Brewing with 100% Oat Malt

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ABSTRACT

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Oats are a cereal with beneficial nutritional properties and also unrealized brewing potential. Furthermore, oats can be tolerated by the majority of people who suffer from celiac disease. Malting of oats produced a malt, which was found suitable for brewing a 100% oat malt beer. The mashing regime, designed by using mathematical modelling, was successfully transferred to a pilot scale plant. The improved lautering performance of oat malt was due to its higher husk content, which also led to a lower extract content in oat wort when compared to barley wort. The protein profile of oat wort, as measured by using Lab-on-a-Chip analysis, revealed that there was no significant difference in the protein profile between oat and barley wort. The fermentation of oat and barley worts followed the same trend; differences could only be seen in the higher pH and lower alcohol content of the oat beer. The flavour analysis of oat beer revealed some special characteristics such as a strong berry flavour and a lower amount of staling compounds when forced aged. This study revealed that it was possible to brew a 100% oat malt beer and that the produced beer was comparable to a barley malt beer.

Key words: Beer, celiac, fermentation, malting, mashing, oats.

INTRODUCTION

Oats are a popular cereal for human consumption. In medieval times, oats were traditionally used in brewing, but were forgotten when the German purity law was introduced in 1516 and the use of this grain outside of Germany was limited[8]. Nowadays, use of oats is regaining interest due to their physiological properties. Oats supply key cardioprotective micronutrients such as folate, magnesium, vitamin B6 and vitamin E[35] and substances with known antioxidant activity[20]. Furthermore, oats can be tolerated by the majority of people who suffer from celiac disease, which requires a lifelong strict gluten-free diet. Whether oats can safely be included in a gluten-free diet has been debated over the last decades. Recent studies on that topic have been summarised in a review[6], which states that most celiac patients tolerate oats. The Scientific advisory board of the Finnish Coeliac Society declared oats acceptable for adult celiac patients in 1997[36].

Germination or malting of cereals has been used for centuries to soften kernel structure, to increase nutrient content and availability, to decrease the content of anti-nutritive compounds, and to add new flavours. Several researchers[11,15,16,33] have investigated the changes occurring during germination/malting of oats. The use of 100% oat malt in brewing has been reported by only few researchers[8,17].

Specifications for brewing cereals are usually a moderate protein and high starch content as well as a high enzyme activity and a low β-glucan content. Oats are rich in protein, lipids and β-glucan and consequently lower in starch than conventionally used barley. Subsequently, oats appear not to be ideal for brewing, although still suitable. However, not only due to the superior nutritional value of oats, their use seems appealing. They have also been recommended as an adjunct due to their higher husk content, which can accelerate lautering[8]. However, not only the higher husk content may be advantageous for the use of oats, but also the generally more uniform shape of the oat kernel, which may lead to a more uniform modification during germination and adequate modification is the key to achieving good lautering performance[1].

The aim of this study was to brew a beer from 100% malted oats (*Avena sativa* L.). An optimal mashing program needed to be developed, which was achieved by using mathematical modelling. In pilot scale brewing experiments, mashing, lautering and fermentation were monitored to evaluate the impact of oat malt on the brewing process. In addition, flavour, sensory and analytical characterisation of the resulting oat beer was carried out. The oat beer was compared to a beer produced from barley malt made under the same conditions.

MATERIALS AND METHODS

Malting

Malting of oats (harvest 2005, Raisio, Finland) was performed four times in a micro malting machine (Joe White Malting Systems, Perth, Australia). The malting process was carried out according to the method described in Klose et al.[17] The four final oat malts were then analysed separately using European Brewery Convention (EBC) methods. The activity of the α-amylase was determined with the Ceralpha diagnostic kit (Megazyme Ltd., Bray, Ireland). Malts were then combined for the mashing

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trials. Malted barley was obtained from the Cork Malting Company, Ireland.

Mashing

A two-level factorial design was applied to generate the optimal mashing regime for oat malt. Three rest temperatures were selected (35, 45 and 62°C) and eight different trials were carried out (Table I). All mashing trials were carried out in a standard mash bath (LB 8 – Electronic, Lochner Labor Technik, Germany). The different worts were heated to 72°C and held until complete saccharification was obtained. Worts were then cooled to 20°C. Resulting worts were analysed with regard to their filterability, extract content, fermentability, viscosity, free amino nitrogen (FAN) content and total soluble nitrogen (TSN) content using EBC methods 8.3, 8.6.1, 8.4, 8.10 and 8.9.1. The protein profile was measured using Lab-on-a-Chip analysis to separate proteins according to their molecular weight. The principle of the Lab-on-a-Chip analysis technique is based on traditional gel electrophoresis that has been transferred to a Chip. This was analysed in an Agilent 2100 Bioanalyzer (Agilent Technologies, Palo Alto, CA) according to Klose et al.[17] For the analysis of the data, the calculation of the models and the interpretation of the results, the program Design Expert 7.1.5 (Stat-Ease, Penzance, U.K.) was used. The optimal mashing regime was verified using a commercially produced oat malt (variety Sang), which was used for brewing a 100% oat malt beer in a pilot scale brewery.

Brewing

Brewing was carried out in a pilot scale brewery (50 L). Oat beer was produced three times and a barley brew was produced as a control using the same mashing, fermentation and filtration procedures. The different malts were milled with a two-roller mill (0.7 mm distance between rollers) and 9 kg of grist was mashed into 32 L of water at 45°C according to the optimal mashing regime, which was achieved from mathematical modelling and slightly modified (see Results and Discussion). After a rest of 20 min, the temperature was increased to 62°C and held for 30 min. A further heating to 72°C was carried out and kept for another 30 min. At this temperature saccharification was monitored every 5 min, until discoloration of iodine occurred. Mashing off temperature was 78°C. Lautering was carried out in a lauter tun. The lauter-rate of the first wort was measured gravimetrically until a final mass of 20 kg. Sparging water was added in such a way to reach a final wort volume before boiling of 55 L. The lauter-rates of these worts were also monitored gravimetrically. In order to provide a reasonable comparison, boiling was performed to reach an extract value of approximately 12% in the boiled worts. Hops (Hallertauer Hercules, Hopsteiner, Mainburg, Germany) were added at the start of boiling, aiming for 18 EBC bitter units. Cold worts were analysed for their extracts and fermentability using an automated beer analyzer (ServoChem Automated Beer Analyzer, Tecator AB, Högenäs, Sweden). The pH values, colour, viscosity, TSN, FAN and β-glucan were analysed according to the EBC-methods 8.17, 8.5, 8.4, 8.9.1, 8.10 and 8.13.1. Fermentation was carried out in Cornelius kegs (20 L) at 11°C by adding a bottom fermenting dried lager yeast (Saflager S-23, Fermentis, France), which was previously rehydrated according to the manufacturer's recommendation with approximately 1×10^7 cells/mL in wort. The fermentation was carried out until the apparent extract did not change significantly. Fermentation was monitored by measuring extract, pH and counting the number of yeast cells (samples were taken approx. 10 cm beneath the liquid surface). Extract was analyzed using an automated beer analyzer (ServoChem, Tectator AB, Höganäs, Sweden). Cell counts were carried out using a haemocytometer (Thoma chamber) and methyl red was employed as an indicator for yeast viability. Fermentation was followed by a maturation period of three weeks at 2°C. Filtration was carried out using a plate filter with standard depth filter sheets (KS80, Seitz). The filtered beer was bottled using a manual bottling unit (Esau-Hueber GmbH, Schrobenhausen, Germany). Bottled beer was stored in the dark at 4°C until analysis.

Table I. Eight mashing trials at 35, 45 and 62°C using rests for 0 or 20 min.

No.	35°C rest	45°C rest	62°C rest
1	0	0	0
2	20	0	0
3	0	20	0
4	20	20	0
5	0	0	20
6	20	0	20
7	0	20	20
8	20	20	20

Beer analyses

The final beer was analysed with regard to extract, alcohol and apparent fermentation using an automated beer analyzer (ServoChem Automated Beer Analyzer), colour was measured according to EBC method 9.6 and foam stability according to NIBEM (MEBAK II, 2.23.3). All analyses were carried out in triplicate and average values including standard deviations are given in the tables and figures. The aroma compounds of the oat and control barley beers were investigated according to MEBAK II method 1.1.1 and taste testing was carried out according to MEBAK II method 2.34.3 (DLG standard). In addition, both beers were analysed for their aging behaviour using gas chromatographic analysis method (PV-GC/MS).

RESULTS AND DISCUSSION

Malting

The brewing process and the quality of the subsequent beer are strongly determined by the quality of the malt. Generally, of special importance to the brewer are extract and nitrogen content, as well as the modification of the malt[3]. Results of oat and barley malt analysis are presented in Table II. Oat malt produced in the micro-malting plant showed lower extract values of 62.1% dm compared to the high extract yields of barley malt (approximately 83% according to EBC). The pH values of congress worts produced from barley malt usually show a pH of 5.6–6.0[28]. Oat based congress worts were at the upper limit of these pH values, with a mean value of pH 5.9. Viscosity of oat congress wort showed relatively high values of 1.81

Table II. Specification of malts used in this study.

	Units	Oat malt micromalting	Oat malt Sang	Barley malt Sebastian
Extract	[%dm]	62.1 ± 0.30	62.3 ± 0.35	83.7 ± 0.29
pH value of congress wort		5.90 ± 0.02	5.99 ± 0.02	5.88 ± 0.02
Viscosity	[mPa*s]	1.81 ± 0.02	1.72 ± 0.07	1.55 ± 0.03
Degree of fermentation	[%] ASBC	80.9 ± 1.29	76.6 ± 0.00	85.0 ± 1.11
Nitrogen	[%dm]	1.72 ± 0.05	1.98 ± 0.05	1.60 ± 0.07
Protein (conversion factor 5.4/5.5)	[%dm]	9.30 ± 0.27	10.67 ± 0.30	8.80 ± 0.39
Total soluble nitrogen	[%dm]	0.63 ± 0.02	0.60 ± 0.07	0.55 ± 0.03
Kolbach index	[%dm]	37 ± 1.71	30 ± 3.00	34 ± 3.39
FAN	[mg/L]	172 ± 9.83	161 ± 15.82	182 ± 13.20
Moisture of malt	[%]	5.1± 0.56	6.2 ± 0.12	3.8 ± 0.20
α-Amylase	[DU]	23 ± 2.79	25 ± 1.38	57 ± 3.26
β-Glucan	[%dm]	0.21 ± 0.01	0.26 ± 0.02	0.30 ± 0.02
Colour of wort	EBC	9 ± 1.20	5 ± 0.03	3 ± 0.45

and 1.72 mPa*s, while barley congress wort had a value of 1.55 mPa*s (at 8.6% extract). The high viscosity value in the oat congress wort might be indicative of possible problems during beer filtering, due to a high β-glucan content. The apparent degree of fermentation in oat malt was 80.9 and 76.6%, whereas in barley according to EBC[4] 4.11.1 values of 83% are achieved. The protein content of oats is usually higher than that of other cereals[19]. For brewing purposes, a high nitrogen content is not advantageous, since it can lead to haze problems in the beer[12]. Hence, in this study a lower-nitrogen oat variety was chosen with a mean value of 1.72%. The protein concentration of grain is typically obtained by multiplying its total nitrogen content by a nitrogen-to-protein conversion factor calculated from the amino acid composition of grain. According to the intensive study of Mossé[29], who analysed several cereals, legumes and oilseeds, a conversion factor of 6.25 as well as 5.83 leads to inaccurate protein content values in cereals. It has been suggested by Mossé[29] as well as Mariotti et al.[23] that the true conversion factor for oats is close to 5.4. For barley, a conversion factor of 5.5 was suggested. These calculations lead to lower protein content values than what is usually known for cereals. Oat malt still showed a relatively high total protein amount of 9.30 and 10.67% as calculated using the 5.4 conversion factor. Soluble nitrogen and the soluble nitrogen ratio (Kolbach index) are indicative of the proteolytic modification of the malt. For barley, well modified malts show Kolbach indices of 35–45%; oat malts with mean values of 37 and 30% are considered to be relatively poorly modified[28]. The importance of FAN for yeast nutrition during fermentation has long been recognised. Although oat malt contains a higher amount of nitrogen, oat worts showed slightly lower free amino nitrogen amounts in wort (172 and 161 mg/L) than barley (182 mg/L). The α-amylase activity in oat malt with 23 and 25 DU was found to be considerably lower than the value in barley malt (57 DU). Similar values for oat malt using the same analysis method have also been reported by Hanke et al.[8]

Mashing

The mashing procedures for barley malt have long been established and can be adapted for specific raw material quality[3]. Since mashing is one of the most important steps in brewing, it is essential to adjust it to the specific malts. Optimised mashing programs have not only been analysed for barley, but also for other grains such as sorghum[7] and buckwheat[39]. Since there are no mashing procedures published for oat malt, it was crucial to study the optimal mashing temperatures for the enzymes from the oat malt used in this study. To minimise the amount of trials needed for such an optimisation, a two-level factorial design was used to generate the best mashing regime for oat malt. Three rest temperatures (35, 45 and 62°C) were selected and rest times were varied over two levels (0 and 20 min). The factorial design chosen for the optimisation of the oat malt mashing program is given in Table I. The specific temperatures were chosen based on the optimal temperatures for barley malt-enzymes. It is known that a rest at 45°C supports cytolytical degradation in barley malt mashes. This degradation process is of great importance to avoid lautering and filtration problems later in the process, which can be caused by high viscosity and/or the formation of filter blocking gels. Usually, increased levels of high molecular β-glucan in the mash are responsible for these problems. In addition, degradation of high molecular weight proteins occurs mainly at temperatures of 45 to 55°C. A rest at 62°C enhances maltose production by β-amylase. Mashing in at lower temperatures such as 35°C can be advantageous, since macromolecules have more time to go into solution, consequently enzymes are already dissolved when their optimum temperature is reached and a higher attenuation limit can be obtained this way[18].

Filterability in laboratory scale of oat wort was found to be considerably slower than that of typical barley worts, using EBC method 4.5.1, but could not be confirmed in pilot brewing trials, where lautering of oats was faster than that of barley. The generally higher fat content of oats[19] might have an influence on the filterability. Furthermore, filtration problems are likely to occur in the presence of β-glucan in the wort. Consequently, if little β-glucan is degraded by β-glucanase during the mashing process, filtration problems occur. Filterability was especially poor in the wort of trial 1, which was most likely due to the fact that no rest at 45°C (the temperature of highest activity for β-glucanase in barley) was performed. Although the β-glucan content of barley and oats is similar[2,21], β-glucanase activity is noticeably lower in oat malt than in barley malt[11]. Thus, the poor filterability of oat wort might be a consequence of this lower activity. However, the importance of an optimal malting regime for a specific grain also has to be considered when discussing filterability. Hence, poor filterability of oat wort could

Table III. Influence of mashing time and temperature on the levels of FAN, TSN and degree of fermentation.

Trial no.	35°C rest	45°C rest	62°C rest	Degree of fermentation (%)	FAN (mg/L)	TSN (mg/L)
1	0	0	0	45.34	93	420
2	20	0	0	70.93	131	590
3	0	20	0	71.09	136	610
4	20	20	0	70.74	151	650
5	0	0	20	75.56	107	520
6	20	0	20	75.41	147	630
7	0	20	20	76.60	148	650
8	20	20	20	76.02	162	690

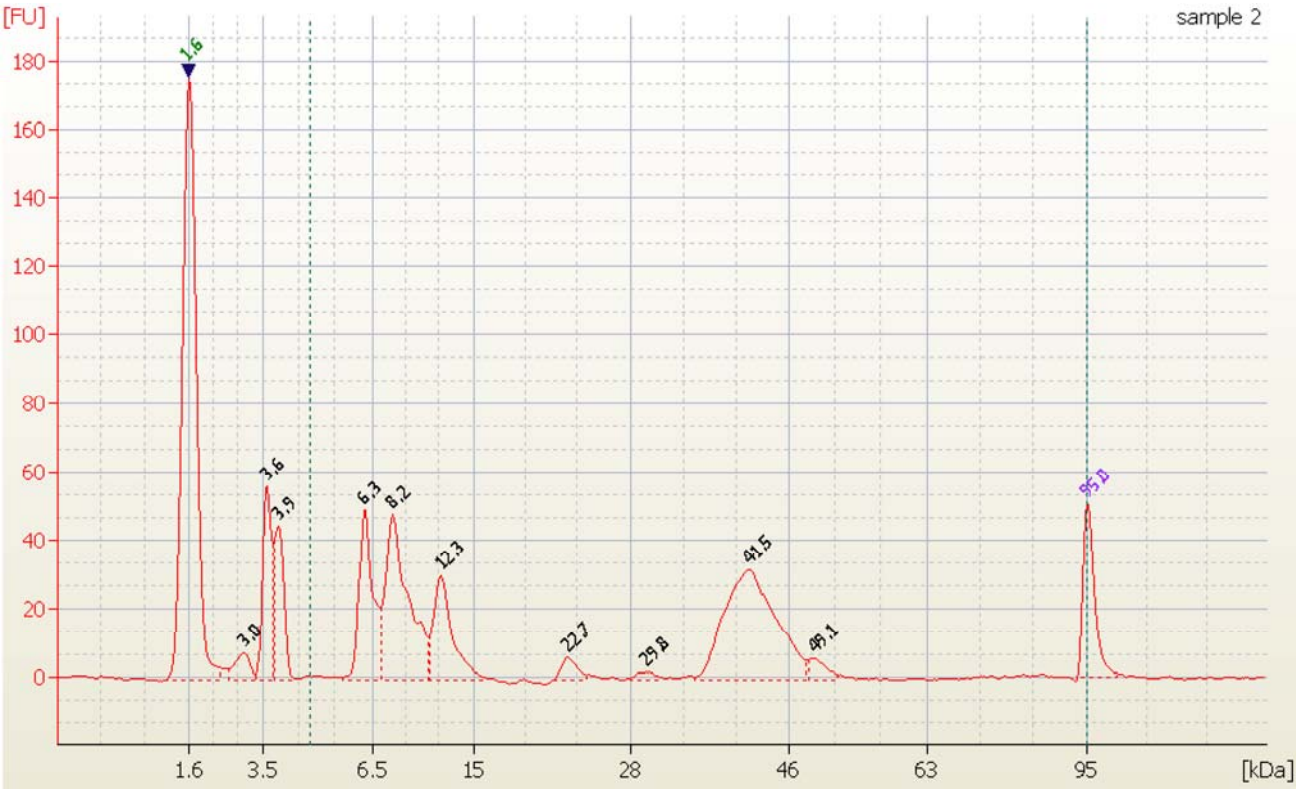

Fig. 1. Electropherogram of the protein profile of oat wort, produced under optimal mashing conditions for oat malt (mash bath).

also be attributed to undermodification. Oat wort extract content ranged from 59.7 to 63.3% (w/w) without any significant differences in the eight trials. Compared to barley malt extract content (approx. 80%), oat malt extract values were considerably lower. This could be attributed to the higher husk content of the oats[19], which lowers the total weight of fermentable extract of the grain.

The degree of fermentation showed significant differences within the eight trials. It could be seen that the lowest values were observed in the wort with no rest at temperatures 35, 45 and 62°C (Table III). In trials 2–4, which included no 62°C rest, the degree of fermentation improved significantly, when at least one of the lower temperature rests (35 or 45°C) was included in the mashing program. This was due to the fact that during the heating of the mash to 72°C, the temperature of 62°C was passed and as a result the β-amylase produced some maltose. Highest values (approximately 76%) were obtained in trials 5–8, which included a rest at 62°C, where β-amylase has its optimum temperature and maltose is produced. Consequently, the significant factor for reaching a high degree of fermentation was the rest at 62°C.

FAN levels also showed significant differences within the trials. The FAN content was lowest when no proteolytic rest at 45°C was held, and it was also poor when no 35°C rest was carried out (Table III). The higher rest temperature (62°C) together with one of the lower temperature rests (35°C or 45°C) increased the amount of FAN. The effects on soluble nitrogen content values were comparable with FAN values. In general, shorter mashing times plus a missing protein rest led to lower TSN, such as in trials 1–3 and 5 (Table III). The worts, which had no 62°C rest, nevertheless resulted in total soluble nitrogen concentrations comparable to the worts with the 62°C rest. These results indicate that the proteases in oat malt still degrade proteins above their optimum temperatures throughout the mashing process[18], although some authors have suggested that barley proteases are inactivated at temperatures higher than 60°C[14]. All mashes showed a similar protein profile, differences could only be seen in the total protein concentration. The protein profile of a typical oat wort is depicted in Fig. 1. Three main protein groups could be detected with molecular weights ranging from 6–15 kDa, approximately 40 kDa and a small pro-

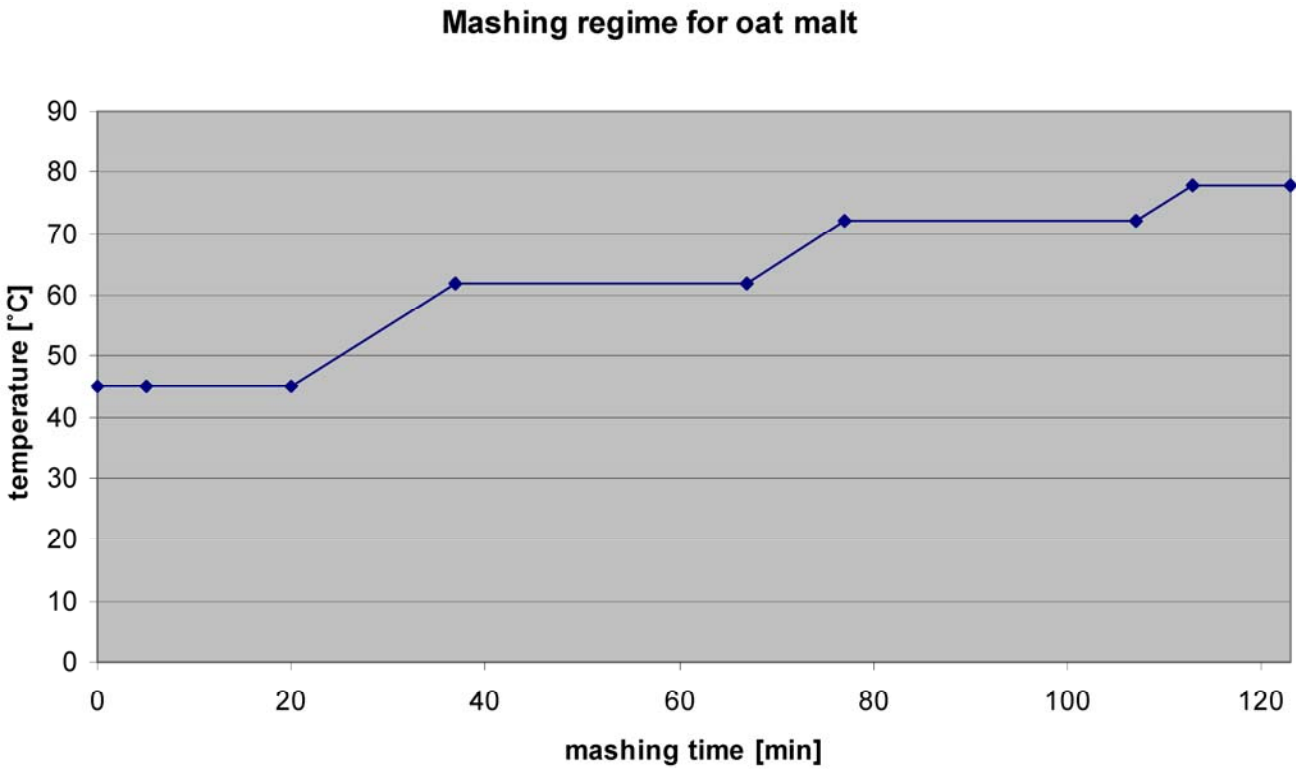

Fig. 2. Optimal mashing regime for oat malt based on two-level factorial design.

tein peak of approximately 22 kDa. The protein profile of the oat wort was similar to that reported for barley wort[17]. The approximately 40 kDa protein, known as protein Z in barley, belongs to the serine proteinase inhibitor (serpin) family, survives the brewing process, and is found in beer[10]. In oats, a trypsin inhibitor with a molecular weight of 43.5 kDa is acting as the cereal serpin[9,27] and can most likely also be found in oat beer[17]. The low molecular weight proteins represent mostly protein breakdown products.

Each response (filterability, extract, degree of fermentation, viscosity, FAN and TSN) was analysed individually with Design-Expert using a 95% confidence interval and each revealed a mathematical model. The software suggested three significant models for the responses of degree of fermentation, FAN and TSN. The selected factors of rest time and temperature revealed no influence on the filterability, extract and viscosity values, so no significant model was found. Therefore, for the optimal mashing program, only the significant models, degree of fermentation, FAN and TSN, were considered. The optimal mashing program, suggested by Design-Expert, which provided the highest values for degree of fermentation, FAN and TSN, was the mashing program of trial 8 (Table I and III), where rests at all three selected temperatures were performed. However, a mashing program without the rest at 35°C also revealed relatively high levels of FAN, which were still in the normal range according to EBC. To achieve the highest values for the degree of fermentation, only the 62°C rest was of importance, hence an elimination of this rest was not considered. Therefore, for a practice-oriented solution as well as for economic reasons, the authors chose the mashing program for oats illustrated in Fig. 2, where the mashing-in temperature was 45°C and the 62°C rest temperature was prolonged for 10 min.

Table IV. Verification of the optimised mashing program using oat malt produced in a micromalting plant (Joe White Malting Systems, Perth, Australia) and commercially produced malt of the variety Sang.

		Mashing with oat malt	
	Unit	**Micromalt**	**Sang**
Extract	%	62.2 ± 0.07	61.9 ± 0.64
Degree of fermentation	%	76.8 ± 0.30	76.6 ± 0.07
FAN	mg/L	148 ± 1.00	154 ± 13.87
Viscosity	mPa*s	1.49 ± 0.01	1.49 ± 0.01
TSN	mg/L	650 ± 8.02	634 ± 8.91

The mashing trials were carried out using the micromalted oats (for specifications see Table II). For brewing, commercially available oat malt (variety Sang) was used. In order to verify the chosen optimal malting program, a trial was repeated using the commercially available oat malt. Results of the new mashing trial, which are shown in Table IV, validated the results from the first mashing trial (see Table III, trial 7).

Pilot scale brewing

Brewing. The commercially produced oat malt was used as the raw material in pilot scale brewing (50 L). A separate trial was performed using barley malt as the ingredient. The mashing procedure (Fig. 2) used for both raw materials was derived from the mathematical modelling and was slightly modified (see *Mashing*). Both raw materials were treated in an identical manner throughout the brewing process. A comparison of the brewing performance of oat and barley malt, during mashing and wort

Table V. Brewing performance and wort characteristics of oats and barley.

		Saccharification (72°C)	Extract (% [w/w])	Viscosity (mPa*s)	pH
Oats	Mash	15 min	na	na	5.79 ± 0.02
	First wort	na	13.42 ± 0.27	2.11 ± 0.15	5.79 ± 0.03
	Preboiled wort	na	8.44 ± 0.04	1.91 ± 0.04	5.82 ± 0.02
Barley	Mash	5 min	na	na	5.70 ± 0.00
	First wort	na	15.84 ± 0.00	2.33 ± 0.50	5.76 ± 0.00
	Preboiled wort	na	11.2 ± 0.00	1.81 ± 0.00	5.81 ± 0.00

Table VI. Cold wort characteristics of oats and barley.

	Unit	Oat wort	Barley wort
Extract	% (w/w)	11.56 ± 0.48	12.01 ± 0.00
Apparent fermentation	% ASBC	72.2 ± 0.01	78.5 ± 0.21
pH		5.58 ± 0.06	5.64 ± 0.03
Colour	EBC units	14.5 ± 0.71	12 ± 0.23
Viscosity	mPa*s	1.91 ± 0.05	1.80 ± 0.00
TSN	mg/L	1,081.6 ± 91.78	845.6 ± 38.61
FAN	mg/L	225 ± 9.99	206 ± 16.52
β-Glucan	mg/L	182.39 ± 13.77	143.72 ± 18.28

processing, is shown in Table V. Results revealed that the pH values of oat malt at mashing-in were slightly higher than those of the barley malt mash. The first worts of oats and barley did not show significant differences regarding pH values. However, in pre-boiled worts the oat pH values again were slightly higher than the ones measured in barley. Nevertheless, both mash pH values lay within the pH range of 5.5–5.8[28], which is commonly observed in commercial brewing. Saccharification of the barley mash at 72°C was achieved within 5 min, whereas oat mashes were starch negative after 15 min. This might have been due to the significantly lower α-amylase activity of the oat malt. Lautering of oat and barley mashes showed differences in the lauter time, which was due to the higher husk content of the oats. The lautering rates were 0.82, 0.82 and 0.83 kg/min in all three brews, which resulted in a total lauter time of 65 min for oat malt, whereas for barley malt a lautering rate of 0.78 kg/min was measured, which resulted in a total lauter time of 72 min.

A higher extract recovery was achieved in the barley control brew. First wort showed an extract level of 15.84%, while first wort in the oat brews showed an extract level of only 13.42%. This could be attributed to the higher husk, protein and lipid content of oats, which lowered the total weight of the fermentable extract of the grain[19]. Moreover, the low extract values of pre-boiled oat wort (8.44%) compared to barley (11.2%) support this assumption.

The viscosity of barley first wort appears to be higher than oat first wort, which was due to the higher extract value in barley. Nevertheless, pre-boiled oat wort showed, despite a lower extract value, a higher viscosity. Characteristics of the cold worts are presented in Table VI. It is noteworthy that oat worts were generally higher in viscosity, TSN, FAN and β-glucan compared to the barley wort. In addition, oat cold wort showed a slightly darker colour than barley wort. As mentioned earlier, oat and barley malts appeared to show similar β-glucan levels (Table II), but β-glucan levels in oat worts were significantly higher than in barley worts. This might be due to the noticeably lower β-glucanase activity in oat malt[11]. Consequently, not enough β-glucan is degraded during mashing and remains in the wort causing a higher viscosity.

Fermentation performance. During fermentation a number of parameters (extract, alcohol development, degrees of fermentation, pH and yeast cell counts) were monitored. Figure 3 shows the alcohol and pH profiles of the oat and barley worts during the 10 day course of fermentation. An increase in alcohol and a pH drop can be seen in both worts. The production of alcohol increased similarly in both worts for the first two days of fermentation. However, the barley control fermentation reached an alcohol level of 4.82% (v/v), which is slightly higher than the oat fermentation with an alcohol level of 4.30% (v/v) after 10 days. The pH dropped in a similar way, but resulted in a pH value of 4.28 in barley and of 4.51 in oats after 10 days. In Fig. 4, the fermentation development and yeast cell count are presented. Both worts behaved in a similar manner, with the only difference in degrees of fermentation that reached higher values in barley than in oats. The maximum number of yeast cells was reached after two days in both worts and decreased significantly until the end of the fermentation.

Characteristics of final beers. The characteristics of the final beers are presented in Table VII. As already seen in the fermentation performance, oat wort was not able to reach the same final attenuation and alcohol values as the wort produced from barley. In addition, the pH of oat beer did not drop as low as in the barley beer. The higher pH values in oat malt worts have also been reported by Hanke et al.[8] and in their trials the pH ranged from 4.65–5.03. The colour in oat beers was slightly higher than in the barley beer, as already seen in the cold worts. This might have been due to the prolonged boiling time of the oat wort compared to the control brew. For a better comparison of the beers, oat wort was boiled longer than barley wort to achieve a similar extract content of the cold worts. Barley control beer showed acceptable foam stability, whereas the foam stability of the oat beer was relatively poor. The generally higher fat content in oats than in barley, and consequently in their worts and beers, might be one possible explanation for the poor foam stability of the oat beers. Another reason could be the higher degree of proteolysis in the oat malt as indicated by higher Kolbach indices in the oat malt.

Aroma compounds of the final beers. The flavour of a beer is of vital importance for consumer acceptance. It has long been established that the type of malt has an important impact on the flavour profile of the beer. In this study, beer was produced from oat and barley malt under identical conditions with the addition of little hops, to emphasise the impact of the grain type itself on the flavour profile of the beer. During the alcoholic fermentation

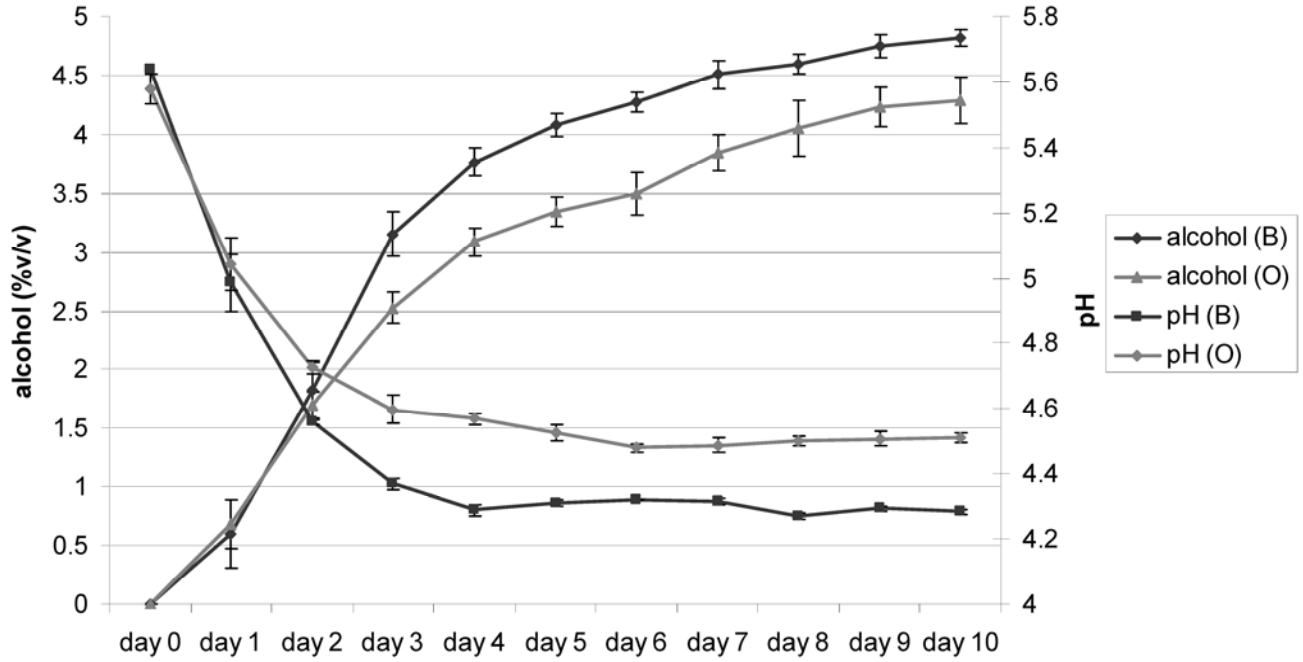

Fig. 3. Alcohol and pH profiles of the oat fermentation (O) and barley control fermentation (B) over the course of fermentation days 0–10.

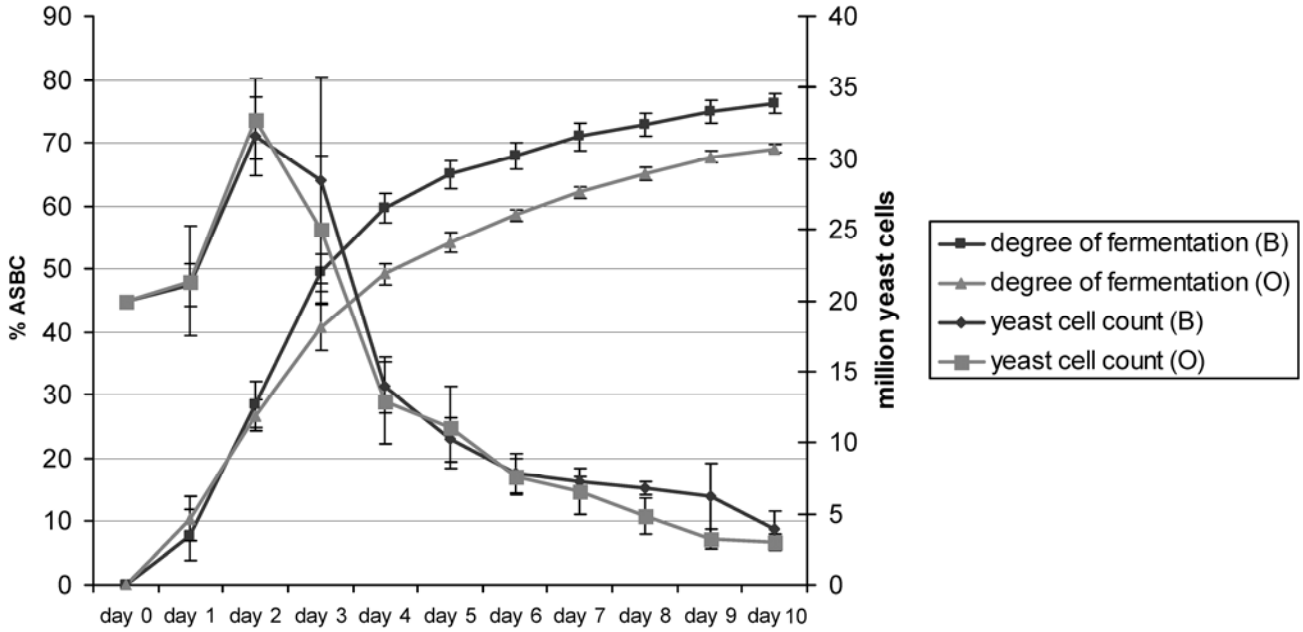

Fig. 4. Degree of fermentation (% ASBC) and yeast cell count profiles of the oat fermentation (O) and barley fermentation (B) over the course of fermentation days 0–10.

Table VII. Characteristics of final beers.

	Unit	Oat beer	Barley beer
Apparent extract	% (w/w)	3.15	2.41
Specific gravity	g/cm^3	1.0123	1.0094
Alcohol	% (v/v)	4.34	4.58
Degree of fermentation	% ASBC	72.1	78.2
pH		4.51 ± 0.02	4.28 ± 0.01
Colour	EBC units	6.4 ± 0.02	5.1 ± 0.14
Foam (NIBEM)	sec	150 ± 2.99	228 ± 1.73

of the wort, the yeast excretes not only the major fermentation products ethanol and carbon dioxide, but also a wide range of flavour compounds including higher alcohols, esters, carbonyls, sulphur compounds and organic and fatty acids[30].

The type of flavour compounds produced by the yeast is dependent on both wort composition and fermentation conditions. Higher alcohols are very important flavour compounds in beer, their production can occur in two dif-

Table VIII. Aroma compounds in oats beer and barley beer.

Name	Unit	Oat beer	Barley beer	Normal range	Normal average	Aroma[26]	Sensory threshold[26]
Acetaldehyde	mg/L	10.0	26.0	2–10	n.a.	green leaves, fruity	10–25
Ethyl acetate	mg/L	10.9	17.9	8–32	18.4	solvent, fruity	30
Propan-1-ol	mg/L	13.0	16.1	4–17	9	alcoholic	800
2-Methyl-1-propanol	mg/L	13.8	20.2	4–57	8	alcoholic	200
Acetic acid 3-methyl-butyl ester	mg/L	0.8	1.4	0.3–3.8	1.72	banana, apple	1.2–1.6
∑ 2- and 3-methyl-1-butanol	mg/L	51.8	65.4	7–34 and 26–123	11 and 36	sweet, banana	65–70
2,3-Butanedione (diacetyl)	mg/L	0.28	0.11	<0.10	n.a.	butterscotch	0.15
2,3-Pentanedione	mg/L	0.11	0.06	<0.05	n.a.	butterscotch, fruity	0.9

Table IX. Sensory evaluation (DLG) of oats beer and barley beer.

	Oat beer				Barley beer			
	Fresh	Description	Forced aged	Description	Fresh	Description	Forced aged	Description
Aroma	4.1	raspberry, yoghurt	3.5	aged	4.1	fruity, apple	2.7	aged
Purity of taste	4.1	raspberry, blueberry	3.5	aged	4.1	fruity, apple	2.5	aged
Mouthfeel	4.3	–	4.3	–	4.3	–	4.3	–
Tingling	4.5	–	4.5	–	4.5	–	4.5	–
Bitterness	4.2	–	3.9	–	4.2	–	3.0	–
Weighed mark	4.2	–	3.83	–	4.2	–	3.15	–

ferent ways. One route is the *de novo* synthesis of carbohydrates through pyruvate, where amino acids are synthesised. The hereby formed α-keto acids are precursors for higher alcohols. The second route, also known as the Ehrlich pathway, is the formation of α-keto acids through the transamination of amino acids. Higher alcohols can be synthesized from the α-keto acid by decarboxylation to the aldehyde and further reduction to the corresponding alcohol. The major higher alcohols in beer are propan-1-ol, 2-methyl-1-propanol, 2-methylbutanol and 3-methylbutanol[30,34,38]. Flavour analyses were carried out on both types of beer. An overview of the aroma compounds is given in Table VIII. The major higher alcohols examined in the oat and the control beer were propan-1-ol, 2-methyl-1-propanol, and the sum of 2- and 3-methyl-1-butanol. According to Meilgaard[25,26], the higher alcohols provide the alcoholic as well as sweet flavours to beer and are commonly found in lager type beers. Oat beer showed considerably lower concentrations of higher alcohols than the barley control beer (Table VIII). A different amino acid composition in the oat worts could have had an influence on the production of higher alcohols.

Esters, which provide fruity and flowery flavours to beers, are the most important aroma compounds in beer and determine beer aroma to a large extent[37]. The concentrations of ethyl acetate and acetic acid 3-methyl-butyl ester (Table VIII) in oat beer were lower than in the control, but within the normal range of common lager beers. In oat beers, both esters were below the threshold, whereas in the barley beer, acetic acid 3-methyl-butyl ester were just above threshold. However, it is known that different esters can contribute to the flavour by synergistic effects and consequently are relevant in beer flavour even below their threshold[25]. Generally esters can be synthesised in different ways. They can be formed via a chemical reaction, but the reaction rate is too slow to account for the amount of esters present in beer. Another route is their synthesis in the yeast cell from alcohol and different forms of acyl-Coenzyme A (CoA). The most common acyl-CoA is acetyl CoA. If acetyl CoA is involved in ester formation, an acetate ester is formed. Different forms of acyl-CoA lead to the formation of fatty acid ethyl esters. In beer, the major esters are ethyl acetate, isoamylacetate, phenylethylacetate and C6-C10 short chain fatty acid ethyl esters[24].

Among the aliphatic carbonyl compounds identified by chromatographic methods in beer and other alcoholic beverages, acetaldehyde is the most abundant component[32]. Acetaldehyde is a common by-product formed during the first days of fermentation and usually is degraded during fermentation and maturation. It is responsible for the young beer-flavour[30]. In oat beer, acetaldehyde (Table VIII) was observed to appear just above the threshold, but in a considerably lower concentration than in the control barley beer.

As aroma components, ketones are of less interest. Nevertheless, two vicinal diketones, 2,3-butanedione (diacetyl) and 2,3-pentanedione are exceptions[32] and very low sensory threshold values have been obtained for diacetyl. According to the values reported, its odour, resembling the smell of butter/butterscotch, can be recognised in concentrations as low as 0.1 ppm[26]. Diacetyl and 2,3-pentanedione are also important aroma compounds of the young beer. Their reduction is only possible with the help of yeast cells, which reduce diacetyl to acetoin and further to butanediol. Butanediol has a very high sensory threshold and is not recognisable in beer[32]. In barley beer, concentrations of diacetyl and 2,3-pentanedione were observed to be below the threshold (Table VIII). Oat beer instead showed concentrations of vicinal diketones above their threshold contributing highly to the aroma of oat beer, whereas the analysed esters and higher alcohols in oat beer were observed in amounts below their threshold and consequently did not contribute to the overall aroma to a large extent.

This was confirmed by sensory analysis, which was performed using a trained taste panel (15 testers). The fresh oat beer aroma was described as having a strong berry-like and yoghurt flavour (Table IX). Barley beer however showed a common apple-like flavour deriving

Table X. Aging indicators of fresh and forced aged oats and barley beer.

Name	Unit	Oat beer		Barley beer	
		Fresh	Forced aged	Fresh	Forced aged
2-Methyl-butanal[a,b]	µg/L	2	3	20	16
3-Methyl-butanal[a,b]	µg/L	7	7	15	16
2-Furfural[c,b]	µg/L	13	19	13	27
5-Methyl-furfural[b]	µg/L	<1	<1	6	4
Benzaldehyde[a,b]	µg/L	<1	<1	1	<1
2-Phenyl-ethanal[a,b]	µg/L	<1	<1	<1	2
Succinic acid diethyl ester[b]	µg/L	<1	1	2	3
Nicotinic acid ethyl ester	µg/L	9	2	<1	5
Phenylacetic acid ethyl ester[b]	µg/L	<1	<1	<1	1
2-Acetyl-furan[b]	µg/L	5	6	5	6
2-Propionyl-furan[b]	µg/L	<1	<1	<1	<1
γ-Nonalacton[b,c]	µg/L	32	79	70	119
Sum of heat indicators	µg/L	45	98	83	146
Sum of oxygen indicators	µg/L	9	10	36	34
Sum of staling indicators	µg/L	59	114	132	194
$\Delta_{\text{heat indicators (aged-fresh)}}$	µg/L	53		63	
$\Delta_{\text{oxygen indicators (aged-fresh)}}$	µg/L	1		–2	
$\Delta_{\text{staling indicators (aged-fresh)}}$	µg/L	55		62	

[a] Oxygen indicator.
[b] Staling compound.
[c] Heat indicator.

from acetic acid 3-methyl-butyl ester. The general impression of both fresh beers was similar with regard to mouthfeel, tingling and bitterness.

Aging characteristics of the final beers. The shelf life of beer is of vital importance for the producer as well as the consumer. It is essential that beer keeps its flavour profile over a significant time period. In this study, the aging indicators of fresh and forced aged oat and barley beer were measured using a PV-GC/MS system. Commonly, the analysis of aging compounds has focused on carbonylic compounds[37]. Carbonylic compounds include (E)-2-nonenal (cardboard flavour), Strecker aldehydes and ketones. Further compounds associated with beer aging are cyclic acetals, heterocyclic compounds (furans, furanones, pyrazines), esters, and sulphur compounds, as well as non-volatile compounds. The formation of staling compounds include the following mechanisms: reactions producing carbonyls, like the oxidation of higher alcohols and of unsaturated fatty acids, degradation of hop bitter acids, Strecker degradation, aldol condensation as well as Maillard reaction, synthesis and hydrolysis of volatile esters, degradation of polyphenols, formation of dimethyltrisulphide etc.[37] The results for the oat and barley beers (Table X) revealed that the Strecker aldehydes, benzaldehyde and 2-phenyl-ethanal, were not detected in considerable amounts in either of the beers. However, the compounds 2-methyl-butanal and 3-methyl-butanal were measured in substantially higher amounts in barley than oat beer and seemed not to increase during beer aging. The heterocyclic heat indicator 2-furfural, which provides a caramel-like and nutty flavour[31], appeared in similar concentrations in both the oat and barley beer and increased during aging, especially in the barley beer. The compound 5-methyl-furfural was not detected in considerable amounts in the oat beer, but was in the barley beer. Both compounds were found to increase with time of storage and temperature and were therefore considered as indicators of heat-induced flavour damage in beer[22]. It should be mentioned that during the brewing process, oat worts were boiled for a longer time than barley worts. For the formation of heat induced staling compounds, the prolonged boiling time of oat worts appeared not to be relevant. The heterocyclic staling compound 2-acetyl-furan, which provides a roast aroma in beer[31], appeared in similar amounts in the fresh and the aged oat and barley beer.

Volatile esters introduce fruity flavour notes and are considered to be highly positive flavour attributes of fresh beer. Certain esters can decrease during storage resulting in diminished fruity flavours in beer. In contrast, other esters such as nicotinic acid ethyl ester are synthesised during (barley) beer aging[37]. Nicotinic acid ethyl ester was found in notably higher amounts in the fresh oat beer than in the barley beer. It decreased during storage of the oat beer, whereas it increased in the barley beer during storage, resulting in a decreased fruitiness of the aged oat beer and an enhanced fruitiness in barley beer.

Cyclic esters or lactones, such as γ-nonalactone (peach-like flavour) tend to increase in concentration and γ-nonalactone especially is considered important for the flavour of aged beer[31,37]. Its original concentration in fresh oat beer was only about half in comparison to the barley beer. However in aged beers, its concentration increased in both beers substantially.

Generally, all heat, oxygen and staling indicators showed lower levels in the fresh and in the force-aged oat beer in comparison to the fresh and force-aged barley beer. Particularly Strecker aldehydes, which indicate oxygen-damage to beer, were found in considerably lower amounts in oat beer than in the barley beer. This might be due to the occurrence of more natural antioxidants in oat malt and thus in the subsequent oat beer. Special antioxidative properties of oats have been known for a long time and phenolic compounds as well as tocols and phytate are regarded responsible for the antioxidant activity[11,15] of oats. The differences between the fresh and forced aged beers present a more positive reaction of oat beer towards staling than barley beer. These results could be confirmed

in a DLG sensory test (Table IX). The overall score of aged oat beer showed higher values than barley beer. Particularly the aroma (odour) and the purity of taste in aged oat beer appeared to be more acceptable than the aged aroma and taste of the barley control beer. Also the bitterness in oat beer remained more acceptable after forced aging (Table IX). Beer bitterness is produced primarily by the hops[13]. During aging of beer, a constant decrease in bitterness is observed, which is partly due to sensory masking by an increasing sweet taste. On the other hand, an increasing harsh after-bitter and astringent note has been reported in aged barley beers[37]. Due to the lower pH in barley beer compared to oat beer, less acceptance of bitterness in aged barley beers seems likely. The influence of the pH in relation to beer astringency during aging has been studied by François et al.[5] and they revealed a large impact of the pH on astringency. The higher the beer pH value was, the lower the perceived astringency.

CONCLUSIONS

Oats are a cereal with unrealized brewing potential. Malting of oats produced not only a malt that is considered to be of higher nutritional value[11,15], but also suitable for brewing a 100% oat malt beer or various speciality beers. It could also be used as lautering aid due to its high husk content[8]. The mashing regime, which was designed using mathematical modelling in a laboratory mash bath, was successfully transferred to a pilot scale plant. The processing of oat malt in the brewhouse did not generate major problems; on the contrary, it was found that the oat mashes lautered faster than the mashes produced from barley malt. The improved lautering performance of oat malt was due to its higher husk content. The increased husk content, together with higher amounts of proteins and lipids, led to a lower fermentable extract content in oat wort when compared to the control barley wort. The lower fermentable extract content consequently led to a lower alcohol content in the oat beer. The protein profile of oat wort, as measured by using Lab-on-a-Chip analysis, revealed that there was no significant difference in the protein profile between oat and barley wort, which had also been reported by Klose et al.[17]. The fermentation of both the oat and barley wort followed the same trend, the only major difference was seen in the higher pH and lower alcohol content of the oat beer. A wide range of beer quality criteria were analysed. Major emphasis was placed on the flavour and sensory evaluation of the oat beer and the control beer. The flavour analysis of oat beer revealed some special characteristics such as a strong berry flavour and a better reaction towards staling, probably due to the presence of more antioxidants. Oat consumption is considered to be safe for most people who suffer from celiac disease and could improve the diet of these patients. Therefore, oats could play an important role in the production of a non-gluten containing beer for these patients. In addition, a beer of a different character is likely to be brewed from oat malt and might in time appeal to new consumers. This study has shown that it is possible to brew a 100% oat malt beer without problems and that the beer produced is comparable to barley malt based beers.

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