8 Wort Boiling

8.1 Why Boil the Wort?

After the wort has been obtained from the spent grains by lautering, sparging, and other processes, the brewer sends the sugar-rich liquid to the boil kettle. The wort contains many of the necessary components needed by the yeast for active fermentation, but potentially lacks the desired flavor profile, and may contain microorganisms and organic and inorganic compounds that are undesirable in the fermentation vessel. Thus, the wort is boiled to adjust the chemistry and biology of the liquid.

While it is often thought that the main reason for boiling the wort is to sterilize it (reduce the number of living microorganisms) or just to allow the hop acids to form the desired bitterness for the product beer, there are a multitude of reasons for heating the wort to these high temperatures. The brewer would not spend the energy, time, and money to perform these tasks if an alternative was available or if a good saleable beer could be made in a different way. As we will see, the number one reason for boiling the wort is the reduction in the number of bacteria, fungi, and mold that may have remained after the mash.

Sterilization of the Wort It is very possible that microorganisms have been introduced into the wort during the mashing process. Often, the mash tun is not completely sealed, the lauter tun may be open to the atmosphere, the mash paddle (if one was used) may not have been perfectly cleaned, and any other number of introductions of airborne microbes may have occurred. While many of these microbes likely do not survive the higher temperatures of the vorlauf, it is quite possible that some have. Heating the wort to boiling for at least 15–20 mins ensures that the number of living organisms in the wort is reduced to almost zero. The high sugar content of the wort also plays against the typical microbe, causing it to be so stressed that application of heat for a short time results in its death.

Increased Maillard Reactions Heating the sugary wort solution increases the rate at which Maillard Reactions occur. We learned about these reactions in Chap. 5

M. Mosher and K. Trantham, *Brewing Science: A Multidisciplinary Approach*,
DOI 10.1007/978-3-319-46394-0_8

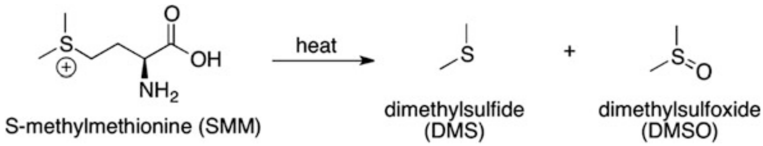
when the malt was kilned; however, the same process can also occur in boiling wort. The wort is packed with sugars, proteins, and amino acids that can undergo the same reactions that happen in malt. In boiling, these reactions produce organic molecules that have flavors resembling caramel, toast, and other rich deep flavors the brewer may want for the particular style of the beer that they wish to make. In addition, the Maillard Reactions also produce molecules that are fairly dark in color. The result is an improvement of the flavor and an overall darkening of the color of the wort. See Chap. 5 for the reactions involved.

Denaturation of the Proteins Any proteins and enzymes that remain after the mash are heated in the presence of relatively acidic (pH 5.0–5.5) water. This results in the reaction of water with the peptide bonds and cleavage of the proteins into smaller pieces. Even those proteins that are only broken a few times are also significantly disrupted such that they cannot form the active sites needed to act as enzymes. The result of this process is the formation of large quantities of amino acids needed for yeast health during fermentation and smaller proteins that can be removed at the end of the boil as trub.

Degassing the Wort While just a side result of the boiling, hot wort can undergo reactions with oxygen in the air quite quickly. Luckily, the brewer knows that oxygen is not very soluble in hot liquids, such that at boiling temperatures, there is almost no oxygen dissolved in the wort to react with any of the sugars or other compounds.

Reduction in Volume After sparging, the wort may not have the correct specific gravity desired by the brewer for the style of beer that they are making. Boiling reduces the volume by evaporating the water in the wort. Typical evaporation rates of 10 % per hour for an open boiling kettle also ensure that the right level of Maillard Reactions is occurring. In some brewing systems, the same effect can be obtained with a greatly reduced boil off of only 2–4 %.

Elimination of DMS Dimethyl sulfide (DMS) results from the decomposition of S-methylmethionine (SMM) under aqueous acid conditions. This small organic molecule has a fairly low flavor threshold and unfortunately, tastes a little like canned corn. While some styles of beer are acceptable with some DMS, it is not a very pleasant flavor in all styles. The precursor molecule to DMS is SMM. SMM is a naturally occurring amino acid found in malt, especially undermodified malt. Boiling the wort causes the SMM to release the DMS, and the evaporation of the wort during the boil also carries much of the DMS away. In a typical boiling process, the maximum amount of DMS possible in a beer is often reduced by 50 %. Fermentation further reduces the amount of this compound. Some of the DMS produced is also oxidized to dimethyl sulfoxide (DMSO), which has a much higher flavor threshold and is difficult to taste at the levels produced. The DMSO can also be reduced in concentration by evaporation of some of the water in the wort.



Formation of Trub Yes, that greenish brown icky stuff at the bottom of the wort after the boil is a necessity. It results from the complexation of proteins and polyphenols (tannins) that can be extracted during the mash. Boiling the wort increases the rate of formation of these complexes. The precipitate begins to form initially as the wort is heated to boiling. The so-called hot break is the formation of large colonies of the trub at the elevated temperatures. The result is an improved clarity with a reduction in the tea-like flavors from the polyphenols.

Reduction of Wort pH As the temperature increases, the reaction rate of the calcium ions (Ca^{2+}) from the water and the diphosphate ions ($H_2PO_4^-$) from the malt increases. The result is the formation of calcium phosphate and hydrogen ions. The calcium phosphate precipitates and is collected with the trub; the hydrogen ions slowly lower the pH of the wort 0.1–0.4 units depending upon the initial pH of the wort. The calcium ions can also form insoluble complexes with larger proteins and help remove them from the wort as well.

$$3Ca^{2+}(aq) + 2H_2PO_4^-(aq) \rightarrow Ca_3(PO_4)_2(s) + 2H^+(aq)$$

The utility of calcium ions in the wort means that some brewers will purposefully add calcium chloride or calcium sulfate to the wort prior to the boil in order to help increase the drop in pH to the desired level. We want to make sure not to reduce the pH too much so that it deviates from the optimal 5.2–5.3 range. Too low and the desired hop reactions (see below) will not take place. Too far away from this range on either side will also affect the yeast's ability to ferment, the flavor of the beer, and the other reactions that are needed to produce a particular style. Coincidentally, the reaction of calcium ions and phosphate ions reduces the pH close to that range as long as our initial pH is close.

Addition of Wort Clarifying Agents Because some of the proteins and protein–polyphenol complexes remain suspended after the boil, addition of a clarifying agent (also known as finings) during the boil is often desired. The higher temperatures of the boil allow the clarifying agent to dissolve completely and help coagulate the proteins, complexes, and other large substances in the wort precipitate. The most common clarifying agent used in this process is carrageenan (when used in raw form it is known as Irish Moss). Carrageenan is a large negatively charged polymer that attracts the positively charged proteins and protein-polyphenol complexes.

Hop Acid Conversion In Chap. 1, we discovered the four main ingredients used in the production of beer. We have explored how water and malt were combined to make the wort and saw the importance of each. During the boil, it is the hops that join the water and malt extract to get us closer to the finished beer. When placed in hot water, the hop oils are extracted from the plant material and interact with the water and other compounds found in the boiling wort. Most importantly, some of the hop oils undergo a dramatic change (as we will see in Sect. 8.5) to become the bittering and preservative agent that we want. If we simply added the hops to the wort when it was cold (known as “dry hopping”), only a very small fraction of the hop oil undergoes the conversion to the important bittering and protective compounds. In fact, even at boiling temperatures only about 35 % of the hop acids undergo conversion after an hour of boiling. This is due to many different factors, including the solubility of the hop acids, the rate of the reaction to form the bittering compounds, and the quantity of dissolved salts in the wort. Interestingly, if the pH is lower than our optimal pH range of 5.2–5.3, the conversion rate is significantly slowed.

Checkpoint 8.1
What are three chemical reactions that take place during the boiling of the wort?

8.2 The Equipment of the Boil

Early beer was likely made by heating wort in whatever vessel was available: ceramic, stone, iron, or even wooden vessels. However, improvements in heating technology have greatly changed since those initial brews. Brewhouses today typically utilize stainless steel kettles with particular characteristics that enhance the transfer of heat into the wort in the most efficient manner possible.

While there is a cost associated with the four ingredients in a typical beer (water, malt, hops, and yeast), the brewer spends most of the operational overhead on heating water. Any efficiencies that can be had in converting the costly energy source (gas, oil, electricity, etc.) into heat and delivering as much of that energy into the water as possible will result in a significant reduction in overhead expenses. Ultimately, this ends up as a greater margin of profit for the company.

In this section, we will explore the characteristics of the boil kettle, their efficiencies, and how it is used in the brewery. Let us start by considering the types of metal that can be employed as heating vessels.

8.2.1 Metals and Heating

When we consider all of the potential options for use as the metal from which to construct our brew kettle, three metals immediately come to mind: aluminum, steel, and copper. Other materials may also be considered based on our experience with cooking in the kitchen, such as ceramic. The characteristics of each of these options for the construction of the brewery must be considered based on the outcome we wish to obtain. In this case, that outcome is to efficiently transfer heat from a source to the wort in the kettle. That heat transfer must be such that our wort can be rapidly warmed to the boiling stage and then maintained there for the duration of the boiling cycle.

Let us examine the characteristics of the four materials we have mentioned and see how they compare. Table 8.1 lists the values for some key parameters that we will need.

The specific heat capacity, defined in Sect. 8.4, is measure of how much heat must be absorbed in order to cause the object to get hotter. Thermal conductivity, on the other hand, is a measure of how that heat is transferred across the metal and into the liquid it touches. Thermal conductivity is measured in watts per meter kelvin. The flow of heat is directly proportional to the thermal conductivity but inversely proportional to thickness of the material. So, as the thermal conductivity gets larger (or the material thickness is reduced) the flow of heat gets greater.

From Table 8.1, we note that ceramics have a fairly large specific heat capacity. In other words, the ceramic must absorb a large amount of heat in order to get hot. They also have a fairly low thermal conductivity, and transfer of heat through a ceramic and into the wort is slow. Overall, ceramics tend to be poor choices for boiling kettles. When heat is applied to them over a long period of time, they do get hot but they stay hot for a long period of time. While this might be good if you are making a casserole, it is difficult to adjust the temperature of the ceramic. Moreover, ceramics cannot be shaped easily by hammering (they are not malleable), and joining two ceramics together is only possible using special glues or mortars. They are corrosion and acid resistant, but the drawbacks concerning their brittleness, difficulty in shaping, and heat transfer characteristics make them not a good choice for a traditional boil kettle.

Table 8.1 Key characteristics of materials for heating

Material	Specific heat capacity (J/kg °C)	Thermal conductivity (W/mK)	Corrosion resistance	Malleability	Weldability	Acid resistance
Pyrex ceramic	~800	30	Excellent	No	Poor	Good
Aluminum	902	205	Excellent	Excellent	Acceptable	Poor
Copper	385	380	Acceptable	Excellent	Good	Acceptable
Steel	450	50	Poor	Good	Good	Poor

Aluminum is a common metal used in inexpensive cookware. While it too has a fairly high heat capacity, the excellent thermal conductivity value and the cost to the consumer is often the reason we see it in the stores. Unlike ceramic, however, aluminum is fairly strong when it is hammered thin, and so a vessel could be made from aluminum. If it is too thin, however, it may bend or stretch unexpectedly during the normal wear and tear of the brewing process. Yet, aluminum's main issue is that it is not very acid resistant and slowly dissolves into the liquid with time. These added metals in the water can impact yeast health later and may have a noticeable flavor profile that is not desired. In short, brewers stay away from aluminum pots.

Copper, on the other hand, has very good heat transfer characteristics. It has a relatively low-specific heat capacity and a fairly high thermal conductivity. So, it does not take much heat to get it hot, and the flow of heat through the metal is very fast. It is malleable and it can be welded together to make a boiling kettle. Copper does have some issues with corrosion (we have all seen the green patina on a copper roof), and it does react with acidic solutions. But, in some cases, the cost of copper and the heat transfer characteristics make this a viable metal to use in the brewhouse.

Steel is not a good option. It does have a low-specific heat capacity, but the flow of heat through the metal is very slow. In fact, it is really not much better than ceramic. The overall heat transfer rate (joules per second) can be made better than ceramic since a steel vessel can be made much thinner. But rusting is a serious issue that is difficult to control, and it is susceptible to the acidic conditions of the wort that would increase the level of iron in the wort to unacceptable levels. So, even though it is fairly inexpensive and can be made into brewhouse vessels, it is not a good choice for a metal.

While some breweries are perfectly happy replacing their copper brewing kettles every so often, most brewers work with a different option that is not in Table 8.1, stainless steel. Stainless steel is an example of an alloy. Let us look more at alloys and see how they stack up to the metals we have just encountered.

Alloys Working with metallurgists, the brewer has found a series of different options based on two of the metals in Table 8.1. The results are mixtures of the metals. These mixtures, called alloys, are simply made by measuring out the correct mix of metals needed, and then melting them in a furnace until they are well mixed together. Alloys have been known for quite some time. In fact, the period from 3300 to 1200 BCE is known as the Bronze Age because of the discovery and use of the very important alloy known as bronze. The good news is that alloys can be formed from an almost infinite set of combinations of metals, and by choosing the metals and their amounts carefully, we can arrive at an alloy that has the properties that we need for our brew kettle.

The metals are mixed together by melting them together in a furnace. The resulting alloy has a much different set of properties than either of the two metals used to make the alloy. For example, when copper is alloyed with tin, we get the alloy known as bronze. Bronze is much harder than copper and as our ancestors found out, it is able to stay sharp when fashioned into a dagger or sword. A copper dagger, on the other hand, would bend too easily and constantly require sharpening. If we mixed zinc with our molten copper, we would end up with the alloy known as brass. Brass is easily molded and can be hammered easily into different shapes. In the right proportions, the brass can even take on the appearance of gold. Both brass and bronze have useful properties; brass is sometimes encountered in fittings used in the brewery. These fitting can be corrosion resistant but sometimes have issues with cracking due to stress.

Steel itself is an alloy of iron and carbon (and other elements in small quantities.) However, if the iron is alloyed with at least 11 % chromium, it forms a special alloy known as stainless steel. There are a multitude of different stainless steel alloys each given a separate designation known as an SAE steel grade (Table 8.2) The SAE grades were developed by the International Society for Automotive Engineers (SAE International) organization. The most commonly used stainless steel is 304 stainless steel that is an alloy of iron containing 18 % chromium and 8 % nickel. It has fairly good corrosion resistance and is somewhat resistant to acids. The second most commonly stainless steel is 316, an iron alloy containing 18 % chromium, 8 % nickel, and 2–3 % molybdenum. The added molybdenum greatly improves the acid resistance of the metal. In fact, where concentrated sulfuric acid would react with 304 stainless at room temperature, 316 stainless is unaffected.

The overall heat capacity and thermal conductivity for stainless steel are not significantly different than plain steel. The relatively low heat capacity means that it will heat up quickly, thus absorbing a relatively small amount of heat energy as it warms. The ability to transfer heat to the liquid it contains is not as good as other metals. However, since stainless steel is relatively strong compared to the other materials mentioned above, the vessel can be made thinner, improving the over energy transfer.

Table 8.2 Selected stainless steel alloys

Group name	Common SAE steel grades	Composition	Pros	Cons
Martensitic	410, 420	12–18 % chromium 0.2–1.2 % carbon	Hard corrosion resistant	Poor welding properties
Ferritic	409, 430	12–18 % chromium <1 % carbon	Corrosion resistant	Thin sheets can be welded
Austenitic	304, 316	18 % chromium 8 % nickel 2–3 % molybdenum <0.08 % carbon	Corrosion resistant Excellent weldability useful temperature range	Oxidizes above 925 °C Chloride ions can etch

For those particularly corrosive environments, it is possible to also get a stainless steel that has a very low carbon content (<0.03 %). Those stainless steels are denoted with an "L" following the code name: e.g., 304 L. These products are very resistant to corrosion compared to the higher carbon content steels, but, for most, if not all, brewery applications, the added expense of this type of stainless steel is not worth the return on the investment.

The stainless steel alloys, in general, are corrosion resistant because the chromium in the metal reacts with oxygen in the air to form an impervious layer of chromium oxide on the surface of the metal that is firmly adhered to the surface of the metal. If the stainless steel is scratched, the layer reforms and the metal is protected again. This is unlike "normal" steel, where the surface of the iron reacts with oxygen to form iron oxides (rust) that flakes off of the metal allowing more of the steel to reaction with the oxygen again.

Checkpoint 8.2
Which of the metals would you use in a pot for making soup? Which metal would not be suitable for extended and repeated use, if the food you were making was fairly acidic (such as tomato soup)? Why are aluminum cooking pots so prevalent on the market?

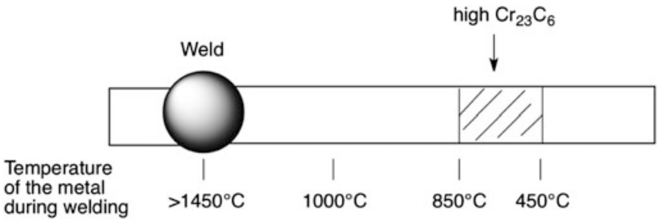
8.2.2 Corrosion

Corrosion is the reaction of a metal surface with oxygen from the air to form a metal oxide. If that metal oxide is not firmly attached to the surface of the metal or flakes off of the metal by mechanical or other means, a pit is formed on the metal. Repeated oxide formation in the same location can result in a hole, crack, or general damage to the structural integrity of the metal vessel.

The brewhouse is a wet corrosive environment for metals. And many different types of corrosion can attack those metals. Those types of corrosion include the following:

- **General corrosion** In this process, the entire surface of the metal reacts with oxygen and slowly corrodes away. The result is a thinning of the metal across the entire surface of the metal.
- **Galvanic corrosion** When two different metals are touching because of a weld, close contact, or otherwise fixed to each other, they can transfer electrons from one of the metals to the other. This enhances the corrosion of the metal that gives up the electrons to the other metal. For example, physical and prolonged contact of zinc metal and steel results in corrosion of the zinc.

- **Erosion** If a liquid is physically pushed against the wall of a vessel or pipe, the constant action of the liquid can erode the interior wall.
- **Cavitation** The collapse of bubbles against the wall of a vessel or pipe can act similarly to the physical erosion of the metal. The force of the bubble collapse can be significant enough to rapidly cause a weakening of the wall of the vessel or pipe.
- **Weld corrosion** When stainless steel is welded, the metal at the point of the weld is heated to approximately 1450 °C. The temperature of the metal depends upon how close the region is to the weld. And where the metal is about 850–450 °C, a chemical reaction takes place. At this temperature range, the carbon in the steel reacts quickly with the chromium to form $Cr_{23}C_6$. Above 850 °C, the $Cr_{23}C_6$ breaks down. Because the chromium is tied up with carbon at this distance from the weld, it cannot react with oxygen to form the protective layer of chromium oxide. Therefore, at this distance from the weld, there is an increased risk of corrosion of the stainless steel.



- **Microbe corrosion** Microbes can form colonies that stick to the surface of the vessels in the brewery. If that colony is not destroyed, it can form a hard plaque that adheres tightly to the surface of the vessel. The microbes can produce corrosive chemicals and slowly corrode the stainless steel in those locations.

The presence of corrosion on a stainless vessel can be very damaging to the vessel. It can form pits on the surface of the vessel that is unsightly, or it can continue hidden in cracks and crevices on the vessel until a fracture occurs. That fracture could result in catastrophic failure of the vessel. Imagine standing next to a 300-barrel fermenter when corrosion causes failure of the vessel! Therefore, it is very important that every brewery has protocols in place to inspect and address corrosion as early as possible.

8.2.3 Methods for Heating

Once the wort is in the boil kettle, it is heated until it reaches its boiling point. How the heat is delivered to the vessel is very important to the brewer. In addition to the cost to produce the heat, the protocols, safety, and design of the vessel are considered. In the typical brewery, two main methods are used to generate the heat: steam and direct-fire.

Steam is produced using a boiler either by heating a container of liquid using gas burners or using electrical heating elements (much like an electric hot water heater.) The water boils and is converted to steam under a slight pressure. The steam is then carried through insulated pipes to the boil kettle. This is a more expensive initial investment and requires additional safety protocols and training for employees on the handling of steam; the overall process has some very useful benefits. First, it is less expensive to operate in the long term. Second, and likely the most useful to the growing brewery, additional boiling kettles need only have a piped connection to the steam source to begin heating.

The design of some boil kettles allows them to be heated directly. In these systems, the gas burners are located underneath the boil kettle and the flames of the burners directly contact the bottom of the boil kettle. This direct-fire method for heating costs less to install, but over time can be more expensive to operate than steam. Moreover, if additional vessels are used in the brewhouse, each must have its own burners and its own supply of fuel to burn.

The disadvantages of both steam and direct-fire kettles reside in the fact that they do generate flue gases from the combustion of fuels. The steam boiler is often more efficient and produces less emissions, but both must be properly ventilated.

Two additional methods for the production of heat must also be considered. As mentioned above, it is possible to either generate steam using an electric heater and a direct-fire kettle can be heated directly using an electric heater. The operation of these heaters can be about as expensive as the use of steam or direct-fire, but the safety protocols for the use of electricity in close proximity to water must be followed. Moreover, electricity is not always produced free of flue gases—electrical power plants might use coal, diesel, or other fuels to generate the electrical energy.

The other method for producing heat is currently being explored: microwave heating. While this method does appear to show promise, it is still in its infancy in the brewing world.

Heat Transfer Characteristics It is important that any heat applied to the boil kettle is transferred efficiently into the wort inside. Heating too slowly and the boiling process can take a very long time to achieve. Heating too quickly and the wort may scorch providing off-flavors and increased color to the finished beer.

When the brewer applies heat to the vessel and it is transferred into the wort, the characteristics of the vessel's construction and the rate of heat transfer can result in one of the two main types of boiling processes. In the extreme, the surface of the vessel is considerably hotter than the wort. If the metal is not very "wettable"—the liquid is not attracted to the surface of the metal—this extreme heating tends to be favored (see Fig. 8.1). Known as film boiling, the surface of the vessel next to the wort becomes superheated and a layer of steam from the wort forms along the vessel but does not form into bubbles easily. This steam can be superheated well beyond the boiling point of the wort. In film boiling, the risk of scorching is significant (see Fig. 8.2).

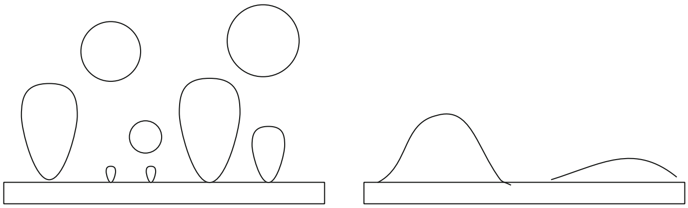


Fig. 8.1 The extremes of heating liquids in metals. The wettable surface allows the bubbles of wort steam to release from the metal. The non-wettable surface holds the wort vapor against the metal causing the vapor to increase in temperature well above the boiling point

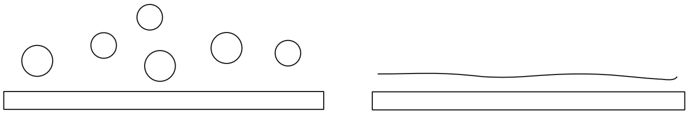


Fig. 8.2 Nucleate versus film boiling. The action of the bubbles in nucleate heating helps cause the liquid to rise in the vessel and evenly distributes the heat throughout the wort. Film boiling does not do this—instead the steam near the surface becomes superheated causing the liquid to scorch

At the other end of the spectrum, the surface of the vessel is barely hotter than the wort and heat is slowly applied. If the metal is wettable—the liquid is attracted to the surface of the metal vessel—bubbles of wort steam easily form. In this case, the bubbles tend to be fairly small and release quickly from the vessel surface. Known as nucleate boiling, this provides the most efficient transfer of heat into the wort.

Stainless steel, despite all of its advantages, is not wettable. Use of this metal as the location to provide heat transfer to wort requires that the heating source is not much hotter than the wort so that scorching is reduced. In addition, adequate mixing of the wort must occur to further avoid the Maillard Reactions from overtaking the wort and that the area of the vessel being heated is not too great. Copper metal, on the other hand, is very wettable. Heat transfer across a copper vessel generates excellent nucleate boiling. While copper's stability toward corrosion and acid is not ideal, the use of copper in a vessel as the area for heat transfer clearly provides a benefit for its use.

8.2.4 Direct-Fire Vessels

A direct-fire vessel is heated by the energy released from combustion of a fuel. Historically, these vessels were made of copper and a fire was built underneath

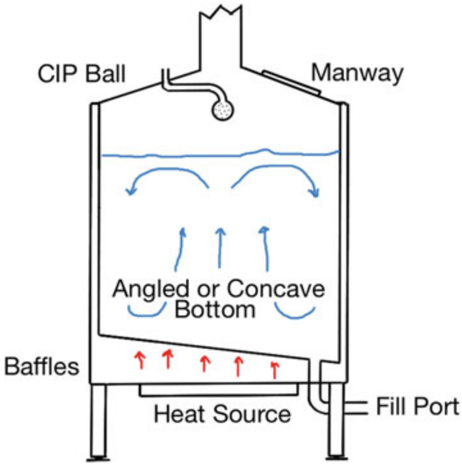


Fig. 8.3 Direct-fired Boil Kettle. The kettle may or may not be open at the *top*. The enclosed kettles often have a hatch near the top for servicing the interior of the vessel. Heat is applied by combustion of a fossil fuel or organic material (*red arrows*), where the baffles help hold the heat close to the vessel. Note the convection that occurs inside the vessel (*blue arrows*)

them using wood, peat, coal, and other combustible materials. In today's world, the heat is applied by combustion of methane (natural gas), propane, butane, diesel, or heating oils. These copper kettles tend to have a concave bottom or shielding that can trap the heat and keep it in contact with the bottom of the vessel to improve heat absorption by the kettle. Control of the heat is accomplished by regulating the temperature of the firebox underneath the vessel (Fig. 8.3).

While copper boiling kettles still exist, many of the newer direct-fired vessels are stainless steel (typically 304). Heat transfer is not as efficient and the risk of film boiling is very significant in these cases. Ensuring that the temperature of the steam is not too much hotter than the boiling wort is needed to avoid scorching.

The heat transfer into the wort causes the warmed liquid to become less dense and rise to the surface of the vessel. This causes colder wort to move into the space vacated by the warmed liquid. Thus, mixing of the wort occurs as it moves from the exterior walls of the vessel and rises to the middle of the vessel. The area of contact of the wort with the bottom of the vessel can be an issue. In these vessels, there is almost always some form of scorching, caramelization of the sugars, or unwanted Maillard Reactions that make their way into the finished product. Boiling of the wort in these vessels also results in evaporation of up to 10 % of the water in the wort per hour. This is necessary to encourage the loss of DMS and other volatile organic compounds, and also concentrates the sugars.

While technically not a direct-fired kettle, it is possible to heat the wort in a kettle of similar design using steam (Fig. 8.4). These steam-fired kettles are surrounded by jackets that circulate steam around the bottom of the vessel and transfer the heat into the wort directly through the sides and bottom of the vessel. Typically, these vessels are constructed of stainless steel and necessitate careful control of the

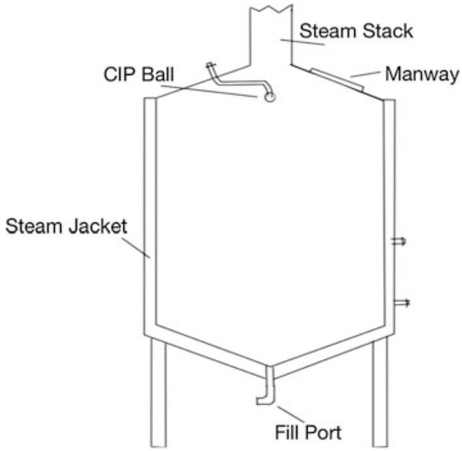


Fig. 8.4 The steam-fired boil kettle. Steam is circulated in jackets around the exterior of the stainless steel vessel. The slightly angled *bottom* helps to cause the liquid inside to rise—mimicking the currents found in the direct-fired boil kettle in Fig. 8.3

heating process to reduce the degree of film boiling that is likely to occur. This type of vessel is very commonplace in the US steam-fired microbrewery.

Checkpoint 8.3
Provide a list of pros and cons for the use of a natural gas direct-fired kettle and for a steam-heated direct-fired kettle.

8.2.5 Calandria

A technological design incorporated the advantages of steam heat and the use of copper materials was used extensively until the mid-1900s. Still used in the USA today, the internal calandria (Fig. 8.5) allows efficient nucleate boiling of the wort. In this system, the wort fills a stack of copper pipes that are surrounded by a stainless steel steam jacket. Steam heat then enters the wort through the copper pipes, causing the warmed liquid to rise in the pipes. Colder wort enters the pipes at the bottom of the stack and rises as it is heated. This pulls more wort into the bottom of the calandria. The movement of the rising wort as it reaches the boiling point eventually becomes significant, such that a deflector plate is required to spread the wort out and direct it back into the bulk of the vessel. In this way, wort circulates up into the calandria, reaches its boiling point, and shoots upwards to the deflector plates. The wort then splashes back to the edges of the vessel and travels downwards toward the bottom of the copper pipes. The wort in a boiling kettle follows this flow pattern on its own. This process, where the wort circulates through the calandria on its own, is known as thermosiphoning.

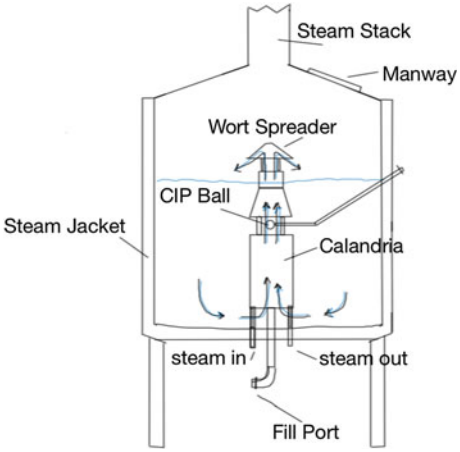
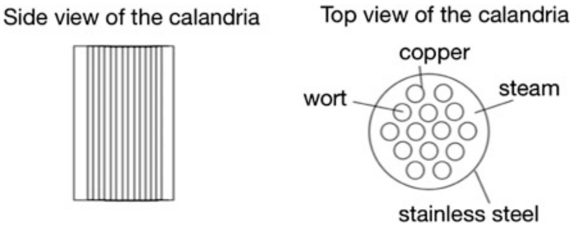


Fig. 8.5 The internal calandria. The copper pipes in the internal calandria must be covered prior to heating the wort. The gap between the calandria and the wort spreader allows efficient distribution of the heat by admitting additional wort into the spreader. Note the currents of the wort in the vessel



Some disadvantages exist with the use of the internal calandria. First, the calandria should be covered with wort. If the steam is applied too early, the wort will boil and not have enough force to eject itself from the copper pipes. Thus, it will overheat and scorch. The time required to fill the vessel with wort can result in a delay in production. Second, the efficiency of heat transfer across copper means that it is very possible that there is some scorching of the wort inside the copper tubes. The resulting layer of caramelized sugars on the copper surface, known as fouling, reduces the efficiency of heat transfer. And third, cleaning of the internal surfaces of the copper pipes inside of the boil kettle is difficult, even when using clean-in-place (CIP) technology.

Workarounds for the disadvantages of the internal calandria have been explored. For example, the wort can be pumped into the base of the copper pipes. In this way, the entire boil kettle does not need to be filled in order to begin the heating process. This system, known as the Stromboli system, works well to decrease the overall processing time and reduces fouling of the copper pipes because of the constant action and flow rate of the wort caused by the action of the pump. Two disadvantages still exist; cleaning the system inside of the boiling kettle is not addressed

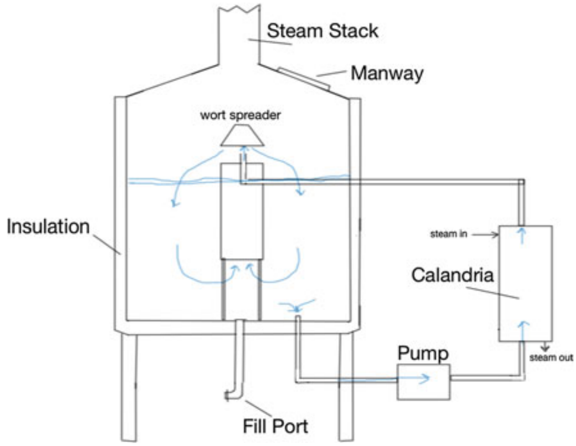


Fig. 8.6 The external calandria. The advantages of the external calandria are the main reason that this heating system is very widely used in brewhouses

with the use of the pump, and the action of the pump on the hot wort can cause problems with adequate trub formation (the force of the pump can disrupt the formation of the complexes of proteins and polyphenols.)

In the mid-1900s, the calandria system moved outside of the boil kettle (Fig. 8.6) to become known as an external calandria. In this system, the wort is pumped into the base of the calandria where it rises into the copper tubes. It is heated and then rushes out of the top of the calandria. It is then piped back into the boil kettle and up into the deflector plate where it splashes into the boil kettle. Actual boiling takes place inside the kettle, but heating occurs exterior to the kettle. In this way, cleaning of the boil kettle is greatly simplified, and because the calandria itself is easily accessed outside of the vessel, it is also much easier to clean.

The use of a pump in the system and other modifications to the copper piping inside the calandria also provide useful advantages. For example, the pumping action helps to keep any fouling of the copper tubes to a minimum. This advantage is clear when one considers that about 10 heating cycles (10 batches of beer) can be performed before the calandria must be cleaned. Also, because the wort is pumped into the calandria, the boil kettle need not be full in order to begin the heating process. To aid in appropriate trub formation, the pumping action can be stopped once the wort is at boiling temperature. The wort at this temperature will thermosiphon through the external calandria.

By far, the biggest advantage to the use of the external calandria is that the evaporation of water from the wort can be reduced to about 5 % per hour while still preserving the necessary reductions in volatile organic compounds such as DMS.

8.2.6 Other Heating Systems

New Belgium Brewing Company, in Fort Collins, Colorado, for example, utilizes a different heating systems for their boil kettle. The system, known as a Merlin®, efficiently boils wort by pumping it from a whirlpool vessel and up through the

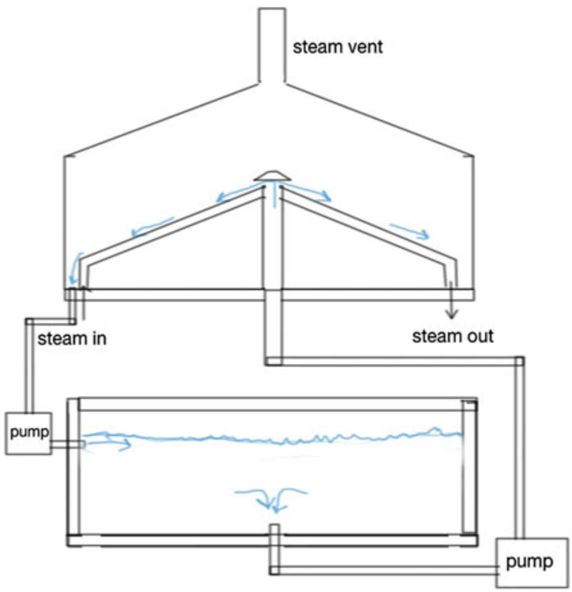


Fig. 8.7 The Merlin® heating system. Wort is heated as a thin film as it passes down the cone in the heating vessel. The hot wort is stored in the whirlpool vessel where trub can be separated as it forms

center of the heating vessel (Fig. 8.7). The wort is then deflected and runs down a steam-heated cone on the inside of the heating vessel. The greatly increased surface area of the wort in contact with the hot cone allows for very efficient evaporation of the wort. Then, after dripping off of the cone, the heated wort is pumped back into the whirlpool vessel to settle.

The wort is injected at an angle on the whirlpool vessel such that the entire contents of the vessel are mixed. The swirling action of the wort causes the trub to move to the middle of the vessel and precipitate. Thus, the trub is removed from the wort while it is being heated.

Evaporation rates in the Merlin® system are very low (~4 %) but contain the same or better reduction in volatile organic compounds. And thorough heating and mixing of the wort occurs with each portion of the wort passing over the heating cone 5–6 times. Because the system is coupled with the whirlpool, minimal time is needed to remove the trub from the wort at the end of the boil.

Checkpoint 8.4
Compare and contrast the use of an external calandria with an internal calandria. What major advantage does the calandria provide over the direct-fired boil kettle?

8.3 Heat and Temperature

So far we have discovered that heat and temperature are important concepts in the design of a boil kettle. This begs some important questions, what is heat? and what is temperature?

Heat is the transfer of energy from one object to another. Temperature, on the other hand, is a measure of the amount of thermal energy stored in an object. In other words, an object with a greater temperature has more energy in it than one that does not. And when an object with a higher temperature is in contact with one that has a lower temperature, some of that thermal energy can be transferred as heat.

Let us consider an example to illustrate the difference between heat and temperature. Assume we are planning making some noodles for dinner. We start by adding the dried noodles to a pot of boiling water, and then, after they have cooked to our liking, we pour them into a strainer to separate the noodles from the water. During this process, it is likely that a mishap could take place. We could spill a drop of the boiling water on our hand, or a slip could cause the entire pot of boiling water to pour on our hand. Which would hurt more? We know that the water in both cases has the same temperature (its nearly boiling when we strain the noodles). But the larger quantity of water would cause a greater burn to our hand because it has more thermal energy based on the quantity of the water. In other words, it can transfer more energy to our hand than can a drop of the water. If we compare the energy transferred in a pot of warm water to the energy transferred in a drop of boiling water, the quantity of the water plays a very large role in how much thermal energy can be transferred.

8.3.1 Types of Energy

There are a variety of forms of energy found in nature. The most fundamental form is energy associated with motion, known as kinetic energy. Anything that is in motion will have associated energy and the amount of energy can be calculated using the equation:

$$KE = \frac{1}{2}mv^2$$

where
m = the mass of the object in kilograms
v = the velocity of that object in meters/second.

The result is a value for the kinetic energy in units of $\frac{kg\,m^2}{s^2}$. This collection of units is known as the unit for energy, the joule. In other words, $1\ J = 1\frac{kg\,m^2}{s^2}$. As an example of the use of the equation, let us consider a 1200 kg (2646 lb) car traveling at 20 m/s (45 mph). The kinetic energy of the car is then:

$$KE = \frac{1}{2}(1200\ \text{kg})\left(20\frac{\text{m}}{\text{s}}\right)^2$$

$$KE = 240,000\frac{\text{kg m}^2}{\text{s}^2} = 240,000\ \text{J}$$

Checkpoint 8.5
Which has more kinetic energy, a compact car (1045 kg) traveling at 10 m/s or a speeding bullet (0.1 kg) traveling at 620 m/s?

Other forms of energy are categorized as potential energy, which we can think of as stored energy. There are several mechanical examples, such as a compressed spring, or a weight suspended very high. All have the potential to “do” something or cause another object to move. Electrical energy, for example, can be viewed as charges in motion (kinetic energy), and chemical energy can be viewed as separated charges: e.g., a battery. There is energy associated with sound waves and, most important to our discussion, there is thermal energy.

The concept of thermal energy can be viewed as the kinetic energy of individual molecules and atoms. When we think of a container of gas, we envision the individual molecules moving around, bouncing off each other and the walls of the container. Each molecule will have an individual speed, and therefore a kinetic energy. A similar concept is held for solids if we view the atoms or molecules connected with each other by small springs. Each atom vibrates, and due to this motion, they will have an associated kinetic energy. Of course, the atoms in a solid are not connected by springs; however, the forces involved between neighboring atoms that hold them together into a solid are similar in concept.

It would be very difficult to describe an object’s thermal energy by measuring or reporting the individual kinetic energy of every atom in the sample. It is more convenient to measure the “average” energy if we want to know the thermal energy of that object (Fig. 8.8). The temperature, then, conveys information about the average energy of the object. Temperature is easy to measure macroscopically with a thermometer.

There are three main temperature scales in use across the world. In the USA, it is very common to find the Fahrenheit scale where the values are represented in °F. This scale is set such that the melting point of ice is 32 °F and the boiling point of water is 212 °C. The number of divisions between these two values makes it easy to report the temperature; hence, the likely reason is that this scale remains in effect in many countries.

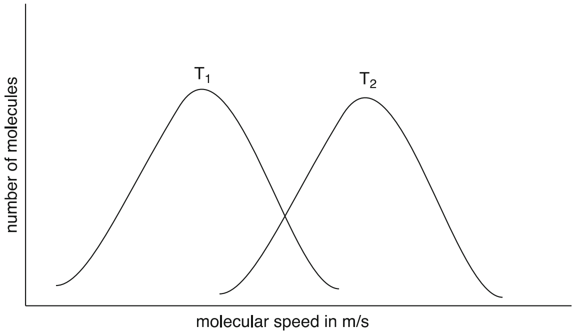


Fig. 8.8 The average molecular speed of the molecules in a hot sample (T_2) is faster than the average molecular speed of the molecules in a cool sample (T_1)

The scientific community prefers the use of the Celsius scale where the values for the melting point of ice is 0 °C and the boiling point of water is 100 °C. The majority of the world, in fact, uses this scale. And, as we will see during our calculations, this is the value that is preferred. As we predict, then, since the mathematical equations use Celsius, and most of the world uses Celsius, this is the scale of temperatures that we will use in this text. We saw this temperature used in the specific heat capacities to describe metals.

Another scale is also used. The temperature could be reported in kelvin. This temperature scale has the same divisions as the Celsius scale, but it is offset by 273.15. So, the melting point of ice is 273.15 K and the boiling point of water is 373.15 K. Note that there is no "°" symbol and the numbers are said out loud as "373.15 K." This scale was created to allow scientists to use positive values for the temperature. It is interesting that the coldest a temperature can be (where the object has zero thermal energy) is 0 K. This temperature was used in the thermal conductivity to describe heat transfer in metals.

It is interesting as well to note that when the thermometer was invented in the early 1700s, many brewers were hesitant to use the new technology. They had been brewing beer quite well by boiling water and waiting a certain amount of time for it to cool to a given temperature for mashing. It was not until Michael Combrune's manual entitled *Treatise on Brewing* in 1758 recommended its use that many brewers started to use the thermometer. It took many years for all of the breweries to recognize the utility of the instrument.

To take us back to our discussion at the start of this section, when we use the words "hot" or "cold" we are generally referring to an object's temperature. And these words are only relative to some other temperatures. But if we consider the atomic model of solids, liquids, or gases, these words would then refer to the average kinetic energy or motion of the atoms.

So what would happen if we place a hot object next to a cold object? The thermal motion of the neighboring atoms will start to cause the "cold" atoms to vibrate, transferring energy to the cold object. The word heat describes this process.

Note that our definition means that objects do not contain "heat." Rather, an object contains thermal energy.

Note as well that the transport of thermal energy does not depend on the total thermal energy of the two objects. Rather, it depends on the average kinetic energy per molecule (temperature!) of the materials.

8.4 Heat Capacity and Heat Transfer

When thermal energy is transferred to an object, the observed temperature change will depend on how much of the material is present. It will also depend on the type of material. The term specific heat capacity addresses how different materials might have different capabilities to store or give up thermal energy.

As an analogy, let us consider two towels used to absorb a spill. A chamois towel can hold considerably more water than a similarly sized kitchen towel. We might say that the kitchen towel has a smaller "water capacity" than the chamois towel. Its also reasonable to say that as the size of the towel increases the more water it can absorb. For towels, the ability to absorb and store water depends on both the type of material and the size of the towel.

Likewise, when thermal energy is transferred to or from an object, factors that determine the total amount of energy transferred are the mass of the object, the temperature change, and a constant that depends on the type of material that makes up the object. This constant is called the specific heat capacity (c).

The definition of specific heat capacity (or just specific heat) is the amount of thermal energy required to raise the temperature of 1 kg of the object by one degree Celsius. For water, that value is 4.184 J/g °C. Table 8.3 lists some selected specific heats for some common materials. The definition means that we can determine the amount of heat change if we know the mass and the change in the temperature of an object:

$$q = m\, c\, \Delta T$$

Table 8.3 Specific heat capacities for selected materials

Substance c (J/kg °C)	*c* (J/kg °C)
Styrofoam™	1300
Aluminum	902
Copper	385
Gold	129
Iron	450
Water	4184
Ice	2030
Malt barley	1674

where

q	heat in joules
m	mass of the object in kilograms
c	specific heat capacity in J/kg °C
ΔT	$T_{\text{final}} - T_{\text{initial}}$, where the temperature is recorded in °C.

From Table 8.3, we note that water has a very large value for specific heat. What does this mean? The definition says that it would take the addition of 4184 J of heat to raise the temperature of 1 kg of water by 1 °C. The addition of the same amount of heat to iron would result in a much greater temperature change for the iron. And as we discovered earlier, a larger change in the temperature of the metal can mean that it is able to transfer some thermal energy to the liquid that touches it.

Another important unit a brewer often encounters is the BTU (British Thermal Unit). This, just like the joule, is a unit used to measure heat. One BTU is equivalent to 1055 J. Burners are often characterized by the *rate* at which they transfer energy. In other words, they are rated by the ability to produce a certain number of BTU per hour. Although it is common to see an advertisement rating a burner at 9000 BTU, this unit is incorrect. The advertiser actually intends to represent the units as 9000 BTU/h, a unit that relates the power of the burner.

8.4.1 Phase Transition: Boiling

We have just discovered the thermal energy changes that are required to increase the temperature of a substance from one temperature to another. However, this only covers the addition (or removal) of that energy while the object stays in its present form. In other words, warming or cooling water is governed by the $q = mc\Delta T$ equation. What happens if the water is converted into steam?

At the boiling point of a liquid, energy that is added into the system is used to convert the liquid into a gaseous vapor. The temperature of the liquid does not change during that process, but it still requires energy to continue boiling the liquid. For example, if we heat a pot of water on the stove until it boils, we have added thermal energy into the water to change its temperature to the boiling point of water. We must continue to add thermal energy to the water to keep it at the boiling point; additional energy is used to convert some of the water into steam. A thermometer in the water would continue to read 100 °C (the boiling point of water) until the pot boiled dry (all of the water was converted into steam). If we remove the pot of water from the stove, it immediately stops boiling.

The amount of thermal energy required to change the phase of a substance can be determined using the equation:

$$q = mC$$

Table 8.4 Latent heat and phase transition temperatures

Substance	Latent heat (kJ/kg)	Temperature of transition (°C)
Water to steam	2260	100
Ice to water	334	0
R134a (refrigerant)	216	−27
Ammonia (refrigerant)	1369	−33

where

q the heat required to change the phase of the entire substance
m the mass of the substance
C the latent heat capacity of the substance per kg in kJ/kg.

Note that the latent heat capacity (C) is *not* the same as the specific heat (c). The latent heat capacity is not related to a specific change in temperature because the temperature of the object does not change as it is converted from one phase or state to another. As we melt ice into water, the temperature remains at 0 °C. As water boils, the temperature of both the water and the steam remains at 100 °C. Table 8.4 lists some useful latent heat capacities and the temperature associated with their phase transition.

For example, let us assume we have 100 kg of water at 100 °C and convert the entire sample to steam. Using the value of the heat capacity for water, we would note that:

$$q = (100\ \text{kg}) \times (2260\ \text{kJ/kg}) = 226{,}000\ \text{kJ}$$

In other words, 226,000 kJ of thermal energy would be required to convert all of the water at 100 °C into steam at 100 °C. While a brewer is definitely not interested in changing all of the liquid wort into steam, the concepts are very useful when we consider the operation of a refrigeration system, which we will cover in Chap. 9.

8.4.2 Power

What is power? Power is defined as the amount of energy that can be transferred in a given amount of time. In our example of a 9000 BTU/h burner, the burner is capable of delivering 9000 BTU per hour or 9,495,000 J/h. These units, however, are not the ones typically encountered when measuring or reporting the power of an object. Instead, the SI unit is the watt (W). A watt is equal to 1 J/s. So, a 9000

BTU/h burner can also be referred to as a 2638 J/s or 2638 W burner. Mathematically we can represent this as:

$$P = \frac{E}{t}$$

where

P power in watts (W)
E energy produced or transferred in joules (J)
t time in seconds (s).

For example, a 1200 W heater could be used to transfer energy into a bucket of water. If the heater was operated for one hour, the amount of energy transferred would be:

$$1200\ \mathrm{W} = \frac{E}{1\ \mathrm{h}}$$

$$1200\frac{\mathrm{J}}{\mathrm{s}} = \frac{E}{1\ \mathrm{h} \times \frac{3600\ \mathrm{s}}{1\ \mathrm{h}}}$$

$$E = 4,320,000\ \mathrm{J}$$

Note in the above example that 1200 W is 1.2 kW and that over an hour this is equivalent to 1.2 kW h. The kW h is just a unit that relates the energy (in kJ). Electrical companies charge for the use of energy based on how many kW h is delivered to your home. For our example, at \$0.12/kW h, we would spend:

$$\mathrm{Cost} = \frac{\$0.12}{\mathrm{kW\ h}} \times 1.2\ \mathrm{kW}$$

$$\mathrm{Cost} = \$0.14$$

or 14 cents to deliver 4,320,000 J to our water. This, of course, assumes that no heat was lost to other objects in the transfer, which is highly unlikely. The container, for one, will absorb some of the heat, as will the air around the container.

Checkpoint 8.6
If 125 kg of water was heated in a boil kettle and the temperature increased from 60 to 95 °C in 1 h, what is the power of the boil kettle in kW?

8.5 Hops in the Boil

As we discovered in Chap. 4, the hop plant is an integral part to our modern interpretation of beer. In fact, almost every batch of beer produced in the USA in today's market contains the compounds found in hops. Knowing about this vital ingredient, the biology of the plant itself and its structure, and how it contributes to the flavor of a beer is very important to understanding the science of brewing.

8.5.1 The Hop Flower Revisited

The female hop plant is the source of the pinecone-shaped flower that a brewer knows as a hop cone. The male plant is responsible for pollination of these cones, but once it has done so, greatly reduces the quantity and quality of the oils found inside the flower. For that reason, the hop farmer abhors the male plants and does everything possible to eliminate them from the field.

Hops, *humulus lupulus*, are an example of a bine. They grow on the farm by extending an annual shoot into the air. That shoot has gripping structures that help it climb by wrapping around twine that has been staked from the base of the underground rhizome to a wire about 20–30 ft in the air. The bine quickly grows up the twine until the plant reaches its maturity and begins producing flowers that look line pine cones.

The structure of the hop flower is interesting. Along the center of the flower is a stick-like structure known as a strig. Extending from the strig are the leaves that encompass the flower and overlap tightly. These leaves, known as bracts and bracteole, protect the oil-bearing portions of the flower. If we peel back the bracts and bracteole, we see these lupulin glands as little yellow dots that are at maturity glisten with the oils highly prized by the brewer (see Fig. 8.9).

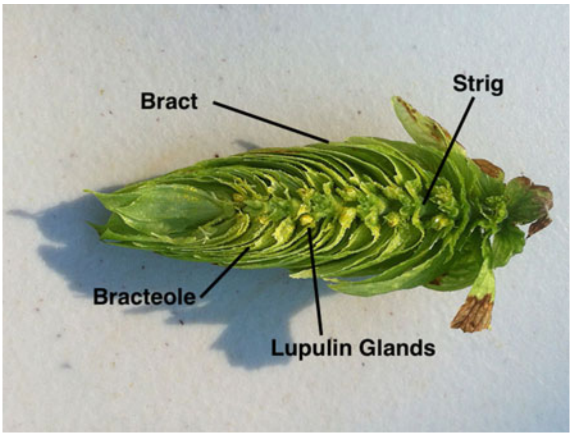


Fig. 8.9 Hop cone structure. The hop cone has been cut away to reveal the structure of the flower. Note the *yellow* lupulin glands near the center of the cone

8.5.2 Hop Oil Constituents

The hop oils contain a very diverse array of compounds. The exact composition of the oils depends not only on the cultivar of hop, but also on the growing conditions for that particular season. The list of compounds contains proteins, water, minerals (such as nickel, zinc, and magnesium), tannins, lipids, sugars, volatile oils, and alpha acids and beta acids.

Volatile Oils The volatile oils include chemical compounds known as terpenes and sesquiterpenes in addition to hundreds of other constituents. These compounds impart odors and flavors associated with the hop flower itself. A key terpene found in hops is myrcene (see Fig. 8.10) responsible for a piney aroma. Important sequiterpenes include farnesene and caryophylene, also responsible for a woody, earthy, or piney aroma.

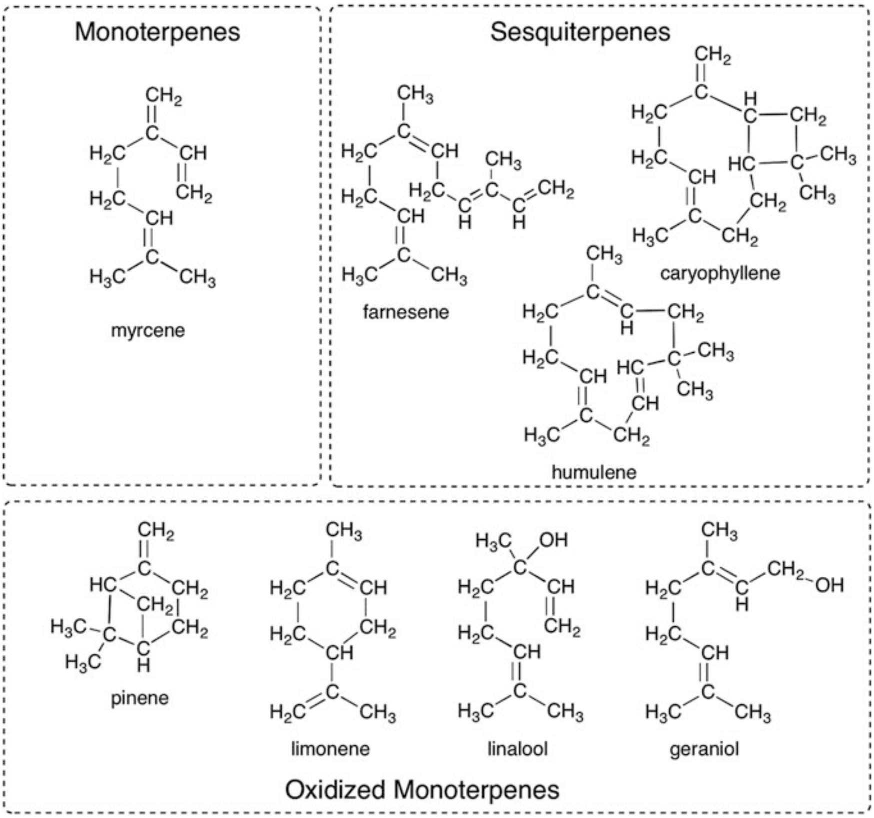


Fig. 8.10 Some of the compounds in the hop oils. These compounds can be broken into two main categories (monoterpenes and sesquiterpenes.) Oxidation and maturing of the hop oil often result in a wide variety of partially oxidized comounds. Some common oxidized monoterpenes are shown here. Note the similarities between each structure

Many of the volatile oils have undergone oxidation in the air to form other compounds, such as geraniol (rose-like or flowery aroma), limonene (lemony aroma), and linalool (flowery aroma). In some hop varieties, the oxidation of the volatile oils has resulted in compounds with cucumber, balsamic, or mushroom-like aromas. In over oxidized, or old hops, these compounds continue to change their structures into compounds that have an “old cheese” or “paper” aroma.

Since the volatile oils are volatile, if the brewer adds them to the boiling wort at the start of the boil, most of the oils will be removed with the steam. Thus, the aroma and most of the flavor that the volatile oils contribute will be removed. In other words, if a brewer wants to capture those aromas and flavors as part of the finished beer, they would wait until the last minute to add the hops to the hot wort (or add them after the wort has been cooled back to room temperature.)

Humulones Another class of compounds found in the oils from the hop cone are the humulones, also known as the **α**-acids (Fig. 8.11). These compounds are prized by the brewer and the hop farmer. In fact, specific cultivars of hops are grown and nurtured to produce extremely high contents of these compounds. They are the compounds that undergo conversion to the bitterness and protective compounds desired in the finished beer.

The general structure of the humulones is illustrated in Fig. 8.10. Three main humulones have been identified that differ in the chain of carbon atoms extending from the central six-membered ring. These compounds are known as humulone, cohumulone, and adhumulone, although the major component of the α-acids is the structure of humulone itself. As the name implies, these compounds are somewhat

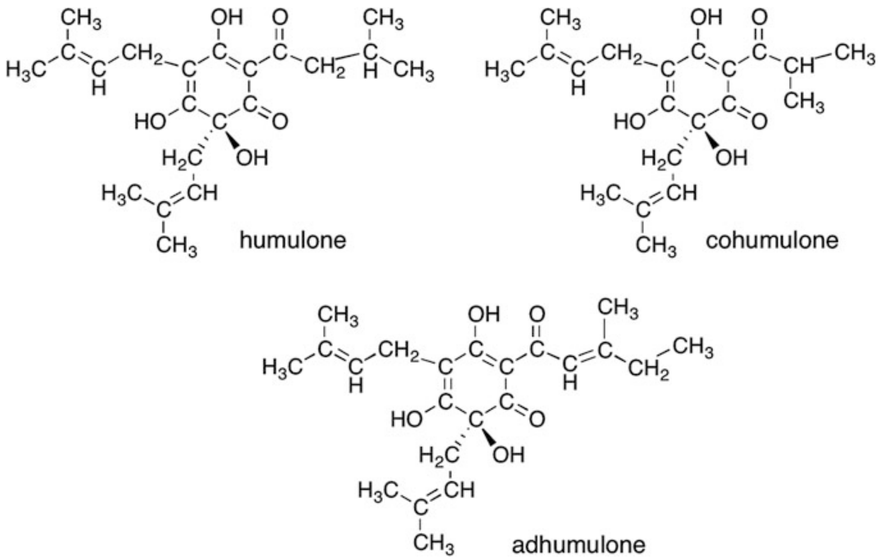


Fig. 8.11 The humulones: humulone, cohumulone, and adhumulone. Can you tell the difference in their structures?

acidic. And because of their structure, they are not very soluble in the acidic conditions of the wort.

Once added to the hot wort, a small amount of the α-acids dissolves and undergoes a reaction. Recent evidence suggests that the reaction requires the presence of the minerals found in the hop cones and in the malt, as the reaction does not proceed if humulone is heated by itself. In any case, the six-membered ring opens during the reaction and the molecule rearranges to a more stable conformation. The ring then closes, but as a five-membered ring system. The result is the formation of cis-isohumulone and trans-isohumulone roughly in a 2:1 ratio depending upon the conditions of the boiling wort (see Fig. 8.12).

The resulting compounds are also known as cis- and trans-iso-α-acids. The iso-alpha acids are intensely bitter and much more soluble in wort than the alpha acids. Unfortunately, though, there is a limit to their solubility that depends upon the amount of maltose, sucrose, and other sugars in the wort. About 100–120 ppm iso-alpha acids appears to be the maximum that can be dissolved. This is not an issue, because the human taste threshold has a hard time telling the difference between bitterness at this level.

In order for the reaction to take place, heat and time are needed. Therefore, the brewer must add the hops at the start of the boil. The longer the hops are in contact with the hot wort, the more of the reaction takes place, and the more bitterness that gets imparted to the finished beer. It should be noted that if the brewer wants both bitterness and aroma, multiple additions of the hops should be done during the boil. The only drawback is that even with prolonged (>60 min) boiling, it is difficult to achieve more than about 35–40 % conversion of the humulone to isohumulone (known as the "utilization rate").

Lupulones In addition to the humulones are a class of compound with a very similar structure known as the lupulones or β-acids. Just like the humulones, ad-

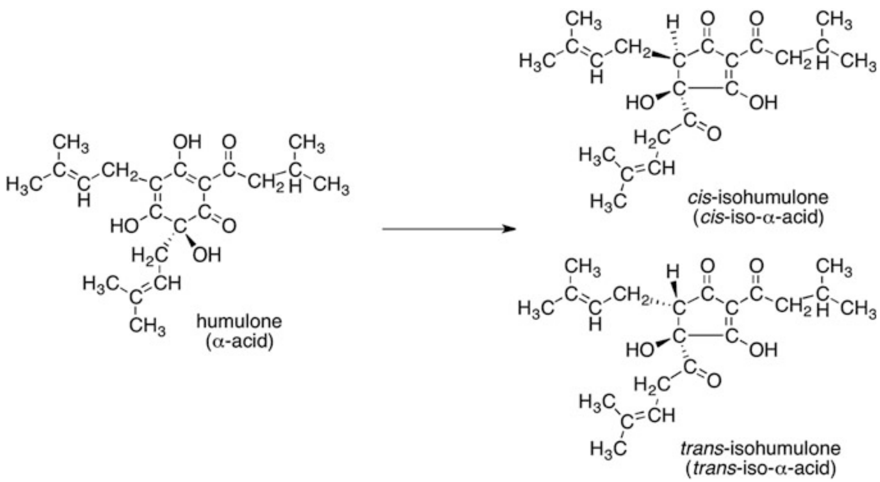
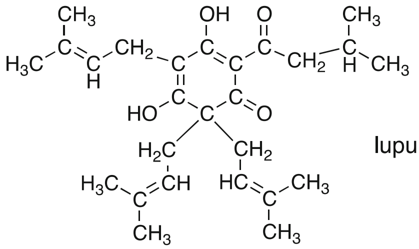


Fig. 8.12 Humulone isomerizes to Isohumulone

and covarieties of these compounds also exit. The lupulones differ greatly from the humulones in that they cannot undergo the ring contraction reaction. In addition, they are not very bitter at all and contribute little to the flavor or aroma of the hops, unless they are oxidized.



The main use for the lupulones is that they can signal whether the hop is a "noble" hop or a "bittering" hop. Ratios of the humulone and lupulone of about 1:1 indicate a noble hop variety. This can be confirmed by a hop oil containing less than 50 % myrcene and a humulene to caryophylene ratio of at least 3:1.

Overall Flavor and Aroma It is the combination of all of the different compounds that give rise to the flavor and aroma of a particular hop oil. With only slight modification of the percentages of the different compounds, the flavor can go from "piney and very harsh" to "grapefruity and pleasant." It is the job of the brewer to select the hops that are appropriate to the style of beer being constructed and confirm that the hops being purchased match the characteristics that are desired.

8.5.3 Modified Hop Oils

Because the conversion of humulone to isohumulone is time-consuming, low yield, and can cause adverse effects in the brew, the brewer may look to a commercial product that provides the same outcome without the use of hops. Research on hop oils and the conversion of alpha acids revealed that the procedure can be completed in the laboratory with excellent efficiency and yield. The result is the modified hop oil.

One modification is to extract the hop oils from the plant material and use the oil directly. This hop extract allows the brewer to reduce the amount of waste products and trub during the boil. The hop oil, when added to the boil, is a little more efficient at the isomerization reaction and can equate to about a 40–45 % utilization rate.

Another modification involves the laboratory-based conversion of the humulone to isohumulone in the hop oil extract. The resulting preisomerized hop oil is nearly 100 % utilized, resulting in a bittering liquid that can be added directly to the wort or to the finished beer. This product is often used to adjust the bitterness of the beer to move the product into the correct specifications for the style.

Other modifications include treatment of the preisomerized hop oil to make either a dihydro, tetrahydro, or hexahyrdo-isomerized oil (Fig. 8.13). Addition of hydrogen atoms using chemical reagents such as sodium borohydride ($NaBH_4$) or hydrogen gas (H_2) allow the hop producer to control the production of any of these products. Each of these has a set of very different properties. For example, the dihydro-isohumulones (also known as rho-isohumulones) are not sensitive to the reaction of light with beer (eliminating the "skunked" flavor associated with a beer left out in the sun). The tetrahydro-isohumulones, where the double bonds have been removed from the molecule, increase the ability of the hop oils to support a thick foam on top of the beer. The hexahydro-isohumulones have both the properties of a light-stable hop oil and an enhanced foam on the finished beer.

As we have noted in this section, the structure of a molecule plays a large role in the properties (such as flavor) of the molecule. And, as we would expect, the bitterness of the reduced isomerized compounds is not exactly the same as before. So care must be taken by the brewer to add just the right amount of these compounds to give the desired flavor for the finished beer.

While some may say that addition of modified hop extracts to the beer is cheating, the results are hard to argue with. Enjoying a cold beer with a very stable foam head on the beach is very hard to complain about.

Chapter Summary

Section 8.1

Boiling wort results in many different outcomes. Sterilization, degassing, and trub formation are accompanied by chemical reactions that improve flavor, color, and the pH of the end product. Hop oil conversion to the iso-alpha acids is also accomplished.

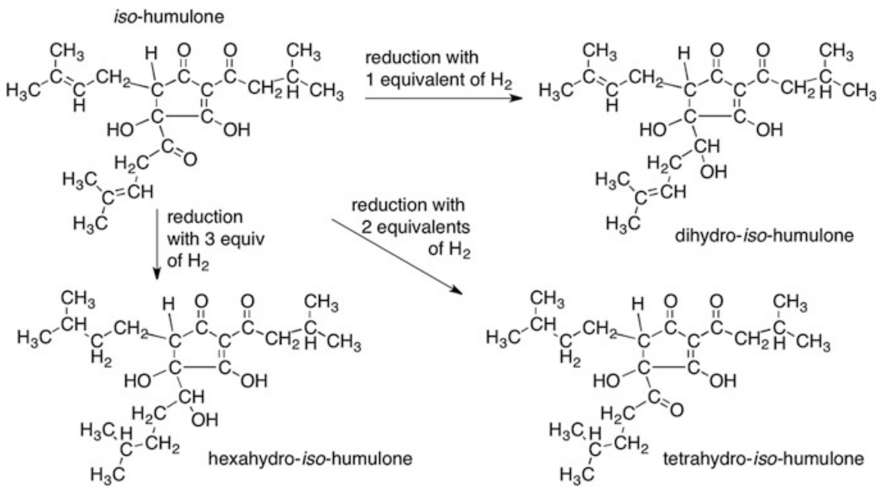


Fig. 8.13 Reduced isohumulones

Section 8.2

Stainless steel is typically used as the metal for boil kettle construction. Corrosion of stainless steel is possible, given the corrosive and acidic environments found in the brewery.
There are different boil kettle designs in use across the globe, each with advantages and disadvantages. New designs are being explored to improve the efficiency of the boil.

Section 8.3

Heat is the transfer of thermal energy. Temperature is a measure of the thermal energy of an object.

Section 8.4

Thermal energy is a form of kinetic energy.
Heat that is transferred can be calculated using the equation: $q = m\,C\,\Delta T$, where q is a form of energy (E).
Specific heat (c) differs for each type of compound and refers to that object's ability to absorb heat. Latent heat (C) is the heat required to change the phase (from solid ← → liquid or liquid ← → solid) of a substance.
The power of a heating system can be calculated using the equation: $P = E/t$.

Section 8.5

The hop cones contain lupulin glands that are the source of extractable oils used in brewing.
Hop oil extracts contain volatile oils, resins, and the alpha acids and beta acids.
Isomerization of the alpha acids results in the bittering and protective agent found in beer.
Preisomerized hop oils are commercially available and allow the brewer to know the exact amount of bittering agent added to the finished wort.

Questions to Consider

1. List the outcomes that result from boiling wort.
2. Which of the outcomes that result from boiling wort reduce the amount of volatile compounds in the wort?
3. Describe, in your own words, what happens to the pH as the wort is boiled.
4. Describe, in your own words, how trub forms and explain the compounds that are found in trub.
5. What is a direct-fired boil kettle?
6. What is a calandria? Sketch a drawing of an internal calandria.
7. Why is copper used inside of a calandria?

8. Why is a copper boil kettle not commonly used in a brewery?
9. Describe the pros and cons for the use of SAE 304 stainless steel versus copper.
10. Use the Internet to find the exact makeup of 316L stainless steel and compare the makeup to 316 stainless steel.
11. In a direct-fired boil kettle that is made from 304 stainless in two halves, the top half is welded to the bottom half to make the final vessel. The rest of the valves, ports, and other items (such as the legs) are then added. Where would you expect to find rust or stress fractures after extended use of this kettle?
12. What advantages would a Merlin® heating system provide over a Stromboli system?
13. Define "heat" and "temperature."
14. What units are used to record heat and temperature?
15. Explain heat and temperature as they relate to walking barefoot on the sidewalk on a hot summer day.
16. Which metal, assuming the same mass, would you expect to absorb more heat, aluminum or iron?
17. If 4500 J of heat was added to water at 40 °C, what would be the final temperature, in °C and in °F?
18. How much heat would be required to raise 255 kg of water from 25 °C to boiling?
19. If 2975 J of heat were added to a 1.0 kg block of metal and its temperature increased from 40.0 to 47.4 °C, what is the identity of the metal (you may need to use Table 8.3)?
20. Calculate the power, in kW of a burner that would do the work outlined in question 17, if all of the heat was transferred into the water and the burner accomplished the job in 35 min.
21. Recalculate question 20, assuming that only 50 % of the heat produced by the burner actually became absorbed by the water.
22. A brewer purchases a burner rated at 22, 000 BTU. How long would it take the burner to heat a 1-kg aluminum pot containing 20 kg of water from 25 to 100 ° C?
23. How much heat would be required to change the temperature of 2.2 kg of water from liquid at 75.0 °C to steam at 120 °C?
24. A brewer elects to warm a 145-g sample of water from 34 to 55 °C by adding 120 g of water at a higher temperature. What would that higher temperature have to be to accomplish that task?
25. A brewer considers the use of a metal in the construction of a boil kettle. The specific heat capacity of the metal is 240 kg/kJ °C and the thermal conductivity is reported as 405 W/mK. On the basis of these values, would this be a suitable choice? Describe the characteristics of heat transfer for this metal.
26. What is the difference between humulone, cohumulone, and adhumulone?
27. Draw the molecular structure of colupulone.
28. The atoms in the structure of pinene are the same atoms found in the structure of myrcene. Can you identify which atoms in pinene match up with the atoms from myrcene?

29. What flavor would you predict from a hop oil that was rich in pinene and in limonene?
30. The –OH at the bottom of the six-membered ring in humulone appears to be missing in the five-membered ring in isohumulone. In the reaction, it is changed into something else. Where is that –OH in the isohumulone structure and what has it become?
31. Why do the lupulones not isomerize? What part of the structure of a humulone, then, would you predict is very important for the isomerization reaction?
32. Identify the similiarities between myrcene and limonene, linalool, and geraniol. Can you determine where the "oxidation" of myrcene has taken place to give rise to each?
33. What portion of isohumulone is likely responsible for causing the light-struck flavor in beer?

Laboratory Exercises

Hop Tea and Identifying Flavors

This experiment is a short introduction to identify some of the key compounds in hops. The hops chosen for the experiment are selected because of the pronounced flavor profile for the particular compound being explored. It is possible, however, to choose different hops based on their availability in a particular area.

Equipment Needed

4 pint Mason jars
potable water
heater (such as a burner, hot plate, or microwave)
4 samples of hops (recommended: Citra, Cluster, Saaz, Northern Brewer).

Experiment

Boil a suitable portion of water. This can be done for an entire class by the instructor, or each laboratory group can warm their own water. In the absence of a burner, hot plate, or other heating devices, it is still possible to extract the hop oils using very hot tap water.
Place a small amount of hops (as pellets) into each of the Mason jars (3–5 pellets is enough), and then add enough hot water to fill the Mason jar approximately 1/4 to 1/3 full. Stir with a spoon or swirl gently. (Caution: hot!)
After 5 min, the aroma of each Mason jar should be recorded. Then, after the hop tea has cooled to just above room temperature, a very small sip of the tea is tasted by the students. The aroma and taste should be recorded.
Match the characteristics of the hops to the compounds that predominate in the hop varieties. Figure 8.9 will assist with the identification of the compounds in the hops.

Determination of Percent Hop Acids in Hops.

This laboratory analysis is based on an ASBC Method (HOPS-6) for the determination of hop acid content in hops. The method works by analyzing the absorbance of an organic extract of the hop oil, because the hop acids absorb ultraviolet light.

Equipment Needed

2 × 250-mL Erlenmeyer flasks
2 tight-fitting corks
Pelletized hops
5.0-mL graduated or volumetric pipet and bulb
100-mL volumetric flask
50-mL volumetric flask
Chemicals:
toluene, methanol, alkaline methanol (0.2 mL of 6.0 M NaOH in 100 mL methanol).

Experiment

Obtain a sample of hops and weigh out 2.500 g of the material (it is important to be as close to 2.500 g as possible). Place the material into a 250-mL E-flask and add 50 mL toluene. Stopper the flask with a cork or other stopper (a rubber stopper is not recommended) and shake by hand for 30 min. Pass this to your laboratory partner when your arm gets tired. (or use a rotary shaker to do the job for you.)
Then, place the flask on the laboratory bench and work on preparing a second sample of the same hops as you did before. The slurry should stand undisturbed for 30 min. This will allow some of the hop solids to settle to the bottom of the flask and leave some of the clear toluene extract at the top.
Withdraw exactly 5 mL of the clarified toluene extract using a graduated or volumetric pipet and dilute this to 100 mL in a volumetric flask with methanol. Dilute 3 mL of the toluene–methanol solution to 50 mL in a volumetric flask using alkaline methanol (0.2 mL of 6.0 M sodium hydroxide in 100 mL methanol) using a plastic pipet.
Then, measure the absorbance of the solution at 275, 325, and 355 nm using the UV–Vis spectrometer. The instrument should be blanked using a blank made from 5 mL of toluene without the hops added. Take your readings as quickly as possible because the hop acids can degrade quickly in light.
Use your readings to determine the percent of alpha acids and beta acids in the hops. The 1.33 factor in the equation relates the dilution of the liquid to the concentration used in the measurement of the samples.

$$\alpha - \text{acids}, \ \% = 0.667 \times (-51.56A_{355nm} + 73.79A_{325nm} - 19.07A_{275nm})$$

$$\beta \text{ - acids}, \ \% = 0.667 \times (55.57A_{355\ nm} - 47.59A_{325\ nm} + 5.10A_{275\ nm})$$

Determination of Wort Viscosity During Boil

This laboratory analysis measures the viscosity of a wort sample as it is being boiled. The effect of evaporation on the sample is observed as are visual comparisons of the wort appearance.

Equipment Needed

250-mL beaker
100-mL graduated cylinder
1L tub for 20 °C water bath
Thermometer
Hot plate
Glass rod for stirring
Viscometer (falling ball or Ostwald)
Wort (prepared by mixing dry malt extract with warm water to a gravity of 1.040 g/mL)

Experiment

Obtain a tub and fill it approximately 1/2 full of tap water. Add either ice or warm water until the temperature of the water in the tub is 20 °C. Maintain that temperature during the course of the experiment.
Obtain 100 mL of wort prepared by your instructor—or prepare it as described above—and place it into the 250-mL beaker. Place the beaker on a hot plate set no higher than 1/2 of full power and stir the solution with a glass rod. While the solution is warming to a boil, measure the viscosity of a water sample using the viscometer. Your instructor will illustrate the method to you. Record the time it takes for the water to pass through the viscometer.
Once the solution on the hot plate has reached a boil, reduce the heat until it just simmers. Occasionally, stir the solution to avoid scorching. Warning: As the solution approaches the boiling point, it may foam significantly. Addition of a drop of vegetable oil, rubbing alcohol, or anti-foam agent will reduce the foaming if it becomes an issue.
After 30 min of boiling, remove the beaker from the hot plate and allow it to cool to room temperature. Then, place it into the 20 °C water bath. Stir or swirl the beaker until the temperature of the wort is the same as that of the water bath.
Then, obtain a fresh sample of wort and determine the time it takes to pass through the viscometer. Repeat that analysis for the boiled wort.

The kinematic viscosity of the wort can be determined by dividing the time for the wort by the time for water and then multiplying the result by 1.0038 (the value of viscosity for water at 20 °C). Use significant figure rules to determine the number of significant digits in the answer.
Compare the viscosities of the preboil and post-boil wort. Compare as well the aroma and the color of the two solutions. Is there a difference? Is it what was expected?