

Master Beekeeper Certification Course: Category #7

By: Louis A. Matej

Date: 1 May 2004

Name: Honey composition, sources and marketable forms.

Subject: Honey Composition and its role in the Biochemistry of Glucose Metabolism and Nutrition.

PROPOSAL

1. Discuss the chemistry and composition of nectar and honey.
2. What are the chemical differences of nectar and honey from various sources?
3. Discuss the process of conversion from nectar into honey.
4. The metabolism of glucose from nectar and honey by bees into heat and energy.
5. Discussion of the importance of providing carbohydrates to bees to maintain nutrition and winter survival.
6. Written paper and to be included as part of an oral presentation discussing the chemistry of bees.

REFERENCES

The Hive and Honey Bee, Dadant & Sons, 1992 Edition, pages 871-890

White, J.W.Jr. and Doner, Landis W. "Beekeeping in the United States Agriculture Handbook Number 335 Revised 1980 Honey Composition and Properties"http://maarec.cas.psu.edu/bkCD/Products_Hive/honey_com.html

Suarez, R.K.; Staples, J.F.; Lighton, J.R.B. and Mathieu-Costello, O. Journal of Experimental Biology 203, 905-911 (2000) "Mitochondrial Function in Flying Honeybees (*Apis Mellifera*): Respiratory Chain Enzymes and Electron Flow From Complex III to Oxygen"

Amend, John R.; Mundy, Bradford P.; Arnold, Melvin T. Saunders College Publishing "General, Organic and Biological Chemistry", Chapter 28, Bioenergetic and Catabolism.....28.3 Carbohydrate Catabolism pages 805-816

ABSTRACT

Honey Composition, Sources and Marketable forms

The sugar concentration in nectar varies from 4% to over 80%. However, the sugar concentration in mature honey averages around 95%.

Honeybees process nectar into honey by removing water biophysically and chemically by absorbing water and passing it from one bee to another and mechanically by fanning to evaporate the stored nectar. This raw honey is composed of a variety of sugars; mainly glucose (dextrose), fructose (levulose), sucrose and maltose, however there are many other chemicals and substances in honey which contribute to its taste, color, pH, viscosity and aroma. Some of these chemicals aid in the ripening and preservation of honey.

When feeding bees sugar syrup in the spring and fall, it is important to maintain the sugar concentration to aid in the survival of the colony by mimicking their intake of nectar and honey. The bees must process sucrose, a disaccharide, by breaking it down into the two monosaccharides, glucose and fructose, with the enzyme invertase (sometimes also called sucrase). This enzyme is secreted into the honey sac of the foraging bee.

Glucose is the primary sugar used for the production of ATP, a high energy chemical used by all life forms including honey bees. The metabolism or catabolism of glucose into heat and energy (ATP) is accomplished in 3 stages: 1) The glycolysis of glucose into pyruvate in the cytoplasm of the cell. This process converts glucose into pyruvate, a chemical readily usable in the biochemical pathways involved in energy production. 2) The pyruvate molecules are coupled with coenzyme A and with the aid of other enzymes in the Krebs or Citric Acid Cycle they are converted into stored chemical energy in the form of reduced NAD and FAD (NADH and FADH). These are exothermal reactions which produce heat and the stored chemical energy is transported from the cytoplasm into the mitochondria of the cells. 3) Oxidative Phosphorylation is accomplished in the mitochondria which releases the stored chemical energy as ATP which is a readily usable form of energy. (For example: wing muscle energy, movement, wax and pheromone secretion, etc.)

The breakdown of glucose produces heat for temperature regulation and is the main source of energy for muscle movement and other metabolic pathways. In contrast, pollen is the primary source of protein and other minerals for growing larva and other necessary biological functions.

A good beekeeper will always be very conscious of the need, availability, and ongoing utilization of carbohydrates in each colony.

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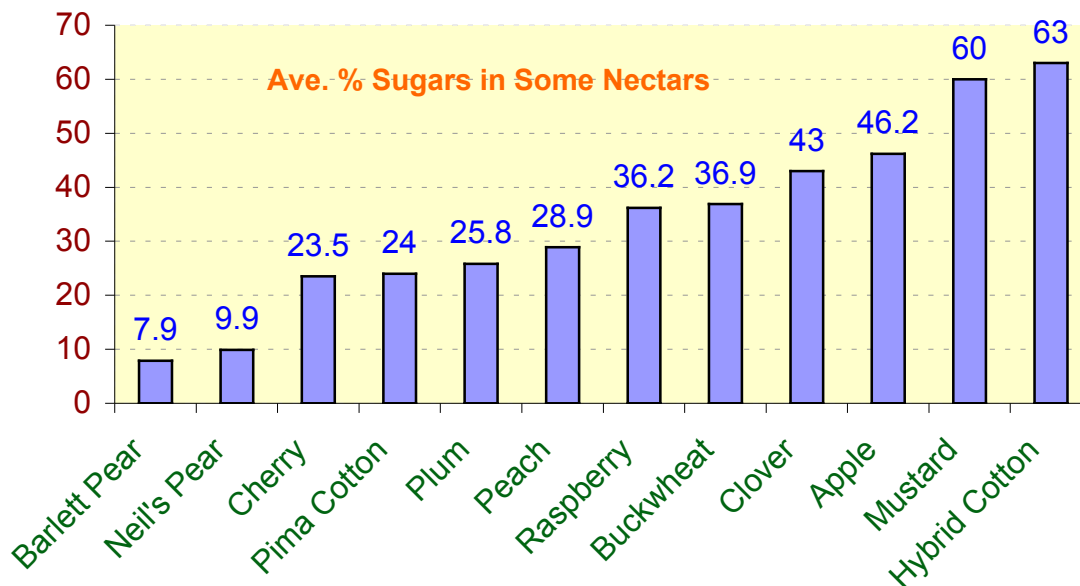
Date: 10 May 2004

Category: Honey composition, sources and marketable forms

Honey Composition and its role in the Biochemistry of Glucose Metabolism and Nutrition

The Chemistry and Composition of Nectar and Honey

It is generally observed that honeybees (*Apis mellifera*) do not forage for nectar which has a total sugar (carbohydrate) content of less than 15% unless absolutely necessary for survival. The sugar content of nectar can vary from as low as 4% to as high as 80% depending on plant species and environmental conditions. The three main carbohydrates in nectar are glucose (dextrose) and fructose (levulose), which are monosaccharides and sucrose (table sugar), which is a disaccharide. The chart below gives the average percentages of some common nectar producing plants.



By removing water from nectar, biophysically and chemically by absorbing water and passing it from one bee to another and mechanically by fanning to evaporate stored nectar, and by adding enzymes and other secretions, the honeybee produces honey. Sealed ripe honey contains a total sugar content between 95% to 99%, regardless of the original nectar sugar concentration. For example: If honeybees collect 5 gallons of nectar at 30% sugar content, they must remove 3.4 gallons of water in order to make honey having a 95% sugar content. For this reason it is important for the beekeeper, when feeding sugar (sucrose) syrup to bees that the solutions mimic as far as possible the nectar gathered in the spring and honey stored for use in the fall and winter.

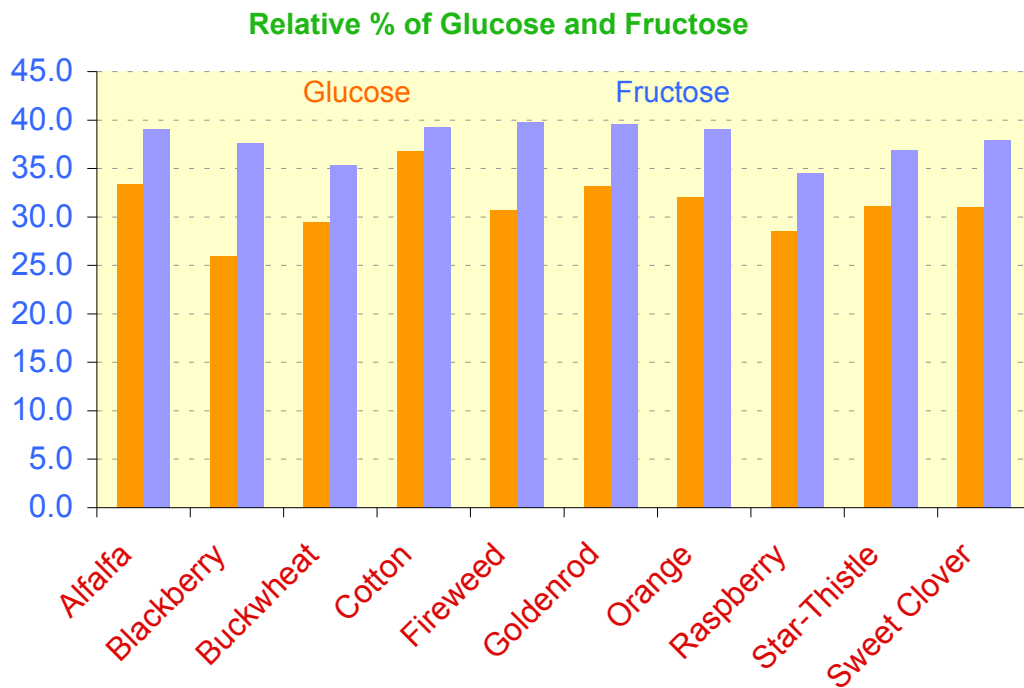
In the picture below, we see two worker bees passing nectar in order to absorb water and add enzymes and other substances:

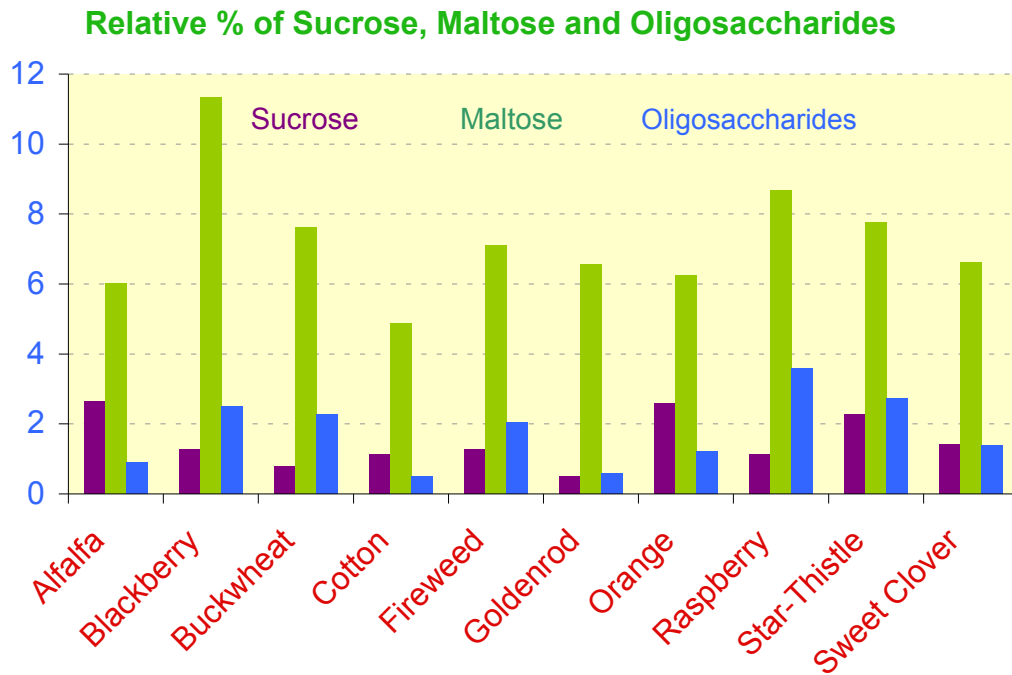


Usually when making sugar syrup in the spring, a beekeeper will add 2 parts of water to 1 part of sugar. In the laboratory, I determined that this mixture amounts to 34.0% total sugar which is similar to the average nectar concentration. In the fall and winter the beekeeper will add 1 part of water to 2 parts of sugar which amounts to 89.4%. This is very close to the concentration of total sugars in honey.

It is interesting to note that in addition to the 3 main carbohydrates mentioned above, honey contains maltose, isomaltose, maltulose, turanose and kojibiose, which are disaccharides and other complex sugars (oligosaccharides, sometimes called “higher sugars”). These are formed during ripening and storage by effects of bee enzymes (specifically invertase).

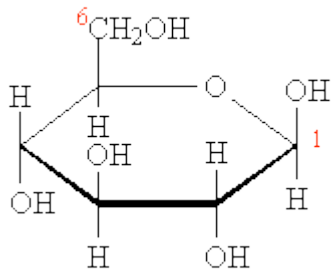
Below are charts showing the relative amounts of fructose, glucose, sucrose, maltose and oligosaccharides found in various types of honey. Note that the relative amounts of fructose to glucose do not vary greatly from one variety to another.



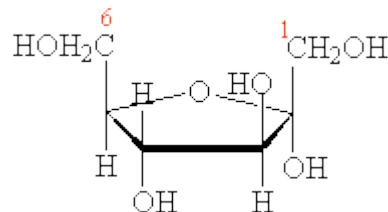


Similarly, the relative amounts of sucrose, maltose and oligosaccharides do not change significantly from one variety of honey to another, varying by only a few percentages.

Glucose and fructose are monosaccharides. The chemical structure of glucose shows that it is a 6 carbon molecule connected at carbons 1 and 5 forming a 6 atom ring structure. Fructose is also a 6 carbon molecule connected at carbons 2 and 5 forming a 5 atom ring structure. (Note: in nature sugars exist in isomeric forms and also exist in both the ring structure as well as in the straight chain structure).

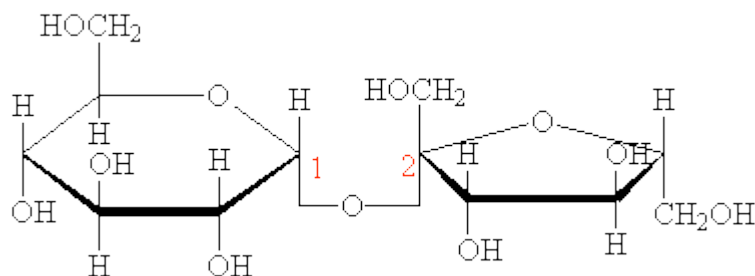


Glucose

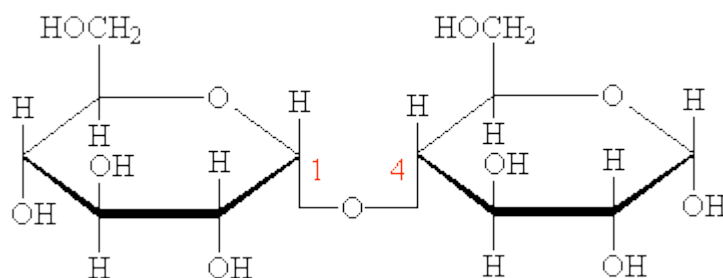


Fructose

Sucrose and maltose are disaccharides. Sucrose is a 12 carbon molecule of glucose and fructose connected by an oxygen atom (glycosidic bond). Similarly maltose is made up of 2 glucose molecules also joined by an oxygen atom.



Sucrose



Maltose

Honey is a supersaturated hygroscopic solution of carbohydrates containing many other chemicals and substances. If you look at all the honey varieties combined, it has been shown that honey contains:

Monosaccharides (70-80%):	Glucose, Fructose
Disaccharides (5.0%)	Maltose, Isomaltose, Sucrose, Nigerose, Turanose, Kojibiose, Maltulose, Trehalose, Gentiobiose, and Laminaribiose
Oligosaccharides (Higher Sugars) (2.0%)	Erllose, Theanderose, Panose, Maltotriose, 1-Ketose, Isopanose, Isomaltosyltetraose, Theanderose, Centose, Isomaltosyl glucose, Isomaltosyltriase and Isomaltosyltaose.
Organic Free Acids (0.2-2.0%)	Gluconic acid (70-80% of all free acids), Acetic acid, Butyric acid, Citric acid, Formic acid, Lactic acid, Malic acid, Oxalic acid, Succinic acid, Fumaric acid, a-Ketoglutaric acid, Pyroglutamic acid, and Maleic acid

Amino Acids (0.2-2.0%)	Proline, Lysine, Histidine, Arginine, Aspartic acid, Threonine, Serine, Glutamic acid, Glycine, Alanine, Cysteine, Valine, Methionine, Isoleucine, Leucine, Tyrosine, Phenylalanine, Tyrtophan
Minerals (0.1-1.5%)	Potassium, Sodium, Calcium, Magnesium, Iron, Copper, Manganese, Chlorine, Phosphorus, Sulphur, Aluminum, Iodine, Boron, Titanium, Molybdenum, Cobalt, Zinc, Lead, Tin, Antimony, Chromium, and Nickel
Vitamins (Trace amounts)	Ascorbic acid (Vitamin C), Riboflavin (Vitamin B2), Panthothenic acid (Vitamin B5), Niacin (Vitamin B3), Thiamine (Vitamin B1), Pyrodoxine (Vitamin B6), Biotin (Vitamin H), Folic Acid (Vitamin B9)
Enzymes	Invertase (sucrase), Diastase (Amylase), Glucose Oxidase, Catalase, Acid Phosphatase.
Enzymes shown to be absent	Lactase, Protease, and Lipase
Esters (trace amounts):	Methyl formate, Ethyl formate, Methyl acetate, Ethyl acetate, Propyl acetate, Isopropyl acetate, Ethyl propionate, Methyl buturate, Ethyl buturate, Isoamyl butyrate, Methyl valerate, Ethyl valerate, Methyl pyruvate, Methyl benzoate, Ethyl benzoate, Methyl phenylacetate, and Ethyl phenylacetate
Ketones and Aldehydes (trace amounts):	Formaldehyde, Acetaldehyde, Propylaldehyde, Butylaldehyde, Isobutylaldehyde, Benzaldehyde, Methylethyl ketone, Isovaleraldehyde, Capraldehyde
Alcohols (trace amounts):	Methanol, Ethanol, Propan-1-ol, Propan-2-ol, Butan-1-ol, Butan-2-ol, Isobutanol, 2-methyl-butan-2-ol, Benzyl alcohol
Lipids (trace amounts)	Glycerides, Sterols, Phospholipids, Oleic acid, Lauric acid, Stearic acid
Trace amounts of beeswax	Beeswax
Microscopic particles	Pollen, Fungal spores, Bacterial spores, and Yeasts

A number of these trace chemicals, especially esters and organic (carboxylic) acids have been used in research to determine their effectiveness in the control of mites.

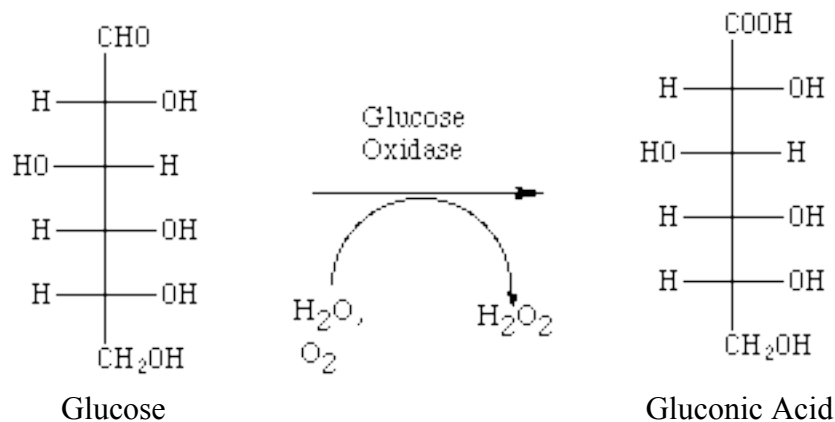
Enzymes:

The four major enzymes in honey are invertase (sucrase, saccharase, or glucosidase), diastase (amylase), glucose oxidase, and catalase.

Invertase is secreted by the honeybee from its salivary glands into the honey sac. This enzyme catalyzes the breakdown of sucrose into glucose and fructose. This reaction is slightly reversible and invertase does not catalyze the synthesis of more complex carbohydrates. This accounts for the disaccharides and oligosaccharides (higher sugars) not found in nectar. The invertase that is present in processed or sealed honey will continue to breakdown sucrose causing some honeys with higher concentrations of sucrose to ripen and mature after storage. Invertase is a key enzyme in preservation of honey.



Another major enzyme in honey is glucose oxidase, which is secreted from the hypopharyngeal gland of the bee into the nectar to assist in the formation of honey. It catalyzes the conversion of glucose to gluconolactone, which in turn equilibrates to gluconic acid. This and other carboxylic or organic acids in honey account for the slightly acid pH and also contribute much to the different tastes in various types of honey. Glucose oxidase activity helps in the preservation of honey by producing hydrogen peroxide which inhibits the growth of bacteria and yeasts.



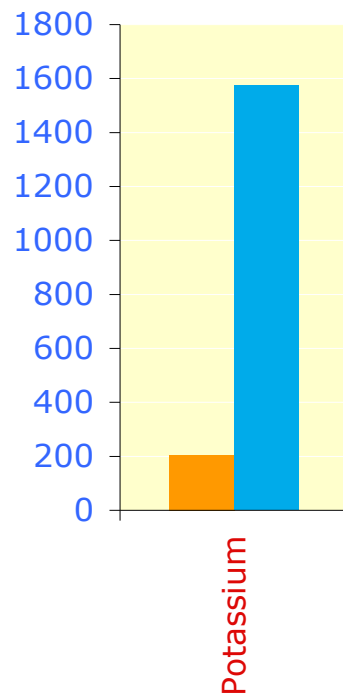
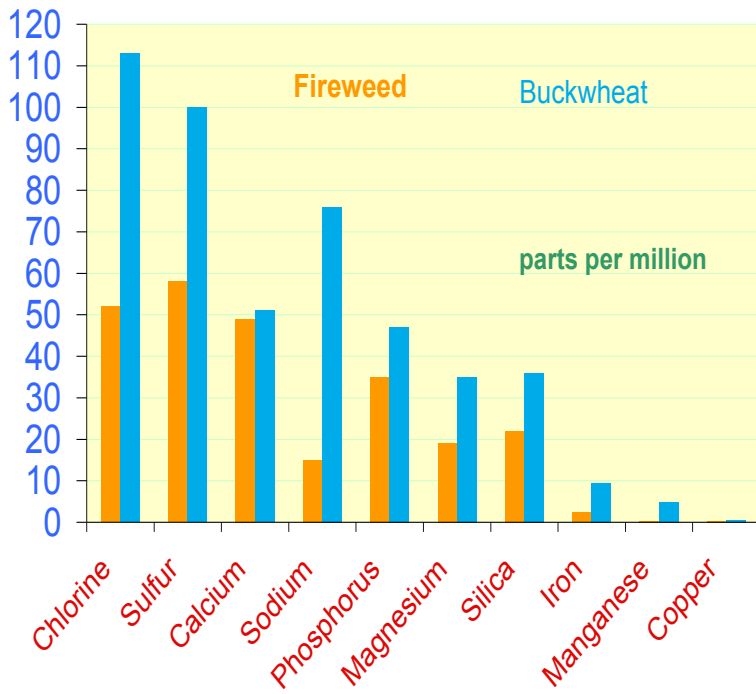
Honey is quite acidic having a pH of between 3.2 and 4.5, which is low enough to have an inhibitory effect on many pathogens. The sweetness of honey offsets the acidic nature of honey. In addition, the hygroscopic nature of honey (its tendency to absorb water) is detrimental toward bacteria or fungal growth because this causes dehydration.

Enzymes in honey breakdown over time and are destroyed with increased heat.

Minerals:

Even though there are a number of compounds in honey which contribute to the variance in color, the 22 minerals found in honey are partly responsible for the range of colors of honey from different sources. These are categorized as water white, extra white, white, extra light amber, light amber, amber, and extra dark amber.

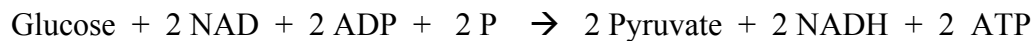
Below are charts showing the relative concentrations of some minerals contained in Fireweed honey (water white) and Buckwheat honey (extra dark amber)



The Metabolism of Glucose by Honeybees from Nectar and Honey into Heat and Energy:
Glucose is the primary sugar used for the production of ATP (Adenosine Triphosphate), which is a high energy chemical used by the honey bee (and most living creatures) for the production of heat and energy. The metabolism or catabolism of glucose into heat and energy (ATP) is accomplished in 3 stages:

1. Glycolysis of Glucose:

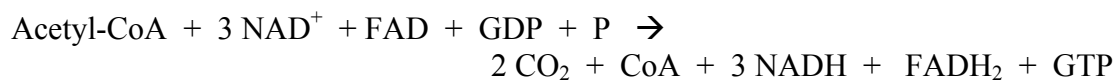
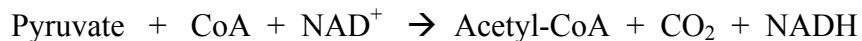
Glycolysis of glucose takes place in the cytoplasm of the cell. This process converts glucose into pyruvate, a chemical readily usable to the honey bee in the biochemical pathways involved in energy production. Pyruvate is a 3 carbon molecule, so for every one molecule of glucose there is produced 2 molecules of pyruvate:



This reaction represents 10 different equilibrium reactions each involving a specific enzyme.

2. The Tricarboxylic Acid Cycle:

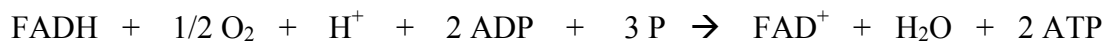
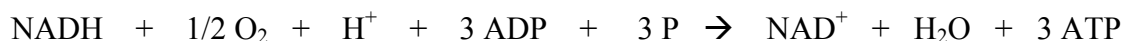
Within the cytoplasm of honeybee cells, pyruvate molecules couple with Co-enzyme A and enter into the Tricarboxylic Acid Cycle or Krebs Cycle (also called the Citric Acid Cycle). The reactions within this cycle are exothermic and heat is produced which the honey bee uses to keep the hive at a constant warm temperature. Excess energy is stored chemically in reduced molecules of NADH (Nicotinamide adenine dinucleotide, reduced form) and FADH₂ (flavin adenine dinucleotide, reduced form). These molecules are high in energy and are then transported to the mitochondria of each cell.



Nine separate equilibrium reactions occur to convert one molecule of pyruvate into heat and stored chemical energy in the form of NADH and FADH₂, each facilitated by an enzyme catalyst.

3. Oxidative Phosphorylation

This final step in the conversion of glucose into energy is accomplished in the mitochondria of each cell. Here the produced NADH and FADH₂ release their stored energy by converting to ATP which is directly used by the cells to allow the bee to move, metabolize other reactions (synthesis of beeswax, pheromones, etc.), fly, etc.



There are 36 ATP molecules produced for every glucose molecule used by the honeybee. During flight, this ATP is used as fuel. It has been found that the metabolic rate derived from

glucose metabolism in the honeybee wing muscles is 3 times as efficient as the rate in the wing muscles of hummingbirds and 30 times as efficient as in active human muscles.

In conclusion, there is an economy of direct heat generation verses stored chemical energy by the honeybee via glucose metabolism. In the winter the bees are not moving very much, yet heat is needed to keep the hive at a constant warm temperature. In the spring not only is heat needed but also more motion from stored energy. In the summer bees do not need as much heat generation but need wing movement for flight and fanning to cool the hive. From the metabolism of glucose heat and motion energy are generated in a very economical way in order to maximize the needs of the colony during times of cold and heat throughout the year.