Rheological Characterization of Honey and Syrup from Different Sources

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ABSTRACT
Syrup is a thick viscous liquid consisting primarily of a solution of sugar in water. Syrup contains large amounts of dissolved sugars which show little tendency to deposit crystals. Its consistency is more like that of molasses. A range of syrups are used in food production. This includes syrups made from agave, cane, corn, glucose etc.

Honey is also a supersaturated solution of sugars with low water content and some small concentrations of bioactive compounds such as phenolic acids, flavonoids etc. Honey is a complex food matrix produced by honeybees from nectar collected from different plants.

In this introductory study, several rheological methods were used to examine rheological properties of syrup and honey. Temperature effect on viscosity is investigated. Amplitude sweeps at different temperatures are used to investigate structural effects in the fluid samples. This knowledge may be of importance in many cases, for instance, during industrial processing of food like pumping and dosing. It is of vital importance to know the flow characteristics of such mechanical- and chemical processes.

INTRODUCTION
Honey and syrup are both key ingredients in the food industry. Honey is almost the only food consumed by humans that is produced by insects. It is an important energy food used as an ingredient in many manufactured foods. Many cereal-based food products contain honey for sweetness, colour, flavour, caramelization and viscosity[1].

The definition of honey in the Codex Alimentarius is as follows: “Honey is the natural sweet substance produced by honeybees from nectar of plants or from secretions of living parts of plants or excretions of plant sucking insects on the living parts of plants, which the bees collect, transform by combining with specific substances of their own, deposit, dehydrate, store and leave in the honeycomb to ripen and mature. Blossom honey is the honey that comes from nectars of plants[2]”.

The definition of glucose syrup according to Codex Alimentarius is as follows: “Glucose syrup is a purified concentrated aquas solution of nutritive saccharides obtained from starch[3].”

Pure honey is an entirely nature product. It contains neither additives nor preservatives. It is one of the most complex mixtures of carbohydrates produced by the nature. The major carbohydrates in honey are fructose and glucose, which account for 65% to 75% of the total soluble solids in honey. This makes honey a supersaturated solution of mainly glucose and fructose. In addition, there are some other mixtures of carbohydrates like disaccharides, trisaccharides and some oligosaccharides[2].

Water is the second most important component of honey. Its content is critical since it affects the storage of honey[4]. The water content depends on numerous environmental factors during production, such as weather conditions and humidity inside the hives. But also, nectar conditions and treatment of the honey during extraction and storage may influence on the water content of honey[5]. In general, honey is composed of about 17-20% water, although some types of honey may have a slightly higher or lower water content

Organic acids constitute 0.57% of honey and include gluconic acid, which is a by-product of enzymatic digestion of glucose. The organic acids are responsible for the acidity of honey and contribute largely to its characteristic taste[6]. Minerals are present in honey in very small quantities, with potassium as the most abundant. Others are calcium, copper, iron, and manganese[5]. Vitamin C, vitamin B (Thiamine) and vitamin B2 complexes such as riboflavin, nicotinic acid, and vitamin B6 (pantothenic acid) are also found. In addition, enzymes like invertase (saccharase), diastase (amylase) and glucose oxidase are also found[7].

Honey is used for a variety of purposes, mainly as food, food ingredients, and as an ingredient in medicine like products. Today, with increasing appreciation of more natural products in many countries, honey has been "rediscovered" as a valuable food. In addition, the nutritional and health enhancing properties of honey are quite a new field of research[2]. But most of the honey sold as food products is used directly as table sweetener or spread.

Honey as a food ingredient deserves serious consideration with its combination of interesting physical properties and fine flavour. It is used both on a small scale as well as at an industrial level. There are many applications within bakery, confectionery, breakfast cereals, dairy, dressings and sauces, frozen foods, meats, snack bars, spread, ice creams, marmalades, jams and many other preserved products[2].

For a long time in human history, honey was the only known sweetener, until the industrial sugar production began to replace it after 1800. Since then, sugar and glucose syrups have a well-established role as key ingredients in the food industry. Because of their competitive price and specific functional properties, they are now used extensively in numerous applications. Glucose syrups are manufactured from starch from various sources. In Europe wheat starch and maize starch have been the most common raw materials, though potato could also be used. The source of starch depends on local availability and price[3].

Light- and dark syrup used in this study, is made by mixing various by-products that arise from the production of white sugar from beet or cane sugar. This syrup is a viscous solution consisting of sucrose, glucose and fructose. The combination of the various sugars prevents crystallization, while the very high sugar content of approximately 80% guaranties a long shelf life. The colour and taste mainly come from smaller amounts of mineral salts and other substances that are naturally present in the raw material. But occasionally salt must be added to create the right flavour profile. Dark syrup normally contains a bit more salt and proteins than the light ones: See **Table 1**.

Scandinavian recipes often use either light- or dark syrup. Made primarily of beet sugar, they are popular liquid sweeteners found in sweet and savoury recipes throughout Sweden, Finland, and Norway.

The lower price of most syrups compared to honey with its relatively high price, has always been a target of adulteration. Detection of invert syrup in honey has been a challenge for more than a century[8]. Whether or not rheological measurements can help to reveal adulteration remains to be seen. But knowledge of rheological properties of food are relevant when designing processing lines regarding influences parameters such as pipes, pumps, tanks etc. Rheological knowledge is also relevant when characterization the structure and the functionality of food like honey and/or syrup. It is a way to understand the structure of the products, or the distribution of its molecular components, especially of macromolecular components. Rheological measurements are also important as predicting structural variations during preparation processes, packaging and storage[9].

Honey`s and Syrups rheological properties are relevant to consumers, honey keepers, processors and handlers since rheological parameters provide useful information that allows the development of new products, optimization of industrial processes and control of quality and even authenticity of honeys.

During storage the honey will crystallize. This is a natural phenomenon. But it involves only glucose, as fructose is characterized by a higher solubility value. The rate of crystallization depends on many factors, like temperature, amount of glucose, fructose and water, glucose supersaturation level, viscosity and presence of preformed crystals or impurities[10]. After some storage the honey will behave very solid. Apparently, crystallized honey contributes to the impression that it is adulterated. But in fact, crystallization is a guarantee that the honey is pure and natural in spite that the crystallization brings about several disadvantages regarding handling and processing. But there are also methods to prevent honey crystallization. This is possible by adding the disaccharide trehalose which is found in all types of honey in different proportions[11,12]. Fortunately, an easy way to get rid of the crystals, is to immerse the jar in hot water for some minutes. Then the solid glucose crystals will redissolve, taking the honey back to its original state.

The viscosity of glucose syrups and honeys is reported to be independent of shear strain. No strain hardening or softening will appear[13]. Although most honeys are Newtonian fluids, interesting shear-thinning and thixotropic as well as anti-thixotropic behaviour have been described for some types of honey. Rheological parameters have also been successfully applied to identify honey adulteration and to discriminate between different honey types[9]. In this introductory study, several rheological methods were used to examine both honey and glucose syrup during heating and storage.

The objective of the measurements reported in this paper was to investigate temperature effect on viscosity of some commercially produced honeys and syrups. Amplitude sweeps at different temperatures are used to investigate structural effects in the fluid samples. This investigation may be of importance in many cases, for instance, during industrial processing of food like pumping and dosing. It is of vital importance to know the flow characteristics of such mechanical- and chemical processes.

FIGURE 1: The 4 different commercial honeys and syrups used in this rheological investigation; 1: Syrup Dark, 2: Syrup Light, 3: Summer Honey from Serbia, 4: Flower Honey from Norway. In addition, a locally produced summer honey from Jeløya south of the Oslofjord was investigated.

TABLE 1: Approximate composition (% w/w) of the commercial honeys and syrups investigated in this study. Values declared by the manufacturers.

Product	Water	Protein	Carbo-hydrate	Starch	Fiber	Salt	kJ pr.100 g
Flower Honey, Norway	19	0	79	0	0	0	1410
Summer Honey, Serbia	17	1	80	0	0	0	1399
Syrup light	14	0.1	85	1	0	0.18	1440
Syrup dark	16	0.5	83	2	0	0.45	1420

MATERIALS AND METHODS

Honey and syrup alternatives

The different types of honey and syrup tested given in **Table 1**, were purchased from ordinary Norwegian grocery stores. In addition, a locally produced summer honey from 2022 at Jeløya in the southern part of the Oslofjord was investigated.

Instrumental analysis and experimental set-up

Two rheometers were used, a Physica MCR301 rheometer (Paar Physica, Anton Paar, Stuttgart, Germany, 2010) fitted with a PP25/P2 plate, and a US200 rheometer (Paar Physica, Anton Paar, Stuttgart, Germany) fitted with a Z4 bob/cup system. Both rheometers were equipped with Peltier temperature controls. The following tests were run:

- Rotational viscosity tests
- Amplitude sweeps
- Varying temperature tests
- Oscillatory tests to monitor sample development (change in G’ and G’’ versus time monitoring crystal growth)

Analysis

The Anton Paar LVR macro was run detecting a 3% reduction in G’ giving the limit of the linear viscoelastic region.

RESULTS AND DISCUSSION

Viscosity

Effects of varying shear rate

The variation of viscosity with varying shear rate is shown in **Fig. 2**. The measurements were carried out at 20 °C. The shear rate was first increased, then decreased to show if any hysteresis occurred.

Only small hysteresis loops show up indicating that there is no significant thixotropic behaviour.

The most viscous sample is the Summer honey, followed by the light and the dark syrup. The Jeløya honey and the Flower honey have a much lower viscosity than the other.

The samples are all slightly shear thinning.

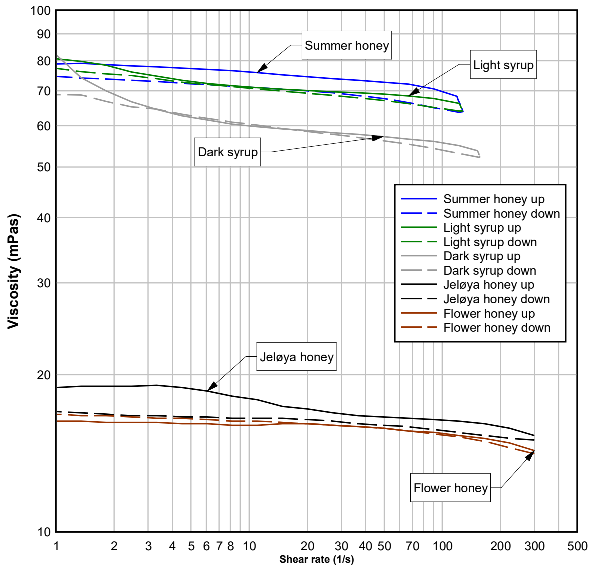

FIGURE 2: Viscosity versus shear rate.

Effects of varying temperature

The effect of temperature variations on viscosity is shown in **Fig. 3.** All the samples exhibit the expected reduction in viscosity with increasing temperature. The syrups are more sensitive to temperature changes than the honeys.

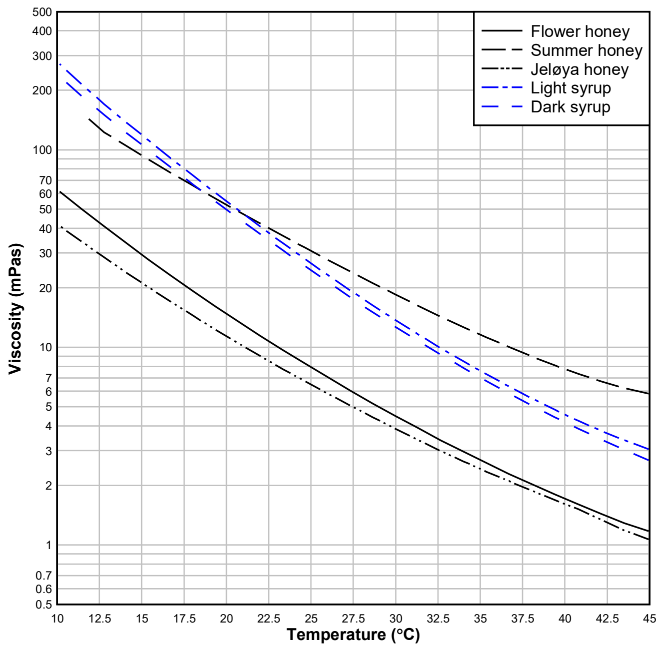

FIGURE 3: Viscosity versus temperature.

Amplitude sweeps - Stiffness, strain limit and strength

Amplitude sweeps were run, and the results are shown in **Fig. 4 and Fig. 5**.
Only the Jeløya honey and the summer honey became viscoelastic solids during the tests, the Summer honey at both 10 and 20 °C, the Jeløya honey only ay 10 °C.

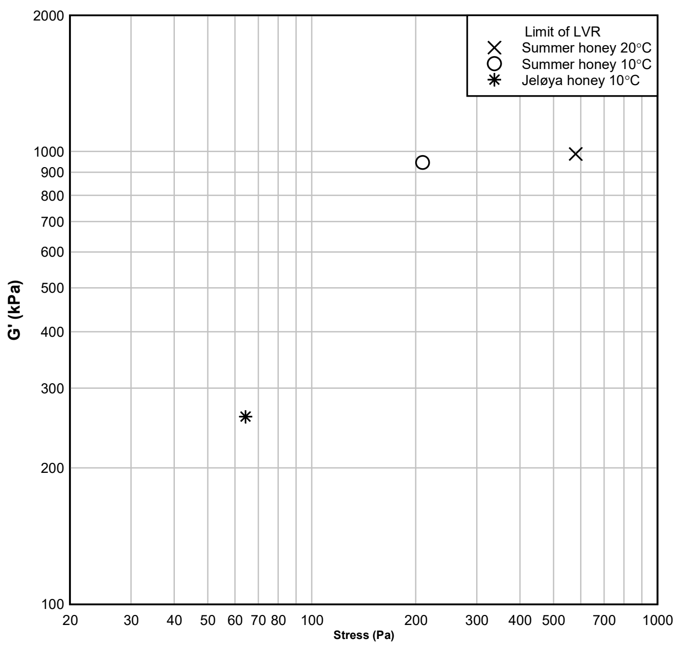

FIGURE 4: G' versus stress. Limit of linear viscoelastic region.

The summer honey is much stiffer that the Jeløya honey, and the Summer honey has a higher strength. The strength seems to increase with increasing temperature.

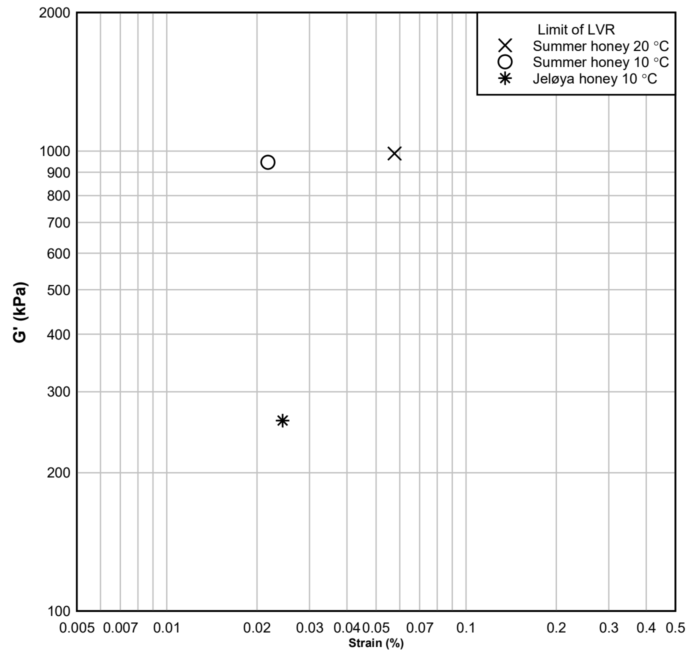

FIGURE 5: G' versus strain. Limit of linear viscoelastic region.

Fig. 5 show that the strain limit of the honeys is between 0.02% and 0.06%.
The Flower honey and the syrups did not behave as viscoelastic solids at the temperatures tested in this study.

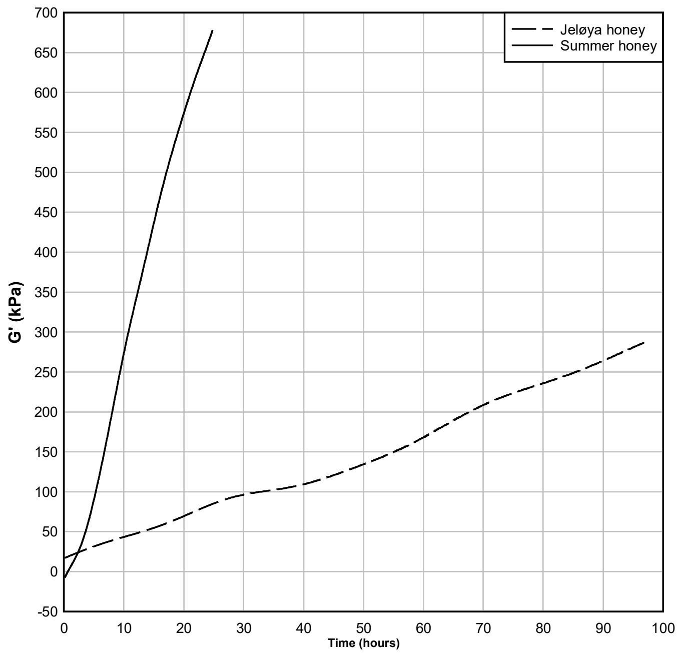

FIGURE 6: Increase in G' versus time.

G', the storage modulus, increases with time as shown in **Fig. 6**, and the process goes on for days. The gradient for Summer honey is as large as 3 Pa/s, while it for Jeløya honey is approximately 0.8 Pa/s. The transient increases in G' were not run until equilibrium as this would take a very long time. This emphasises the requirement for good experimental planning.

Our next rheological challenges will be to study the above-mentioned processes more in depth in different food products.

CONCLUSIONS

The conclusions of this screening study can be summarized as follows:

- Honey is a complex product. It contains neither additives nor preservatives. It is one of the most complex mixtures of carbohydrates produced by the nature. Crystallization goes on for days and weeks. Test programs will hence be very time consuming. Experimental setups are challenging and require careful knowledge-based planning.
- Honey and syrups exhibit normal temperature dependent behaviour.
- Some of the honeys are viscoelastic solids at room temperature.
- All the syrups were viscoelastic liquids at room temperature.
- The honeys and syrups were slightly pseudoplastic.
- The samples had a thixotropic behaviour.

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