Introduction

Beer is one of the oldest produced beverages in the world, and has been made from barley for at least 5,500 years[1]. Though modern beer is a far cry from its ancient predecessor, the overall process remains composed of similar steps derived from saccharification of cereal grains.

The first step in modern brewing is the mash, in which crushed grains are mixed with hot water to activate native barley amylases. These enzymes then convert complex polysaccharides into smaller, fermentable oligosaccharides. The mixture of water and sugars (wort) is separated from the spent grains and transferred to a boiling kettle, and is then boiled. Hops are added to the boiling wort, which causes the isomerization of alpha acids, lending bitterness to beer, which balances the sweetness caused by residual sugars. After boiling, the wort is cooled and transferred to a fermentation vessel, where a yeast culture is added to ferment the wort into “green beer.” This unfinished beer is then filtered, carbonated, and aged. This entire process is outlined below (Figure 1).

Because of the complexity of the complete brewing process, there are multiple opportunities for the application of NMR in brewery quality control. NMR and multivariate analysis have been applied as quality control measures previously[2,3], but never throughout the entire brewing process. In conjunction with a commercial brewing company, this project represents an investigation of the consequential chemical effects, brewers would be able to determine if there was an introduction of oxygen to the brewing stream. The increase in all carbohydrate resonances indicated that during the mash, amylase enzymes were responsible for the conversion of insoluble polysaccharides to water soluble oligosaccharides. Of these, malt-oligosaccharides experienced the largest relative increase, which could be used to determine mash conditions, as variations in temperature ranges influence proportions of mono- di- and trisaccharides present in the sweet wort.

Despite the relative constant concentration of the labeled organic and amino acids, lactic acid increased dramatically throughout the mash and sparge. The increasing amount of this acid could be indicative of an active population of lactic acid bacteria during the mash, which could potentially directly influence the flavor of a finished beer, as well as the pH of the wort, which could influence fermentation behavior of S. cerevisiae.

Results & Discussion

Step 1: The Mash

The following data represent samples taken from multiple batches of the same beer. Labeled chemical species serve as representatives of identifiable compounds, along with illustrations of the inferences a chemist can draw by using these compounds.

Materials & Methods

Beer was acquired directly from an East coast brewery. Sample volumes were 175µL (straight runs) & 500µL (yophosphilated). Degassed beer samples were brought to a final sample volume of 0.75µL with deuterated water. Exactly 10mg of internal quantitation standard (maleic acid) was added to samples for quantitation. Samples were run on a Mercury VX 300 spectrometer operating at 299.681 MHz. Spectral Parameters: pw=67.5°, d1=7°, aS=88°, T=27°C, n=256 (straight runs) & n=128 (yophosphilated) Spectra were processed in MrOva (ver. 8.2-0.16261) and Chemometrics were performed in Eigenvector (ver. 6.1)

Future Work

The next step will be to build multivariate batch reaction models to identify outliers in the brewing process. Identification of natural versus introduced bacteria could be used for quality control measures during the boil step. For example, kojibiose, a product of the carmelization of glucose, is a potential indicator for the condition of a beer while boiling, as excessive carmelization and browning can influence the color and flavor of a finished beer.

Acknowledgements

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Citations

2. Almeida, C. et. al. (2006). Composition of Beer by ¹H NMR Spectroscopy: Effects of Brewing Site and Date of Production

Figure 1: Complete brewing process. Image credit: BBC News http://news.bbc.co.uk/2/hi/business/5273828.stm

Figure 2: Spectra of carbohydrate region of samples pre- and post-boil. The increase of lactic acid was marginal, and could be attributed to the metabolic activity of introduced yeast or residual lactic acid bacteria. In the event that production was due to lactic acid bacteria, the amounts were minimal and could be easily measured and assessed by NMR.

Figure 3: Principal Component Analysis of brewing stream. Samples were from two separate mash in/out (Postboil & Postboil samples) and kettle steps. The increase of lactic acid was marginal, and could be attributed to the metabolic activity of introduced yeast or residual lactic acid bacteria. In the event that production was due to lactic acid bacteria, the amounts were minimal and could be easily measured and assessed by NMR.

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In conjunction with a commercial brewing company, this project seeks to utilize NMR and chemometrics to describe the full chemical changes that occur during the brewing process, as well as variations occurring between separate production lots. Equipped with the knowledge of brewing process variables and their consequential chemical effects, brewers would be able to use NMR as a quality control measure to not only identify when production issues occur, but also where and why they occur.

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