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Electrochemical esterification in distilled liquor via gold catalysis and its application for enhancing ester aroma of low-alcohol liquor

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ABSTRACT

The development of low-alcohol liquor (Baijiu) can represent a tool to solve the problems of excessive alcohol intake. However, low-alcohol liquor has an insufficient ester aroma and a bland taste due to the alcohol dilution process. This study proposes an electrochemical catalysis technology to catalyze the esterification reaction between the acid and alcohol in liquor, thereby enhancing the ester aroma of low-alcohol liquor. In the electrochemical conversion process, the gold electrode with a certain potential promotes the formation of carbocation intermediate from corresponding carboxylic acid, thereby improving the esterification reaction efficiency. The key finding is that the total ester content of liquor treated using this technology is increased by more than 20%, and a strong ester aroma is attained. This study clarifies the electrocatalytic mechanism of the esterification reaction in liquor, and provides a new idea for making low-alcohol liquor become more attractive for aroma and taste aspects trying to obtain an alternative product contributing to the public health.

1. Introduction

Excessive alcohol intake has a close relationship with many diseases and is a major risk factor for the global disease burden (Rehm et al., 2017). In many European countries, particularly Eastern European countries, the per capita alcohol consumption has significantly reduced, mainly due to the implementation of alcohol control policies and the development of low-alcohol liquor (Rumgay et al., 2021). Low alcohol beverages are growing at a rapid rate due to major awareness about serious long-term effects of drinking (Liguori et al., 2018; Mellor et al., 2020). However, in Asian countries, such as China, alcohol consumption is still growing (Im et al., 2019). In particular, the consumption of high-alcohol liquor (Baijiu) has accelerated the increase in alcohol consumption in China (Huang et al., 2021). Baijiu, a typical Chinese distilled liquor, fermented with sorghum alone or a mixture of corn, rice, wheat, peas, millet, and sorghum (Liu and Sun, 2018). It is a transparent alcoholic beverage with a high ethanol content, usually ranging from 45% to 65% in volume. In addition to implementing alcohol control policies, the development of low-alcohol liquor can represent a tool for solving the problems of excessive alcohol intake. However, low-alcohol liquor has an insufficient ester aroma and a bland taste, thus its market attractiveness is insufficient (Yang et al., 2021). Low-alcohol liquor usually uses high-alcohol liquor as the raw material, and the alcohol content is controlled below 40% through mixing the liquor and water (Liu and Sun, 2018). While the production process dilutes the alcohol, it also dilutes the ester content and reduces the ester aroma of the liquor. Therefore, establishing a method for enhancing the ester aroma is beneficial for developing low-alcohol liquor and reducing the amount of alcohol consumption (Cerrillo et al., 2019; Hong et al., 2020).

The typical strategy for enhancing the ester aroma of low-alcohol liquor mainly includes mixing and blending different base liquors and adding foreign substances (Z. Wang, Xu, Cai, Yue, Yuan and Gao, 2020). The source of liquor blends is usually the base liquor. Relying only on the mixing and blending of different base liquors cannot solve the universal problem of reduced ester aroma of low-alcohol liquor (Liu and Sun, 2018). In addition, the national standard "Glossary of Baijiu Industry," which released in 2021 in China, states that no food additives should be used in liquor, and flavored liquor (flavored Baijiu) is excluded from the classification of Baijiu (Xu et al., 2022). Hence, lack of technology to enhance the ester aroma restricts the development of the low-alcohol liquor industry, which has a major demand in China's food industry.

The Chinese national standard "Strong-flavor Baijiu" (GB/T 10781.1-2006) (Zhou et al., 2021) stipulates that the total ester (calculated in terms of ethyl acetate) for low-alcohol liquor should be no

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less than 1.5 g L^{-1}. Enhancing the ester aroma of low-alcohol liquor means increasing the content of some esters (such as ethyl caproate and ethyl acetate). Under the premise of not adding edible alcohol and non-self-fermented colors, aromas, and taste substances (as stipulated in the national standard for liquor), the speed of spontaneous esterification in liquor is extremely slow (Shi et al., 2017). Therefore, catalysis of liquor esterification is an effective strategy to increase its ester content (Ramos et al., 2021). Moreover, the catalysis process of the esterification between alcohol and acid generally requires additional catalysts, such as a strong acid (sulfuric acid) or strong base (sodium hydroxide) (Borges and Díaz, 2012; Tao et al., 2011), which is obviously unsuitable for liquor production.

In view of the above-mentioned difficulties, this study proposes an electrochemical catalysis technology to catalyze the esterification reaction between the acid and alcohol in liquor, thereby enhancing the ester aroma of low-alcohol liquor. Studies have proven the application feasibility of electrochemical catalysis technology in the food field (Manikandan et al., 2018; Wang et al., 2014). In this study, an inert metal electrode (e.g., gold electrode) and an inert platinum electrode are used as the working and counter electrode, respectively. The electrodes only serve as catalysts to transfer electrons and do not dissolve into the liquor. Thus, this technology meets the premise of not adding foreign substances to the liquor and solves the above-mentioned difficulties of traditional strategies. It is confirmed that the electrochemical catalytic esterification technology using a gold electrode with a certain applied voltage to promote the formation of carbocation intermediates remarkably improves the efficiency of the esterification between acids and alcohols. The total ester content of liquor treated using this technology is increased by more than 20% compared to untreated liquor, and a strong ester aroma is attained. This study clarifies the electrocatalytic mechanism of the esterification in liquor, and provides a new idea for enhancing the ester aroma of low-alcohol liquor trying to obtain an alternative product contributing to the public health.

2. Materials and methods

2.1. Materials

Baijiu samples were collected from the Baijiu manufacturer (Xiangjiao Group Ltd., Shaoyang, China), were directly collected from the pottery jars with home-made extractors. Mention of the brand name does not imply research contact with the manufacturer, nor for advertising purposes. The alcohol content of raw Baijiu sample was higher than 63%, thus the low-alcohol Baijiu was obtained through mixing the raw Baijiu sample and a certain amount of ultra-pure water (with a resistivity of 18.2 MΩ·cm^{-1}), according to the dilution technology that commonly used in Baijiu industry (Liu and Sun, 2018). The model liquor contains 40% ethanol (in volume ratio) and 4% desired acids (in volume ratio). The reference standards (24 compounds in total) for gas chromatography were purchased from Merck (Darmstadt, Germany). HPLC-grade solvents were purchased from Aladdin (Shanghai, China) and used without further purification.

2.2. Electrochemistry

A typical three-electrode electrochemical configuration was used in this work, performed with the electrochemical workstation (product number CHI660E, CH Instruments, Inc., Shanghai, China). A polycrystalline gold electrode (CHI101) with a radius of 1.0 mm was employed as the working electrode, a platinum wire (CHI115) as the counter electrode, and an Ag/AgCl electrode with a saturated KCl solution (CHI111) as the reference electrode. Before the electrochemical measurement, the gold electrode was polished with 1 μm, 0.5 μm, and 0.03 μm alumina slurry to obtain a smooth surface and washed with sulfuric acid, ethanol, and water respectively. To avoid oxidation caused by oxygen, the oxygen dissolved in the electrolyte was removed from the sample by passing of nitrogen gas not less than 15 min before the recording of the chronoamperometry curve. Chronoamperometry with applied potential (0.20 V, 0.35 V, 0.50 V, 0.65 V, and 0.80 V) was used for the electrochemical treatment. The chronoamperometry curves were shown in Fig.S1 in support Information.

2.3. Gas chromatography (Arbitrating method)

According to the arbitrating method stipulated in Chinese national standard (GB/T 10345-2007), gas chromatography with authentic internal standards was selected for the constituent analysis of Baijiu. Gas chromatography was performed using the Agilent 7890B gas chromatography (Agilent Technologies Co. Ltd.). The qualitative identification was performed by comparing retention times between authentic standards and targeted compounds, and quantitative analysis was performed using internal standards, 2-ethylbutyric acid and n-pentyl acetate (chemically similar to the analytes of interest). 0.1 mL internal standard was mixed in 4.9 mL Baijiu sample. An Agilent CP-Wax 57 CB capillary column (0.25 mm × 50 m × 0.2 μm) was used for gas chromatography separation, with a flow rate of 1.0 mL min^{-1}. Gas chromatography parameters were well-optimized. The initial oven temperature was maintained at 40 °C and held for 5 min, 50 °C held for 6.5 min, 90 °C held for 5 min, 130 °C held for 2 min, 190 °C held for 1.4 min, finally 195 °C held for 20 min. The analytical precision of gas chromatography was determined in triplicate for both intraday and interday, shown in Tab. S1 in supporting information. As seen, the relative standard deviation (RSD) values for quantification of those compounds in this study are at a comparatively low level (<3.1%).

2.4. Sensory evaluation

Sensory evaluation of Baijiu samples were evaluated by trained sensory tasters according to Chinese national standard (GB/T 33404-2016). Tasters were extensively trained in descriptive sensory analysis. A total of 12 experienced tasters (6 males and 6 females) aged from 20 to 45 years participated in evaluation team and voted on appearance, aroma, taste, style, and comprehensive scores of electrochemically treated samples and untreated samples. In each test session, the samples were randomly presented to the tasters. The sensory experiments were repeated three times to ensure the accuracy of the sensory evaluation results. The sensor array of the electronic tongue is composed of a multiple working electrode (six inert electrodes: platinum, gold, tungsten, titanium, nickel, and silver electrode), an Ag/AgCl electrode reference electrode, and a platinum counter electrode for standard three electrode systems.

2.5. Other methods

Total dissolved solids (TDS) of treated Baijiu was measured in triplicate by a Xiaomi TDS meter (Xiaomi Technology Co., Ltd, Beijing, China), and pH value of treated Baijiu was measured in triplicate by an acidity meter (PHSJ-3F, INESA Scientific Instrument Co., Ltd). The contents of total acid and total ester were measured according to Chinese national standard (GB/T 10345-2007). Optimized conformations of carbocation intermediates were obtained using the molecular mechanics MM2 force field by Chem3D ultra 16.0 software (shown in Fig. S2 in supporting information). Charge distributions in carbocation intermediate and transition state were calculated using Extended Huckel Charge in the Chem3D ultra 16.0 software.

2.6. Statistical analysis and data treatment

The reported data is the mean value of triplicate measurements ($n = 3$, error bars indicate standard deviations). The asterisk indicates the P value (*$P < 0.05$ and **$P < 0.01$, compared with the control), and is estimated by one simple *t*-test. Statistical analysis was performed with the software Origin 2020 (OriginLab Co., Northampton, USA).

3. Results and discussion

3.1. Influence of electrochemical treatment on composition variation and liquor aroma

In our previous study, the impact of electrochemistry on the overall properties of liquor was confirmed (Xiong et al., 2020; Zheng et al., 2021). Therefore, we further examined the influence of the electrochemical treatment on the interconversion relationship between those components and the overall aroma of liquor. In the electrochemical process, pure liquor (without addition of any ionic electrolyte) was used as the electrolyte, and the ionisable organic acids in liquor ensured the smooth current loop during electrolysis. Quantification of the main aroma compounds in untreated and electrochemically treated Baijiu are shown in Tab. 1. As shown in Fig. 1a, changes in the contents of the main compound in the electrochemically treated Baijiu (with the treated potential of 0.20 V, 0.35 V, 0.50 V, 0.65 V, and 0.80 V respectively) can be divided into two groups based on the cluster analysis of the heat map, which visually reflects the content changes of these quantified compounds. The quantified compounds in the two clusters showed similar trends to those of n-pentanoic acid and n-amyl alcohol (cluster 1, with a fluctuant trend), ethyl acetate (cluster 2, with an increasing trend), respectively. As shown in Fig. 1b and c, after treatment, the content of the main alcohols and acids in the liquor did not show statistically significant change, whereas there was a significant change in the ester content (Fig. 1d). For example, the contents of sec-butyl alcohol and n-pentanoic acid show a fluctuant trend, changed no more than 5%, while the contents of ethyl acetate (with the odor threshold of 32600 $\mu g \cdot L^{-1}$) (Liu and Sun, 2018) and ethyl hexanoate (with the odor threshold of 55 $\mu g \cdot L^{-1}$) (Liu and Sun, 2018) show an increasing trend, increased by 34.3%, and 13.7% respectively. Esterification is a dehydration reaction, forming esters from alcohols and acids, oxidation is relevant here because the alcohols can be oxidized to form acids. Even the oxygen dissolved in the electrolyte was removed from the sample by passing of nitrogen gas. Oxidation may be electrochemically enhanced because peroxide species can be formed from the water and the alcohols can be directly oxidized. Therefore, the precursor acid content of the ester components with increased content was no more than 5% before and after the electrochemical catalysis process, which may be contributed to the oxidation of alcohols. The significant change in the ester content caused by electrochemical treatment confirmed the influence of electrochemistry on liquor components. Considering the important correlation of non-volatile substances (especially the organometallic compounds) to Baijiu aroma, electronic tongue was used to distinguish patterns for the aroma compounds in Baijiu. The impact of electrochemistry on the overall aroma of liquor was investigated by the electronic tongue and the principal component analysis (PCA) of the electronic tongue data is shown in Fig. 1e. As seen, PCA data points in the two group are distributed separately, and have demonstrated a significant difference between the liquor before and after the electrochemical treatment. Further, the experienced tasters in the sensory evaluation team conducted a blind evaluation of the liquor before and after the treatment (shown in the insert in Fig. 1e) and the following conclusions were derived: Firstly, Baijiu is soft and harmonious before the treatment and has an outstanding taste and strong ester aroma after the treatment; Secondly, the strong ester aroma taste of liquor after treatment can be attributed to the increase in ester content of the liquor, particularly attributed to the increase in ethyl hexanoate, which has a low odor threshold of 55 $\mu g \cdot L^{-1}$ (Liu and Sun, 2018). The detailed radar graph of appearance, aroma, taste, style, and comprehensive scores, which described the influence of electrochemical treatment on the sensory profile of Baijiu, is shown in Fig. 2. The main difference between electrochemically treated Baijiu and untreated Baijiu is reflected in aroma. The aroma of Baijiu gradually strengthened with the applied potential increasing. Sensory evaluation is consistent with the gas chromatography results. It should be noted that Baijiu is rich in many flavor components, including alcohols, acids, and esters, which can be mutually converted (Liu and Sun, 2018). The chemical reaction mechanism of the electrochemical treatment of liquor is still unclear based only on the change in the contents of the abovementioned substances. The interconversion relationship between those components requires further elucidation.

Table 1
Quantification of the main flavor compounds in untreated and treated Baijiu (0.20 V, 0.35 V, 0.50 V, 0.65 V, and 0.80 V; 20 min) using the arbitrating method stipulated in Chinese national standard (GB/T 10345-2007).

No	CAS	Name	Retention time/min	Untreated sample mg/100 mL	Treated sample (mg/100 mL)				
					0.20V	0.35 V	0.50 V	0.65 V	0.80 V
1	75-07-0	Acetaldehyde	5.60	51.87	54.32	52.32	60.32	65.56	65.46
2	141-78-6	Ethyl acetate	7.75	64.04	68.32	70.54	84.23	84.89	86.18
3	105-57-7	Acetal	7.90	13.61	17.69	13.32	18.32	17.65	18.21
4	67-56-1	Methanol	8.34	7.85	6.62	7.18	6.88	6.43	6.9
5	105-54-4	Ethyl butyrate	12.18	13.08	14.28	13.92	16.84	16.62	16.02
6	78-92-2	2-Butanol	12.32	3.40	3.82	3.98	3.87	3.23	3.53
7	71-23-8	Propyl alcohol	12.83	15.48	15.88	15.2	15.38	15.67	15.96
8	78-83-1	Isobutyl alcohol	15.26	8.87	8.29	8.61	8.82	9.2	9.21
9	539-82-2	Ethyl valerate	16.28	4.84	5.1	4.88	5.28	5.26	5.62
10	6032-29-7	2-Pentanol	16.72	0.82	0.83	0.82	0.84	0.82	0.84
11	71-36-3	1-Butanol	17.93	11.54	11.6	11.28	11.23	11.8	11.81
12	123-51-3	3-Methyl-1-butanol	20.76	4.42	4.37	4.91	4.32	4.2	4.49
13	123-66-0	Ethyl hexanoate	21.32	116.83	120.39	126.71	126.83	130.21	132.01
14	71-41-0	n-amyl alcohol	22.79	1.15	1.12	1.09	1.1	1.1	1.09
15	97-64-3	Ethyl lactate	27.37	97.05	97.19	97.29	98.36	98.18	98.71
16	111-27-3	Hexyl alcohol	28.12	4.75	4.82	4.76	4.82	4.8	4.81
17	64-19-7	Acetic acid	32.48	58.58	58.68	59.37	60.38	60.34	60.64
18	79-09-4	Propanoic acid	35.35	4.06	4.28	4.36	4.49	4.42	4.45
19	79-31-2	Isobutyric acid	36.12	0.80	0.76	0.8	0.75	0.76	0.75
20	107-92-6	Butyric acid	37.71	9.63	9.37	9.58	9.28	9.23	9.2
21	503-74-2	Isovaleric acid	38.81	0.75	0.74	0.76	0.74	0.76	0.75
22	109-52-4	Pentanoic acid	40.53	2.65	2.65	2.67	2.65	2.66	2.67
23	142-62-1	Hexanoic acid	42.76	54.83	54.9	54.86	54.92	54.9	54.99
24	111-14-8	Heptanoic acid	45.30	1.03	0.82	0.95	0.76	0.8	0.64

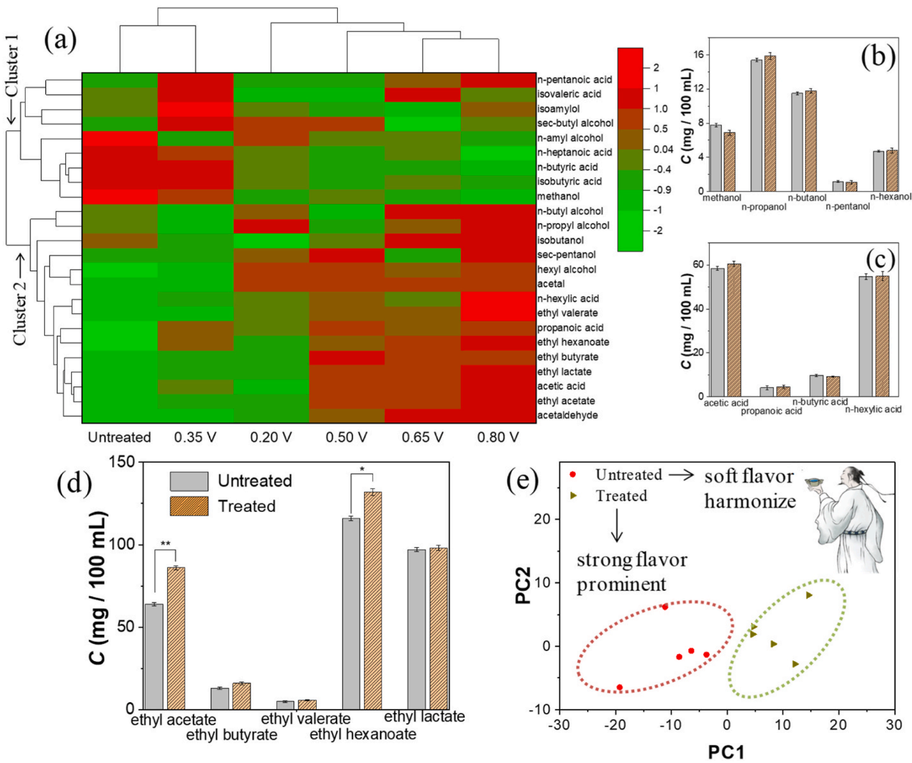

Fig. 1. (a) Heat map of main compound contents in electrochemically treated and untreated Baijiu (treated potential, 0.20 V, 0.35 V, 0.50 V, 0.65 V, and 0.80 V, for 20 min). The content of the main alcohols (b), acids (c), and esters (d) before and after the electrochemical treatment (0.8 V, 20 min). (e) Principal component analysis of the treated and untreated Baijiu, the insert shows the taster comments. Ethanol concentration in the Baijiu: 40% in volume ratio.

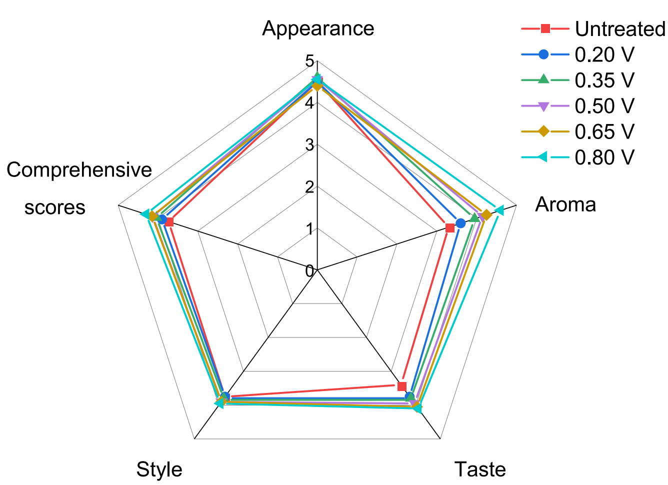

Fig. 2. Radar graph of appearance, aroma, taste, style, and comprehensive scores. Description of the influence of electrochemical treatment on the sensory profile of Baijiu, with treated potential of 0.20 V, 0.35 V, 0.50 V, 0.65 V, and 0.80 V respectively.

3.2. *Investigation of the composition variation in the electrochemical process with model liquor*

The model liquor with clear ingredients (ethanol, water, and a mixture of specific ingredients) was used as the research object to explore the interconversion relationship between Baijiu components in the electrochemical process. Firstly, the model liquor containing ethanol, water, and lactic acid was prepared, and its pH was tested in real-time to monitor the progress of the esterification reaction. As the esterification reaction progresses, the acid (e.g., lactic acid) is consumed and the pH value increases. As shown in Fig. 3a, the increase in pH value became more evident with prolonged duration of electrochemical treatment; a higher electrochemical treatment potential resulted in a larger increase in the pH value. The higher potential group (0.65 V and 0.80 V) produced a significant difference from the control group after electrochemical treatment of 5 min, and the lower potential group (0.20 V, 0.35 V, and 0.50 V) presented a significant difference from the control group after 10 min of treatment. Similarly, the total dissolved solids (TDS) in the model liquor were monitored in real-time to assess the progress of the esterification reaction. As the esterification reaction progresses, lactic acid is consumed to produce ethyl lactate, resulting in an increase in the TDS value (the solubility of ethyl lactate in ethanol/water mixture is lower than that of lactic acid). As shown in Fig. 3b, the TDS value increased along with an increase in the electrochemical treatment duration; a higher electrochemical treatment potential resulted in a more noticeable increase in the TDS value. In addition, the change of TDS value follows a similar trend with the change of pH value. The above results confirmed the promotional effect of electrochemical treatment technique on the esterification reaction based on the real-time changes in the pH and TDS values. Further, the concentrations of lactic acid and ethyl lactate in the model liquor were measured and shown in Fig. 3c. As seen, the content of lactic acid decreased steadily along with the increase of processing time of electrochemical treatment, while the content of ethyl lactate increased steadily along with the increase of processing time, which confirmed the transformation from lactic acid to ethyl lactate by the esterification process. In the earlier publication it was found that the spontaneous oxidation in the Baijiu aging process contributed to the increase of ester content (Deng et al., 2020). The reaction rate of spontaneous oxidation, caused by the dissolved oxygen, is extremely slow, and a long period of time (at least three years) is required for the Baijiu aging process. However, in the case of electrochemical treatment, the promotion of ester content can be finished within 25 min, which reflects the feasibility of the proposed method.

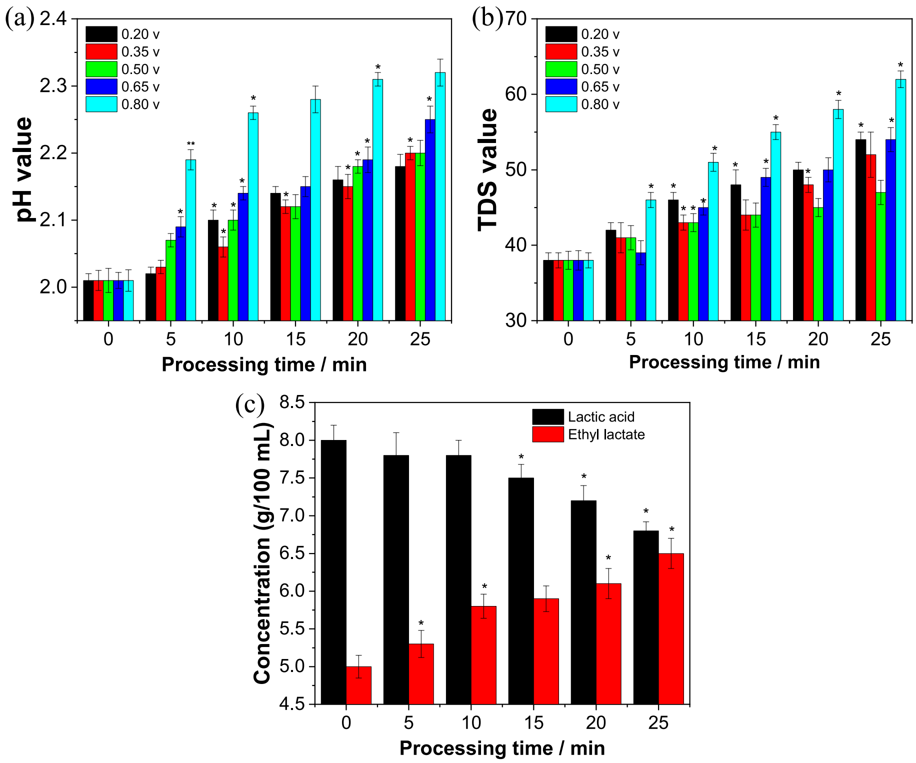

Fig. 3. (a) The correlation between pH value and electrochemical treatment potential (0.20 V, 0.35 V, 0.50 V, 0.65 V, and 0.80 V), with incremental processing time (0 min, 5 min, 10 min, 15 min, 20 min, and 25 min). (b) The correlation between TDS value and electrochemical treatment potential (0.20 V, 0.35 V, 0.50 V, 0.65 V, and 0.80 V), with incremental processing time (0 min, 5 min, 10 min, 15 min, 20 min, and 25 min). Liquor ingredients: 40% ethanol in volume ratio, 4% lactic acid in volume ratio. (c) The correlation between the concentration (lactic acid, ethyl lactate) and the processing time of electrochemical treatment with a potential of 0.80 V.

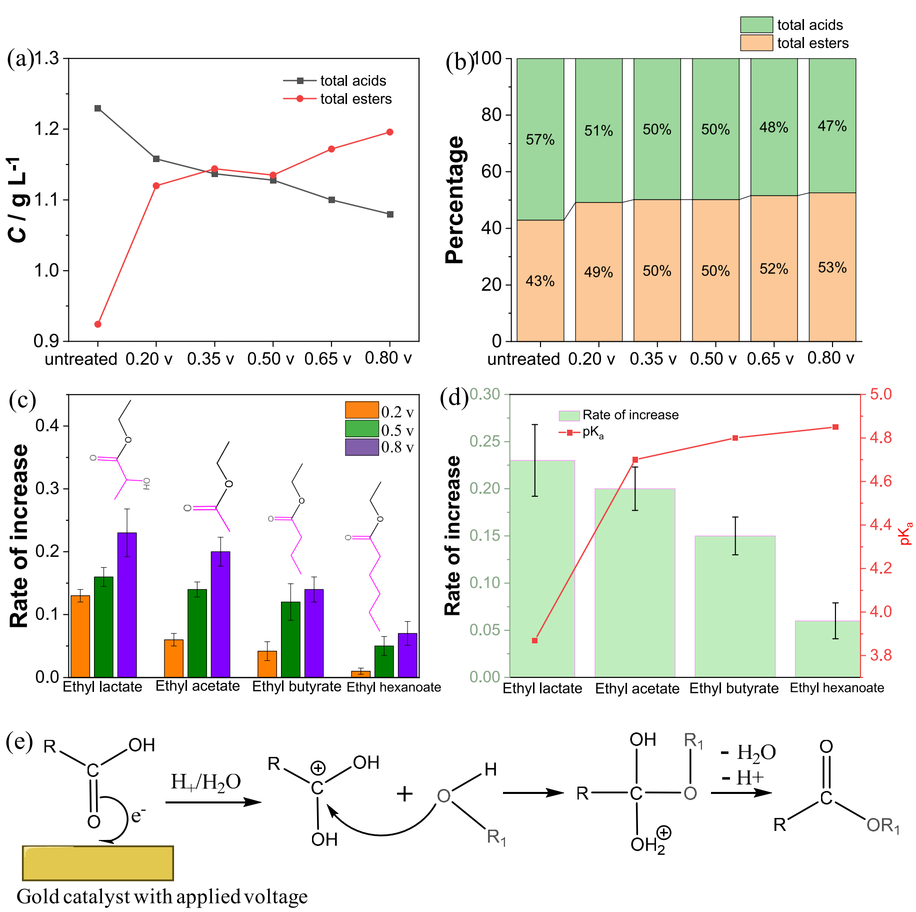

Fig. 4. (a) The content of total acid and total ester in the model liquor applied with increasing potentials. The lines (in red or black) are provided to guide the eyes. (b) The calculated proportions of acids and esters in the model liquor applied with increasing potentials. (c) The increase in the ratios of the characteristic esters in Baijiu, ethyl lactate, ethyl acetate, ethyl butyrate, and ethyl hexanoate. (d) The correlation between the increase in the ratio of the ester and the acidity (described as pK_a) of the corresponding acid. (e) Schematic representation of the reaction mechanism of the electrochemically catalyzed esterification. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

3.3. Elucidating the reaction mechanism of the electrochemically catalyzed esterification

The national standard method was used to test the content of total acid and total ester in the model liquor with clear ingredients. Compared to the control group (untreated group), each group with an applied potential exhibited a decrease in the total acid content; a higher processing voltage resulted in a more prominent decrease in the total acid content (black dots in Fig. 4a). On the contrary, compared to the control group (untreated group), each group with an applied potential exhibited an increase in the total ester content; a higher processing voltage resulted in a more noticeable increase in the total ester content (red dots in Fig. 4a). The above results highlight the conversion from acid to ester. The proportions of acids and esters in the model liquor were calculated, shown in Fig. 4b. As seen, the control group (untreated group) contained 57% acid and 43% ester. This indicates that the esterification reaction between acid and alcohol in the model liquor reached equilibrium and the extent of spontaneous esterification is relatively low. Namely, the ester content is relatively low, and 57% of the acid is not converted to the corresponding ester. And the reaction rate of further esterification is extremely slow under natural conditions. After the electrochemical treatment, the acid content significantly reduced, whereas the ester content significantly increased, showing a trend of acid to ester conversion (shown in Fig. 4b). At the same time, the conversion trend increased with an increase in the processing voltage. After 0.8 V treatment for 20 min, the acid content decreased from 57% to 47%, and the ester content increased from 43% to 53%. The ester content is increased by 23.2%. In the typical process of Baijiu production, longstanding aging is used to improve the ester content, and the increased ester content is less than 20% after five years of aging (Zheng et al., 2021). As can be seen, the improvement of ester content caused by electrochemical treatment is of great significance to enhance Baijiu quality. Similarly, we tested the increase in the ratios of the other three esters, ethyl acetate, ethyl butyrate, and ethyl hexanoate. The model liquors containing ethanol, water, and desired organic acids (acetic acid, butyric acid, or hexanoic acid) were prepared. These organic acids were selected for the reasons: compounds that contributed to the main aroma of Baijiu, and compounds that related to the quality indicators according to national standards of Baijiu. As shown in Fig. 4c, after 0.8 V treatment for 20 min, the results showed a remarkable conversion from organic acids to the corresponding esters by esterification. The ratios of ethyl acetate, ethyl butyrate, and ethyl hexanoate increased by 20.0%, 14.2%, and 7.5%, respectively. Generally, the efficiency of an active site of the catalyst can be expressed as the turnover frequency (TOF), which quantifies how many catalytic cycles proceed per unit of time and per site (Watzele et al., 2021). Thus, the TOF value of surface gold atom with applied voltage was calculated according to eq (1).

$$\mathrm{TOF} = \frac{\text{generated ester (mol)}}{\text{surface Au atom (mol)} * \text{Time (h)}} \tag{1}$$

TOF values for ethyl lactate, ethyl acetate, ethyl butyrate, and ethyl hexanoate were $4.6 \times 10^5\ h^{-1}$, $3.5 \times 10^5\ h^{-1}$, $2.4 \times 10^5\ h^{-1}$, and $1.4 \times 10^5\ h^{-1}$ respectively. The TOF values in the electrochemical conversion were higher than that in the typical inorganic catalysis of gold ($5.0 \times 10^4\ h^{-1}$ referenced to the exposed gold) (Comotti et al., 2004; Ye et al., 2019), suggesting that the catalytic efficiency of voltage-pulsed gold was higher than that of typical inorganic gold. In the case of ceria-supported gold, the TOF value of esterification was enhanced upon incorporation of water in the feed stream (Mullen et al., 2017). In the case of K_2CO_3-supported gold, the TOF value of esterification was enhanced upon the formation of gold nanoparticle (Lianyue Wang, Li, Dai, Lv, Zhang, & Gao, 2014). The influence of environmental factor is clearly evident on the TOF value of gold. It can be suggested that the applied potential enhanced the TOF value of gold in the case of electrochemical esterification in liquor.

Under weak acid conditions, the speed control step of the esterification reaction between the acid and alcohol is the formation step of carbocations (Kazansky, 1999). The acidity of the acid is correlated with the ease of carbocation formation (Williams and Lawton, 2010). Therefore, the correlation between the increase in the ratio of the ester and the acidity of the corresponding acid is shown in Fig. 4d. It can be seen that the smaller pK_a value resulted in a larger increase in the ratio of the ester. The catalytic activity for ester formation follows the expected order (ethyl lactate > ethyl acetate > ethyl butyrate > ethyl hexanoate) according to the relative value of pK_a. This result suggests that the electrochemically catalyzed esterification reaction has undergone the step of carbocation formation.

In order to further clarify the role of the gold electrode with the applied voltage in catalyzing the esterification reaction, computational method was used to optimize the configuration of the carbocation intermediates corresponding to the above four acids and analyzed the charge distribution of the carbocation intermediates (Fig. S2). Carbocation intermediates are stabilized by the inductive effect of groups bonded to the molecular center, thus reducing the charge of reactive intermediates (Ouellette and Rawn, 2018). The calculated charge distribution using extended Huckel method (Tromer and Freire, 2013) was shown in Tab. S2. As seen, among the four carbocations, the charge of the carbon atoms in the carbocation is as follows: lactic acid (0.687 eV), acetic acid (0.710 eV), butyric acid (0.723 eV), and hexanoic acid (0.703 eV). The charge of carbocations is significantly reduced after being adsorbed on the gold electrode surface: lactic acid (0.082 eV), acetic acid (0.108 eV), butyric acid (0.098 eV), and hexanoic acid (0.099 eV). This suggests that the gold electrode applied with a voltage can not only transfer electrons but also stabilize the carbocations, thereby reducing the energy barrier and accelerating the progress of the esterification reaction.

Therefore, the reaction mechanism of the electrochemically catalyzed esterification can be summarized as follows, as shown in Fig. 4e: The electrochemically catalyzed esterification reaction is a nucleophilic substitution reaction, where the hydrogen ion and carboxyl group in the carboxylic acid form a carbocation intermediate. On the gold electrode surface, the energy barrier of the chemical reaction formed by the carbocations is relatively low, which promotes the formation of carbocations. The nucleophile (alkoxy group) attacks the carbocation on the gold electrode surface, loses a water molecule and a hydrogen ion to form an ester.

In summary, model liquor with a clear composition was used to verify the catalytic mechanism of the electrochemical technology. From a technical point of view, this study establishes a method to increase the content of esters in low-alcohol liquor. This technology was also applied to high-alcohol liquor (53% ethanol concentration, in volume ratio). After high-alcohol liquor is processed, its ester content is significantly increased. The electrochemical esterification technology proposed herein targets the reaction of alcohol and acid and is effective for both the low-alcohol and high-alcohol liquors. Most of the important esters in the liquor are converted from ethanol and corresponding acids, and ethanol has a much greater concentration (usually >35% in volume ratio) than other acids. Therefore, the degree of increase in ester content is related to the initial concentration of acidic substances, which has almost no correlation with ethanol. This issue needs to be considered when the technology is applied to liquor production as the initial concentration of acidic substances is related to the final ester content. Moreover, the liquor quality is not only related to the ester content but also related to the content of other types of aromatic substances (e.g., acids, alcohols, and aldehydes). Therefore, from an application point of view, the electrochemical esterification technology needs to be used in conjunction with the blending technique to obtain the high-quality and low-alcohol Baijiu.

4. Conclusions

This study proposes an electrochemical catalysis technology to catalyze the esterification reaction between the acid and alcohol in liquor, the total ester content of liquor treated using this technology is increased by more than 20%, and a strong ester aroma is attained. The influence of electrochemical catalysis on the composition variation was investigated with model liquor, which confirmed the transformation from acids to esters. It is found that the gold electrode with a certain potential promotes the formation of carbocation intermediate from corresponding carboxylic acid, thereby improving the esterification reaction efficiency. In short, this study provides a new method for developing low-alcohol liquor and propose a new idea for solving the problem of excessive alcohol intake owing to Baijiu.

Data availability

The data that support the findings are available from corresponding author upon reasonable request.

CRediT authorship contribution statement

Zihao Wang: Investigation, Validation. **Ayuan Xiong:** Investigation, Validation. **Yougui Yu:** Writing – review & editing, Supervision. **Qing Zheng:** Conceptualization, Writing – review & editing, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.crfs.2022.10.003.

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