A. Symes, F. Van Opstaele, G. De Rouck and P. Oliveira

Advanced hop products designed for sustainable brewing and improved taste and aroma in different beer styles

Breweries can have up to 30 % beer loss due to process inefficiencies. Recently, hop extracts have been explored to offer standardized, cost-effective and a sustainable alternative to brewers. This study aimed to test new hop extracts applied in three main beer styles to showcase potential advantages to brewing. Hop extracts were applied into: 1) one lager wort stream for differentiation into lager and ale beers; into 2) one non-alcoholic beer, and into 3) one specialty beer style, Indian Pale Ale (IPA). Following the application of selected hop extract blends, the resulting beers were submitted to sensory analysis and their profiles compared. Results showed that, when applied to lager wort, brewing solely with hop extracts (naturally pre-isomerized bittering and post-fermentation aroma extracts) successfully delivered true-to-style lager and ale beer profiles. Bittering hops from alpha and beta skewed the aroma towards floral/herbal and citrus/lemon, respectively. Aroma hop extracts contributed towards citrus enhancement in lager, and stone fruit/floral in ale. Overall, hop extracts improved hop bill efficiency when compared to hop pellets. In non-alcoholic beer, sweetness was modulated, worty notes masked, and mouthfeel improved. In IPA, a blend of post-fermentation extracts (Amarillo®/Cascade/Citra®) significantly increased positive attributes (fruity, sweet, floral, and citrus). Also, it was possible to deliver a characteristic dry hop taste impact, while significantly reducing the brewing time. The selected hop extract blend delivered positive taste impact across all beer applications.

Descriptors: brewing efficiency; advanced hop extracts; functionality; sustainable hop bill

1 Introduction

Brewing has been a traditional industry due to the brewer's devotion to using known raw materials. However, both brewing and hop industries have faced an unprecedent demand for efficiency and flexibility due to recent supply chain disruptions. In 2020, significantly less beer was produced globally, with a need to store greater quantities of hops, while currently experiencing market volatility due to geopolitical tensions. These factors forced the industry to look towards solutions and trigger brewing technology innovation programs. This necessary evolution fostered greater efficiency into hop taste solutions, when compared with traditional four-vessel brew-houses, as breweries review processes, recipes and shorten the route to market of new developments. Nevertheless, the global beer growth is projected to rise between 2.5 – 3.5 % by 2028, mainly lead by China, North America and Western Europe, with emerging markets, such as, Asia, South America and Mexico making a significant contribution to the global recovery [2]. Thus, new opportunities to drive innovation, process, recipe optimizations, and adopting more sustainable technologies are expected, with no use of organic solvents, pesticides, or chemical processing, using instead natural foodstuff resources and recycling streams from nature occurring processes. There are great expectations from the modern consumer to experience new, unique, full-flavored beers, with hop-forward styles being top ranked. US craft brewers are leading the market, setting the global trend [43].

As it is well known, hops can serve multiple applications in beverages, providing antimicrobial properties, bitterness, aroma, flavor, as well as additional functionality to beer [55]. Additionally, hops can be used to increase yield, improve bitterness quality, mouthfeel, head retention, and even prevent light-struck off-notes [29]. Hops have been seen to act as an antioxidant and contribute with health promoting active compounds, such as 8-Prenylnaringenin, xanthohumol and polyphenols as natural additives [4, 32, 45]. As such, it's important to define the required hop application at the start of the recipe creation process. Two decades ago, hop utilization rates of about 33 % with an occasionally hopback in the whirlpool were typical. Nowadays, an extensive range of different hop products are available which allow significant yield improvements. This means there is less waste, allowing brewers to optimise their process and be more sustainable.

The number of hop varieties and products available to experiment on is increasing, and, contrary to the trend over the last years, it is likely that the average amount of hops used by brewers will not

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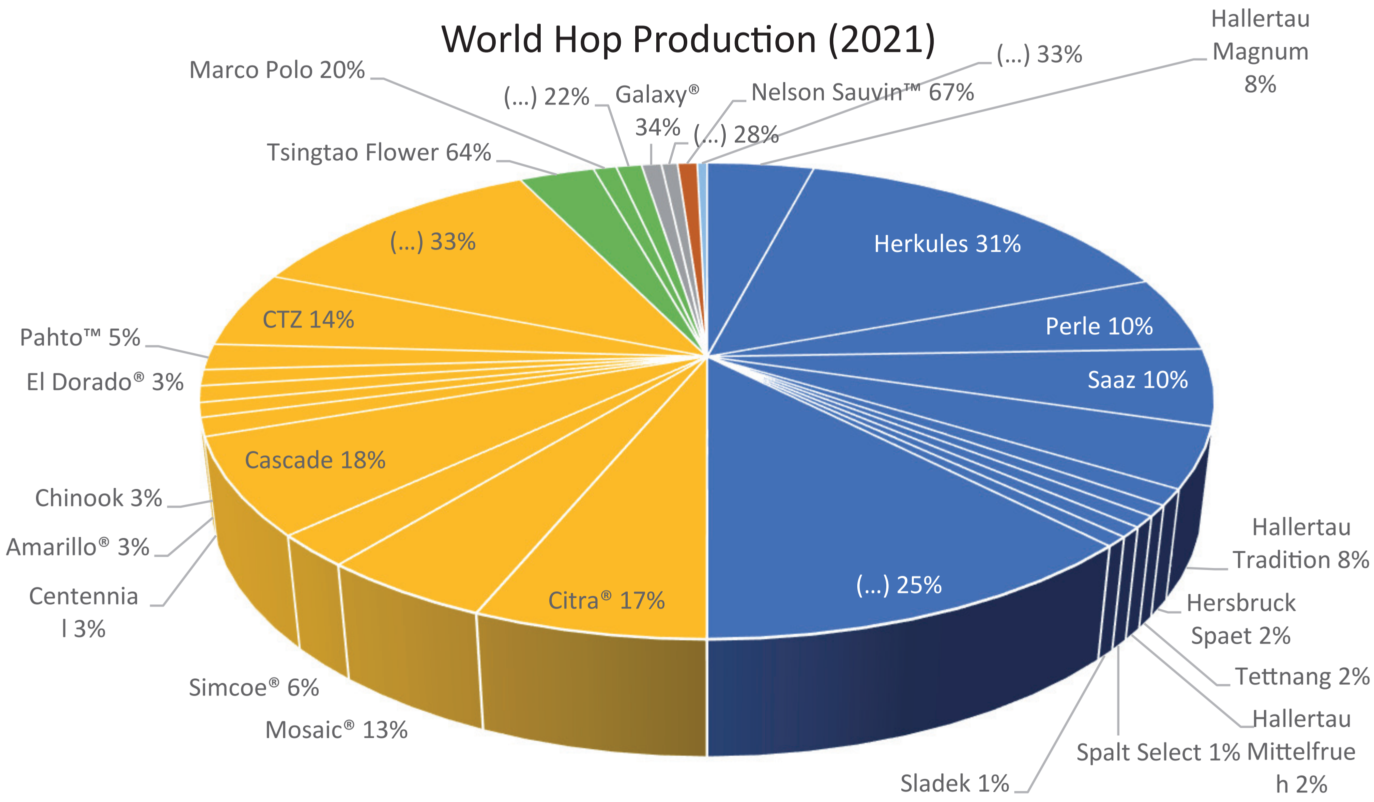

Fig. 1 **World hop production in 2021, including the top produced varieties from each region [3, 17, 19]**

increase (currently over 660 g/hL). Instead, advanced hop products are expected to provide more sustainable and efficient solutions for brewers to use [30, 57].

Consequently, the value of hops has changed from bittering to offering a dual purpose by also focusing on aroma hop varieties. Globally, hops split is now roughly 60/40, aroma and bitter, respectively [3, 17, 19]. Over 70 % of the world hop crops are growing in EU and US. US especially, has experienced a complete market shift, from 20 % to 80 % of aroma hop acres. There are currently nine hop varieties produced worldwide surpassing a total of 5,000 metric tons, as seen in figure 1. These are Perle, Saaz and Hallertau Tradition, as aroma hops; Magnum and Herkules, as bitter varieties, from EU. From US, Citra®, Mosaic® and Cascade as aroma hops, and CTZ as bitter.

The pelletizing of hops is a standard process since the 1960s [21, 26, 46, 49], with the technology applied to hops evolving since then. It is well known that hops quickly loose quality attributes, so, growers will bale and dry hops immediately after harvest and store them below 0 °C to retain their freshness. T90 pellets (10 % of the hop bract removed) retain all natural lupulin and cone material, have a longer shelf life, reduced storage, and are easier to handle, when compared to whole cones. Yet, containing most of the cone insoluble material, and require a kilning stage that significantly reduces the hops' volatile components. As such, using lupulin concentrated powder/pellets that, contain less vegetable material, less bitterness, and more intense hop flavors is advantageous. For example, using T45 pellets, with 55 % of the bract being removed. Also, it is possible to deep-freeze hops (at about – 30 °C) and separate the bract, which limits the heat exposure. A nitrogen-rich environment used during the separation and pelletizing process avoids oxidation reactions, and, in this case, T45 pellets gain interest to be used in dry-hopping, when manufactured from aroma varieties. Examples of these products in the market are cryohops and wethops [8, 27].

The goal of sustainable hop extraction is the quantitative recovery of active substances, namely, soft resins (bittering), polyphenols, essential oils (i.e., hydrocarbons, oxygenated compounds, and sulfur-containing compounds), in a concentrated format. In order to achieve this, advanced techniques combining different sample preparation methods, extraction, and separation techniques are required, using green technology with solely hop material as a source to allow a clean label in beer applications [32, 34, 57]. This has motivated the progress of the hop extraction technology.

Hop extracts have been produced on a large scale since 1970s [55]. First, using steam and alcohol liquid mixtures. Conventional aqueous extraction with pure organic solvents can use different temperatures and mixtures for optimum extraction. Ethanol is an efficient polar extraction solvent as it dissolves a broad range of hop components, but implications with its high flammability and export tax may cause restrictions. An ethanol extract (or resin extract) results in aqueous and resin fractions that are standardized for alpha-acids. The aqueous phase includes polyphenols, soft resins, and other water-soluble constituents such as linalool (low-molecular-weight hydrocarbons), proteins, and mineral salts, with higher polarity. The recovery of sesquiterpenes (humulene and caryophyllene) is about 90 % as their boiling points are higher. The resin extract will contain hard resins (about 40 different polyphenols). This type of extract is useful when applying shorter boiling times at lower temperatures as it dissolves and isomerizes rapidly. Losses of up to 50 % remain unavoidable for myrcene and other monoterpenes [6, 7]. Linalool glucosides and other glycosidically-bound hop aroma compounds, and aroma precursor markers, such as thiols, are also extracted and of interest [6, 7, 22, 23, 54, 55].

Steam distillation is also commonly used to standardize extracts, and to extract water soluble compounds and essential oils (e.g., monoterpenes such as myrcene, linalool, limonene, and β-pinene). However, this technique has a relatively low extraction power and often requires longer exposure to higher temperatures, resulting in low-boiling-point aroma compounds to evaporate. Also, beta-myrcene will dimerize and result in poor steam-distilled oil stability. Alternatively, vacuum evaporation allows the use of lower temperatures, and thus avoids additional losses. Washings are effective at solubilizing polar aroma compounds, but also extract other constituents, and require further stabilization and separation techniques for selectivity. Hydrosols from cold extractions are a good option to explore as the resulting extract is similar to what happens during dry hopping beer [56]. Water is the cleanest solvent that can be used, but has a limited extraction capability, and it is not microbiologically stable, hence, it also requires further stability processes such as acid, heat, or pressure stabilization.

The choice of an appropriate extraction solvent is a key factor for a clean label solution and a good extraction efficiency. This depends on several other factors including its dissolving power, selectivity, flammability, volatility, and cost. Methylene chloride was the preferred solvent for hop extraction until 1980, and then replaced by alcohol and CO_2, which are by-products of beer [55]. Suitable extraction solvents are non-toxic, food grade and listed in the EU Extraction Solvents Directive 2009/32/EC; compliant with EU regulation 1223/2009; EU Regulation 1334/2008; 178/2002 and FDA 21 CFR 117 (see Table 1). When considered as food additives, these must conform with the carryover principle that permits the presence of a food additive in a compound to be carried over to the final beverage, imparting no technological function, in accordance with the Article 20 and 18 of the Food Regulation 1333/208. Several EU regulated additives can be used in the beer category ((EC) No 1333/2008). Nonetheless, from a consumer perspective and improved clean label it's important to restrict the use to naturally sourced ingredients from water, yeast, hops, and malt ingredients, which is often rated of premium quality, when compared to commonly referred as "reconstituted beverages".

The use of carbon dioxide (CO_2) gases in the sub- or supercritical state as extracting solvents is an established practice for ten years and has been shown to be a valid and versatile substitute to organic solvents of a highly nonpolar character (e.g., hexane and pentane) [25, 55]. Additionally, as a by-product of fermentation, with no combustion of fossil fuels, it is therefore an environmentally friendly source contributing towards a circular economy. Its usage allows residue-free solvent removal. The first extracts developed were mainly intended for additions in the brewhouse (kettle and whirlpool), but with recent technology advancements a range of new extracts are available today for post-fermentation additions [18, 20, 58].

Liquid CO_2 (lCO_2) extracts provide an oil profile similar to ethanol extracts, free from hard resin and polyphenols, with a lower pro-

Table 1 List of permitted carriers and extraction solvents in beverages and flavoring extracts (EU Extraction Solvents Directive 2009/32/EC; EU regulation 1223/2009; EU Regulation 1334/2008)

Solvent	CAS number	CP 20 °C	Boiling Point (°C)	Flash Point (°C)	Usage in Beverages	Solubility in Water, %	Taste	Advantages/ Disadvantages
CO_2	124-38-9	0.07	-56	N/A	QS; GMP	As carbon dioxide: 0.16 g/100 mL (20 °C)	Neutral taste/ aroma at atmospheric conditions	Solvent free residue as by-product from fermentation; tunable; strong extraction power/selectively; high Capex investment; specialized operators.
Ethyl alcohol (Ethanol)	64-17-5	1.20	78	13	QS; GMP	Fully miscible	Alcoholic like	Strong extractability power; not allowed in halal/non-alcoholic formulations; high export tax; high flammability.
Ethyl acetate	141-78-6	0.58	77	-4	GMP	8.3 g/100 mL (20 °C)	Sweet, fruity aroma	Positive synergy taste impact when formulated within flavoring preparations; limited solubility;
Isopropyl alcohol (Isopropanol)	67-63-0	2.43	82	12	10 ppm	Fully miscible	Alcoholic slight bitter taste	Alternative for non-alcoholic applications; limited extraction power; extract profile shift.
Water	7732-18-5	1.00	100	N/A	QS	Fully miscible	Neutral taste/ aroma	Clean label and ready to drink; requires additional microbially stability; low extraction power.
Propylene glycol	57-55-6	56	187	107	1000 ppm	Fully miscible	Neutral taste/ aroma	Good alternative to non-alcoholic formulations; low extract power/selectivity; volatile market cost; dissolves hydrophobic substances; auto preservation.
Glyceryl triacetate (Triacetin)	102-76-1	23	258	138	QS	6.1 g/100 mL (20 °C)	Neutral to slight bitter	Non-polar solvent; good to formulate with essential oils; Miscible in ethanol; limited water solubility; bitter taste.
Glycerol (Glycerin)	56-81-5	1412	290	176	QS	Fully miscible	Odorless with sweet taste	Good alternative to non-alcoholic formulations; Low extract power/selectivity; High viscosity; auto-preservation.

portion of the monoterpene hydrocarbon beta-myrcene and only low-molecular-weight, saturated liquids are present while the fresh spice/oil rich character is preserved [35]. This extract is mainly used to replace dry hopping aromatization of beer, suitable for cask and bottle post-fermentation additions [35]. Parameters such as temperature, pressure, CO_2-flow rate, and extraction time can be regulated to control the extract's quality specifications, manufacturing costs and its ecological impact [32, 36, 47]. Typical conditions used at 5 – 15 °C, 60 – 65 bar, while lower temperature enables the branched chain esters profile of hops. The ICO_2 hop extract provides satisfactory hop oil yield of 0.5 – 10 mL/100 g with 95 % of alpha and beta acids, and can also extend the beer shelf-life [48].

The advantage of using supercritical CO_2 (scCO_2) is its high selectivity towards extracted compounds, suitable for the isolation and fractionation of volatile and nonvolatile ingredients. Its strong penetrability and solvating power will extract oleoresin from hops at 200 – 300 bar, 40 – 50 °C [35]. Flow rates of about 1000 – 2500 kg/h and pressures at 500 bar can be used, which yield about 1 % higher, when compared with 300 bar extractions. Sesquiterpenes hydrocarbons are susceptible to auto-oxidation, and mainly epoxides are formed, such as beta-caryophyllene epoxide and alpha-humulene-1-2-epoxide [16]. An accelerated solvent extraction will extract soft resins. Typically, extraction plants pump pressurized ICO_2 via a heat exchanger through the extractor containing the hop biomass. Following, the homogeneous extract mix is separated through pressure reduction into the gaseous CO_2 and the liquid extract phase. Next, the fractionation of the extract happens by reducing the pressure step-by-step, at 80 to 100 bar or in subcritical conditions [36, 47]. For example, Marynka variety had optimum extraction parameters from essential oils using a trap at 5 °C, extraction pressure at 85 °C and dynamic extraction time of 10 min [16]. The highest content of essential oil compound extracted was alpha-caryophyllene (2.89 %).

Liquid aroma hop extracts can limit the vegetative matter in brewing, as well as increasing selectivity of taste/aroma active compounds. Nevertheless, certain pre-requisites are mandatory to develop cost-effective solutions, namely, having access to premium raw material quality, with an essential oil content over 1 mL/100 g hop [41]. When optimized, there is a multitude of applications, addition points and dosage rates that will suit different purposes and different beer styles, as well as endless combinations if we take into consideration hop compound synergies [12, 14]. Excluding monovarietal applications, most of the developments take a minimum of three to four hop varieties to create outstanding roundoff tastes in beer, with notable hop character, depth, and complex lingering. Associated with a consistent formula engineered, the addition point and incorporation into the brewer's recipe, in harmonization with all ingredients is key to the final beer overall quality [10].

New advanced hop products have the potential to offer smart and efficient options to improve hop conversions in brewing. As such, in this paper we aimed to explore these advantages in beer application, when compared to more traditionally used T90 pellets and bittering extracts. The selection and blend designed from the aroma hop extracts is new and reported for the first time in a method paper. Three beer applications will be assessed: 1) Optimization and differentiation using lager wort, brewed, and differentiated into respectively, lager and ale beer styles. Two naturally pre-isomerized bitter hop extracts and one flowable extract will be used, and the impact of post-fermentation hop aroma extracts, compared to T90 pellet brews; 2) Optimization of non-alcoholic beer with sensory defects using post-fermentation hop extracts; and, lastly, 3) Optimization of a specialty beer style, IPA, using post-fermentation extracts to deliver taste and aroma premiumization.

2 Materials and methods

Hop Extracts have been produced and kindly provided by Totally Natural Solutions Ltd (TNS), Kent, UK. Bitter extracts: HA-46006 HopAlpha NISO 25 % (containing 25 % naturally pre-isomerized alpha acids); Flowable extract for brewhouse addition: HopGain® FLOE (flowable CO_2 hop extract prepared from hop pellets with no bitter acids); BE-47007 HopBeta HULU 20 % (containing 20 % naturally pre-isomerized hulupones). Aroma hop extracts: HZ-48003 HopZero® Clarity; HS-42003 HopShot® Citrus; HB-44015 HopBurst® Amarillo®; HB-44002 HopBurst® Cascade; HB-44012 HopBurst® Mosaic®; HB-44044 HopBurst® Nectaron®; HB-44005 HopBurst® Citrulicious; HS-42030 HopShot® Nelson Sauvin™. All extracts from hop cones, in 45 – 99.9 % w/w monopropylene glycol.

Non-alcoholic beer batch was freshly brewed, produced via de-alcoholization and characterized with typical sensory defects, namely: sweaty, meaty, and yeasty off notes. Specialty beer reference was commercially available West Coast style IPA (5.0 %ABV) style – dry hopped with Amarillo®, Cascade and Mosaic® hops; sensory profile: citrus aroma of zesty grapefruit, a bitter hop character and a dry hoppy finish.

Hop oil extraction and composition: T90 hop pellets were distilled according to the standard EBC method 7.10. Following, hop oil composition was analyzed by Gas Chromatography – Mass Spectrometry (Agilent) and the main fractions presented as myrcene, caryophyllene, farnesene, and humulene, adopted from EBC method 7.12.

Brewing trials were completed at Ghent University pilot-brewery. A brewing batch size of 50 hL was produced to create the lager wort. Wort mashing-in at 64 °C for 30 min; following a 20 min rest at 74 °C; and mashing-off at 78°C. Kettle boiling was complete in 30 min, with 5 g/hL of HopGain® FLOE added. Wort was transferred to the whirlpool with 5 g/hL of HopGain® FLOE added. The wort was then divided equally into 50 L fermentation vessels, for differentiation into lager and ale beers. Fermentation and beer production was performed in duplicate. The primary lager fermentation used dry yeast SafLager W-34/70 German Lager Dry Yeast (Fermentis) at 12 °C; followed by two days conditioning, and additional four days at 3 °C for dry hopping infusion. The primary ale fermentation used dry yeast SafeAle™ K97 (Fermentis) at 18 °C; followed by two days conditioning at 20 °C and additional four days at 3 °C for dry hopping infusion. Dry hopping and hop oil extracts were added twice at the fermenter, at the start and end of fermentation.

Reference lager beer (LAGER REF T90) had a total hop bill of 300 g/hL, in equal ratio of T90 Citra®, Cascade, and Amarillo®. Reference ale beer (ALE REF T90) had a total hop bill of 980 g/hL of

T90 Nectaron®. Lager trial beer (LAGER TRIAL OIL) had a total hop extract dosage of 75 g/hL with equal parts of Citra®, Cascade, and Amarillo®. Ale trial beer (ALE TRIAL OIL) had a total hop extract dosage of 95 g/hL in 5:3 ratio, respectively, Nectaron® and Nelson Sauvin™. HopAlpha NISO 25 % was added post-fermentation, prior bottling at 8.2 g/hL (equivalent to 19.5 IBU contribution). The final beer bitterness was 15.8 ± 1.5 IBUs (1 IBU equals 1 mg/L).

Sensory Analysis – The sensory characterization of beers was performed with an internal TNS panel of eight experienced hop tasting panelists. Panel was trained using standard AROXA™ Certified Flavor Standards. Sensory attributes have been locked as per TNS Hop Lexicon. Descriptive profiling has been used to characterize the aroma and taste of beers. Beers were tasted blind in a dedicated 10-booth sensory facility. Flavor and aroma descriptive analysis was performed in triplicate; a scale of 0 – 9 was used to rank specific attributes which include fruity- tropical, fruity – stone fruit, citrus – lemon, citrus – other, floral, herbal, spicy, grassy, woody, resinous and sulfur (e.g., DMS).

3 Results and discussion

3.1. Lagers and wort differentiation

Despite the significant growth of specialty beer styles with craft brewing, lagers are still the prevalent beer globally. A fundamental advantage in bright lager production is the possibility for wort's harmonization and its re-formulation using hop extracts to enable increased output at full industrial scale. Additionally, a lager differentiation by readjusting the original gravity with malt extract, adding hop extracts post-fermentation, can also multiply into different beer styles, from premium hoppy lagers with citrus and fruity taste distinctions, towards ales, and specialty styles such as IPA and NEIPA. A typical dosing flowrate of 300 – 500 hL/h is successfully achieved within automatic dosing systems.

For this experiment, one wort lager stream was produced and separated into multiple kegs to differentiate into different beers, using liquid hop extracts. The beers were then analyzed and compared with the corresponding references using T90 pellets. Firstly, two different naturally pre-isomerized bitter liquid extracts, namely, HopAlpha NISO 25 % and HopBeta HULU 20 %, were applied in separate beers. Figure 2 shows the beer sensory profiles brewed with both bittering hop extracts added individually. Figure 2A shows the taste impact, and figure 2B shows the aroma impact. Both bitter hop extracts were dosed post-fermentation, namely, naturally isomerized alpha 25 % (REF NISO), dosed at 8.2 g/hL, and light stable hulupones 20 % (REF HULU), dosed at 12.5 g/hL. Hop pellets were not used in these recipes, which allowed to reduce the boiling time to 30 minutes. This means the hop extracts were more energy efficient to use compared to the hop pellets. Results show that both bitter hop extracts provided high quality bitterness to the beer and had a similar taste profile. NISO contributed for a fruity-fermented character and HULU provided a clean, sharp bitterness with hoppy notes. The beer with HULU 20% skewed aroma towards a citrus lemon and fruitiness character which can be an interesting application for beer styles where the aim is to reduce herbal and spicy attributes. These findings support previous studies where it is shown that the beer sensory bitterness perception and its quality is influenced by multiple chemical drivers in addition to iso-alpha acids [24]. Both beer profiles were rated as credible representative of lager styles. Despite the absence of aroma extracts, the addition of FLOE at late-whirlpool has contributed to a subtle hop aroma, which might be a solution to consider with exclusive additions to the brewhouse. Dosing HULU 20% as light stable bitter hop extract is a valid option for beer in clear packaging.

Secondly, the same lager wort was used to brew additional beers, namely, one ale, and one lager, solely using liquid hop extracts. Brews using T90 pellets were used as reference to compare with beer trials. Beer characteristics are shown on table 2. Figure 3 shows the sensory profiles from the brewing trials, comparing reference brews using T90 pellets (REF T90) for dry hopping, with brews using hop extracts (TRIAL OIL), in double dry hopped (DDH) lager and pale ale styles. NISO was dosed post-fermentation, at

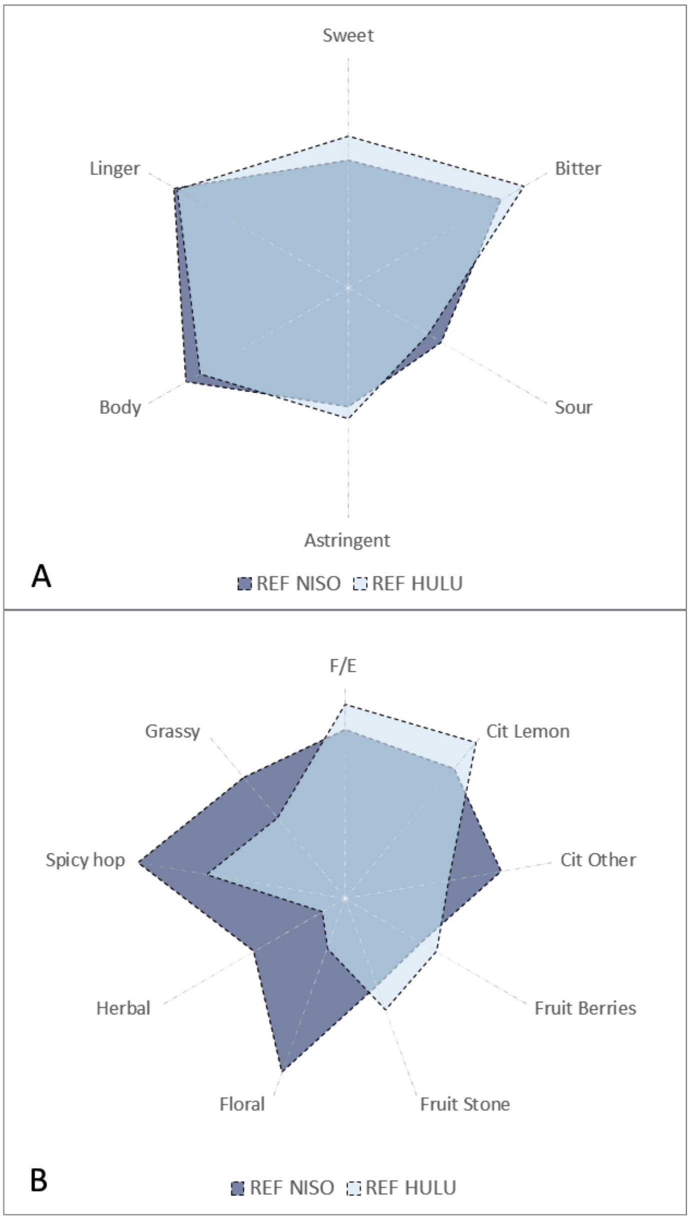

Fig. 2 **Beer sensory spider diagrams: comparing NISO vs HULU additions as bitter hop extracts to bright lager beers. Taste impact shown on 2A, and aroma impact shown on 2B**

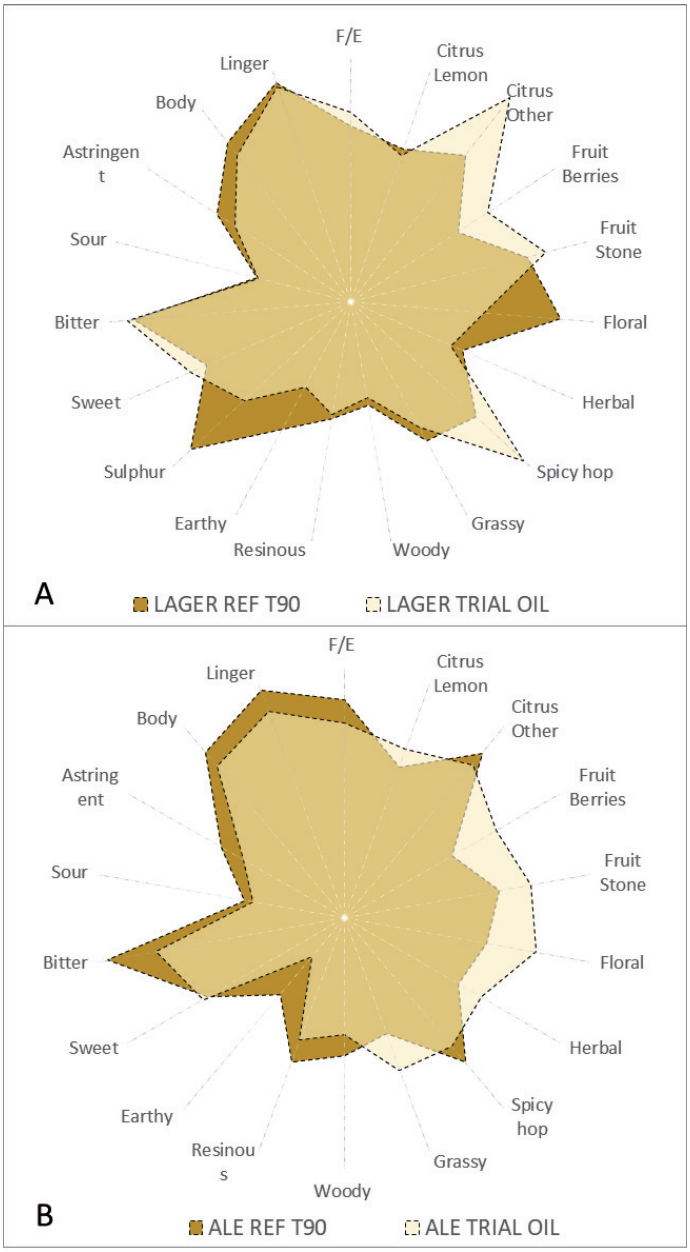

Fig. 3 **Beer sensory spider diagrams comparing T90 brews vs hop extract additions to the same wort. In bright lager (3A), and in pale ale (3B) styles, respectively**

8.2 g/hL, in both lager and ale recipes. The hop bill in lager was reduced to less than 10 % w/w, from 900 g/hL (T90) to 75 g/hL (equivalent hop extract). The ales hop bill was reduced in the same magnitude, from 1100 g/hL (T90) to 95 g/hL (equivalent hop extract). The sensory results have shown that the beers were significantly different in sensory character.
The bitterness and earthy resinous and woody attributes were reduced when using hop extracts; however, the bitterness quality rated higher. DDH lager using hop extracts, had significantly less sulphury and floral character, with increased citrus, spicy and fruitiness roundness. These beers had a pleasant, fruity, tropical, and citrusy aroma. The addition of aroma hop extracts to lagers allows to explore additional lager-plus concepts in a faster and safer way. DDH ale achieved a rounder fresher and pleasant taste overall, when compared to the reference. The aroma was described as fruity candy with amplified floral and stone fruit subtleties. In addition to the positive final beer organoleptic characteristics, one of the main process benefits upon brewing with hop extracts, was the significantly reduction in resident time required in maturations vessels due to dry hopping. In these brews, a reduction of four days conditioning was achieved.

Lager recipes contain modest aroma hop quantities, and thus the optimization focus is on bittering efficiency, transitioning additions from kettle to post-fermentation, which allows to recover up to 60 % of IBU and better alpha yield. As such, the hop taste impact is easily harmonized. Further advantages include a significant reduction in boiling time with no isomerization required, improving filtration capacity due to reduced hot trub, hence significantly faster brew time.

A future sustainable approach to explore brewing options in the lager space is the use of “noble hop” variety types, as opposed to the actual noble hops. Noble hops represent the traditional European hops, namely, Saaz, Spalt, Tettnanger, and Hallertau Mittelfrüh, generally characterized by a distinct herbal and floral aroma and a subtle spicy flavor with a smooth bitterness (3–5.5 %). These are mainly used to brew European lagers, such as Pilsners and Helles. Replacing these with hop type extracts with taste parity will allow brewers to avoid terroir influences, potential crop infections and seasonal climate changes, which can make noble hops difficult to source given their popularity. The fractionation and formula design of hop extracts can match certain varieties or variety mixes at pre-determined ratios. The same principle can be applied to certain hop varieties with reduced hop oil yield or crop availability to favor sustainable sources.

3.2. Low alcohol and beer functionality

The non-alcoholic market amounted to US$ 31.92 billion in 2022, with expected annual grow over 13% (CAGR 2022-2025) with expected volumes of 9,214 million liters by 2025 [51]. The technical requirements for these beer styles, including low to no alcohol and low calories, are mainly to address sensory defects with the expectations for the taste parity as per the regular full alcohol and caloric reference beers [5, 50]. Most of arrested fermentations will leave a sweet worty taste, and low carbohydrate beers are often characterized as thin liquids, lacking depth and a long-lasting taste and mouthfeel. While there is still no match for the replacement of alcohol, the functionality delivered by hops have the potential

Table 2 **Beer characterization using an Anton-Paar beer alcolyzer 3001:**

Beer Description	**Alcohol % (v/v)**	**Er (Real Extract) % (w/w)**	**p (Original Extract) % Plato**	**RDF % (w/w)**
REF NISO/HULU	5.19 ± 0.09	4.07 ± 0.09	11.95 ± 0.22	67.38 ± 0.09
LAGER REF T90	5.48 ± 0.07	3.74 ± 0.01	12.07 ± 0.10	70.41 ± 0.34
LAGER TRIAL OIL	5.36 ± 0.04	4.20 ± 0.00	12.32 ± 0.06	67.36 ± 0.13
ALE REF T90	6.70 ± 0.03	4.34 ± 0.04	14.39 ± 0.08	71.48 ± 0.10
ALE TRIAL OIL	6.13 ± 0.06	5.04 ± 0.02	14.21 ± 0.10	66.30 ± 0.11

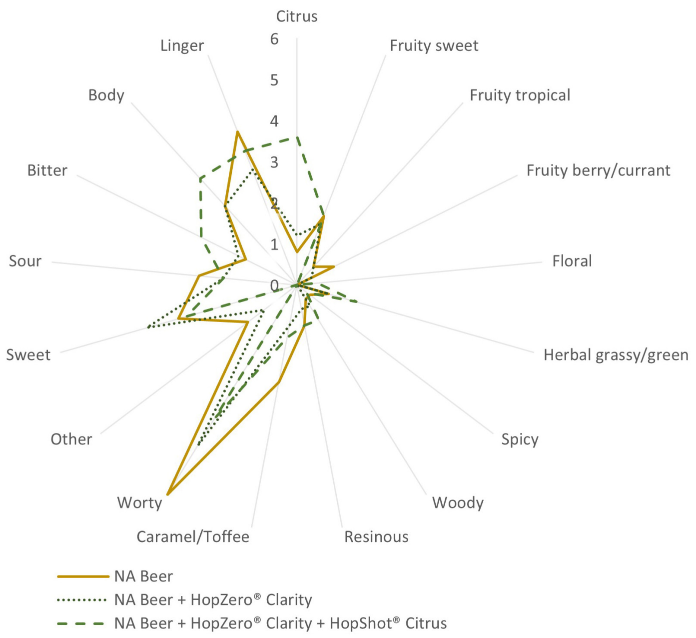

Fig. 4 **Profile optimization of zero alcohol beer (NA Beer) using hop extracts**

to fill the taste gap with their synergistic and masking effects when combined with volatile and nonvolatile beer constituents. Other options would be able to address beer sensory defects via food additives, such as hydrocolloids or flavorings with modifying properties (FMP). However, these are not derived from hops, and thus not considered for this study.

Figure 4 shows a practical taste optimization example using a non-alcoholic beer with significant taste defects. The addition of hop extract in dotted line (HopZero® Clarity, at 10 g/hL) has masked the worty and yeasty notes present in the beer base (brown line). The addition of a second fractionated hop extract in green line (HopShot® Citrus, at 10 g/hL) rectifies the hoppiness top note and spikes citrus and sweet fruitiness attributes. It also increased the beer mouthfeel and full flavor taste perception. In this case, the two hop fractions combined have seen to deliver functionality to the beer base and thus improving sensory attributes. By making use of neutral tasting hop fractions, such as HopZero® Clarity, it was possible to increase the mouthfeel perception upon swallowing. Hop extracts improved beer sensory attributes such as fruity-citrus notes, as seen in previous studies [33].

3.3. Specialty beer and dry hop optimization

Hops can have a significant impact on taste and recipe cost of hop-forward beer styles, mostly due to inefficiencies related to dry hopping. Using hop pellets for dry hopping is inefficient due to the low amount of hop oil/active compounds in pellets (0.5 to 4 % dry weight). Hence, it is of interest to further optimize the brewing processes. Therefore, the potential replacement of pellets used in late-whirlpool and dry hop bills, by post-fermentation hop extracts, has been investigated.

Different hop varieties will impact significantly on the perceived intensity and character of beer key sensory attributes [10, 40]. Hops used to brew specialty beer styles will typically have significantly higher myrcene levels and consistently lower quantities of herbal, woody, and spicy-forward hydrocarbons (Fig. 5), which explains the application into the correspondent beer style brewed. Recent aroma varieties such as Mosaic®, Simcoe®, Galaxy®, Centennial, Citra® and Amarillo® contain a substantial amount of monoterpene alcohols (linalool and geraniol) contributing with a pleasant fruity and floral aroma [53]. Furthermore, Mosaic®, Citra® and Amarillo® are regarded as geraniol precursors and free geraniol dominant hops. Cascade is characterized by floral or fruity monoterpene alcohols (linalool, geraniol, and β-citronellol) and their derivatives (geranyl acetate and geranyl isobutyrate) [31, 53]. Galaxy® and Nelson Sauvin™ have a relatively large number of volatile thiols (e.g., 4MSP, 3S4MP and 3SH). Additionally, it has been reported that 3S4MP could enhance the flavor intensity of other hop-derived flavor compounds as a flavor enhancer in Nelson Sauvin™ (e.g., 3S4MPA, isobutyric ester (2-methylbutyl isobutyrate), linalool, and geraniol). Simcoe® also contains a large amount of thiols (4MSP and 3SH), especially 4MSP [41, 44]. The opposite is noted for traditional (German) varieties, which are spicier, more herbal and the major odor-active compounds include common hop odorants, such as myrcene, (3R)-linalool, and 2- and 3-methylbutanoic acids [37].

Figure 6 shows the sensory profile spider diagram from a typical IPA beer style (5.0 %ABV), which was dry hopped with Amarillo®, Cascade and Mosaic® T90 hop pellets (solid brown line). After profiling this reference beer, the objective was to optimize its taste and aroma, namely, to amplify its positive sensory attributes, applying post-fermentation hop extracts, with full traceability to the original hop varieties. The reference beer was further spiked with a hop extract blend, and the sensory diagram is shown in the dashed green line. Results show that the spiked beer was characterized with a significant increase in citrus, fruity sweet, and floral aroma, as well as a significantly sweeter taste. The hop aroma fingerprint was optimized by increasing oxygenated fractions, using terpene alcohols, respectively expressing the fruity, citrus, and floral at-

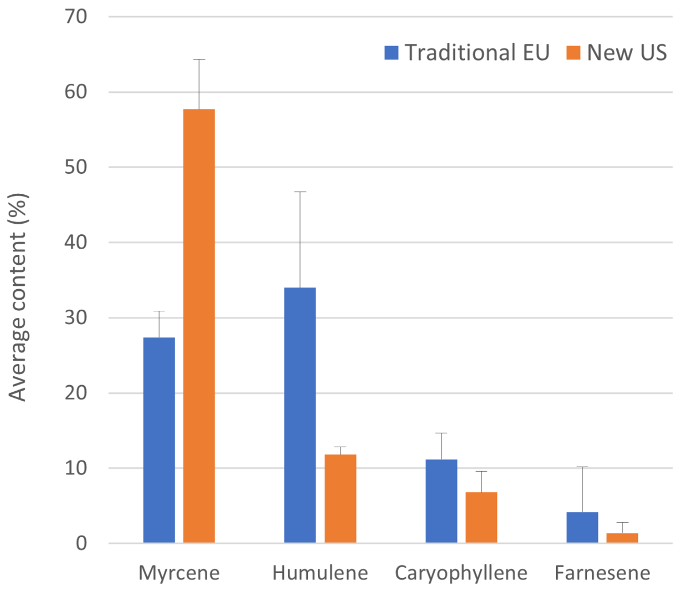

Fig. 5 **Differences in the average oil composition of five top rated hop varieties from traditional varieties produced in EU, compared to more recent hop varieties, from US**

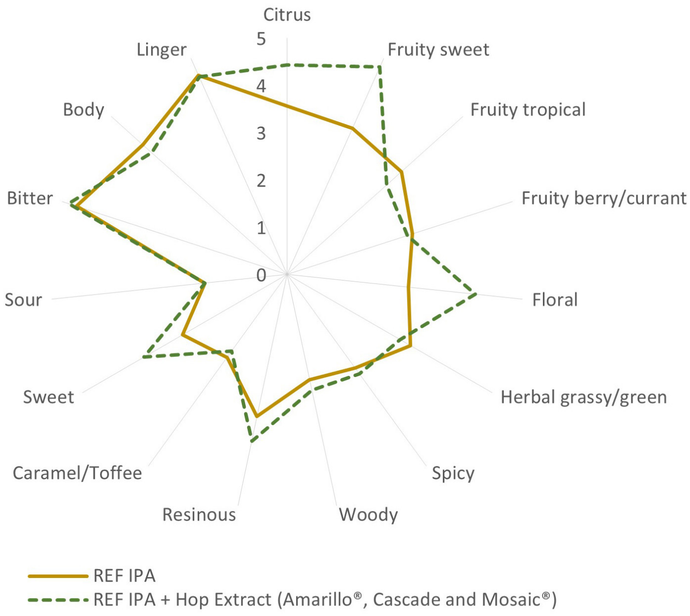

Fig. 6 **IPA style beer optimized using post-fermentation hop extracts**

tributes. Consequently, the hop extract blend allowed to reduce/modulate woody and herbal compounds, such as monoterpenes and sesquiterpenes, as well as the bitterness impact.

Table 3 includes a list of the main hop volatile compounds divided by its main taste contribution to beer. The solution was an increase of floral-estery and fruity-citrusy compounds, to the detriment of herbal-woody compounds. This effect has been explored in previous studies [34, 59]. It was also reported a slight increase in resinous taste perception indicating a possible limit threshold in dosage rates which should be monitored to avoid any interference in the overall beer profile.

In this case, an enriched estery hop fraction and post-fermentation addition would serve as an alternative to additional T90 hop pellets, with no changes at the brewhouse or fermentation, which simplifies the hop bill application. Furthermore, the hop extracts significantly increased maturation vessel capacity, while reducing occupancy and contact times to hops given the instant solubility upon dosage. The resulting aroma fingerprint of hops in beer depends on the quantity and quality of the hop dosage, the time of addition, and a comprehensive profiling, of a wide range of key compounds. All these compounds are influenced by the synergies with beer constituents with different volatilities and sensory thresholds to consider. Therefore, sensory, and analytical analysis are essential resources to validate taste solutions.

A good reference to have for the overall aroma is the odor activity value (OAV), defined as the ratio of the concentration of the odor-active compounds to its respective odor threshold. So, odor-active compounds exhibiting an OAV ≥ 1 may contribute to aroma. Most odor-active compounds in hops include linalool, geraniol, β-damascenone, β-citronellol, esters, and organic acids. Following, also S-methyl hexanethioate, methyl dec-4-enoate, caryophyllene, and humulene. Up to 80 % of essential oil from hops is composed of hydrocarbons myrcene, humulene and caryophyllene. Terpene hydrocarbons contribute to beer flavor in dry hopped beers. For instance, myrcene has a threshold of 30 ppb in beer and is one of the main hop aroma contributors, and, about 400 ppb provides a characteristic piney resinous hoppy profile. The myrcene contribution to beer profiles is generally described by brewers as typical "dank IPA". Moreover, as previously studied, a β-myrcene fraction induce an intense 'crushed grass, sap' aroma [13]. Ketones can help to increase fruity fermented notes, with 2-nonanone and 2-deacanone, but one should be wary of the cheesy, waxy notes contribution. Conversely, carboxylic acids such as butanoic, octanoic or heptanoic acids contribute with off-notes and should be avoided.

4 Conclusion/Summary

The findings in this work have shown that advanced hop products are versatile and can be used in different brewing applications, such as lager wort differentiation, to successfully brew true-to-style beers. Naturally pre-isomerized bitter extracts delivered high quality bitterness and after taste to ales and lagers. Aroma hop extracts, added post-fermentation, delivered distinct hoppy taste and aroma characteristic top notes. Adding liquid hop extracts in

Table 3 **Main volatile compound indicators generally found in hops and its aromatic sensory contribution. Adapted from Nickerson and Engel and updated with previous studies [1, 15, 28, 36, 38]**

Floral-Estery Compounds	Citrus-Piney Compounds	Herbal-Woody Spicy Compounds	Fruity-Citrusy Compounds
Geraniol	β-pinene	β-myrcene	β-damascenone
Geranyl acetate	α-pinene	β-caryophyllene	β-citronellol
Geranyl isobutyrate	α-cadinene	α-pinene	Limonene
Linalool	Limonene	β-ocimene	α-ylangene
β-ionone	α-Muurolene	α-copaene	3-methyl-2-buten-1-ol
Linalool	Nerol	β-humulene	3-methyl-2-butenal
Nerol	/3-Selinen β-selinene	2-methylpropyl	
Caryophyllene oxide	α-terpineol	Calamenene	2-methylbutyl propanoate
		β-farnesene	2-methylpropanoate
		Humulene epoxide II	Methyl 4-decenoate
		Camphere	2-methylpropyl-2-methylpropionate

brewing recipes provided advantages on liquid dosing, shorter boiling and dry hop infusion timings as well as improved filtration capacity. Hop extract blends designed have shown a clear positive taste synergy due to its natural difference in affinity and polarity [41]. In addition, upon linearization, can provide cost-effective all-in-one solutions to match T90 pellet hop bills, and simplifying the raw material handling and dosing upon brewing. Following studies should explore new bespoke liquid hop extracts for specific beer styles with direct conversion from pellets.

Trials reported in this study will support brewers to experiment, combine and convert recipes from hop pellets, towards new liquid aroma hop extracts. Standardized soluble liquid solutions avoid further reformulations, easier handling, while contributing to brand consistency and simplified supply chain. Additionally, brewers will be able to control reactions such as oxidation and hydrolysis, avoid losses via evaporation, washing out, or by adsorption onto the biomass. Rectifying shifts in profile due to terpenoids biotransformation, avoiding hop creep, and addition of standardized haze can be explored [9, 11, 52].

Future hop innovations are expected to provide: 1. Consistency in core aroma hop varieties and existing established beer portfolio, allowing process optimizations and brewers to monitor a wider range of active taste components; 2. Extension lines, innovate and re-think the usage of by-products such as waste hop, and offer value-added hop products; recover aroma molecules as restauration aromas to use as building blocks in specific engineered hop formulas. In addition to hop oil, the usage of both hard resins and various water streams should continue to be explored to achieve a full usage of hop material. Concentrated and standardized active taste and aroma hop compounds can result in less beer staling character and extended shelf-life [42, 58].

From a sustainability view, a decrease in indirect/direct carbon footprint emissions is expected throughout the value chain. The partnership and vertical integration between growers and manufactures is determinant for accessibility to hops globally. The brewing industry ambition is to reduce the carbon footprint of beers from an average of 500 g/L CO_2 to 50 g/L CO_2 by 2050. Therefore, switching to environmentally friendly technology is key for the business strategy, as well as finding renewable ways to eco-friendly brew, to reduce water footprint, and to consider returnable, reusable, or recyclable packaging [39]. This new market dynamic reflects the industry evolution over the recent years. The expected recovery growth by premium tasty hop-forward beers sets off the brewing and the hops industry towards an optimistic future. We should expect hop-forward beers and premiumization to prevail, expanding the offer beyond the traditional brewer's portfolio within the beer category.

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