

**PHYSICO-CHEMICAL AND FUNCTIONAL
PROPERTIES OF SYRUPS DERIVED FROM OIL
PALM TRUNK (*Elaeis guineensis*) SAPS
COMPARED WITH COMMERCIAL SYRUPS**

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UNIVERSITI SAINS MALAYSIA

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PALM TRUNK (*Elaeis guineensis*) SAPS
COMPARED WITH COMMERCIAL SYRUPS**

by

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LIST OF SYMBOLS AND ABBREVIATIONS

C	Carbon
EFB	empty fruit bunch
H	Hydrogen
L	Liter
M	Molarity
mg	Milligram
ml	Mililiter
mPa.s	miliPascal second
N	Normality
O	Oxygen
OPT	oil palm trunk
OPF	oil palm frond
Pa.s	Pascal second
S	Sulphur
T	Temperature
wt	Weight
μ M	Micromolar
μ m	Micrometer
$^{\circ}$ C	degree Celsius
$^{\circ}$ Brix	degree Brix

**SIFAT FIZIKAL-KIMIA DAN BERFUNGSI SIRAP DIPEROLEHI
DARIPADA SAP BATANG KELAPA SAWIT (*Elaeis guineensis*)
DIBANDINGKAN DENGAN SIRAP KOMERSIAL**

ABSTRAK

Dalam kajian ini, sap kelapa sawit daripada batang yang segar (OPT_{0sap}) dan sap kelapa sawit daripada batang yang disimpan selama 60 hari (OPT_{60sap}) dijadikan sirap. Sap ini diperah menggunakan mesin pemerah khas yang menggabungkan prinsip mengupas, menghancurkan dan memerah. Sirap daripada batang-batang ini (OPT_{0sy} dan OPT_{60sy}) dibandingkan dengan sirap komersial seperti sirap maple (M_{sy}) dan dua jenis sirap glukosa (G_{1sy} dan G_{2sy}) dari segi sifat-sifat fizikal, kimia dan berfungsi. Sirap nipah (N_{sy}) digunakan sebagai sirap kawalan. Peratusan penghasilan sirap adalah tinggi bagi OPT_{60sap} dibandingkan dengan sirap-sirap yang lain dengan nilai 11.9 % (vol/vol) tetapi lebih rendah daripada N_{sy} (13.08 %). Warna kesemua sirap dapat disusun sebagai OPT_{60sy} > OPT_{0sy} > M_{sy} > N_{sy} > G_{1sy} > G_{2sy} daripada paling gelap kepada paling cerah. Nilai kelikatan OPT_{0sy} dan OPT_{60sy}, 0.99±0.03 dan 0.99±0.07 mPa.s, adalah jauh berbeza daripada kelikatan sirap komersial. Jumlah pepejal larut bagi sirap-sirap dalam kajian ini adalah diantara 66 sehingga 82 °Brix. Jumlah air di dalam semua sirap adalah dalam lingkungan 20% hingga 31%. Berdasarkan kajian jumlah gula, gula utama di dalam OPT_{0sy}, OPT_{60sy} dan G_{2sy} adalah glukosa, manakala sukrosa adalah gula utama di dalam N_{sy} dan M_{sy}, dan maltosa adalah gula utama bagi G_{1sy}. Sirap OPT_{0sy} dan OPT_{60sy} mempunyai jumlah phenolik 825.35 and 885.57 mg GAE/100g lebih tinggi berbanding N_{sy}, M_{sy}, G_{1sy} and G_{2sy}. Aktiviti memerangkap radikal bebas bagi OPT_{0sy} dan OPT_{60sy} adalah tinggi daripada N_{sy}, M_{sy} dan G_{2sy}

dengan nilai askorbik asid 79.39 ± 0.89 dan 83.87 ± 0.62 VCEAC mg/100g dan nilai vitamin E 122.92 ± 1.38 dan 129.87 ± 0.96 TEACmg/100g masing-masing. Sifat aliran bagi OPT_{0sy} dan OPT_{60sy} adalah mirip model Herschel-Bulkley. Penggunaan OPT_{60sy} dalam penghasilan tofi menghasilkan tofi yang berwarna gelap dan mempunyai nilai kecerahan 29.35 ± 1.00 seperti tofi daripada G_{2sy}, 29.06 ± 0.28 . Hasil daripada ujian sensori, penerimaan terhadap tofi daripada OPT_{60sy} adalah tinggi dengan skor daripada 5 hingga 5.9 daripada 7 untuk semua sifat. Skor yang tertinggi bagi tofi daripada OPT_{60sy} adalah bagi warna (5.93) dan aroma (5.67). Kesimpulannya, penghasilan sirap daripada batang kelapa sawit adalah sesuai sebagai pilihan lain bagi penggunaan pemanis sedia ada.

**PHYSICO-CHEMICAL AND FUNCTIONAL PROPERTIES OF SYRUPS
DERIVED FROM SAPS OF OIL PALM TRUNK (*Elaeis guineensis*)
COMPARED TO COMMERCIAL SYRUPS**

ABSTRACT

In this study, freshly squeezed oil palm trunk sap (OPT_{0sap}) and 60 days stored oil palm trunk sap (OPT_{60sap}) was processed to produce syrup. The saps were collected using a squeezing machine that designed with principles of peeling, shredding and squeezing. The respective syrups (OPT_{0sy} and OPT_{60sy}) were compared to commercial syrups of maple (M_{sy}) and two types of glucose (G_{1sy} and G_{2sy}) in terms of physico-chemical and functional properties. Nipa syrup (N_{sy}) was used as control. The yield percentage for production of OPT_{0sy} was high as compared to other syrups with 11.9 % (vol/vol), but lower than N_{sy} (13.08 %). The colour of the syrups ranked as OPT_{60sy} > OPT_{0sy} > M_{sy} > N_{sy} > G_{1sy} > G_{2sy} from the darkest to lightest. The viscosity of the OPT_{0sy} and OPT_{60sy}, 0.99 ±0.03 and 0.99 ±0.07 mPa.s, were significantly different from all the other syrups. The total soluble solids of all the syrups were in between 66 to 82 °Brix. The moisture contents of the syrups were from 20 to 31%. Based on the sugar content analysis, major sugar for OPT_{0sy}, OPT_{60sy} and G_{2sy} was glucose, while major sugar for N_{sy} and M_{sy} was sucrose, and for G_{1sy} it was maltose. The OPT_{0sy} and OPT_{60sy} have high total phenolic content of 825.35 and 885.57 mg GAE/100g which were significantly higher than other syrups. Free radical scavenging activities of OPT_{0sy} and OPT_{60sy} were significantly higher than N_{sy}, M_{sy} and G_{2sy} with vitamin C values of 79.39 ±0.89 and 83.87 ±0.62 VCEAC mg/100g and vitamin E values of 122.92 ±1.38 and 129.867 ±0.96 TEAC mg/100g respectively. The flow behaviour

of OPT0_{sy} and OPT60_{sy} was best fit to Herschel-Bulkley fluid model. Incorporation of OPT60_{sy} in the toffee production produced toffee that was dark in colour with lightness value of 29.35 ± 1.00 (L*) that is similar to toffee from G2_{sy} (29.06 ± 0.28). From the sensory analysis, the acceptance for toffee from OPT60_{sy} was high with score of 5 to 5.9 out of 7 for all attributes. The highest score for toffee from OPT60_{sy} were for colour (5.93) and aroma (5.67). In conclusion, the production of syrup from oil palm trunk sap is possible as an alternative of commercial sweetener.

CHAPTER 1: INTRODUCTION

1.1 OVERALL VIEW

Palm oil industry is one of the major contributors of the agricultural sector in Malaysia. In fact, of those 4.8 million tons of palm oil produced globally in the year of 2008, 88% were originated from Malaysia and Indonesia (Kosugi et al., 2010). The source of palm oil is from the fruits of the oil palm tree. Thus, large scale plantation of oil palm trees is the key to produce enormous amount of palm oil. About 20% of the land that is reserved in Malaysia for agricultural purposes is utilized for oil palm plantation (World Growth, 2009). However, the fruits produced by the oil palm tree contain edible oil until the period of 20 to 25 years only (Yamada et al., 2010). After this period, the tree will either grow too tall for the fruits to be harvested or unable to produce fruits due to the aging factor. Consequently, the tree will be chopped down and replanted to continue producing palm oil.

The phenomenon of tree chopping will contribute to large amount of biomass waste. The waste produced in the year of 1997 alone had reached 13.2 million tons, which include empty fruit bunch, trunk and oil palm frond (Kamaruddin et al., 1997). Specifically, based on a recent study carried out by Wan Asma et al. (2010), 3.7 million trunks of oil palm wastes will be produced annually by replanting the tree between the years of 2009 and 2030. Additionally, the amount of oil palm wastes will increase, which predicted to arise from the 5.10 million hectares of oil palm tree plantations by the year of 2020 (Jalani et al., 2002).

Most of the oil palm waste was decomposed by burning that resulting in environmental pollution (Lim et al., 1997; Kabashi et al., 2007). In order to curb this problem, researchers had widely investigated on utilising the oil palm waste. Some examples of the applications were utilizations of the empty fruit bunch in the papermaking industry (Astimar et al., 2002; Tanaka et al., 2002) and in the production of medium-density fibreboard (Ridzuan et al., 2002). Additionally, oil palm trunk and frond were used in the manufacturing of fibre plastic composite (Liew et al., 2000), blackboard (Mohamad et al., 2001) and particleboard (Hashim et al., 2011). Most of the researches were focused on utilising the fibre from the oil palm waste.

However, during the process of shredding or pressing the trunks to get the fibre, the sap inside the trunk will be concurrently squeezed out. About 70 % of the weight of oil palm trunk is the sap, where it is being wasted by disposing without further use. Currently, the utilisation of the sap was concentrated on the bioethanol and lactic acid productions. The sap is collected using a specially designed squeezing machine that is designed with principles of peeling, shredding and squeezing altogether (Murata et al., 2013). The collected sap is either filtered or centrifuged to remove insoluble solids. The sap contains 6.67 % sugar with glucose as the main component, and fructose, sucrose, arabinose and galactose were present in a significant amount (Yamada et al., 2010). Furthermore, the sap was also reported to have amino acids, organic acids, minerals and vitamins (Kosugi et al., 2010).

The high content of sugars (6 °Brix) in the sap creates an opportunity for it to be used as syrup in the food industry. Besides, two of the widely used plant

syrups, namely maple and birch are produced from tree sap. Maple sap contains only 1.3 to 3.3 °Brix of sugar (Clément et al., 2010) and birch sap has sugar concentration of 0.5 to 1.1 °Brix (Kallio, 2013). The higher concentration of sugar in oil palm trunk sap suggests that the yield of syrup produced is higher.

Syrups have been used as a flavouring agent and sweetener for confectioneries and bakery products (Phaichamnan et al., 2010), binding agent for production of muesli bars and glazing agent in producing glossy surface for bakery products (Hull, 2010). From the combination of large amount of sap with suitable chemical composition, this study was conducted to measure the potential use of the oil palm trunk sap as an ingredient in food industry. The sap was centrifuged, subjected to heat treatment, subsequently the physical, chemical and functional properties of the sap and syrup were analysed. The syrup was incorporated into a confectionery product and the effects of incorporation on the quality of the product were then studied.

In general, this study consists of three stages. The first stage was the analysis of saps from different trunk storage time on both physical and chemical properties. The second stage was the production of the syrups from the saps. Nipa syrup was used as a control at this stage. These syrups were then analysed for physical, chemical and functional properties with commercial syrups, maple and glucose, for comparison. The third stage was the incorporation of the syrup in a confectionery product (toffee). At this stage, toffee produced using only glucose syrup was the control. The effects of partial replacement of the glucose syrup with other syrups were analysed for the selected properties, namely water activity, colour, texture and sensory.

Lastly, the general aim of this study was to characterise the saps and syrups produced from oil palm trunk. The specific aims of this study were as stated in subchapter 1.2.

1.2 OBJECTIVES

The specific objectives of this study are as listed follows:

- 1.2.1 To study the physical and chemical properties of saps from oil palm trunk under different storage time, and to compare the outcome with nipa sap.
- 1.2.2 To produce syrup from oil palm trunk sap using boiling process, subsequently characterise and compare the physical, chemical and functional properties of oil palm trunk syrup with commercial syrups.
- 1.2.4 To study the feasibility of using oil palm trunk syrup in confectionery item (toffee), and compare the effects on water activity, colour, texture and sensory properties with toffee made from commercial syrups.

CHAPTER 2: LITERATURE REVIEW

2.1 Fundamentals of oil palm

2.1.1 Overview of the tree

African oil palm or scientifically known as *Elaeis guineensis* (Figure 2.1) is one of the most common type of oil palm tree planted in Malaysia. The African oil palm tree originates from the family of Arecaceae that is widely found in the coastal area between Senegal and north Angola. This plant is similar to many other types of palm trees, namely coconut (*Cocos nucifera*) and nipa (*Nypa fruticans*). In local terms, it is known as ‘kelapa sawit’ in Malaysia and ‘kelapa ciung’ in Indonesia. Oil palm tree also grows wildly in riverine forests and freshwater swamps due to being native to tropical rain forests region (Lim, 2012).



Figure 2.1: African oil palm tree (Schmidt, 2007a)

Oil palm tree naturally can tolerate temporary flooding or fluctuating water table, but it grows well under the environment of unlimited availability of water (Lim, 2012). However, the tree will only produce palm oil until the age of 20 to 25

years (Schmidt, 2007b; Lee & Ofori-Boateng, 2013). Beyond this period, the tree will be chopped down for replantation, producing a large amount of biomass waste.

2.1.2 Oil palm plantation and biomass waste in Malaysia

As of year 2010, it had been reported that 4.6 million hectares of land in Malaysia were planted with oil palm trees. These plantations produced 16.99 million tons of crude palm oil and 2.01 million tons of crude palm kernel oil (MPOB, 2015). Despite producing a large amount of palm oil, the vast plantation area will require replantation after a stipulated period that will generate large amount of biomass wastes. The abundant biomass wastes include empty fruit bunch (EFB), oil palm frond (OPF) and oil palm trunk (OPT).

Empty fruit bunch is the leftover of the bunch where the fruits were removed for palm oil production in the palm oil mill (Lee & Ofori-Boateng, 2013). In Malaysia, 15.8 million tons of EFB were produced annually (Sumathi et al., 2008). The production frequency of EFB is more frequent compared to other types of wastes, as EFB is produced during the harvesting period along with the palm fruits. It was reported that EFB are used as a source of nutrients in the plantation area due to its inherent production of xylose (Rahman et al., 2006).

In terms of OPF, it is part of the felled tree during the replantation period. Locally, the biomass waste of OPF was reported to be approximately 54.17 million tons in the year of 2010 and 54.24 million tons in 2011 (Wan Zahari et al., 2004). Due to the large amount of OPF being produced annually, many researches were conducted on OPF for the production of binderless board (Laemsak & Okuma, 2000), and pulp and paper (Wanrosli et al., 2007)

Finally, the OPT is a biomass waste arising from the oil palm replantation process. The OPT is usually 6 to 9 metres long (Abdul Khalil et al., 2007) and a diameter of 45 to 65 cm (Lee & Ofori-Boateng, 2013), with high moisture and starch contents. Approximately 3.7 million trunks are predicted to be produced annually until the year of 2030 (Wan Asma et al., 2010). On the other hand, it had been reported that 13.5 million tons of OPT were produced in the year of 2011, with an expected increase of 50 % by the year of 2020 (MPOB, 2012; Lee & Ofori-Boateng, 2013). It was reported that most of these oil palm trunk was decomposed by burning (Lim et al., 1997; Kabashi et al., 2007; Shahirah et al., 2015) which is causing environmental problems such as air pollution.

Various investigations had been conducted to utilise this renewable source, thus improving the waste management of palm oil industry. About 40 % of the OPT are being used in plywood and furniture production (Abdul Khalil et al., 2010). Many of the OPT applications involve the dry matter of the OPT, despite 70 % of the trunk weight consists of watery compound (sap).

2.1.3 Oil palm trunk sap

Oil palm trunk sap is collected during the pressing of the trunk. Kosugi et al. (2010) conducted a study on the characteristics of the oil palm trunk sap. The resulting outcome of the study showed that the oil palm trunk sap contains 6.67 % of sugar (glucose and fructose). Besides, it also contains amino acids (serine, glutamic acid and alanine), organic acid (malic acid, maleic acid and citric acid) and vitamins (vitamin C and B). These components are the factors that make the sap a suitable raw material for syrup with appropriate nutritional values.

Besides, Yamada et al. (2010) proved that the reducing sugar content in the sap significantly increases when the trunk is stored at ambient temperature (<60days). On the other hand, the sucrose content decreased. These changes were triggered by amylase and other enzymes that were present in the trunk (Chang & Ryan, 1987; Wang et al., 2000; Maruyama et al., 2009; Yamada et al., 2010). Over time, the enzymes reacted with the sucrose and starch contents in the stored trunk, subsequently altered the sugar contents in the pressed sap. The study was conducted by storing the trunk at ambient temperature for 120 days with the sap being analysed in the interval of 30 days. A decrease in sugar concentration was observed with prolonged storage of the saps because of fermentation (>60days).

Since the sugar contents of the sap changes proportionally to the storing period of the trunk, there is a possibility that other physical and chemical properties of the sap change as well. Therefore, the first stage of this study is to investigate the changes in physical and chemical properties of the sap at period of day 0 (fresh sap) and day 60 (stored trunk). This is based on the study conducted by Yamada et al. (2010), day 60 sap has the highest sugar content, and hence our main interest in the sap is the sugar.

The previous study found that OPT can produce sap that contains sugar and vitamin, thus there is a possibility for it to be used in the food industry. It has been reported that approximately 70 % of the weight of the trunk arises from the sap (Yamada et al., 2010). Considering the sugar contents of the OPT sap, it can be potentially used as an alternative type of sweetener. Besides, the local abundant supply of the trunk secures a cheaper production cost for this alternative sweetener.

It was reported that the trunk is sold at RM8 to RM18 with every trunk can produce up to 200 to 250 L sap (Wan Asma et al., 2010).

There were several researches carried out on the utilization of the sap, namely the production of ethanol and lactic acid bacteria (Kosugi et al., 2010), characterisation of the sap (Yamada et al., 2010), hydrogen production by bacteria (Noparat & Prasertsan, 2011) and carbon feedstock for bacterial growth (Lokesh et al., 2012). Nevertheless, none of the past investigations involved the use of the sap as an ingredient in food probably because the initial total soluble solid of the untreated trunk's sap is low (4 to 6 °Brix).

2.2 Syrup

Syrup is defined in Collins English Dictionary as a concentrated solution that is made of sugar and meant for cooking or eating. On the other hand, syrup is also defined as a thick solution of sugar (sucrose) in water, mixed with other ingredients and used as a medium for medications toward ingestion (Saunders Comprehensive Veterinary Dictionary, 2007). Besides, honey that naturally contains a concentrated amount of sugar in water is also considered as syrup (Manley, 1998).

There are many types of commercially available syrups in the market, including maple syrup, birch syrup, glucose syrup and high fructose corn syrup. Syrups are being used extensively in the food industry as sweetener, flavour agent, bodying agent and colouring agent (Hull, 2010). For every application, appropriate properties of the syrup are taken into account to match the needs of the specific

role. Therefore, it is important to understand the entire set of properties of the syrup to enable the application and production to be more economical. The summary of variety of commercial syrups is presented in Table 2.1.

Table 2.1: Variations of commercial syrups.

Type of syrup	Major sugar	Sugar concentration (% wt/wt)	Reference
Maple	Sucrose	66	Greweling, 2007
Glucose	Glucose	> 20	Hull, 2010
HFCS	Fructose	40 – 90	Manley, 1998

2.2.1 Maple syrup

Maple syrup is a product of concentrating the colourless maple sap collected from maple tree (Li & Seeram, 2010). Maple syrup is produced from 30.3 to 34.1 million litres annually by the United States of America (15 %) and Canada (85 %). There are several types of maple trees that are used to produce maple syrup, namely sugar maple, red maple and black maple, also scientifically known as *Acer saccharum*, *Acer rubrum* and *Acer nigrum*, respectively (Perkins & van den Berg, 2009). Maple tree is native to North America and Canada. It is planted widely for commercial production of maple syrup, especially in the area of Nova Scotia, Minnesota, south of Ontario, Quebec and West Virginia (Heiligmann et al., 2006).

The production processes of maple syrup are as follows. Firstly, maple sap is collected from the trunk through a taphole. The taphole is designed by inserting a metal tapping device into the trunk at the height of 0.08 to 0.178 metres above the

ground and approximately 0.04 to 0.06 metres depth. The sap that is produced will be collected either by placing a container at the end of the taphole or a tube that links all the sap directly to a collection tank (Perkins & van den Berg, 2009). In South Korea, the sap is known as ‘garose’, which means ‘tree that is good for bones’ is consumed raw without processing it into syrup for health benefits (Yuan et al., 2013).

The sap contains mainly water and sugar, and other sub-components including amino acids, organic acids and phenolic compounds (Thériault et al., 2006). Sucrose is the major sugar component in maple sap at 96 % to 99 % of the content. The sap is usually slightly acidic with pH rating of 6.5 to 7.0, with wide pH variation of 3.9 to 7.9 (Perkins & van den Berg, 2009). During the production of syrup, the sap is evaporated to approximately 66 % dissolved-solid content (Greweling, 2007) through vacuum or under normal atmospheric pressure.

The syrup is classified into several grades based on the density, flavour, clarity and colour. The colour and clarity are interrelated and measured using spectrophotometer light transmittance at 560 nm (Perkins & van den Berg, 2009). Figure 2.2 shows the type of maple syrup that was used in this study.



Figure 2.2: Maple syrup

The colour falls between very light yellow amber and near black, while the clarity varies from less than 25 % to more than 75 % of light transmittance (Table 2.2). Generally, the colour considered darker as the redness increases.

Table 2.2: Classifications of maple syrup based on the Canadian and American standards (Source: Perkins & van den Berg, 2009).

Light transmittance	Canadian grading		American grading	
≥75.0%	Canada No.1	Extra light (AA)	U.S. Grade A	Light amber
60.5–74.9%	Canada No.1	Light (A)	U.S. Grade A	Medium amber
44.0–60.4%	Canada No.1	Medium (B)	U.S. Grade A	Dark amber
27.0–43.9%	Canada No.2	Amber (B)	U.S. Grade B for reprocessing	
<27.0%	Canada No.3	Dark (C)	Substandard	

2.2.2 Nipa syrup

Nipa syrup originates from nipa palm (Figure 2.3), or commonly known in Malaysia and Indonesia as nipah. Scientifically nipa palm is known as *Nypa fruticans* Wurmb, it is the only species of the genus within the same family of oil palm (*Elaeis guineensis*) and sugar palm (*Arenga pinnata*), otherwise known as Arecaceae. Nipa plant was first found in South Asia i.e. Sri Lanka, Bangladesh and South East Asian, northern Australia and Pacific Islands (Lim, 2012).

Nipa palm is a type of palm that does not have a trunk. However, the leaves can grow up to 10 meters in height above the ground, while the stem (rhizome) develops beneath the ground. The plant grows in saline mud and estuarine river

waters, as well as occasionally in the presence of water, as long as the soil is damp (Lim, 2012).



Figure 2.3: Nipa palm (Lim, 2012)

The sap that is used for syrup production in this study is collected from the young inflorescence, which is part of the palm right before the flower opening phase. The sap can be collected from alive and felled palm. The flower that later turn into fruits is chopped off for collection (Figure 2.4), consequently allowing the sap to be tapped (Lim, 2012). Nipa sap is usually used to produce vinegar, toddy or palm wine (Jirovetz et al., 2001), sweetener (Lim, 2012) and drinks (Nur Aimi et al., 2013).



Figure 2.4: Fruits of nipa palm (Lim, 2012)

The sap have high amount of sugar, making it suitable to be produced into syrup. Sugar is the major compound of the sap with 14.5 wt % of the total of 15 wt % of the chemical composition (Tamunaidu et al., 2011), with sucrose being the prominent sugar compound. Based on its accessibility, the nipa sap was selected as a control mechanism in this study. In addition, it is hope that the finding of this study can contribute to the existing information on nipah.

2.2.3 Glucose syrup

Glucose syrup, also known as corn syrup is a type of sweetener that is commonly used in confectionery productions. Glucose syrup is widely used in food industry, for example, as colouring agent in toffee (Greweling, 2007), sweetener in beverages (LeBlanc et al., 2009) and doctoring agent in hard boiled candy (Hull, 2010). The syrup is considered to be GRAS (generally recognized as safe) under the US Code of Federal Regulations (CFR) 21, Section 184 (Hobbs, 2009).

Glucose syrup is defined as a solution of starch origin and saccharides concentrated, which have the dextrose equivalent (DE) of more than 20 %, at least 70 % of dry matter, and less than 1 % of sulphated ash that is based on dry matter (Hull, 2010). The production process of the syrup is through hydrolysis method for edible starch, i.e. corn starch and potato starch with the presence of enzyme or acid (Greweling, 2007). The details of the hydrolysis process for starch will be discussed in subchapter 2.2.3 (a).

Glucose is the prominent sugar component in glucose syrup with some traces of maltose and oligosaccharides (Vaclavik & Christian, 2008). Glucose syrup that is commonly used in confectioneries production has 42 DE, where the syrup type is known as ‘Confectioners Glucose’ (Hull, 2010). Glucose syrups that are produced at different DE may have variation in properties. For example, glucose syrup of 42 DE is less sweet than 63 DE. Besides, the addition of gum in the syrup affects the viscosity, and thus alters the application of the syrup. Therefore, two sets of glucose syrups from different manufacturers, with the same DE, but different viscosities were used in this study (Figure 2.5 (a) and (b)).

Although the glucose syrup tastes sweeter than sucrose, the syrup still differ in many aspects compared to sucrose. In other word, glucose and fructose (monosaccharides) are different type of sugar as compared to sucrose (disaccharide). Therefore the properties of viscosity, saturation point, reaction with other compounds (e.g. protein) and hygroscopicity are different as well.



Figure 2.5 (a): Queen's Glucose syrup



Figure 2.5 (b): Karo's Glucose syrup

As a result, many aspects need to be considered if glucose syrup is intended to be used as a replacement for sucrose. These comparative studies were carried out in the second and third stages of this thesis, where the OPT syrup was compared to the syrup with sucrose and syrup with glucose as major sugar.

2.2.3 (a) Starch hydrolysis

Starch hydrolysis is the process where the starch polymers are cut into shorter chains under certain conditions (Fennema, 1996). The hydrolysis process on starch may vary according to the amount of enzyme or acids that are being used, consequently producing different type of products. Thus, to classify the product of starch hydrolysis, the amount of starch conversion is determined by using their DE.

In this case, DE represents the different degrees of starch hydrolysis. Total conversion of starch into invert sugars is expressed as 100 DE and no conversion of starch is presented as 0 DE (Greweling, 2007). Maltodextrin is the hydrolysis product with 20 DE or less (Damodaran et al., 2008), while hydrolysates is the product of hydrolysis with 80 DE or more (deMan, 1999). In addition, degree of

polymerization (DP) of the starch can be found from the DE rating, where the relationship can be expressed as $DE = 100/DP$ (Damodaran et al., 2008). The DP is inversely proportional to DE due to the lower polymer rating in high DE rated syrups.

During hydrolysis, starches that contain polymers of amylose and amylopectin are added with either enzyme or acid, or both. Moreover, with the presence of heat, the glycosidic bonds of the starch are broken, subsequently producing oligosaccharides, disaccharides and monosaccharides (Fennema, 1996). Hydrochloric acids and enzymes, including α -amylase, glucoamylase, β -amylase and pullulanase are usually used as the hydrolyzing agents for glucose syrup production. An additional enzyme of isomerase is used in the production of high fructose corn syrup.

The use of enzymes in starch hydrolysis is based on the desired DE, because different enzymes produce different amount of glucose. Sometimes, acid-enzyme hydrolysis is used to produce 63 DE syrup, which is sweeter than 42 DE and less sweet than and 95 DE syrups (Hull, 2010). In addition, acid hydrolysis costs less than hydrolysis that uses enzymes, because the enzyme itself is costly. However, enzyme hydrolysis produces more specific products compared to acid hydrolysis (Hull, 2010).

2.2.4 High fructose corn syrup (HFCS)

High fructose corn syrup (HFCS) is a product of breakdown of glucose syrup. Thus, it can be considered to originate from edible starch. In fact, similar to glucose syrup, HFCS is classified as GRAS in CFR 21, Section 184.1866 (Hobbs, 2009).

The HFCS is produced through isomerization process of glucose in glucose syrup, with the presence of enzyme i.e. glucose isomerase, that converts the glucose to fructose. The first product of the isomerization process is HFCS with 42 % of fructose with 58 % of glucose contents (Fennema, 1996). The HFCS that possesses this amount of fructose is also known as the ‘first generation HFCS’ (Hull, 2010). However, higher amount of fructose is always desired, which can be achieved by passing the HFCS through cation-exchange resin that separates fructose from glucose, and thus concentrating the fructose content (Damodaran et al., 2008).

The HFCS with high content of fructose that varies between 40 % and 90 % produces sweeter syrup compared to the glucose syrup (Manley, 1998). Fructose, in general, is sweeter than glucose, while twice sweeter than sucrose. In addition, fructose can be processed by the human body without the use of insulin (Edwards, 2000). These properties are some of the reasons that make HFCS commonly used as a sweetener in the beverage industries (Rippe, 2014).

2.3 Sugar

Sugar is the major component of syrup that contributes carbohydrates for living organisms. Carbohydrate is present in plant, animal tissue and microorganisms under various forms. Glycogen is a form of carbohydrate that is stored in animal organisms. In the case of plant organisms; starch is a stored form besides sucrose, glucose and other oligosaccharides, and cellulose is a structural form of carbohydrate (deMan, 1999). Simpler forms of carbohydrates can be divided into two segments, namely disaccharide and monosaccharide. For

disaccharide, sucrose is the most important form, while glucose and fructose are important forms for monosaccharide, where both types are present in syrup at different amounts.

2.3.1 Sucrose

Sucrose is commonly known as granulated sugar, white sugar and also table sugar. Commercially, it is produced from the juice of sugar cane or sugar beet, which is refined and processed into crystals (LaBau, 2012). Disaccharide (group of sugar in which sucrose is part of) is composed of two monosaccharide molecules that are bind together through glycosidic bond. As for sucrose, the reducing end of glucose is bonded to the reducing end of fructose, hence resulting in the non reducing compound of sucrose.

One of the characteristic of sucrose is that it is highly soluble in acid medium, resulting in quicker acid hydrolysis compared to other oligosaccharides. This condition was due to the carbonyl-to-carbonyl bonds of glucose and fructose in the sucrose molecule as illustrated in Figure 2.6 (deMan, 1999).

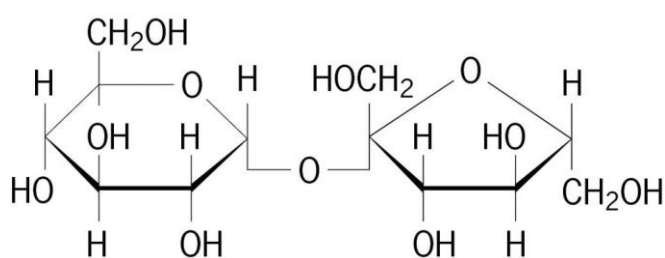


Figure 2.6: Molecular structure of sucrose (McGraw Hill, 2002)

Sucrose is soluble in water, but becomes insoluble when the concentration reaches a saturation point of approximately 66 % at room temperature. This characteristic causes the solution to be unstable for microorganisms' growth (Edwards, 2000). However, the solubility of sucrose will increase with the rise of

temperature (Varzakas et al., 2012). Sucrose undergoes partial decomposition if heated (without nitrogenous compounds and limited or no water) to 210 °C, where a non enzymatic browning will occur through a process called caramelisation (deMan, 1999).

Sucrose is considered as a traditional sweetening agent that is purely sweet, with non-digestible carbohydrate in its original form, however becomes digestible upon hydrolysed into monosaccharide (Varzakas et al., 2012). Sucrose can be converted into glucose and fructose through a hydrolysis process. With the presence of acid or enzyme, sucrose will be broken into 1:1 ratio of glucose and fructose. In fact, as sucrose solution boils, a small amount will be converted into glucose and fructose (Edwards, 2000).

2.3.2 Glucose

The most important form of monosaccharide is glucose that is naturally found in fruit juices, honey and blood (Varzakas et al., 2012). It is from the class of aldose of monosaccharide, besides galactose and mannose. This is because glucose has a functional group of aldehyde at one end, which gives the glucose ability to reduce (deMan, 1999). Glucose can be fermented under the conditions of anaerobic and aerobic (Stick, 2001; Collins, 2006; Brown, 2008; Varzakas et al., 2012). The structure of glucose is illustrated in Figure 2.7.

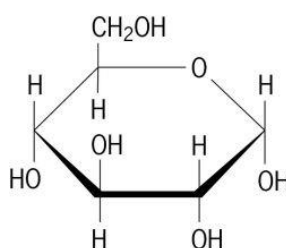


Figure 2.7: Structure of D-glucose (McGraw Hill, 2002)

Glucose is highly soluble in water, moderate in ethanol and insoluble in organic solvent (Belitz et al., 2009). These properties give glucose the characteristic of hygroscopicity, limiting its usage in dry products and as well as a sucrose replacement during formulations of products. Glucose is produced through acid or enzyme hydrolysis of starch from either corn or potato, and also by acid hydrolysis of cellulose (Varzakas et al., 2012). Glucose is a monomer of various disaccharides i.e. sucrose, lactose and maltose, and polysaccharides i.e. glycogen, starch and cellulose.

2.3.3 Fructose

Fructose is part of the ketose class of monosaccharide and sorbose (Varzakas et al., 2012). The classification is due to fructose having a functional group of ketone at one end, making it a reducing sugar. As a result, fructose molecule forms a pentagon shape, despite having six carbon atoms. The structure of fructose is depicted in Figure 2.8.

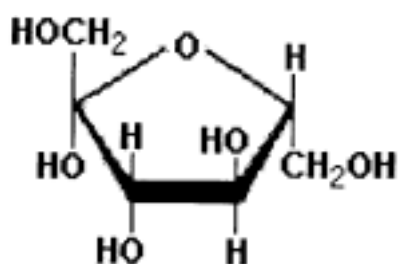


Figure 2.8: Structure of fructose (Gibson et al., 2007)

Fructose is the sweetest natural sugar and is the most abundant type of ketose sugar (deMan, 1999), where it is naturally found in fruit juices and in honey together with glucose (Varzakas et al., 2012). Fructose can be produced from the hydrolysis of inulin (deMan, 1999; Collins, 2006; Brown, 2008; Varzakas et al.,

2012). In the food industry, fructose is produced from the starch of high fructose corn syrup through an extended enzymatic reaction called isomerization of glucose syrup.

2.4 Reactions of sugar

The solution from sugars is unstable, where it undergoes various kinds of reactions, namely isomerization, dehydration, polymerization, caramelisation, Maillard reaction and crystallisation (deMan, 1999). The instability also depends on the compounds that are present in the solution and the conditions that the solution is subjected to. During syrup production, the major processes will affect the types of sugar that will be present and the physical properties of the syrup, namely colour and viscosity.

During the boiling of OPT sap into syrup and toffee making, caramelisation and Maillard reaction are important. Besides, crystallization is the important reaction of sugar during storage. This is because the OPT sap is reported to have reducing sugars, disaccharide and amino acids (Kosugi et al., 2010) that are the reactants of these three reactions.

Caramelisation and Maillard are complex reactions to the sugar containing foods either during the processing stage or storage (Varzakas et al., 2012). However, these reactions are intended depending on the type of the product. For example, dark colour formation in toffee production is desired (Maillard reaction), while it is undesired in other cases of loss of nutrients and protein value (BeMiller & Whistler, 1996; Varzakas et al., 2012).

2.4.1 Caramelisation

Caramelisation is a non enzymatic reaction involving the formation of caramel pigment, without the presence of nitrogenous compound. Although caramelisation occurs when sugar is subjected to heat treatment, it still requires very high temperature of around 200 °C. The caramelisation occurs in a sequence of reactions that involve the changes of polyhydroxycarbonyl compounds (reducing sugar and sugar acids) as the temperature increases. The final product of caramel pigment is formed as the temperature reaches 210 °C, where this reaction is independent of the presence of oxygen (Varzakas et al., 2012).

However, there are two conditions that control the specific end product of caramelisation reaction; which are (i) the type of sugar that is being used and (ii) the condition during process. Aromatic compounds will be produced if the caramelisation process involves heating of sucrose in alkaline catalysts. This process promotes the production of aromatic compounds, namely dihydrofuranones, cyclopentenolones, cyclohexenolones and pyrones. Besides, coloured pigments will be formed as glucose syrup is heated in the presence of sulphuric acid and ammonia (Belitz et al. 2009) for production of commercial caramel colour.

In general, the first stage of caramelisation is the development of reducing sugar. At the temperature of around 160 °C, sucrose is converted to glucose and fructose and as the heating continues, a compound known as caramelan ($C_{25}H_{30}O_{18}$) is formed. This compound has a characteristic of bitter taste and is soluble in water. Further heating of caramelan compound will result a compound named caramelen. The caramelen ($C_{36}H_{50}O_{25}$) is water soluble

compound that melt at high temperature of 154 °C. More heat treatment will produce caramelin ($C_{125}H_{188}O_{80}$), very dark, nearly insoluble compound, the final product of caramelisation reaction (deMan, 1999). The caramel colour is the formation of these coloured compounds.

In conclusion, the caramelisation reaction is a product of sugar fragmentation and degradation processes. Caramel flavours are the side products of these reactions, namely diacetyl (buttery flavour), acetic acid, formic acid, acetylformoin acetylformoin (4-hydroxy-2,3,5-hexane-trione) and 4-hydroxy-2,5-dimethyl-3(2H)-furanone (Jurch & Tatum, 1970; deMan, 1999). The summary of caramelisation reaction is presented in Figure 2.9.

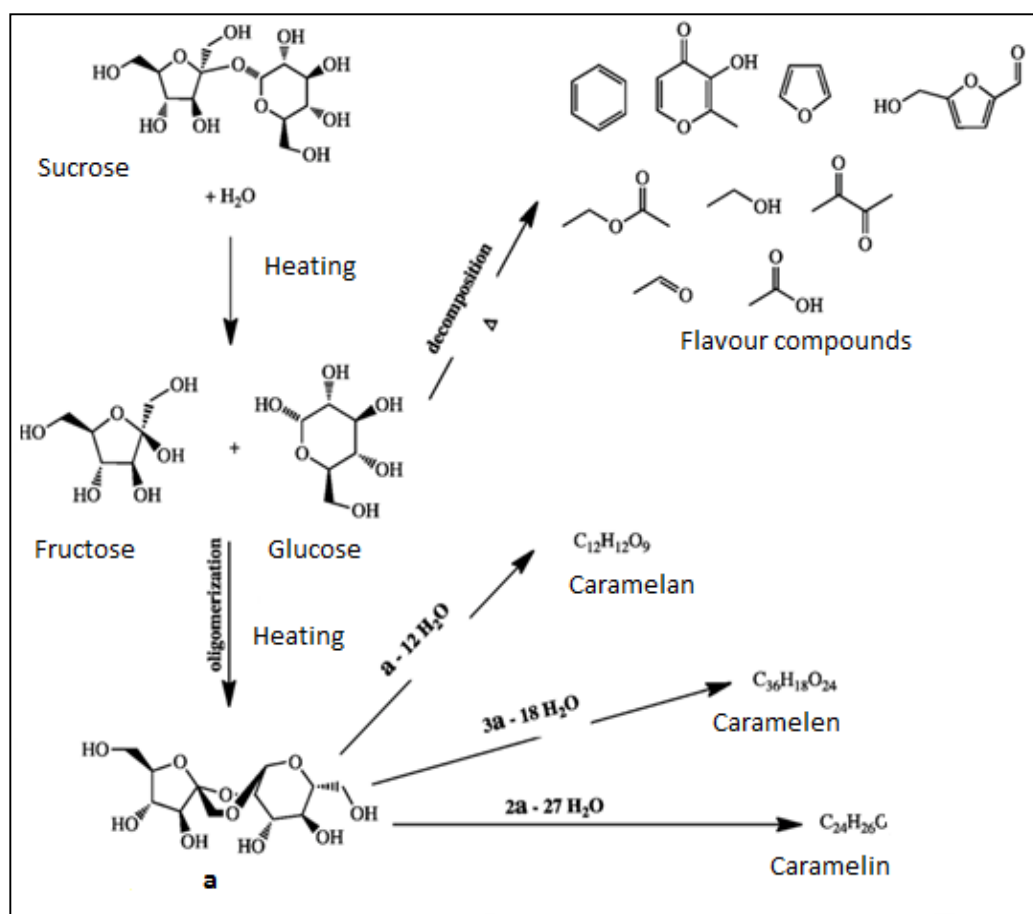


Figure 2.9: Summary of caramelisation reaction (The Chemistry of Caramel, 2011)