J. Inst. Brew., January-February, 1992, vol. 98, *pp.* 37-41

LIQUID CO_2 AND ETHANOL EXTRACTION OF HOPS
PART I: EFFECT OF HOP DETERIORATION ON EXTRACTION EFFICIENCY AND EXTRACT QUALITY

By I. S. Daoud and S. Kusinski*

(Brewing Research Foundation, Nutfield, Redhill, Surrey, RH1 4HY)

Received 19 March 1991

Deteriorated hops were extracted with liquid carbon dioxide (LCO_2) and with ethanol. The degree of hop deterioration influences both the extraction efficiency and the composition of the resulting extracts.

Key Words: *Extraction, deteriorated hops, liquid carbon dioxide, ethanol, extract quality, beer flavour.*

INTRODUCTION

The process for extracting hops with an organic solvent or liquid carbon dioxide has to cope with a variable agricultural material. Apart from varietal and seasonal variations, the processor has to take into account the loss of alpha-acids (deterioration) during handling and storage, even though methods have been devised to minimise this deterioration, such as pelleting, vacuum packing and cold storage. Ideally hops should be pelletised as rapidly as possible after harvest and the pellets cold stored. In practice it is not always possible to extract all the hops in a very short time and for the plant to remain idle for the rest of the year. Consequently hops are stored under a variety of circumstances and may lose some of their alpha-acids.

The nature and extent of hop deterioration can influence extraction performance, the quality of the extracts and the flavour and quality of beers. In the present studies hops were allowed to deteriorate under ambient and cold storage conditions and then extracted with liquid carbon dioxide and ethanol to establish the effects of deterioration on:

(i) the efficiency of extraction, and
(ii) the composition of extracts.

EXPERIMENTAL

Storage of Hops

Commercial packs which contained 25 kg of hop pellets were stored at either ambient temperature (0-35°C) or in a chilled store at 4°C for up to 20 weeks. Three vacuum packs of hop pellets were prepared from the same batch of Target hops. Packs (P1) and (P2) contained pellets prepared two months after harvest, while for pack (P3) the hops were pelleted one month later. Prior to pelleting the hops were stored at ambient temperature. The packs were ruptured to speed up the rate of deterioration. Pack (P1) was stored at 4°C and packs (P2) and (P3) were stored at ambient temperature. At regular intervals during the storage trial the hops were analysed for alpha-acids content by LCV.

Methods of Extraction

(a) LCO_2 Extraction

A twin column pilot scale extractor was used to extract hops for 7-8 hours at a temperature of 7°C and at a pressure of 700-800 psig, using LCO_2 flowrates between 20 and 35 kg/hr. A description of the plant is given elsewhere.[4] Commercial hop pellets were milled through a 1 mm sieve using a Wiley Knife mill. Up to 4.3 kg of the powered hops were then packed into each extraction column, which could be used separately or in series. The liquid leaving the columns was passed into an evaporator at 40°C where the CO_2 was boiled off. The extract was collected periodically by opening the tap at the bottom of the vaporator. The gaseous CO_2 was passed through a column packed with activated charcoal before being discharged to atmosphere.

(b) Ethanol Extraction

Hop cones and pellets were milled through a 1 mm screen using a Wiley Knife mill. 1.5 kg of the milled hops was placed in a 10 litre glass jar and 5 litres of AR quality ethanol was added. The jar was fitted with a lid and the contents stirred vigorously for 5 hours at 30°C. The mixture was filtered through a Buchner Funnel and the residual hops were washed with 500 ml of ethanol. The filtrate was sorted for 24 in a refrigerator. The hop residue was returned to the glass jar, covered with 3 litres ethanol and mixed thoroughly before being left unstirred at 30°C. After a further 24 hours the contents of the glass jar were filtered through a Buchner Funnel and the residue washed with 1 litre ethanol. The two filtrates were combined and the resulting solution evaporated slowly under reduced pressure to remove the ethanol.

Analytical Methods

The following analytical methods were used for hops and hop extracts.

- Alpha-acids by LCV[5], Column Chromatography (CC)[3] and HPLC[2].
- Beta-acids by CC[3] and HPLC[2].
- Total resin[3], by solubility in methanol (ether extract).
- Soft resin[3], by solubility in hexane (ether extract).
- Hard resin[3], = total resin—soft resin.
- Hop oil[5], by steam distillation using IOB still.
- Fats and waxes[6], by solubility in cold methanol.
- Water content[1], by distillation.

RESULTS AND DISCUSSION

Methods of Analysis

The extraction efficiency is defined here as the percentage recovery of the alpha-acids present in the hops at the time of extraction. The recovery is measured as the difference in the alpha-acids contents of hops as charged and the spent hops. Although it is not specific for alpha-acids, the Lead Conductance Value (LCV) is the measurement most widely employed for adjusting hop rates, assessing hop utilisation and estimating the brewing value of many hop products. Specific methods for the determination of alpha-acids include CC and HPLC analysis. Due to the observed differences between LCV and the CC determination of the alpha-acids content of deteriorated hops, both analyses were used.

Accuracy of Data

Pellets of Target hops were milled and extracted with liquid CO_2 under normal operating conditions. Ten determinations each of the LCV content of hop powder, extract and spent hops, showed that the variations around the mean values were ±0.1%, ±0.5% and ±0.3% respectively. These variations resulted in the extraction efficiency having a variation of ±3%.

---

*Present Address: University of Nottingham, Chemical Engineering Department, Nottingham.

Maximum Extraction Efficiency

Examination of the results of a large number of exhaustive extractions, showed that the minimum residual LCV in the spent hops was around 0.5%. Therefore the achievable extraction efficiency has an upper limit less than 100% and depends on the LCV of the hops at the time of extraction. Fig. 1 shows the upper limit of the extraction efficiency as it varies with the LCV content of the hops at extraction. Imposing the effect of the variation in the analytical results, transforms the extraction efficiency line into a band. Most of the experimental extraction data fall within this band, with the exception of a few runs where 100% extraction efficiencies were recorded. Fig. 1 shows clearly that the maximum extraction efficiency which can be achieved increases slightly with the LCV of the hops at the time of extraction.

The Effect of Storage on the Degree of Deterioration

Fig. 2 shows that the rate of loss of LCV was greatest for the hops which were pelleted after 3 months of ambient storage (P3). The other ambient stored pellets (P2) showed an intermediate rate while the LCV of the cold stored pellets (P1) remained steady for some months before showing signs of deterioration. The degree of deterioration is taken as the percentage drop in the LCV of the hops, based on the value at the time of preparing packs (P1) and (P2), i.e. 2 months after harvest.

The loss of beta-acids with storage was found to be similar to that of the alpha-acids (Table IV). Previous work[7] on the storage of Bullion hops showed the same trend.

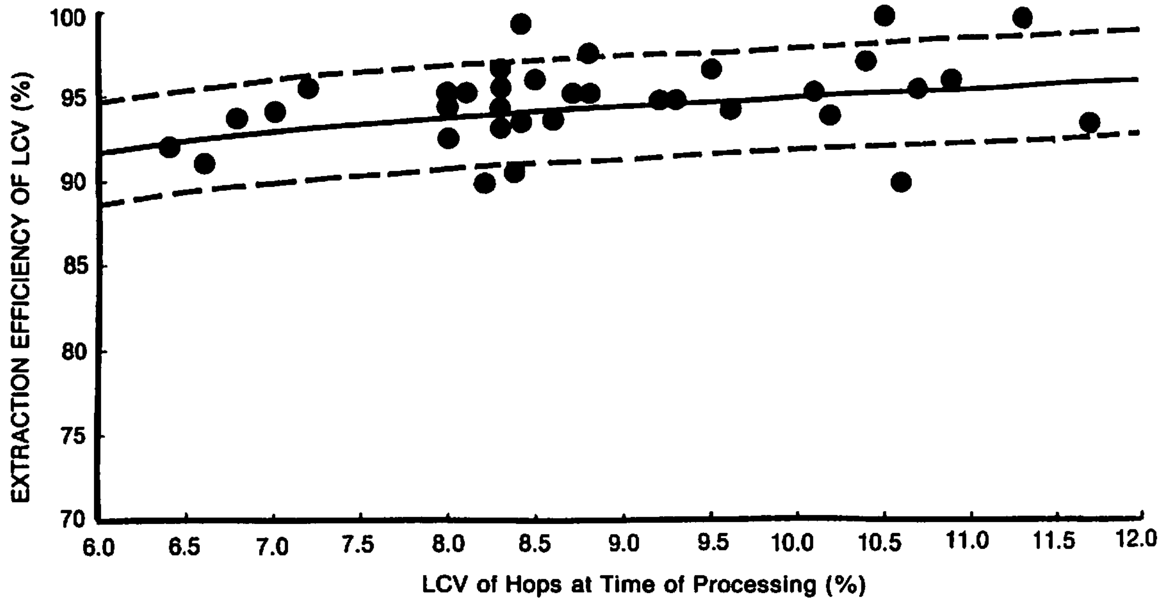

FIG. 1. Extraction efficiency versus LCV content of hops at processing, various hop varieties.

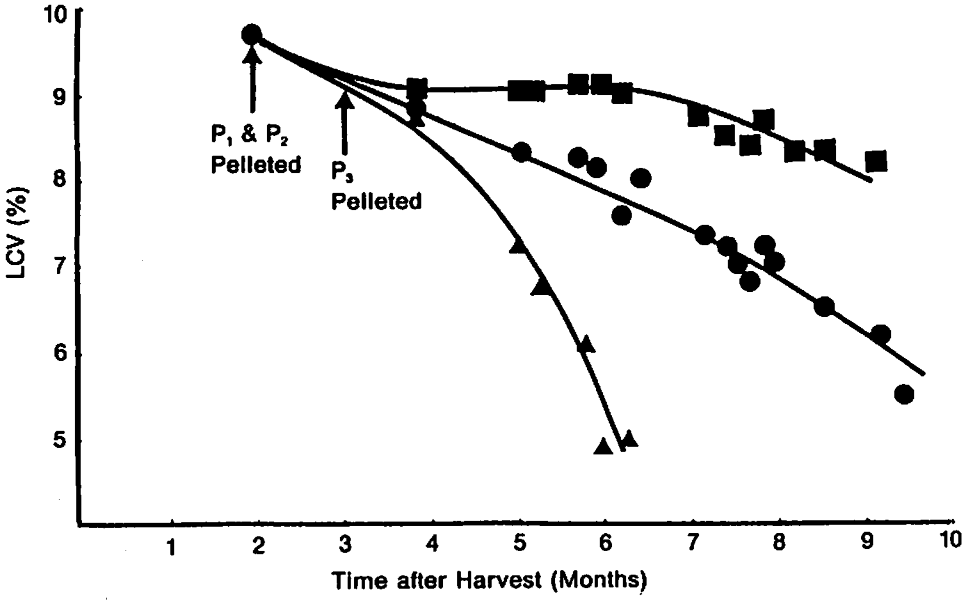

FIG. 2. Change in LCV content with storage period of Target pellets stored at ■: 4°C (Pack P1), ●: ambient temperature (Pack P2), ▲: hops stored at ambient conditions for 3 months before pelleting (Pack P3).

TABLE I. The Effect of Hop Deterioration on the Extraction Efficiency—(1982 Target Hops)

Storage Method	Period days	LCV	% Deterioration LCV**	Alpha-Acids Extraction Efficiency % LCV	CC
Cold	0	9.7	—	94	93
(P1)	62	9.1	6	96	94
	166	8.4	13	95	94*
Ambient	60	8.8	9	97	93
(P2)	104	8.3	14	94	92
	114	7.9	18	92	90
	129	6.8	30	94	91*
	137	5.1	47	86	80*
Ambient	56	8.7	10	96	94
(P3)	98	6.7	31	90	90
	125	5.2	46	85	82

*Determined by HPLC

**Based on alpha-acids at receipt (two months after harvest) of 9.7% by LCV and CC.

P1: Hops stored at ambient temperature for two months after harvest before pelleting, boxes ruptured.

P2: Hops stored at ambient temperature for two months after harvest before pelleting, boxes ruptured.

P3: Hops stored at ambient temperature for two months after harvest before pelleting, boxes ruptured.

Effect of the Degree of deterioration on Extraction Efficiency

The stored hops were extracted with LCO_2 at various intervals and the extraction efficiencies achieved are listed in Table I together with the LCV content of the hops at the time of processing. Table I shows that extraction efficiencies based on CC analysis are a little lower than those based on LCV. It can be seen from Fig. 3 that up to 30% deterioration, the extraction efficiencies fall within the band of maximum extraction efficiencies established on Fig. 1.

Clearly any deterioration has the effect of lowering the LCV content of hops at the time of extraction and therefore reduces the maximum achievable efficiency (Fig. 1). In addition very high levels of deterioration result in further lowering of the maximum achievable extraction efficiency since deterioration products interfere with extraction.

Liquid CO_2 and ethanol Extraction of Hops

A number of varieties of hops were extracted with LCO_2 and with ethanol to compare the qualities of the resulting extracts. The extractions were taken to exhaustion. The LCO_2 extraction efficiencies were the same in the case of milled pellets (Table II), while in the case of very deteriorated milled hop cones, the extraction efficiencies were higher with ethanol (see Table III). In both cases the extraction efficiencies based on CC and LCV analysis were found to be similar.

Ethanol extracted a greater weight of material from hop pellets than did LCO_2, i.e. the yields of total extract were higher (see Table II). However, since both solvents extracted all material measured as LCV, ethanol must extract additional non bittering material such as hard resins and chlorophyll.

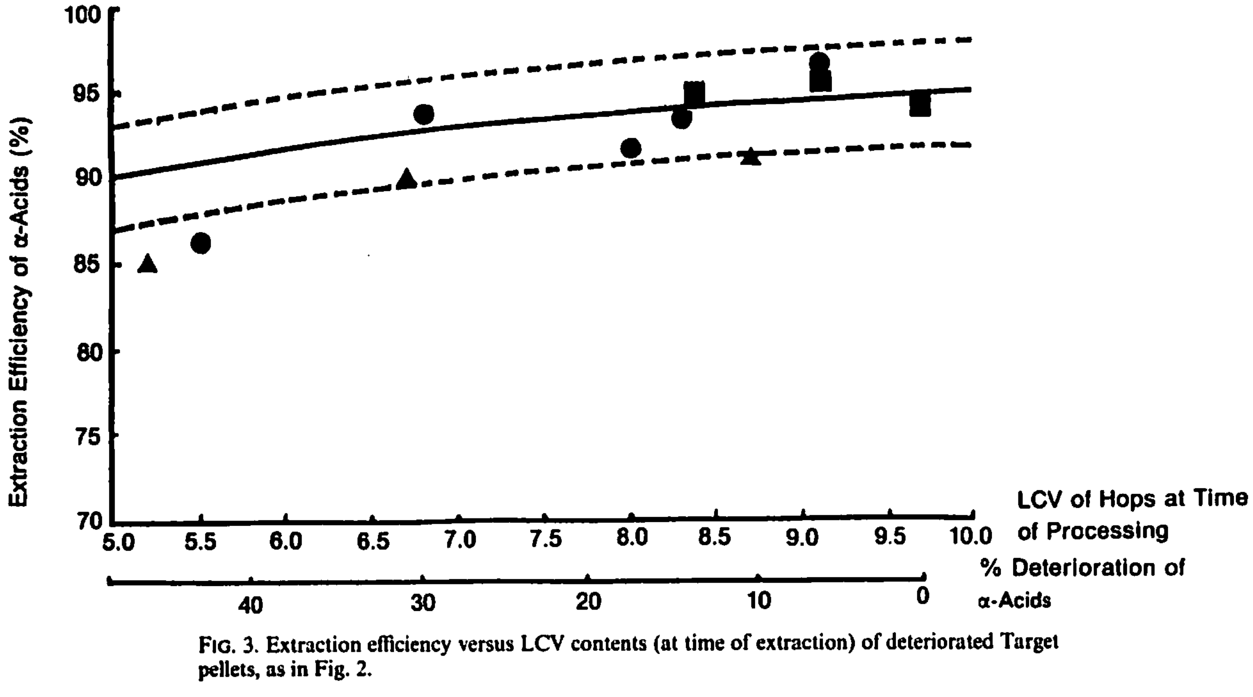

FIG. 3. Extraction efficiency versus LCV contents (at time of extraction) of deteriorated Target pellets, as in Fig. 2.

TABLE II. Extraction of Hop Pellets with LCO_2 and Ethanol

	LCV Received %	% Deterioration* LCV	Solvent	Extraction Efficiency % LCV	Extraction Efficiency % CC	kg extract/kg hops	Yield kg α-acids/kg hops LCV	Yield kg α-acids/kg hops CC
Yeoman Pellets	11.3	5.0	LCO_2	100	100	0.223	0.113	0.107
Cold Stored			E	100	100	0.322	0.113	0.114
Yeoman Pellets	11.3	5.8	LCO_2	100	100	0.227	0.107	0.111
Ambient Stored			E	100	100	0.351	0.100	0.104
Target Pellets	8.3	32.5	LCO_2	99	89	0.168	0.084	0.052
Ambient Stored			E	89	99	0.300	0.075	0.078

LCO_2: Liquid Carbon Dioxide.
E: Ethanol.
*: Based on LCV at harvest.

TABLE III. Extraction of Deteriorated Milled Cone Hops with LCO_2 and Ethanol

Hop Variety	LCV Received %	% Deterioration* LCV	Solvent	Extraction Efficiency LCV	Extraction Efficiency CC
Bullion	5.6	25.3	LCO_2	88	88
			E	99	99
Challenger	3.2	39.6	LCO_2	90	90
			E	98	95
Northdown	4.8	—	LCO_2	86	90
			E	99	99

LCO_2: Liquid Carbon Dioxide.
E: Ethanl.
*: Based on LCV at harvest.

TABLE V. Analysis of Liquid CO_2 and Ethanol Extracts—Yeoman Cold Stored Pellets

Solvent	Hops LCV %	Extract LCV %	Extract β-Acids %	Extract Oil ml/100 g	Extract Moisture %
LCO_2	11.3	50.7	24.7	5.8	2.1
E	11.3	34.1	18.8	3.2	2.8

Quality Aspects of Hop Extracts

(a) Effect of Hop Deterioration on the Quality of LCO_2 Extracts

The composition of LCO_2 extracts obtained from target hop pellets at various degrees of deterioration is shown in Table IV. The amount of alpha-acids in the extract changed from 47% in extract from the least deteriorated hop pellets to 31–36% in extract from the most deteriorated. This reflects the fact that as deterioration increases there is less alpha-acids available in the hops for extraction. The yield of total extract did not decline to the same extent as did the alpha-acids, and consequently the ratio of alpha-acids to total extract decreased with increased percent deterioration (Tables II & IV).

The fraction of uncharacterised material in the extracts increased from 10–15% as the deterioration progressed to a level of 36%. It is likely that the uncharacterised material recovered in the extract is a product of the deterioration process. A comparison of the results from the two batches of ambient stored pellets (P2, P3) shows that the extracts from P3 pellets (i.e. hops stored at ambient temperatures for 3 months before pelleting) had the greater amount of uncharacterised material at the same level of deterioration. This suggests that pelleting cone hops at harvest or as soon as practicable would avoid an increase in uncharacterised material in the extracts.

The beta-acids content of the extract also decreased as the percentage deterioration with respect to beta-acids increased (Table IV).

Overall LCO_2 extracts from Target hops would be expected to contain about 10–20% uncharacterised material providing that the deterioration of the hops being extracted is below 30% (based on the alpha-acids content at harvesting).

TABLE IV. The Effect of Hop Deterioration on the Composition of Resultant LCO_2 Extracts—(1982 Target Hops)

Storage Method	% Deterioration LCV	% Deterioration β-Acids* CC	Hop Oil ml/100 g	Moisture %	α-Acids %	β-Acids %	Fats & Waxes %	Total Soft Resin %	Uncharacterised Material %
Cold; (P1)	0	0	5.6	2.95	47.3	25.0	1.2	84.9	12.6
	13	17	4.4	1.68	45.3	23.8	1.3	84.5	15.4
Warm; (P2)	9	2	5.8	2.85	46.7	26.2	5.0	81.6	10.0
	30	4	3.6	2.10	42.5	28.7	4.1	89.0	20.0
	47	49	3.7	2.20	36.0	22.7	4.4	85.7	22.6
Warm: (P3)	10	13	6.2	2.14	44.2	22.6	3.2	82.8	16.0
	31	38	4.9	2.67	37.1	20.6	4.6	85.0	27.6
	46	68	5.5	0.80	30.9	17.3	4.4	84.1	35.9

P1, P2, P3: see Table I.
*Based on β-acids at receipt of 5.3% by CC.

(b) Liquid CO_2 and Ethanol Extracts

The analysis of the LCO_2 and ethanol extracts for Yeoman hop pellets is given in Table V. The proportions of alpha-acids (LCV), beta-acids and oil, in the LCO_2 extract is higher than the ethanol extract which is the result of the greater selectivity of LCO_2 as a solvent.

CONCLUSIONS

The maximum achievable extraction efficiency of alpha-acids depends upon the alpha-acids contents of the hops at the time of extraction. Specifically, maximum extraction efficiency increases with alpha-acid content. Consequently, hop deterioration leads to lower extraction efficiencies. This situation is exaggerated for highly deteriorated hops when the products of deterioration interfere with extraction. For example, with Target hops having deterioration levels in excess of 30%.

Hop deterioration also results in lower quality extracts as exemplified by lower percentages of bittering material and increased percentages of uncharacterised material.

The extraction of hops with ethanol and with LCO_2 provided similar recoveries of alpha-acids. Higher bulk extract yields are obtained with ethanol although the increase does not comprise bittering material.

Acknowledgements The authors thank the Director of the Brewing Research Foundation for permission to publish this paper, Miss M. Polack for some of the experimental work, and Mr I. M. Laws, Mr B. Blake and Mr J. Shaw for their technical assistance.

REFERENCES

1. American Society of Brewing Chemists, *Methods of Analysis*, 1976.
2. Buckee, G. K. *Journal of the Institute of Brewing*, 1985, **91**, 143.
3. European Brewery Convention, *Analytica*, 1975 (Revised 1980).
4. Grimmett, C. M., *Chemistry and Industry*, 1981, 359.
5. Institute of Brewing, *Analysis Committee, Recommended Methods of Analysis*, 1977 (Revised 1982).
6. Sharpe, F. R., Grimmett, C. M., Laws, D. R. J. and Bett, G. *Journal of the Institute of Brewing*, 1980, **86**, 234.
7. Whitear, A. L. *Journal of the Institute of Brewing*, 1966, **72**, 177.