Control of Off-Flavors From Fermentation

Many beer flaws are the result of unwanted fermentation flavors. Yet the control of these unwanted flavors can be difficult because so many factors influence the amount and type of fermentation by-products that accompany ethanol production. After all, a miscalculation in the proper types or proportions of malt and hops may result in a failure to produce the desired beer style, but the beer may still be delicious to drink. However, even the most expertly executed recipe may yield an utterly undrinkable brew if fermentation goes awry.

The following discussion describes five common fermentation derived flavor compounds known as fusel alcohols, esters, aldehydes, diacetyl, and various sulfur containing compounds (sulfur dioxide, hydrogen sulfide, and dimethyl sulfide) and how certain fermentation parameters (principally temperature, aeration, wort composition, pressure, and pitching rate) influence their creation or suppression.

Summary of International Beer Flavor Terminology[1,2,3]

Flavor Compound	Meilgaard Flavor Tier	O - odor T - taste W - warming	Descriptors
Fusel alcohol	0110	OTW	Alcoholic, spicy, wine-like, vinous
Esters, Aldehydes	0120	OT	Solvent-like, plasticizers, lacquer-like
Esters	0130	OT	Fruity, banana, apple, solvent-like
Acetaldehyde	0150	OT	Green apple, bruised apple
Diacetyl	0620	OT	Butterscotch, buttermilk
Sulfur Dioxide	0710	OT	Striking match
Hydrogen Sulfide	0721	OT	Rotten egg
Dimethyl Sulfide	0732	OT	Cream corn, cooked vegetable

Flavors from Fermentation

Fusel Alcohols: The primary alcohol produced by brewers yeast is relatively tasteless ethanol. However, yeast must metabolize other wort constituents besides sugar to support cellular activities that ensure yeast growth and health. Included among these wort constituents are amino acids, which are involved with the production of fusel alcohols (a.k.a., fusel oils, higher alcohols).

Fusel alcohols are more aromatic than ethanol and are associated with descriptors such as alcoholic, vinous, spicy, hot, and even solvent-like. In general, conditions that promote rapid yeast growth foster fusel alcohol production.

<u>Factors That Increase Fusel Alcohols</u>[4]

- Increased dissolved oxygen (↑ growth through yeast cell membrane synthesis)
- Stirring/convection currents (↑ growth through good contact between yeast and nutrients)
- High fermentation temperature (↑ growth through increased yeast metabolic activity)
- High gravity wort (greater than 13°P)
- Low pitching rate (creates increased demand for amino acids in yeast reproduction)
- Low-pressure fermentation (↑ growth through lower build-up of inhibitory CO_2)
- Yeast type (certain strains, especially ale-types, produce more fusel alcohols)

[1] Meilgaard
[2] FlavorActiV
[3] Bickham
[4] Kunze, p. 303

Although very high amino acid levels may lead to higher fusel alcohol content,[5] it is generally accepted that fusel alcohols are produced when the aforementioned growth stimulators create demands for amino acids (which are used as building blocks for protein synthesis) beyond the quantity of amino acids available in the wort.[6,7] Protein synthesis includes the creation of intermediary products that become protein when combined with the specific amino acid for a particular protein. If the required amino acid is missing, the intermediary product is converted to a fusel alcohol. This process may also explain why fusel alcohol production increases as the percentage of nitrogen-free glucose adjuncts increases, and the maltose fraction decreases[8,9].

High starting wort gravity (especially over 13°Plato) increases fusel alcohol production; however, many modern commercial breweries have moved toward high gravity brewing (≈ 16°Plato) because it increases plant capacity. They also employ other parameters to shorten fermentation time such as increased fermentation temperatures in tall cylindrical fermenters. Warmer temperatures increase yeast metabolic activity and stirring created by convection currents in tall fermenters creates better contact between yeast cells and nutrients. Because high gravity, warm temperatures, and stirring can increase fusel alcohol production, brewers using any of these parameters may increase fermentation tank pressure because pressure is inhibitory to fusel alcohol production. (As will be discussed later, increased gravity and temperature can also increase ester production, and over pressure is also a means to inhibit ester formation.)

Yeast strains also have varying propensities to produce fusel alcohols. Infections by wild yeast or bacteria may also increase fusel alcohol. Top-fermenting ale yeast are well known for producing more fusel alcohols than bottom-fermenting lager yeast, much of which has to do with lager yeasts' ability to ferment at cooler temperatures. For this, and the other aforementioned reasons, warm fermented ales with high starting gravities like barleywines are likely to exhibit high levels of fusel alcohols, especially those fortified with glucose to boost their alcohol content. Conversely, cool-fermented, all-malt lagers of normal starting gravity are likely to produce fewer fusel alcohols. Lager yeast generally produce 60-90 mg of fusel alcohol and ale yeast often more than 100 mg/L. Because levels of 100 mg/L cause noticeable flavor consequences, ales are well known for their spicy character relative to lagers.[10]

Esters: Esters are responsible for fruity aromas in beer and are important flavor contributors, particularly in top-fermenting ales. However, high levels of fruity esters are usually unwanted when producing lager beers. At excessive levels, esters become unpleasant and can even take on a solvent-like character. Three factors influencing ester levels are yeast strain, wort composition, and fermentation conditions.

<u>Factors That Increase Ester Production</u>[11]

Yeast

- Strain (various strains have different ester production characteristics)
- Flocculent yeast
- Pitching rate (either high or low rate, depending on yeast strain)
- Genetic and physiological instability of yeast (yeast performance can change with re-pitching)

Wort Composition

- Decreased dissolved oxygen (restricts yeast growth)
- Decreased free unsaturated fatty acids, i.e. lipids (increased availability of Acetyl CoA for ester production relative to yeast growth; increased AATase (ester enzyme) activity)
- Increased gravity (reduces oxygen solubility, increased level of alcohol cosubstrate)
- Increased zinc levels (stimulates breakdown of α keto acids to fusel alcohols)

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[5] Narziss, 205
[6] Narziss, p. 202
[7] Campbell, p. 68-69
[8] Schmidt & Kluba, p. 391
[9] Narziss, p.205
[10] Kunze, p. 303.
[11] Dufour, et. al., pp. 218-227

Fermentation Conditions

Increased temperature (higher levels of fusel alcohols; stimulates activity of AAtase)
Decreased pressure (lowers CO_2 saturation – high CO_2 inhibits Acetyl CoA)
Decreased stirring (reduces yeast growth)
Drauflassen (stimulates ester enzyme activity)

Esters are the result of an enzyme-catalyzed combination of an alcohol (either ethanol or fusel alcohol) and a fatty acid. In general, most factors that promote yeast growth inhibit ester formation. Acetyl CoA, which is involved in the synthesis of enzymes for ester production, also participates in the synthesis of fatty acids and amino acids for yeast growth. When factors favoring growth (O_2, lipids, stirring) are present, Acetyl CoA is directed toward yeast growth and away from the creation of enzymes for esterfication.[12] Other conditions (high fermentation temperature and *Drauflassen*, meaning "adding to", as in adding new wort to an actively fermenting tank) stimulate the activity of ester creating enzymes. Finally, conditions that increase the level of fusel oils (high temperature, zinc) contribute to esterfication.[13] Many important esters are formed from fusel alcohols as well as ethanol, and the increased level of certain fusel alcohols increases the material for the production of these esters.

Ester formation is quite complicated and dependent on many interrelated variables. Furthermore, certain conditions affect the formation of various esters differently, which may increase one ester while decreasing another. While lager yeast generally produce lower ester levels than top-fermenting yeast, the lower ester levels may be attributable to cooler lager fermentation temperatures, since all lager yeast strains may not produce lower ester levels than ale yeast when fermented at warmer top-fermenting temperatures. There is contradictory evidence as to the effect of pitching rate on esterfication, and the optimal pitching rate to maximize esters may differ by strain.[14]

Carbon dioxide pressure during fermentation is a common way of influencing ester production. High levels of CO_2 inhibit Acetyl CoA activity that causes ester production. Tall cylindrical tanks not only increase hydrostatic pressure (i.e., the weight of the beer increases the pressure on the liquid at the bottom of the tank that increases the solubility of CO2), but they also produce natural stirring by convection currents that limit esterfication. Conversely, Bavarian Weizen brewers who try and maximize ester production prefer shallow open fermenters that reduce pressure and convection currents.

Aldehydes: Fermentation by brewer's yeast can be very simply described as the conversion of sugar to ethanol and carbon dioxide, accompanied by the production of lesser quantities of other by-products (e.g. esters and fusel alcohols described above) and intermediary compounds such as aldehydes. When yeast convert sugar to alcohol, the sugar undergoes intermediary changes including conversion to acetaldehyde before becoming alcohol. For this reason, the quantity of acetaldehyde first increases and then declines, which makes high levels of acetaldehyde a common green beer flavor and a good indicator of beer maturity. Acetaldehyde and other carbonyl compounds are responsible for the typical grassy, rough, and cidery flavors found in beer before maturation.[15]

[12] Dufour, et. al., p. 216.
[13] Dufour, et. al., p. 224.
[14] Dufour, et. al., p. 219.
[15] Patino, p.316.

Methods to Influence Acetaldehyde Levels in Beer[16, 17,18]

Causes of Higher Acetaldehyde levels from Primary Fermentation

- Intense fermentation
- Increased temperature during fermentation
- Increased pitching rate
- Increased pressure during fermentation
- Minimal aeration
- Stirred fermentation

Causes of Reduced Acetaldehyde Levels after Primary Fermentation

- Intense secondary fermentation and conditioning
- Warm conditioning
- Increased yeast concentration during conditioning
- Minimize aeration

Since the creation of acetaldehyde is an intermediate step in ethanol production, successful control includes proper secondary/maturation practices that allow the yeast to reduce acetaldehyde to alcohol. Essential to this reduction is the carryover of enough living and healthy yeast cells through primary fermentation and maturation. Elevated acetaldehyde levels may result from diminished yeast activity brought on by early cooling, non-vital cells, or removing yeast from green beer by filtration prior to complete maturation. Ensuring that yeast remain healthy and in sufficient quantities to complete fermentation starts with the rapid onset of active fermentation provided by a sufficiently large and vigorous yeast population supported by adequate pitching rates and strong wort aeration. Because aldehydes are easily volatized even at low temperatures, they are readily carried off by evolving CO_2. Pressurized fermentation that traps CO_2 retains higher acetaldehyde levels, which must be reduced in the conditioning process.[19]

It is also noteworthy that the intrusion of oxygen into packaged beer can cause alcohol to convert back to aldehydes, which is a contributor to stale beer flavors. Other catalysts, including light, can create other oxidative pathways that result in the creation of aldehydes and stale flavors.[20] For these reasons, it is important to avoid the uptake of oxygen after the start of fermentation, especially in packaging, and protect packaged beer from light and heat.

However, the slow oxidation of alcohol is sometimes a desirable process that provides the unique character to sherry, a fortified wine that is allowed to oxidize. Controlled oxidation of tannins can soften the astringency of red wine. Esterfication of harsh fusel alcohols during aging also leads to improved flavor and aroma. Barleywines and imperial stouts are also examples of "big" beers that may also be purposely "laid down" to increase the complexity of these beers through the aging process.

Diacetyl: Another important flavor compound produced by yeast during fermentation is diacetyl, which has a butterscotch aroma and slick mouthfeel. Diacetyl is derived from α-acetolactate, an intermediary compound in yeast biosynthesis of the amino acid valine needed for cell growth. However, once α-acetolactate is in beer, it not only can be converted to valine, but also to diacetyl. Therefore, if sufficient valine already exists, the production of α-acetolactate for valine synthesis is repressed, which then

[16] Kunze, p. 302
[17] Patino, p. 317.
[18] Narziss, p. 206
[19] Narziss, p. 244. Acetaldehyde levels may decline by 20-70% during lagering.
[20] Narziss, p.324.

leads to lower levels of diacetyl.[21] Warm fermentation temperatures and high levels of aeration that foster cell growth requiring amino acids (i.e., valine) create increased levels of diacetyl. However, in the later stages of fermentation/conditioning, yeast also convert diacetyl to much less offensive and intense flavor compounds. Therefore, it is important to retain enough healthy yeast at the end of primary fermentation for conditioning to clean up the diacetyl. Adequate pitching rates and aeration are important for diacetyl control, as well as avoiding low amino nitrogen adjuncts. Removing yeast from young beer by filtration or chilling the beer before diacetyl reduction has been completed can also lead to increased diacetyl levels. Although high initial temperatures stimulate diacetyl production, high temperatures during conditioning also stimulate yeast activity that aids in the removal of diacetyl when oxygen is excluded. This is why some lager breweries allow the temperature of young beer to rise by as much as 10°C or more for 1 to 2 days before beginning cold conditioning (diacetyl rest). A variety of bacteria, wild yeast, and mutated brewers yeast also produce diacetyl, so good sanitation and yeast-handling techniques are also important to diacetyl control.

Sulfur Compounds: Yeast require sulfur for the synthesis of cell protein. Wort contains sources of sulfur including inorganic sulfate in water and sulfur-containing amino acids, peptides, and protein from malt. Sulfur compounds important to beer flavor develop in part from the synthesis of amino acids and the reduction of inorganic sulfur.[22] In general, the concentration of these yeast produced compounds increases with increasingly unfavorable fermentation conditions. Among these compounds are sulfur dioxide resembling a struck match and the particularly offensive hydrogen sulfide resembling the aroma of rotten eggs.

Sulfur dioxide (SO_2), is a common signature of many European lagers. It also has natural antioxidant and antimicrobial properties and acts as a reserve against the production of aldehydes during beer storage.[23] In fact, exogenous sulfites are widely used in wine production because of their antimicrobial and antioxidant properties. Yet, in excessive quantities SO_2 may be unwanted. The loss of SO_2 increases with increasing storage temperature.[24] Lagering reduces the amount of SO_2 through various chemical reactions; however, bunging conditioning tanks causes a more limited reduction in SO_2 since lesser amounts of volatized SO_2 can be carried off by escaping fermentation gas.[25] The most important means to reduce the formation of SO_2 during fermentation is by 1) sufficient levels of yeast nutrients in wort, 2) an increased amount of lipids, 3) intensive aeration, 4) vital yeast, and 5) the removal of hot and cold trub.[26]

Hydrogen sulfide (H_2S) occurs during alcoholic fermentation. A deficiency in nutrients for yeast growth leads to higher H_2S levels. For this reason beers made from adjuncts may be more susceptible to elevated H_2S levels.[27] Fortunately, H_2S is easily volatized and normally only a small fraction remains in beer, which is usually below the flavor threshold. Increased lagering temperatures and fermenter height contribute to the evolution of the H_2S from the green beer. High levels of H_2S also may be indicative of infection of the wort by outside microbes.

Although not principally derived from fermentation, dimethyl sulfide (DMS) is another common sulfur compound having an aroma of cream corn or cooked vegetables. DMS is also produced by fermentation, but like other sulfur compounds, proper fermentation conditions do not allow problematic levels to remain in the beer. In most cases, DMS originates from the precursor S-methyl methionine (SMM) produced by malt during germination.[28] When heated in excess of 65-70°C, SMM is converted to DMS, with increased heating driving off the DMS. This is why highly kilned malts produce worts with less DMS than light colored ones. Boiling temperatures allow the SMM in wort to convert to DMS and then carry off the volatized DMS with escaping steam vapor. However, when DMS has not been fully volatized during boiling (e.g. because of a non-vigorous boil, an insufficient boiling time, or a covered kettle), SMM can still

[21] Campbell, p. 69-70.
[22] Narziss, p. 204.
[23] Almeida, p. 191.
[24] Ibid.
[25] Narziss, p.208.
[26] Ibid.
[27] Ibid.
[28] Narziss p. 171.

be converted to DMS in the whirlpool, but the DMS will not be volatized because the temperature is below boiling. For this reason, extended whirlpool stands should be avoided, and the wort chilled as rapidly as possible after hot break separation. DMS, like diacetyl, can also be a by-product of bacterial infection.

Conclusion

Although the flavor compounds discussed may be desirable at low levels depending on the beer style, at excessive levels they become offensive. In general, there are some common means to control the flavors described in this discussions, although it must be recognized that the pathways leading to these compounds are complex and interdependent, and the guidelines are not always hard and fast rules. Yet, implementing good and repeatable brewing and fermentation practices will lead to higher beer quality and better consistency. These practices can provide the proper environment for yeast to grow and ferment, while avoiding the stress factors that give rise to off-flavors.

Several good practices include:

- Produce worts with the proper level of amino acids and balance of wort sugars that generally favor maltose over glucose.

- Provide an adequate quantity of healthy yeast cells for fermentation and maturation through sufficient pitching rates and aeration levels. Conversely, after fermentation starts, further intrusions of oxygen should be avoided.

- Maintain the correct fermentation temperature, especially avoiding excessively high temperature levels. Although fermentation temperatures vary by strain, caution should be exercised when fermenting lager yeasts in excess of 50°F and especially in excess of 55°F. For ales, caution should be exercised over 70°F, and especially in excess of 75°F. Furthermore, the solubility of oxygen decreases with increasing wort temperature. At high temperatures, it is difficult or impossible to dissolve sufficient oxygen for the yeast.

Furthermore, other common sense practices beyond fermentation management will further add to successful brewing:

- Avoiding stale malts and hops,
- Using clean de-chlorinated water with the proper balance of minerals, especially calcium,
- Proper temperatures and pH applied throughout a brewing process that avoids the uptake of oxygen, and
- Sanitary conditions that exclude unwanted microbes and keep the wort free of taints from cleaners and sanitizers.

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