TECHNICAL PRINCIPLES FOR CARAMEL APPLICATION: ANALYSIS OF GASTRONOMIC AND CHEMICAL

FUNDAMENTALS

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Abstract

The application of caramel has existed since millenary times, originating in China with rudimentary blown figures. However, up to the present time, the complex artistic figures that are presented in the competitive world gastronomic scenarios or as part of gastronomic sophistication are served in the most exclusive A&B establishments. For this study, a thorough qualitative bibliographic review has been carried out to support and substantiate the culinary chemical principles of components, reactions and process of elaboration of caramel. Concluding in the first instance that sugars are susceptible to reactions such as caramelization due to high temperatures, which leads to the melting point of the carbohydrate to melting and generates compounds related to the characteristics of smell, taste but especially, the dark color of

this food; chemical products such as furfural, melanoidin's, furans, furanone, lactones, pyrones, aldehydes, ketones and more that give the identifying characteristic to the final sweet product.

Keywords: caramel, sugar, ascorbic acid, tartaric acid, acetic acid, blowing, modeling, satin, stretching, spinning, spinning

Resumen

La aplicación en caramelo existe desde tiempos milenarios, con origen en China con rudimentarias figuras sopladas, hasta llegar a la actualidad las complejas figuras artísticas que se presentan en los competitivos escenarios gastronómicos mundiales o como parte de sofisticaciones gastronómicas servidas en los establecimientos de A&B más exclusivos. Para este estudio, se ha realizado una profunda revisión bibliográfica de carácter cualitativo, con el fin de sustentar y fundamentar los principios químico culinarios de componentes, reacciones y proceso de elaboración del caramelo. Concluyendo en primera instancia que los azúcares son susceptibles de reacciones como caramelización debido a las altas temperaturas, lo que conlleva a que al alcanzar el punto de fusión del carbohidrato este se derrita y se genere a la vez compuestos relacionado con las características de olor, sabor pero sobretodo del color oscuro propio de este alimento; productos químico como furfural, melanoidinas, furanos, furanonas, lactonas, pironas, aldehídos, cetonas y más que le dan la característica identificadora al producto dulce final.

Palabras clave: caramelo, azúcar, ácido ascórbico, acido tartárico, ácido acético, soplado, modelado, satinado, estirado, hilado

1. INTRODUCTION

The elaboration of caramel dates back to ancient times, according to biblical evidence from the time of Noah when fruit juices were reduced to concentrate the sugars. However, with the introduction of sugar from India, the panorama for this food changed to industrialized levels.

Nowadays, gastronomy is compared to fashion in the world; every year, new gastronomic trends emerge, and gastronomic professionals must continually reinvent themselves to create new products, recreate new techniques and innovate culinary concepts. There are international gastronomic consultancies that launch their forecasts on the novelties, trends and expectations of the market.

The year 2020, 2021 and 2022 have been changing, where confinement and isolation forced the human being to create new habits of enjoyment of the table as the gastronomic shows, which is where you enjoy with the senses, where the customer seeks above all new experiences that go beyond the menu, and is that food has ceased to be a necessity to become a gastronomic adventure.

That said, it implies that gastronomic professionals go beyond their limits and look for those culinary techniques hidden from the view of the kitchen; being the case of the caramel technique, which is the cooking of sugar until obtaining a malleable texture that allows the elaboration of artistic pieces for exhibition or consumption.

2. DEVELOPMENT

2.1. Caramel

Few culinary processes are more dramatic than caramelization, but transforming white sugar into a rich caramel is simply heat work (Farrimond, 2017).

How does sugar respond to heat?

Caramelization is not melting but rather the "thermal decomposition" of sugar to create something completely new. When hot enough, the sugar molecules smash into each other so violently that they break apart before transforming into thousands of new fragrant molecules, ranging from spicy and bitter to subtle and buttery. There are two techniques for making caramel: wet and dry.

The drying technique is less versatile but is easy to do as it simply involves heating the sugar in a heavy-bottomed pan. The sugar turns a molten amber, then turns brown, and its molecules break down, losing their sweetness. The caramel is at its best when dark amber and can be poured over nuts for a brittle or as a sauce base.

Sugar is a sculpting material. Add a little moisture and heat and get a wide range of moldable consistencies: creamy, crunchy, brittle and rock-hard.

2.1.1. Components

Water

Considered the solvent of water-soluble components, reactant and reaction medium. The role of water as a determining agent of food texture is based on the dipolar character of its molecule (Tur Marí, 2008).

The moisture content of the caramel, as well as in all food matrices, determines how it behaves to a great extent. The more water there is in the food, the more the growth of microorganisms and the probability of chemical and enzymatic reactions will be favored (Martinez et al., 2000).

Water serves as a slowing and homogenizing tool in the caramelization process.

In these sweets, stability problems are aggravated by the fact that foods saturated with sugars and very hygroscopic tend to absorb water from the environment during and after baking.

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The base ingredients of caramel are sucrose, glucose syrup and water, known as honey or syrup in the mixing stage. It can be produced at atmospheric pressure, which requires a final temperature of 150 °C to achieve the desired final concentration and the minimum moisture content for storage (Treybal, 1999).

White sugar or sucrose

It is known as sucrose, table sugar or common sugar. McGee, in 2008, indicates that it is formed by a glucose molecule and a fructose molecule, which is obtained mainly from sugar cane as well as from the beetroot Beta vulgaris subspecies vulgaris Altissima Group,

They belong to the carbohydrate group, a group that also includes starches.

There are two groups of sugars: monosaccharides and disaccharides,

Sucrose is the most abundant organic chemical in the world. Its partial hydrolysis is commercially exploited in the inverted sugar used in beverages, as it reduces the sugar needed to provide a given sweetness. In addition, this sugar has a very high degree of solubility, a great capacity for hydration, and is less hygroscopic than fructose; all these characteristics make it used in the preparation of various foods (Badui, 2006).

Table sugar contains 99.5% sucrose, making it possible to produce a crunchier and more stable caramel, and the more refined the sugar is, the lower the moisture level in its structure since, through this refining process, the residual traces of sucrose are eliminated.

Sugars have a special affinity for water, dissolve easily in it and form temporary but strong bonds with water molecules in their vicinity, thus sugars retain moisture in baked dishes, prevent frozen desserts from solidifying into a solid block of ice, form an adherent matrix that holds food particles together in preparations such as marzipan and granola bars, maintain a moist, glossy appearance in glazes, and help preserve fruits by robbing moisture from spoilage microbes and preventing their growth.

Boiled sugar

If the sugar is boiled until almost all the water evaporates, it solidifies as it cools. This process allows decorative pieces to be made from sugar boiled at 149°C or higher, which is shaped while still hot. Sugar that is boiled to form a syrup undergoes a chemical change called inversion; inverted sugar resists crystallization. The amount of sugar inverted depends on the amount of acid present. Just enough cream of tartar or glucose is added to the syrup to form a mass of extremely fine sugar crystals, which gives the fondant its pure white color. This technique is also used when working with icing sugar. If too much cream of tartar or glucose is used, too much sugar is inverted so that the sugar becomes too soft and sticky to work with and does not harden sufficiently upon cooling. If not enough cream of tartar or glucose is added, too little sugar is inverted, and the sugar is too hard, so it is complicated to work and breaks easily.

The temperature at which the syrup is boiled is important; the higher it is, the harder the sugar will be. The temperature used is 149 to 157°C. When the temperature exceeds 159°C, the sugar begins to caramelize. Cooking at a lower temperature gives a softer sugar that is easier to work with; it does not keep its shape or keep well.

Regarding the temperature and the addition of cream of tartar or glucose, it is important to take two more precautions. When first boiled, it discolors more rapidly than pure sucrose. Therefore, acid or glucose should not be added until the syrup reaches a temperature of 104 to 110°C (104 to 110°F). Secondly, the syrup should be boiled rapidly over moderate heat because if it is boiled slowly, it will have more time to discolor and will not be a clear white color (Gisslen, 2012).

High purity sugar

It is a high-quality sugar resulting from a double crystallization and filtration process using animal bone charcoal and inert earth. The sugar is bleached by physical processes, not by chemical processes, resulting in a minimum sucrose content of 99.8% (El Tiempo, 1994).

This high-purity sugar is appreciated for its purity, color, cloudiness, ash and sediments. It is also used in producing soft drinks, juices and soft drinks, confectionery, sauces and preserves, liqueurs, dairy products, bakery and pastry products, food in general and medicines.

Isomalt, Isomalt, Isomaltitol or Isomalt

Isomalt is a disaccharide sweetener composed of glucosorbitol and glucomannitol, known to withstand high baking temperatures of up to 180°C with a melting temperature of 110°C.

Larrea (2021) indicates the following properties of Isomalt:

- White, crystalline, odorless and with good stability.
- It is obtained from sucrose by enzymatic action, transforming it into isomaltulose, which is subsequently hydrogenated. Isomalt contains two different disaccharide alcohols: glucomannitol and glucosorbitol. The molecular changes in these steps make Isomalt chemically and enzymatically more stable than sucrose.
- Stable at high temperatures, it can be heated without losing its sweet taste or decomposing. This
 makes it suitable for products that undergo heat treatments, such as baking.
- Low hygroscopicity absorbs very little water, which prevents products made with Isomalt from becoming sticky, making it important and practical in producing candies, where it avoids having

to wrap them individually. In addition, another advantage derived from this property is that, as the products do not absorb moisture, they have a longer shelf life.

- Isomalt improves flavor transfer in foods. It dissolves more slowly in the mouth, so treats made with Isomalt have a longer-lasting flavor. In addition, Isomalt does not have the "cooling" effect of other polyols, which is sometimes undesirable.
- Sweetening power similar to sorbitols, although this depends on its concentration, temperature and the form of the product in which it is used. Its low sweetness is a characteristic to be taken into account.
- Non-cariogenic. It can even help to heal incipient caries lesions thanks to the stimulation of salivation in the mouth.
- It does not produce an increase in blood glucose or insulin levels.
- The sensory properties of Isomalt make it an ideal ingredient in products such as candies, chocolates, baked goods, hard candies, toffees, chewing gums, nutritional supplements, cough drops and throat lozenges.
- It can be used without limit in the maximum quantity (Quantum satis), as long as good manufacturing practices are followed.
- A certain prebiotic effect on bifidobacteria is attributed to it.
- Synergies: good qualitative and quantitative synergies with intensive sweeteners, giving the
 product body, texture and a mild sweetness, while intensive sweeteners raise the sweetness level
 to the desired level in the product. Isomalt can mask the bitter aftertaste of other intensive
 sweeteners.

It is also appreciated for its elasticity, malleability and neutral flavor.

Glucose

Also called dextrose, it is a simple sugar and is the most common sugar from which living beings directly extract chemical energy. Glucose is found in various fruits and honey but is always mixed with other sugars. It is the structural unit from which starch chains are built. It is most often found as the sweet substance in corn syrup, which is made by breaking down starch into individual glucose molecules and small chains of glucose. A chain of two glucose is called maltose. Compared to table sugar or sucrose, glucose is less sweet and water-soluble and forms a lower solution. It melts and begins to caramelize at approximately 150°C. (McGee, 2008)

This ingredient can absorb or give up moisture. Therefore it is used in the preparation of whipped and fermented doughs as a preserved product; it is also used in sugar decorations such as gum paste, fondant, pastillage and even plastic chocolate due to its elasticity, facilitating the handling of these preparations. In addition, it is used in the ice cream industry since it prevents recrystallization and enhances the creamy consistency; it is also used as a stabilizer in the production process.

It is present in fruits, the most abundant organic compound in nature, being found in free form or combined form. Its use in confectionery is as an ingredient in sugar toppings. The advantages it offers, it is resistant to decomposition, requires little time to dissolve, is easily digestible, enhances flavor and gives a smoother consistency to products (Shendurse & Khedkar, 2016).

For the production of blown caramel, the standard use is 10 to 20% of the total weight of sugar; however, there is evidence of uses of up to 40%.

Ascorbic Acid

Among the most important acid sugars is ascorbic acid or vitamin C, which is found mainly in fruits. In addition to its nutritional relevance, it gives rise to several chemical reactions that produce yellow pigments in foods containing (Badui, 2006).

Tartaric

It is found in avocados, grapes and grapefruit. It shifts the balance of the system to the flavilium form, with glutathione acting as an antioxidant and used as a sequestrant and flavoring agent. (Badui, 2006)

Acetic

It is a product derived from yeast, reduces the strong acid taste, and is more soluble. They have been used for centuries to preserve foods and improve their sensory properties. (Badui, 2006).

Citrus

It is present in practically all vegetables. It is present in the form of crystals, and it is very soluble in water; it is used as a metal sequestrant that can cause the oxidation of terpenes responsible for the aroma of these products; it helps the action of antioxidants and also as a flavoring agent (Badui, 2006).

Acids are naturally occurring, so over the years, the safety of their consumption has been proven. In this case, most countries do not restrict their use; the only limitation is related to consumer acceptance (Badui, 2006)

Acids act as catalytic agents in the caramelization process; they are generally found naturally, which is why they have been used throughout the years, and their implementation is safe for human

consumption. The relationship it has with caramel is that the addition of acid accelerates the caramelization process and helps as a preservative and flavoring.

Under acidic conditions, the enolization and isomerization of monosaccharides occur under slower kinetics than those in alkaline media. Reactions such as caramelization by heating at low pH values involve dehydration of the sugar molecules, forming cyclic compounds responsible for non-enzymatic browning (Belitz & Grosch, 1997).

Dyes

Due to the composition and artistic purposes of the candy, the ideal colorants are water-soluble, preferably in gel form, to keep water activity in the formulation to a minimum.

2.2. Reactions to the candy

2.2.1. Caramelization

Non-enzymatic browning, in general, is the name given to the browning of a food product due to any reaction that does not pertain to enzymatic activity. Although these include various reactions, such as lipid oxidation or ascorbic acid degradation, non-enzymatic browning is mainly associated with carbohydrate degradation reactions, such as caramelization and Maillard reactions (BeMiller and Whistler, 1996).

Sugars are considered wonderfully resistant materials, unlike proteins which denature and coagulate easily, fats which go rancid in contact with air and heat, and starch chains, which break into shorter chains of glucose molecules; sugars are small and stable molecules. As a result, they mix easily with water, tolerate the heat of boiling and, when sufficiently concentrated in water, readily bind to each other and form pure, solid masses or crystals. This tendency to form crystals is how pure sugar is obtained from plant juices; thus, various types of sweets are made (McGee, 2008).

The caramelization reaction is the name given to a set of reactions that occur in carbohydrates when exposed to elevated temperatures without the presence of amino groups from proteins. Factors affecting the reaction are pH, salts and the carbohydrate concentration (mainly sucrose) in the solution. At the beginning of the reaction, in caramelization, there is hydrolysis of sucrose to break down this disaccharide and produce glucose and fructose. As further degradation of these products occurs, other compounds are formed, with a special preponderance of 5-hydroxymethylfurfural (HMF). The typical brown color developed during caramelization is attributed to the production of polymeric products during the reaction; HMF and furfural are known as precursors of such polymers (Quintas et al., 2007).

Caramelization is the browning reaction known as pyrolysis, which occurs when sugars are heated above their melting point. The reaction occurs at both acidic and alkaline pH, and is accelerated by adding carboxylic acids and some salts (Pauletti et al., 1999).

The dehydration of sugars in the caramelization process generates many chemical compounds; furfural and its unsaturated derivatives are produced, which polymerize with themselves or with other similar substances to form the macromolecules of pigments called melanoidins. During this transformation, several low molecular weight and highly odorous compounds are also synthesized, such as furans, furanone, lactones, pyrones, aldehydes, ketones, acids, esters and pyrazines, as well as others with conjugated double bonds that also absorb radiant energy and thus produce colors.

2.2.2. Crystallization

This is the name given to the chemical reactions that occur when sugar is heated to the point where its molecules begin to break down. This destruction triggers a remarkable series of chemical creations. From a single type of molecule in the form of simple sweet but colorless and odorless crystals, the cook generates hundreds of new and different compounds, some of which are small sour or bitter or intensely aromatic fragments, while others are large, flavorless aggregates, but with an intense brownish color. The more the sugar is cooked, the less sugar and sweetness remain, and the darker and more bitter it gets (McGee, 2008). So, the higher the cooking temperature, the more the sugar degrades.

Syrup performance in the cold water test	Syrup boiling point ^o C	Jams
Filament	102 - 113	Syrups, compotes
Soft ball	113 - 116	Fondant, fudge
Firm ball	118 - 121	Candies
Hard ball	121 -130	Marshmallows, nougat
White fracture	132 - 143	Taffy
Hard fracture	149 - 154	Butter fudge
Γ	160 - 168	Hard candies, toffee
	170	Light caramel for syrups, color and taste
	180 - 182	Cotton candy
	188 - 190	Dark caramel
	205	Black candy

Tab	le 1.	Sugar	points
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* Above 165 °C, the sugar syrup is more than 99% sucrose. It no longer boils, but begins to decompose and caramelize. Boiling points depend on altitude. For every 305 meters above sea level, 1°C must be subtracted from the boiling points indicated.

Prepared by: Authors

Source: (McGee, 2008)

Invert sugar is a mixture of two simple sugars, dextrose and levulose, resulting from sucrose's separation. It is produced naturally in bee honey, which is why this product is so sweet; a slight increase in sweetness is perceived due to the hydrolysis of sucrose.

2.3. Techniques

Yarn

It is a skein of thin, hair-like sugar strands used to decorate cakes and showpieces. Since it does not keep well, spun sugar should be prepared before it is used. It gradually absorbs moisture and becomes sticky. Sooner or later, this moisture will cause the sugar to dissolve (Gisslen, 2012).

Its application is for desserts, and it can be colored with colorants, preferably in gel form, to minimize water activity and avoid deterioration of the piece.

Molding

It is a clear, boiled sugar that can harden in different forms. Although it is usually molded in flat sheets like glass, it can be poured into molds of various shapes (Gisslen, 2012). It is customary to color the candy, even before pouring it.

It works with stainless steel or silicone molds, preferably on a lightly oiled marble slab.

Blowing

Known as *blown sugar*. They are considered the most complex artwork due to the rigorous technique, perfectly crafted candy dough, and the practice time to develop the skill.

Experts prefer to boil the syrup at a lower temperature, 143 to 149°C, so the sugar is a little softer. However, boiling at 157°C makes harder finished pieces that keep better (Gisslen, 2012).

It requires a lot of artistic skill and practice. This type of sugar is the same as the preparation of the sugar stretched. The only difference is that the sugar must be cooked at a temperature between 150°C and 157°C, which facilitates the subsequent blowing of the sugar.

The processes for this type of caramel are various and depend on the preferences of the chefartist (Marín, 2011) proposes two cookings, one at 125°C and adding ascorbic acid, and then cooking up to 155°C.

Stretching

Known as *pulled sugar, it* is considered the most difficult candy to achieve due to the great mastery of the material. There are three steps to follow: cooking the material, drawing the sugar to achieve a satin finish and assembling the artistic piece (Sebess, 2007).

This type of caramel is used for elaborating ribbons or ribbons of a single color or amalgamated, which allows one to admire the perfection of handling temperatures and textures.

Casting

It is the most used for assembling structures and bases for artistic assemblies. The cast sugar can be opaque or translucent; once the caramel has reached a temperature of 150°C to 160°C, pour slowly into molds of various shapes, and once cold, remove the molds.

Spun sugar

It is a skein of thin, hair-like sugar strands used to decorate cakes and showpieces. Since it does not keep well, spun sugar should be prepared just before it is used. It gradually absorbs moisture and becomes sticky. Sooner or later, this moisture will cause the sugar to dissolve. (Gisslen, 2012).

Satin

When the caramel is repeatedly stretched, air particles enter the caramel, resulting in golden, coppery, pearly and pearlescent reflections. When heated, it melts, and when cooled, it crystallizes and hardens. Finally, the pieces are glued together with heat or melted caramel.

3. Process

3.1. Sequence of the process

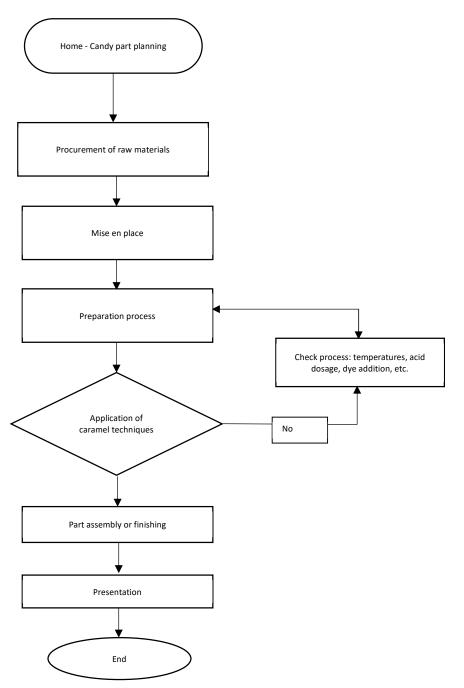


Figure 1. Flow chart of manufacturing processes and applications in Carmelo. Source: Own elaboration

Procedure for the production of blown caramel

The general procedure applies to spun sugar, stretched sugar, etc., as proposed by the author (Gisslen, 2012), with some observations for the styles indicated below.

- a. Pour the sugar and water into a large saucepan.
- b. Place the mixture over low heat and stir gently until the sugar dissolves.

- c. When the sugar dissolves, turn the heat moderately high and stop stirring.
- d. Place a sugar thermometer in the pan.
- e. While boiling the sugar, keep the sides of the pan free of crystals with a brush wet.
- f. When the temperature reaches 104 to 110°C, add the acid dissolved in a little water or glucose.
- g. Boil rapidly until it reaches the desired temperature.

Spun sugar

Prepare the workplace by placing two lightly oiled sticks at the edge of the table so that they protrude 30 to 60 cm. They should be parallel, 30 cm apart. Put enough paper on the floor under the sticks so that they drip there. To spin the sugar, you need a wire whisk with the ends cut off. You can also use a fork, but it is not as efficient. When the temperature reaches 104 to 110°C, add the acid dissolved in a little water or the glucose. Boil quickly until it reaches the desired temperature. (Gisslen, 2012).

Molded sugar

Prepare a mold, bend a metal strip to give it the desired shape and place it on a marble slab. If you are going to make round figures, use a metal ring. For small circles or other shapes, cookie cutters can be used. To prevent the hot syrup from dripping from under the strip, attach it to the marble on the outside with any material, such as plasticine. Lightly oil the inside of the strip and the marble slab. Prepare a syrup exactly the same for the stretched caramel. Pour into the mold until it has the desired thickness. Let it cool for 5 minutes. Slide a spatula under the mold to loosen the sugar from the marble, and let it cool completely until it is hard and brittle (Gisslen, 2012).

4. Equipment and Work Tools

Table 2. Working tools

Detail	Description of use	Reference image
Infrared lamp 1800WW	Place the candy so that it is under the light bulb and activate the infrared light so that it starts to heat up. In this way, the candy will receive enough heat to keep it at an optimum temperature.	
Silpat	Place the caramel on the tray; it can withstand temperatures up to 250° C.	

Dryer	It must have cold air to cool the piece of caramel as it takes the desired shape.	
Candy thermometer	Stainless steel sleeve Glass body with red alcohol 80°C - 200°C	
Cannulas or suffusion pump for candy	It is worked under a lamp, stretching and folding it to distribute the air bubbles and homogenize the heat.	
Kitchen torch	It should be kept a few centimeters away from the caramel to avoid burning; it is used to caramelize a surface.	
Airtight container	To preserve the candy decorations, use a hermetically sealed plastic or glass container to protect the candy.	S S S S S S S S S S S S S S S S S S S

Source: Own elaboration.

5. Conclusions

The application in caramel is considered one of the most complex gastronomic arts to be captured in a final piece due to the demand for mastery of techniques such as blowing, spinning, stretching, molding and modeling, as well as expertise in temperatures and proportions of components; and finally the recognition of reactions produced in the caramel.

The more refined the sugar is, the lower the level of humidity in its structure and the starches are eliminated from the sucrose in the photosynthesis process, as well as the impurities, which is why it is advisable to use a high-purity sugar for caramel work to achieve higher quality in the piece.

The caramelization reaction is a culinary chemical that occurs in carbohydrates, especially in sugars such as sucrose. This reaction generates many compounds that cause changes in sensory characteristics, especially in color, through the melanoidin pigments that give these foods their characteristic dark color.

This study aims to become the theoretical, technical and analytical foundation of the application in caramel, with projection to future bromatological analyses and subsequent publications of high relevance.

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