Hops and hop products

Although hops were not added to the first beers, now all modern beers are hopped.
Hops contribute to the flavour and appearance of beer.
They provide beer with its characterististic bitterness and aroma.

Technical Summary 11

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Continuing this series of technical summaries for the Institute & Guild's AME candidates.

The function of hops in brewing.

Hops are exclusively used to provide aroma and bitterness in beer. They add the following properties:

- Provide the bitter taste in beer (with alpha acid the principal precursor)
- The oils provide aroma.
- Modify yeast performance during fermentation.
- Contribute to beer texture (mouth-feel)
- The bacteriocidal properties protect beer against some biological spoilage organisms.
- Reduce over foaming during wort boiling.
- Aid in protein coagulation during the boil.
- Act as a filter medium when a hop back is used.
- Foam active agent in beer improving foam performance and cling.
- Cone hops contribute tannins which may increase the reducing power of a beer, and hence its resistance to oxidative staling. Tannins may also contribute to a tendency to produce chill haze.

Hops *(Humulus lupulus)* belong to the family *Cannabinaceae*.

The part of the hop plant used for brewing is the inflorescence (that is a modified branch) of the female plant, which matures to produce a strobile - commonly called a cone. This contains small yellow granules called lupulin glands. These glands contain the hard and soft resins and the essential oil. The soft resins are converted into the bitter substances in the beer and the essential oils impart the "hoppy" character .

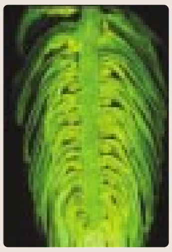

Figure 1. Cross section of a hop cone.

It is the soft resins (soluble in hexane) that are most important in brewing, and these consist of alpha acids, beta acids and un-characterised soft resins.

The alpha acids and beta acids provide the bittering principals. These acids are largely insoluble in cold water and are more soluble in boiling water. However during wort boiling, the alpha acids are isomerised into iso-alpha acids that are much more soluble.

The beta acids are less soluble and are largely unchanged during wort boiling, and hence contribute little to the final bitterness of the beer, unless they are oxidised to hupulones in which case they will also contribute bitterness. See Figure 2.

The amount of alpha acid added is calculated from the weight and concentration in the raw hops or hop product used, and when using hops added to the kettle, the utilisation decreases throughout the brewing process:

Typical recovery rates of iso-alpha acid during brewing with cone hops.

Process Stage	Recovery of alpha acid
At the end of Wort Boiling	50 – 55%
At the end of Fermentation	35 – 40%
Bright Beer	25 – 30%
After dispense	20% of bitterness can segregate into foam.

The reasons for loss of iso-alpha acid from conventional hops in brewing are:

- The nature (duration and vigour) of the boil.
- Only around 50% is isomerised from alpha to iso-alpha acid during wort boiling.
- Iso-alpha acid is absorbed by the trub (hop debris/protein) during hot wort clarification.
- Iso-alpha acid is absorbed by the yeast and lost in beer foam (fermenting heads)
- Iso-alpha acid is lost in beer foam and absorption by the final filters.

Whole hops

Whole hops are added to the kettle, and separated through a hop strainer or hop back. Although used by a number of traditional brewers they can be difficult to handle and store in a modern brewery, and many brewers prefer to use hop products.

Whole hops cones are cleaned to remove unwanted stems and leaves before being dried and baled. They are generally stored cold (circa 5°C) to reduce the loss of alpha acid.

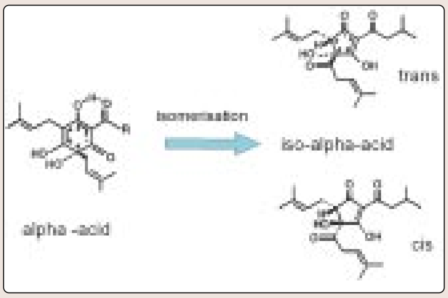

Figure 2. Isomerisation of alpha acid into iso-alpha acid.

Since they are not usually blended each bale will have a unique alpha acid content depending on the variety season and growing area.

Whole hops also tend to give the poorest alpha acid utilisation during boiling (25% to 30%) since they have higher quantity of vegetative material and the alpha acid is less readily available. The higher the content of vegetative material, i.e. the greater the bulk of hop debris, then the greater the potential to retain wort with higher wort losses during wort clarification at the end of boil. There is usually

Table 1. Summary of benefits from using whole hop

Preparation	Bales from growers
Major use	Bitterness and aroma
Method of use	Direct addition to kettle during boiling or cask for dry hopping

Composition	%	
Total resins	15	**Advantages:**
Soft resin – alpha acids	(8)	Traditional form
beta acids	(4)	Free from extraction solvents
Hard & uncharacterised resins	(3)	Standard aroma & bittering product
Essential; oils	0.9	Aids hot break formation & settling
Tannins/polyphenols	4	
Protein (N x 6.25)	15	**Disadvantages:**
Water	10	Bulky and expensive to store
Monosaccharides	2	% alpha and aroma varies each year
Lipids and waxes	3	Subject to loss of alpha and aroma on storage
Amino acids	0.1	Possible contaminates from debris and pesticide
Pectin	2	Low utilisation (25 – 30%)
Ash	8	Higher losses of wort in spent hops
Cellulose & lignin	40	Costs of disposal of spent hops

Resins and oils will vary according to variety

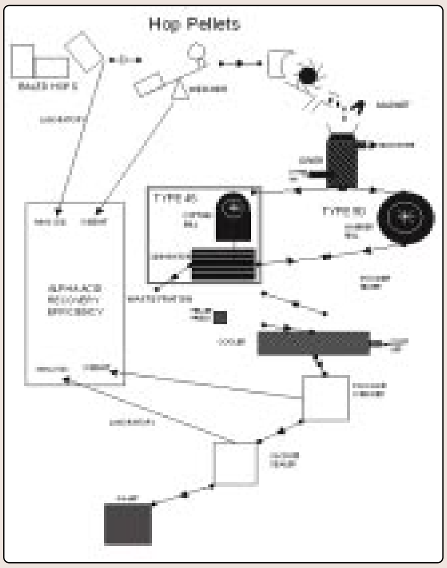

Figure 3. Manufacturing process of pelletised hop products.

an associated cost to remove the spent hop material. See Table 1.

Pelletised Hops

Pelletised hops are made by milling whole hops and compressing the hops into pellets. These are generally packaged under vacuum or in an inert gas such as nitrogen to reduce the rate of deterioration. Pelletised hops are available as:

- regular pelletised hop, (type 90 pellets)
- enriched pellets (type 45 pellets), where some of the vegetative (non-alpha acid bearing material) is removed to give a constant product with a much higher alpha acid. See Figure 3.

Hops of the same variety but with differing alpha contents are often blended to give a standard product with a constant alpha acid appropriate for each variety and growing season.

Pellets are added to the kettle where the alpha acid is isomerised during wort boiling.

Table 3. Summary of benefits from using iosmerised hop pellets

Preparation	Magnesium oxide is added to milled hops and gently heated before being palletised and vacuum packed
Major use	Bitterness with good aroma properties
Method of use	Direct addition to kettle during boiling – can be added part way through the boil

Composition	
Similar to Type 90 pellets	**Advantages:**
	Similar to hop pellets
Almost all the alpha acid is converted to	Better keeping properties
the equivalent magnesium iso-alpha acid.	Better utilisation (50 to 60%)
Slight reduction in beta acid content	
Presence of magnesium and magnesium oixide	**Disadvantages:**
	Similar to hop pellets
	MgO could be perceived as a chemical addition
	Low utilisation (25 – 30%)

Pelletised hops generally yield 2 to 3 % improvement in utilisation over the equivalent whole hops (between 27% and 32% utilisation – but sometimes up to 40%).

Milling makes the alpha acid more readily accessible, with less vegetative material there is also a lower entrained wort loss, which can be further decreased through a trub recovery system.

Wort clarification is usually carried out in whirlpool vessel and the trub (including the spent pelletised hops) is often recovered and sold along with the spent grains. See Table 2.

Isomerised hop pellets

The pellets for isomerised hop production are produced in a similar way to standard pellets (see Figure 3) with about 2% magnesium oxide added during the pelletising process. These "stabilised" pellets, packed in an inert atmosphere are heated to 50°C for approximately 14 days, when up to 99% of the alpha acids are isomerised in situ, giving wort utilisation rates of 80 to 90%, and final beer utilisation rates of up to 70%

The handling and processing of isomerised pellets is similar to regular pellets. See Table 3.

Hop Products

Beside whole hops (hop cones) and pelletised hops, other hop products and extracts are used either as alpha acids added to the kettle or as isomerised iso alpha acids added to the kettle or after fermentation. Hop oils and hop bittering products can be added after fermentation to give a dry hop character, or to modify the character of the final beer.

Processed hop products represent a convenient and controlled system for adding both bitterness and aroma character to beer, and can be useful for adjusting beers produced outside specification.

Their benefits include:

- Reduced bulk
- Reduced transport costs
- Reduced storage costs
- Potential for automating hop addition in the brewery
- Uniformity - (can be standardised to % iso-alpha acid value)
- Greater stability (long term storage)
- Improved utilisation (pellets up to 10%: Post fermentation bitterness up to 70% improvement)
- Reduced beer and wort losses
- Improvements in beer quality and consistency
- Decreased level of polyphenols/tannins
- Decrease (or absence) of nitrates
- Decrease (or absence) of pesticide residues

These potential benefits have to be balanced against:

- Increased production/processing costs
- Possible inclusions of solvents and toxic residues (not with CO_2 extract)
- Purist/public attitudes to the use of processing and solvents
- Possible adverse effects on beer quality and taste.

All of the products are derived from whole hops in the first instance, and are generally used to help the Brewer overcome the effects of aging, storage and consistency problems.

Hop extract

It is possible to extract the soft resins in a variety of solvents, thus obtaining a concentrated solution of alpha and beta acids as well as uncharacterised soft resin.
Two typical solvent systems are used:
Organic: Principally Ethanol; and Hexane
Carbon Dioxide: Liquid and Supercritical Carbon Dioxide. See Figure 4.

Table 2. Summary of benefits from using pelletised hop

Preparation	Leaf hops are cleaned, milled, palletised and vacuum packed
Major use	Bitterness and aroma
Method of use	Direct addition to kettle during boiling

Composition	
Type 90 pellets – similar to leaf hop but may be	**Advantages**:
standardised for alpha	Traditional product
Lower moisture content	Free from extraction solvents
Better utilisation through ruptured resin glands	Standard aroma & bittering product
	Aids hot break formation & settling
	Significant reduction in volume
Type 45 pellets – increased alpha due to	Improved storage properties
concentration of lupulin gland.	Improvement in % hop utilisation
Between 40 to 50% of vegetative material	Easier disposal of spent hop debris
is removed	
Resin/oil concentration is approximately double.	**Disadvantages:**
	Bulky than extracts
	Possible contaminates from debris and pesticide
	Low utilisation (25 – 35%)

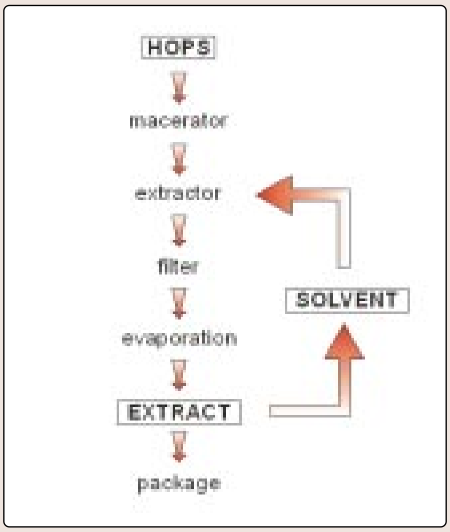

Figure 4. Process flow chart for the manufacture of hop extracts.

The main organic extractants are strong solvents and extract plant pigments along with the soft resin. After extraction the solvents are boiled off, to leave concentrated resins containing alpha acids for addition to the kettle. Solvent extracts are increasingly falling from favour because of perceived problems with residue, although ethanol does not have this disadvantage.

Carbon dioxide is a more selective extractant removing less of the water soluble components. Supercritical CO_2 (operating typically above 250 to 300 bar and below 40 to 45°C) has the properties of both gas and liquid, and is a more polar solvent extracting more plant material than the sub-critical CO_2. The latter often known as liquid CO_2 operating at 50 bar and 10 to 15°C is a relatively mild non-polar solvent, like hexane, but gives lower overall extraction efficiency with a higher yield of alpha acid. See Figure 5.

The immediate availability of the hop resins in the extracts added to the wort is favourable for utilisation (overall in the range of 35% - 45%), and the material is free from or has greatly reduced nitrate and pesticide residues. Liquid CO_2 extracts also contain much of the hop essential oils, but the immediate availability of the hop oils decreases their survival during boiling, which may be detrimental to beer flavour.

Standardisation of alpha acids in hop extracts (normally 30% alpha, but sometimes 25% or 45%) can easily be achieved. A "pure resin extract" (P.R.E.) is usually obtained first using optimum extraction conditions to produce the best yield of alpha acids from a particular batch of hops (normally in the range of 40 - 55 % alpha in the P.R.E. extract).

The P.R.E. is then diluted to the required standard before final packaging by the addition of either glucose or corn syrup, or, more rarely (because of storage stability problems) with a hot water extract of the hop material, which will contain some of the hop sugars, tannins, polyphenols etc.

Further fractions of carbon dioxide extract

Table 4. Summary of benefits from using hop extracts

Preparation	Resins and oils are extracted from the hops using solvents which are then driven off.
Major use	To provide bitterness to beer
Method of use	Direct addition to kettle during boiling

Composition	Whole hops	Organic solvent extract	Super critical CO_2	Liquid CO_2
Total resin	12 – 20%	15 – 60%	75 – 90%	70 – 95%
Alpha acid	2 – 12%	8 – 45%	27 – 55%	30 – 60%
Beta acid	2 – 10%	8 – 20%	23 – 33%	15 – 45 %
Essential oils	0.5 – 2%	0 – 5%	1 – 5%	2 – 10%
Hard resins	2 – 4%	2 – 10%	5 – 11%	None
Tannins	4 – 12%	0.5 – 5%	0.1 – 5%	None
Waxes	1 – 5%	1 – 20%	4 – 13%	01 – 10%
Water	8 – 12%	1 – 15%	1 – 7%	1 – 5%

Advantages:
Less bulk storage
Good storage properties (several years)
Improved utilisation (45 to 65%)
Reduced pesticide residues
Minimal wort/beer losses

Disadvantages:
Different brewing operation compared to whole hops
Solvent extract
Solvent residue (minimal)
Altered aroma profile
Presence of "chemicals"
Supercritical CO_2
Altered aroma profile
Highest cost of extraction
Possible impurities
Liquid extract CO_2
Lower yield than supercritical
Higher cost per unit alpha than other extracts.

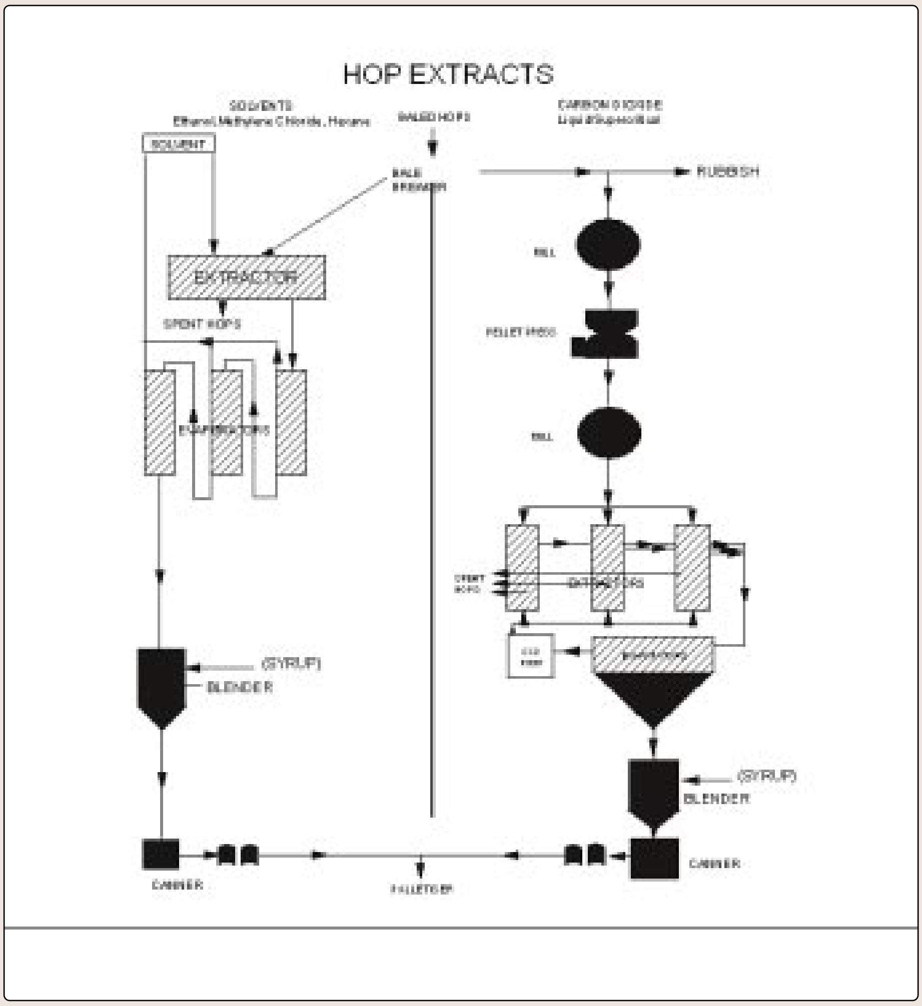

Figure 5. Schematic of plant used to manufacture of hop extracts.

Table 5. Summary of benefits from using isomerised kettle hop extracts (IKE)	
Preparation	Pure resins undergoes controlled heating with alkali metal salts which isomerises most of the alpha acid.
Major use	To provide bitterness and late hop character to beer
Method of use	Direct addition to kettle during boiling
Composition	Similar to pure resin extract- 90% of the alpha acid is isomerised
Supercritical CO_2	Essential oil components absent
Liquid extract CO_2	High levels of purity
	Contains similar amounts of essential oils as the leaf hop

Advantages:	Disadvantages:
Easy to handle and store	Restricted to those varieties processed
Standardised constant product	Considered to be "chemically processed"
Precise control of bittering	
Retains aroma contribution	
High utilisation (50 to 75%)	
High purity/ minimal residues	
Minimal wort/beer losses	

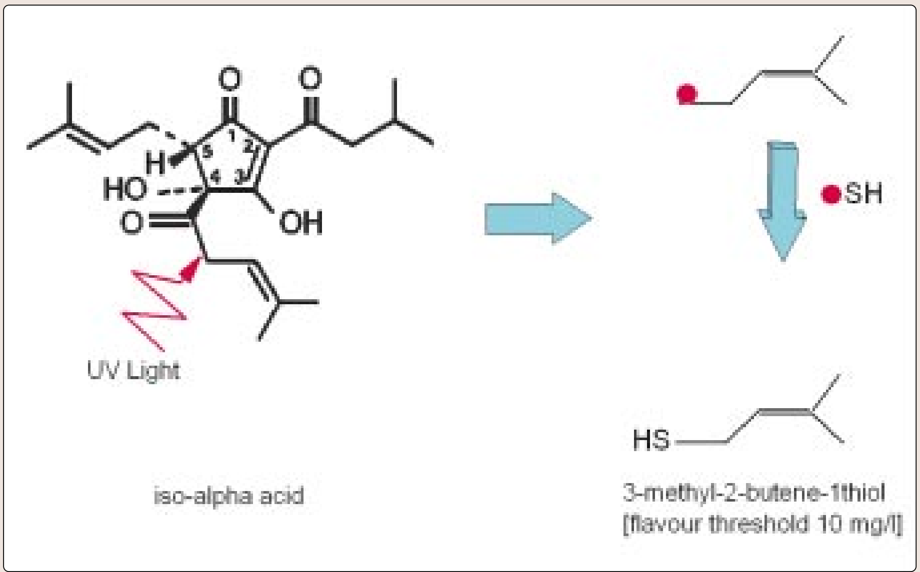

Figure 6. Production of light struck flavours (3-methyl-2-butene-1-thiol).

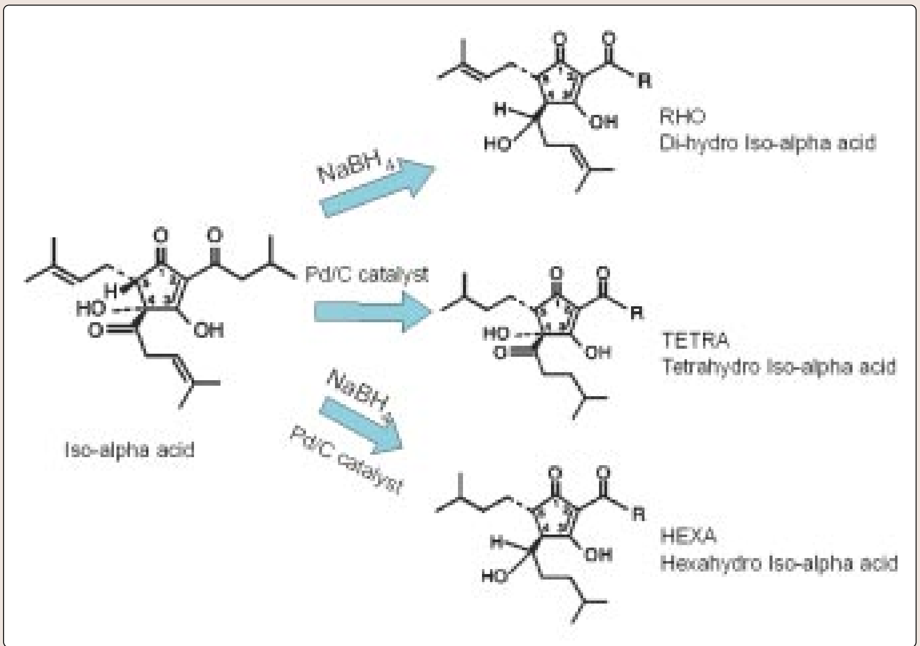

Figure 7. The production of reduced iso- alpha- acid compounds from iso alpha acid.

can be used for separating the hop oil fraction from whole hops, so that the oils can be used for dry hopping. The alpha acid can also be used to produce isomerised kettle or post fermentation hop bittering extracts, thus enabling all the brewing properties of the hop to be recovered. See Table 4.

Isomerised kettle hop extracts.

In order to improve utilisation it is possible to pre-isomerise the alpha acid before wort boiling. Alpha acid can be isomerised by heating with an alkali metal carbonate while still in the resin form to produce pre-isomerised kettle extract (IKE). If it is made with potassium salts it is usually called PIKE; if it is made with magnesium salts, MIKE.

The benefit of isomerised kettle extract is its ease of use, standard utilisation being around 70%, but it is relatively expensive. See Table 5.

Isomerised hop extract.

As well as adding the isomerised extracts to the kettle where there are still losses due to absorption by the trub and yeast, it is possible to add isomerised extracts post fermentation (PFB - post fermentation bitterness), when the utilisation of alpha will be higher.

It is usual to use a pure alpha acid, which has been separated from the soft resin, purified and isomerised externally to produce potassium or magnesium salts of the iso-alpha acid by heating. The isomerised extract is water based and is standardised to 20% or 30% isomerised iso-alpha acids from which a utilisation of 70% to 95% or greater can be expected.

The material left behind in the soft resin is called the "base extract" and contains oils, beta-acids, and other resin materials plus impurities; it is often added to the kettle during boiling to:

1. prevent excess foaming or over boiling
2. to add tannins and hop oils
3. to provide a source of non isohumulone bitterness
4. to provide hop compounds to ensure fermentation proceeds normally

As PFB isomerised extracts contain only iso-alpha acids, they contribute no flavour character other than pure bitterness to the beer.

The extracts are often used to adjust for lack of kettle bitterness or to supplement non-isomerised hops in high gravity brewing (thus achieving better utilisation).

When PFB isomerised extracts are used as the sole source of bitterness, base extract should also be added to the kettle to give other elements of hop character to the beer. See Table 6.

Reduced hop extract

In the presence of sunlight (UV/visible radiation), conventionally hopped beers produce a "skunky" or "light struck" flavour. For this reason many beers are packaged in light proof or brown glass which is opaque to the radiation. See Figure 6.

Light struck flavours develop when the iso-alpha acid molecule splits stimulated by UV light, and the free side chain bonds with a free sulphur radical. If the weak double bonds are reduced the iso-alpha acid cannot be photolysed and the reduced hop compound is not susceptible to the light strike effect.

A variety of reduced compounds have been developed from both alpha and beta acids which are not prone to light struck taints while at the same time providing bitterness to beer. The mechanisms and structures are shown in Figure 7.

As well as providing different levels of bitterness, some of the reduced humulones have an effect in enhancing beer foam character.

The products are usually marketed at concentrations of between 5% and 20% in aqueous solution.

If a brewery uses clear glass and reduced iso-humulone, it is necessary to exclude all sources of conventional hop (iso-alpha acid) below 0.2ppm. Iso alpha acid can be carried over from all vessels, pipework and in pitching yeast. It is usual to keep a pure strain of yeast or use freshly cultured yeast to avoid any carry over.

If it is only being used for its foam enhancing properties, the reduced iso material may safely be used in conjunction with conventional hopping regimes. See Table 7.

Table 6. Summary of benefits from using isomerised (post fermentation bittering (PFB) extract

Preparation	Alpha acid extract from the resin is convert to alkali metal salt of iso-alpha acid in buffered water solution.
Major use	Provides all parts of the hop bitterness
Method of use	Added in line post fermentation

Composition	%	**Advantages:**
Alpha acids (HPLC)	0 – 0.8	Easy to handle and store
Beta acids	0 – 0.3	No aroma contribution
Aroma compounds	absent	Standard bittering product
Iso alpha acid (30% solution)	29 - 31	High utilisation (70 – 95%)
Potassium carbonate buffer	68 - 70	Easy adjustment of bitterness
Specification		**Disadvantages:**
pH (1% solution)	9.0 – 9.5	Expensive
Haze (1% solution)	0 – 5 EBC	No hop aroma contribution
Gushing test	None	Reduced kettle hop addition which contributes to hot break
		Reduced hop character in beer
		“Chemically processed”

Table 7. Summary of benefits from using reduced hop compounds

Preparation	Reduction of iso-alpha acid or beta acids
Major use	Light strike resistance and foam improvement in beer
Method of use	Added post fermentation

Advantages:	**Disadvantages:**
Traditional form	Costly
Free from extraction solvents	Utilisation lower (45 – 55%)
Standard aroma & bittering product	Chemically processed
Aids hot break formation & settling	If aroma is required it has to be added separately

The reduced iso compounds have different benefits

Reduced iso product	**Bittering power**	**Foam stability**
Standard iso alpha acid	100	Standard +
Dihydro - iso alpha acid	60 – 80	Much greater +++
Tetrahydro- iso alpha acid	160 – 180	Greater ++
Hexahydro- iso alpha acid	100	Standard +

Resins and oils will vary according to variety

Table 8. Summary of benefits from using hop oils and late hop essence

Preparation	The oil fraction from whole liquid CO_2 extraction of hops is further extracted and purified by vacuum distillation. Essences are fractionated from whole oil by column chromatography.
Major use	Enhance hop aroma and flavour in beer
Method of use	Added post fermentation

Composition	
Hop oils	Pure varietal oils or blends, semi refined
Late Hop Essence – Spicy	Principally terpenes and sequiterpenes
Late Hop Essence – Floral	Principally ketone fraction

Advantages:	**Disadvantages:**
Easy to handle and store	Oil require top be emulsified before use
Standardised constant product	Essences are very costly
Available in variety of specific or generic forms	Some drinkers can detect the difference in dry hop character between hop oils and whole hops
Provides means of precisely adjusting and controlling late hop character	Extraction dosage rates are critical
Less change in hop character over time than with cone hops	

Hops and hop essence

Most of the hop products considered so far have been used to enhance the bitterness fraction in beer, but hops are also a source of hop oil aroma and these can be separated by steam distillation or by CO_2 extraction. The oils are ideal for post fermentation addition where they give dry hop aroma to beer, retaining much of the aroma character of the original hop variety.

Hop oils are usually added in the form of an emulsion (with a food grade emulsifier), marketed in concentrations between 1,000 and 10,000 ppm of pure oil, or by re-dissolving in liquid CO_2 and directly injecting this solution into a beer main.

Other developments of hop oil addition techniques involve the adsorption of oils on to the surface of finely divided silica, and the retention of oils inside the ring structure of b-cyclodextrin molecules. Both these methods entrap the oil in a solid (powder) form, which readily releases the oils in to beer on contact with water.

With column chromatography it is possible to fractionate the whole hop oil into late hop essence, which may itself be divided into spicy and floral fractions:

- Late hop essence Spicy – contains terpene and sesquiterpene oxides which produces spicy flavour in beer, improves mouthfeel and enhances perceived bitterness.
- Late hop essence Floral - contains ketone fraction which imparts light floral notes improving the fragrance rather than the taste of the beer. See Table 8. ■

● Further Reading

Neve R.A. – *Hops* published by Chapman and Hall

IoB Blue Book on Hops

O'Rourke T – *IOB Blue Book* – Brewhouse and Brewing Materials – (in print)

Morris Hanbury Jackson LeMay Ltd. technical literature

Brewing Science Vol 1 ed J.R.A. Pollock – various sections

Malting and Brewing Science – Hough, Briggs and Stephens

New Brewer July 1994

Moir M (1988) Development in Hop Usage, *Ferment* Vol 1 No 3,

O'Rourke T – Back to Basics – *Brewers Guardian* April 1998.