Effect of Electron Beam Radiation on Main Aroma Components of Chinese Baijiu

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***Abstract*—Aging process plays an important role in high quality liquor production. The liquor natural aging process usually takes a very long time, which causes serious financial burden for wineries. Therefore, much efforts have been paid to develop new technologies for shortening aging time. In this work, the effect of electron beam radiation on main aroma components of Baijiu is investigated in detail. The factors of radiation doses and storage time or/ conditions are taken into consideration. Results show that the main aroma component is hexanoic acid ethyl ester, whose content can increase after radiation without depending on the radiation dose changes. Both the dissolved O_2 of liquor and storage temperature have strong effect on the liquor radiation aging process. The number of the aroma components decreases with increasing of radiation dose, and this phenomenon is more obvious for the group of radiation at N_2 condition. Comparing to the control group, both the ester species and the hexanoic acid ethyl ester content decrease with storage time going, but the specie numbers of alcohol, ketones, alkane and others increase, even back to the initial level of just the end of radiation. Though the results indicate that the aged Baijiu by radiation technique shows a return back tendency in a certain degree after a period of storage time, the Baijiu still is aged with fast and high efficient after radiation. This report can provide some basic data for the application of radiation technique in the liquor aging, and open a new window for liquor aging technique research.**

***Index Terms*—radiation, liquor, aging, aroma component**

I. Introduction

Chinese Baijiu is a traditional distilled liquor and regards as one of the most famous distilled spirits in the world, alongside brandy, gin, rum, vodka and whiskey [1]. Traditional Baijiu productive process contains six major steps: material preparation, daqu making, alcoholics fermentation, distillation, aging and blending [2], [3]. Baijiu is containing abundant volatile components such as organic acids, esters, lactones, phenols, heterocycles, terpenes and aromatic compounds [4]. But, the young liquor generally contains hydrogen sulfides, mercaptans and sulfides derived from sulfur-containing amino acid metabolism, as well as small amounts of acetaldehyde, acrolein, crotonaldehyde, methanol, free ammonia, and other low boiling point substances [5]. The low boiling point aldehydes and sulfides are the origin of “peppery”, “harsh”, “green” and “raw” [6], [7]. Thus, the aging process is needed to improve the liquor quality [8], [9]. In general, the natural aging process takes usually a very long time from six months to a few years, thus it inevitably causes serious financial burden for wineries. Therefore, scientists have put many emphasis on shortening the aging time. For physical methods, Ma *et al.* revealed that the liquor treated by high-gravity had qualities equivalent to the liquors aged naturally for more than two years [6]. Zhu *et al.* found that high pressure treatment could accelerate the natural aging process for Chinese Baijiu [10]. Many other physical methods, such as microwave, ultrasonic, laser, radiation, electric field, were also used to shorten the aging time successfully [3], [11]-[15]. For chemical methods, ozone could accelerate the aging process of distilled spirits [16]. And Ortega *et al.* reported that oxidative aging was an important acceleration in the aging of sherry white wine [17]. For biological methods, Cortes *et al.* found that Saccharomyces cerevisiae race capensis G1 could shorten the aging time [18]. Peinado *et al.* also reported that the traditional biological process by which sherry wines aging time can be accelerated by using submerged Sacch aromyces cerevisiae var. capensis strain cultures previously grown in glycerol [19].

Compared with chemical or biological methods, the physical method has the biggest virtue that maintaining the nutritional content of fermented food to the utmost, which is known as green processing technology [20]. Among many physical methods, laser or irradiation (X-ray, electron beam or gamma irradiation) maturation with

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a fast (<1 min) and high efficient property can't change the temperature of liquor body so as to hold the flavor [13], [21]-[23]. It's reported that the flavor of liquor by laser aging showed a return back tendency after a long time storage [13]. However, there are rare researches about the effect of time on the flavor of liquor aging by irradiation technology. Therefore, the main ester content changes of Baijiu aged through high energy electron beam is investigated in detail here. The radiation doses, radiation environment, storage time and other conditions are taken into consideration. Through the work, it will give a further evaluation on the application potential of radiation technology in liquor aging, and provide some basic data and guidance for brewing industry.

II. Materials and Methods

A. Materials and Characterization

Chinese Baijiu with 52 percentage of alcohol provided by Hubei University of Technology is brewed through Chinese traditional solid-state fermentation technology; ethanol (AR), ethyl caproate (99%) is purchased from Macquaries Co., Ltd; other relative reagents are all analytical grade and used without any treatment. A 10 MeV linear electron accelerator (IS2A) is the radiation source in this work (a dose rate of 1 kGy). The main aroma components of liquor is measured by a gas phase chromatography (Agilent-GC/MS), and liquor sample pretreatment as follows:

Taking 4mL liquor in a 20mL beaker, then 6mL distilled water and 1.0g NaCl are mixed in the beaker. The extraction fiber head (after activating at 270℃ for 30min) is inserted the mixed solution. After balance for 5min at 45℃ in the water bath, the extraction head is pushed, and then kept the headspace extraction about 40min at 45℃. Finally, the extraction fiber head is inserted into the injection port and desorption about 3min.

GC/MS measure conditions: Injection port temperature 250℃, interface temperature 250℃, pressure 7.6522 psi; total flow: 4mL/min, column flow:1 mL/min; the initial column temperature is 50℃ with keeping time 2min, then heat to 250℃ with a speed of 10℃/min, and keep 7 min at 250℃.

B. Experimental Method

1) Effect of radiation doses on the Baijiu aging

The Baijiu is packaged about 30mL with PE bags (10×15cm) under air and nitrogen environment before being irradiated. The packaged Baijiu (3 samples of one dose) are exposed to radiation doses of 1, 3, 6kGy, respectively. Next, the volatile matter species and contents are measured through a gas phase chromatography.

2) Effect of storage time on the Baijiu aging

Based on the above results, one dose (3kGy) is selected and used to the packaged Baijiu, then the Baijiu aroma components are characterized at 10 days (0.3 month), 1 month and 5 months after storage under room temperature and low temperature (4℃), respectively. Then, the storage time and condition effecting on the Baijiu aging is investigated. According to the previous experiment, the alcohol and hexanoic acid ethyl ester are exposed to high energy electron beam, then the mechanism is preliminarily studied firstly through a contrastive analysis of species changes of each group substances.

3) Sensory evaluation

The sensory evaluation of Baijiu is a qualitative and quantitative evaluation method based on the sensory descriptive analysis technique (Chinese standard, GB/T12313). The color, fragrance, taste and character of Baijiu is scored by using liquor flavor wheel and digital scale (Chinese standard, GB/T33405 2016). Among them, color refers to the clarity of the liquor appearance; fragrance refers to the liquor's aromas, including grain, fragrance, bad and aged aromas; taste is sourness, sweetness, fullness, harmony, purity and durability; character refers to typicality of liquor style.

C. Statistical Analysis

Data are reported as mean values +s.e.m of multiple determinations. Statistical significance in the difference is evaluated by analysis of variance (ANOVA) or Kruskal-Wails-test method after One-sample Kplmogorov-Smirnov Npar-test and Homogeneity of Variances test and all statistical calculations are carried out by *SPSS* software.

III. Results and Discussion

As we know, the special flavor of liquor mainly depends on the kinds and contents of the volatile matter [13]. Here, we measure the volatile matter kinds and contents of Chinese Baijiu before and after radiation in detail. From the results, it can be seen that the species of liquor are over 100, and the main aroma component is hexanoic acid ethyl ester with a content over 55% (Fig. 1 and Fig. 2). Therefore, we research the content change of hexanoic acid ethyl ester as the representative of effecting of radiation doses on the liquor. Compared to the control group, the hexanoic acid ethyl ester content increases from 55.08% to about 63.59% significantly after radiation in air condition without depending radiation dose. Similarly, for radiation under the N_2 condition, the hexanoic acid ethyl ester content of liquor reaches about 70%, and also does not depend on the radiation dose (Fig. 1). In addition, the radiation effect on the single alcohol or/ hexanoic acid ethyl ester is almost negligible within radiation dose range in this work, their purity is still over 98.51% and 99.75% after radiation, respectively. Thus, it concludes that electron beam radiation can improve the content of hexanoic acid ethyl ester in liquor without depending on radiation dose.

However, there is a significant change in the number of main species before and after radiation. For radiation under the air condition (Fig. 2a), compared with control group, the species of alkane and others for radiation groups show an obvious decrease except of ester, acids and alcohols, but kinds of ketones increase. For radiation under the N_2 condition (Fig. 2b), compared with control group, the numbers of ester, alcohols, ketones and alkane and others for radiation groups decrease, especially the number of ester species and alkane and others have a great decrease. Therefore, it's inferred that the main aroma components of liquor become purer for radiation at N_2 condition than that for radiation in air condition. The hexanoic acid ethyl ester content for radiation at N_2 condition increases more than that for radiation at air condition, but the number of alkane and others for radiation at N_2 condition decreases much more than that for radiation at air condition. It can be attributed to the effect of dissolved O_2 in the liquor on the radiation decomposition products. When high energy electron beam is exposed to liquor, the water will be degraded and produced many free radicals as followings: H_2O*, e-aq, •H and •OH [24]. In addition, the redox capacity of e is stronger than that of H atom. The dissolved O_2 of liquor in air condition is more than that in N_2 condition. When the dissolved O_2 reacts with e from electron beam, the e content of the liquor will decrease, and thereby reduces the radiation effect. Therefore, there is a greater increasing content of hexanoic acid ethyl ester and decreasing of the number of main aroma component for radiation at N_2 condition than that for radiation liquor in air condition. Consequently, compared with the control group, the flavor of Baijiu with different radiation conditions is improved more obvious (Table I). Interestingly, the flavors of liquor being irradiated under air-condition are richer and better than that at N_2-condition, which might be attributed to the more of aroma components of liquor irradiated in air-condition than that of liquor irradiated at N_2-condition.

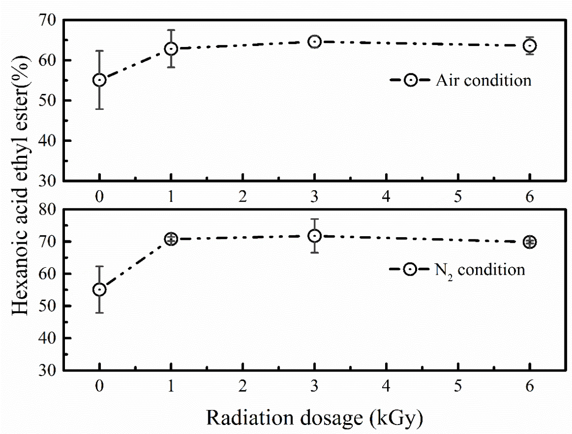

Figure 1. Radiation doses effect on the content of hexanoic acid ethyl ester under different conditions (n=3, all data represent means +s.e.m).

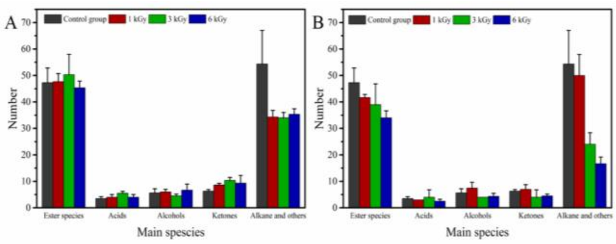

Figure 2. The aroma component changes of liquor by different radiation doses (A for air condition, B for N_2 condition, n=3, all data represent means +s.e.m).

TABLE I. The Sensory Evaluation of Liquor after Radiation at Air or N_2 Conditions by 3 kGy Radiation Dose.

Sample (score)	Color (10)	Fragrance (25)	Taste (50)	Character (15)	Total (100)
Control group	10	18	40	13	81
Air-condition	10	23	46	13	92
N_2-condition	10	23	42	13	89

Fig. 3 shows the content change of hexanoic acid ethyl ester with storage time going under different conditions after radiation. For the liquor irradiated at air condition, comparing to the initial level, the hexanoic acid ethyl ester content gradually decreases with storage time going at both normal and low temperature (Fig. 3). The hexanoic acid ethyl ester content reaches the lowest value at 5 months, but is still higher than that of the control group (Fig. 1). Comparing to group of storage at normal temperature, the content decreasing speed of the hexanoic acid ethyl ester is lower than that at low temperature. For the liquor irradiated at N_2 condition, comparing to the initial level, the hexanoic acid ethyl ester content almost does not change till to 5 months with storage time going at both high and low temperatures. And it also can be seen that the best condition is low temperature storage after radiation by N_2 protection.

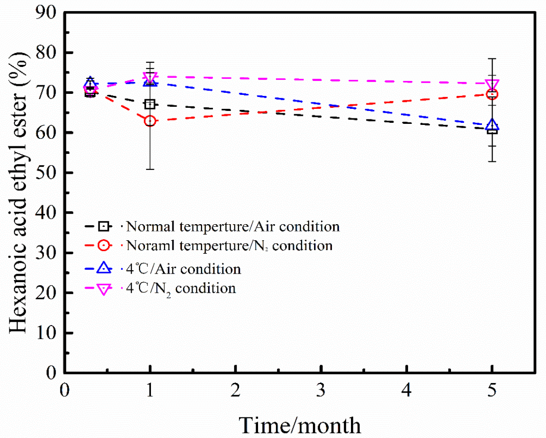

Figure 3. The hexanoic acid ethyl ester content changes with storage time increasing under normal temperature and 4℃ after high energy electron beam radiation (n=3, all data represent means +s.e.m).

The species change of main aroma component with storage time going is also measured, and results are shown in Fig. 4. Comparing to the group of 0.3 month, the species number of main aroma for the group of 1 month decreases obviously. (Fig. 4). Interestingly, with the storage time further increasing to 5 months, the ester species continually decrease for all experimental groups, but the species of alkane and others increase to almost the level of the group of 0.3 month. What's more, the species of alcohols and ketones also show a slight increase in the storage time of 5 months, even return to the initial level (Fig. 1 and Fig. 4). Those results agree with the content change of hexanoic acid ethyl ester (Fig. 3). Therefore, both the increase of main species and the decrease of ester species and content with storage time going show that the special flavor of liquor aging is not stable and a return back tendency after radiation technique, but the content of the hexanoic acid ethyl ester for radiation aging groups can keep a higher level than that of control groups after 5 months storage under all conditions.

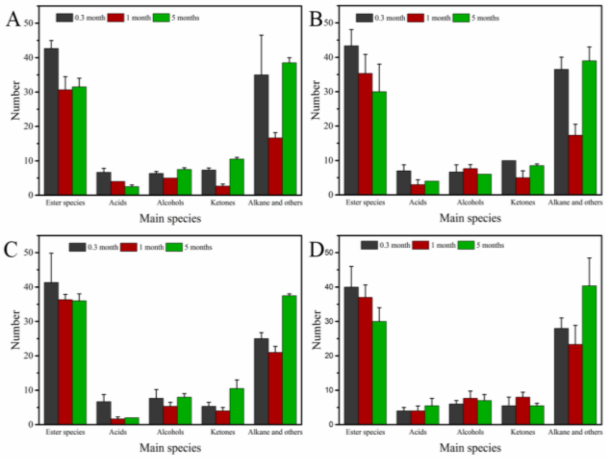

Figure 4. The specie change of main aroma component with storage time going after radiation (A for air condition storage at normal temperature; B for air condition storage at 4°C; C for N_2 condition storage at normal temperature; D for N_2 condition storage at 4°C; n=3, all data represent means+s.e.m).

IV. Conclusion

The main aroma component of Baijiu here is hexanoic acid ethyl ester. The hexanoic acid ethyl ester content of Baijiu aging by radiation technique can increase without depending on the radiation doses, but the number of main aroma components decreases obviously after radiation. Though the flavor of Baijiu aging by radiation technique shows a return back trend in a certain degree with storage time going, the Baijiu is still aged. Therefore, radiation technique can be used to age liquor, but the storage condition and time of the aged liquor need to consider to keep a high quality flavor. It will be much more efficient in liquor aging if radiation technique can combine with other aging techniques and appropriate storage conditions.

Conflict of Interest

The authors declare no conflict of interest.

Author Contributions

Long Zhao and Jun Yang indicate the experiment and revise the manuscript; Wei Qi and Yumeng Huang carry out all experimental work, analyze data and finish the initial manuscript.

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