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Matthew Sheehan, Austin Montgomery, Julie M. Goddard, and Gavin L. Sacks

Department of Food Science, Cornell University, Ithaca, NY, U.S.A.

ABSTRACT

Newer sour beers are often packaged in aluminum cans, but the compatibility of sour beer and its major acids (lactic, acetic) with cans is unclear. In an initial study, commercial sour beers were packaged in cans containing one of four different liners (bisphenol A (BPA) epoxy, two BPA–non-intent (BPA-NI) epoxy, and acrylic). Corrosion, as measured by dissolved aluminum and visual degradation of the liner, was positively correlated with concentrations of lactic acid, acetic acid, and decreased pH value. After 48 wk, aluminum concentrations up to 58 mg/L were observed in one sour beer, or nearly 100-fold greater than typical dissolved aluminum concentrations in non-sour beers. Liner type did not affect corrosion. In a subsequent model sour beer study with two acrylic liners and one BPA-NI liner, molecular SO_2 positively correlated with corrosion, but only at concentrations 5-fold higher than the maximum expected in sour beers. Other added components (chloride, copper, ethanol) did not affect corrosion. Addition of acetic, lactic, and phosphoric acid in varying equinormal combinations to a non-sour beer demonstrated that acetic and lactic acids (average dissolved aluminum = 2.54 mg/L following storage) promote corrosion more than phosphoric acid (average dissolved aluminum = 0.47 mg/L). Titratable acidity (TA) correlated well with corrosion, with increased dissolved aluminum observed at TA > 6 g/L as lactic acid equivalents. Organic acid corrosivity was hypothesized to relate to the proportion of acid in its neutral form, and thus these findings are relevant to producers of other beverages with high levels of organic acids.

KEYWORDS

Aluminum can packaging; BPA-NI; can liner; corrosion; epoxy; sour beer

Introduction

Sales of sour beers, also called "tart" beers or ales, have grown considerably in the last decade, with revenue rising by 40% per year during both 2018 and 2019.[1] Compared to other beers, sour beers are characterized by their sour taste, their relatively high titratable acidity (TA) concentrations (5 g/L or more, as lactic acid equivalents) and their low pH (3.0 to 3.9).[2,3] The major acids in sour beer are reported to be lactic acid (1.9 to 8.9 g/L) followed by acetic acid (0.3 to 1.4 g/L), with lesser amounts of succinic and citric acids.[4,5] By comparison, the TA of non-sour beer styles is reported to be < 200 mg/L, and pH 4–5.[6,7] The high levels of lactic and acetic acids in sour beers are typically produced by spontaneous or inoculated mixed cultures of *Saccharomyces*, non-*Saccharomyces* yeasts like *Brettanomyces*, and multiple genera of lactic acid and acetic acid bacteria.[2,8–11] Alternatively, beers may be soured through other means like direct lactic acid addition.[12]

Sour beers have been traditionally packaged in glass, but in recent years many producers have increased their use of aluminum beverage cans in response to consumer demand. However, it is well reported that beer and other acidic beverages will corrode unprotected aluminum through the following reaction.[13]

$$2\ Al^0{}_{(s)} + 6\,H^+{}_{(aq)} \rightarrow 2\ Al^{3+}{}_{(aq)} + 3\,H_2 \qquad (1)$$

Corrosion reactions will increase dissolved aluminum (Al(III)), which can impact bone development and the brain among other health effects,[14,15] and can reduce beverage quality and affect flavor through haze formation (through reaction with proteins or other macromolecules) or increased astringency.[16–18] Corrosion may also ultimately lead to leakage and loss of the hermetic seal.[19] Beverages may contain other components known to directly accelerate corrosion (copper, chloride), or indirectly accelerate corrosion by damaging the liner (ethanol).[19,20] Other unwanted reactions between beverage components and aluminum cans are also reported, e.g. sulfites in wines appear to react with aluminum to form hydrogen sulfide (H_2S).[21]

To slow corrosion, aluminum beverage cans are internally coated with a thin polymeric liner to prevent direct contact between beverage and metal. Starting around 1960, beer cans with BPA (bisphenol A) based epoxy liners became standard,

CONTACT Gavin L. Sacks gls9@cornell.edu
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although in recent years BPA – non intent (BPA-NI) materials like acrylic and non-BPA epoxies have become more common due to health concerns associated with BPA.[22–25]

Based on concentrations of dissolved aluminum (a proxy for can corrosion), most beers appear well-suited for packaging in cans. For example, one survey of commercial beers reported that the range of dissolved aluminum observed in canned beers (0.04 to 0.33 mg/L) was comparable to the range observed in bottled beers (0.05 to 0.22 mg/L).[26] Notably, aluminum concentrations in canned beer are below those observed for canned soft drinks, which in one survey averaged over 0.5 mg/L and were as high as 10 mg/L.[27] The higher aluminum content of soft drinks could be due to their lower pH (often < 3.0, as compared to > 4.0 for standard beer styles), which would promote corrosive reactions.[28]

To the authors' knowledge, and in contrast to standard beer styles, there is no prior work on the corrosivity of sour beers towards beverage cans. The pH of sour beers is somewhat higher than in typical soft drinks, but the acids found in sour beers (lactic, acetic) are not common in canned beverages and their compatibility with different can liners (BPA-Epoxy, BPA-NI-Epoxy, acrylic) is unknown. This work evaluated the corrosivity of sour beers with varying levels of organic acids, along with the effects of other sour beer components and liner types.

Experimental

Chemicals

Glacial acetic acid (99.7% min.) and phosphoric acid (85% purity) were purchased from VWR Analytical (manufactured by BDH, Radnor, PA). DL-Lactic acid (> 85%) was obtained from Thermo Scientific (Waltham, MA). Sulfuric acid (25% v/v) from BDH Chemicals and citric acid monohydrate (99% purity) were purchased through VWR (Radnor, PA). Potassium metabisulfite (i.e., KMBS, $K_2S_2O_5$, 99%) was obtained from Chem Products (Portland, OR). Ethanol (EtOH), 70% v/v, was purchased from Koptec (King of Prussia, PA). Calcium chloride (97% anhydrous, powder), DL – malic acid (99% purity), copper sulfate (99%), sodium sulfate (99% anhydrous, granular), and potassium hydroxide pellets (KOH, 85% w/w) were purchased from Sigma Aldrich (St. Louis, MO). Sodium chloride (99%) was purchased from Calbiochem (San Diego, CA). L-(+)-tartaric acid (99.7% purity) was produced by J.T. Baker (St. Paul, MN). An electric glue skillet and B-2001 hot glue pellets were from FPC Corporation (Wauconda, IL). Deionized, distilled water with a resistance of 18.2 MΩ • cm at 25 °C was produced using a Milli-Q system (Millipore Sigma; Burlington, MA).

Nitrogen liquid and gas (N_2, Ultra High Purity) cylinders were supplied from Airgas USA LLC (Elmira, NY). A 500 mL LN_2 sprayer was obtained from US Solid (Cleveland, OH).

Aluminum cans

For screening studies to evaluate the corrosivity of commercial sour beers and model sour beer solutions, aluminum cans (355 mL; 3004 alloy) were provided by a single industry partner (Manufacturer A). Cans had one of four liner types; BPA based epoxy, acrylic, and two versions of BPA-NI epoxies. These are referred to as BPA-Epoxy-A, Acrylic-A, BPA-NI-Epoxy-A1, and BPA-NI-Epoxy-A2. The can liner thickness was the thickest liner available from the manufacturer, and the thickness recommended by each manufacturer for corrosive beverages.

For studies on a non-sour beer with added acids, cans were provided by two different manufacturers; Manufacturer A provided BPA-NI-Epoxy and acrylic-based "BPA-NI Gen 1," lined cans, and Manufacturer B provided acrylic lined cans. These are referred to as: Acrylic-A, Acrylic-B, and BPA-NI-Epoxy-A.

For all studies, the same source of can ends were used (5000 series alloy, BPA Epoxy 202LOE B64 style, American Canning, Austin, TX).

Canning protocol

During canning, 355 mL of beer was dispensed directly from a keg into cans, a few drops of LN_2 were added to remove headspace O_2, and the can was immediately topped with a lid and seamed using a MK16 double seamer (Oktober Design; Grand Rapids, MI). Seam quality was validated using a standard industry protocol consisting of measuring the seam thicknesses at four different points (first operation (0.187-0.193 cm), second operation (0.107-0.117 cm), cover hook (0.135-0.157 cm), body hook (0.140-0.191 cm)) at three locations around the seam (Oktober Design Seaming Manual 2020).[29] Total package oxygen (TPO) was measured using a Fibox 3 LCD trace O_2 meter with a DP-PSt6 oxygen dipping probe (PreSens, Regensburg, Germany) and determined to be <1.5 mg O_2/L for the tested cans.

Beer compositional analysis

TA, pH, SO_2, organic acid, and alcohol analyses were performed at the Cornell Craft Beverage Analytical Laboratory (Geneva, NY). The pH was measured using an Orion Star A211 meter (Thermo Scientific, Waltham, MA). Titratable acidity (TA) was measured with a Hanna Instruments (Smithfield, RI) HI901W automatic titrator by titrating to pH = 8.2 and results were expressed in lactic acid equivalents. Free and total SO_2 was measured by a Hanna Instruments HI901W automatic titrator.

For organic acids, lactic, malic, and tartaric acid were determined by HPLC (Shimadzu Prominence) fitted with a Phenomenex Rezex ROA Organic Acid H + column (300 mm) and guard column (50 mm). The injection size was 20 µL. The aqueous mobile phase (0.0005 N H_2SO_4) was isocratic and the flow rate was 0.5 mL/min. The total run time was 35 min. The column was maintained at 45 °C (model CTO-20AC). Detection was performed by a photodiode array detector, also held at 45 °C (model SPD-M20A), with quantitation at 210 nm. Acetic acid was determined by enzymatic assay on a BioSystems SPICA using a vendor provided kit (Admeo, Napa, CA; part #23930).

Alcohol by volume was determined by GC-FID (Agilent 6890 N, 7638B autosampler). For each analysis, 900 µL of 2% butanol was added to 100 µL of beer sample prior to injection on a GC column (Phenomenex Zebron ZB-WAXplus, 30 $m \times 0.25$ mm × 0.25 µm). The injection size was 1 µL, and injections were split at a 50:1 ratio. Constant pressure (138 kPa) was maintained over a run. Helium was used as a carrier gas (2.2 mL/min flow rate). Runs were isothermal (180 °C) and required 8 min total run tine.

Dissolved Al and Cu were analyzed at a local facility (USDA-ARS Holley Center, Ithaca, NY) using a Thermo Scientific iCAP 6500 series system for inductively coupled plasma-atomic emission spectroscopy (ICP-AES) by a protocol described elsewhere.[30]

Corrosion studies of commercial sour beers

Nine sour beers were obtained either in glass bottle or stainless steel keg format from a local retailer in Ithaca, NY, or directly from a local brewery. Each beer was given a sequential numeric code (**1**, **2**, … **9**), and their initial chemistry is reported in Table 1. All samples were purchased commercially except the sample directly acquired from the brewery (**9**) which was selected due to its high acetic acid content. Sour beers were then packaged in cans containing one of four liners (BPA-Epoxy-A, Acrylic-A, BPA-NI-Epoxy-A1, and BPA-NI-Epoxy-A2) using the protocol described above ("Canning protocol"). Two storage replicates were prepared for each beer × liner × timepoint combination. Following seaming, cans were stored at 20 °C in an upright position in the dark for 2, 6, 24, and 48 wk.

Corrosion measurements

For characterizing corrosion, can tops and bottoms were removed with a Gryphon C-40 band saw, then the body was cut vertically with scissors. Visible corrosion for each can was scored on a 1 to 5 scale, as described previously.[21] Briefly, cans with little visible corrosion were scored "1", and those with the maximum observed level of corrosion were scored "5" (Supplementary Figure 1). Dissolved aluminum concentrations were measured via ICP-AES according to the protocol described earlier.

Table 1. Composition of the nine commercially sourced sour beers used in the long-term study.

Sample ID	pH	ABV (% v/v)	Lactic Acid (g/L)	Acetic Acid (g/L)	Al (mg/L)	Cu (mg/L)
1	3.21	4.24	5.68	n.d.	0.12	0.12
2	3.46	5.40	5.84	n.d.	0.20	0.03
3	3.44	4.59	3.76	n.d.	n.d.	0.14
4	3.30	4.84	5.00	n.d.	0.46	0.13
5	3.37	9.45	5.46	n.d.	0.45	0.60
6	3.05	4.04	7.55	n.d.	0.30	0.10
7	3.36	4.79	3.24	n.d.	n.d.	0.12
8	3.49	5.67	3.00	1.08	0.33	0.20
9	3.45	7.09	4.61	9.01	n.d.	0.10

Multifactor screening of sour beer components for corrosivity

A bottled American light lager (4.2% ABV) was purchased from a local store, and 8 g/L lactic acid and 8 g/L acetic acid were added to create a base sour beer with high corrosivity. Other potential corrosive components were added based on a fractional factorial design generated in JMP Pro 16 (SAS Institute, Inc., Cary, NC). The potential corrosive components evaluated included ethanol (range of 4.2 – 10% v/v; adjusted with 70% v/v ethanol), pH (3.2 – 4.2; adjusted with KOH), free SO_2 (0 - 30 mg/L; adjusted with KMBS stock solution), sodium (0 - 150 mg/L; adjusted with sodium sulfate stock solution), chloride (0-250 mg/L; adjusted with calcium chloride stock solution), and copper (0 - 1 mg/L; adjusted with copper sulfate stock solution). Four middle points were included in the fractional factorial design, shown in Supplementary Table 1. Samples were canned using the procedure listed above and stored at 20 °C for 12 wk. Following storage, corrosion was evaluated by measurement of dissolved aluminum by ICP-AES.

Corrosivity of organic acid mixtures during long term storage

A commercial American light lager (4.2% ABV) was spiked with different acid combinations (lactic, acetic, phosphoric) such that the total acid content was equinormal (0.17 N). A total of nine different combinations were used (Supplementary Table 2). For each acid combination treatment, the pH was adjusted to one of two values (3.0 and 3.5) using dropwise addition of concentrated KOH, for a total of 18 beer treatments. The treatments were then canned with three different liners (BPA-NI-Epoxy-A, Acrylic-A, and Acrylic-B) in triplicate. After 24 wk of storage at 20 °C, dissolved aluminum was measured by ICP-AES, as described in the following section.

Statistical analysis and software

Statistical analysis was done via JMP Pro 16 and JMP Pro 17 (SAS Institute, Inc., Cary, NC). Analysis of variance ($\alpha = 0.05$) was used to evaluate the effects of sour beer components, liner, and storage time on aluminum can corrosion. A p-value < 0.05 was used to determine significant differences among treatment groups.

Results and discussion

Corrosivity of commercially produced sour beers and correlation with beer components

Nine sour beers sourced from industry collaborators were characterized for pH, alcohol, lactic acid, acetic acid, and copper, then repackaged into cans with one of four liners. Initial Al was < 0.5 mg/L in all sour beer samples. Dissolved Al was measured after 2, 6, 24, and 48 wk storage at 20 °C, and the increase in dissolved Al (calculated as [Al at time point X] – [initial Al]) was used as a proxy for corrosion. Dissolved Al increased in all canned beverages in a time-dependent manner, with measurable increases in dissolved Al occurring for all beers somewhere between 6 and 24 wk (Figure 1). The greatest Al increase for each sour beer was observed at the last time point (48 wk), with the largest value observed in **9** (43.2 ± 4.7 mg/L) followed by **6** (9.3 ± 1.0 mg/L). These two values were well above the maximum increase in average Al observed in wines stored in BPA and BPA-NI epoxy cans for up to 32 wk (< 2.5 mg/L)[21] and also well above typical concentrations observed in other canned and bottled beers (~0.1 mg/L).[26] For beer **9**, consumption of a 355 mL (12 oz) serving per day would equate to ~15 mg/day Al, or ~100 mg/week. This value approaches the World Health Organization recommended total weekly intake of <2 mg Al/week per kg body weight, or <150 mg Al/week for a 75 kg person.[34] As a caveat, this sour beer was not commercially released due to its high acetic acid content (see next section), and the dietary Al from the highest commercially available sour beer (**6**) was only ~3 mg per 355 mL serving.

Interestingly, no significant difference in dissolved Al was observed among the three liner types (acrylic, BPA epoxy, BPA-NI epoxy) at any timepoint (ANOVA, $p > 0.05$; Supplementary Table 3). This contrasts with previous work on canned wines, where much greater H_2S, dissolved Al, and visible corrosion were observed in wines stored in acrylic lined cans after as little as four weeks. The corrosive component of wines is hypothesized to be sulfites (especially the molecular SO_2 form), and there was visible evidence in this previous work of a direct reaction and degradation of the acrylic liner in high molecular SO_2 wines.[21]

All sour beers had pH values, alcohol content, and lactic acid (Table 1) comparable to those reported in earlier literature.[4,5] Cu concentrations in the current study fell within the range of values reported in a different survey.[31] Acetic acid values were generally comparable to previous studies (<2 g/L)[4,5] with the exception of sample **9**, which contained

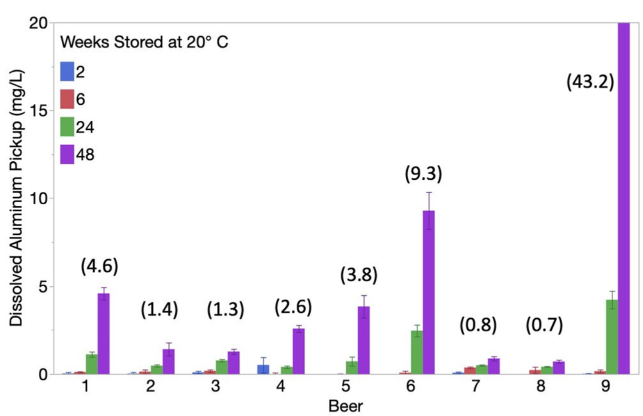

Figure 1. Increase in dissolved aluminum following storage (2 to 48 wk) of different sour beers. Values represent the averages for four different lined aluminum beverage cans values, with technical storage replicates for each can liner. Error bars represent one standard error from the mean. Values shown in parentheses are the mean dissolved aluminum pickup for each beer after 48 wk.

9 g/L acetic acid, considerably greater than values in earlier reports, and also well above the rejection threshold for acetic acid in red wine of 0.9 g/L.[32] This beer was provided directly by a brewery and was later destroyed because it was deemed commercially unsalable.

Acetic acid was strongly correlated with dissolved aluminum (R^2 = 0.838, $p < 0.001$), although this was due to the very high acetic acid content of sample **9** (Figure 2). Linear regressions of [component] vs [dissolved aluminum in at 48 wk] were performed for all other components, with sample **9** excluded. Dissolved aluminum was correlated inversely with pH (R^2 = 0.695, $p < 0.001$) and positively with lactic acid (R^2 = 0.602, $p < 0.001$). No other components correlated with dissolved aluminum (Figure 2).

Visible evidence of corrosion in the form of liner blistering was observed only after 48 wk of storage and only for two of the sour beers – **9** (highest acetic acid) and **6** (highest lactic acid). Blistering occurs due to formation of H_2 gas concurrent to aluminum oxidation and dissolution (Equation 1), and these two beers also had the greatest increase in dissolved aluminum during storage (Figure 1). Representative images of BPA-Epoxy and BPA-NI Epoxy can interiors are shown in Figure 3. Images from a lower acid sour beer (**1**) with no visible liner damage are shown for comparison. For **6** and **9**, blistering is evident in the neck region of the can for both BPA and BPA-NI liners. Blistering is also evident in the body of BPA-NI Epoxy cans (Figure 3, top) but not BPA Epoxy cans (Figure 3, bottom). Despite these visible differences, no significant difference was found between the mean dissolved aluminum increase in BPA-epoxy and BPA-NI Epoxy cans after 48 wk of storage ($p > 0.05$; Wilcoxon Each Pair test). This result suggests that most of the dissolved aluminum increase is arising from the neck regions.

Screening of potentially synergistic corrosive compounds in beers

The long-term storage trial with commercially sourced sour beers suggested that low pH and/or high concentrations of acetic and lactic acids accelerated corrosion. Prior to performing long-term storage trials to investigate the role of pH and different acids, a screening experiment was performed using a fractional factorial design to determine if other beer components (ethanol, molecular and free SO_2, sodium, chloride, copper) could also accelerate corrosion. Suggested limits for these components are provided by can manufacturers,[33] although recent work on canned wine suggested that only pH, molecular SO_2, and free SO_2 were correlated with corrosion after 4 to 8 months of storage.[21]

The correlation coefficients for all variables studied with dissolved aluminum are reported in Table 1. After 12 wk of canned storage in BPA-NI-Epoxy-A cans, the component that was best correlated with dissolved aluminum was molecular SO_2 (Table 1 and Figure 4) with 2.3-fold higher dissolved aluminum observed for sour beers with the highest molecular SO_2 (2.4 mg/L) vs. samples with no added SO_2. A similar observation was made in canned wine, where

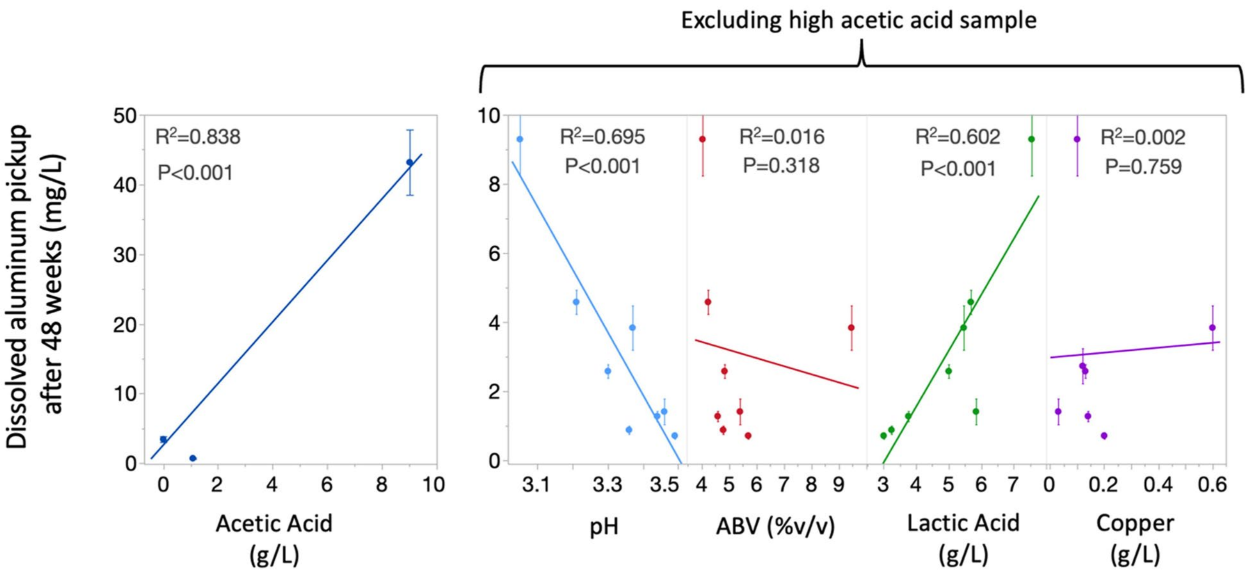

Figure 2. (Left) linear regressions of dissolved aluminum increase vs acetic acid concentrations of nine sour beers; (right) linear regressions of dissolved aluminum increase vs. pH, alcohol by volume (ABV), lactic acid, and copper of eight sour beers, with the highest acetic acid beer **9** excluded. Dissolved aluminum was determined after 48 wk of storage, and values represent the average observed for four different can liners with two replicate cans per liner. Error bars represent one standard error from the mean.

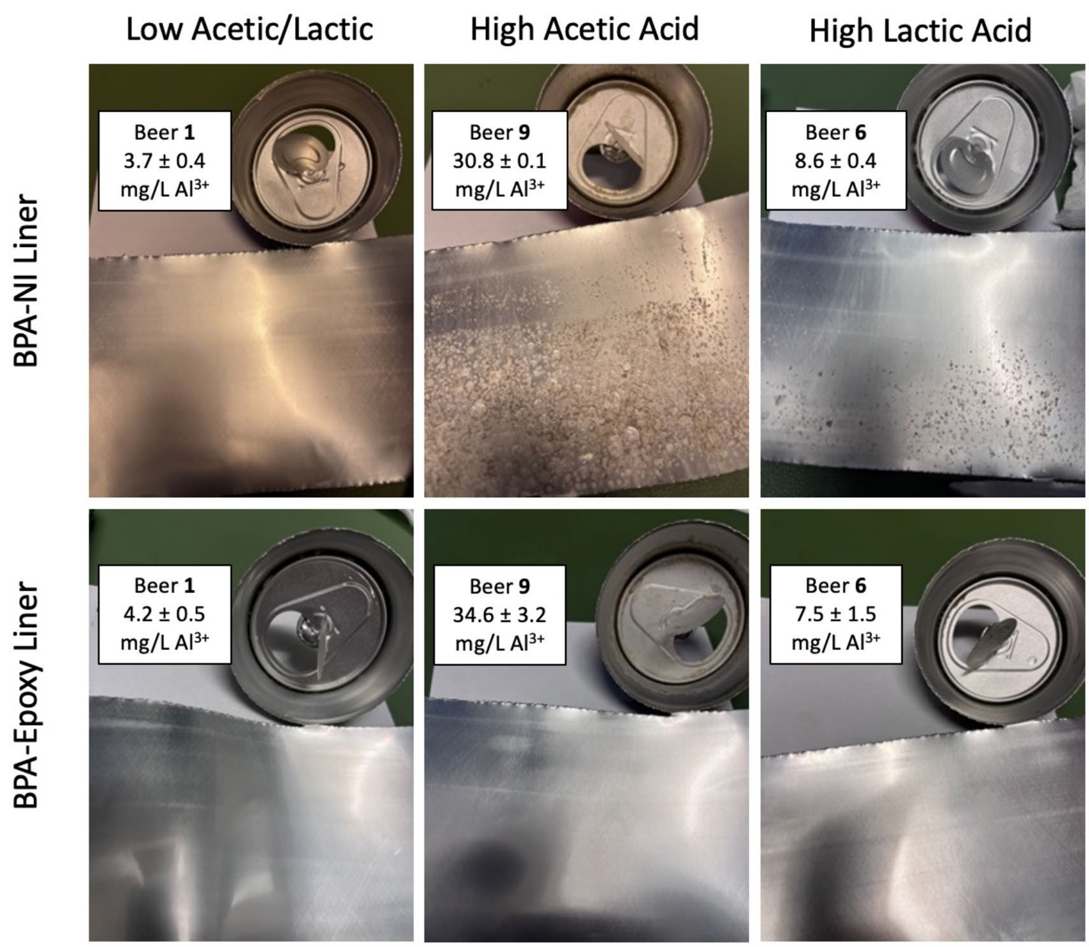

Figure 3. Interior of BPA-NI Epoxy (top) and BPA Epoxy (bottom) cans following 48 wk of storage at 20 °C for representative sour beers (**1**, **9**, **6**) with varying concentrations of acetic acid and lactic acid. Dissolved aluminum increases following storage are reported for each can and sour beer concentration (mean ± one standard error). Following storage of sour beers **6** and **9**, BPA Epoxy cans show evidence of visible blistering only in the headspace/neck region, while BPA-NI Epoxy shows evidence of blistering in both the body and neck regions of the can.

molecular SO_2 was the best predictor of dissolved aluminum, H_2S production, and visible damage to the liner.[21] The range of molecular SO_2 used in this study (0 to 2.4 mg/L) is realistic for wines, but is much higher than those typically observed in beer, where producers in most countries strive to keep total SO_2 concentration < 10 mg/L (or 10 ppm) to avoid declaring their use on packaging.[34] Assuming a beer pH of 3 (the lowest observed in our study) and all total SO_2 exists in its free form, a total SO_2 concentration of 10 mg/L corresponds to a molecular SO_2 ~0.5 mg/L. However, free SO_2 was below detection limits in all commercial sour beers evaluated in this study (< 2 mg/L; data not shown). Thus, molecular SO_2 is <0.1 mg/L in these commercial sour beers, and unlikely to contribute to increases in dissolved aluminum.

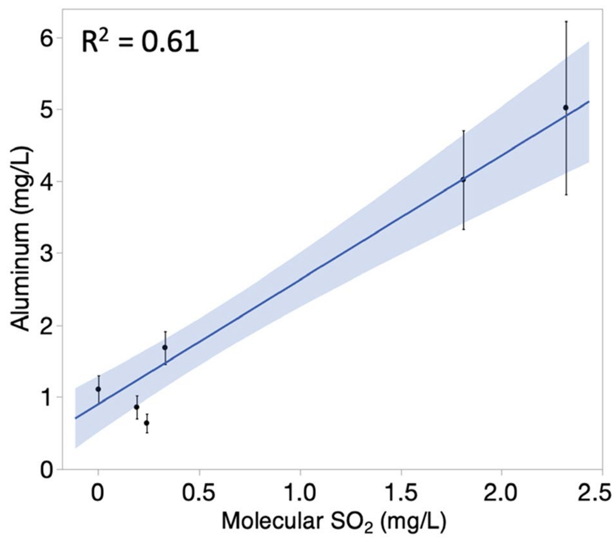

Figure 4. Correlation of dissolved aluminum with molecular SO_2 (p-value <0.05) in the multi-factorial screening experiment.

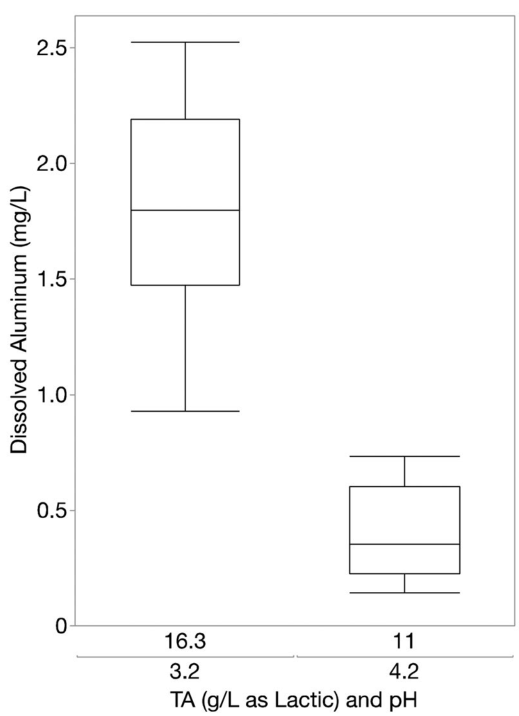

Figure 5. Dissolved aluminum as a function of pH in the multi-factorial screening experiment. Only samples with no SO_2 addition are included.

Because of the large effect of SO_2 on corrosion, the data were reanalyzed using only samples with no added SO_2. With this reduced data set, the only components correlated with dissolved aluminum were pH and TA ($p < 0.05$). The Pearson correlation coefficients for all compositional parameters with dissolved aluminum, excluding SO_2 samples, are shown in Table 2. The lower pH (3.2) and higher TA (16.3 g/L) samples had 5-fold higher concentrations of dissolved aluminum (Figure 5). Because pH and TA were adjusted simultaneously through dropwise addition of concentrated KOH, it was not possible to decouple these two parameters.

Other parameters (alcohol, chloride, copper, or sodium) had a negligible or non-significant effect on corrosion (Supplementary Figure 2). Very high ethanol (~80% ABV) concentrations are reported to accelerate can corrosion through swelling and delamination of the liner,[19] although no effect was observed at more typical alcohol concentrations found in wine.[21] Similarly, chloride and copper are reported to accelerate corrosion at high concentrations and/or in the absence of a polymeric liner,[20,33] but not with lined aluminum.[36] Analogously, no effect on dissolved aluminum was observed with beverages containing chloride and copper concentrations comparable to this study, as was also observed with wine.[21] As noted previously, the sulfhydryls present in fermented alcoholic beverages may complex copper ions, decreasing their activity and presumably their corrosivity, too.[21]

Visual corrosion in cans following storage was scored on a 1 - 5 scale. Examples of each rating are shown in Supplementary Figure 1. The visual corrosion ratings after 12 wk were well correlated with dissolved aluminum (Figure 6, R^2 = 0.73). Generally, moderate to high visible corrosion (corrosion score ≥ 3) was only observed when dissolved aluminum exceeded 2 mg/L. There was a progression of visible corrosion in which corrosion started near the seam (Figure 7, Step 1), and then extended vertically down the length of the can down the can (Figure 7, Step 2). In the most damaged cans, visible blistering and liner degradation were primarily observed in the can neck (Figure 7, Step 3), comparable to long term studies of sour beers sourced from commercial breweries (Figure 3). Little to no visible damage to the underside of the can lids was observed in all solutions, likely because of the can lids possessed a thicker liner (~9 µm). Similarly, studies on high alcohol hand sanitizer

Table 2. Correlation coefficients for pairwise regressions of beer components vs. dissolved aluminum.

Pearson Correlation Coefficients	ABV	pH/TA	Sodium	Chloride	Copper	Molecular SO_2
All samples	0.009	−0.616	0.059	0.072	−0.106	0.712
Only "no SO_2 added" samples	0.401	−0.905	−0.249	−0.055	−0.285	n/a

observed negligible damage to the can lids, with blistering primarily observed in the neck region of the can body.[19]

Effect of specific acids on aluminum corrosion

Based on results described earlier, corrosion in sour beers was best correlated with lower pH, higher TA, and higher concentrations of individual organic acids (acetic, lactic). However, these factors are also well correlated with each other, and it was unclear which factor(s) were likely to be causative of the observed corrosion. To address this question, sour beers were prepared by spiking an American light lager with equinormal (0.17 N) mixtures of three acids (phosphoric, acetic, and lactic) in varying ratios, and then canned and stored for 24 wk in one of three liners. After storage, beer in the Acrylic-B cans had a two-fold higher concentration of dissolved aluminum ($p < 0.05$) than solutions stored in the Acrylic-A and the BPA-NI-Epoxy-A cans, which performed similarly. As noted earlier, these differences are much lower than the differences observed between epoxy and acrylic liners for canned wine.[21]

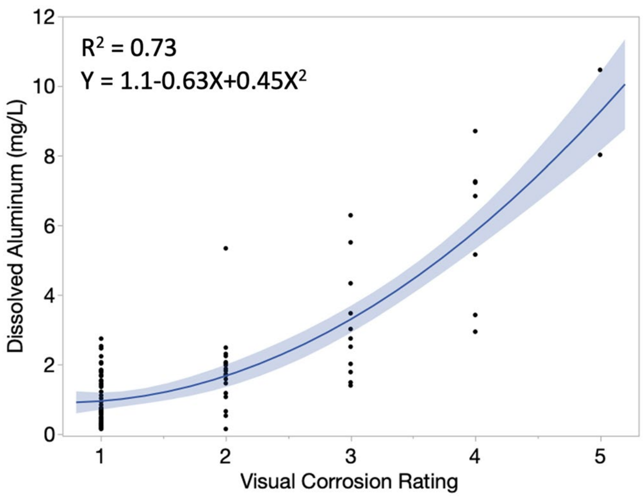

Figure 6. Regression of dissolved aluminum and visible corrosion rating for model sour beers from the fractional factor design evaluation of parameters affecting corrosion. Each point represents one sample, and each combination of parameters had three technical replicates.

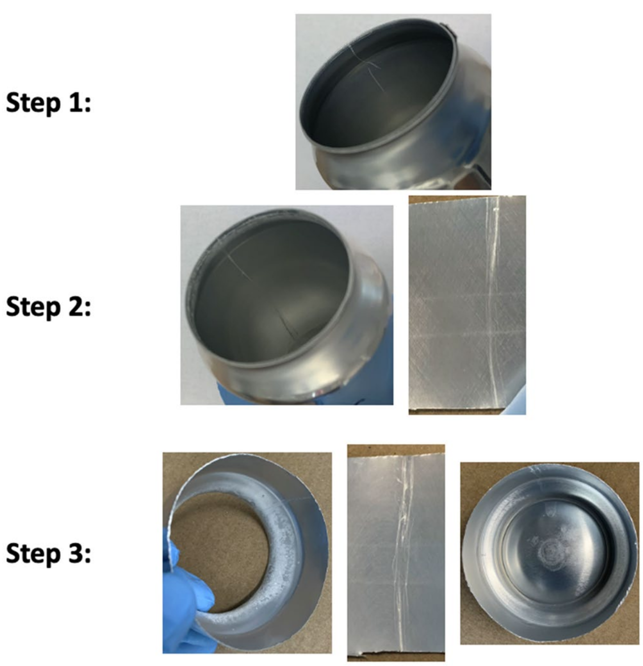

Figure 7. Progression of visual corrosion in BPA-NI-Epoxy-a cans during storage. More advanced steps correlated with higher dissolved aluminum.

The summed concentration of lactic and acetic acids was well correlated with dissolved aluminum after 24 wk storage (Figure 8), with an even stronger concentration observed between the concentration of undissociated lactic and acetic acid with dissolved aluminum ($R^2 > 0.85$, Figure 9). By comparison, phosphoric acid ($pK_{a1} = 2.1$) exists almost entirely in its charged hydrogen phosphate (HPO_4^-) form at beverage pH. Previous work with canned wine noted that that the concentration of neutral forms of SO_2 ("molecular SO_2") was the best predictor of H_2S formation and corrosion.[21] Speculatively, the neutral, undissociated forms of acetic and lactic acids may be better able to permeate pores in the liner than charged species, resulting in greater corrosion.

An increase in dissolved aluminum is observed once the sum of undissociated acetic and lactic acids is > ~6 g/L as lactic acid equivalents. At lower concentrations of undissociated acids, the sour beers had dissolved aluminum concentrations comparable to a control American light lager stored in can (0.30 mg/L) and slightly higher than the control lager stored in glass bottle (0.085 mg/L). However, from a practical standpoint, determination of undissociated lactic and acetic acid concentrations is not trivial, as it requires measurement of individual acids (e.g. by HPLC or enzymatic methods), followed by calculating the undissociated proportion based on the pH and the Henderson-Hasselbalch equation. A simpler approach is to use titratable acidity (TA) as a proxy for undissociated acids. Although TA will also include protons from charged polyprotic acids, e.g. HPO_4^-, we observed good correlation ($R^2 > 0.7$) between dissolved aluminum and TA for the Acrylic-A and BPA-NI-Epoxy-A cans (Figure 10), with an increase in dissolved aluminum over baseline observable at TA > 6 g/L as lactic acid

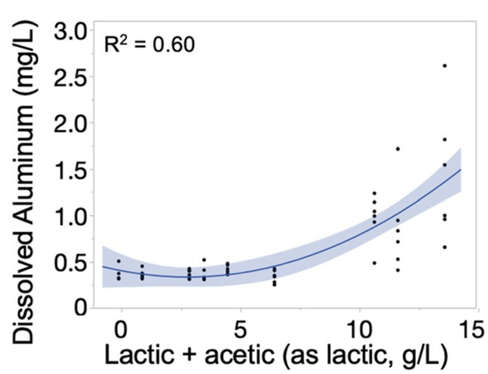

Figure 8. Dissolved aluminum as a function of total lactic and acetic acid after 24 wk of storage in Acrylic-a cans.

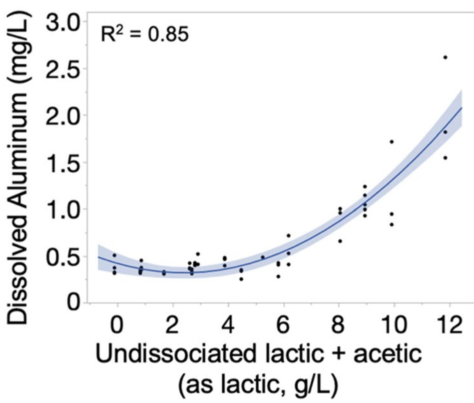

Figure 9. Dissolved aluminum as a function of undissociated lactic and acetic acid after 24 wk of storage in Acrylic-a cans.

equivalents. A weaker correlation between TA and dissolved aluminum was observed for Acrylic-B cans (Figure 10), although this may be explained by the considerable can-to-can variation in dissolved aluminum. Finally, pH was not a good predictor of can corrosion (Figure 11), further suggesting that organic acids (and not free protons) are involved in corrosion of lined beverage cans.

Although this current work is the first to demonstrate the corrosivity of acetic and lactic acid in sour beers, this report has certain limitations. Our work demonstrates that acetic and lactic acids are especially corrosive as compared to phosphoric, but other non-volatile acids (e.g. citric, malic, fumaric) were not tested. A mechanistic explanation for the corrosivity of acetic and lactic was not established, although the hypothesis that the volatility of these acids facilitates

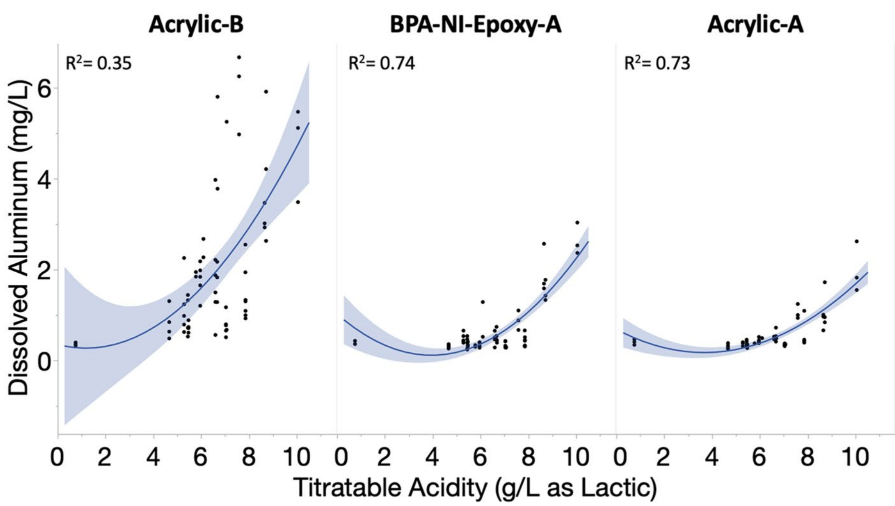

Figure 10. Correlation between titratable acidity (TA) and dissolved aluminum by liner type after 24 wk of storage.

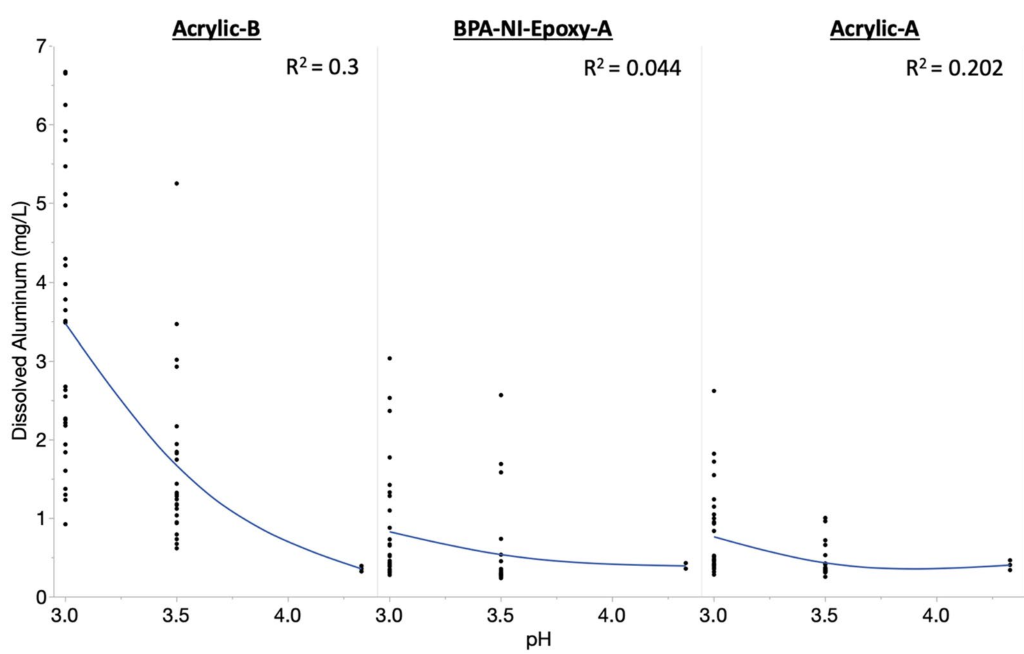

Figure 11. Correlation of dissolved aluminum with pH of model sour beers for three liner types. Each point represents one beer after 24 wk of storage.

their passage through the liner should provide a good starting point for future work. The impact of can storage on sensory properties of the sour beers was not evaluated and would likely be of interest to many sour beer producers.

Conclusions

Canned sour beers will accumulate higher concentrations of dissolved aluminum (up to 40 mg/L after 48 wk) than typical concentrations reported in conventional canned beers (<0.5 mg/L). Increases in dissolved aluminum appeared to arise from corrosion of the aluminum can body, especially the neck region, and were correlated with visible damage to the liner. The increase in dissolved aluminum did not differ among liner type (BPA Epoxy, BPA-NI epoxy, and acrylic), for commercial beers, but did correlate with the total concentration of lactic and acetic acid. Addition of acids to non-sour beer samples suggested that the neutral forms of these organic acids are well correlated with corrosion, and that titratable acidity (TA) may be a simpler but effective metric for predicting the corrosivity of sour beers. This work is a step towards evidence based determination of factors causing corrosion in other canned beverages with high levels of volatile acids, and therefore the ability to prolong their shelf-life.

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ORCID

Matthew Sheehan http://orcid.org/0009-0005-2985-7344
Austin Montgomery http://orcid.org/0009-0003-2566-7397
Julie M. Goddard http://orcid.org/0000-0002-3644-0732
Gavin L. Sacks http://orcid.org/0000-0002-1403-0505

Literature cited

[1] Hurt, J. **2020**, March 11. *Beer Drinkers Are Growing Sweet on Sour Beers.* https://www.forbes.com/sites/jeanettehurt/2020/03/11/beer-drinkers-are-growing-sweet-on-sour-beers/.

[2] Dysvik, A.; Rosa, S. L. L.; Rouck, G. D.; Rukke, E.-O.; Westereng, B.; Wicklund, T. Microbial Dynamics in Traditional and Modern Sour Beer Production. *Appl. Environ. Microbiol.* **2020**, *86*(14), e00566-20. DOI: 10.1128/AEM.

[3] Jackson, G.; Klassen, A. **2019**. *Achieving Balance in Sour Beer: Understanding and Adjusting Titratable Acidity*. The Beverage People. https://www.thebeveragepeople.com/pdf/webbeerpdf/Adjusting-Titratable-Acidity-in-Sour-Beer.pdf (accessed Aug 21, 2024).

[4] Tenhovirta, S. **2019**. The Effects of Lactic Acid Bacteria Species on Properties of Sour Beer. URN:NBN:fi:hulib-201906122666; http://hdl.handle.net/10138/303018.

[5] Tipler, A.; Reuter, W. M.; Chadwick, L. *The Analysis of Lactic and Acetic Acids in Sour Beers by HPLC with PDA Detection*. **2015**. https://resources.perkinelmer.com/lab-solutions/resources/docs/app-analysis-of-lactic-and-acetic-acids-in-sour-beers-by-hplc.pdf (accessed Aug 21, 2024).

[6] Coote, N.; Kirsop, B. H. Factors Responsible for the Decrease in pH During Beer Fermentations. *J. Inst. Brew.* **1976**, *82*(3), 149–153. DOI: 10.1002/j.2050-0416.1976.tb03739.x.

[7] Park, J. M.; Shin, J. A.; Lee, J. H.; Lee, K. T. Development of a Quantitative Method for Organic Acid in Wine and Beer Using High Performance Liquid Chromatography. *Food Sci. Biotechnol.* **2017**, *26*(2), 349–355. DOI: 10.1007/s10068-017-0047-9.

[8] Dusart, A.; Ryckaert, J.-P.; Collin, S. Comparative Investigation of Flavors in Red and Brown Flemish Beers: Key-Role of Brettanomyces and Torrefied Malts in Ethylphenols Occurrence. *J. Am. Soc. Brew. Chem.* **2022**, *81*(3), 357–365. DOI: 10.1080/03610470.2022.2109380.

[9] Herkenhoff, M. E. The Probiotic Paradox: Thriving in High-Hopped Sour Beer. *J. Am. Soc. Brew. Chem.* **2024**, 1–9. DOI: 10.1080/03610470.2024.2350108.

[10] Rochefort, L.; Caille, O.; Nedervelde, L. V. Sequentially Pitching Lactic Acid Bacteria and Active Dry Yeasts for Sour Beer Production. *J. Am. Soc. Brew. Chem.* **2023**, *82*(2), 141–149. DOI: 10.1080/03610470.2023.2215665.

[11] Shayevitz, A.; Abbott, E.; Zandycke, S. V.; Fischborn, T. The Impact of Lactic and Acetic Acid on Primary Beer Fermentation Performance and Secondary Re-Fermentation during Bottle-Conditioning with Active Dry Yeast. *J. Am. Soc. Brew. Chem.* **2021**, *80*(3), 258–269. DOI: 10.1080/03610470.2021.1952508.

[12] Weikert, J. **2016**. *The Art of Tart: The Many Ways (Both Quick and Slow) to Make Sour Beer.* Beer and Brewing. https://beerandbrewing.com/the-art-of-tart-the-many-ways-both-quick-and-slow-to-make-sour-beer/.

[13] Sivits, C. G. **2021**. *Consumer Demand and Covid Push Large-Format Sour Beers into Cans.* Vinepair. https://vinepair.com/articles/sour-beer-cans/ (accessed Aug 21, 2024).

[14] Kawahara, M.; Konoha, K.; Nagata, T.; Sadakane, Y. Aluminum and Human Health: Its Intake, Bioavailability and Neurotoxicity. *Biomed Res. Trace Elem.* **2007**, *3*(18), 211–220.

[15] Reilly, T.; Mierczynski, P.; Suwanto, A.; Krido Wahono, S.; Maniukiewicz, W.; Vasilev, K.; Bindon, K.; Mierczynska-Vasilev, A.; Kilmartin, P. Using Zeolites to Cold Stabilize White Wines. *Aust. J. Grape Wine Res.* **2023**, *2023*, 1–12. DOI: 10.1155/2023/7259974.

[16] Beveridge, T.; Wrolstad, D. R. E. Haze and Cloud in Apple Juices. *Food Sci. Nutr.* **1997**, *37*, 75–91.

[17] Chira, K.; Jourdes, M.; Teissedre, P.-L. Cabernet Sauvignon Red Wine Astringency Quality Control by Tannin Characterization and polYmerization During Storage. *Eur. Food Res. Technol.* **2011**, *234*(2), 253–261. DOI: 10.1007/s00217-011-1627-1.

[18] Wang, Y.; Zajac, A. L.; Lei, W.; Christensen, C. M.; Margolskee, R. F.; Bouysset, C.; Golebiowski, J.; Zhao, H.; Fiorucci, S.; Jiang, P. Metal Ions Activate the Human Taste Receptor TAS2R7. *Chem. Senses.* **2019**, *44*(5), 339–347. DOI: 10.1093/chemse/bjz024.

[19] Thomson, E. L.; Bullied, A. R. Corrosion Resistance of Aluminum Beer Cans Containing Hand Sanitizer. *J. Am. Soc. Brew. Chem.* **2020**, *78*(4), 279–283. DOI: 10.1080/03610470.2020.1784634.

[20] Soares, B. M. C.; Dantas, S. T.; Anjos, C. A. R. Corrosion of Aluminum for Beverage Packaging in Acidic Media Containing

Chlorides and Copper Ions. *J. Food Process Engineering* **2017**, *40*(6), e12571. DOI: 10.1111/jfpe.12571.

[21] Montgomery, A.; Allison, R. B.; Goddard, J. M.; Sacks, G. L. Hydrogen Sulfide Formation in Canned Wines under Long-term and Accelerated Conditions. *Am. J. Enol. Vitic.* **2023**, *74*(1), 0740011. DOI: 10.5344/ajev.2022.22051.

[22] Chen, D.; Kannan, K.; Tan, H.; Zheng, Z.; Feng, Y. L.; Wu, Y.; Widelka, M. Bisphenol Analogues Other Than BPA: Environmental Occurrence, Human Exposure, and Toxicity-A Review. *Environ. Sci. Technol.* **2016**, *50*(11), 5438–5453. DOI: 10.1021/acs.est.5b05387.

[23] Krieg, H.; Gadhia, H. An Overview of Can Liner Types and Measuring Techniques. *MBAA TQ.* **2021**, *58*(4), 214–218. DOI: 10.1094/TQ-58-4-0211-01.

[24] Maffini, M. V.; Rubin, B. S.; Sonnenschein, C.; Soto, A. M. Endocrine Disruptors and Reproductive Health: The Case of Bisphenol-A. *Mol. Cell. Endocrinol.* **2006**, *254-255*, 179–186. DOI: 10.1016/j.mce.2006.04.033.

[25] Tickner, J. A.; Simon, R. V.; Jacobs, M.; Pollard, L. D.; van Bergen, S. K. The nexUs between Alternatives Assessment and Green Chemistry: Supporting the Development and Adoption of Safer Chemicals. *Green Chem. Lett. Rev.* **2020**, *14*(1), 23–44. DOI: 10.1080/17518253.2020.1856427.

[26] Sharpe, F. R.; Williams, D. R. Content, Chemical Speciation, and Significance of Aluminum in Beer. *J. Am. Soc. Brew. Chem.* **1995**, *53*(2), 85–92. DOI: 10.1094/ASBCJ-53-0085.

[27] Duggan, J. M.; Dickeson, J. E.; Tynan, P. F.; Houghton, A.; Flynn, J. E. Aluminium Beverage Cans as a Dietary Source of Aluminium. *Med. J. Aust.* **1992**, *156*(9), 604–605. DOI: 10.5694/j.1326-5377.1992.tb121455.x.

[28] Vargel, C. *Corrosion of Aluminum* (2nd ed.). Elsevier Science: Oxford UK, **2020**.

[29] Anonymous. *Model 7 Operation Manual*. Oktober Can Seamers. Grand Rapids, MI, **2020**.

[30] Zhou, S.; Okekeogbu, I.; Sangireddy, S.; Ye, Z.; Li, H.; Bhatti, S.; Hui, D.; McDonald, D. W.; Yang, Y.; Giri, S.; et al. Proteome Modification in Tomato Plants upon Long-term Aluminum Treatment. *J. Proteome Res.* **2016**, *15*(5), 1670–1684. DOI: 10.1021/acs.jproteome.6b00128.

[31] Osorio-Macías, D.; Peñarrieta, M. Evaluation of Copper Content in Beers Obtained from Retail in Sweden. *J. Brew. Distilling.* **2017**, *7*, 1–4. https://doi.org/10.5897/JBD2017.0049.

[32] Corison, C. A.; Ough, C. S.; Berg, H. W.; Nelson, K. E. Must Acetic Acid and Ethyl Acetate as Mold and Rot Indicators in Grapes. *Am. J. Enol. Vitic.* **1979**, *30*(2), 130–134.

[33] Coetzee, C. *The Winemaker's Guide to Wine in a Can*; Winetech: Suider Paarl, SA, **2021**.

[34] Guido, L. F. Sulfites in Beer: Reviewing Regulation, Analysis and Role. *Sci. Agric. (Piracicaba, Braz.)* **2016**, *73*(2), 189–197. DOI: 10.1590/0103-9016-2015-0290.

[35] Soares, B. M. C.; Anjos, C. A. R.; Faria, T. B.; Dantas, S. T. Characterization of Carbonated Beverages Associated to Corrosion of Aluminium Packaging. *Packag. Technol. Sci.* **2016**, *29*(1), 65–73. DOI: 10.1002/pts.2187.

[36] Soares, D. S.; Bolgar, G.; Dantas, S. T.; Augusto, P. E. D.; Soares, B. M. C. Interaction between Aluminium Cans and Beverages: Influence of Catalytic Ions, Alloy and Coating in the Corrosion Process. *Food Packaging and Shelf Life*, **2019**, *19*, 56–65. DOI: 10.1016/j.fpsl.2018.11.012.

[37] Evaluation of Certain Food Additives and Contaminants. **2007**. WHO Technical Report Series. (940), 33–44.