Journal of Food Engineering 116 (2013) 138–143

Contents lists available at SciVerse ScienceDirect

Journal of Food Engineering

journal homepage: www.elsevier.com/locate/jfoodeng

An approximate shelf life prediction of elaborated lager beer in terms of degradation of its iso-α-acids

Dieudonné Nimubona, Carlos A. Blanco *, Isabel Caballero, Antonio Rojas, Cristina Andrés-Iglesias

Dpto. Ingeniería Agrícola y Forestal (Área de Tecnología de los Alimentos), E.T.S. Ingenierías Agrarias, Universidad de Valladolid, 34004 Palencia, Spain

ARTICLE INFO

Article history:
Received 1 August 2012
Received in revised form 19 November 2012
Accepted 22 November 2012
Available online 1 December 2012

Keywords:
Lager beer
Trans-α-acids
Iso-α-acids isomers
Activation energy
Trans-/cis-ratios
Degradation kinetic

ABSTRACT

A 3-l laboratory-scale beer production protocol was designed and developed to produce beer. Concentrations of cis-/trans-iso-α-acids were quantified by HPLC. The trans-/cis-ratio varied from 0.62 to 0.49 after accelerated aging from 4 °C to 50 °C. The degradation of trans-iso-α-acids in elaborated pale lager beers followed first order reaction and this degradation conforms to the Arrhenius equation. The activation energy (E_a) and frequency factor (A) for trans-iso-α-acids in elaborated pale lager beer ranged from 69.2 kJ mol^{-1} and 1.88 × 10^{10} days^{-1} for trans-isocohumulone to 74.4 kJ mol^{-1} and 1.3642 × 10^{11} days^{-1} for trans-isoadhumulone. The higher value of E_a demonstrated greater temperature sensitivity of trans-iso-α-acids during accelerated storage. The average half life of trans-iso-α-acids in elaborated pale lager beer was found to decrease from 471 days to 12 days when temperature increased from 4 °C to 40 °C. Using the activation energy of trans-α-acid degradation and the temperature profile of the accelerated aging, a mathematical model was employed to predict the loss of iso-α-acids, when the initial concentration of iso-α-acids in the product is known. The results obtained in the investigation can be of great importance to the industry in predicting the alteration of beer bitterness during warm periods and in tropical countries where summer temperature can reach 40 °C.

1. Introduction

Every brewer aims at a pleasant and consistent beer flavour by selection of high-quality raw materials and application of a controlled production process. Hop-derived beer bitterness is considered as a primary flavour attribute of beer and therefore accurate determination of beer bitterness is of great importance for each brewer. However, many beer constituents can contribute to some extent to beer bitterness, such as catechins and anthocyanogens (Zhao et al., 2010) or hop-derived isoxanthohumol (Fritsch et al., 2005).

It is generally recognised that the main bittering principles of beer are the hop-derived iso-α-acids (Jaskula et al., 2010). The iso-α-acids are important for beer foam stability and cling (Hughes, 2000; Kunimune and Shellhammer, 2008) and, in addition, they also act as an effective beer preservative due to pronounced antibacterial properties (Benitez et al., 1997; Sakamoto and Konings, 2003; Suzuki et al., 2006; Vaughan et al., 2005; Blanco et al., 2006; Blanco et al., 2007). However, it seems that the relative sensitivity of hop-sensitive and hop-resistant bacteria to trans-isohumulone is maintained at different pH values (Blanco et al., 2007).

Flavour instability during storage remains one of the most important quality problems of beer (Vanderhaegen et al., 2006, 2007; Schutte et al., 2008). Flavour instability is relevant to both ales and lagers, but pale lager beers seem to be especially sensitive to flavour deterioration (De Cooman et al., 2000; Clark et al., 2011). Hundreds of constituents form the complex beer matrix and, inevitably, chemical reactions lead to changes both in the composition of beer, and in features related to taste and flavour (Kanauchi et al., 2011). Thus, beer quality is constantly altered during storage. It seems impossible to exert rigid control over this phenomenon, since not all factors that affect flavour changes can be excluded. The concentration of oxygen or reactive oxygen species can be limited by applying good brewing practices and light absorption can be prevented to a great extent by using appropriate packaging. Nevertheless, thermal energy inherently provokes reactivity, which is determined by the temperature to which beer is exposed. Furthermore, oxidation reactions may occur if compounds with suitable redox potentials are present (Huvaere et al., 2003). The degradation of bitter substances during storage is represented by the evolution of trans- and cis-α-acid concentrations (Intelmann and Hofman, 2010). Levels of the trans- form of iso-α-acids in beer decrease with beer storage time, while those of the cis-form remain unchanged (Kappler et al., 2010). Araki et al., 2002 found that the trans-/cis-ratio, based on peak areas, was similar for fresh beers regardless of the beer specification, but it decreased in aged beer,

* Corresponding author. Fax: +34 79108302.
E-mail address: cblanco@iaf.uva.es (C.A. Blanco).

0260-8774/$ - see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.jfoodeng.2012.11.019

to extents differing between beers (Araki et al., 2002). Generally, the trans-isomers are less bitter than the cis-counterparts (Hughes, 2000; Hughes et al., 1997). Trans-isomers are also reported to be more prone to oxidation than their cis-counterparts and thus less stable (De Cooman et al., 2000; Jaskula et al., 2009).

Usual pH values of bottom fermentation beers at the end of fermentation are between 4.2 and 4.4, rarely 4.0 or less. The importance of the control of finished beer pH is well accepted since the influence of pH on beer flavour, and physical and microbiological stabilities is clearly recognized. The pH of beer has a very marked influence on the development of lactic organisms; low pH inhibits their growth. On the other hand, colloidal haze is accelerated by low pH. Taylor (1990) showed that pH control during brewing has a relative significance by stimulating yeast growth and wort buffering capacity on beer pH, and the consequent influence on beer flavour, potential haze stability, and head formation ability (Kaneda et al., 1997).

Food spoilage is due to a set of chemical, physical and microbiological processes that affect a number of characteristics of the food. Shelf life assessment can be done by studying the evolution of some selected parameters over a period of time (Singh, 1994) and so the status of food is determined by the damage it has suffered. The knowledge of the rules that determine these changes is a necessary tool to develop the model to be used in shelf life experiments.

The use of a chemical kinetic approach to define models of changes in food quality was suggested by Kwolek and Bookwalter (1971) and Ferrer (1986). These models are very important to understand the extent of a specific chemical reaction and the rate at which the changes occur, and also to be able to optimize food processing or storage conditions. In addition, the knowledge and control of kinetic parameters can greatly improve thermal processing conditions in terms of maximizing the rate of generation of desired flavour compounds or suppressing the rate of formation of off-flavour or undesired products (Soares et al., 2004).

On the other hand, the Arrhenius equation expresses the influence of temperature on the reaction rate in studies of the life of foods. Through this equation and with the kinetic expressions of the different orders of reaction, one can construct a mathematical kinetic model describing the deterioration of food during storage, taking into account the influence of temperature on different degradation processes (Saguy and Karel, 1980). The development of these models allows us to obtain activation energies of concrete processes of deterioration from experimental values of indicator parameters of these processes. These data allow estimation of the lifetimes at different storage temperatures (Lai and Heldman, 1982).

To gather more information concerning the relationship between the quantities of iso-α-acids, storage temperature, and the shelf-life period, a kinetic study could be performed. The most commonly used simplified kinetic models, reported in the literature to describe the kinetics of compound formation through pure iso-α-acids degradation, are first-order ones (Malowicki and Shellhammer, 2005). Data on the kinetics of iso-α-acids in beer degradation during storage, and particularly at high temperature are almost non-existent.

The aim of this study was to study degradation kinetics in elaborated pale lager beer as a result of changes in iso-α-acids. Trans-iso-α-acids, which are more unstable than their cis counterparts (De Cooman et al., 2000), were quantitatively monitored by tracing alterations in profiles of the iso-α-acids as a function of aging temperature with High Peformance Liquid Chromatography (HPLC). To promote trans-iso-α-acids degradation, elaborated pale lager beer samples were submitted to forced aging experiments, in which temperature was the only technological parameter to be changed. The kinetic parameters of the trans-iso-α-acids, E_a and A were calculated. The results would be used to predict the iso-α-acids degradation in beers during storage.

2. Materials and methods

2.1. Material

The malted barley (Beka, Nevada, Scarlett and Prestige) used was kindly donated by Intermalta, S.A, (Pamplona, Spain) and malted barley Cargill was donated by Cargill España, S.A. Malt division (Madrid, Spain). The pelleted hop (Nugget) used was kindly donated by S.A. Española de Fomento del Lúpulo (León, Spain). Bottom fermenting brewer's yeast *Saccharomyces cerevisiae* Saflager S-23 was provided by DCL Yeast LTD, England.

2.2. Pale lager beer production in the pilot brewery

Five brews were made with five different barley malts (Cargill, Beka, Nevada, Prestige and Scarlett), mineral water, hop pellets and yeast.

The malt was milled in Perten Laboratory Mill 3303 (Perten Instruments AB, Huddinge, Sweden) to break apart the grain kernels, increase their surface area, and separate the smaller pieces from the husks. The resulting grist was mixed with heated water in a process known as "mashing". During this process, natural enzymes in the malt break much of the starch down into sugars, which play a vital part in the fermentation process. Mashing took one and half hours, and during this time various temperature rests (waiting periods) activate different enzymes depending on the type of malt used, its modification level, and the objectives of the brewmaster. The activity of these enzymes transforms the grain starches into dextrines and then into fermentable sugars such as maltose.

Initially, the grist was mixed with 2 l of preheated mineral water at 37 ± 2 °C with stirring (123 rpm) for 20 min in a 5-l capacity steel recipient. A mash rest at ca. 40 °C activates beta-glucanase, which breaks down gummy beta-glucans in the mash, making the sugars flow out more freely later on in the process. The temperature was increased to 47 °C in 10 min and held at 47 ± 2 °C for 20 min. A mash rest from 47 °C to 55 °C activates various proteinases, which break down proteins that might otherwise cause the beer to be hazy. Next, the temperature was raised to 65 ± 2 °C in 10 min and maintained during 20 min. A mash rest temperature of 65–71 is used to convert the starches in the malt into sugar, which is then usable by the yeast later in the industrial brewing process. Finally the mash temperature was raised to 78 ± 2 °C for a 10 min period at a rate of 1 °C per min (known as a mashout) to deactivate enzymes.

Mashing was followed by wort separation and sparging until the desired wort amount was achieved. Wort boiling at 100 °C required 60 min. Bittering and aroma hops were added 10 min after the beginning and also at the end of wort boil.

Wort was clarified and cooled to pitching temperature with a refrigerated immersion cooling coil (JP Selecta, Model 398, Barcelona, Spain). Pitching temperature was 28 °C for the bottom fermenting yeast.

Fermentation was performed in a 3-l bioreactor system at 10 °C for 10 days. After beers reached the final attenuation degree, temperature was gradually reduced to 4 °C, the conditioning temperature. Conditioning lasted for three weeks in the bioreactor. The pale lager beers produced were Beka (B), Cargill (C), Nevada (N), Prestige (P) and Scarlett (S).

2.3. Reagents and chemicals

International Calibration Standard (ICS) for HPLC analysis of iso-α-acids (IAA) were purchased from Labor Veritas (Zürich,