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Novel Boiler Water Treatment Using Green Chemistry Saves Water and Energy

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ABSTRACT

Purified tannin has been proven to save significant energy and water when used as a boiler water treatment. Purified tannin protects boilers from corrosion and scale, allowing operation well above ASME guidelines for water quality and, thereby, improving their efficiency. The functional properties of tannins have been studied, and the mechanisms of boiler protection verify empirical field results. A case study involving a California regional brewery demonstrates how purified tannin saves water and energy.

Introduction

Tannins have a history of use as boiler water treatments dating back to the mid-1800s. The story goes that a sack of potatoes was accidentally left inside a boiler after a cleaning and dramatically improved the condition of the boiler upon the next inspection. Extracted from plants, tannins are renewable, nontoxic, nonflammable, and biodegradable compounds that have made a recent comeback as a boiler water treatment in the form of purified tannin from tree bark. There are many possible applications of purified tannin, including as a steam boiler treatment product commonly used in the brewing industry. Most other boiler treatment products currently in use incorporate phosphates, phosphonates, polymers, sulfite, and other hazardous chemicals—many of which are mined and are facing limited supply and price inflation.

Boiler water treatments are designed to prevent corrosion of equipment, prevent scaling of heat-transfer surfaces, and conserve water and energy. The exciting thing about refined tannin is its exceptional ability to perform at much higher cycles of concentration (COC), which leads to a reduction in both water and energy consumption (Fig. 1).

COC represents the accumulation of dissolved minerals in the boiler water and is calculated as the total dissolved solids (TDS) in the boiler water divided by the TDS in the feed water. Higher COC results in lower blowdown: Blowdown (as % of feed water) = 1/COC × 100. Purified tannin can reduce blowdown by as much as 50–80%, water use by 8–20%, energy use by 1–5%, and greenhouse gases by 1–5%.

Clozit (6) is an on-line platform that provides a report on expected savings achievable due to a reduction in boiler blowdown when switching to refined tannin. Its credibility is certified by the Natural Gas Technologies Centre (NGTC) in Quebec, Canada. The savings calculated for a regional brewery and a paper mill are presented in this article.

Effective boiler treatment needs to achieve the following:

- Scavenge oxygen
- Inhibit corrosion
- Inhibit scale
- Minimize carryover

Purified tannin-based boiler treatments achieve all of these goals. Discussion of the functional properties of tannin as an oxygen scavenger, corrosion inhibitor, and scale inhibitor and the unique property of preventing carryover are presented, along with examples of calculations of savings at a regional brewery and for a larger boiler system at a paper mill.

Purified Tannin as an Oxygen Scavenger

The removal of dissolved oxygen is critical to prevent pitting corrosion of boiler systems. Various chemicals (oxygen scavengers) are used to remove residual oxygen following any mechanical

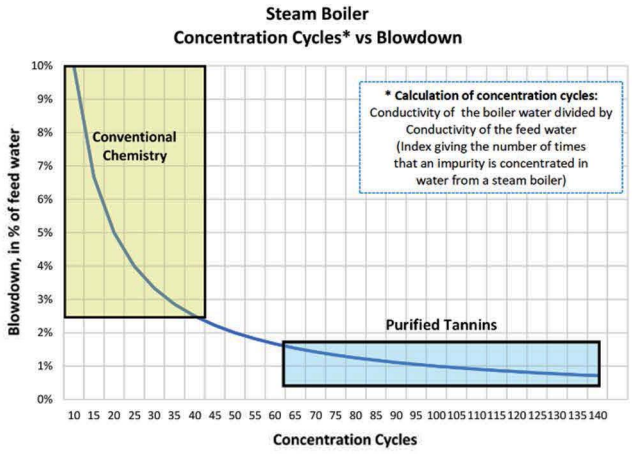

Figure 1. Higher cycles of concentration (COC) result in lower blowdown rates.

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removal of oxygen. The most widely utilized oxygen scavenger is sodium sulfite because of its low cost, USDA acceptance, and comparable safe handling. Refined tannin has the ability to remove oxygen at reaction times similar to catalyzed sulfite and typically requires only 2 ppm tannin/1 ppm dissolved oxygen (versus 7.88 ppm sodium sulfite/1 ppm O_2).

Purified tannin, relative to sulfite, contributes very little to TDS (Fig. 2); TDS contributions from chemistry can be significant. Fewer dissolved solids added by the chemical itself translates to a lower starting point (feed water TDS) when calculating COC.

Purified Tannin as a Corrosion Inhibitor

The goal of a water treatment program is to create conditions that minimize the corrosion of steel in the boiler; this is usually referred to as being, "passivated." Passivation is a term used in industry to describe an oxide film with reduced reactivity that protects the underlying metal from corrosion. Some researchers have defined passivation as the creation of a barrier to additional oxidation; others have defined passivation as the absence of corrosion. Passivation in boiler and boiler feed-water systems involves the creation of a protective layer of metal oxide on the surface of the steel. In boilers, it is widely accepted that the formation of a continuous, adherent layer of magnetite (Fe_3O_4) is the most desirable form of iron oxide in boiler systems because it helps protect against general corrosion (i.e., rust [Fe_2O_3]) (7). Magnetite, which is important in corrosion protection of steel, was one of the first substances whose crystalline structure was determined by X-ray. At high pH, temperature, and pressure, similar to the conditions found in a boiler, steel test coupons rapidly develop a strikingly different appearance in the presence of tannins. Typically, the surface is visibly smoother and more adherent, with noticeably less spalling of magnetite than in control samples.

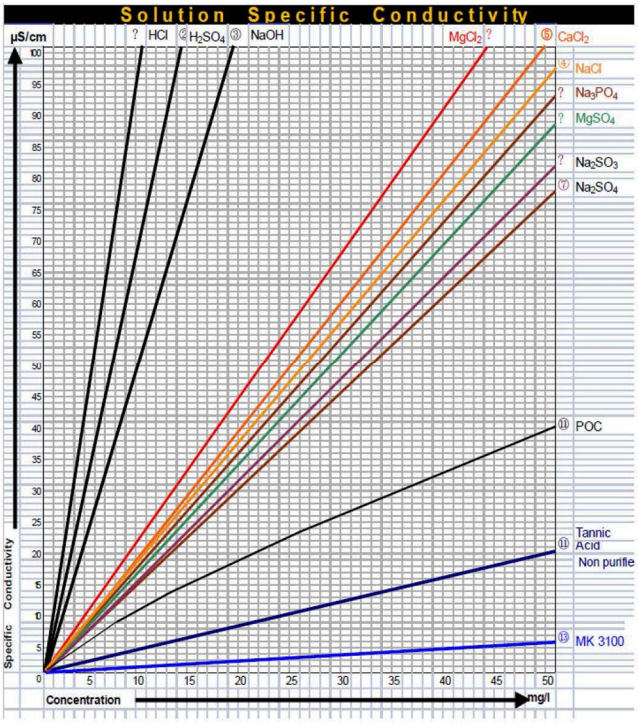

Figure 2. Purified tannin (MK 3100) contributes much less conductivity to boiler water than other ions.

The microstructure of these passivation layers was studied (1) using scanning electron microscopy coupled with energy dispersive spectroscopy, as well as grazing incidence X-ray diffraction. Their corrosion behavior was studied using potentiodynamic polarization and electrochemical impedance spectroscopy. The magnetite layer that was formed with refined tannin showed improvements in thickness, reduced porosity, adherence, and crystal composition and structure and is consistent with improved corrosion protection (Fig. 3).

Purified Tannin as a Scale Inhibitor

Scale on boiler heat-transfer surfaces increases energy consumption. The thickness and composition of the scale determines energy loss (Fig. 4), but in general, thin layers of scale dramatically affect energy costs. Scale can also lead to hazardous conditions, failure of equipment, and costly repairs.

Boiler water treatment typically consists of both external (e.g., water softening) and internal treatments. Internal treatment typically consists of the use of chelates, dispersants, or sludge con-

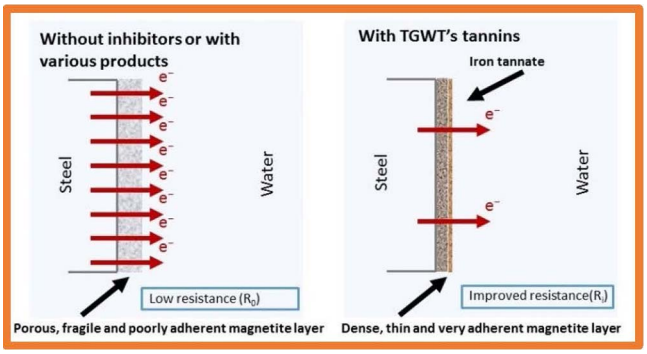

Figure 3. Model of a smooth, thin, adherent, and dense iron tannate passive oxide layer compared with a typical magnetite passive oxide layer.

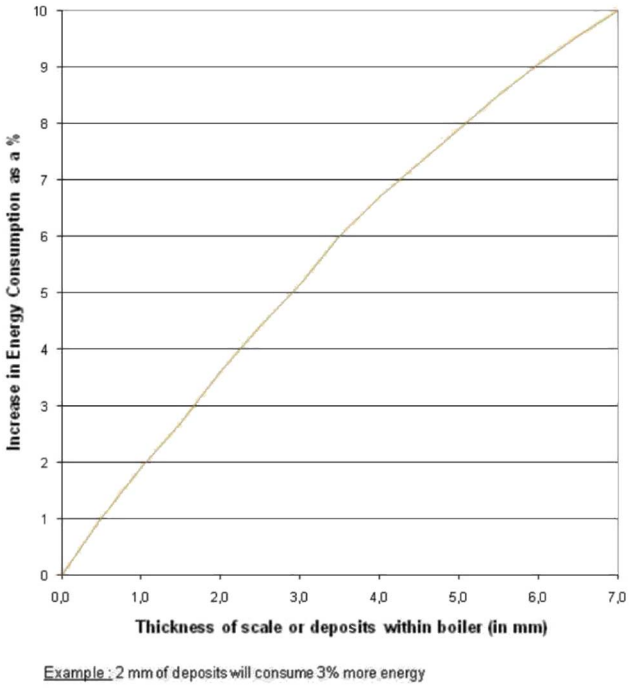

Figure 4. Energy consumption associated with the thickness of scale deposits on boiler tubes.

ditioners in the form of phosphates, phosphonates, polymers, and other chelates. These chemicals prevent scaling by precipitating, solubilizing, or modifying the minerals that cause scaling.

Purified tannin inhibits the phenomena of scaling by stabilizing and precipitating scale-forming salts. Tannin reacts with minerals in a boiler to form ligno-complexes (chelates). Tannin also deposits a dynamic film on the metal by adsorption and desorption, and scaling minerals are rejected and remain suspended in the water. Concentrations can be very high without risk of scaling. Studies (4) have shown that tannin has a dispersive effect on silica, which minimizes the propensity of precipitation and subsequently decreases the scaling potential. Anecdotal experience has shown that purified tannin allows significantly higher COC and demonstrates visible removal of previously deposited scale.

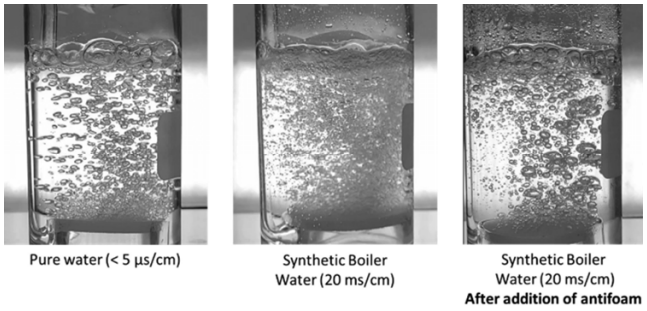

Figure 5. A silica/silicone oil antifoam prevents inhibition of coalescence.

Purified Tannin Reduces Foaming and Carryover

Carryover is any contaminant that leaves the boiler with the steam. Entrained boiler water that "carries over" contains dissolved solids and possibly some suspended solids. Carryover results from incomplete separation of steam from the steam–water mixture in a boiler. Mechanical and chemical factors can contribute to incomplete separation. Carryover can cause equipment damage and result in inefficient heat transfer.

The ASME/ABMA set the boiler water guidelines for dissolved solids, alkalinity, and other factors for purposes of steam

TGWT
LES GARS DU TANNIN
THE TANNIN GUYS

STEAM BOILERS WATER TREATMENT SAVINGS REVIEW
2022-08-30

CASCADES CABANO
Témiscouata-sur-le-lac, Québec
Éric Moreau
Cell.: 1-418-860-7674
eric_moreau@cascades.com
Startup: June 1, 2011

TOTAL SAVINGS (*based on an inflation rate of 2% per year)

1 year	11 years 2 months
$222,792	**$2,757,261**

GHG (CO2 EQUIVALENT)		MAKE-UP WATER		SEWER WATER	
1 year	11 years 2 months	1 year	11 years 2 months	1 year	11 years 2 months
699 t/year	7,806 t	24,015 m3/year	268,168 m3	27,214 m3/year	303,890 m3
$20.00/t	$24.87/t	$1.00/m3	$1.24/m3	$1.00/m3	$1.24/m3
$13,981	**$173,028**	**$24,013**	**$297,184**	**$27,211**	**$336,762**
SAME AS REMOVING FROM THE ROAD 152 MID-SIZE CARS	SAME AS REMOVING FROM THE ROAD 1,697 MID-SIZE CARS	SAME IN VOLUME AS 1,057 TANKER TRUCKS	SAME IN VOLUME AS 11,803 TANKER TRUCKS	SAME IN VOLUME AS 1,198 TANKER TRUCKS	SAME IN VOLUME AS 13,378 TANKER TRUCKS

FUEL (SAVINGS PER YEAR)

Oil nº6	215,950 liter/year	$0.55/liter	$118,773
Biomasse	1,484 t/year	$23.00/t	$34,132

SAME AS HEATING FOR 1 YEAR 729 RESIDENTIAL HOUSES (1500 SQUARE FEET)

FUEL (SAVINGS SINCE 11 years 2 months)

Oil nº6	2,411,442 liter/year	$0.68/liter	$1,469,928
Biomasse	16,571 t/year	$28.60/t	$422,416

SAME AS HEATING FOR 1 YEAR 8,141 RESIDENTIAL HOUSES (1500 SQUARE FEET)

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Figure 6. Savings in fuel, greenhouse gas emissions, make-up water, and sewer water at a large pulp and paper mill.

quality. The use of purified tannin allows boiler operators to successfully run water treatment programs that far surpass these recommended limits. For example, the ASME/ABMA recommended limit for conductivity for boilers under 300 psi is 5,400 µS. Purified tannin has been run in successful programs at up to 20,000 µS, while maintaining or improving steam quality. Refined tannin has been proven to produce higher quality steam (less entrained water) than other traditional water treatment programs on which ASME/ABMA guidelines base their recommendations. When running higher COC in a boiler, the potential for scaling and carryover (foaming) are orders of magnitude higher and must be prevented. A recent study (3) was conducted to determine the roots of chemically induced carryover in boilers and how tannin mitigates carryover.

Table 1. Before and after mass flow rate chart for Bear Republic

Conventional Chemistry	Flow Rate	Refined Tannin Chemistry	Flow Rate
Make-up conductivity	380	Make-up conductivity	380
Feedwater conductivity	70	Feedwater conductivity	56
Boiler conductivity	2,500	Boiler conductivity	12,000
Load	20%	Load	20%
Steam load (lb/hr)	1,035	Steam load (lb/hr)	1,035
Cycles	35	Cycles	250
Blowdown	3%	Blowdown	1%
Returned condensate	80%	Returned condensate	80%
Feedwater rate (lb/hr)	1,065	Feedwater rate (lb/hr)	1,042
Blowdown rate (lb/hr)	29.8	Blowdown rate (lb/hr)	0.073
Condensate returned (lb/hr)	828	Condensate returned (lb/hr)	8.28
Make-up rate (lb/hr)	236	Make-up rate (lb/hr)	2.14

The study (3) explored foaming in boilers and the relationship between bubble coalescence inhibition (bubbles coming together to form a larger bubble) and foaming (Fig. 5) and explored why tannin-based products reduce or eliminate carryover. Pure water forms large steam bubbles. Inhibition of coalescence (i.e., promoting small bubbles) occurs with high-TDS waters and leads to carryover. Small bubbles increase the likelihood of carryover through three paths: 1) bubble rising speed; 2) the volume of small versus large bubbles serving as nucleation sites when pressure drops occur; and 3) the ejection of small droplets when a small bubble bursts (like a fizzing soda on your upper lip). It was shown that when the total ionic strength reaches a critical value, inhibition occurs, and small bubbles appear to cause foaming.

Chemco Products Company

TOTAL SAVINGS
DETAILED CALCULATION ON SAVINGS

1 year	5 years	10 years
$4,220	$21,961	$46,208

	SAVINGS %	SAVINGS	BEFORE	AFTER PURIFIED TANNIN
FUEL USAGE	1.6 %	204 MMBtu/year	12,700 MMBtu/year	12,496 MMBtu/year
FUEL COST	1.6 %	$1,675	$104,140	$102,465
GREENHOUSE GASES EMISSIONS	1.6 %	11 t	679 t	668 t
GREENHOUSE GASES COST		$0	$0	$0
MAKE-UP WATER USAGE	11.8 %	30,831 gal/year	260,993 gal/year	230,162 gal/year
MAKE-UP WATER COST	11.8 %	$234	$1,984	$1,749
SALT COST FOR SOFTENED WATER	11.8 %	$59	$500	$441
ENERGY LOST IN SEWER WATER	86.3 %	44 MMBtu/year	51 MMBtu/year	7 MMBtu/year
SEWER & WASTERWATER COST	86.3 %	$1,393	$1,615	$222
TESTING LABOR TIME	30.0 %	39 hours	130 hours	91 hours
TESTING LABOR COST	30.0 %	$858	$2,860	$2,002
WATER TREATMENT PROGRAM	0.0 %	$0	$4,000	$4,000

	SAVINGS %	SAVINGS	BEFORE	AFTER PURIFIED TANNIN
STEAM PRODUCTION	1.4 %	137,226 lbs/year	9,543,298 lbs/year	9,406,072 lbs/year
THERMODYNAMIC STEAM QUALITY	1.5 %	1.0 %	98.2 %	99.6 %
STEAM QUALITY IMPROVEMENT	100.0 %	118 MMBtu/year	0 MMBtu/year	118 MMBtu/year
STEAM TO PREHEAT DEAERATOR/FEED TANK	7.4 %	1.0 %	7.0 %	7.0 %
ENERGY TO PREHEAT DEAERATOR/FEED TANK	7.4 %	43 MMBtu/year	575 MMBtu/year	532 MMBtu/year
CYCLES OF CONCENTRATION	600.0 %	214	36	250
BLOWDOWN RATE	85.7 %	2.4 %	2.8 %	0.4 %
BOILER EFFICIENCY	1.6 %	1.0 %	63.2 %	64.3 %

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Figure 7. Clozit calculations for Bear Republic Brewing.

Tannin forms particles of the right size and hydrophobicity to act as antifoam particles. A possible mechanism for this antifoam action is that a tannin particle forms a bridge between two bubbles and, due to its hydrophobicity, makes the liquid dewet and, thus, perforates the bubbles.

Case Study at Bear Republic Brewing Company, Cloverdale, CA

Purified tannin has proven to be an excellent boiler water treatment for industrial steam boilers for over four decades. For example, Cascades Cabano pulp and paper mill implemented tannin treatments more than 11 years ago and found it greatly improved their efficiency. Since then, they have amassed $2,760,00 in overall savings, while running at 100–200 cycles and maintaining excellent steam quality with a condensate return conductivity of 5–10 µS (Fig. 6).

Bear Republic Brewing Company is a regional brewery located in Cloverdale, CA, and probably serves as a better illustration of what tannin treatment can offer the brewing industry. This community was one of the most heavily impacted during the ongoing California drought beginning in 2013. In January of 2014, the California State Health Department listed Cloverdale as one of 17 communities expected to run out of water. Fortunately, Cloverdale was able to add capacity to their water system; however, water remains in short supply. Because of this, water savings and wastewater treatment have been a high priority at their production facility in Cloverdale. In 2018, in an effort to save water, Bear Republic introduced Tanguard DA from Chemco Products to their 150 horsepower Cleaver Brooks boiler to generate 40 psi steam. The before and after mass flow rate chart is shown in Table 1.

Bear Republic Implementation, Safety, and Maintenance

Tanguard DA replaced three conventional products: a sulfite-based product, a scale inhibitor product, and an amine product. Tanguard DA incorporates an ammonia-based amine into the one-drum formulation for condensate treatment. One of the three existing chemical pumps was utilized to inject Tanguard DA into the feed-water tank based on the feed-water pump activation. Tanguard DA is not regulated by the DOT, and tannin is made from natural, sustainable trees, as opposed to the more hazardous, regulated, and mined traditional products it replaced. (Note: Tanguard DA is corrosive in its packaged concentration and proper handling and PPE should be used.)

Increasing the COC index from 35 to 250 reduced blowdown and, thereby, dramatically reduced the volume of chemistry needed to treat the boiler. This reduced shipping related costs, inventory of chemicals on-site, and hazardous materials handling by personnel.

The residual concentration of Tanguard DA in the boiler can be measured by color comparator or, more accurately, with a handheld colorimeter. Typically, the residual Tanguard DA level is targeted at 175–225 ppm in the boiler. A minor pump adjustment is made to increase or decrease residual levels. Boiler blowdown is monitored and controlled by conductivity. A range of 11,000–12,000 µS is targeted, and the operator bottom blows the boiler to keep conductivity below 12,000 µS. Increasing the COC reduced blowdown enough that the surface blowdown valve was no longer utilized, and boiler conductivity was able to be more simply controlled by minimal bottom blowdowns. Tanguard DA eliminated drop testing for inhibitor levels, sulfite levels, and alkalinity levels. Proper water softening is critical with Tanguard DA, as with any water treatment program.

Summary of Treatment at Bear Republic Brewery

Savings, as calculated by the on-line platform Clozit (6) are presented in Figure 7. The overall savings generated by changing the water treatment program from traditional to Tanguard DA was about $4,000—enough to pay for the water treatment program chemicals and service.

Due to a higher percentage of condensate return, the boiler was already achieving high COC with conventional chemistry. The introduction of Tanguard DA increased that to 250 COC and an average conductivity of 12,000 µS. Feed-water temperatures averaged about 180°F (lower temperatures require higher dosages of Tanguard DA to scavenge oxygen). Blowdown rates with Tanguard DA were significantly reduced, and associated energy, water, and wastewater savings have been enjoyed. The boiler was in good condition prior to Tanguard DA, but during the annual inspection in December 2020 after two years of Tanguard DA treatment, John Powell, boiler inspector for Hartford Boiler Inspections, commented that the water side looked better than any boiler of this size he had seen. In particular, he was impressed by the formation of the beneficial, passivating layer of magnetite on the tubes (Fig. 8). The presence of visible magnetite on the tubes indicates the absence of scale and corrosion and the safe, efficient operation of a boiler and steam production.

Figure 8. Boiler tubes during inspection at Bear Republic Brewing in 2022, showing unscaled tubes in good condition.

Summary

Breweries can substantially reduce water and energy consumption by implementing a refined tannin water treatment program for their steam boilers. Refined tannin saves these resources by reducing blowdown through increased COC of the boiler water beyond what is recommended by the ASME/ABMA guidelines and, thereby, is breaking new ground in sustainability. Although refined tannins have been used and studied for several years, it is still considered new technology to the U.S. market and a new avenue for breweries to save water in an industry where water savings are valued and ever more difficult to find. The steam system is often described as "the heart of the plant," and the water treatment program is critical for its efficiency and longevity. An understanding of how refined tannin safeguards the equipment and improves efficiency, along with the experience of other breweries, is needed to build confidence in this new technology. Refined tannin, when applied properly and accompanied by good maintenance practices, has been shown to achieve the traditionally desired results of scale prevention, oxygen scavenging, and corrosion inhibition, while introducing the benefit of minimizing carryover at higher COC.

Refined tannin not only saves water and energy resources but is easily converted from a traditional treatment program. Maintenance of the tannin program is simple and minimizes the chemistry needed for treatment, the time needed for testing and blowdowns, and chemical handling. Tannins are made from a natural, sustainable source that is not regulated by the DOT and are easier to source.

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