STATE OF THE ART IN LOW-ALCOHOL BEER PRODUCTION

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ABSTRACT

Alcohol-free beers are usually characterized by a worty off-flavor and a lack of the pleasant fruity aroma found in regular beers. The available published analytical data on ester and aldehyde levels in alcohol-free beers confirm these defects. The comparison presented here shows that all processes currently used to produce this type of beverage fail to yield a satisfactory product. Neither ethanol removal nor limited fermentation is suited for producing a pleasant-tasting alcohol-free beer. New studies are needed to devise new strategies based on better identification of compounds contributing to the worty off-flavor and better knowledge of yeast physiology.

KEYWORDS

Alcohol-free beer, cold contact process, worty off-flavor, ester, carbonyl compounds

INTRODUCTION

Production of alcohol-free and low-alcohol beers is usually regarded as an answer to increasingly restrictive road and driver safety regulations. Belgian legislation contains provisions for two kinds of low-alcohol-content beers: beers with less than 0.1% v/v alcohol are termed "alcohol-free", and a threshold of 0.6% v/v is set for "low-alcohol" beers.

In 1988, the estimated market for low-alcohol beers was about 100,000 hl in Belgium and 3,000,000 hl in Europe (13). In 1992, the European production of alcohol-free and low-alcohol beers increased by 900,000 hl, these beers accounting for 4% of the European beer market (Brauwelt International 1993/III). Yet Belgian consumption of low-alcohol beverages decreased markedly from 1995 to 1996 (by 17 %; Le Journal du Brasseur, 1997), mainly owing to insufficient organoleptic quality: worty flavors, lack of body and aromas, occasional sulfide factors (10).

Brewing a low-alcohol beverage means deviating the yeast fermentation so as to limit the most abundant by-products without losing minor aromas like esters or fusel alcohols. This review compares the main industrial fermentation processes used in alcohol-free beer production and examines the chemical composition of such beers as opposed to regular beers.

PROCESSES FOR ALCOHOL-FREE BEER PRODUCTION

The most usual way to produce low-alcohol beers is to modify the normal brewing process so that fermentation is limited and almost no ethanol is produced (usually less than 0.5 % v/v, 17). "Stopped" fermentation (or checked fermentation), where the yeast is removed before full attenuation, can be distinguished from "limited" fermentation, where yeast metabolism is restrained. Usually, no extra plant or process is needed, but fine control of the process is required. In the cold contact process (CCP), alcohol-free beers are produced from usual worts cooled to 0-1 °C before pitching (30). Primary metabolism is slow under these conditions, although many biochemical reactions can take place. Carbonyl compounds suspected of imparting the worty flavor are partly removed while some esters are synthesized. Off-flavor adsorption may also occur. The pH does not fall as low as usual, however, so the wort must be acidified either chemically or by immobilized lactic bacteria (26). In the latter case, the lactic acid taste of the final product advantageously masks undesirable worty flavors (19). Two strains of cocci have been selected by Narziss (20) for their ability to confer a pure acid flavor and a slightly honey-like smell.

CCP is currently applied to low-density worts in immobilized yeast reactors (1, 16, 15, 29, 33, 35). Arrested batch fermentation is a simple operation, but one difficult to control when producing alcohol-free beers. The main advantage of immobilization is the high yeast density achieved in steady-state conditions. Immobilized cells systems were firstly proposed for rapid fermentation and maturation (22). They have benefited from improved process engineering (optimized volumetric productivity, easy separation and recovery of the biomass) and associated parameters such as flocculation (34), limited contamination owing to a high density population and limitation of cell diffusion (29). Actually, the metabolism of immobilized yeast cells may be modified as a result of mass transfer limitations and waste product accumulation (8). Growth stops because of oxygen deficiency and high ethanol content in the immediate vicinity of the cells. Although similar to a no-growth state, such systems allow both significant reduction of several carbonyls (2) and esterification of higher alcohols (21).

When producing alcohol-free beers by immobilization technique, the ethanol level of the out-flowing beer can be adjusted to a threshold value by adjusting the temperature (often to below 1°C ; 1, 33) and residence time (often to less than 30 hours ; 1, 33). Production is usually continuous for several months without regeneration. Immobilization carriers must be inert, cheap, stable, reusable, non toxic and supporting high yeast cell concentration. Carriers used in brewing can be divided into three groups (6,7) according to their mechanism of action : gel entrapment (calcium alginate, carrageenan beads) ; adsorption on an inert support (DEAE cellulose, 15) or entrapment in a pre-formed carrier such as porous glass (sintered glass, 1). Other techniques such as covalent attachment, cell aggregation are mentioned occasionally but not applied. Ruhaut (28) compared several immobilization carriers. A recently developed approach is colonization of the internal surface of silicon carbide rods (12). Ongoing research focuses on both for primary fermentation (14) and immobilization carriers.

Ethanol can also be removed from regular beers by distillation, vacuum-distillation (11), dialysis (3) or reverse osmosis (36). Dealcoholization has recently been coupled with continuous production (5). Such methods yield beers with 0.05 % v/v ethanol, but these beers often lack the fruity flavors of regular beers, owing to insufficient discrimination between small molecules. Furthermore these expensive techniques, especially distillation, can favor synthesis of compounds responsible for an undesirable worty aroma and color.

All the above-mentioned processes can be improved by using (17) :

- cold water malt extracts, obtained under 60°C to avoid amylase-catalyzed starch hydrolysis ;
- high temperature mashing which also limits amylase activity ;
- the "spent grains method", i.e. re-mashing of spent grains (with or without acid hydrolysis) (17, 5)
- high gravity brewing which disproportionately increases the yeast ester synthesis
- the Barrett patent method, combining beer produced from low gravity worts and flavors vented from high gravity wort fermentation (18)
- carefully selected yeasts like *Saccharomycodes ludwigii* unable to ferment sugars like maltose (20)

CHEMICAL COMPOSITION OF ALCOHOL-FREE BEERS IN COMPARISON WITH REGULAR BEERS

Major compounds of alcohol-free beers

Table 1 shows conventional analyses of commercial alcohol-free beers. Usually brewed with an initial gravity of 6.5 - 7.4 °P, the real beer extract often remains above 5 - 7 °P except when ethanol is removed. These sugar-rich beverages (maltose being the main sugar, see Table 2) are also characterized by a higher pH (4.4 -4.9) than regular beers.

Table 1. Conventional analysis of commercial alcohol-free beers

Brewing method	CCP bottom yeast[1]	CCP top yeast[1]	CCP special yeast[1]	Ethanol removal reverse osmosis[2]
Original gravity (°P)	7.42	7.31	6.51	2.48
Ethanol (wt. %)	0.51	0.42	0.38	0.40
Apparent extract (°P)	6.15	6.25	5.56	1.68
Real extract (°P)	6.41	6.47	5.75	1.83
Attenuation (%)	17	15	15	32
Color (EBC)	10.7	7.0	9.7	-
pH	4.87	4.45	4.35	-
Bitter substances (EBU)	35	27.4	23.5	12.3
DMS (ppb)	26	40	60	-
Total diacetyl (ppb)	0.10	1.4	0.09	-

From ([1]) Narziss *et al.*, 1992 and ([2]) Kavanagh *et al.*, 1991

Table 2. Sugar in alcohol-free beer produced by an immobilized yeast/CCP process

Sugars	in-flowing wort (g/100g)	out-flowing beer (g/100g)	change in concentration (g/100g)
glucose	0.58	0.61	+ 0.03
fructose	0.10	0.25	+ 0.15
sucrose	0.40	0.16	- 0.24
maltose	5.05	5.00	- 0.05
maltotriose	0.92	0.92	0.00
total (°P)	7.05	6.94	- 0.11

From van Iersel *et al.*, 1995

Aroma compounds of alcohol-free beers

Esters are known to impart the fruity flavor to regular beers (see Table 3).

Table 3. Concentration and flavor thresholds of current esters and fusel alcohols in lager beer

Compounds	Concentration (ppm)	Flavor threshold (ppm)
Fusel alcohols		
n-propanol	4-17	800
isobutanol	4-57	200
active amylalcohol	7-34	65
isoamylalcohol	25-123	70
2-phenylethanol	5-102	125
Esters		
ethylacetate	4-48	33
isobutylacetate	0.03-0.25	1.6
isoamylacetate	0.8-6.6	1.6
2-phenylethylacetate	0.1-1.5	3.8
ethylhexanoate	0.1-1.5	0.23
ethyloctanoate	0.1-1.9	0.9

From Renger *et al.*, 1992

When regular and alcohol-free beers are compared as regards their ester and fusel alcohol concentrations, few if any fruity aroma compounds are detected in the latter, whatever the production process (Figure 1, 23). Our results confirm data of Schur (30) who detected a total ester level below 1 ppm after a CCP fermentation (see Table 4). According to Narziss (20), high level of higher aliphatic alcohols could be obtained in a 0.45% ethanol beer by using *Saccharomycodes ludwigii* to ferment a 7.5 °P wort. Unfortunately, high levels of acetoin and diacetyl were also high.

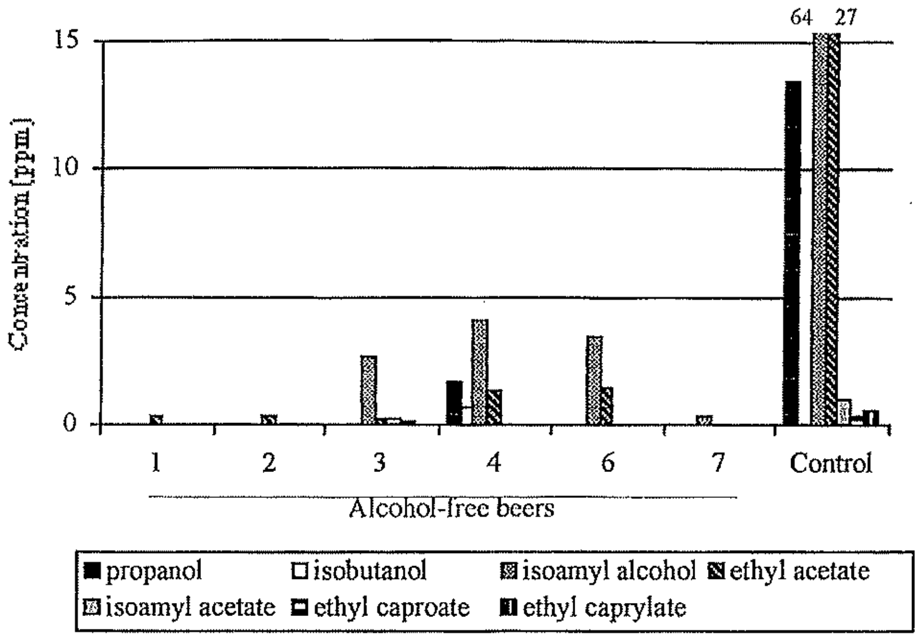

Figure 1. Headspace analysis of 7 commercial beers. Beer 1 and 2 have been distilled and the Barrett Process was applied to beer 2. Beer 3 was produced in an immobilized yeast reactor. Beers 4 and 6 were issued from a cold contact process and beer 7 from limited fermentation. Control was a regular lager beer.

According to Muller (18), one should take advantage of the disproportionate synthesis of esters in high density brewing. By increasing the wort gravity from 10 to 20 °P it is possible to increase the acetate ester concentration 3- to 4-fold while only doubling ethanol production. Higher levels of n-propanol and isobutanol are also reported. The Barret patent method (see above) thus appears as a promising way to improve the fruity character of low-alcohol beers.

Table 4. Production of fusel alcohols and esters in a CCP fermentation

Compounds	Initial concentration (ppb)	Final concentration (ppb)
isobutanol	150	350
isopentanol	180	380
2-phenylethanol	210	130
isoamyl acetate	0	70
ethyl butyrate	0	10
ethyl caprylate	0	60
ethyl caproate	0	75
isoamyl caprylate	0	6
isoamyl caproate	0	6
phenylethylacetate	0	15
total	540	1102

From Schur, 1983

Wort carbonyl compounds have long been considered responsible for the worty aroma or "unfermented beer" flavor of alcohol-free beers. They are present in the raw materials or produced in the brewhouse (4). Before mashing, cabonyl levels depend on the type of malt used, increasing with increasing kilning temperature. Branched aldehydes can additionally be produced through mashing when the temperature is raised. High losses are expected to occur during boiling (chemical transformation, removal by water vapor), but Strecker degradations will regenerate such aldehydes during the clarification step. When a thermal desorption cold trap system was used to measure carbonyl compound levels in commercial low-alcohol beers (Figure 2, 23), beers obtained by limited fermentation displayed a higher 3-methylbutanal concentration (22 to 56 ppb and above) than either dealcoholized or regular beers (17 ppb for regular beers). Table 5 also shows the evolution of several carbonyl compounds during a cold contact process. Again, although removed to a certain extent (levels reduced by 15 to 99%), worty-flavor-imparting compounds remained after fermentation. Narziss (20), using *Saccharomycodes ludwigii*, reached similar conclusions.

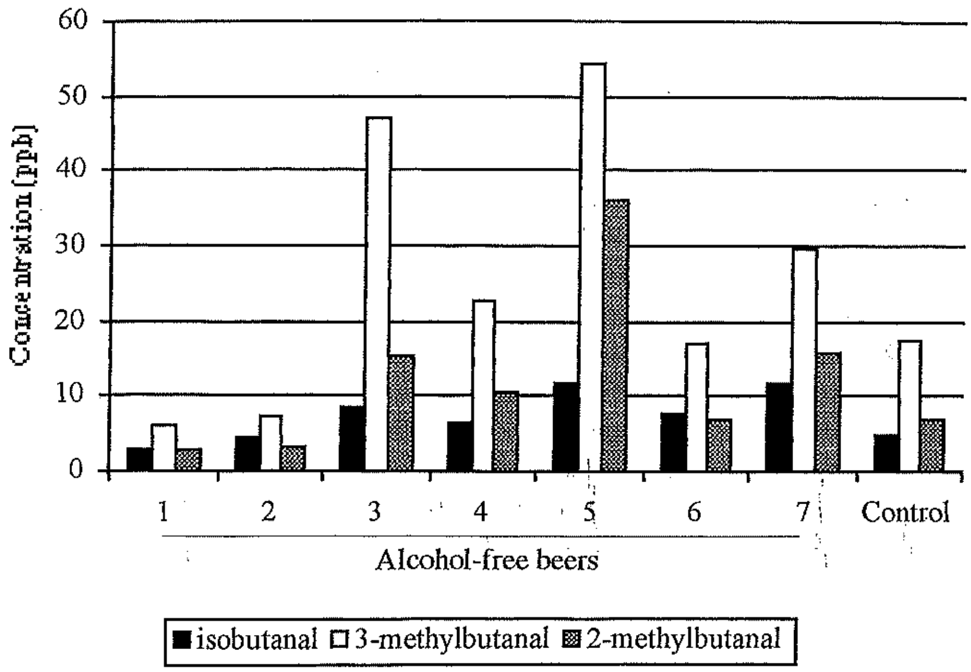

Figure 2. TCT analysis of 8 commercial beers. Beer 1 and 2 have been distilled and the Barrett Process was applied to beer 2. Beer 3 was produced in an immobilized yeast reactor. Beers 4, 5 and 6 were issued from a cold contact process and beer 7 from limited fermentation. Control was a regular lager beer.

Table 5. Reduction of carbonyl compounds during a CCP fermentation (1) and immobilized yeast/CCP process (2)

Compounds	Initial concentration (ppb)	Final concentration (ppb)	% reduction
furfural[1]	480	280	42
benzaldehyde[1]	12	8	33
methional[1]	18	8	55
trans-2-nonenal[1]	12	+	99
pentanal[1]	13	11	15
2-hexenal[1]	5	2	60
2-octenal[1]	2	+	99
2-methylbutanal[2]	87.4	19.1	77.9
3-methylbutanal[2]	344	101.2	70
heptanal[2]	7.6	3.9	49

From (1) Schur, 1983 and (2) Collin *et al.*, 1991

Other compounds may contribute to the off-flavor of alcohol-free beers. Proline is one of the major amino acids in wort and beer. Proline and hydroxyproline possess secondary amino groups protecting them from usual Strecker degradation (31, 32). Yet, they can react with α-dicarbonyl compounds like pyruvaldehyde to be further decarboxylated, the resulting salt cyclizing to form 2-acetylpyridine (Figure 3). Such compound may contribute to the baked bread or "cracker like" aroma found in some low-alcohol beers.

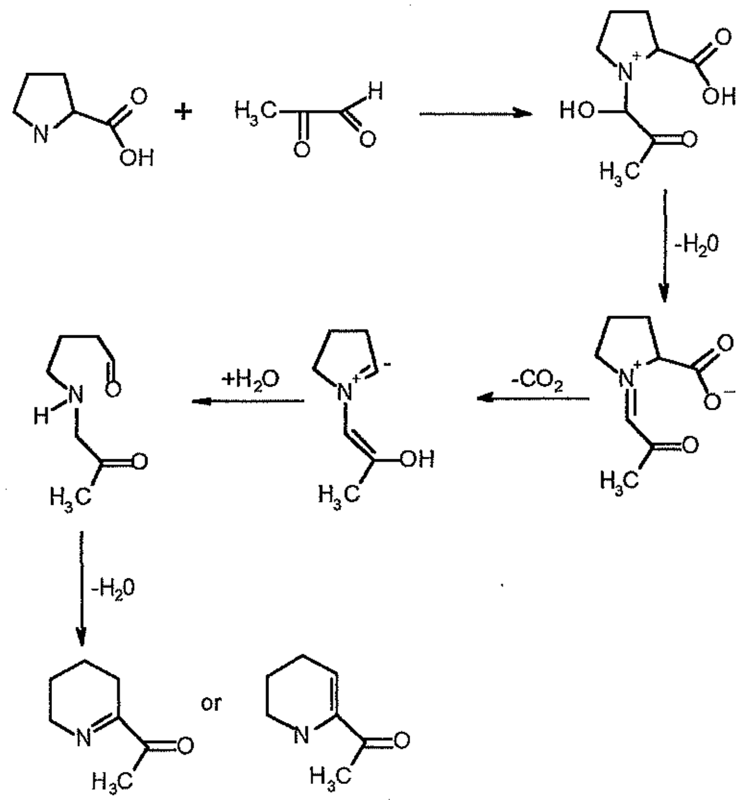

Figure 3. Potential mechanism of formation of 2-acetylpyridine derived compounds from proline and pyruvaldehyde.

HOW TO IMPROVE ALCOHOL-FREE BEER FLAVORS

Potential solutions to the lack of flavor and off-flavor of alcohol-free beers depend on the process applied by the brewer. To make flavorful alcohol-free beers by dealcoholization, the ethanol removal system should be able to discriminate between ethanol and other beer volatiles.

To improve CCP fermentations, we need more information about yeast physiological changes linked to low temperature stress (9).

But first, efforts must be made to identify all compounds contributing to the worty off-flavor (24). By studying their evolution through the production processes it should be possible to pinpoint critical steps at which improvements might be made. Another seemingly promising approach would be to select yeasts unable to produce ethanol but capable of reducing the unpleasant worty flavor.

Eventually, development of efficient ethanol substitutes may significantly improve the likeness of alcohol-free beers to regular beers, not only in terms of "body" (10, 13,19) but also as regards optimization of flavor retention and flavor thresholds (25,27).

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