k_5)t} \right]}{\varepsilon(k_4+k_5) - (k_1+k_2+k_3)} \tag{8b}$$

$$C_C = C_{Bo} \left\{ \frac{k_3 \left( 1 - e^{-((k_1+k_2+k_3)t)} \right)}{(k_1+k_2+k_3)} - \frac{\varepsilon k_2 k_5 \left[ \frac{\left( 1 - e^{-((k_1+k_2+k_3)t)} \right)}{(k_1+k_2+k_3)} + \frac{\left( 1 - e^{-\varepsilon(k_4+k_5)t} \right)}{\varepsilon(k_4+k_5)} \right]}{\varepsilon(k_4+k_5) - (k_1+k_2+k_3)} \right\} \tag{8c}$$

$$C_G = C_{Bo} \left\{ \frac{k_1 \left(1 - e^{-(k_1+k_2+k_3)t}\right)}{(k_1+k_2+k_3)} - \frac{\varepsilon k_2 k_4 \left[ \frac{\left(1 - e^{-(k_1+k_2+k_3)t}\right)}{(k_1+k_2+k_3)} + \frac{\left(1 - e^{-\varepsilon(k_4+k_5)t}\right)}{\varepsilon(k_4+k_5)} \right]}{\varepsilon(k_4+k_5) - (k_1+k_2+k_3)} \right\} \quad (8d)$$

Equ. (7) could be expanded as

$$Q_{pyrolysis} = k_1 C_B \Delta h_1 + k_2 C_B \Delta h_2 + k_3 C_B \Delta h_3 + k_4 C_T \Delta h_4 + k_5 C_T \Delta h_5 \quad (9)$$

Substituting Eq. (8a) and (8b) into Eq. (9), one arrives at

$$Q_{pyrolysis} = C_{Bo} \left\{ \left( k_1 \Delta h_1 + k_2 \Delta h_2 + k_3 \Delta h_3 \right) e^{-(k_1+k_2+k_3)t} + \frac{\left( k_4 \Delta h_4 + k_5 \Delta h_5 \right) k_2 \left[ e^{-(k_1+k_2+k_3)t} - e^{-\varepsilon(k_4+k_5)t} \right]}{\varepsilon(k_4+k_5) - (k_1+k_2+k_3)} \right\} \quad (10)$$

where:

$$k_i = A_i \exp \left[ \left( \frac{-E_i}{RT_o} \right) \right] \quad i = 1-5$$

For isothermal condition

and

$$k_i = A_i \exp \left[ \left( \frac{-E_i}{R(T_p + \beta t)} \right) \right] \quad i = 1-5$$

For non-Isothermal condition

**Table 1.** Kinetic constants used in the simulations

i	Reaction	A <sub>i</sub> (s <sup>-1</sup> )	E <sub>i</sub> (kJ/mol)	Source
1	Biomass→Gas	1.3×10 <sup>8</sup>	140	[18]
2	Biomass→Tar	2.0×10 <sup>8</sup>	133	[18]

3	Biomass→Char	$1.08 \times 10^7$	121	[18]
4	Tar→Gas	$4.28 \times 10^6$	107	[19]
5	Tar→Char	$1.0 \times 10^6$	107	[19]

**Table 2.** Change in enthalpy values used in the simulations.

i	Reaction	$\Delta h_i$ (kJ/kg)	Source
1	Biomass→Gas	-418.0	[18]
2	Biomass→Tar	-418.0	[18]
3	Biomass→Char	-418.0	[18]
4	Tar→Gas	42.0	[19]
5	Tar→Char	42.0	[19]

#### 4. RESULTS AND DISCUSSION

Following the two-stage parallel reaction model in Fig. 1, it has been stated that as the biomass particle is heated and its temperature increases, thermal decomposition occurs according to primary reactions giving out gas, tar and char as products. Sequentially, a secondary reaction occurs where the tar decomposes to give out gas and char. Based on the fact that the amounts of each of biomass pyrolysis product vary depending mainly on the zone temperature, the influences of heating conditions on the heat of biomass pyrolysis and the particle residence time are investigated.

Fig. 2 depicts the effects of heating rate on the heat of pyrolysis. The heat of the pyrolysis first shows endothermic peaks and follows by exothermic peaks at different temperatures for the different heating rates. It can be stated that the first set of peaks (endothermic peaks) corresponds to the main pyrolysis process, while the second set of peaks (exothermic peaks) are due to the small weight loss step between the range of temperatures shown in the figure. It should be noted that the higher temperatures correspond to the char stabilization step. An endothermic thermal effect prevails in the initial stage of the primary pyrolysis process. The secondary reactions of non-volatile primary decomposition products are exothermic and influence the global heat of wood pyrolysis [17]. The presence of two separate reaction steps with different heats of reactions and the exothermicity of secondary char graphitization have been reported in literatures [17]. Figs. 3-6 show that as the heating rate increases, the particle residence time in the reactor decreases and high heating rates favours the production of tar and gas. Therefore, as shown in the Table, length of heating and its intensity affect the rate, extent and sequence of pyrolysis reactions, and composition of the resultant products.

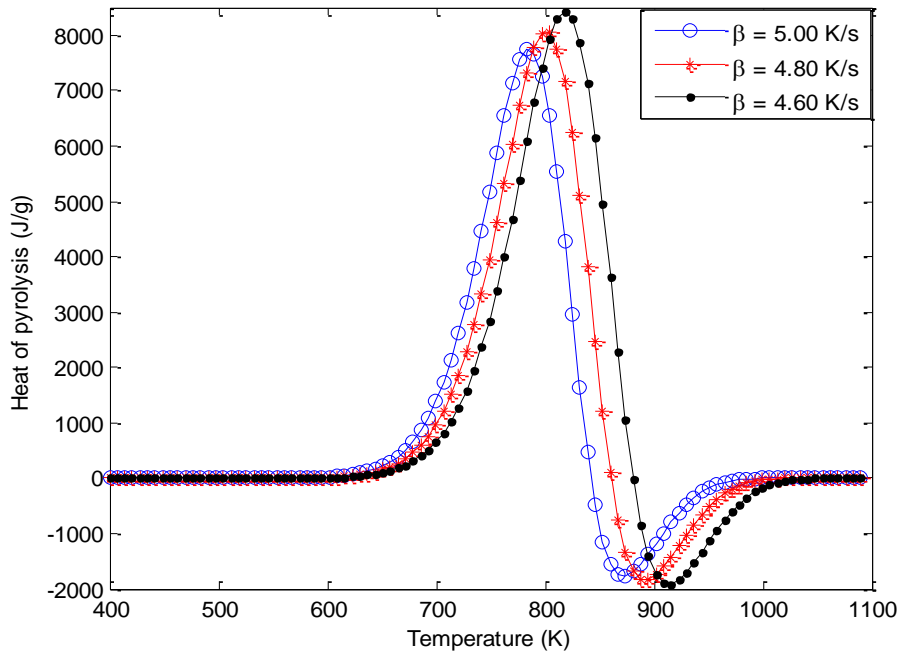


Fig. 2. Effects of heating rate on heat of pyrolysis

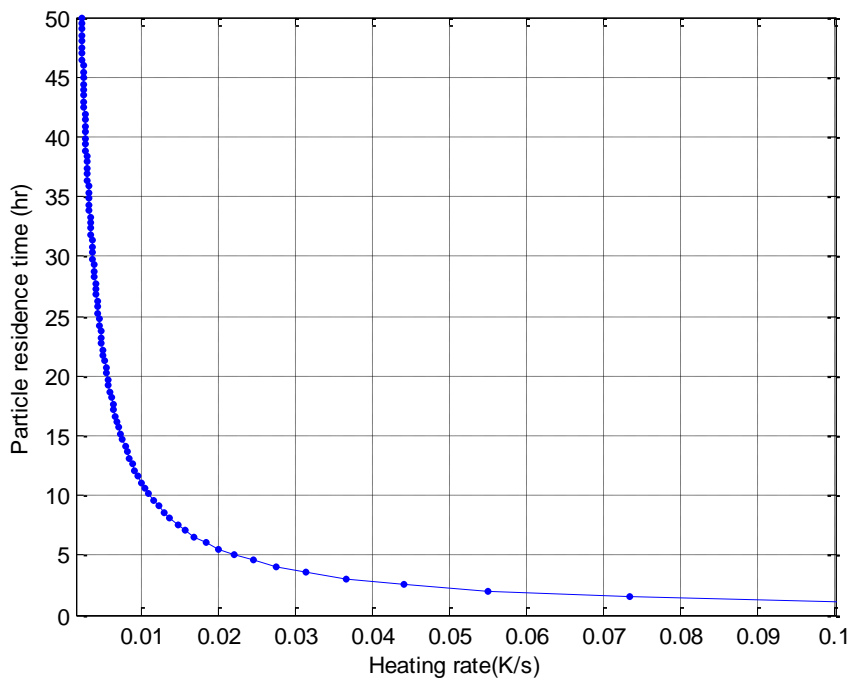
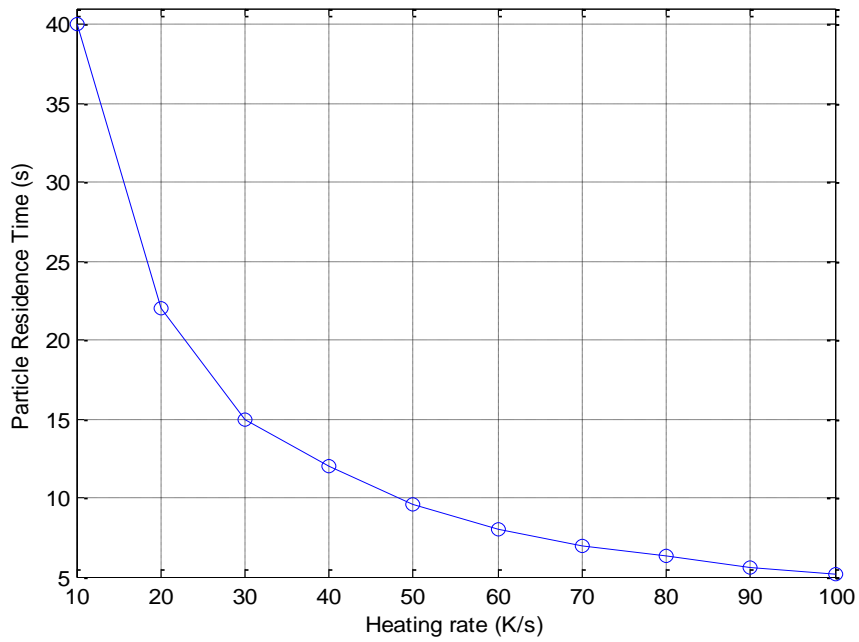
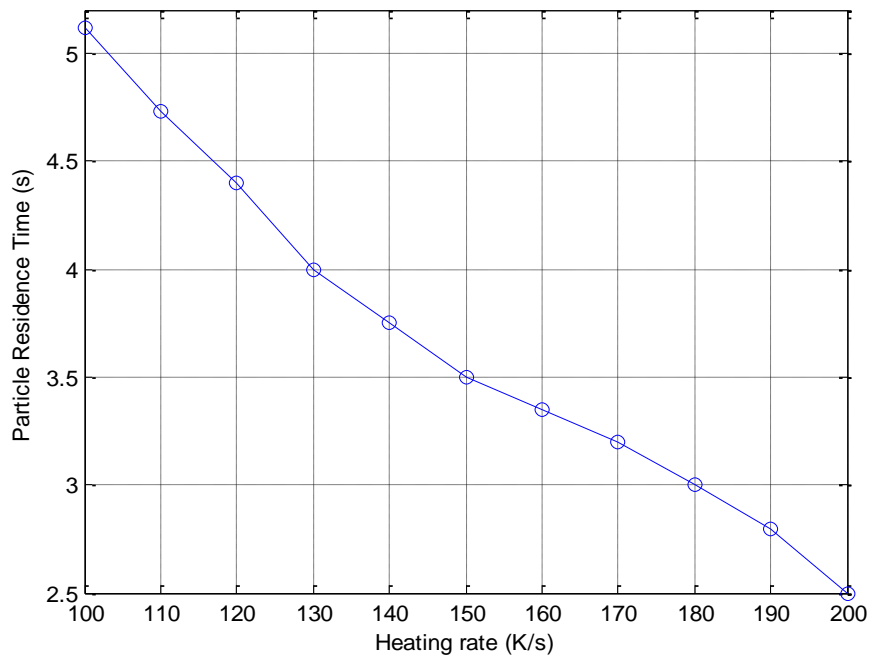


Fig. 3. Variations of biomass particle residence time very low heating rates

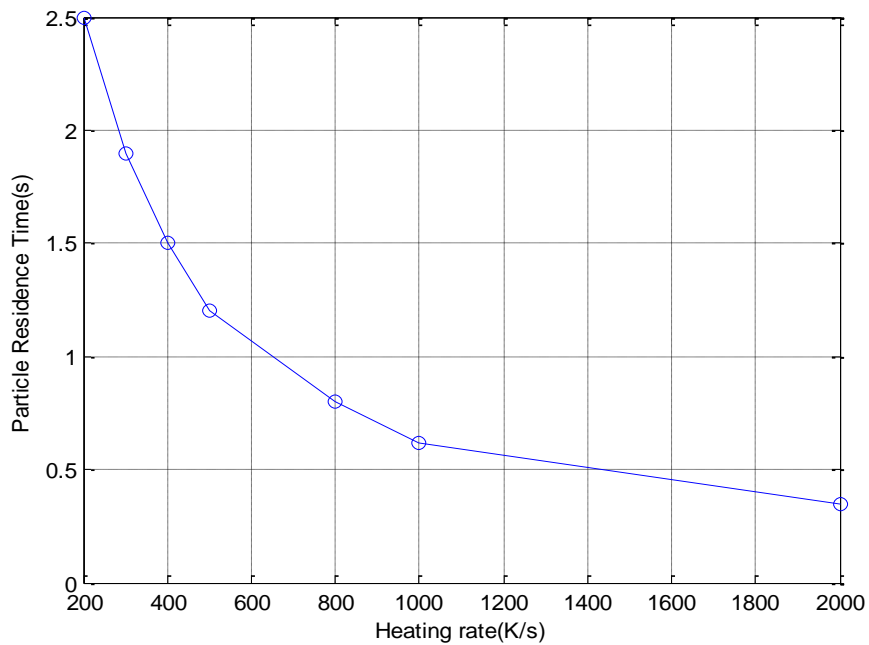


**Fig. 4.** Variations of biomass particle residence time with heating rates of 10-100K/s



**Fig. 5.** Variations of biomass particle residence time heating rates of 100-200K/s





**Fig. 6.** Variations of biomass particle residence time with heating rates 200-200K/s

**Table 3.** Pyrolysis conditions for different pyrolysis technologies

Pyrolysis technology	Residence time	Heating rate	Temperature (°C)	Product
Carbonization	days	very low	400	charcoal
Conventional	5-30 min	low	600	oil, gas, char
Fast	0.5-5s	very high	650	bio-oil
Flash-liquid	< 1s	high	< 650	bio-oil
Flash-gas	< 1s	high	< 650	chemicals, gas
Ultra	< 0.5s	very high	1000	chemicals, gas
Vacuum	2-30 s	medium	400	bio-oil
Hydro-pyrolysis	< 10s	high	< 500	bio-oil
Conventional	< 10s	high	< 700	chemicals

## 7. CONCLUSIONS

In this work, analytical model of heat of pyrolysis under isothermal and non-isothermal heating conditions has been presented. The developed analytical solutions are used to investigate the effects of heating conditions on the heat of biomass pyrolysis and particle residence time.

The heat of the pyrolysis first showed endothermic peaks and followed by exothermic peaks at different temperatures for the different heating rates. Also, as the heating rate increases, the particle residence time in the reactor decreases and high heating rates favoured the production of tar and gas.

The length of heating and its intensity affect the rate, extent and sequence of pyrolysis reactions, and composition of the resultant products. The work has a lot of practical importance and physical significance in industrial pyrolysis and in the design of biomass gasifiers or reactors

### Nomeclature

$A_1; A_2; A_3; A_4; A_5$  frequency factor, 1/s

$Bi_m$  Modified Biot number

$C$  concentration,  $kg/m^3$

$E$  activation energy, J/mol

$K$  thermal conductivity, W/mK

$k_1; k_2; k_3; k_4; k_5$  rate constants, 1/s

$Q$  heat of pyrolysis, J/Kg

$R_g$  universal gas constant, J/mol

$t$  time, s

### Subscripts

B virgin biomass

G gases

C char

T tar

G gas

o initial

f final

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