Determination of Essential Oil in Hops and Hop Products[1]

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ABSTRACT

This paper describes a method for the determination of the essential oils of hops and hop products. A modification of the Wright and Connery method using 100 g of ground hops in 3 L of water has been found to give excellent results. Only 4 hr is required to bring about complete distillation of the oil in ground hops and hop products. Such a method may be suitable as a standard method.

Key words: Distillation, Essential Oil, Ground Hops, Lupulin, Refrigerated Storage, Rolling Boil

An essential oil is one of the contained volatile oils found in plants that is capable of imparting odor and, often, other characteristic properties. Another definition states that an essence is a substance distilled or otherwise extracted from a plant and believed to possess its virtues in concentrated form. Essential oils of plants are those that are readily vaporizable, that is, volatile. Volatile oils are distinguished from fixed oils such as liquid fats found in plant seeds, which are nonvolatile.

The essential oil of hops is a complex material. Modern capillary gas chromatography can separate as many as 120 components in hop oil. The major components include myrcene, humulene, caryophyllene, and farnesene. Classification of hop varieties can be accomplished by examination of such components (3,4,5). The ratio of various components may determine whether the hop is classified as an "aroma" hop (2). Such relationships are also useful in the selection of new hop varieties. Composition of oil may be of greater interest to brewers than total oil content. Useful relationships involving quality are based on accurate, reliable quantitative analysis.

In the late 1940s, studies of hop oil quality were initiated by Robert Wright and Frank Connery of Ballantine & Sons, Newark, NJ. Evaluation of hop aroma was based on the quantity of hop oil available and its aromatic quality (6). Their method of hop oil determination used 300 g of ¼-in. milled hops in a 12-L flask with 6 L of water added. This was boiled for up to 6 hr. In 1970 the Analysis Committee of the European Brewery Convention adopted a method consisting of placing a maximum of 100 g of hops, separated by teasing, not grinding, in a 5-L flask with 3 L of water (3). The period of distillation was 3 hr. In an unpublished paper, Likens, Nickerson, and Wright recommended distilling 250 g of whole hops with 5 L of water for 6 hr.

As can be seen, the methods published to date vary significantly. The purpose of this work is to establish a method that can be used by all laboratories. Recently, interest has increased in the essential oil of hops and hop products. Some brewers are including oil content in hop purchase specifications. It is important, therefore, to have a method which will give the same results to each laboratory seeking such information.

EXPERIMENTAL

The *Methods of Analysis* of the ASBC (1) does not contain a section dealing with determination of oil. The John I. Haas company has been using a method that has given accurate, reproducible results over many years of use. The method is a modification of the Wright and Connery method (6). Coarsely ground hops (100 g) are distilled in 3 L of water for 4 hr. Equipment consists of a 5,000-ml round-bottom boiling flask with standard taper 45/50 outer joint for ease of sample introduction. A reducing adapter standard taper 24/40–45/50 is used to connect the flask to a distilling receiver suitable for trapping oil. Distilling receivers of 5 and 12.5 ml capacity are available. A 41 × 300 mm Allihn condenser (Corning, Corning, NY) connects to the receiver. A variable auto transformer is necessary to control the heat of a 5,000-ml capacity heating mantle. The heating mantle is one of the most important parts of the equipment. The heat must surround the boiling flask in order to achieve rapid boil. The 600-W mantle brings the mixture to a boil in 30 min. The maximum high heat setting is used to achieve rapid boiling, and then the heat is reduced to maintain a rolling boil. Water is the only reagent required; tap water is satisfactory. When determining the oil content of hop extracts, it is helpful to add Teflon chips to promote gentle boiling.

Samples of hops are prepared for analysis by grinding in a #3 commercial-size Universal food chopper using a three-bladed knife for a coarse grind. Such a cutter is designed to chop material into rather large pieces.

RESULTS AND DISCUSSION

The essential oil of the hop is found in the structure known as lupulin. The lupulin glands, about 0.15-mm in diameter, make up about 20% of the weight of the hop cone. Oil in the lupulin can be about 7.5% of the weight of the lupulin. An experiment was conducted in which 20 g of ground lupulin and 20 g of the same lupulin, unground, were each placed in 1,500 ml of water and distilled for 7 hr. The quantity of distillate was measured at 30-min intervals. The data in Figure 1 show that the rate of distillation of duplicate samples is exactly the same for both the ground and the unground lupulin. This would seem to indicate that rupturing the lupulin by grinding is unnecessary for fast, efficient distillation of the essential oil. Other experiments showed that coarse grinding of whole hops is indeed necessary. An examination of the ground hops showed about 10% of the sample consisted of pieces larger than ¼ in., 15% were between ¼ and ⅛ in., and 75% of the pieces were less than ⅛ in. This is not truly coarse, but this is the type of grind obtained with the equipment described above. Over 95% of the grind of a six-bladed knife passed through a ⅛-in. screen. Grinding allows the hops to achieve a rolling boil, which is the secret to efficient distillation. Whole hop cones tend to form a layer that is static during boiling, preventing complete distillation.

The data in Figure 2 show the results of a study of the relation between sample size and yield of oil using 3 L of water. The 50 g, ground and unground, and the 100 g, ground and unground samples yielded the same amounts of oil, although completion of

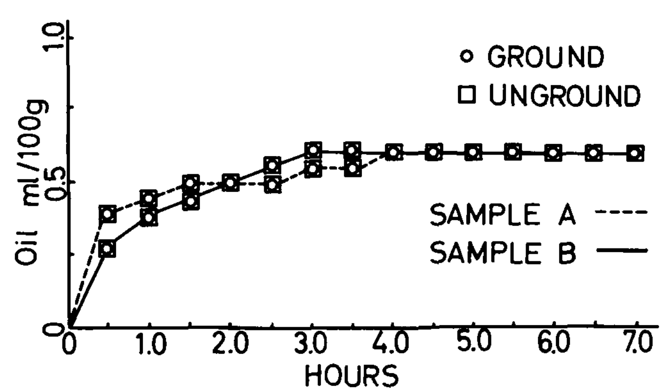

Fig. 1. Distillation rates of ground and unground lupulin.

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distillation was faster in the ground samples. The 200 g unground sample yielded only 85% of the yield of the 200 g ground sample after a 7-hr boil. This is because the unground sample was unable to achieve the rolling boil essential to complete distillation. A sample of 50 g of unground hops in 3-L of water gave a suitable rolling boil that brought about excellent distillation of the oil. We consider 50 g to be an inadequate amount of hops to represent a normal size shipping lot of hops; 100 g of ground hops in 3 L of water is preferred. An alternative to this would be the distillation of 100 g of whole hops in 6 L of water.

Additional studies were performed to compare the rate of distillation in 100 g hop samples, ground and unground. Figure 3 shows a typical result from a Galena hop. The distillation in 3 L of water was complete at 4 hr with the ground hop, but only 87% of the available oil had distilled from the unground hop. After 7 hr, the unground hop yielded only 96% of its potential oil. Each data point is an average of three points. This observation was the same in all samples of Galena, Eroica, and Brewer's Gold, but was not true of Cluster hops. At 4 hr only about 75% of the oil had distilled in the ground or the unground samples of Cluster hops and 6–7 hr were required for complete distillation.

Hop material is constantly changing. It is well recorded how heat can change the brewing value of hops. The same is true of hop oil. Figure 4 shows the effects of room temperature storage on hops over a two-month period. Analysis of four varieties of hops demonstrated the changes of oil yield that can result from both refrigerated (3°C) and room temperature storage (24°C). Refrigeration does not stop the reduction of oil yield, but it does slow it down. The Cluster and Bullion stored at room temperature lost 50% of their oil in the two-month period. On the average, 18% of the oil was lost under refrigeration compared to 43% under room temperature conditions of storage.

Hop samples ground and then placed in refrigerated storage lost oil considerably faster than unground samples in refrigerated storage. As indicated by Figure 5, about 50% of the oil yield was apparently lost from ground hops after seven-weeks refrigerated storage compared to 20% from unground hops. Ground hops stored under refrigeration and unground hops at room temperature appeared to lose about the same amount of oil.

Hop oil distills readily from hop extracts and hop pellets. Whole hop pellets (100 g) were distilled in 3 L of water. Hop extract (20 g) was placed on 4×4 in. sheets of weighing paper, rolled, and put into 3 L of water. Extracts made with hexane or methylene chloride as the extracting solvents contained nearly 100% of the oil found in the original hops. Hop extracts made from Galena or Brewer's Gold can contain up to 7.0 ml of oil per 100 g of extract. A Cluster extract may contain up to 4.0 ml/100 g. Oil content in hop extract does not undergo changes similar to that of hops in storage over a period of time. The oil content of hop extract stored at room temperature for six months remained relatively constant. The oil content of hop pellets tended to drop as with ground hops refrigerated over a period of time. A sample of concentrated pellets containing 2.1 ml/100 g when pelletized dropped to 1.3 ml/100 g after four months in refrigerated storage. This is a loss of 38% of the oil yield. A regular pellet made from a hop containing 1.8 ml/100 g in

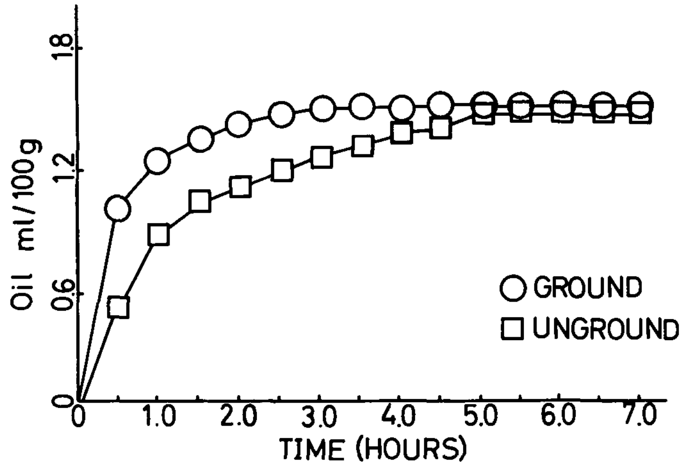

Fig. 3. Distillation rates of 100 g of ground and unground hop samples in 3 L of water. Each data point is an average of three points.

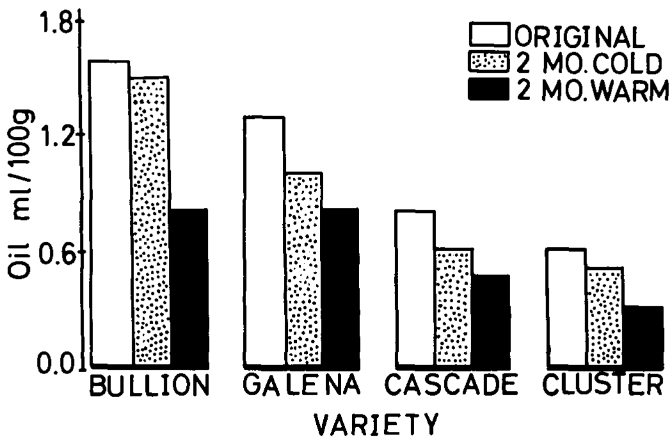

Fig. 4. Effects of room temperature and refrigerated storage on oil yields of hop samples.

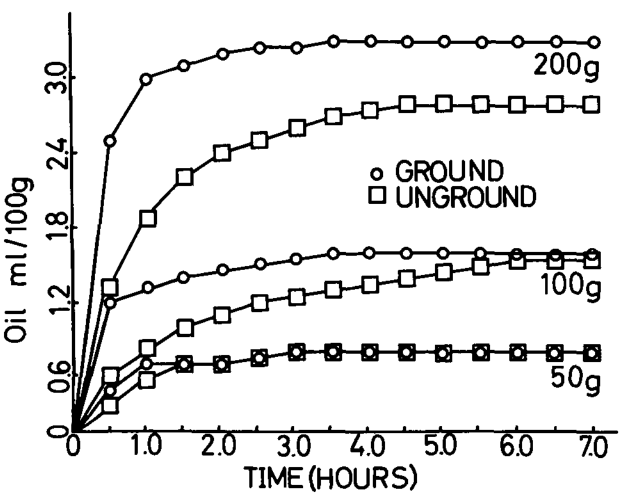

Fig. 2. Distillation rates of 50, 100, and 200 g of ground and unground hop samples in 3 L of water.

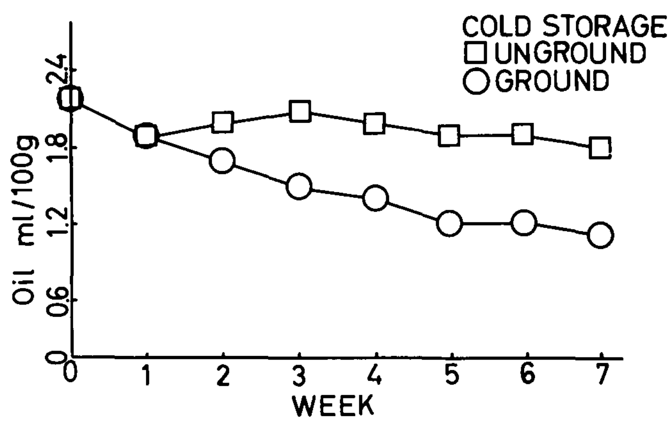

Fig. 5. Effects of grinding on oil yield of hop samples.

October dropped to 1.3 ml/100 g in April, a loss of 28% under refrigerated conditions of storage.

The essential oil of the hop cone is ever changing. The processes of harvest, kilning, and baling all act to reduce the essential oil content of hops. The oil is altered so that it is no longer as volatile as the original oil. Oxidation, polymerization, or some unknown process may be responsible for this change.

When determining the essential oil content of hops and hop products, it is important to remember that hop oil is unstable. Ground hop samples should not be stored before analysis, even if placed in refrigeration. The need to coarsely grind hops before distillation has been established. Grinding the hops promotes a rolling boil in the distillation process. This boiling is a physical process that allows complete entrainment of the available oil in the steam. The 4-hr distillation of a 100 g sample of coarsely ground hops in 3 L of water is a method which can be used by all laboratories for accurate, reliable results.

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