The role of oxygen in brewing

We live in an oxygen-rich environment for it comprises 21% of the air we breathe. Oxygen is chemically very reactive and combines readily with nearly all other elements. Elements reacting with oxygen are said to be oxidized. Oxidation reactions tend to be accelerated by heat with the most vigorous reactions leading to combustion and burning.

Technical Summary 3

The third in this series of technical summaries for the Institute & Guild's AME candidates. By Tim O'Rourke.

Nearly all plants and animals require oxygen for respiration with the removal of waste gas, carbon dioxide. Oxygen is a key component of organic compounds.

Biological systems in brewing.

The malting process involves the germination and partial growth of cereal seeds (usually barley). To survive these seeds have to live in an oxygen rich environment and the waste gas produced during respiration has to be removed. Air is blown through the grain at various stages in the malting process:

- In barley storage air is blown through the grain to prevent carbon dioxide build up.
- During steeping the wet steeps are aerated to keep the steep water saturated and to agitate the growing barley. During the air rests in steeping air is usually sucked through the bed to bring in fresh oxygen and to remove carbon dioxide.
- During germination humidified air is blown through the bed to vent carbon dioxide and keep the piece cool.
- Once the green malt is kilned the living part or embryo is killed and the malt has no further need for oxygen.

The other living organism used in beer is yeast. Although fermentation itself is an anaerobic process (occurs in the absence of air – see below), yeast cells require oxygen for growth

Anaerobic respiration:

Sugar → Alcohol + Carbon dioxide + Energy (ATP)

Molecular oxygen is taken up by yeast at the start of the fermentation and is used by the cell to synthesise sterols and unsaturated fatty acids which are essential components of the yeast's membrane. The need for oxygen can be removed if sterols (e.g. ergosterol) and unsaturated fatty acids (e.g. oleic acid) are added directly to the wort.

In terms of releasing energy, aerobic respiration is more efficient than anaerobic respiration. However in yeast the temptation to use the available oxygen for aerobic respiration is suppressed through a mechanism described as the Crabtree effect. In the presence of glucose sugars (above 1% by weight) yeast (*Saccharomyces spp*) uses glucose to produce alcohol and uses the oxygen to produce the necessary lipid compounds.

The presence of insufficient lipid compounds will lead to a defective fermentation due to inadequate yeast cell reproduction, which in turn will lead to:

- Slow and sticking fermentations
- Off flavours – e.g. poor removal of diacetyl and acetaldehyde
- Poor yeast crop in terms of quantity and vitality
- Low ester formation

Excess oxygen will lead to:

- Rapid fermentations
- Excessive yeast growth and hence beer losses
- Higher ester production – giving fruitier flavoured beers

Oxygenating the wort

Wort is usually aerated in line on transfer between the wort clarification vessel (whirlpool tank) through the wort cooler to the fermenting vessel prior to yeast addition.

Most breweries oxygenate the wort on the cold side after the wort cooler (see table below).

It is surprisingly difficult to get oxygen to dissolve in water (or wort). There are several systems available which include:

- Aeration in the mid section of two stage wort cooler to benefit from the turbulent flow conditions of a plate heat exchanger.
- Use of stainless steel and ceramic candles in the cold wort line to produce micro bubbles.
- The use of in line static mixers to promote turbulent flow
- The use of venturi systems which produce pressure increase to forcing gas into solution.

In any system only part of the gas supplied is dissolved. A good aeration system should also include a measuring device appropriately located sufficiently far from the injection point so that it accurately measures the dissolved oxygen and can feed back to control system.

The amount of dissolved oxygen required depends on the yeast strain and the original gravity of the worts. Traditional ale and lager worts were usually not collected higher than 1045 (12% Plato) and required 6 to 8 ppm dissolved oxygen.

With high gravity brewing original gravities have increased up to 1080 (20% Plato) and require dissolved wort oxygen levels of 16 ppm or higher.

From the table below it can be seen it is impossible to provide this level of dissolved oxygen from air alone and pure oxygen injection is used.

Oxidation reactions

Oxidation and reduction reactions take place all the time. Since we live in an oxygen rich atmosphere products are continually being slowly oxidised.

A molecule which loses electrons it is said to have been oxidised. If one molecule loses an electron then another molecule must accept that electron. The molecule which accepts the electrons it is said to be reduced.

Solubility of oxygen in water and in wort at different temperatures and at atmospheric pressure.

	Temperature (°C)				
Oxygen concentration (mg/l)	0	5	10	15	20
Saturated water	14.5	12.7	11.2	10.0	9.9
Saturated 12% Plato wort	11.6	10.4	9.3	8.3	7.4

Ref Moll – Beers & Coolers

Comparison of benefits between hot and cold wort aeration

Benefits from hot wort aeration	Benefits from cold wort aeration
Sterilises air	Better oxygen solubility in cold
Better mixing through wort cooler	Lower risk of wort oxidation
	Little oxygen is consumed due to chemical reactions with wort
	Lower risk of off flavours and instability
Limitations from hot wort aerations	**Limitations from cold wort aerations**
Lower solubility of oxygen	Air must be sterile before addition
Risk of wort oxidation	Separate oxygen mixing system is required
Some of the oxygen will be consumed through wort oxidation reactions.	
Risk of oxidised off flavours (garlic and staling) developing in the beer	

In this context oxygen is willing to accept free electrons and hence acts as an oxidising agent, but in that process oxygen itself will be reduced.

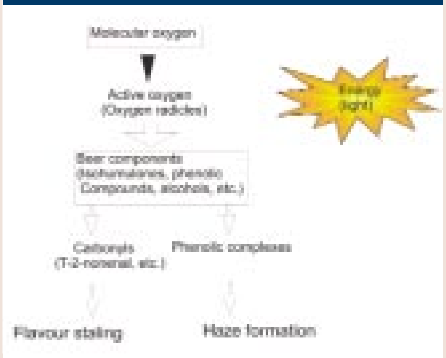
Oxygen usually exists in a triplet state ($^3O_2$) and in this form is not very reactive. Oxygen has to be activated by energy (light or heat) or catalysed by metals (copper or iron etc) when it forms highly reactive radicals such superoxides and hydroperoxyl radicals.

The radicals rapidly react with wort and beer components to produce oxidized compounds some of which have an impact on the final product e.g:

- Flavour staling compounds particularly carbonyls – for example trans 2 nonenal
- Accelerated chill and permanent haze formation through oxidation of polyphenols.
- Increase of beer astringency through oxidation of polyphenols
- Increase in beer colour through oxidation of polyphenols.

The proposed mechanisms for these changes is shown below.

Fig 1. Proposed beer staling mechanism



Taken from: Kaneda H. et al MBAA Technical Quarterly 1999 No 1.

These oxidative changes are almost inevitable, and have a marked influence on the flavour and aroma of beer. The only control the brewer has is to influence the rate at which these changes occur and hence the length of time the beer can exhibit its optimum flavour profile.

Flavour changes observed in a typical beer due to oxidation over time.

Fig 2. Typical changes in flavour character with ageing

Oxygen control and minimising product oxidation.

Brewing materials

The processing and storage of brewing materials have been implicated in promoting staling There is particular reference in the literature to the production of lipoxigenase enzyme during malting which is thought to increase the lipid content of the wort.

Possibly more important, is the role of raw materials is in providing compounds which promote staling such as lipids or providing compounds which give reducing power to shield the wort and beer from oxidation. (e.g. compounds such as melanoidins and polyphenols;)

Brewhouse

Mash and wort oxidation has been the subject of considerable study and most of the brewhouse manufacturers have designed brewhouse operating and transfer systems to minimize the uptake of oxygen:

- Mashing and mash transfer systems to the bottom of the vessels
- Sparge and lauter re-circulation systems to introduce the wort below the liquid level.
- Avoidance of systems with forced aeration during boiling.

All these designs reduce oxygen ingress. However by far the largest uptake of oxygen comes from the brewing water (in mashing and sparging) which unless de-aerated will contribute around 30 ppm oxygen per kilo of malt mashed.

Brewhouse oxidation produces a measurable increase in oxidised compounds (lipids and polyphenols) but it is not certain how much this may contribute to ageing in the packaged beer. Oxidation will use up the reducing potential in the mash and wort, producing beers with lower reducing potential, which would notionally be more prone to more rapid oxidation.

There are a number of contradictory articles in the literature dealing with wort and mash oxidation. In many systems the wort or mash was artificially aerated to produce an unnatural result. Research on a pilot scale looking at mash oxidation by comparing normal brewing (less than 40 ppm oxygen per kilo of malt mashed) with very reduced oxidation (1 ppm oxygen per kilo of malt mashed) did not produce beers with improved flavour stability. However some process differences between the beers was noted:

- A better lauter tun run off was obtained with less oxidized mash with lower levels of oxidised protein as a result of less disulphide bridging between the polypeptides. Oxidised proteins polymerise by forming disulphide bridges (see Figure 3).
- Poorer beer foam performance was observed from the lower oxidised mash. The mash with less mash oxidation produced a beer with a higher reducing potential.
- Higher levels of oxidation increased the colour of the wort and beer produced. The beer produced from mash with higher levels of oxidation had lower beer polyphenol content (not at a significant level)

Fermentation

Air or oxygen is added just prior to fermentation to stimulate yeast growth. Live active yeast has a huge capacity to adsorb oxygen and it is rapidly assimilated before any chemical oxidation can occur. At the end of fermentation the green beer is totally anaerobic and free from oxygen.

Beer Processing

After fermentation beer is venerable to oxidation. While active yeast is still in suspension much of the oxygen can be scavenged. In the absence of active yeast, oxidation will occur leading to the staling reactions described earlier. Measures must be taken to avoid oxygen ingress:

- All tanks should be blanketed with inert gas (carbon dioxide or nitrogen)
- De-aerated water should be used to chase through beer transfers.
- All additions and dilutions should use de-aerated water.
- Flush all bends and fittings with de-aerated water
- Attention should be paid to prevent leaks at pump surfaces, joints etc where air can gain access
- Pipework should be designed to be fully purged.
- Processing large volumes of beer into large tanks helps minimise oxygen pick up.
- Automation should be used to turn off pumps when vessels and dosing pots run empty.
- Inert gas used to undercover flush of centrifuges

Fig 3. Oxidation of proteins through the formation of disulphide bridges

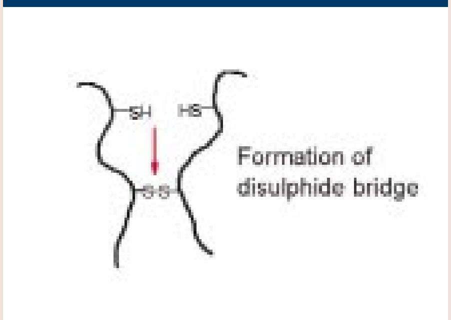
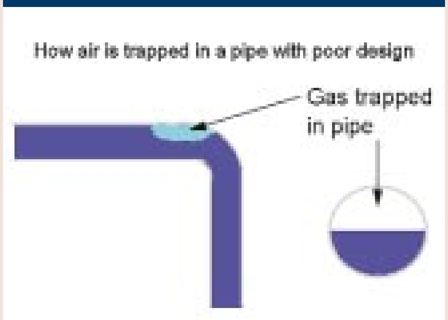


Fig 4. How air can be trapped in a bend with poor design



- Effective oxygen removal from de-aerated water.

Poor pipework design can lead to oxygen pickup (see Figure 4).

Through careful operation and good process designs oxygen pickup can virtually eliminated. Beer should be presented to the packaging lines with less than 50 ppb dissolved oxygen.

Packaging (small pack filling)

Inevitably during small pack filling (bottling and canning) a small amount of oxygen pick up is inevitable. Developments in packaging line design have been made to minimise exposure to oxygen:

- Counter pressure filler bowl with inert gas
- Flushing can or double pre evacuation of bottles with inert gas
- Fobbing control and gas flushing to reduce air in head space
- Packaging lines surrounded by inert gas tunnels
- The use of oxygen scavenging barrier crown corks can provide protection against oxidation,

With the latest technology designed to reduce oxygen pickup it is now possible to produce beers with less than 100 ppb total in package oxygen. All Brewers should be capable of achieving less than 500 ppb. total in package oxygen.

Keeping the oxygen content down in the finished product makes a very significant contribution to delaying the onset of staling.

Anti-oxidants

The brewer can also increase the anti oxidant capacity of the beer. Providing the beer with compounds, which compete with flavour active compounds to be oxidised by the oxidising agents present:

- As stated earlier raw materials have a profound effect on the staling capacity of a beer. The use of dark malts and high hop grists give beer better keeping qualities.
- Naturally conditioned beer has yeast present in the final package and the yeast cells are able to scavenge residual oxygen picked up during filling.
- Sulphur dioxide is an anti-oxidant produced during fermentation. The levels of naturally occurring SO2 can be boosted during fermentation by deceasing yeast growth through:
  - Lower fermentation temperatures
  - Reduced wort aeration
  - Reduced pitching rate
  - Reduced original gravity
  - Increased sulphate additions to the mash
  - Producing bright worts
- Anti oxidants such as sulphur dioxide and ascorbic acid (or sodium ascorbate) can also be added to the beer, usually prior to packaging. It is found that the two anti-oxidants added together is the most effective method of use.
- Avoidance of metal ions, particularly iron and copper will reduce the rate of oxidation. This can be controlled through specifications on materials such as syrups and kieselguhr, and by diverting pre-coat liquors to drain to wash the filter bed out.,

Beer in Trade

Most beer leaving the Brewery shows little signs of ageing. It is during storage in the supply chain that flavour deterioration occurs.

Most light beers (Lagers and Pale Ales) show symptoms of ageing within three months of packaging even though they are given a nominal shelf life of 12 months, sometimes more. The flavour stability of darker beers are better for the reasons listed earlier.

Process improvements make a significant contribution to improving the flavour stability of beer in trade, but the major improvements could result through better handling of beer in the supply chain;

- Does the beer have to have a 12-month shelf life ? The supermarkets can turn perishable products around in a few days.
- The best before date gives limited information about the product. One major Brewer is now providing a packaging date enabling consumers to judge the freshness of the beer.
- Cold / cool storage of beer in the supply chain reduces the rate of oxidation.
- If cold storage cannot be achieved then it is certainly necessary to avoid warm storage. Beer held at 30°C will stale 25 times faster than the same beer held at 0°C.

However there is a note of caution. Not all consumers dislike the "oxidized/stale " tastes of beer. Many North American consumers associate this taste with imported brands from Europe and other areas and are less impressed when presented with the fresh beer!

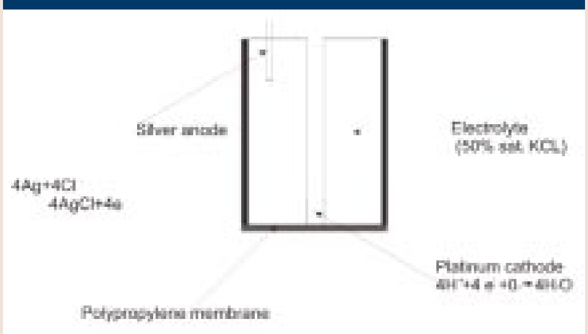
Measurement

To be able to control something it is necessary to be able to measure it.

There are a number of reference methods in IGB list of recommend methods. Two methods that are commonly use in the industry are:

- Shake out air methods use caustic soda to adsorb the CO_2 and measures the head space air. This method cannot be used with nitrogen gas top pressure or mixed gas carbonation.
- The Indigo carmine method, where the indigo carmine dye reacts with oxygen to produce a blue colour.
- The platinum electrode which is capable of detecting oxygen in solution and is available for both laboratory and in line use.

Fig 5. The platinum electrode



The platinum electrode is the industry standard for measuring dissolved oxygen in line and in the laboratory (see Figure 5).

However "It is not the oxygen that we should measure …rather the impact of the oxygen". It is therefore necessary for Brewers to taste their products through the shelf life to assess how well the beer survives ageing.

Summary

Oxygen has an impact throughout the malting and brewing process.

It would not be possible to malt barley or ferment wort without the contribution from oxygen, and without oxygen we would not be around to enjoy the beer either !

However, oxygen reacts with many compounds present in mash, wort and beer, which have an impact on the final and keeping quality of the product.

There is still some disagreement over the importance of oxidation of the mash and wort production, but there is no disagreement that oxidation post fermentation is damaging to both the taste and colloidal stability of the beer. ■

● Further Reading

1. Moll *"Beers and Coolers"*

Prof Dr Annemuller G. et al *Brauwelt International* Volume 19 April 2001

O`Rourke T Australia and NZ Institute of Brewing Convention March 1992

Prof Bamfort C. *Brewers Guardian* April 2000

Kaneda H. et al *MBAA Technical Quarterly* 1999 No 1.