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RESEARCH ARTICLE

Experimental Investigation of Pyrolysis Process of Agricultural Biomass Mixture

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Abstract

This paper describes an experimental investigation of pyrolysis process of agricultural biomass mixture, without the addition of inert gas. The mixture consists of corn stalk, wheat straw, soy straw and oat straw with equal mass fractions. During the experiment, the mass of biomass sample inside the reactor was 10 g with a particle diameter of 5-10 mm. The sample in the reactor was heated in the temperature range of 24-650ºC at average heating rates of 21, 30 and 54ºC/min. The sample mass before, during and after pyrolysis was determined using a METTLER P1000 digital scale. Experimental results of the sample mass change indicate that the highest yield of pyrolytic gas, achieved at 650ºC, was in the range from 74 to 81%, while char yield ranged from 19 to 26%. Heating rate of biomass mixture sample has significant influence on the pyrolytic gas and char yields. It was determined that higher heating rates in the reactor induce higher yields of pyrolytic gas, while the char mass reduces. Condensation of pyrolytic gas at the end of the pyrolysis process at 650ºC produced 1.3-1.8 g of liquid phase. The results obtained represent a starting basis for determining material and heat balance of pyrolysis process as well as agricultural biomass pyrolysis equipment.

Keywords

pyrolysis · agricultural biomass mixture · reaction temperature · gas yield

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1 Introduction

Biomass can be defined as matter composed of plant material, including products, by-product, waste and residues of the plants. Biomass is a renewable energy source which can be used as a substitute for fossil fuels. In Vojvodina (Republic of Serbia), the most common are plant residues in agricultural production. Energy balance plan for Vojvodina predicts that the content of solid biomass, principally harvest residues, is around $35000 \cdot 10^{12}$ J of heat and 360 GWh of electrical energy per year [1]. Table 1 reviews biomass potential based on agricultural production in Serbia.

Tab. 1. Review of agricultural biomass potential in the Republic of Serbia [2]

Crop	Acreage 10^3 ha	Yield t/ha	Total biomass 10^3 t
Wheat	850	3.5	2975.00
Barley	165	2.5	412.50
Oat	16	1.6	25.60
Rye	6	2.0	12.00
Corn	1300	5.5	7150.00
Sunflower	200	4	800.00
Soy	80	4	320.00
Rapeseed	60	5	300.00
Hop	1.5	1.6	2.40
Tobacco	3	1.0	3.00
Orchards	275	1.05	288.75
Vineyards	75	0.95	71.25
Total	3031.50	32.70	12360.50

The main area for crops production is the northern part of the country (Vojvodina), with production of corn, soy, barley, rye, wheat and other (Fig. 1).

There is a significant difference in the quality of agricultural biomass depending on the regions and seasons. Table 2 shows proximate analysis of the agricultural biomass from different regions in the Republic of Serbia. The same table also shows melting temperatures of ash for the discussed biomass that

Tab. 2. Proximate analysis of agricultural biomass in the Republic of Serbia [5]

	Soy straw	Rapeseed	Wheat straw	Corn stalks
Moisture, W (wt%)	8.35-39.95	8.84-18.19	8.28-9.90	7.26-9.79
Ash, A (wt%)	3.92-15.82	3.95-5.88	5.89-12.53	2.26-5.52
Fixed carbon, C_{fix} (wt%)	14.06-20.27	17.88-18.52	18.15-18.29	14.45-17.95
Volatiles (wt%)	69.06-81.40	76.24-77.53	69.18-75.96	76.52-80.67
t_1 - sintering temperature (°C)	1185	1100	880	1010
t_2 - softening temperature (°C)	1310	1270	920	1040
t_3 - hemisphere temperature (°C)	1420	1400	1100	1075
t_4 - flow temperature (°C)	1450	1420	1160	1100

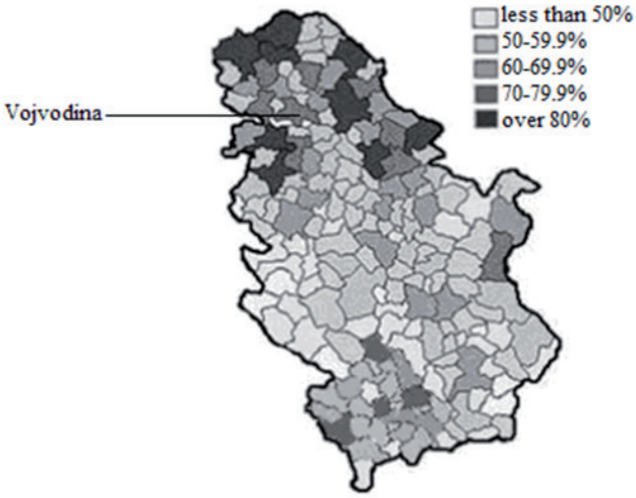

Fig. 1. The geographic distribution of biomass energy potential in Serbia [3, 4]

are determined by using the standard SRPS CEN/TS 15370-1:2009. It can be seen that all biomass species have different mass fractions of moisture, ash and volatile matter. Judging by the value of ash melting temperature, wheat and soy straw are significantly different in the way that soy straw has high values of melting temperature, while wheat straw has lower values. This can adversely influence the combustion process of agricultural biomass and its utilization. A large number of authors investigate this issue and there is a lot of different literature data on biomass chemical composition. From the aspect of biomass combustion kinetics and process modelling, the most important data refer to mass ratio of volatiles and char content. [6-8]

The main biomass thermal conversion processes are combustion, gasification, pyrolysis and liquefaction. Pyrolysis of biomass is the heating of solid biomass in an inert atmosphere to produce gaseous products (mainly CO_2, H_2, CO, CH_4, C_2H_2, C_2H_4, C_2H_6, benzene etc.), liquid products (tars, high molecular hydrocarbons and water) and solid products (char). Experimental study of biomass pyrolysis process has been carried out by many researchers [9-13].

Slow pyrolysis (slow heating rate) has been practiced for many years and requires relatively slow reactions at low temperatures to maximize solid char yield. A number of different approaches are being developed in order to optimize an efficient pollution-free system [9].

Liquid fuel production by fast pyrolysis is a promising technology. High yields of liquid products can be obtained under optimized conditions of pyrolysis process. Pyrolysis oil consists of water and a complex mixture of organic compounds that are condensed and collected after the pyrolysis step. The time and temperature profile between formation of pyrolysis vapours and their quenching influences the composition and quality of the liquid product [10].

Shuangning et al. [11] studied the kinetics of corn stalk pyrolysis. Kinetic parameters were determined (activation energy E = 33.74 kJ/mol and frequency factor k_0 = 1013 s^{-1}) in the temperature range of 477-627°C. Mani et al. [12] are also investigating kinetic parameters of wheat straw pyrolysis. They were considering three stages of wheat straw pyrolysis process (Stage 1, Stage 2, Stage 3). The stage 1 represents drying, which is not considered as part of pyrolysis process. The kinetic parameters, such as activation energy (kJ/mol), frequency factor (l/min) and order of the reaction for the three stages considered were: E_1=69 kJ/mol, E_2=78 kJ/mol, E_3=80 kJ/mol, $k_{01}=2.57\cdot10^{12}$, $k_{02}=3.97\cdot10^{7}$, $k_{03}=3.17\cdot10^{6}$, n_1=2.3, n_2=0.65, n_3=0.27, respectively. It was noted from the order of the reaction that the second stage of the pyrolysis curve corresponds to the degradation of cellulose and hemicellulose, and the third stage to the lignin degradation. The same authors discussed the effect of reaction temperature on oat straw pyrolysis products [13]. They noted that bio-oil yield increased at lower temperatures (40.5% at 450 °C), while the pyrolysis gas yield (42% at 550 °C).

The literature data [9-24] on pyrolysis modelling and kinetics cannot anticipate precisely enough the yield and distribution of pyrolysis products. Mehrabian et al. [25] utilised a one-dimensional single particle model to investigate the effects of radiation temperature, moisture content, particle size and biomass physical properties on the heating rate in biomass particles during pyrolysis. It was shown that the heating rate is mainly affected by the radiation temperature and the particle size.

Tab. 3. Proximate and ultimate analysis of agricultural biomass [28]

	Proximate analysis				Ultimate analysis (wt%, dry basis)					
	Moisture	Ash*	Fixed carbon C_{fix}	Volatiles	Carbon C	Hydrogen H	Nitrogen N	Total Sulphur S	Oxygen O**	Lower heating value H_d (kJ/kg)
Corn stalk	13.17	11.52	16.60	60.23	48.23	8.18	0.81	0.18	31.08	16291
Wheat straw	14.77	7.80	16.35	62.23	48.23	8.30	1.09	0.19	34.38	16590
Soy straw	12.08	3.02	18.74	66.52	53.05	7.78	0.89	0.16	35.10	17465
Oat straw	12.22	15.06	15.38	59.18	44.82	7.88	1.20	0.14	30.89	16676

*Dry basis

** Oxygen content was calculated

Reviewed literature doesn't provide data on gas chromatography and thermogravimetric analysis of pyrolysis process of agricultural biomass mixture. Hence, the scope of this paper is to investigate the influence of pyrolysis temperature and heating rate on pyrolytic gas and char yields of biomass mixture. This kind of investigation is very imoportant for national economy of the Republic of Serbia considering high yields of agricultural biomass. In addition, the Republic of Serbia is interested in admittance to European Union (EU) and signed Memorandum of Integration into the EU energy market. Thus, it accepted the obligation to follow EU politics and programmes. In order to achieve that, it is necessary to create technical and economical conveniences from using agricultural biomass to stimulate electricity production.

2 Apparatus and Experimental Procedures

2.1 Raw material

Agricultural biomass from Vojvodina (Republic of Serbia) was used as experimental sample. The sample is a mixture of four different kinds of agricultural biomass (corn stalk, wheat straw, soy straw and oat straw) equal mass fractions (2.5 g of each kind). Proximate and ultimate analysis of agricultural biomass was performed at the Institute of Lowland Forestry and Environment, University of Novi Sad. The results of biomass composition analysis are presented in Table 3. The analysis was determined according to ASTM standards [26, 27].

2.2 Experimental facility for agricultural biomass pyrolysis

The scheme of laboratory facility used for the pyrolysis of agricultural biomass mixture and the data collected at measuring points (M.P.) are demonstrated in Fig. 2. The laboratory facility is designed and constructed in the Institute for Energetics, Process Technique and Protection of Environment at the Faculty of Technical Sciences in Novi Sad. The facility was previously used for the investigation of the corn stalk pyrolysis [29]. During the construction of experimental facility, materials resistant to high temperatures were used as well as materials resistant to corrosion.

The construction of furnace and reactor enable examining of batch (non-continuous) pyrolysis, combustion and gasification processes with maximum reaction temperature of 700 ºC. Light furnace isolation and small reactor mass also enable sample measuring during the experiment. The electrical furnace, with 410 mm of height, outer diameter of 320 mm and inner diameter of 150 mm, is coated with insulant (rock mineral wool) and surrounded by three separately controlled electrical heaters with total power of 4.5 kW which heat the reactor vessel with the biomass sample to the desired temperature. Reactor vessel for the biomass is 200 mm high and with inner diameter of 72 mm.

During the experimental investigation of biomass pyrolysis process, the following instruments were used:

– *Measuring the sample mass*

Instrument: Digital scale METTLER P1000
Measurement range: 0-1000 g
Measuring error: 1000 g ± 1 g

– *Measuring the temperature of pyrolysis gas*

Instrument: Digital temperature sensor Testo 925 with type K probe (NiCr – Ni)
Measurement range: 50-1000 °C
Measuring error: ±0.2%

During the experimental investigation of pyrolysis process of agricultural biomass mixture (without the addition of inert gas), initial sample mass was 10 g with particle diameter of 5-10 mm. The mixture samples were placed into the biomass sample container and then into the electrical furnace. The heating process was performed by using electrical heaters, and after achieving the temperature of 650°C, that temperature was maintained within a narrow range around 650°C until the sample mass in the reactor stabilized. The container with the biomass sample was attached to the scale by means of a flexible connection between the scale and the container. During the heating process, the relationship between changes in mass, temperature and time was annotated. After the experiment, char and liquid phase mass were measured.

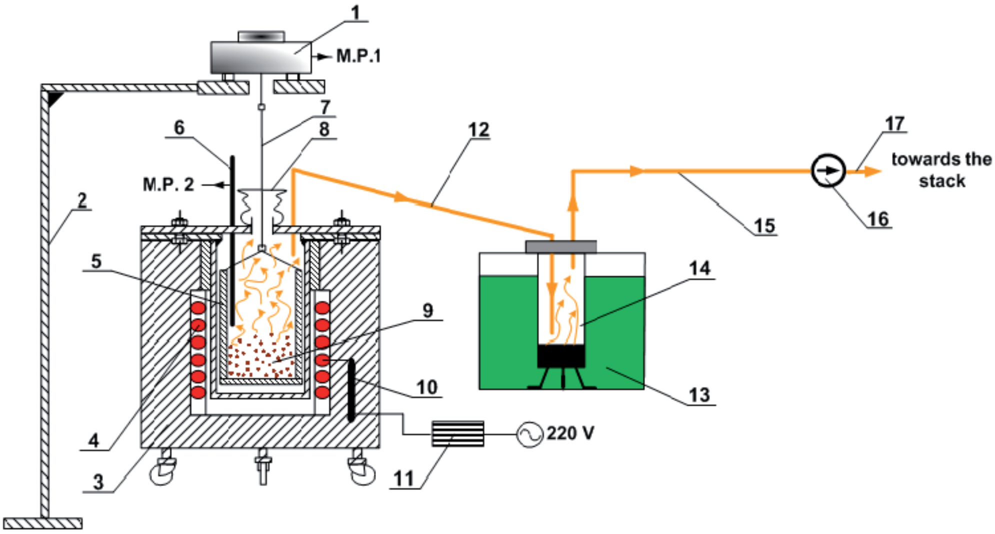

Fig. 2. The scheme of experimental facility (and metering points) for agricultural biomass pyrolysis

(1) – digital scale, (2) – scale stand, (3) – electrical furnace, (4) – electrical heaters, (5) – container for agricultural biomass sample, (6) – thermocouple (device for measuring temperature in the biomass container), (7) – flexible connection between the scale and biomass container, (8) – flexible teflon wrap, (9) – agricultural biomass sample, (10) – temperature control sensor,(11) – temperature controller, (12) – flow of gaseous pyrolysis products, (13) – cooler, (14) – bottle for liquid phase separation, (15) – dry gaseous pyrolysis products, (16) – pump, (17) – gas emission into the atmosphere

3 Results and discussion

The process of biomass mixture pyrolysis was continuous, carried out in dynamic conditions, with controlling the temperature and mass of the sample. The samples were subjected to the temperature range of 25-650°C, and the average heating rates were 21, 30 and 54°C/min. All the experiments were conducted at atmospheric pressure. Prior to pyrolysis, the biomass was shredded to fractions of 5-10 mm. In order to obtain precise results of the sample analysis, the experiment was repeated five times, and the sample had the same mass of 10 g for each experiment. Mean values of the measuring results are presented in Table 4.

3.1 Effect of pyrolysis temperature

The effect of pyrolysis temperature on char and pyrolytic gas yield of agricultural biomass mixture, at different heating rates, is shown in Table 4.

It can be seen that lower temperatures (<150°C) imply slower process of the sample decomposition and the main product is char. At higher temperatures (150 – 550°C), the mixture sample decomposition is faster, with significant char reduction and gas yield increase. Above 550°C, there is a stabilization in char and pyrolysis gas yield. It is obvious that pyrolysis temperature has significant effect on pyrolysis gas yield. The decrease of char

Tab. 4. Devolatilization characteristics of agricultural biomass mixture (particle size: 5-10 mm)

Pyrolysis temperature (°C)	Heating rate 21°C/min		Heating rate 30°C/min		Heating rate 54°C/min	
	Volatiles content m_{gas}/m_0	Char content m_{char}/m_0	Volatiles content m_{gas}/m_0	Char content m_{char}/m_0	Volatiles content m_{gas}/m_0	Char content m_{char}/m_0
50	0	1	0	1	0	1
100	0.04	0.96	0.02	0.98	0.0	1
150	0.10	0.90	0.04	0.96	0.01	0.99
200	0.22	0.78	0.07	0.93	0.01	0.99
250	0.38	0.62	0.13	0.87	0.02	0.98
300	0.60	0.40	0.31	0.69	0.08	0.92
350	0.64	0.36	0.57	0.43	0.11	0.89
400	0.66	0.34	0.70	0.30	0.22	0.78
450	0.68	0.32	0.73	0.27	0.34	0.66
500	0.70	0.30	0.75	0.25	0.51	0.49
550	0.71	0.29	0.77	0.23	0.70	0.30
600	0.72	0.28	0.79	0.21	0.72	0.28
650	0.74	0.26	0.81	0.19	0.75	0.25

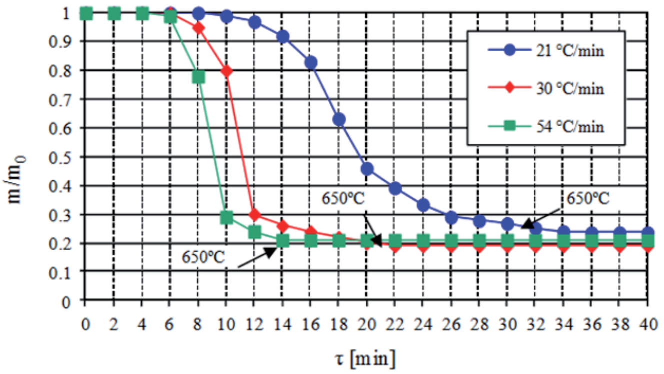

Fig. 3. Mass loss curve for the sample of agricultural biomass mixture as a function of reaction time and heating rate

yield with temperature increase can be explained with either greater decomposition of the sample at higher temperatures, or with secondary decomposition of char.

3.2 Effect of heating rate

Experimental investigation of the effect that the heating rate of the sample in the reactor has on pyrolysis products yield is shown in Figure 3. Three different heating rates in the reactor were investigated: 21, 30 and 54ºC/min. Obtained results imply that the increase of the heating rate of the mixture sample inside the reactor during pyrolysis process, leads to decrease of char yield and increase of pyrolysis gas yield. Higher char yields at lower heating rates are consequence of slow reactions that occur in the reactor. Duration of the pyrolytic process was 14, 21 and 31 min with heating rates values of 54, 30 and 21ºC/min, respectively. After that, mass ratio m/m_0 stabilizes. The mass of pyrolytic gas, char and liquid phase, obtained by measuring after the pyrolysis process, was in the range 7.4-8.1 g, 1.9-2.6 g, 1.3-1.8 g, respectively. Mean value of pyrolytic gas separation rate was 0.24 ,0.38 i 0.53 g/min with heating rates values of 54, 30 and 21 ºC/min. Mass ratio of char and biomass mixture sample was in the range 0.19-0.26 kg/kg at pyrolytic temperature of 650 ºC. The mass ratio primarily depends on moisture, carbon and hydrogen fraction in the sample. At higher pyrolysis temperatures the ratio is smaller because of lower fractions of moisture and volatiles. Char yield decrease with heating rate increase can be explained with the fact that faster heating of the sample in the reactor leads to faster depolymerization of solid material to primary volatiles, while at lower heating rates, dehydration is more stable.

Biomass mixture decomposition can also be described by the following differential equation:

$$-\frac{dm(\tau)}{d\tau} = k \cdot \left(m(\tau) - m_\infty\right), \qquad (1)$$

where m_0 is initial sample mass, $m(\tau)$ is mass at time τ, m_∞ is ultimate char yield and k is chemical reaction rate constant.

The solution of equation 1 is:

$$m(\tau) = m_\infty + (m_0 - m_\infty) \cdot e^{-k \cdot \tau}. \qquad (2)$$

The chemical reaction rate constant is defined as:

$$k = k_0 \cdot \exp(-E / R \cdot T), \qquad (3)$$

where k_0 is pre-exponential factor, E is activation energy and R is gas constant.

Kinetic parameters (E, k_0, k and reaction order n) from pyrolysis process of agricultural biomass has been investigated by many researchers [11-13].

There is not enough literature data regarding pyrolysis process of agricultural biomass mixture (corn stalk, wheat straw, soy straw and oat straw), while experimental investigation of individual kinds of agricultural biomass, such as corn stalk, wheat straw and oat straw has been conducted by many researchers. Pyrolytic gas yield values obtained through experimental investigation of pyrolysis process of agricultural biomass mixture are tested by comparing them to the results obtained by other researchers, which is presented in Table 5. It can be observed that the pyrolytic gas yield obtained by experimental investigation of biomass mixture pyrolysis is similar to the pyrolytic gas yield of individual kinds of agricultural biomass. Significant misalignment can be noted when comparing our experimental results to forest residues. Higher mass fractions of volatiles and moisture in forest residues in comparison to agricultural biomass give higher gas yields in pyrolysis process.

Tab. 5. Pyrolytic gas yield obtained by experimental investigation of biomass mixture pyrolysis and comparison to literature data

Pyrolysis temperature (°C)	Gas yield (dry pyrolytic gas + bio-oil) (wt.%)			
	Experimental value (mixture, heating rate 21 ºC/min)	Literature data [16] (Corn cob, heating rate 30 ºC/min)	Literature data [30] (Corn stalks, heating rate 10 ºC/min)	Literature data [31] (Forest residue, heating rate 10 ºC/min)
350	64	66	60	42
400	66	71	65	71
500	70	75	71	78
600	74	76	72	81

4 Conclusion

The experimental investigation of agricultural biomass pyrolysis was conducted on mixture of corn stalk, wheat straw, soy straw and oat straw with equal mass fraction. The mixture sample mass was 10 g with particle diameter 5-10 mm. The heating rates in the reactor were 21, 30 and 54ºC/min. Investigation of pyrolysis process of biomass mixture indicated higher yields of pyrolytic gas yield at higher temperatures and higher rates of heating the sample in the reactor. The highest gas yield was achieved at 650ºC and it ranged from 74 to 81 %, while the char yield was in the range 19-26%. Condensation of pyrolytic gas at the end of the pyrolysis process at 650 ºC produced 1.3-1.8 g of liquid phase. In order to evaluate pyrolytic gas yield obtained through pyrolysis of agricultural biomass mixture, it was compared with pyrolytic gas yields obtained through pyrolysis of other biomass kinds. It can be observed that the yields were similar. More significant misalignment has been noted with forest residues.

High yields of pyrolytic gas (74-81%) obtained by pyrolysis process of agricultural biomass mixture at 650°C and large abundance of agricultural biomass in Vojvodina (Republic of Serbia) show promise in applying these technologies. If the ratio of pyrolytic gas yield obtained by this experimental investigation were to be excepted and applied to industrial pyrolysis of total biomass amount in the Republic of Serbia, estimated at 12360.50×10^3 t (Table 1), it would denote generating 9146770 t to 10012005 t of pyrolytic gas annually. It gives a great opportunity for the Republic of Serbia to compensate its deficit in renewable energy sources, especially by using agricultural biomass which is very significant for national economy of the Republic of Serbia.

Nomenclature

A	ash mass fraction in agricultural biomass (%)
C	carbon mass fraction in agricultural biomass (%)
C_{fix}	fixed carbon mass fraction in agricultural biomass (%)
E	activation energy, kJ/mol
H	hydrogen mass fraction in agricultural biomass (%)
H_d	lower heating value, kJ/kg
k	chemical reaction rate constant, 1/s
k_0	pre-exponential factor, 1/s
m	mass of the sample inside the reactor that changes over time, g
m_0	initial sample mass, g
N	nitrogen mass fraction in agricultural biomass (%)
O	oxygen mass fraction in agricultural biomass (%)
S	sulphur mass fraction in agricultural biomass (%)
t	reaction temperature, °C
t_1	sintering temperature, °C
t_2	softening temperature, °C
t_3	hemisphere temperature, °C
t_4	flow temperature, °C
W	water mass fraction in agricultural biomass (%)
τ	reaction time, min
CH_4	methane volume fraction in pyrolysis gas (%)
CO	carbon monoxide volume share in pyrolysis gas (ppm)
CO_2	carbon dioxide volume fraction in pyrolysis gas (%)
H_2	hydrogen volume fraction in pyrolysis gas (%)
O_2	oxygen volume fraction in pyrolysis gas (%)
EU	European Union
M.P.	measuring point
SRPS CEN/TS 15370-1:2009	Designation for standards and related documents established by the Institute for Standardization of Serbia (ISS). Solid biofuels – Method for the determination of ash melting behavior.

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