COMBINED ORGANIC ACID LEACHING AND TORREFACTION AS PINE WOOD PRETREATMENT BEFORE FAST PYROLYSIS

by

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Reducing pine wood particle size is beneficial for acid leaching (shorter leaching time, smaller equipment size) and also for pyrolysis (low pyrolysis time, high oil and sugar yields). Torrefaction helps to improve the energy efficiency of grinding. However, it is not well established whether alkali and alkaline earth metals can still be removed effectively, after torrefaction, by leaching with an acetic acid solution, while keeping high oil and sugar yields. To investigate this, an experimental study was carried out combining torrefaction (290 °C, 20 minutes) and subsequently acid leaching of pine wood as pretreatment step before fast pyrolysis of the feedstock at 530 °C. The oil, char, gas, water, pyrolytic lignin, light oxygenates and levoglucosan yields were compared with the results obtained from fast pyrolysis of untreated pine wood and acid leached pine wood at 530 °C. In addition, pyrolysis vapors were condensed step-wise into two distinguished fractions (condensation $T = 80\,^{\circ}C$) to increase the levoglucosan concentration up to 45 wt.% with or without applying torrefaction as pretreatment.

Intra-particle reactions during torrefaction are more profound in the presence of alkali and alkaline earth metals. Cellulose and lignin derived products (e.g. levolucosan (~0.2 kg/kg pine wood) and pyrolytic lignin (~0.11 kg/kg pine wood) were not affected by the torrefaction pre-treatment of acid leached pine wood. In general, torrefaction of acid leached pine wood followed by fast pyrolysis showed similar total organics, char, gas, light oxygenates and produced water yields compared to fast pyrolysis of acid leached pine wood. Contrary, when acid leaching is applied after torrefaction the organics (dry bio-oil) and light oxygenates yields are quite comparable to the results of untreated pine wood fast pyrolysis.

Key words: *pine wood, fast pyrolysis, stepwise pyrolysis, acid leaching, alkali and alkaline earth metals*

Introduction

Fast pyrolysis is a promising process for the production of transportation fuels and valuable chemicals from lignocellulosic pine wood [1-3] . For fast pyrolysis, fast particle heating rates, moderate temperatures (450-500 °C) and short hot vapor residence times (1-2 seconds) are required in the absence of oxygen [4-6]. As a result, it is possible to produce 50-75 wt.% of bio-oil. Grinding is required to obtain an appropriate particle size to induce fast heat and mass transfer. Reducing the particle size of Lignocellulosic pine wood requires significant amounts of energy due to fibrous tenacious nature, which results in an increase in costs [7]. Torrefaction as a

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pine wood pretreatment step reduces the energy demand for grinding the pine wood [8-11]. Torrefaction of pine wood has also been studied in combination with fast pyrolysis [4]. It turned out that when torrefaction was applied before pyrolysis it was possible to increase the concentration of certain specific groups of compounds *e.g.* and individual species (*e.g.* levoglucosan, acetic acid) in the pyrolysis step, while maintaining the overall oil yields (sum of torrefaction and fast pyrolysis). Note, the overall oil yield (sum yields of torrefaction and fast pyrolysis) only stays constant when the torrefaction temperature does not exceed 300 °C.

Pine wood naturally contains alkali and alkaline earth metallic (AAEM) species [12, 13]. The presence of AAEM during pyrolysis catalyzes ring-fragmentation and dehydration reactions of the carbohydrates. This favors the char, water, gas and light organic yield while decreases the organic oil and sugar yield [14-16]. Sugars are an interesting renewable feedstock for the production of chemicals like levulunic acid, and levulinic esters [17] and bioethanol [18]. Organic acid leaching of several pine wood species is successfully applied to reduce the AAEM content which results in a significant increase, not only in the oil yield, but also in the sugar yields [19-22]. An extensive discussion about the effects of the acid leaching process on pyrolytic yields and the bio-oil characteristics can be found elsewhere [20-22] .

It is important to mention that acid leaching of the AAEM's goes much faster when small particles are used [2], which requires extensive grinding. In previous work, the leaching experiments with diluted acetic acid (mass fraction 10) showed that the removal of AAEM from ball milled particles (< 125 μm, containing no fibrous structure) was almost instantaneous (< 2 minute) whereas the AAEM removal from cylindrical rods (diameter 27 mm with length of 5, 10, or 40 mm) took hours or even days. From these results it can be concluded that the AAEM removal rate is determined by mass transfer in the pine wood pores (filling the pores with liquid and diffusion of AAEM/acid inside the pores to the bulk liquid), rather than mass transfer in the cell wall [2]. Therefore, the particle size is an important parameter. In addition, small particles requires large amounts of electrical energy for the grinding. As discussed earlier torrefaction can decrease the energy requirements for grinding. However, so far it is not known if the AAEM still can be effectively removed using pyrolytic acid leaching after torrefaction and if the organic oil and sugar yield remains high after fast pyrolysis of acid leached torrefied wood.

Oudenhoven *et al*. [22] impregnated AAEM (*K* and *Na*) into untreated pine wood and compared the results with experiment in which the AAEM were simply added *external* to the fluidized bed. The AAEM were added into the fluidized bed as salt or as AAEM rich char from straw. There presented results showed a significant decrease of the organic yield due to the AAEM both inside the pine wood structure as well as externally added. Based on the results it is not clear if the AAEM only catalyze the reactions of the produced vapors or also alter the condensed phase reactions (solid and possibly liquid). To answer this question, in the present contribution two step pyrolysis experiments of untreated and acid leached pine wood were performed in which the AAEM are only present in the first step and the temperature is chosen so that cellulose decomposes mainly in the second step. In this way the AAEM do not get in contact with the levoglucosan vapors, which are not present during the first step. By doing this we can study if the AAEM influences the condensed phase chemistry of cellulose.

Two main experiments were carried out: torrefaction at 290 °C of acid leached pine followed by fast pyrolysis of the solid product at 530 °C and torrefaction of untreated pine at 290 °C, where after the solid product is acid leached followed by fast pyrolysis at 530 °C. The obtained results are compared to one step fast pyrolysis of untreated and acid leached pine wood.

Materials and Methods

Materials

In this study, pine wood (Lignocel 9, purchased from Rettenmaier & Söhne GmbH, Germany) was used as lignocellulosic feedstock. The pine wood was grounded using a knife-mill and sieved to obtain a particle size of 0.5-2 mm and dried at 105 °C for 24 hours. Additionally, silica sand with a diameter of 212-300 μm, particle density of 2600 kg/m^3 and bulk density of 1600 kg/m^3, was used as fluidized bed material in the fast pyrolysis experiments. Levoglucosan and D-(-)-xylose was obtained from sigma Aldrich (> 99%). Acetic acid (99.7%) and Acetol (98%) was also purchased from Sigma Aldrich. D-(-)-Fructose was obtained from Fluca (> 99%) and Guaiacol was obtained from SAFC (98%).

Experimental Methods

Acid Leaching

Acid leaching was carried out using sieved untreated pine wood and the same pine wood obtained after torrefaction. The use of synthetic acidic solution to remove AAEM's has previously been validated [2]. The properties of this aqueous acidic solution together with the experimental conditions of the acid leaching experiments are summarized in tab. 1. Acid leaching experiments were carried out in a 50 L reactor. The pine wood (0.10 g dry pine wood per 1 g of leaching solution) was added to the reactor and the slurry was mixed with a flat blade stirrer (660 rpm) combined with a baffle mounted on the reactor wall. The acid leaching temperature was 90 °C. After 2 hours, the leaching solution was drained from the reactor through a perforated plate (pore size 0.5 mm), leaving the solid pine wood particles inside the reactor. Then, the pine wood was rinsed with milli-Q water to remove the remaining acid solution, which still contained a considerable amount of the AAEM. The rinsing was repeated till the pH was around 7. After the rinsing step, the pine wood was dried at 105 °C in an oven for 24 hours. To determine the concentration of the inorganics left in the pine wood, the ash content was determined under dry oxidation conditions (575 °C for 24 hours). The ash composition was determined by X-Ray Fluorescence (XRF).

Table 1. Operational conditions of acid leaching and fast pyrolysis experiments

Acid Leaching Solution Properties	[wt.%]
Acetic acid (SAFC, 99.5 wt.%)	10
Acetone (Assink Chemie, purity> 99.5 wt.%)	3.75
Ethanol (Assink Chemie, purity 99.8 wt.%)	3.75
Guaiacol (SAFC, purity >98 wt.%)	1.5
Propionic acid (SAFC, purity >99.9 wt.%)	1.5
Demineralized water	79.5
Acid Leaching Process	
Run Time [minute]	120
V_{vessel} [L]	50
$V_{\text{leaching liquid}}/M_{\text{pine wood}}$	10
Stirrer speed [rpm]	660
$T_{\text{acid leaching}}$ [°C]	90
Fast Pyrolysis Process	
Run time [minute]	45-60
$M_{\text{sand,initial}}$ [kg]	1.0
$\Phi_{\text{v,N2}} / \Phi_{\text{m,pine wood}}$ [Nl/g]	1.5
T_{reactor} [°C]	530
τ_{vapors} [s]	1.6-1.9
U/U_{mf}	2.5
$T_{\text{outgoing gas 1st condenser}}$ [°C]	80
$T_{\text{outgoing gas 2nd condenser}}$ [°C]	0

Torrefaction and fast pyrolysis

Fast pyrolysis experiments were carried out batch-wise in a fluidized-bed bench-scale reactor, explained in detail in our previous studies [21, 22]. The operational conditions are summarized in tab. 1. A brief description of the operational procedure follows; hot sand (530 °C) was fluidized inside the reactor using nitrogen. During a period of 30-40 minutes, 150 g of wood or torrefied wood was fed manually via a gas lock system consisting out two valves into the fluidized bed reactor in batches of 2-5 g together with 4-8 g of sand. After the last feeding, the bed was maintained at 530 °C for 15 minutes before cooling down to ensure full conversion of pine wood. The char was removed from the gas/vapor stream using two wire-mesh filters (pore size 9 μm and 5 μm). The vapors were condensed in two fractions using an electrostatic precipitator (ESP), operated at 80 °C (outgoing gas temperature), and a double-walled glass condenser called intensive cooler (IC), operated at -5 °C (outgoing gas). The non-volatile gases passed through a gas filter (10 μm) to collect the remaining liquid (± 2 wt.% of total oil) and, then ventilated to the atmosphere. Every 10 or 20 minutes, a gas sample was taken from the outgoing gas stream to analyze the produced gases by micro gas chronomatograph. During torrefaction, pine wood was essentially pyrolyzed at 290 °C in the same fluidized bed reactor. At the end of the torrefaction experiment, the reactor was quickly cooled down by feeding large amounts of cold sand to the reactor. The average pine wood particle residence time in the hot reactor of the first step was estimated to be around 20 minute [4]. The torrefied pine wood was recovered by sieving, in order to remove the sand, and subsequently dried in the oven at 105 °C for 24 hours. This torrefied wood was used as a feedstock for the fast pyrolysis experiments performed at 530 °C. Because not all sand could be removed from the torrefied wood, six random samples were taken from the torrefied wood mixture after sieving and burned to determine the actual torrefied wood content. In this way it was possible to determine the actual amount of torrefied wood fed during fast pyrolysis at 530 °C.

All pieces of the set-up were weighted carefully before and after each experiment to complete the mass balance. The char yields were calculated by weighing the char collected in the filter and the sand bed minus the amount of sand at the start of the experiment and the empty filter.

The bio-oils were condensed in the ESP and IC during the experiments and collected in attached bottles. The amount of bio-oil was determined by weighing the bottle and ESP with the bio-oil and subtracting the weight of the empty bottle and ESP. When the water content of both condenser fractions are known the water production can be calculated and the related organic yield as well. In the end, these data were used to complete the mass balance and to calculate the yields. The (cumulative) yields for torrefaction and fast pyrolysis experiments are always expressed on basis of the amount of dry pine wood fed to the first step (torrefaction).

Analytical techniques

The techniques used to analyze the feedstock and the pyrolysis products are summarized in tab. 2. The following gasses were measured, H_2, CO, CO_2, CH_4, C_2H_4, C_2H_6, C_3H_6, and C_3H,8 using gas chromatography (micro GC, Varian CP 4900). The ash composition of the pine wood was determined with XRF Spectroscopy (Phillips PW 1480 spectrometer). Karl Fischer titration (Metrohm 787 KF Titrino, titrant Hydranal Composite 5) was performed to determine the water content in the bio-oils. The identification and quantification of levoglucosan was achieved by GC-MS analysis (GC 7890A MS 5975C Agilent Technologies) equipped with a capillary column (Agilent HP-5MS, HP19091S-433). Samples were dissolved in acetone (50 mg oil/g acetone) and filtered before analysis (Whatman 0.2 μm filter). Total water-insoluble compounds in the liquid product of the first condenser were measured by cold water precipitation (≤ 2 °C). Since the obtained bio-oil was very viscous, 1 g of bio-oil was dissolved in 1 g of ethanol. The solution was added drop wise into 40 g of ice cooled demi water. The solution and water insoluble compounds were filtered using filter paper Grade 597 1/2 folded filters 50 mm (Sigma Aldrich) and after filtration the filter paper and water insolubles were dried at room temperature. After subtracting the pre-weighted dry filter the water insolubles weight could be determined. The water insoluble are hereafter referred to as pyrolytic lignin.

Table 2. Summary of the methods used to analyze the bio-oil

Property/Compounds	Method
Ash content	575 °C, dry oxidation
Ash composition	XRF
Evolved gas analysis	Micro GC
Water content	Karl Fischer
Water-insoluble compounds (pyrolytic lignin)	Cold water precipitation
Levoglucosan, Guaiacol, Acetol, Actic acid	GC-MS

Table 3. Characterization of the pinewood used in this study

	Acid leached pine wood	Acid leached pine wood	Acid leached torrefied pine wood
Moisture (wt.%)	8	< 1	< 1
Alkali metals (ppm)			
Na^+	60	2	8
K^+	398	9	13
Mg^{2+}	387	9	17
Ca^{2+}	1771	68	92
Ash (dry, wt.%)	0.37	0.08	0.09

Results

The moisture and AAEM content of the different feedstocks can be found in tab. 3. After organic acid leaching the pine wood was dried to a water content below 1wt.%. As can be observed after torrefaction of pine wood at 290 °C, the AAEM's can still be removed effectively via organic acid leaching.

In addition, the pine wood was leached with torrefaction liquid collected in the 2nd condenser in a separate dedicated experiment following the same procedure as described in section *Acid leaching* only using real torrefaction liquid and 10 gram of untreated pine wood. The Na^+, K^+, Mg^{2+} and Ca^{2+} concentration was effectively reduced to 7, 12, 22, 73 ppm, respectively, after leaching with torrefaction liquid.

Char, organics, gas, and water yields

Table 4 shows the char, organic, water and gas yields for untreated and acid leached pine wood. The same table shows the cumulative product yields of torrefaction plus fast pyrolysis. In

Table 4. Lumped pyrolysis products yield obtained by pyrolysis and stepwise pyrolysis of untreated and acid leached pine wood; temperature for torrefaction 290 °C and was 530 °C in the second step

Nr	Feed	Char yield[a]	Organic yield[a]	Water yield[a]	Gas yield[a]
1	Pine untreated 20->530	0.10 (0.12)	0.50 (0.50)	0.12 (0.13)	0.28 (0.25)
2	Pine leached 20->530	0.08	0.58	0.09	0.25
3	Pine leached and torrefied 20->290	0.64[b]	0.19	0.04	0.11
4	Fast pyrolysis 290->530	0.09	0.38	0.05	0.14
3+4	Sum of leaching, torrefaction and fast pyrolysis	0.09	0.56	0.09	0.25
5	Pine torrefied 20->290	0.63[b]	0.21	0.06	0.10
6	Leached + second step 290->530	0.13	0.30	0.05	0.16
5+6	Sum of torrefaction, leaching and fast pyrolysis	0.13	0.51	0.11	0.26

[a] Yield based on original pine wood fed in first step [kg/kg pine wood initial pine wood d.a.f.]. Gas yield by difference.
[b] Solid product obtained after torrefaction

one case the pine wood is acid leached before torrefaction and in another case the pine wood is first torrefied and then acid leached. Between brackets the reproducibility results can be seen (Nr.1). It can be concluded that the reproducibility is sufficient enough for trend detection based on a single experiment.

The product yields for fast pyrolysis of acid leached wood and the accumulative yields of torrefaction of acid leached wood followed by fast pyrolysis are comparable. The product yields for fast pyrolysis of untreated wood and the cumulative yields of torrefaction of wood followed by acid leaching and fast pyrolysis are comparable. It can be observed that the additional water, when the pine wood is leached after torrefaction, is solely produced during torrefaction when the AAEMs are thus still present in the pine wood.

Acetic acid, acetol, guaiacol, and pyrolytic lignin yields

Table 5 shows the acetic acid, acetol, guaiacol and pyrolytic lignin production for pyrolysis of acid leaching of pine wood before and after torrefaction following by fast pyrolysis at 530 °C. When acid leaching is applied, the acetic acid production decreases in depend of direct fast pyrolysis of pine wood or first applying a torrefaction step. In the presence of AAEM's more acetic acid is produced during torrefaction, 1.4 *vs*. 0.9 wt.%, respectively. However, as it can be seen in tab. 5, the production of acetic acid did not differ in the second step because the AAEM content after torrefaction and acid leaching was equally low (180 and 30 ppm), see tab. 3. The liquid in the 2nd condenser (T_2^{nd} condenser = 20 °C) contained between 6 and 10 wt.% of acetic acid for both 1 step pyrolysis experiments and torrefaction. Therefore, also the torrefaction liquid can be effectively used for acid leaching.

It is already known that the presence of AAEM favors the ring scission reactions that results in the production of light components such as acetol [24]. Indeed, when acid leaching is applied the acetol production is lower compared to untreated pine wood. This is also the case when torrefaction and acid leaching are included as pretreatment step prior to pyrolysis.

Table 5. Acetic acid, Acetol, Guaiacol and Pyrolytic lignin yield obtained by pyrolysis and stepwise pyrolysis of untreated and acid leached pine wood; temperature was for first step pyrolysis 290 °C and was 530 °C in the second step.

Nr	Feed	Acetic acid yield[a]	Acetol yield[a]	Guaiacol yield[a]	Pyrolytic lignin yield[a]
1	Pine untreated 20->530	2.5	1.2	0.9	15.9
2	Pine leached 20->530	1.5	0.5	1.0	12.7
3	Pine leached and torrefied 20->290	0.9	0.1	0.8	0.8
4	Fast pyrolysis 290->530	0.4	0.2	0.7	10.0
3+4	Sum of leaching, torrefaction and fast pyrolysis	1.3	0.3	1.5	10.8
5	Pine torrefied 20->290	1.4	0.7	0.9	2.8
6	Leached + second step 290->530	0.4	0.2	1.0	8.81
5+6	Sum of torrefaction, leaching and fast pyrolysis	1.8	0.9	1.9	1.6

[a] Yield based on original pine wood fed in first step [kg/kg pine wood initial pine wood d.a.f.].

Water-insoluble fraction of the bio-oil, also known as pyrolytic lignin, mostly contains the lignin derived oligomeric compounds. Table 5 shows the total yield of the water-insoluble compounds. Comparing untreated and pretreated wood in pyrolysis of untreated pine wood, there is ~3% of absolute difference between the water insoluble yields. At this point it is not known if the total production of lignin derived oligomers is also lower because the composition of the oil has changed significantly (*e.g.* levoglucosan) and therewith possibly also the solubility of these oligomers in bio-oil. This in turn will definitely change the equilibrium of these oligomers during cold water precipitation (extraction). Unequivocally, the production of water pyrolytic lignin was higher in the second step of the process. This is not surprisingly since lignin starts to decompose at around 120-280 °C and covers a wide temperature range until 500 °C, with a maximum decomposition rate between 350-450 °C. On the other hand, application of acid leaching prior to torrefaction decreased the production of the water insolubles from 2.8 to 0.8 wt.% in the torrefaction step. Nevertheless, during torrefaction the lignin start to react already at temperatures around 290 °C leading to overall lower accumulative pyrolytic lignin yields.When torrefaction is applied a profound effect on the guaiacol yield was observed. Although, the yield of guaiacol is still low, the guaiacol yield nearly doubled compared to pyrolysis without torrefaction (Nr 1 and 2). The increased production of guaiacol can be ascribed to the initial production of guaiacol during torrefaction at low temperature (290 °C). Guaiacol start decompose into catechol and phenols at temperatures above 360 °C . Acid leaching seems to have a negligible effect on the quaiacol yield.

Levoglucosan yield

In tab. 6. it can been seen that the cumulative levoglucosan yield, in the case of acid leaching, for one step (20→530 °C) and torrefied wood pyrolysis (20→290→530 °C) is quite similar. This is in agreement with the work by Westerhof *et al.* [4] showing no significant effect on the cumulative levoglucosan yield for one step and two step pyrolysis (first step 290 °C) for untreated pine wood. It can be observed that when acid leaching is applied after or before torrefaction a comparable cumulative levoglucosan yield is obtained. This means that no extensive *liquid/solid* phase reactions did take place leading to significant lower levoglucosan yields. Obviously, the main decomposition reactions of cellulose found place during fast pyrolysis and not during torrefaction. In all cases only small amounts of AAEM's were present during fast pyrolysis. To conclude with respect to the levoglucosan yield, the presence of AAEM's during torrefaction does not influence the outcome of pyrolysis at 530 °C. Note, at higher torrefation temperature and likely also longer torrefaction times (and the combination) significant lower organics and sugars will be produced [4]

Table 6. Levoglucosan yield and levoglucosan concentration ESP, (T_{reactor}= 530 °C, $T_1^{\text{st}}{}_{\text{cond}}$= 80 °C) torrefaction ($T_{\text{reactor}}$= 290 °C)

Nr	Feed	Levoglucosan yield wt.%[a]	Levoglucosan concentration wt.%[a]
1	Pine untreated 20->530	3.4	14.8
2	Pine leached 20->530	17.6	47.8
3	Pine leached and torrefied 20->290	2.5	19.6
4	Fast pyrolysis 290->530	17.9	44.7
3+4	Sum of leaching, torrefaction and fast pyrolysis	20.4	
5	Pine torrefied 20->290	0.9	4.3
6	Leached + second step 290->530	18.5	40.5
5+6	Sum of torrefaction, leaching and fast pyrolysis	19.4	

[a] Yield based on original pine wood fed in first step [kg/kg pine wood initial pine wood d.a.f.].
[b] Levoglucosan concentration 1st condenser (80 °C).

To produce a sugar rich oil, acid leaching, torrefaction and fractional condensation of the produced vapors were combined. Table 6 shows the concentration of levoglucosan in the first condenser operated at 80 °C. No levoglucosan was observed in the second condenser operated at

20 °C. This is in agreement with Westerhof *et al*., [4] that levoglucosan can concentrated in this condenser by stripping off the water and light compounds and collect them the second condenser [23]. The highest obtained concentration of levoglucosan was 47.8 wt.%. The high concentration of levoglucosan is beneficial in subsequent purification before further usage in application (*e.g*. chemicals production). An techno-economic evaluation of the acid leaching process as pretreatment step in pyrolysis is provided by Oudenhoven *et al*. [2].

Conclusions

Acid leaching (*e.g*. torrefaction liquid) can bring the AAEM content down to below 130 ppm before and after torrefaction. During torrefaction a considerable amount of water and acids were already produced and thus not collected as fast pyrolysis oil. The benefits of grinding torrefied wood has some implications namely cooling down (at least to some extend) of the torrefied wood is required before grinding. Cooling the torrefied wood is probably also required when it is acid leached preventing the requirement of high pressure systems. Nevertheless, torrefaction of acid leached pine wood followed by fast pyrolysis showed similar overall product yields compared to fast pyrolysis of acid leached pine wood without torrefaction. Contrary, when acid leaching is applied after torrefaction the cumulative organics and light oxygenates yields are quite comparable to the results of fast pyrolysis of untreated pine wood without torrefaction. The yield of pyrolytic lignin decreased from 16 to around 11 wt.% when acid leaching was applied with and without torrefaction as pretreatment step whereas the Guaiacol yield increased significantly.

Compared to one step pyrolysis of acid leached pine wood at 530 °C no significant differences were observed in levoglucosan yields when the pine wood was acid leached before or after torrefaction prior to pyrolysis at 530 °C. Pyrolysis vapors were condensed into two distinguished fractions (condensation $T = 80$ °C) to increase the levoglucosan concentration up to 47.8 wt.% with a yield of 20 wt.% (kg/kg pine wood) simplifying considerably its recovery.

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