A Review of Alternate and Efficient Methods to Produce Beer without Hops

Adhiraj Pathania[1] Savreet Kaur Bains[2] Paviter Bakshi[3] Mohit Sharma[4]
[1,2,3]Student [4]Assistant Professor (Guest Faculty)
[1,2,4]Dr. SSB UICET, Panjab University, Chandigarh, India [3]GGDSD College, Panjab University, Chandigarh, India

Abstract— Various alternate ingredients are used in place of hops with little effect on organoleptic properties in the production of beer. The brief history of the beer industry and the latest establishment up of local craft beers. Hops are available only in damp temperate regions of the world. The other part of the world then has to import it for the production of beer which makes it expensive. This study shall help the brewers to use alternate versions of hops to keep the cost low without changing the attributes of the beer much, various comparisons with the standard hops are conducted, also use of enzymes- assisted brewing process compared with conventional methods.

Keywords: Hops, Alternate to hops, Nigerian vegetables, Brewery history, proximate analysis, Bittering, Enzyme

I. INTRODUCTION

A hop plant Humulus lupulus beer flowers are called hops. The plant is a member of the flowering plant family Cannabaceae, (also called seed cones or strobiles). They are used mainly in beer asa bittering, flavouring, and stabilization agent, to which they impart floral, fruity, or citrus flavours and aromas in addition to bitterness. In other drinks and herbal remedies, hops are also used for various purposes. We have taken five substituents of hops which are Nigerian hop extracts, Garcinia Cola (bitter cola), Azadirachta indica (Neem), Vermonia amygeldaine (bitter leaf) and Gongronema latifolium (heckle). They are easily available in Nigerian local markets. The chief objective of this study is thus to compare the vegetables that can be used as a substitute to commercial hops by: a) Brief history of beer industries, latest trends and notable mergers in the brewery industry. b) analyzing proximate analysis for both the vegetable substitutes and hops. c) study the extracting of resinous components and essential oils. d) Look into the consequences of different type of solvent used for extraction, effects of temperature and period of storage on the bitterness index of these vegetables. e) Physio-chemical properties of the extracts, ANOVA for comparison of phytochemicals in the isomerized hop and the Nigerian bitter vegetables, Post hoc test for comparison of isomerized hop extract and those of Nigerian plants. f) Changes in the efficiency of beer production when assisted by enzymes. Nonnutritional plant chemicals are phytochemicals that have preventive properties for protection from disease. They have the bioactive compounds found in plant food which are natural for example leaves, nuts, stems and roots [1]. Alkaloids, Tannins, Saponins, Terpenoids, Oxalates, Trypsin, Flavonoids Glycosides, inhibitors etc. are examples of phytochemicals. Alkaloids contain compounds that contain low molecular weight nitrogen due to the presence of alkaline metabolites in plants improve tress from biotics and abiotic alkaline components or by influencing pollinators and pollinators dispensing of seeds and fruits. Defensive tactics involve predator repellence by toxicity or taste of bitterness included fix or alter via the antioxidant system [2],[3]. Tannins (or tannoids) another group of phytochemicals which is a class of astringent polyphenolic biomolecules, that bind to and proteins and various other organic compounds precipitate amino acids and alkaloids included [4]. Another type of Saponins are glucosides of foaming characteristics that are phytochemicals too. Characteristics containing polycyclic aglycones annexed to one or more side chains of sugar. The Aglycone the part that is also called sapogenin is either a steroid (C27) or a triterpene (C30) [5]. Natural substances and oxalates are a phytochemical class that is present in the food and bind macronutrients like calcium throughout our digestive tract and help in easy defecation by voiding excreta form bowels. Oxalate, to which it is not bound calcium passes from the skin into the blood as a waste product. Kidneys in which the urine exits the body [6]. Acid phytic, Inositol hexaphosphate (IP6), or phytate, is also known as a potent antioxidant that helps to get the body off the ground. Certain contaminants and heavy metals [1]. Inhibitors of trypsin are phytochemicals that decrease the biological availability of active trypsin, an enzyme necessary for many nutrients, animal and humans included too [3]. References to Haemagglutinin to a substance which causes agglutination of red blood cells, a mechanism referred to as haemagglutination [2]. That acts on the cardiac muscle's contractile force both because they tend to interrupt functions, the bulk are highly toxic to the heart [1]. Cyano-glycosides approximately 90 % of the larger plant community accounts for Toxins referred to as cyanogens [7]. Potential poisoning of alkaline Cyanoglycosides derives from enzymatic degradation to degradation. Free hydrogen cyanide (cyanogenesis) is made, resulting in acute intoxication of cyanide. Such glycosides are detected as in some species, secondary metabolites [8]. For hydrogen, inorganic cyanide, also called prussic acid, is a colourless and highly poisonous compound fluid. [9]

II. EMERGENCE OF BEER INDUSTRY IN THE SOCIETY

The corporate control started in the British market of brewing where a businessman Charles Chlore [10] bought 75% share of Watney Maan, a leading brewery chain that was at its peak around the 1960s. This sudden and unexpected news led to the closing of many local breweries. The closing down of neighbourhood breweries continued going in the post-war period until the beginning of the 1980s, the quantity of nearby and self-ruling brewing companies across the world diminished at a steady rate, while major corporate players rose in the public market wherever on the planet. The local traditional brewhouses and pubs which were very eminent little time ago started disappearing, mostly purchased by international players or they stopped their activity as profits

became quite less. The rise of international and larger brewers started in the 1970s and 1980s where several amalgamations originated and bloomed as a result of many large acquisitions and companies having affiliations with them. In the US itself, this expansion continued. For example, in the USA a lion shares i.e. 75% of the market was in the hold of just four organizations were Coors Brewing Company, Miller Brewing Company, Anheuser-Busch and Pabst during the 1980s. In the United Kingdom, Scottish & Newcastle, Bass, Watneys/Grand Metropolitan, Whitbread Beer Company, Allied-Lyons and Courage are six dominating national brewers which controlled the production as well as they took the task of distribution of beer because these companies had acquired the great number of local pubs and breweries in the state.[11] Subsequently, further merger and acquisition activity persisted, the notable and crucial ones were the formation of Scottish & Newcastle and its acquiring Courage company which soared its share to 30% of UK beer production in 1995. Conversely, a failed attempt of M&A (merger and acquisition) activity by Bass and Whitbread followed their retreatment from the British market. Meanwhile in Europe, Guinness (later Diageo), Heineken and Carlsberg dominated the market. By the end of the century, four global leaders which were notably Anheuser-Busch having a quarter (25%), Interbrew (13%), Heineken (12%) and AmBev (later Inbev, 10%) made up 60% of the world production of beer in volume. [12] The scale economies of plant level were crucial determining factors of national-level merger and acquisitions but international trade of beer (as opposed to production) is very less as beer is a low-value product and also bulky. The distribution, branding, advertising and credibility of the brand increased with firm-level economies with the help of mergers and acquisitions as it promoted synergy. [13] Some studies appreciated and recognized the influential role that broadcasting and branding exert on the beer industry, and suggest that 'behavioural lock-in' which is a type of theory of behaviour between consumer and producer which has also aided the exposure of global brands. [14]

Ironically, the current scenario has seen an ascent in the number of micro and craft breweries wherever on the planet which was mainstream in the past too but limited to nations. In 1980, the soaring number of breweries in the UK jumped from 142 to 1,113 in 2012. More growth was recorded in the US within the same period, from 92 to 2751 it saw a high jump in the opening of breweries. [15] Similar to numerous other European nations, such as Italy, Belgium, Germany, and Spain. What left the space for new players and created condition for speciality markets focusing on their requirement is the low preference of consumers in the heavy concentration processes in the brewing industry; policies in support of small business and entrepreneurs, such as cheap loans, rate reassurance and financial handout made available by local governments; and an increased level of finesse and refinement in consumers tastes, more tilted towards making a unique quality and niche products.[15],[16],17],[18]

III. PROCESSING OF VEGETABLES TO POWDER

Fresh vegetables are first stalked, sorted, cleaned by washing and then dried by simple air and oven drying. [19] Before the next step of grinding the plant material is cooled and then milled either by using a gibbon model or hammer mill. When the powder is ready, it is generally packed in the packaging material of usually thickness 0.06mm.

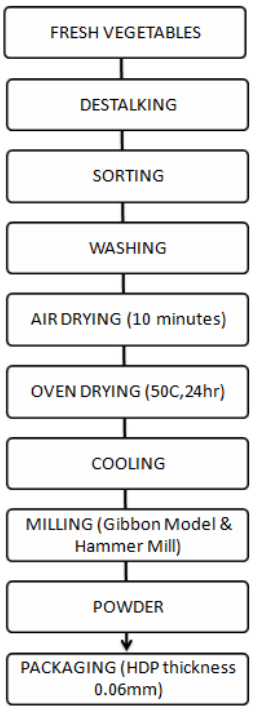

Fig. 1: Vegetable processing into powder

IV. PROXIMATE ANALYSIS

Proximate analysis is a quantitative analysis of the macromolecules present in a compound. The materials for the experiment were taken from the research lab and the local market. Hops were provided by the African Breweries Ltd. and chemicals from associations The Association of Official Analytical Chemists. And the Institute of Brewing [20]

A. Proximate analysis of vegetable samples compared with that of hops.

It analyzes the vegetable's proximate research data to those of industrial hops. It is found that Gongronema latifolium is the species with the highest fat content and is approximately six-folds the value of the commercial hop. This partially explains why Okafor et.al [20] reported that beer brewed with Grongonema latifolium had a poor foam head although it has almost the same protein content which is responsible for foaming here the fat plays its part. The moisture content of all the plant species do not vary largely when compared with the hops but least in hops i.e.10 (% dry wet basis). Vernonia amygdalina has the highest protein content of 16.34 (%dwb) yet the overall effect of protein to fat ratio annuls the protein's flex to increase foam heads. Considering crude fibre mainly dietary fibre hops are dominating but the DF or dietary fibre content of other plants is not too low. Present in the smallest percentage, they play a vital role as prebiotics. Prebiotics are those good bacteria that catalyse our intestinal purgation. In the case of beer, these are soluble fibre and thus helps in binding the food material in the intestinal tract and aids in intestinal emptying. Ash content is higher in Gronginima

latifolium i.e 14.6 and Garcinia cola, 13.62 (%dwb) whereas 8.9 (%dwb) in case of vernonia amygdalina, very close to that of hops i.e. 8 (%dwb). Garcinia oils also have the highest proportion of essential oils 1.16 (%dwb) when compared to others and also 0.5 in the case of hops. Oils impart the aroma and odour to the beer. Comparable results for the total resin values for Grongonemalatifolium, Vermonia amygdalina and Azadirachta indica were also analysed in the paper. [21]

B. Resin components of fresh vegetables and hops.

Resins are formed when the plant secretes a fluid which when exposed to air ossifies. Resins have a significant effect on the taste of the beer as it imparts a bitter flavour to the beer, especially soft resins. There are two types of resins: soft raisins and hard resins categorised based on their solubility in different solvents. Hard resins are soluble in diethyl ether and soft ones in cold methanol. It is found that all vegetables have higher values than hops for hard resins. And in the case of soft raisins, Grogonema latifolium has the highest resin content i.e. 18.6 (total resins=22.95) even higher comparative to hops i.e. 16.13 (total resins=18.16). In the case of hops, these resins are composed of two similar chemical groups α acids (humulones) and β acids (lupulones). None of them is bitter intrinsically but isomerised α acids and oxidized β acids are. During the later process of boiling worts, these α acids are converted into iso α acids that are largely responsible for the bitterness of the beer. Garcinia kola somewhat exhibits different composition from others and thus contain low resin content of 8.24 out of which soft resins comprises 6.07. [22] These values indicate that more rapidly than commercial. hops the vegetables can oxidize or deteriorate.

Percentage composition dry weight loss					
Constituents	Grongonema latifolium	Vernonia amygdalina	Garcinia cola	Azadirachta indica	Hops
Total resins	22.95	18.6	8.24	15.07	18.16
Soft resins	18.6	13.32	6.07	10.28	16.13
Hard resins	4.35	5.43	2.17	4.79	2.03

Table 1: Resin Components Table

C. Bittering potentials of water and organic solvent extracts of the vegetables and hops.

Bittering potentials of water along with distinct organic solvents extracts of the vegetable species as well as hops were calculated and analysed. IBU is the international bitterness units for measuring the amount of bitterness content induced due to the action of isomerised alpha acids or other bitterness compounds. The more the IBU, the more the beer will be bitter in taste. The scale of IBU generally ranges between 5 to 120, 5 being the lowest and 120 which is a very high bitterness level in beer. Most beers fall in the level between 15-80. The art of producing beer is just to rightly balance the ingredients and taste. Here is the potential of different species checked when dissolved in water and other organic solvents. Analysing the values demonstrate that in their amount of bitterness, the vegetables vary. Low bittering values were given by water extracts i.e. 18.4 with grongonema latifolium. 14.34 with vernonia amygdalina, 12.1 with garcinia cola and 14.12 with Azadirachta indica. Compared to hops that possess the value of 38.96, the value of the alternative plant species used is generally observed as low. While organic fat solvent extracts produced far higher values. Again, grongonema latifolium (42 in ethanol, 47.43 in acetone, 48.64 in toluene) has almost near bittering potentials of solvent extracts to hops that exhibit IBU value of 46.58 in ethanol, 48.46 in acetone and 49.96 in toluene. The high bittering essence of organic extracts recommends the end from vegetable tissues of meddling fat and other lipid materials. The results matched a report that claims that for bittering constituents of hops extraction non-polar solvents are beneficial. [23] Other alternative Vernonia amygdalina have bitterness potential of 38.61, 48.85, 46.96 in ethanol acetone and toluene respectively. IBU values of Garcinia cola are somewhat not in the focal vicinity of values rendered by hops as it yields IBU of 12.1 in water, 28.24 in ethanol, 29.4 in acetone and 30.66 in toluene. It doesn't mean that it can't be used as an alternative to hops, but yes it will impart a variation in taste, bitterness, aroma and mouthfeel of the generated beer.

D. Six Changes in the efficiency of beer production when assisted by enzymes.

The exogenous enzymes can be used with unmalted barley as an alternative to malting. [24] The losses in the malting processes would be prevented, although the energy and materials are needed to produce the enzyme mixture. In the industrial fermentation process, they are produced or manufactured in which fermentation is carried out and the yeast converts part of the protein in broth into enzymes. After fermentation, a rotary vacuum drum filter is used for the separation of enzymes from different biomass. The biomass is sterilized, dried, and sold as a fertilizer which has its economic importance. The enzyme liquor coming out of the rotary vacuum drum filter is purified secondly by ultrafiltration and concentrated by the process named reverse osmosis. The enzyme liquor contains 7% protein and 93% water is afterwards mixed with glycerol to stabilize the enzyme solution. glycerol concentration of 30%.is the final product produced by this process.

The Grassmann diagram explains the energy flows of the conventional malting process. [25] The main product stream has chemical exergy more than the exergy destroyed which is 77% of the total, so it is an energy-efficient process. The total exergy loss for processing is 518 MJ/100 kg malt, of which 380 MJ is destroyed and 138 MJ is wasted. [26] In the kilning process, high-quality energy is required for removing water which takes up the most energy. Subsequently, around 7% of dry matter is lost during malting due to respiration and the removal of rootlets.

E. Effect of temperature and period of storage on the bitterness levels of Water, Ethanol, Acetone, Toluene

Discussing the influence of the temperature of storage and the duration of storage on the degrees of vegetable bitterness. All the vegetal plants and hops were checked periodically at the intervals of 4 weeks, 8 weeks and 12 weeks and different

temperatures in various solvents. The findings demonstrate that hops have greater stability in storage than vegetable extracts. The stability of bitterness is observed to be varying with the temperature of the vegetable, extractant variety, type of vegetable and storage period. The highest losses in bittering potential among vegetables were shown by Grongonema latifolium.

Temp.	Water	Ethanol	Acetone	Toluene
27 ±1^{0}C	49.94	28.29	26.58	19.50
7 ±1^{0}C	10.72	4.70	4.98	3.79
0 ±1^{0}C	8.99	3.49	3.55	3.14

Table 2: Effect on Temperature on Reduction in Bitterness Level of Grongonema Latifolium with Different Solvents.

Temp.	Water	Ethanol	Acetone	Toluene
27 ±1^{0}C	33.94	26.28	24.23	17.47
7 ±1^{0}C	7.31	4.62	4.34	4.44
0 ±1^{0}C	6.14	3.28	3.14	3.04

Table 3: Effect on temperature on reduction in bitterness level of Verninia amygdalina with different solvents.

Temp.	Water	Ethanol	Acetone	Toluene
27 ±1^{0}C	21.39	14.40	17.61	10.46
7 ±1^{0}C	5.59	3.98	3.53	3.30
0 ±1^{0}C	4.22	2.86	2.53	2.09

Table 4: Effect on temperature on reduction in bitterness level of Garcinia cola with different solvents.

Temp.	Water	Ethanol	Acetone	Toluene
27 ±1^{0}C	24.97	19.04	13.98	13.81
7 ±1^{0}C	7.08	4.40	4.01	3.65
0 ±1^{0}C	4.43	3.11	2.96	3.04

Table 5: Effect on temperature on reduction in bitterness level of Azadirachta indica with different solvents.

Temp.	Water	Ethanol	Acetone	Toluene
27 ±1^{0}C	7.46	4.28	3.94	3.33
7 ±1^{0}C	3.46	1.77	1.42	1.54
0 ±1^{0}C	2.16	1.59	1.41	1.20

Table 6: Effect on temperature on reduction in bitterness level of HOPS with different solvents.

In general, however, the loss of bitterness was less for organic solvent extracts than for water extracts stored at the same time, temperature and duration.

Most organic solvent extracts also preserved more than 70 per cent of their original bitterness after 12 weeks of storage at ambient temperature, whereas water solvent extracts experienced a 50 % reduction in their bitterness levels. Results also suggest that freezing and chilling storage when compared to ambient temperatures showed fewer losses in bittering capacity. This is in line with Grant (1977) and Hough et al [25],[26],[27],[28] (1982) reports that said that cold storage provided hop bitterness with greater stability than elevated temperature storage. Generally, with the period of storage increment, bitterness levels get decreased.

V. COMPARISON OF PHYTOCHEMICALS

The isomerized hop in the sample is produced by Ritchies et al, other samples are milled and vacuum dried at 50℃. 200 gm of each plant product prepared was then preserved in desiccators for the analysis. [27]

A. ANOVA for comparison of phytochemicals in the isomerized hop and the Nigerian bitter vegetables.

ANOVA stands for Analysis of Variance. It is an analysis tool that bifurcates the total variability found in the data into two sets. One is systematic factors and the other one is random factors. The basic understanding of this method is an analysis of variance found in different data sets by gaining information about the relationship between dependent and independents variables. The outcome of the ANOVA formula is the F statistic or F-ratio given by the formula: [29]

The formula for ANOVA is:

$$F = MSB/MSE$$

Where:

F= ANOVA coefficient

MST= Mean sum of squares due to treatment

MSE= Mean sum of squares due to error

If there is no real difference observed between tested groups, it is termed as a null hypothesis. P-value is "The Probability" for the "Null Hypothesis" to be "True". The null hypothesis treats everything the same and everything equal. There are many statistical tests which include T-test (comparison of the mean), F test (comparison of variance), ANOVA (Analysis of Variance) etc. P-value (any value from 0 to 1) e.g. =0.1 means 10 out of 100, the null hypothesis will be true. The experimenter should decide the level of significance before starting the experiment. P value> level of significance, the null hypothesis is accepted. Here, the test p-value is 0.633 which is higher than 0.05. Then, enough proof exists to accept the Null hypothesis and the inference that there is no significant discrepancy between the examined samples. [29]

The data demonstrated that A. Indica has the highest degree of value of significance of 0.618, which indicates that the sample of all the plants is the nearest in resemblance to isomerized hop. Furthermore, the significance value of G. kola to isomerized in the ranking of values, hop is 0.605, the second value of importance among the other values. [30]

The implication is that G. kola is also close to isomerized hop, but not as close to isomerized hop as A. Indica. Other specimens, i.e. Amygdalina, V. and G. latifolium have significance values of less than 0.605 but greater than 0.05. That demonstrates that the samples are not significantly distinct from isomerized hops. [30]

The test's p-value is 0.645, which is greater than 0.055 and then, to conclude, we have enough proof. There is no variation between the samples. (Hop leaf, G. kola, A. indica, V. amygdalina, and V. amygdalina) of interest for G. latifolium) [30]

The numerous comparisons made using the post hoc test. It revealed that A. Indica has the highest value for significance of 0.637, which means this plant is the nearest among the plant's anything to the hop Leaf (control). Additional extracts, i.e., G.kola, Amygdalin, and with G.latifolium have values of significantly less than 0.637 but over 0.05. This demonstrates that the plants do not differ greatly from hop leaves. [30]

VI. CONCLUSION

The four Nigerian vegetables Garicinia Kola (bitter cola), Azadirachaindia (Neem), Vermonia amygeldaine (bitter leaf) and Gongronema latifolium (heckle) which were substituents

of hops have very much potential to be alternatives, Azadirachaindia (Neem), Vermonia amygeldaine (bitter leaf) and Gongronema latifolium (heckle) due to their high bitterness levels, whereas the Garicinia Kola (bitter cola), due to its high value of essential oils which play a vital role in imparting aroma and flavour to the beer. The cold temperature will ensure bitterness for a longer time. Stopping the oxidation of vegetables by pelletizing the powders and the vacuum packing. There is no significant difference in phytochemical constituents such as tannin, phytate, saponin, cardiac glycoside, cyanogyloside and hydrogen cyanide between the hop and the vegetables (Nigerian). The extracts from vegetables can be used as substituents for beer brewing. G.latfolium have the highest chances for the substitute for hop extract and V.amygdalina, the closest option for hop leaf extract. Various efficient processes such as Dry hopping, hop bittering and aqueous extraction process. These results are noted and concluded that the combined process of the aqueous extraction process and hop bittering is most economical and efficient. The enzymes help in reducing the environmental problems of the hop brewery industry. The mergers and acquisitions in the brewery industry in the firm-level economies support synergy.

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