

HEAT TREATMENT OF CARBOHYDRATES TO PRODUCE CARMEL  
COLOR

KHALIZATUL RADHIAH BT KASIM

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Faculty of Chemical Engineering & Natural Resources  
University Malaysia Pahang

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## ABSTRACT

Caramel colors are brown powders or viscous liquids that are used to impart yellow to dark brown and have been used in carbonated beverages, distilled liquors, wines, pharmaceutical, extracts, bakery products, candy, soups, and baked beans for decades. This color additive can be prepared from various sources of carbohydrates such as glucose, corn, molasses, wheat, and tapioca hydrolysates by controlled heat treatment in the presence of certain reactants. The purpose of this study is to produce caramel color from different sources of carbohydrates as well as investigate the effect of pH on the development of the browning reactions. In this study, two set of experiments were conducted. The first is production of caramel color from glucose solution. Glucose sample of different pH are pre-heated in water bath at 100°C and further heated at caramelization temperature of 121°C in paraffin bath. The color development was monitored using U-1800 Hitachi UV-Visible Spectrophotometer. The second experiment is production of caramel color using starch hydrolysates produced from acid hydrolysis of corn starch by microwave heating. In this particular experiment, the starch concentration was varied to study the effect of starch concentration. Different length of heating time for microwave assisted hydrolysis of starch was used. As a result, the color intensity was observed highest at pH 8, in lower concentration of starch, 0.7 g/ml and 10 minutes of microwave heating. Hence, it is concluded that alkaline condition is a suitable reaction medium to produce caramel color while the required time for caramelization completion is 1.5 hours.

## ABSTRAK

Warna karamel ialah serbuk perang atau cecair likat yang biasanya digunakan untuk memberi warna kuning atau coklat tua dalam pembuatan minuman berkarbonat, arak, farmaseutikal, ekstrak, produk bakeri, gula-gula, sup, dan kacang panggang. Bahan pewarna ini dapat disediakan daripada pelbagai sumber karbohidrat seperti glukosa, jagung, molases, gandum, dan ekstrak ubi kayu secara pemanasan terkawal dalam kehadiran reaktan tertentu. Tujuan kajian ini adalah untuk menghasilkan warna karamel daripada sumber-sumber karbohidrat yang berbeza di samping bertujuan untuk menyiasat kesan pH ke atas penghasilan warna karamel. Kesan kepekatan larutan kanji ke atas penghasilan warna caramel juga merupakan salah satu fokus dalam kertas ini. Dalam kajian ini, terdapat dua set eksperimen telah dijalankan. Eksperimen pertama adalah menggunakan glukosa sebagai sumber karbohidrat di mana sampel glukosa pada pH berbeza dipanaskan dalam rendaman air di 100°C dan kemudian dipanaskan pada suhu pemrosesan karamel iaitu 121°C dalam parafin. Penghasilan warna diperhatikan menggunakan UV Hitachi U-1800 Visible Spectrophotometer. Eksperimen kedua dilakukan dengan menggunakan kanji yang dihasilkan daripada hidrolisis tepung jagung menggunakan asid di dalam gelombang ketuhar. Dalam eksperimen ini, pelbagai kepekatan larutan kanji disediakan untuk mengkaji kesannya terhadap penghasilan warna karamel. Tempoh pemanasan untuk kanji di dalam gelombang ketuhar dimanipulasikan. Keputusannya, warna karamel yang terang telah diperhatikan di pH 8 serta pada kepekatan kanji yang rendah, 0.7 g/ml dan waktu pemanasan di dalam mikrogelombang selama 10. Kesimpulannya, medium alkali sesuai untuk penghasilan warna caramel dan masa untuk penghasilan warna caramel yang sempurna ialah 1.5 jam.

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**LIST OF ABBREVIATIONS**

4-MeI	4-methylimidazole
5-HMF	5-(hydroxymethyl)-2-furaldehyde
DAP	monohydrogenphosphate
DE	Dextrose equivalent
EBC	European Brewery Convention
FDA	Food Drug and Administration
GLC	Gas-Chromatography Liquid
GRAS	Generally recognized as safe
HCl	Hydrochloric acid
HMW	High molecular weight
LMW	Low-molecular weight
THI	2-acetyl-4-(1,2,3,4-tetrahydroxybutyl)imidazole
UV	Ultra-violet

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## **CHAPTER 1**

### **INTRODUCTION**

#### **1.1 Research Background**

The first and commercial caramel color was produced in Europe about 1850 (Chappel and Howell, 1992). Caramel color first gained commercial importance as an additive in brewery products (e.g., porter, stout, dark beers, and ales) and as a colorant for brandy. In 1858, the French chemist M. A. Gelis authored the first known published technical study of caramel color. Later in 1863 in United States, caramel color has become an item of commerce before regulations affecting their use were introduced (Chappel and Howell, 1992).

Caramel color is one of the most essence researched commodities in the world today. It has been published in thousands of literature studies with a wide range of topics. Its benefits and applications have been, and continue to be, widely studied and discussed extensively. The use of synthetic coloring agents has been avoided at from a standpoint of their safety problem, while caramel is a well-known material used in many industries as a natural harmless coloring agent and it appears as a promising substitute therefore at the present time. Its use in food industries required no limitations since it is classified as 'generally recognized as safe' (GRAS) substance by Food Drug and Administration (FDA).

In industrial scales, caramel colors are always highly concerned in the field of food industry either as a flavor ingredients or a coloring additive. Ever since, caramel is designed for these purposes and its manufacture for commercial use is an important technological process that takes place under rather strictly controlled

conditions and selected ingredients. Therefore, demands of the caramel quality improvement and controls as well as the market are increasing.

### **1.1.1 Caramel Color**

Caramel colors are brown powders or viscous liquids that are used to impart yellow to dark brown and have been used in carbonated beverages, distilled liquors, wines, pharmaceutical, extracts, bakery products, candy, soups, and baked beans (Fetzer, 1938). It accounts for more than 80% (by weight) of all colorants added to the foods we consumed (Kamuf et al., 2003). This color additive can be prepared from various sources of carbohydrates such as glucose, corn, molasses, wheat, and tapioca hydrolysates by controlled heat treatment in the presence of certain reactants (Pintea, 2008). Different reactants such as acids, alkalis, salts, ammonium salts and sulfites can be added depending on the type of caramel color.

### **1.1.2 Classes of Caramel**

Caramel color is a versatile food colorant. It is produced to have a broad spectrum of target consumers. Therefore, it is classified into four classes of caramel according to types of reactant and its color intensity as shown in Table 1.1:

- i. Caramel Class I (plain or spirit caramel):  
Prepared by heating carbohydrates with or without acids or alkalis; no ammonium or sulfite compounds are used.
- ii. Caramel Class II (caustic sulfite caramel):  
Prepared by heating carbohydrates with or without acids or alkalis in the presence of sulfite compounds; no ammonium compounds are used.
- iii. Caramel Color III (ammonia caramel):  
Prepared by heating carbohydrates with or without acids or alkalis in the presence of ammonium compounds; no sulfite compounds are used.
- iv. Caramel Color IV (sulfite-ammonia caramel):

Prepared by heating carbohydrates with or without acids or alkalines in the presence of both sulfite and ammonium compounds.

**Table 1.1:** Codex Classification of Caramel Colors

Table I. Codex classification of caramel colors				
Parameter <sup>a</sup>	Class I – E150 a	Class II – E150 b	Class III – E150 c	Class IV – E150 d
Color intensity	0.01–0.12	0.06–0.10	0.08–0.36	0.10–0.60
Total nitrogen (%)	<0.1	<0.2	1.3–6.8	0.5–7.5
Total sulfur (%)	<0.3	1.0–3.5	<0.3	1.4–10.0

<sup>a</sup> Expressed on a solids basis.

### 1.1.3 Properties of Caramel Color

The most importance properties when dealing with caramel color are tinctorial power, stability and compatibility with food which depend on types of reactant used and technical conditions such as time, temperature, moisture content and pressure.

Since caramel color is a result of a complex chemical composition, the complete characterization of caramel is a difficult task (Delgado-Vargas and Paredes-Lopez, 2002). However the color properties can be characterized by the tinctorial power which is a function of color strength. Higher tinctorial power shows the higher color strength of a caramel and hence, darker color. The tinctorial power can be measured using the following formula:

$$\text{Tinctorial power} = K = K_{560} = A_{560}/cb$$

where A = absorbance at specified wavelength,

c = concentration (g/l),

b = cell thickness

Alternatively, the color properties can also be characterized using hue index;

$$\text{Hue index} = 10 \log (A_{510}/A_{610})$$

which is inversely proportional to tinctorial power. Hue index measures the redness of the caramel color. The higher redness gives higher hue index but lower tinctorial power and vice versa. Similarly, the color strength of caramel could also be represented as the color intensity which also is the measure of absorbance at 610 nm, over a 1-cm path length, of an aqueous solution of 1g caramel color solids/litre. The 610-nm wavelength was selected because most of the data correlating absorbance with color strength, as determined by the European Brewery Convention method (WHO, 1976), were generated using this length (Licht et al., 1992).

The stability of a caramel depends on the charge carried by reactants in a caramel. If reactants in a type of caramel are all negatively charged, then the color is stable. In contrast, if the reactants consist of negatively and positively charge molecules, then the caramel color will coagulate and this result in unstable caramel color (Kamuf et al., 2003). The valuable functional properties of caramel to slowly absorb oxygen can stabilize the colloidal system which in turns prevents haze formation and facilitates flavor retention (Chappel and Howell, 1992).

The compatibility of a caramel color can be defined as the absence of flocculation, precipitation and haze formation (Pintea, 2008). This again relates with the stability of caramel color. A stable colloidal system will prevent precipitation or coagulation which usually happens between oppositely charged molecules. A caramel color is said to be compatible when the particles of the caramel color must have the same charge as the colloidal particles of the product to be colored. For example, a soft drink contains negatively charged colloidal particles, and therefore, a negative caramel color should always be used (Gelis, 1858).

#### **1.1.4 Importance of Caramel Color**

Caramel color has a significance value as food additives that act as a provider for food coloring and pleasant odor to foods. The importance of caramel color lies on its valuable functional properties. Therefore, caramel color is widely used in the beverages industry to gives color to drinks. In US, more than 80% of caramel is used

to color drinks such as colas and beers due to its ability to prevent haze formation in beers and improve the shelf lives of beverages. In fact, the addition of caramel color to blended whiskeys can compensate the color loss produced by neutral spirits during the mixing. In other areas of application, caramel also contributes its color in the confectionery product, baked goods, cereals, desserts and spice blends (Pintea, 2008).

### **1.1.5 Caramelization**

The process that leads to production of caramel color is referred as caramelization. Caramelization is a kind of non-enzymatic browning (Tsai et al., 2009). It is usually formed when sugars are being heated at high temperature above 80°C and pH range of 3 to 9 without amino groups (Davies & Labuza, 2005; Kroh, 1994) either dry or in concentrated solution, either alone or with certain additives. Caramelization reactions include changes in the ring size of monosaccharides, breakage and reformation of glycosidic bonds, dehydration, introduction of double bonds and the formation of anhydro rings. Caramel color can also be obtained through maillard reaction (nonenzymatic browning) (Kamuf et al., 2003). In general, the formation of caramel involves condensation reactions in which water molecules are lost (Benhura et al., 1999).

The caramelization of carbohydrates polymer and their mixtures with low-molecular-weight sugars is of particular interest for food processing not only because of the caramel flavor and color, but also because the changes in sugar structure and the liberation of water during the caramelization reaction could have a potentially significant effect on the mechanical and barrier properties of the carbohydrate system. In particular, the water liberated during caramelization could decrease the glass transition temperature of the amorphous carbohydrate matrix (Johanna & Job, 2006).



## 1.2 Problem Statement

Caramel color are produced from the carefully controlled heat treatment of carbohydrates such as dextrose, invert sugar, lactose, malt syrup, molasses and starch hydrolysates. Carbohydrate sources must be rich in glucose because caramelization occurs only through the monosaccharide.

The hydrolysis of starch using conventional heat treatment with hydrochloric acid, HCl require long time and high energy as well as the low conversion.

Thus in this research, a compact microwave oven is used to hydrolyze starch added hydrochloric acid which requires less than 10 minutes at lower energy.

## 1.3 Objectives

- i. To produce caramel color from different sources of carbohydrate.
- ii. To study the effects of pH and time on caramel color intensity.
- iii. To determine the optimum time required for caramelization reaction completion.
- iv. To produce caramel color from corn starch hydrolyzed in microwave oven.

## 1.4 Scopes of Study

- i. Two sources of carbohydrates; glucose and corn starch were used in this research.
- ii. A Sharp compact microwave oven with a frequency of 2.45 GHz is used for starch hydrolysis.
- iii. The production of caramel color in this research is conducted at pH of 8 and pre-heating temperature of 100°C.
- iv. This research is focused on Ammonia caramel which is caramel class III.

## **CHAPTER 2**

### **LITERATURE REVIEW**

#### **2.1 Introduction**

A lot of studies have been done upon caramel color. For the past decades, scientists have conducted numerous experimental studies on the manufacturing of caramel color with the purpose of developing the highest quality of caramel.

The color can be produced or manufactured from various carbohydrates raw material in any container (reactor) to effect caramelization. Years of experience and experimentation have conveyed a greater understanding of the caramelization process so that caramel color manufacturers today use highly controlled processes that provide a uniform and reproducible product. The manufacture process of caramel color requires careful control of temperature, pressure and pH to ensure that the brown color obtained has high tinctorial power and remain unchanged over extended period.

Therefore, a lot of improvements have been applied to the process in terms of reactor, raw material and operating conditions such as pH, temperature and reactant concentration since these are among factors that affect quality of caramel color.

During the manufacture, unsaturated reactive species created by the dehydration of carbohydrates polymerize to form high molecular weight constituent (HMW). Low-molecular weight (LMW) products are also formed by degradative reactions. The latter is said to be the caramel color markers in which it is used for caramel color characterization in various studies.

## 2.2 Caramel Color Manufacture

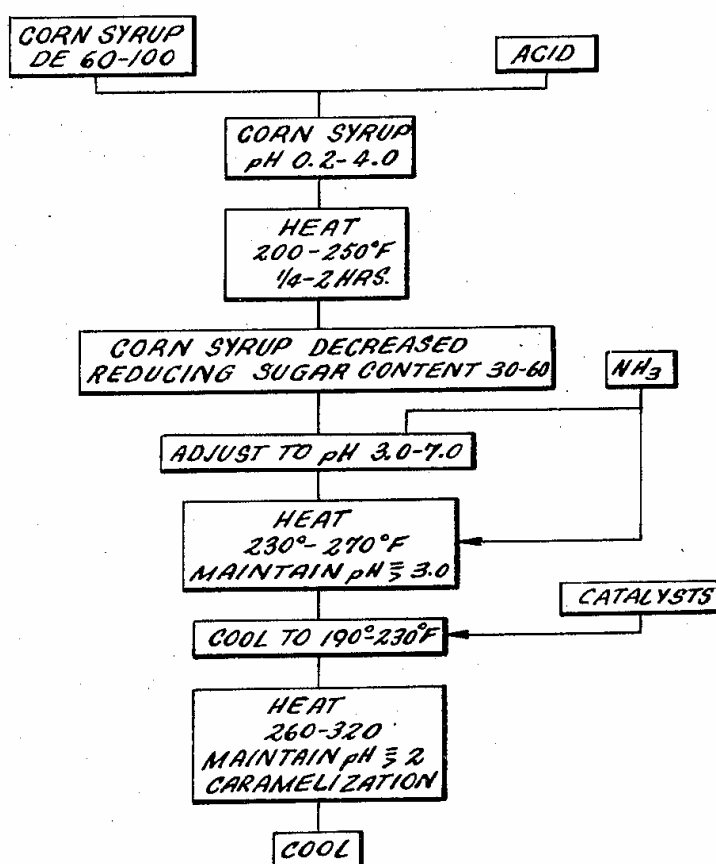
Caramel color was originally made by heating sugar to certain temperatures up to about 204°C until 15% of the initial weight was lost (Chappel and Howell, 1992). This natural colorant has been manufactured from various carbohydrates such as cane sugar, molasses, glucose, fructose and honey. Glucose and fructose are the sugars that caramelize readily. Though the process of caramel color manufacture has been published in thousand of literatures in many countries, efforts still continues in exploring new method or material for the process. Hence, various method of preparing caramel color will be discussed hereafter.

The manufacture of caramel color had been described briefly by Myers and Howell in their literature *Characterization and Specifications of Caramel Colour: An Overview*. According to the literature, sufficient amount of carbohydrate is added to the reaction vessel at a temperature range of 50°C to 70°C. Once the temperature is increased to 100°C, reactants are then added and heating continued until the desired temperature is reached. The desired pressure for this process is 0 kg/cm<sup>2</sup> for open-pan process and 5.3 kg/cm<sup>2</sup> for closed-pan process. Since the process is exothermic, temperature controlled is crucial. After obtaining the desired color intensity, system is cooled either by flash cooling; or flooding of external or internal reactor cooling coils; or passing the product through a heat exchanger; or directly adding water to the product. Upon cooling, the product temperature is approximately 80°C. It is filtered through a leaf-type or plate-frame filter coated with diatomaceous earth or simply filtered through a fine (100-mesh) screen. Finally, the filtrate is pumped into a holding tank and the pH and specific gravity are adjusted accordingly to meet user specifications (Myers and Howell, 1992).

In a research of caramel color preparation, Meisel invented method to manufacture caramel color in continuous process in order to improve caramel color quality that had been processed in batch reactors. In his study, Meisel used a heat exchanger consists of a jacketed tube equipped with scrapers rotating at high speed to maximize the heat transfer to carbohydrate liquor (Meisel, 1969). With reference of two carbohydrate materials; starch hydrolysate and sucrose, he discovered that caramelization of carbohydrates can be carried out on a continuous basis in shorter

time. He also stated that by using heat exchanger where continuous agitation of the carbohydrate liquor passing therethrough, it is possible to carry out the process at higher temperature for the same amount of reagent.

In different studies, a commercial method of producing caramel color was employed from hydrolysis products of starch or other suitable carbohydrates to provide a product of high acid fastness or stability in acid solution and in more economical way (Longenecker, 1952; Fetzer, 1956). Longenecker described the process in Figure 2.1.



**Figure 2.1:** Manufacture of Caramel Color

As illustrated in Figure 2.1, a corn syrup having a content of 60 to 100% of reducing sugar or D.E (dextrose equivalent) is first acidified to a low pH range of 0.2 to 4.0 before pre-heated at 200 to 250°F for 2 hours. The pre-treatment decreases the D.E content by 20 to 35 % to a value between 30 to 60 %. Anhydrous ammonia is then added as the neutralizing agent to bring the pH up to a value between 3.0 and 7.5.

After the addition of ammonia the liquid is further heated to a temperature of about 230°F to 270°F for a period of 15 minutes to 2 hours. Upon completion the desired time, the solution is cooled to within the range of 190°F to 230°F. If the solution is to be cooled to a lower temperature, then it is uneconomical. After the addition of final catalyst for instance sulfite compound, the liquid is heated to high temperature within the range of 260°F to 320°F and held until the desired caramelization is achieved or the required tinctorial power is obtained.

Preparation of caramel color from fruit waste has received significant attention from researchers. Sugary saps obtained from African oil palm (*Elaeis guineensis*) and wine palm (*Raphia hookeri*) had been analyzed and processed into caramel color by acid-heat treatment in the presence of ammonia (anhydrous) (Umerie, 2000). The acid-heat treatment in this process is fundamental to affect dehydration and polymerization of the sugars in the samples (Fetzer, 1964; Longenecker, 1952). The addition of ammonia (anhydrous) with continuous heating gives the desired product of concentration between 30-40°Bé. The use of sugary saps is believed to reduce cost and increase the availability of caramel.

The formation of caramel color from polysaccharide has been carried out by hydrolyzing the unusual carbohydrate to its monosaccharide. It has been proven in the production of caramel color from polysaccharide material extracted from the fruit of *Azanza garckeana* in the presence of ammonium salts. The mucilage is extracted from *Aganza garckeana* fruit with water and heated at 130°C until the brown color (caramel) is formed (Benhura et al., 1999). The heating process takes place in a VWR Scientific heating block set using 2.5 ml vial for a period of desired time. In the same study, the authors also prepare a larger scale of *Azanza* extracts and heated them in a stainless steel pot wherein samples were removed periodically in order to monitor the formation of caramel color. The formation of caramel color from this material would open opportunity to use fruit waste as a renewable resource in the caramel manufacturing as it may reduce cost as discussed earlier.

Processing of caramel color from malted tubers of *Cyperus esculentus* was reported by Umerie and Enebeli in 1996. The caramel produced from the malted tubers of *Cyperus esculentus* appeared as brown-black syrup. Kilning at temperatures up to 120°C produced a 'special malt' (Kneen, 1967) and from this the caramel was

also obtained. Hence, the caramel should find applications where it will add body, flavour or colour, as in some bakery products, non-alcoholic malt beverages, dark beers and in condiments production. It might then be developed for other applications (Umerie and Enebeli, 1996).

In particular applications; the food-colorant industry and the tobacco industry, the desired product in caramel color manufacture is the polymeric material and not the numerous volatile and semi-volatile compounds formed in such reactions (Lauterbach et al., 2002). The polymeric material is formed from the reactions of reducing sugars with ammonia and ammonium salts in Parr bomb at 93°C for 2.5 h.

### **2.3 Parameters that Affect Caramel Color**

In the production of caramel color from the usual carbohydrate materials, the formation of color depends on the nature of the starting material, its concentration, temperature, pH and the nature of catalysts that may be used (Benhura et al., 1999; Defaye et al., 2000). Hence, in this section, the parameters that affect the caramel color properties are discussed.

#### **2.3.1 Types of Starting Material and Initial Concentration**

The functional properties of caramel color such as color intensity and stability are primarily determined by the starting materials which in turn determine the chemical composition of the caramel. The usual carbohydrates used in the manufacture of caramel color are sucrose and starch hydrolysates of corn, wheat and tapioca.

Functional caramel color can only be produced from carbohydrates containing high glucose content because caramelization initially proceeds through monosaccharides (Pintea, 2007). For this reason, carbohydrates with a dextrose equivalent (D.E.) of less than 60 must be pretreated by acid hydrolysis to increase

glucose content. Acid hydrolysis tends to reduce or eliminate structural variation in starches of different vegetable origin. When sucrose is used, it is inverted to the monosaccharides before caramelization (Myers and Howell, 1992). Starch hydrolysate is one of the preferable sources of carbohydrates since it contain high dextrose equivalent (D-glucose) concentration which produces highest quality of caramel color (Burdock, 1997).

Benhura et al., 1999 described that formation of caramel color in a closed vials, where water was not allowed to evaporate off, the formation of color depended on initial concentration of polysaccharide extract. When concentration of polysaccharide was increased from 1 % to 5 % and 10 %, there was a corresponding increase in the formation of caramel color.

In acid hydrolysis of starch, Khan et al., 1979 confirmed that the formation of D-glucose or dextrose equivalent is increased with increasing starch concentration.

### **2.3.2 Type of Catalyst**

Myers and Howell in their paper stated that type of catalyst play a vital role in determining the final composition of the end product. For instance, Caramel Class I and Caramel Class II whereby no ammonium compound is added usually require higher temperature than that of required by Caramel Class III and Caramel Class IV. This phenomenon happens due to ammonium compounds ability to initiate the dehydration reactions of sugars that are critical to color formation more readily than do non-ammonium reactants such as hydroxides and carbonates used to prepare Caramel Class and II. Thus, the use of ammonium compounds permits the manufacture of products of higher color intensity than does the use of non-nitrogenous reactants.

In a research of caramel color prepared from polysaccharide, the effect of ammonium salts on the formation of caramel color was studied. In the presence of ammonium acetate and ammonium carbonate, the development of a brown color was less than in the control samples where no ammonium salts were added. However, the

presence of ammonium chloride and ammonium sulphate resulted in some improvement in the development of caramel color (Benhura et al., 1999).

Formation of polymeric material (2, 6-deoxyfructosazine) from a reaction between reducing sugar and ammonia and ammonium salts is enhanced when monohydrogenphosphate (DAP) is used as caramelization catalyst at constant pH of 8 (Lauterbach et al., 2002). This reactivity is likely due to the fact that the monohydrogenphosphate anion can act as both an acid and a base.

### 2.3.3 pH of Reaction Medium

A study on effect of starting material discovered that monosaccharides exhibited much more rapid brown caramel formation in alkaline condition (Anjadouz et al., 2001; Benjakul et al., 2005). In a recent research, fructose is observed to develop browning pigments more significantly at a pH of 7 and 10 but formed very few of brown pigments at a pH of 3 (Tsai et al., 2009).

In studies by Willits et al. (1958) and Buera et al. (1987), glucose browning monitored at pH values ranging from 3 to 9 and 4 to 6 respectively shows higher browning reactions in alkaline condition. The higher the basicity of solution, the higher the browning intensity.

In the case of polysaccharides of extracted *Azanza* fruit, the formation of caramel color is enhanced by suitable ammonium compound and at low pH of 4 since the quantity of reducing sugars is generally low (Benhura et al., 1999).

However, caramel color has good functionality across a wide range of from 2 to 10. Most caramel color ranges from 2 to 5 but as for caramel color that has been neutralized prior to spray drying, the pH is found to be 8. Commercial liquid caramel color should possess a pH of 5 to provide good stability (Burdock, 1997).

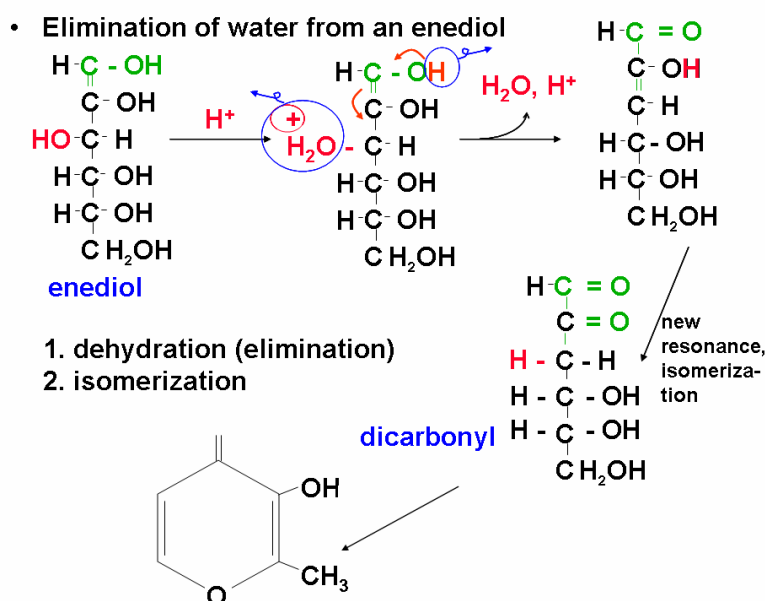


### 2.3.4 Temperature

Burdock (1997) stated that browning reaction increase rapidly with time to a higher final value with increasing temperature . A pH value of 4 to 6 is used for caramelization in system at lower temperature of 45 to 65°C (Buera et al., 1987).

### 2.4 Mechanism of Caramelization

Caramelization comprises the reactions involved in the thermal decomposition of carbohydrates, in particular reducing mono- and disaccharides. Various stages of the caramelization reaction may be discerned (Kroh, 1994). The first step in most caramelization reactions involves internal reorganizations with the carbohydrates which are known as enolizations. The second step comprises the formation of the anhydro form of the carbohydrate via the elimination of a water molecule. This is followed by variety of chemical reactions which depend strongly on the precise sugar composition, sample conditions like pH and the temperature. In these intermediate stages, most of the volatile compounds associated with caramel flavor are formed.



**Figure 2.2:** Reaction mechanism of caramelization reaction