Chapter 1
History of glucose syrups

Glucose syrups are clear colourless viscous liquids, derived from starch, but, who first produced a glucose syrup, when, where and why, or was it all a lucky discovery?

1.1 Historical developments

The glucose industry was born in Russia, in 1811, when a German chemist **Konstantin Gottlieb Sigismund Kirchoff**, working in Russia, showed to the Russian Imperial Academy of Science in St Petersburg three flasks. According to a report of this meeting (Memoires de L'Academie Imperiale Des Science de St Petersburg, **4**, 27, 1811), one flask contained syrup produced artificially from vegetables (potatoes, wheat and buckwheat). The second contained some 'sugar' obtained from this syrup by drying, and the third contained a syrup made from the 'dried sugar'. But, there was no mention in this report of how Kirchoff had made the syrup. Fortunately, this was revealed in the Philosophical Magazine of 1812 (Vol. 40, July to December).

Evidently, Kirchoff discussed the results of his experiments with an eminent Swedish chemist, **Prof. Jons Jacob Berzelius (1779–1849)** of Stockholm, who then told The Royal Institute, in London, about Kirchoff's experiments, and that the different vegetables had been heated with sulphuric acid to obtain the syrup. At the suggestion of **Sir Humphry Davy (1778–1829)**, Kirchoff's experiments were repeated at the Royal Institute, and produced similar results to those of Kirchoff. It was however, not until 1814, that the Swiss chemist, **Nicolas Theodore de Saussure (1767–1845)** showed that the syrups produced by Kirchoff contained dextrose.

To this day, we still do not know why Kirchoff carried out these experiments, or what he was trying to achieve, although there have been many suggestions. Kirchoff was born on 19 February 1764 in Teterow Germany. In 1792, Kirchoff was working in St Petersburg as an assistant in a chemist's shop, and became a chemist in 1805. He was then elected an Associate of The Russian Academy of Science in 1807, and became an 'Adjunct', or member, of The Academy in 1809. According to the Memoires de L'Academie Imperial Des Science de St Petersburg, **4**, 27, 1811, at that time, Kirchoff was working on the analyses of different geological minerals. This suggests that Kirchoff was not a food chemist, and that his discovery of glucose syrups – a sweet product, was purely a fortuitous accident for the food industry. Because of Kirchoff's interest in minerals, and the fact that St Petersburg had a thriving porcelain industry, there is the possibility that he was looking for an alternative adhesive or flux to use in the gilding of porcelain. Gum Arabic had been used as the adhesive in the early days of the gilding process, but that was replaced by honey in the mid-eighteenth century (private correspondence with The V & A Museum, London).

Basically, gold leaf and honey were ground together to form a paste, which was then painted onto the glazed porcelain. Essentially, the honey was acting as a flux, to improve the adhesion of the gold to the porcelain.

However, in 1811 with Napoleon Bonaparte wagging war all over Europe, both honey and sugar became very scarce, and according to Daniel Green's book, 'CPC Europe – A family of food companies' (1979), the price of sugar in Berlin in 1811 was £45 per hundredweight, which in today's money (2007) would have equated to £14.98 per pound (£33.00 per kilo). With this high price of sugar, it is not surprising that honey, which had previously been used in the porcelain industry as an adhesive for gilding, would now be used as an alternative to sugar for sweetening. Therefore, it is possible that Kirchoff with his knowledge of chemistry and minerals would have had the perfect background to look for an alternative adhesive to honey, so as to keep the St Petersburg porcelain industry in business. The fact that he ended up with a sweet sticky product was, like so many scientific discoveries, a very fortuitous discovery. The immediate impact of Kirchoff's discovery can be gauged from the report in the Philosophical Magazine (1812), which mentions that Kirchoff's work was adopted 'on a large scale in the Russian Empire, as the price of cane sugar had increased so much and the supply was so uncertain'. So the sweet sticky substance which Kirchoff had inadvertently made became a useful alternative to sugar. And that was the start of the glucose industry.

In 1812, Kirchoff was elected an Extraordinary Academician in Chemistry. This encouraged him to continue his research into starch, which resulted in 1816, with the discovery that enzymes were also capable of breaking down starch. Kirchoff died, in his adopted country of Russia, in St Petersburg on 14 February 1833, aged 69.

Some people have suggested that glucose was discovered by an unknown German. Kirchoff was a German, and we know that he discussed the results of his glucose experiments with Prof. Berzelius before they were published. As Kirchoff was a member of several scientific societies, it is quiet possible that he also discussed his results with other interested scientists, hence the origins for the suggestion that an unknown German discovered glucose syrup. This unknown German I would suggest was in fact K.C.S. Kirchoff. It is interesting to note that the initials of Kirchoff vary in different publications. The reason for this is that the Russians spell Konstantin with a 'K', whilst Western Europe spells it with a 'C'.

Coincidentally to Kirchoff discovering how to make glucose syrup, **Napoleon Bonaparte** asked the French government for 100,000 French Francs (equivalent to £162,303 in 2005), as a prize for anybody who could make sucrose from an indigenous French plant. The reason for this request was that the successful British blockade of the French ports, prevented sucrose being imported from France's overseas colonies. Napoleon's reaction to this successful blockade was typical of a politician, he issued an embargo on all merchandise from England and her colonies to give the impression that the sugar shortage in France had nothing to do with the successful blockade! The prize of 100,000 Francs was won by a French analytical chemist, **Louis-Joseph Proust (1754–1826)** in 1810 for producing 'sugar' from grapes (Memoires de L'Academie des sciences, belles-lettres et arts d'Anger, 14, 1997–1998, pp. 225–246.). Napoleon also awarded Proust with the Legion d'Honneur. However, the 'sugar' which Proust had produced was not sucrose, but dextrose.

It would be another three years before sucrose was produced from a French plant. On 2 January 1813, Napoleon was told that **Benjamin Delessert (1773–1847)**, from Plassy, near Paris, had succeeded in making loaves of white sugar (so called because the sugar was moulded into the shape of a loaf). Delessert had produced the sucrose from the root of the sugar beet plant – *beta vulgaris altissima*. This was the start of the sugar beet industry in France and a political time bomb – a development which, some 164 years later, would have a considerable influence upon the future development of the European glucose industry. As for Delessert, he did not receive a 100,000 Francs. However, in recognition of his work, Napoleon gave Delessert his own Legion d'Honneur sash (Sugar and All That . . . A History of Tate & Lyle, 1978, p. 21). Delessert name has however been immortalised by giving his name to the 'Dessert' course of restaurant menus.

The UK glucose industry started in 1855, when a Frenchman **Alexandre Mambre (1825–1904)** started to produce solid glucose in Spitalfields, London. In 1876, he moved production to Hammersmith. Whilst there had been a starch industry in the United Kingdom, since about 1600, the starch was used mainly for laundry and textile purposes – there had been no attempt to use the starch for making glucose.

Alexandre Mambre was the son of a French farmer, and was born in 1825, in Valenciennes, Northern France. It is believed that the reason he came to England in 1855 was to secure a patent to produce brewing sugars made from potatoes, and he knew that in England, his patent would be protected, whereas in France, this would not have been the case. Mambre was, however not alone in producing 'brewing sugars', but these other producers were using sucrose as their starting material, and produced an invert-type product for use in brewing, mainly for adding colour to the beer. In 1850, there was a tax on sugar used in beer, therefore, it is possible that by using these products for colouring, tax would have been avoided, and this might also be a reason why British beers at that time had a very characteristic dark colour.

In about 1861, Mambre changed the spelling of his name to Manbre, and died in England, in 1904. The company which he started would eventually become Manbre and Garton, which was subsequently purchased by Tate & Lyle in 1976, who then closed the company, selling off the glucose assets in 1980 to Cargill.

In the United Kingdom, prior to 1962, sugar had been taxed, on and off for several years, because it was an easy tax to collect direct from the producer, and glucose syrups, together with molasses and saccharin, were included within this taxation, which was known as Excise Duty. Therefore, in a typical glucose refinery, there would have been a room, known as 'The Tank Room', in which an excise officer would have been permanently stationed. It was his private kingdom, which nobody was allowed to enter, so as to ensure that there was no interference with the collection of the Excise Duty.

Each Tank Room would contain a minimum of two tanks, each of a known volume. All syrups leaving the refinery would have to go into one of these tanks, and once the tank had been filled, the excise officer would note the volume and temperature of the syrup in the tank. Next, he would measure its specific gravity, using a hydrometer. From these three measurements, the officer would calculate the solids present and hence the amount of duty to pay. Then, and only then, would the syrup be allowed to go forward to the next processing stage, that is evaporation. For ease of handling, the solids of the glucose syrup entering the Tank Room would have been about 40%.

The duty in 1960 was five shillings and four pennies (5s 4d), per hundredweight (112 pounds), based on syrup solids. This would have been equivalent to 27 pennies per hundredweight, or £5.40 per ton in decimal currency. For a syrup containing 80% solids, the duty would have been £4.32 per ton, on a product which was selling at about £40 per ton, excluding duty. This duty would also have applied to dextrose. A monthly return of the daily production would be prepared, and the total duty payable for that month by the glucose manufacturer would then be paid to the local collectors' office. For a refinery producing 100 tons of syrup per day, at 80% solids, 30 days a month, the duty would have been £12,960 per month, or £155,520 per year.

If the syrup was exported, or used in a product, which was exported, then the Excise Duty could be recovered from HM Customs and Excise. Fortunately, for the UK glucose industry, the excise duty on sugar, molasses, glucose syrups and saccharin was abolished in 1962.

1.2 Analytical developments

As Kirchoff's discovery grew into an industry, technology was borrowed from several other different industries, particularly from the sucrose industry, with many different people contributing to the process and to the methods of analyses – both physical and chemical.

Following **de Saussure's** confirmation that Kirchoff's glucose syrup contained dextrose, the German chemist **Herman von Fehling (1812–1885)**, in 1848, worked out a method for determining the total reducing sugars in a syrup, using a solution of alkaline tartrate and copper sulphate – the well-known Fehling's Titration. Since dextrose and the other sugars present in a glucose syrup are reducing sugars, this meant that the infant glucose industry now had a method for determining the total reducing sugars present in a glucose syrup – what we now refer to as the dextrose equivalent (DE) of the syrup. Or, to put it another way, how far the starch had been broken down. The principle behind the Fehling's method is that reducing sugars convert the blue alkaline copper sulphate solution to a red precipitate of cuprous oxide. It is interesting to note that the glucose syrup industry used this method, although slightly modified (see below), for over 100 years to run its process and to characterise its products. And it is still a recognised method for determining reducing sugars.

The Fehling's method had several major drawbacks. One was the determination of the end point of the titration. In 1923, two British chemists, **Joseph Henry Lane (1883–1951)** and **Lewis Eynon (1878–1961)**, both of whom had a background in sugar beet technology, and who ran their own analytical consultancy (established in 1910), suggested the addition of methylene blue as an internal indicator to improve the recognition of the end point. The Fehling's method then became known as the Lane and Eynon method.

Other drawbacks of the Fehling's method are that the titration is carried out using a boiling solution, and is time consuming, taking about forty-five minutes for three titrations. Additionally, the detection of the titration's end point is very dependent upon the skill of the analyst – it is not the easiest of titrations to perform. In 1979, **M.G. Fitton**, who worked for Corn Products, Belgium, showed that the DE could be measured using a cryoscope (freezing point osmometer), with result being available within two minutes, and as it is an automatic determination, it did not rely on the eyesight of the analyst to determine the end point. This method uses the principle of sugars depressing the freezing point of a solution. One drawback of this method is that the other soluble substances present in the syrup, typically sodium chloride resulting from pH adjustments of the syrup, will also depress the freezing point. With the introduction of de-ionised (de-min) syrups, it is necessary to calibrate the cryoscope for both de-ionised and non-deionised syrups. It should be appreciated that the cryoscope will only determine the DE of a syrup – ideal for a lot of routine production analyses, and, like the Fehling's method, it will not determine which sugars make up the DE. For determining the individual sugars which make up the DE, the industry had to wait for the next major analytical development – chromatography. The word 'chromatography' is derived from the Greek, and means 'colour writing'.

In 1850, the German chemist **Friedlie Runge (1794–1867)** was the first person to separate dye colours using paper chromatography, but it was the Russian botanist **Mikhail Tswett (1872–1919)**, who recognised that chromatography could be used as a method for separating different substance, and in 1910 published details describing the process. The method was further developed by **Archer Martin (1910–2002)** and **Richard Synge (1914–1994)** in the early 1940's. In 1941 Martin then suggested the possibilities of high-pressure liquid chromatography (HPLC). In 1946, **Stanley Partridge (1913–1992)** developed the use of partition paper chromatography for the examination of sugars, and in 1948, so as to separate larger amounts of sugars than was possible using paper chromatography, **Hough, Jones and Wadman** used columns of cellulose. Thirty years later, in 1978, this pioneering work would be used on an industrial scale to produce fructose syrups containing up to 90% fructose, by replacing the cellulose with ion exchange resins.

Whilst both paper and thin layer chromatography, together with gas–liquid chromatography, were used as research tools for sugar analyses, the real breakthrough for the glucose industry came in 1973 when the American chemists **Brobst, Scobell and Steele**, working for A.E. Staley Manufacturing Company, Decatur, IL, U.S.A. (now part of Tate & Lyle Americas Inc), produced a viable automatic HPLC which could quickly determine the sugars present in a glucose syrup. As the system is computer compatible, the DE of the syrup can be calculated, and if a blend of syrups and sucrose have been used, the ratios can also be calculated, together with any process inversion. Besides being quick, this method does not use any expensive or dangerous solvents – just de-ionised water, making it both cheap and safe to operate. This was a major step forward in the analysis of glucose syrups, especially as the industry can use either an acid or a combination of both acid and enzyme to produce glucose syrups, which have the same DE, but have totally different sugar spectra and hence different properties and processing characteristics. By comparing the different sugars present in a syrup, it is possible to get an indication of how the syrup has been produced.

The development of HPLC by **Brobst, Scobell and Steele** was invaluable for the next major development in the glucose industry, namely the commercial development of high-fructose glucose syrups. HPLC also enabled the accurate analyses of different sugars, alcohols, polyhydric alcohols and other products present in syrup blends, or in finished products. It is a very versatile and powerful analytical tool, and invaluable to any applications chemist.

The use of the cryoscope and HPLC within the glucose industry have now almost totally superceded the Fehling's method for characterising a glucose syrup.

In the early days of the glucose industry, to quickly determine the solids present in a syrup, the industry used the Baumé hydrometer. The Baumé hydrometer was invented in 1768 by a French chemist, **Antoine Baumé (1728–1804)**, who worked in the French alkali industry, where he used it to determine the solids of different solutions used in the saltpetre, bleaching and sal ammoniac processes. The Baumé hydrometer is still used today in the production of glucose syrups as a quick method for measuring the solids in starch slurries and glucose syrups, as well as in other process streams. It is a very simple and inexpensive piece of equipment. Because of the way that the Baumé hydrometer was adopted by the glucose industry, there were some inconsistent readings, therefore the glucose industry standardised on a 'modulus' of 145 for its hydrometers, and is the constant used to convert specific gravity into degrees Baumé.

The Baumé hydrometer having originating from the alkali industry is standardised using a solution of common salt. In 1835, to make the hydrometer more suitable for the sugar industry, a German chemist, **Karl Joseph Von Balling (1805–1868)**, recalibrated the Baumé scale so that it could read sucrose solids – to give us degrees Balling. In 1854, an Austrian mathematician **Adolf F. Brix (1798–1870)**, improved the accuracy of the Balling scale to give us the well known Brix Solids. And finally, in 1918, **Dr Fritz Plato**, a German, made further improvements and corrections to the Balling scale to produce the Plato tables, which are now used extensively in the brewing industry. Basically, the Balling, Brix and Plato scales are identical up to the fifth and sixth decimal place. In summary, the glucose industry uses the Baumé scale, whilst the sugar industry uses the Brix scale. The brewing industry, however, uses the Plato scale, possibly due to it being more accurate, which is financially important when dealing with the paying of duty on beer.

Today, for a more accurate determination of glucose syrup solids, the glucose industry uses a refractometer. As well as being more accurate, the refractometer is also quick and easy to use. The instrument works on the principle that a single ray of light is diffracted when it passes from one substance to another. The amount of diffraction can be related to the amount of solids present in the syrup. The most common refractometer used in the industry is the Abbe refractometer, which was developed by a German physicist **Ernst Abbe (1840–1905)**. Originally, he was Professor of Optical Physics at the University of Jena, and directed research at the Carl Zeiss factory from 1866. He became a partner in 1875, and on the death of Carl Ziess in 1888, became the director of Carl Zeiss. The solids of a glucose syrup which are determined using a refractometer are referred to as 'The RI Solids'. The temperature at which the determination is made should always be stated. It is therefore standard practice for the refractometer to be temperature controlled.

1.3 Process developments

Running parallel with developments in analytical methods were improvements in the production of glucose syrups. In Europe, the glucose industry was based on either potato or wheat starch, because both of these starches were readily available within Europe. In North America, however, the glucose industry which also used potato and wheat starch, started to look at the possibility of using maize (corn) of which there is a plentiful supply, and in 1841, **Thomas Kingsford (1796–1869)**, an English immigrant, developed an alkaline process to obtain starch from maize. In the year 1875, an Italian, **M.M. Chiozza** developed a process in which the maize was soaked or steeped in a solution of sulphur dioxide. **Dr Arno Behr** of The Chicago Sugar Refining Company used this sulphur dioxide steeping process to replace the Kingsford alkaline process and is still used by the industry today. At that time, American companies produced either starch or glucose syrups, but in 1883, The Chicago Sugar Refining Company started to produce both glucose syrups and starch, and this is possibly the start of the glucose industry, as we know it today, a totally integrated starch and syrup operation.

One of the advantages of using either maize or wheat as a raw material for making starch is that both can be easily stored and transported before being processed. Potatoes, on the other hand, like sugar beet, have to be harvested in a 'campaign'. Whilst potatoes can be stored for a limited time in a clamp in a field, ideally, they should be processed as soon as they have been harvested, with the resultant starch being dried, and then stored. The dried starch can then be made into a slurry before being converted into a glucose syrup.

With the industry being able to produce syrups, the production of crystalline dextrose, the end product of starch hydrolysis, was proving more difficult. The production problems were eventually solved in 1923 by **W.B. Newkirk**, who worked for Corn Products, Argo, USA, by devising a process of controlled crystallisation. This involved seeding a dextrose rich syrup, and allowing it to cool with continuous agitation with the dextrose crystals being recovered using a centrifuge.

When acid is used to make glucose syrups which have a DE higher than 60, the resulting syrup has an undesirable off taste. The problem of this undesirable off taste was solved in 1938 by **Dale and Langlois**, who worked for A.E. Staley, Decatur, IL, USA. They used 'fungal enzymes' derived mainly from moulds of aspergillus to further change the sugar spectrum of a conventional acid converted 42 DE syrup to produce the very successful 63 DE syrup. This syrup is sweeter than a conventional 42 DE syrup, and enabled glucose syrups to be used in many new and different applications, other than confectionery products. In 1951, **Langlois and Turner** further developed the use of their 'fungal enzyme' for the production of dextrose. This development was a major advance in dextrose production and would mean the end of the conventional acid process for making dextrose. All future dextrose production would use either a combination of acid and enzyme or purely enzymes. The 'active ingredient' in Langlois and Turner's 'fungal enzymes' was glucoamylase, sometimes referred to as amyloglucosidase or AMG for short.

The next major milestone in the industry occurred in 1957, when **Richard Marshall** and **Earl Kooi**, discovered the existence of an enzyme which could be used to convert dextrose into fructose. Since fructose is approximately 50% sweeter than sucrose, this discovery had a major impact on the glucose industry – the glucose industry could at long last, compete with the sucrose industry, on a sweetness for sweetness basis. This discovery had possibly the greatest commercial impact on the glucose industry than any other discovery.