

## Tribo-rheology of alcoholic and non-alcoholic beer

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## ORIGINAL ARTICLE

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# Tribo-rheology of alcoholic and non-alcoholic beer

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## Abstract

The analysis of mouthfeel is an important but challenging area for objective study. The use of human tasting panels presents issues of comparability between studies together with ethical limitations on consumption. Here, tribo-rheology was used in the analysis of lubrication of seven beer styles in their standard and low/no alcohol formats. Tribo-rheology was used to generate Stribeck curves showing the frictional characteristics and differences between the beers. Some possible causes for the differences in lubrication were evaluated including varying concentrations of ethanol, maltose, maltodextrin and sodium chloride. This work demonstrates statistically significant differences in lubrication between low/no alcohol beers and standard strength beers from the same producer. To conclude, the results and differences in lubrication are discussed in terms of molecular detail.

## Keywords:

tribology, tribo-rheology, low-alcohol, mouthfeel, beer

## Introduction

Low and no alcohol beers represent a small but growing market. The increasing consumption of no and low alcohol beers has highlighted historical quality issues which may inform modern products. Progress with methods of production has aimed to remedy defects with the early low and no alcohol beers categorised into volatile flavour, nonvolatile flavour and mouthfeel.

Production methods for low and no alcohol beers have changed since the early methods which used heating to remove ethanol, resulting in an undesirable product with significant loss of aroma and oxidative damage (Sohrabvandi et al. 2010). Modern production methods use technology to remove alcohol or to produce beers with low alcohol. The ethanol removal strategies are typically either thermal or membrane methods. The brewing methods use an altered grist or the use of non-standard yeasts unable to utilise maltose (Bellut and Arendt 2019). The products of these approaches have different advantages and disadvantage (Rettberg et al. 2022). Further, methods can be combined to produce a more desirable low or no-alcohol beer.

The quantification of flavour is challenging. Generally, gas chromatography with mass spectrometry is conducted on beers (Charry-Parra et al. 2011) and has been used to assess quality in low alcohol beers, primarily in terms of volatile organic aroma compounds related to aroma and flavour. This is due to the older methodologies of ethanol removal, which typically involved heating (Brányik et al. 2012), and the loss of volatile flavour molecules. Other methods of analysis include liquid chromatography with mass spectrometry (often tandem mass spectrometry) which is used for non-volatile organic acids, saccharides and other relevant molecules (Araújo et al. 2005). These compounds are important in taste, particularly sweetness, sourness and bitterness. Although gas chromatography is capable of measuring many of these compounds it can require significant processing and derivatisation reactions, which add complexity when compared to liquid chromatography (Otter and Taylor 1967).

Although more challenging than measuring absolute quantities of compounds but key for the of quality

is subjective and oral processing has been shown to have high variability among individuals. (Hiiemae and Palmer 2003). Defects in mouthfeel vary, depending on the method of dealcoholisation or low alcohol brewing methodology, where low gravity mashing yields a wort low in fermentable sugar and a beer of low alcohol content. This leads to a low final gravity with little residual sugar and, as final gravity has been shown to correlate with mouthfeel fullness (Langstaff et al. 1991), a low original gravity beer would be expected to have a thinner mouthfeel. Alternatively incomplete fermentation of higher gravity wort can be utilised which may result in significant flavour defects (Perpète and Collin 1999). These limited fermentation beers exhibit a high specific gravity due to incomplete attenuation and a positive mouthfeel, but an overly sweet taste with low levels of volatile aroma molecules (Perpète and Collin, 2000).

The contributors to mouthfeel are less well defined than volatile aroma compounds. Early work to define mouthfeel properties focussed on carbonation, fullness and after feel (Langstaff and Lewis, 1993), which sought to describe the exact nature of the oral properties of a product. The molecular contributors to these properties were from a wide range of chemical classes and the reasoning for their contribution varied. For example, chloride ions were predicted to increase the indirect perception of mouthfeel, by initiating  $\alpha$ -amylase production and by being shown to positively correlate with perceived fullness (Langstaff et al, 1991). This is not an effect that can be measured using currently available instrumentation, as there is no capacity to simulate the release of enzymes although inorganic salts may have their own friction reducing effect in tribology.

The dextrin level in beer has been considered a major factor in mouthfeel perception (Langstaff and Lewis 1993) although the ratio of lengths of the glucose polymer has been shown to play a significant role beyond that of concentration (Krebs et al. 2019). Using a trained, tasting panel it is possible to differentiate the change in mouthfeel beyond pallet fullness, providing a more useful distinction for process and product adjustments (Krebs et al. 2019).

Although ethanol concentration is considered a major and positive contributor to the perception of mouthfeel, it is seen to lower viscosity when in water (Khattab et al. 2012). Although more recent work looking at altered ethanol concentration in the same beer showed a more complex interaction with higher levels being more positively received highlighting individual perceptive differences to be a key factor (Ramsey et al. 2018).

Recently, attributes and scores for 24 beers from a trained panel have been compared to the concentrations of different compounds (Agorastos et al. 2023). This yielded a strong ( $r=0.84$ ) correlation between the levels of iso- $\alpha$ -acids and bitterness, while polyphenol content was weakly ( $r = 0.59$ ) correlated with drying. Iso- $\alpha$ -acids significantly to bitterness (Caballero et al. 2012) but polyphenols are known to be the major contributor for drying/astringency in wines (Laguna and Sarkar 2017), suggesting beer has different behaviour to wine. Furthermore, Agorastos et al. (2023) noted that ethanol was not a major contributor to mouthfeel, as it was not correlated with attributes other than a sensation of 'burning'. It was also observed that spiking with sugar (isomaltulose) did not contribute to mouth coating (Agorastos et al. 2023). These insights suggest that with human tasting panels, directly attributing a single molecule or class of molecules to a descriptor has variable success in the context of beer.

Human factors vary widely, with measured values for tongue movement varying from 2.1 to 32.4 millimeters per second (mm/s) across 165 individuals with the highest being 305.7 mm/s (Hiimae and Palmer 2003). This wide range of speed is expected to result in different lubrication properties and mouthfeel (Sarkar and Krop 2019) even when presented with the same product. Additionally, the force applied between hard pallet and the tongue varies between individuals and, based on stages of swallowing, ranges from 0.01-90 Newtons (Prinz et al. 2007). It was also observed that the force varied significantly depending on exact location on the tongue.

Classically, analysis of beer was conducted by trained panels using predefined descriptors (Langstaff and Lewis 1993) which have been compared with

quantitative measurements of friction and wear with tribometers (Fox et al. 2021). However, the exact relationship between lubrication and mouthfeel is difficult to define and descriptions from participants vary depending on the substance being measured (Batchelor et al. 2015; Laguna et al. 2017).

Lubrication properties determined by tribometer can be used to assess the predicted oral properties of liquid products (Batchelor et al. 2015; Cai et al. 2017; Godoi et al. 2017; Mills et al. 2013) and solids/semi solids (Samaroo et al. 2017; Ningtyas et al. 2019). Specifically, the use of tribometers has been reported in the measurement of the lubrication properties of beer (Fox et al. 2021) and wine (Laguna and Sarkar 2017).

The choice of surfaces is of key importance in tribology-based techniques and presents a dilemma for researchers as reproducibility is contrasted with the relevance to biological systems. Of course, the most appropriate 'life system' would be a hard pallet and tongue system, animal tongues being used as a soft surface with a standard moving surface (Ranc et al. 2006). Aside from ethical concerns, biological materials tend to be highly variable between organisms of the same species - let alone genus – which makes comparisons between a pig or other animal tongue and that of a human being challenging. As such, most studies opt for an artificial surface; most commonly polydimethylsiloxane (PDMS) is used (Laguna et al. 2017), although other silicone elastomers have been successful (Mills et al. 2013) together with roughened tape (Godoi et al. 2017).

Recently, the use of dedicated tribology instruments has been expanded to include rheometers with tribology attachments. Accordingly, tribo-rheology functions in a similar manner, measuring the friction between two surfaces in the presence of a lubricant, but the rheometer enables the inclusion of accurate sliding speeds. The hybrid machine also provides cost and space saving as the instrument has dual functionality. Tribo-rheology is a new technique, so little literature is available of specific systems using this technology. This system provides a method for analysing beer to assist in quality comparisons of low and no alcohol beverages with standard beers.

## Materials and Methods

Water for HPLC gradient analysis, ethanol for HPLC, sodium chloride (analytical reagent grade), maltose monohydrate (analytical reagent grade) was obtained from Fisher Scientific with maltodextrin 4-7 dextrose equivalent (Average 6.5 DE) from Sigma Aldrich. SYLGARD 184 elastomer kit (Dow Corning) was used to fabricate tribology surfaces. Commercial bottled beers were purchased from a supermarket and measured on opening. Poly-ethersulfone syringe filters (0.22 µm, from SLS) were used to remove particulates from model test samples. Beers were not filtered but were allowed to settle for 48 hours before opening and use.

### Instrumentation

Discovery hybrid rheometer HR-1 (TA Instruments) with 3 Balls on Plate top geometry (aluminium) (TA Instruments). Bottom sample holder was a locally produced 3D printed resin cup (Supplementary Figure 1). The axial force was fixed at 1 N (+/- 0.1).

A Melter Toledo handheld density meter Densito (accuracy +/- 0.001 g/mL) was used for measurement of specific gravity based on an average of three measurements per sample.

### Tribology measurements

Tribology was conducted using a TA instruments Discovery Hybrid Rheometer with 3 Balls on Plate attachment, this geometry consists of three ¼ inch diameter stainless steel hemispheres screwed into the flat plate attached to the main shaft with an aluminium spring beam coupling. Torque is measured while a constant axial force is maintained from the tribology attachment (1 N) and sliding speed is varied between 0.15 and 150 mm/s, temperature was maintained at 20°C for all experiments. Torque is then used to calculate friction coefficient designated  $\mu$ , by the equation:

$$\mu = M \div dFN$$

Whereby M is torque (Nm), d is arm length (0.015 m) and FN designates the normal force (N).

### PDMS production and conditioning

PDMS disks were produced from SYLGARD 184 elastomer kits by mixing part A 10:1 with part B (w/w), which was mixed and degassed, before being poured into 3D printed resin moulds to a depth of 4 mm (~4g). This was then cured at 100°C for 35 minutes as per the manufacturers recommendations, disks were sonicated with deionised water before use and only used for one measurement before being replaced.

### Statistical analysis

Analysis was performed using Microsoft Excel 16 with Analysis ToolPak, one tailed t tests were conducted and P values of <0.05 were considered significantly different.

## Results and discussion

Stribeck curves which plot the frictional characteristics of a liquid lubricant were generated using a hybrid rheometer for a range of commercially beers of several styles (Table 1). Beers were compared to values obtained with deionised water. Figure 1a shows the observed friction for two India pale ale beers, both from the same brewery, with a declared ABV of 0.0% (IPA0) and 5.0% (IPA5). A clear difference is observed between the samples, where the 5% ABV beer demonstrates a lower level of friction at all but the highest speeds, continuing to be statistically significant even at the highest test speed ( $p=0.04$ ) when compared to water. The 0% ABV product is less distinct from water, as significant differences are only observed in friction between 0.6 and 75 mm/s sliding speeds. Low lubricity is a known feature of some low and no alcohol beers and is demonstrated by the differences observed in this comparison.



**Table 1.**

Beer composition and codes.

Style	% ABV	Specific gravity (g/mL)	Abbreviation
IPA	0	1008.2	IPA0
IPA	5	1005.7	IPA5
Amber ale	0	1013.1	AA0
Amber ale	4.3	1008.7	AA5
Lager	0	1016.3	LA0
Lager	4.6	1004.6	LA46
Lager	0.5	1015.0	LA05
Pale ale	0.5	1024.8	PA05
Pale ale	4.3	1007.0	PA43
Milk stout	0.5	1028.3	MS05
Milk stout	4.3	1016.4	MS43
German wheat	5.3	1007.0	GWB53
German wheat	0	1017.4	GWB0
Citrus pale ale	0.5	1013.9	CPA05
Citrus pale ale	4.5	1005.1	CPA45

In contrast, other tested beers did not show such differences, the amber ales (AA0, 0% ABV and AA5, 4.3% ABV) (Figure 1b) do not demonstrate a statistical difference at any tested speed but are both distinct from water at all speeds below 75 mm/s. This similarity demonstrates a successful matching of lubricity between the two products from the same brewery. Similarly, the two milk stouts (MS05, 0.5% ABV) and MS43, 4.3% ABV) exhibited similar lubricity, despite the stouts being from different breweries. Figure 1c demonstrates the Stribeck curves obtained for these products, this style is expected to contain a high residual sugar content obtained by the addition of lactose. This was apparent in MS43 (4.3% ABV) with a specific gravity (SG) of 1.0164, while the average SG in the standard beers (containing alcohol) was 1.0078 (Figure 2). The difference is less apparent with the low and no alcohol beers, where the SG of the 0.5% ABV milk stout was 1.0283 compared to the average of 1.0172. The high specific gravity of the low alcohol beers is expected and is generally a by-product of their limited fermentation process (Sohrabvandi et al. 2010) or from post fermentation addition of sugars.

German wheat beer is known for its mouth feel and tribo-rheology analysis was performed (Figure 1d) on two samples from the same brewery, one at 5.3% ABV and the other 0.5% ABV. This data shows

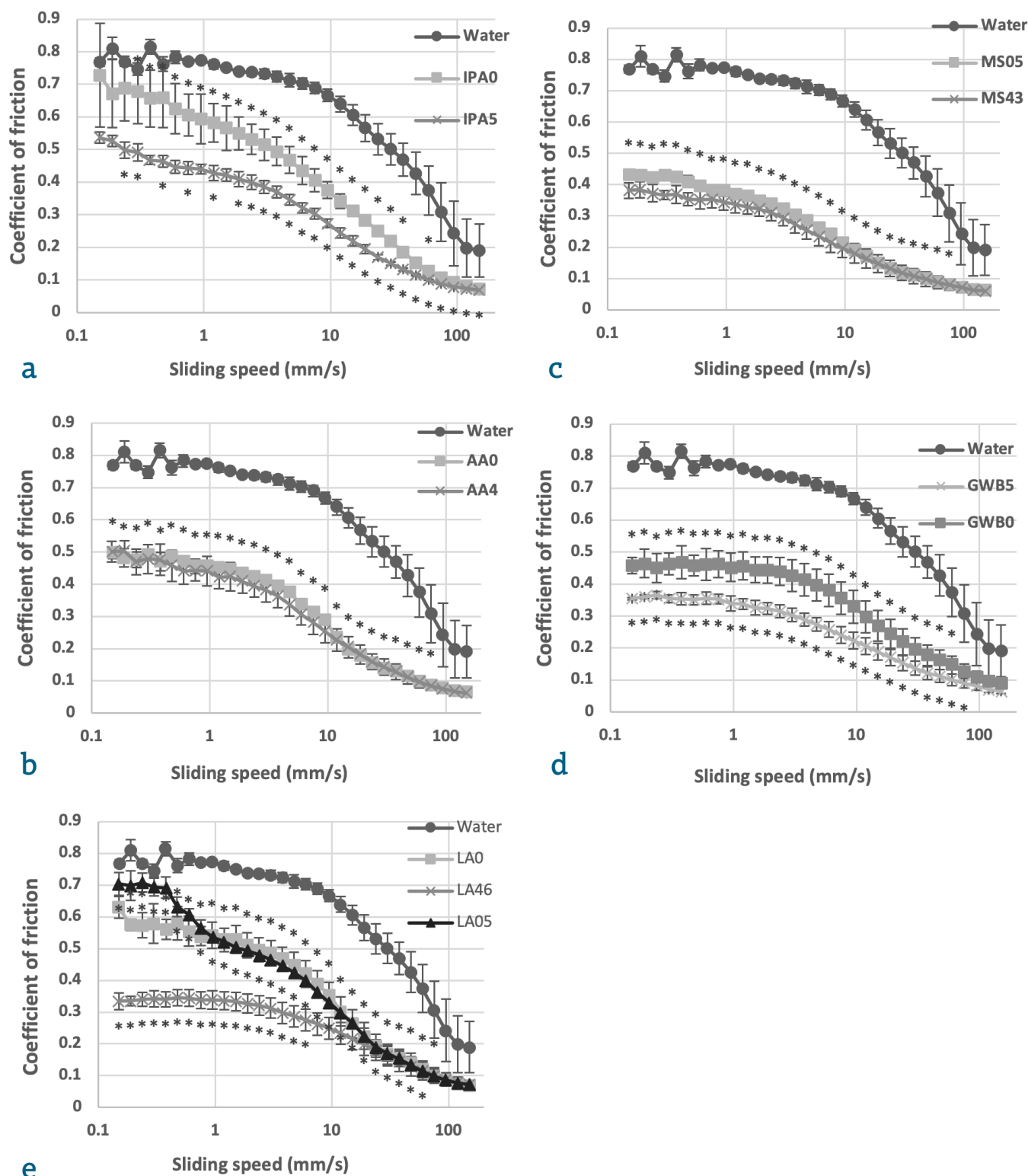
significantly higher lubrication was observed with GWB53 at almost all rolling speeds, whereas the level of lubrication shown by the low alcohol GWB05 is also significant, yielding a statistically relevant difference when compared to water at all speeds below 75 mm/s. This is likely to be explained by the specific gravity of this product (1.0174) containing 53 g/L carbohydrate.

Lager style beers have a milder taste profile compared to ales with reduced bitterness and hop impact (Furukawa Suárez et al. 2011). This can be advantageous in producing low alcohol products as subtle flavours are not as adversely affected by limited fermentation or ethanol removal strategies. Conversely, such beers are less well 'protected' to any off flavours. Accordingly, a standard strength European lager (LA46) and the same brewers 0.0% ABV (LA0) products were compared (Figure 1e). This again shows a significant difference between the standard (4.6% ABV) and the alcohol-free products. In this case, the difference was observed in the lower speed region which has greater relevance to oral processing, with 10.34 mm/s being reported as the mean speed of movement during swallowing of liquids (Hiiemae and Palmer 2003). However, the variation and range were significant between individuals. Further to this, a second low alcohol lager (LA05) was obtained but produced by a different brewery. This showed a similar profile to that with LA0, except at speeds of 0.37-0.18 mm/s where a significant difference was observed between LA0 and LA05. Here, the LA05 with 0.5% ABV showed increased traction, which was not expected, as ethanol produces a lubricating effect (Mills et al. 2013).

The trends reported in Figure 1 differ from the work reported by Fox et al (2021) in that the friction curves for the alcohol-free beers exhibited lower friction factors than the 'standard' products. However, here none of the low/no alcohol products had lower friction coefficients than the products containing alcohol. None of the beverages reported by Fox et al (2021) were used in this study so direct comparison between methods is not possible. However, Fox et al (2021) used a glass ball surface with PDMS pegs, whereas in this work three stainless steel balls on plate with flat PDMS discs was used. It is possible that the differences reflect the different surface chemistry of glass versus stainless steel and/or the

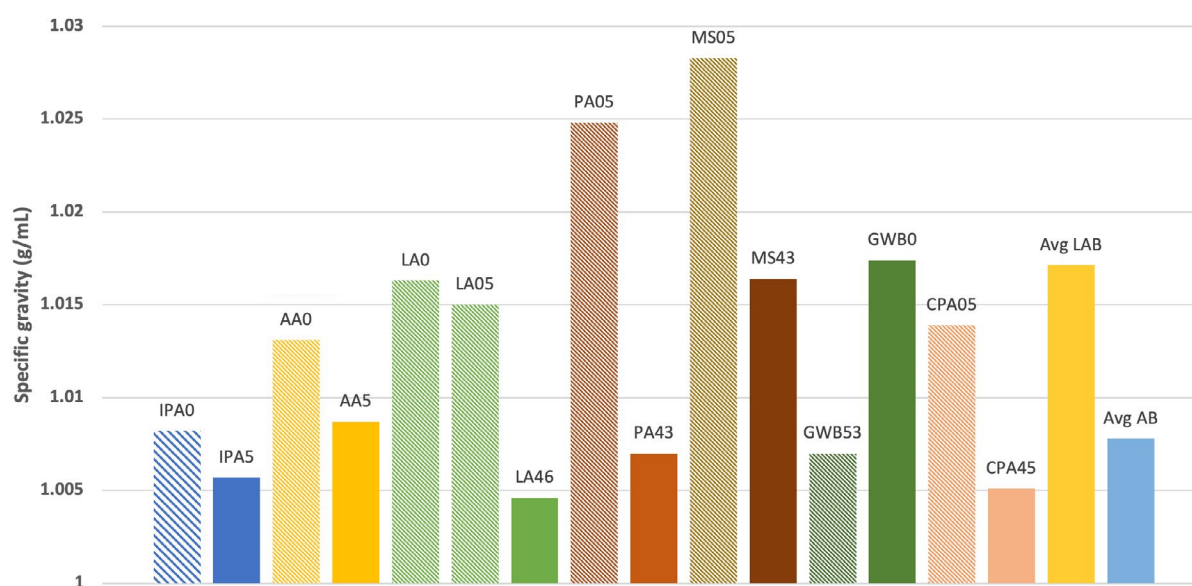
**Figure 1.**

Stribeck curves generated from 3 Balls on Plate tribo-rheology on PDMS surface with water, (a) India pale ale, IPA0 and IPA5; (b) amber ale, AA0 and AA4, (c) milk stout, MS05 and MS43, (d) German whet beer GWB0 and GWB5, (e) lager LA0, LA46 and LA05 as lubricant ( $n=3$ ). Star markings denote significant difference from water ( $p<0.05$  in one tailed T test)



**Figure 2.**

Specific gravity of beers used in this work.



different application of force for apparatus with a single ball on pegs compared to three balls on a disk. This does suggest that choice of equipment may have a role in measurements and suggests some standardisation on methodology or calculation of conversion factors would be of benefit.

To investigate the variations within the data reported here, solutions of compounds found in beers were analysed using the same process as the beers. Ethanol was chosen as this is the most obvious change between the products. **Figure 3a** shows the Stribeck curves obtained with a series of ethanol concentrations. Interestingly, low ethanol (0.5% ABV) is seen to significantly increase the friction at lower speeds (<7.5 mm/s), suggesting there may be a threshold where low concentrations of lubricating substances are less lubricating than when they are absent. This concentration has a direct relevance to this study as many low alcohol beers are reported at 0.5% ABV. This data suggests a possible explanation for the difference between lagers LA0 and LA05, with the small amount of ethanol (0.5% ABV) increasing friction. While the increased friction between the two beers is not identical to that of 0.5% ABV and water, the overlap suggests a possible link.

At a concentration of 1% (v/v) ethanol almost no significant difference in lubrication is observed from water, indicating the threshold for neutral effect is between 0.5 and 1% for this lubricant. At 5% ABV, significant lubrication differences are observed at

almost all speeds compared to water. This level also suggests an interesting although unintentional outcome of fermentation, where 5% ABV is at the lower end of levels that yield a significant difference in friction but is a common ethanol level in beer. This would require deeper investigation, particularly in more complicated systems but could represent an interesting avenue of investigation.

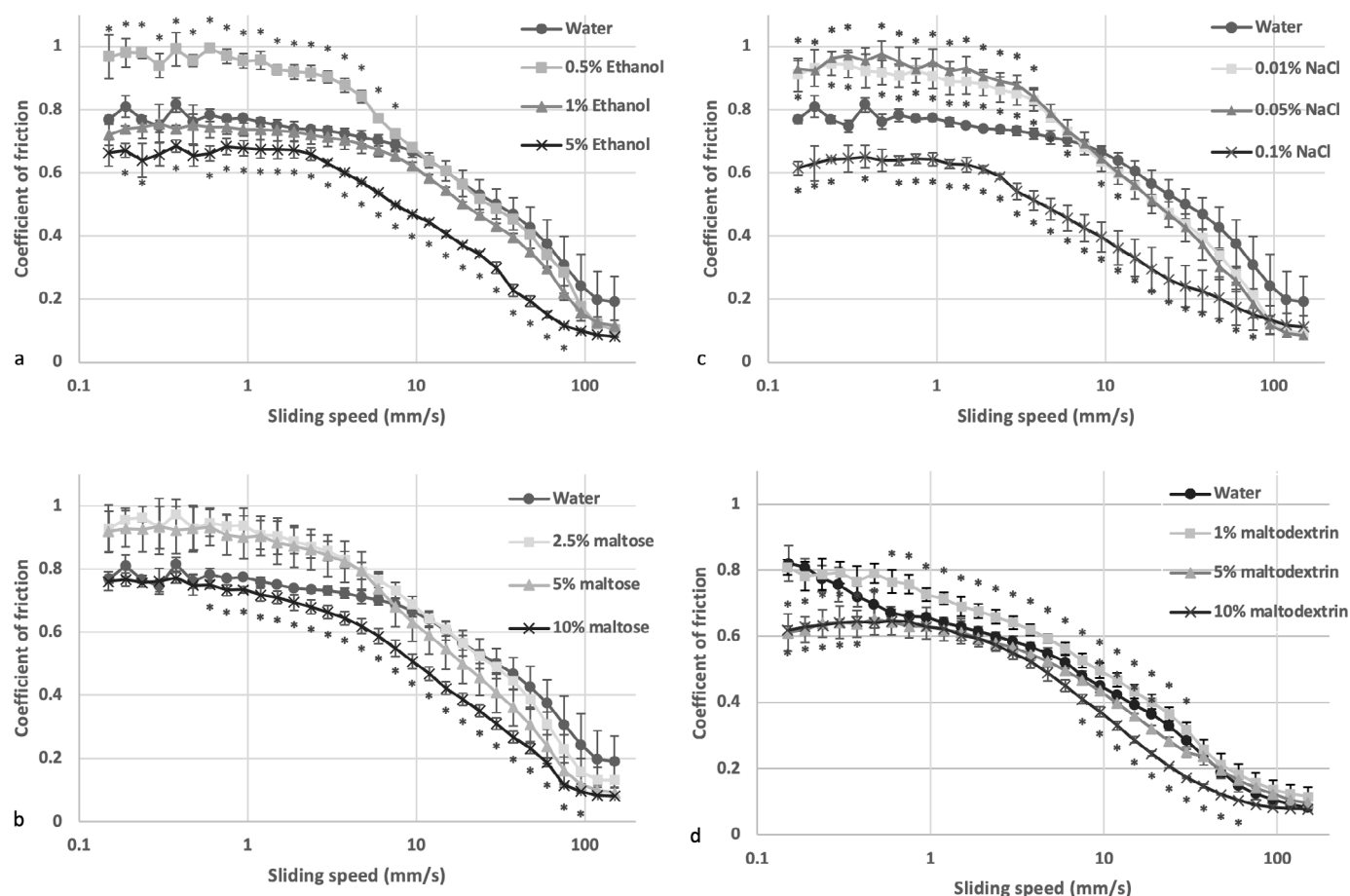
Maltose was used as a model for residual sugars, although the remaining sugars in beer can be more diverse (Otter and Taylor 1967). Stribeck curves were obtained for different concentrations of maltose (**Figure 3b**). These results show a similar pattern to ethanol, where at low concentrations and low speeds, traction is increased. Although for maltose, the concentration is higher (0.5% versus 2.5-5%) the change is statistically significant at more points of speed.

Previous work has demonstrated a role for longer chain polymeric saccharides (dextrins) in the sensory perception of beers (Krebs et al. 2019). Maltodextrin (4-7 DE) was tested (**Figure 3d**), and a similar profile was seen to maltose with the lowest concentration exhibiting lower lubricity than water. Although with maltodextrin the sliding speed range for significant difference was faster, covering a greater portion of the tested speeds. Interestingly both solutions (5, 10%, w/v) show similar behaviour at lower speeds but are significantly different at higher speeds. Although 5% solutions were not



**Figure 3.**

Stribeck curves generated from 3 Balls on Plate tribo-rheology on PDMS surface with water, and (a) ethanol (v/v), (b) maltose (w/v) and (c) sodium chloride (w/v) in water as lubricant ( $n=3$ ). Star markings denote significant difference from water ( $p<0.05$  in one tailed T test).



significantly different from water, the 10% solutions were. This is consistent with data from previous studies where 50 g/L maltodextrin was the lowest concentration with any significant effect on mouthfeel (Krebs et al. 2019).

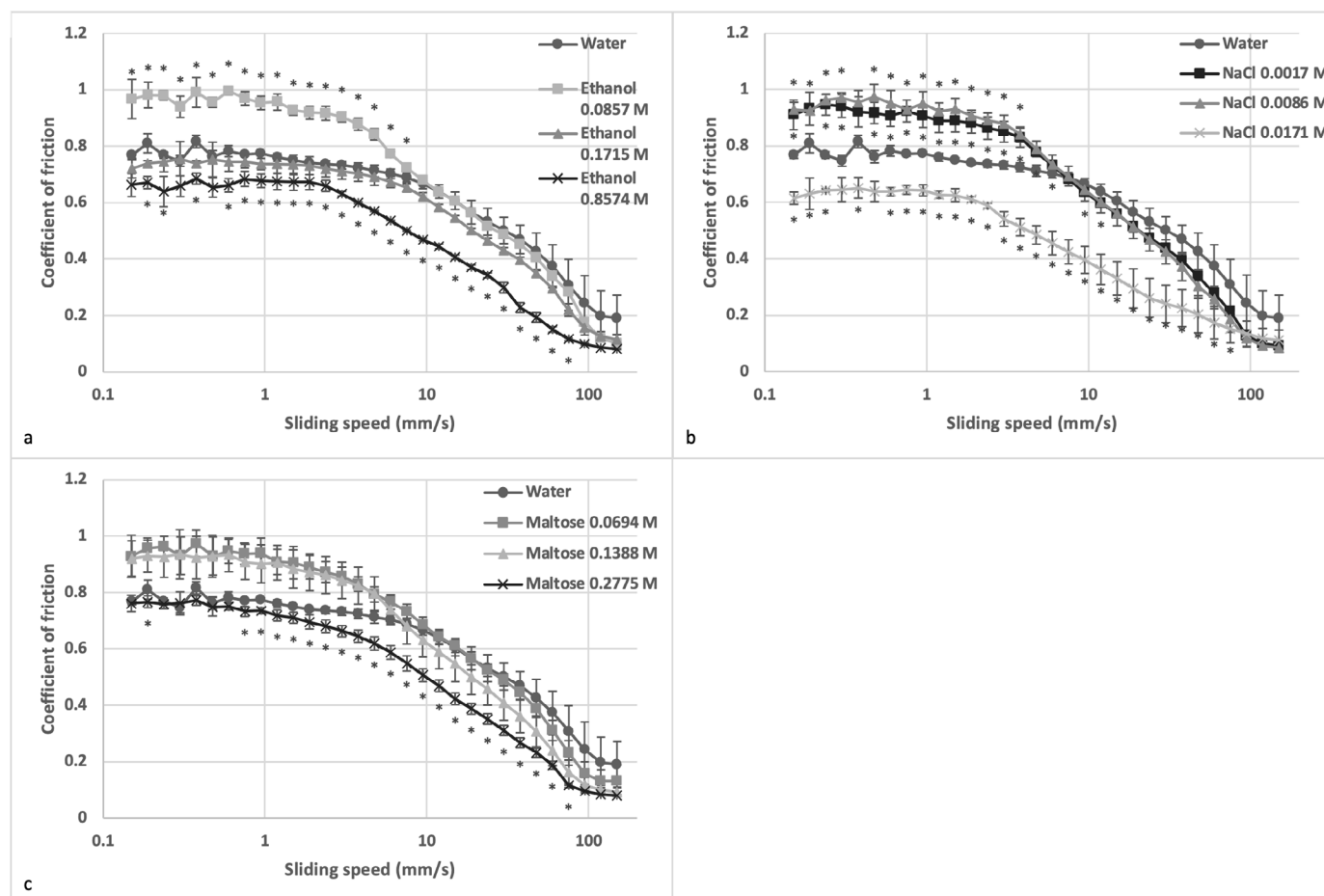
Simple inorganic salts have been shown to demonstrate lubrication behaviour in solutions (Mills et al. 2013), so solutions of sodium chloride were analysed at a range of concentrations. Figure 3c shows the results with sodium chloride used as a substitute for mineral content. The inorganic composition of beverages varies significantly, depending on the local water or remineralisation of purified water (Krennhuber et al. 2016). Similarly, the total salinity can vary significantly, and the work reported here is not intended to replicate any specific product or style but represents a simple model for inorganic content of beers. The data in Figure 3c shows that at low concentration, lubricants can increase friction.

The mineral content in beer (both alcoholic and non-alcoholic) is 363-700 mg/L (Krennhuber et al. 2016), suggesting the levels applied here are applicable to commercial products.

The explanation for why different molecules have varied thresholds as lubricants is due to differences in molecular mass where there are similar levels of molecules present. To explore this, the Stribeck curves were replotted as molar concentrations (Mol/L) (Figure 4). From this, it is apparent that sodium chloride provides greater lubrication per molecule than other tested molecules. Ethanol and maltose are similar at lower concentrations (0.0857 Mol/L and 0.0694 Mol/L) but diverge at higher levels. The increases in friction are likely from boundary chemical films related to elastohydrodynamic lubrication where film formation is dependent on viscosity together with chemical properties of the surface and the lubricant (Hsu. 2004).

**Figure 4.**

Stribeck curves generated from 3 Balls on Plate tribo-rheology on PDMS surface with water, and various concentrations of ethanol (a), sodium chloride (b) and maltose (c) in water solutions M/L as lubricants ( $n=3$ ). Star markings denote significant difference from water ( $p<0.05$  in one tailed T test).



The concept of monolayer film lubrication is primarily applied to fatty acids, siloxanes and thiols in Langmuir-Blogett films. These films are only seen to behave as solids when the molecular spacing is equal to or smaller than the size of the film forming molecule. When not under these conditions the film behaves as a liquid monolayer rather than a solid one. These liquid layers are more resistant to failure as the molecules are able to move under stress without causing total disruption of the system but only under relatively light stress levels (Hsu, 2004). This natural flexibility along with the ability to self-repair by diffusing back into the monolayer allows molecules to provide physical lubrication for surfaces. The presence of a range of differently sized molecules allows for easier formation of layers by tessellation (or tiling) of the different sizes, shapes and polarities to produce the most thermodynamically stable result. An important consideration with mixed monolayers is the compatibility of molecules, as it is expected that

some functional groups will reduce binding and tessellation of other molecules (Hsu 2004). This is important in complex systems such as beer, where many different molecules are present and competing for binding spaces. It has been demonstrated that competitive binding from poorly compatible molecules produces inferior lubrication to single component systems (Nakayama and Studt 1991). With many different molecules, the formation of crowded Langmuir-Blogett films may become more likely as the gaps between bound molecules are filled creating a more uniformly covered surface. However, this will be dependent on molecule compatibility and relative concentrations. These binary interactions at surface interfaces are difficult to predict and may be concentration independent if binding is blocked or inhibited by the other molecules.

The application of Langmuir-Blogett film theory to heterogeneous wear surface systems - where two

different materials are abraded against one another - is less commonly observed as much of this work is applied to metal-metal based wear interactions. Oral tribology requires a softer surface to be used as one of the tribopairs, which allows scope for substances to form lubricating surfaces on one of the pair but not the other. This pairing-based system also brings the possibility of two entirely different monolayers, one adsorbed to the metal and the other to the PDMS or other soft surface, further complicating the study of complex mixtures. In this case, analyte-analyte interactions are determined as the two different monolayers abrade and interact with each other, or form more complex chains from the original surfaces, producing effects unique to that mixture of lubricants and tribopairs only visible at speeds where elastohydrodynamic effects do not dominate.

## Conclusions

Tribology provides an effective methodology for measuring lubrication properties of beer and allows for investigation into causes of observed differences. In this work, Tribology was used to demonstrate differences in lubrication behaviour between Indian pale ales, German wheat beers and lager beer with different alcohol levels, reflecting the loss of lubrication performance provided by ethanol content. The method was also able to demonstrate that measurements of alcohol-free amber ales, milk stouts and two lager beers closely match the standard strength products suggesting compensation for the lack of ethanol as a lubricant has occurred in the different formulations. This method presents a mechanism for more complex artificial systems to be examined to elucidate causes of differences in the physical properties of products as well as functionality in validating brewing techniques in attempting to mimic specific desirable lubrication properties.

## Author contributions

**Thomas Holt:** methodology, validation, formal analysis, writing (original draft, review and editing).

**Tom Mills:** methodology, writing (review and editing), supervision, funding acquisition.

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