PRODUCTION OF XANTHOHUMOL ENRICHED HOP EXTRACTS USING CARBON DIOXIDE AS SOLVENT AT PRESSURES UP TO 1000 BARS

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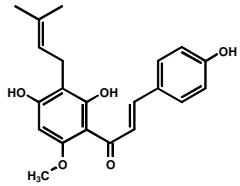

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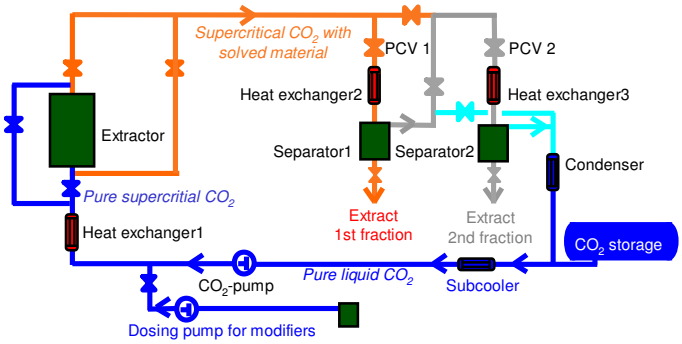
Introduction
Hop polyphenols cannot be extracted with carbon dioxide under the conditions used for common hop extracts destined for the application in the brew house. Also the prenylated flavonoid xanthohumol belongs to this substance group and it is not extractable at 250 bars. Xanthohumol has shown a significant anticarcinogenic potential in in-vitro tests and at present clinical trials are carried out to try to confirm this in-vivo (1).
Two possibilities using solvents with different polarities for the enrichment of xanthohumol are described (2). Either an ethanol hop extract is extracted with carbon dioxide or the spent hops of the extraction with carbon dioxide are extracted by means of an ethanol/water mixture to separate xanthohumol from the hop bitter acids.
In both cases at least two solvents are needed to utilise their different polarities. And furthermore the first method requires a carrier material as an aid. Moreover an alternative method is suggested using only carbon dioxide as solvent.

Extraction
It is well known that the solubility of substances in supercritical carbon dioxide depends on the pressure and temperature of the solvent. Higher pressure and therefore higher density often improves the solubility of substances. Beyond this changes in interactions allow to extract molecules which are difficult to dissolve at lower pressures. Most of the larger production facilities work with pressures up to 300 bars. The principle of the plants looks similar according to the following scheme.



Process
The pump compresses the CO_2 to the desired pressure and the solvent is tempered to extraction conditions in the heat exchanger 1. The carbon-dioxide flows either from the bottom to the top of the extractor or vice versa. The plant can be operated with a 2-step separation or with 2 parallel separators.
The loaded gas is depressurized at the PCV 1 (pressure control valve) to the separation pressure of the first separation step. Heating or cooling follows in heat exchanger 2 to adjust the separation conditions. Parts of the dissolved material fall out and are collected in separator 1.
At the PCV 2 the gas pressure from the separator 1 is reduced to the CO_2 storage pressure and the carbon-dioxide is set to the required temperature of the second separation step by heat changer 3. The substances are separated in separator 2.
The regenerated solvent is then liquefied in a condenser and subcooled and recirculated to the CO_2 pump.
A dosing pump allows additions of modifiers between CO_2-pump and heat exchanger 1 to change the solvent conditions of the carbon dioxide.
The following table shows the equipment of the extraction plant and the parameters which can be used for extraction and separation.

Plant design
The main data of the extraction plant are the following:

extraction volume:	50 l
extraction pressure:	70 - 1000 bars
extraction temperature:	5 - 120 °C
mass flow of CO_2:	180 - 300 kg/h
dosing of modifiers:	0 -7 l/h
separation pressure separator 1:	65 - 300 bars
separation pressure separator 2:	60 - 65 bars
temperatures in the separators:	15 - 120 °C
Separation, flow of solvent:	serial or parallel

The xanthohumol enriched hop extract
For the production of a xanthohumol enriched hop extract spent hops of the conventional extraction with carbon dioxide are extracted a second time by means of carbon dioxide but now at pressures up to 1000 bars (3).
The product is a dry dark green extract containing between 10 and about 30 % xanthohumol. The wide area of the xanthohumol content depends on the separation conditions chosen. With this technique about the half of the xanthohumol put in is extractable. Besides xanthohumol hard resin compounds such as humulinic acids and hulupones make up the essential parts of the extract. The extract is totally soluble in ethanol or in polyethylene glycol 200 and can be dosed in all stages of the brewing process or into non-alcoholic beverages.

Dosing of xanthohumol
Xanthohumol addition during wort boiling is insufficient because it is partly isomerised and only about 10 % as xantohumol (40% as xanthohumol + isoxanthohumol) can be found in the finished wort. But in order to guarantee normal shelf-life it is recommended to add it before filtration. Nevertheless it has to be taken in account that up to 90 % of xanthohumol can be absorbed at the filter. Dosing after the filtration may lead to turbidity in the beer or the beverage.
To improve the content of xanthohumol in beers brewed according the German purity law a process for wheat beers, which has been known for a long time, was applied in the St. Johann research brewery with two hl cast volume (3). The basic beer fermented to completion and maturated is mixed with bottom-fermented yeast before it is filled into bottles or kegs with 5 to 10 % feed mainly in the form of finished wort.
In the case on hand the xanthohumol enriched extract is mixed with a solution of hot yeast wort and afterwards it is cooled immediately. In the mixing tank the mixed feed is homogenised with the “basic beer” and this is filled into bottles or kegs. Through this process the excretions of xanthohumol are avoided during the brewing process and beers with xanthohumol contents of approximately 2.5 to 3 mg/l can be produced which complies with the solubility level of xanthohumol in beer.
Four beers with different bitter levels were produced according this process. All four beers were altogether awarded good marks when they were tasted in the well trained panel of the research brewery. The addition of xanthohumol to the mixed feed did not produce any negative or strange ratings.

Resumé
The technique to gain a xanthohumol enriched extract by means of using carbon dioxide as the only solvent is shown. Examples how to dose this extract to beer or beverages are described. The bitterness of beers and non-alcoholic beverages to which the xanthohumol enriched extract was added was judged as good.

References
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