Journal of Leather Science and Engineering

RESEARCH

Open Access

Evaluation and improvement of the oxidative stability of leather fatliquors

Yue Yu[1], Min Huang[1], Jiaqi Lv[1], Yunhang Zeng[1*], Qingyong Sun[2] and Bi Shi[1,3]

Abstract

Fatliquor oxidation may give leather unpleasant odor, and excessive amounts of Cr(VI) and volatile organic compounds. The accurate evaluation and improvement of the oxidative stability of fatliquors are of great significance to high-quality leather manufacturing. We proposed a set of practical methods for evaluating the oxidative stability of fatliquors on the basis of oxidation induction time, change in iodine value (Δ IV), and change in acid value (Δ AV) under accelerated oxidation conditions (at 100 °C with 10 L/h of air). Oxidation induction time is a highly sensitive marker for quantifying the oxidative stability of fatliquors, and Δ IV and Δ AV that are low cost and easy to operate are useful in evaluating the oxidative stability of fatliquors when the oxidation induction time is less than 22 h. The number of double bonds in fatliquors is an important factor affecting oxidative stability. The sulfation modification of fatliquors that greatly reduces double bonds and the addition of antioxidants, especially butylated hydroxyanisole and butylated hydroxytoluene, markedly improve oxidative stability of fatliquors.

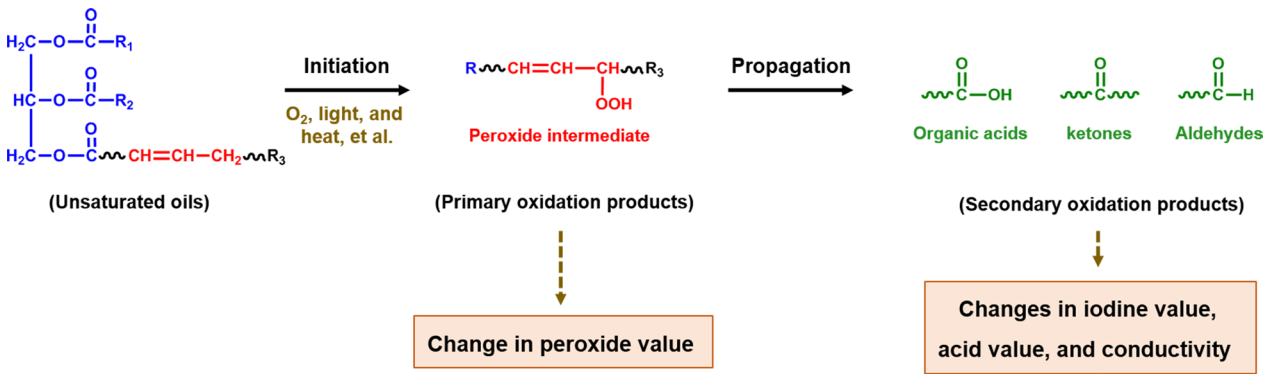
Keywords: Leather fatliquor, Oxidative stability, Natural oil, Modification, Antioxidant

1 Introduction

Fatliquors are one type of the most used leather chemicals and act as lubricants to increase the dispersity and movability of collagen fibers in leather, playing an important role in improving the physical properties, such as softness, fullness, strength, and extensibility, of resultant leathers [1–3]. Fatliquors are generally divided into three types by structure and source: (1) natural vegetable oils and animal fats; (2) chemically modified products of vegetable oils and animal fats; and (3) synthetic oils/fatliquors [4, 5]. Natural vegetable oils and animal fats and their modified products account for 50%–80% of the total amount of fatliquors because they can endow leather with excellent softness and grease touch [6]. However, fatliquors derived from natural vegetable oils and animal fats may give leather unpleasant odor, and excessive amounts of Cr(VI) and volatile organic compounds (VOCs) [7, 8]. The main reason is that natural vegetable oils and animal fats containing double bonds are easily oxidized into unstable hydroperoxides and thereby promote the conversion of Cr(III) to Cr(VI) [9] and generate small molecular VOCs after decomposition [10]. Therefore, the oxidative stability of fatliquors must be improved for manufacturing high-quality leathers. Currently, the oxidative stability of fatliquors is assessed by sensory evaluation of the color and odor changes in fatliquors that are stored for a long period. As a result, an objective evaluation methodology for evaluating the oxidative stability of fatliquors is lacking, and thus a systematic understanding of factors affecting the oxidative stability of fatliquors and rational design of oxidation-resistant fatliquors is limited.

Oil oxidation has received considerable attention in the food industry because it adversely affects the flavor and color of food and reduces shelf life [11, 12]. The oxidative stability of oils is usually evaluated by detecting the primary and secondary oxidation products of oils [13]. As shown in Scheme 1, the active methylene group next to the double bonds of oils is prone to oxidation under oxygen, light, heat, and other external conditions and

*Correspondence: zengyunhang@scu.edu.cn
[1] National Engineering Laboratory for Clean Technology of Leather Manufacture, Sichuan University, Chengdu 610065, China
Full list of author information is available at the end of the article



Scheme 1 Possible oxidation pathway of unsaturated oils

generates primary oxidation products, such as hydroperoxide intermediates [14]. Unstable hydroperoxides are then further decomposed into secondary oxidation products that are small molecular VOCs, such as organic acids, ketones, and aldehydes [15]. Hydroperoxides, organic acids, and the disappearance of double bonds in oils lead to the changes in peroxide, acid, and iodine value of oils, respectively. Thus, these parameters are conventional indicators for predicting the oxidative stability of oils used in food [16–18]. Moreover, an ISO 6886 standard for evaluating the oxidative stability of food oils has been established [19], in which conductivity caused by the secondary oxidation products of oils is monitored during an accelerated oxidation process for the determination of an oxidation induction time.

Inspired by the above evaluation methods, we investigated whether oxidation induction time and iodine, acid, and peroxide values of oils are suitable for evaluating the oxidative stability of leather fatliquors. Typical fatliquors were first treated in an accelerated oxidation system, and then oxidation induction time and changes in iodine value (Δ IV), acid value (Δ AV), and peroxide value (Δ PV) during oxidation were determined and compared for the selection of suitable indicators that can be used in evaluating oxidative stability. The preferred indicators were subsequently used in investigating the effects of modification methods and antioxidants on the oxidative stability of fatliquors, formulating effective strategies for improving the oxidative stability of fatliquors (Additional file 1: Fig. S1), and providing theoretical guidance for the development of high-quality and oxidation-resistant fatliquors.

2 Materials and methods

2.1 Materials

Fatliquors, namely, synthetic oil (the scientific name is phosphate ester, synthesized by the reaction of long-chain fatty alcohol and P_2O_5), castor oil, freshwater fish oil, rape oil, deep sea fish oil, sulfated rape oil, sulfonated rape oil, oxidized–sulfited rape oil, and phosphated rape oil, were of industrial grade and provided by Decision Chemical Co., Ltd (Sichuan, China). Butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT), tannic acid (TA), and vitamin C (VC) were of analytical grade and purchased from Aladdin Biochemical Technology Co., Ltd (Shanghai, China). All the other reagents were of analytical grade and purchased from Chengdu Kelong Chemical Co., Ltd (Chengdu, China).

2.2 Accelerated oxidation tests for fatliquors

2.2.1 Apparatus

A simple experimental apparatus for analyzing the oxidative stability of fatliquors was designed and built according to ISO 6886 [19] with some modifications to reduce the cost of apparatus. As shown in Fig. 1, air pump, gas flow meter, silica gel drying tube, sample bottle, and absorption bottle were connected in sequence with a latex tube. A certain amount of fatliquor sample was placed in a sample bottle, which was incubated in an oil bath at 100 °C. A stream of purified air was pumped into the sample at a flow rate of 10 L/h to accelerate the oxidation of fatliquor. During oxidation, the sample was taken out of the sample bottle for testing, and the gases released from the fatliquor, together with air, were imported into the absorption bottle containing 50 mL of deionized water. The conductivity of the absorption solution was monitored in real time with a conductivity tester (S230 SevenCompact™, Mettler Toledo, Switzerland) for the analysis of oxidation induction time.

2.2.2 Determination of oxidation induction time

Synthetic oil, castor oil, freshwater fish oil, rape oil, and deep-sea fish oil (20.0 g each) were separately oxidized at 100 °C with 10 L/h of air with an apparatus, as shown

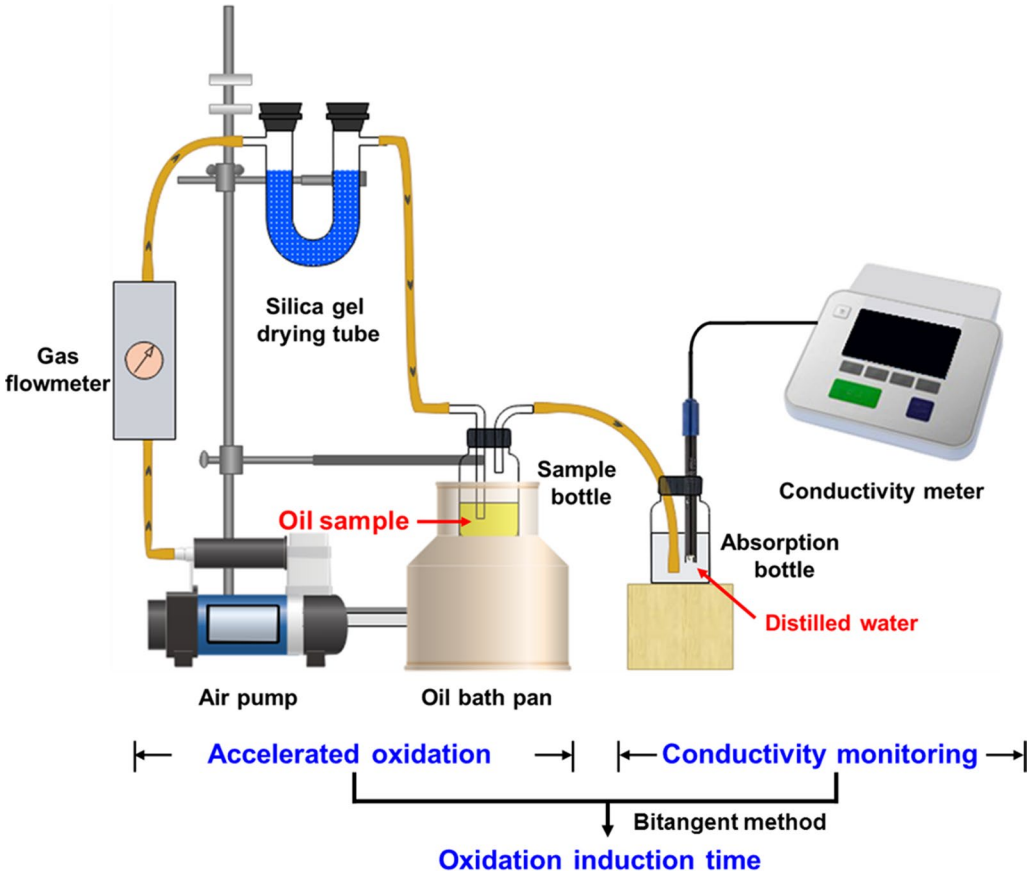


Fig. 1 Experimental apparatus for the acceleration of fatliquor oxidation

in Fig. 1. The conductivity of the absorption solution was recorded every 10 min with a conductivity tester. Then, a conductivity curve was plotted over time, and the oxidation induction time (unit: h) of the fatliquor sample was obtained using the bitangent method [19].

2.2.3 Determination of Δ IV, Δ AV, and Δ PV

Synthetic oil, castor oil, freshwater fish oil, rape oil, and deep-sea fish oil (50.0 g each) were separately oxidized at 100 °C with 10 L/h of air for 12 h with the apparatus, as shown in Fig. 1. Then, a certain amount of an oxidized sample was used for determining iodine value according to ISO 3961 [20], acid value according to ISO 660 [21], and peroxide value according to ISO 3960 [22]. The iodine, the acid, and peroxide values of the five fatliquors before accelerated oxidation were measured as initial values. Then, the Δ IV, Δ AV, and Δ PV of the fatliquors were obtained by calculating the differentials of the three indicators before and after oxidation.

2.3 Attenuated total reflection Fourier transform infrared spectrum of modified rape oils

Rape oil, sulfated rape oil, sulfonated rape oil, oxidized–sulfited rape oil, and phosphated rape oil were placed in a freeze dryer (Beta 1–8 LDPlus, Christ, Germany) for moisture removal. Then, each fatliquor sample was dropped into the center of a sample cell of the infrared spectrometer (Nicolet IS10, Thermo Fisher, USA) for the collection of infrared spectra within the range of 400–4000 cm^{-1} at a resolution of 0.5 cm^{-1}. Cumulative scans were performed 32 times [23].

2.4 Accelerated oxidation tests for modified rape oils

Accelerated oxidation tests were separately carried out on sulfated rape oil, sulfonated rape oil, oxidized–sulfited rape oil, and phosphated rape oil, and their oxidation induction time, Δ IV, Δ AV, and Δ PV were determined with the apparatus and methods described in Sect. 2.2.

2.5 Accelerated oxidation tests for sulfated rape oil with antioxidants

Sulfated rape oil was mixed with 1 wt% (based on the weight of sulfated rape oil) BHA, BHT, TA, and VC successively. Accelerated oxidation tests were carried out on the mixture, and oxidation induction time, Δ IV, Δ AV, and Δ PV were determined according to the apparatus and method described in Sect. 2.2.

3 Results and discussions

3.1 Establishment of methods for evaluating the oxidative stability of fatliquors

One purpose of this work was to propose effective methods for evaluating the oxidative stability of fatliquors. The oxidation induction time, Δ IV, Δ AV, and Δ PV of the five typical fatliquors, which have different levels of oxidative stability, were first detected, and the relationship between each indicator and the oxidative stability of fatliquor was analyzed. The suitable indicator for the evaluation of the oxidative stability of the fatliquors was determined.

The unsaturated bonds of fatliquors can react with halogens in an addition reaction and can thus be estimated with iodine value [20]. The initial iodine values of the five fatliquors in Fig. 2 indicated that the natural oils followed the order deep sea fish oil > rape oil > freshwater fish oil > castor oil according to the number of double bonds, and the synthetic oil almost had no double bonds. Given that the oxidation of natural oils mainly occurs in the active methylene groups next to double bonds (Scheme 1) [14], a high number of double bonds usually results in low oxidative stability [24]. The five fatliquors varied in number of double bonds and thus had different levels of oxidative stability.

A long time is needed to oxidize fatliquors under ambient conditions. Thus, the oxidation induction time, Δ IV, Δ AV, and Δ PV of the fatliquors in our study were determined under an accelerated oxidation condition (100 °C and 10 L/h of air). The small molecular organics released from the fatliquors during the accelerated oxidation process were purged into water. The procedure led to an increase in water conductivity (Fig. 1), which was then plotted over time. The oxidation induction time of the fatliquors was obtained using the bitangent method, as shown in Fig. 3. Here, oxidation induction time represented the time when the formation of oxidation products rapidly begins to increase rapidly. As shown in Fig. 3a, there were no sharp rises in the conductivity–time curve of synthetic oil because synthetic oil has no double bonds (Fig. 2; iodine value, 0.8 g/100 g) and is difficult to oxidize into small molecular organics even at a high temperature and in an oxygen-enriched environment. As shown in Fig. 3b–e, the conductivity–time curves of the natural oils contained two periods. The first period (the slow growth of the conductivity–time curve) is known as the induction period, during which the oils slowly absorbed oxygen and peroxides formed. The second period (the rapid growth of the conductivity–time curve) is referred to as the tainted odor and flavor period, in which the oils rapidly absorbed oxygen and peroxides were dissociated into aldehydes, ketones, and low fatty acids [19]. The oxidation induction time of four natural oils (Fig. 3f) obtained from the conductivity–time curves in Fig. 3b–e followed the order castor oil (13.0 h) > freshwater fish oil (10.2 h) > rape oil (9.3 h) > deep sea fish oil (5.3 h). The comparison between Figs. 2 and 3f showed that the oxidation induction times of fatliquors were negatively correlated with their initial iodine values, indicating that fatliquors with more double bonds required shorter times to be oxidized and the fatliquor with a high initial iodine value, that is, a large number of double bonds, had a low oxidative stability, which is consistent with results of oils obtained in previous studies [24]. Thus, the oxidation induction time can be used as a quantitative indicator for evaluating the oxidative stability of fatliquors.

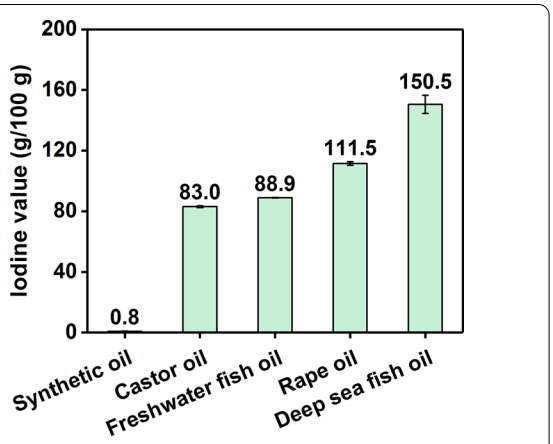


Fig. 2 Initial iodine value of synthetic and natural oils

The oxidation of oils causes changes in their iodine, acid, and peroxide values [14, 15]. After accelerated oxidation for 12 h, the Δ IV, Δ AV, and Δ PV of the five fatliquors were analyzed, and the results are listed in Fig. 4. The Δ IV, Δ AV, and Δ PV of synthetic oil were close to zero because it had no double bonds and was thus difficult to oxidize. The Δ IV of natural oils followed the order deep sea fish oil > rape oil > freshwater fish oil > castor oil (Fig. 4a). The Δ IV of natural oils was positively correlated with their initial iodine values because the oils with more double bonds are easier to be oxidized and caused sharper decreases in the number of double bonds. The Δ IV accurately characterized the decrement of double bonds and was thus suitable for describing the

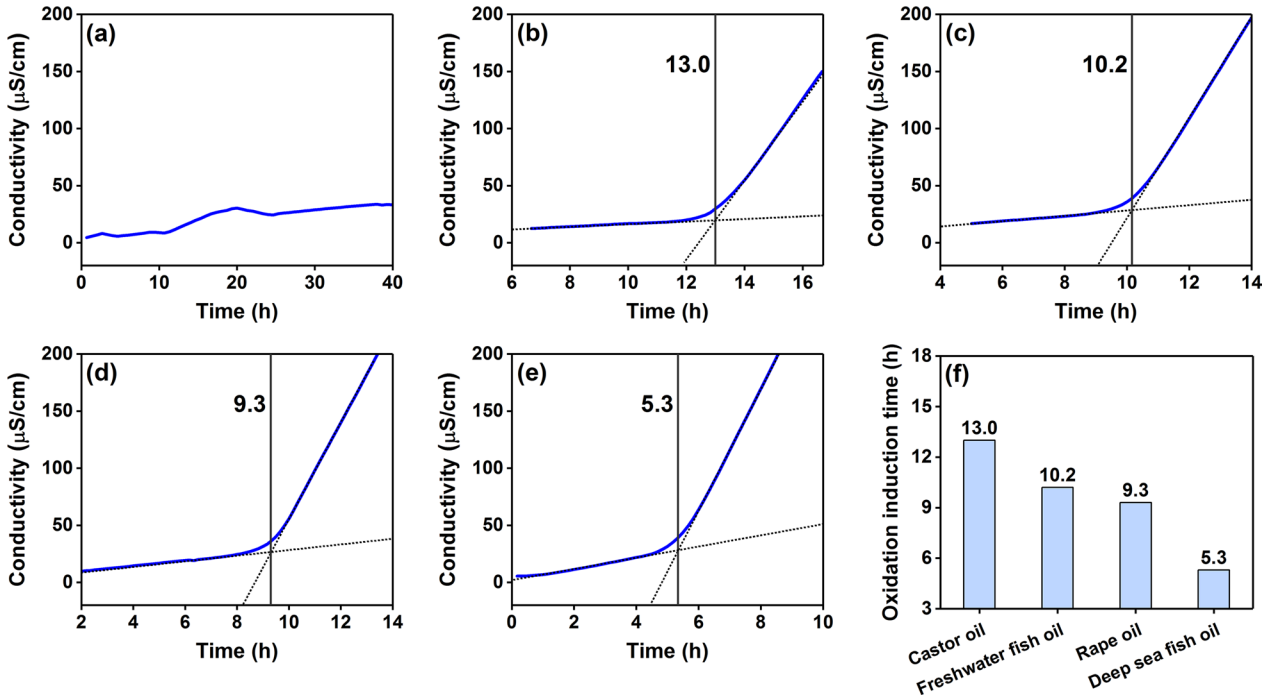


Fig. 3 Conductivity–time curves of synthetic oil (**a**), castor oil (**b**), freshwater fish oil (**c**), rape oil (**d**), deep sea fish oil (**e**), and the oxidation induction time of the natural oils (f), under accelerated oxidation conditions (100 °C, 10 L/h air)

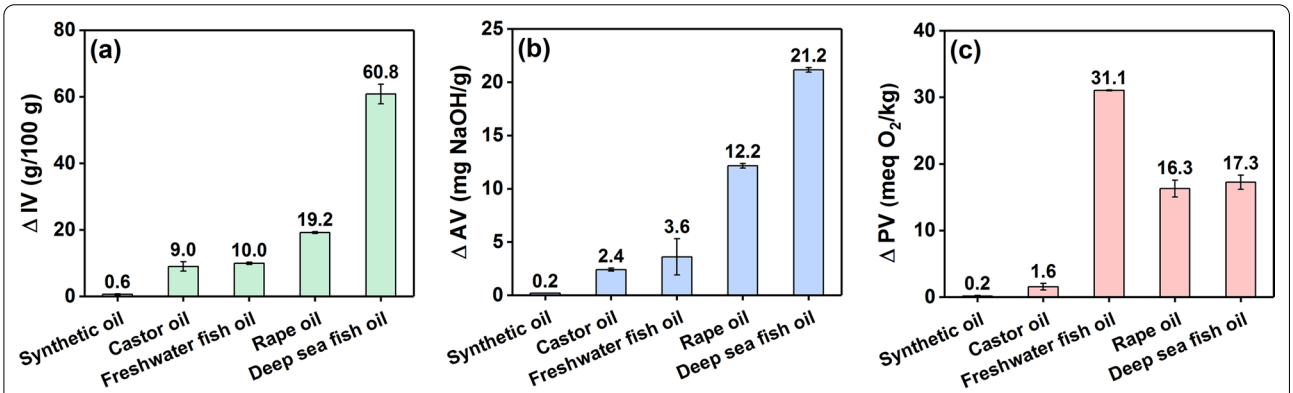


Fig. 4 Changes in iodine value (**a**), acid value (**b**), and peroxide value (**c**) of synthetic and natural oils after accelerated oxidation (100 °C, 10 L/h air, 12 h)

oxidative stability of the fatliquors. The Δ AV of natural oils showed a positive correlation with the initial iodine value of the oil (compare Figs. 2 with 4b) because oxidation of the oils with more double bonds proceeded more smoothly and more small molecular organic acids were generated. Therefore, the Δ AV is also a simple indicator for evaluating the oxidative stability of the fatliquors.

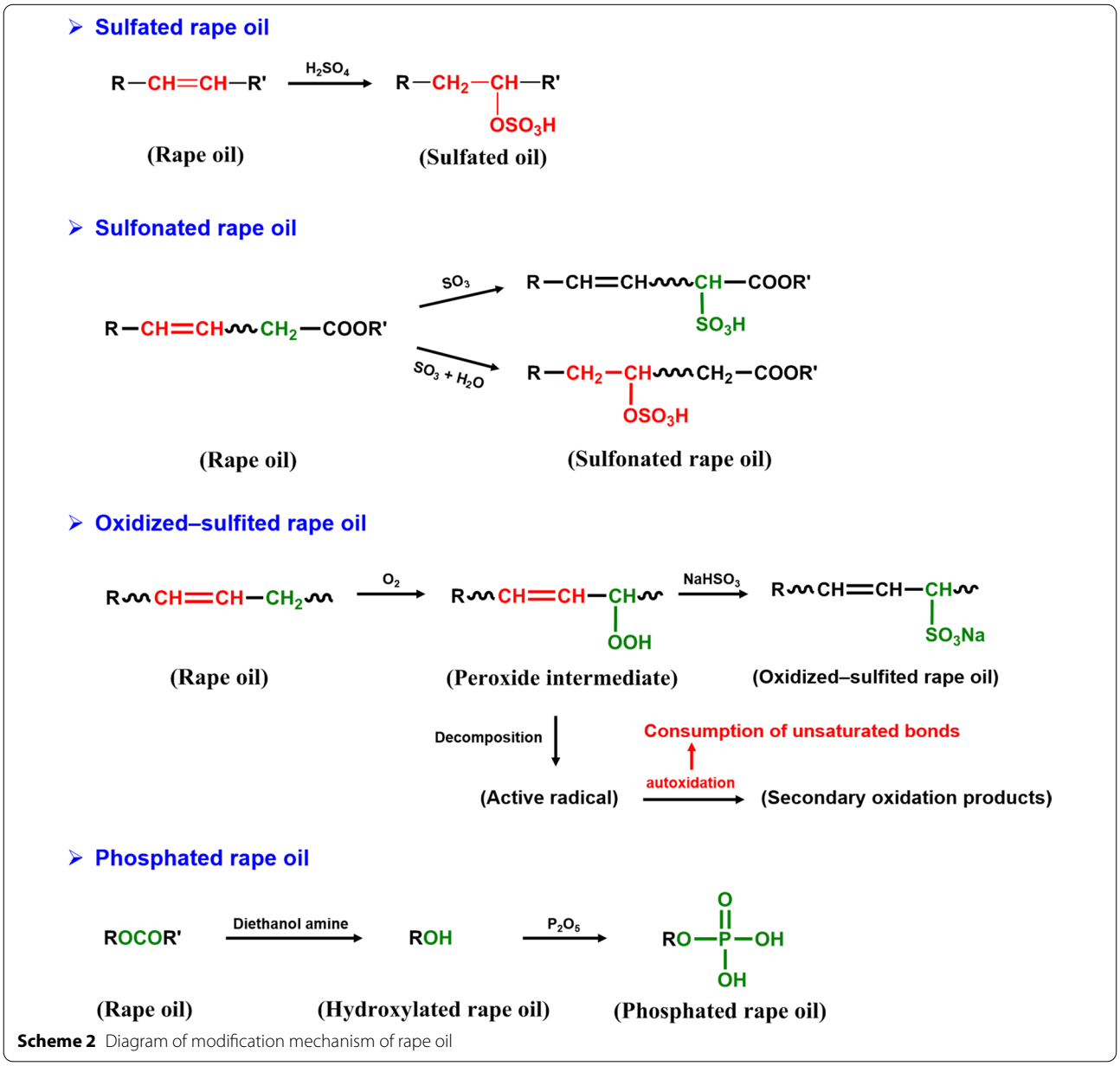
The peroxide values of natural oils increased after accelerated oxidation test (Additional file 1: Fig. S2[c]), but no clear correlation was found between the Δ PV (Fig. 4c) and initial iodine value. The reason was that peroxide is only an intermediate product during oxidation and easily decomposed into secondary compounds [25]. Thus, although the Δ PV can indicate the occurrence of an oxidation reaction and formation of peroxide intermediates, it was unsuitable for evaluating the oxidative stability of fatliquors.

In summary, the number of double bonds of fatliquors that can be characterized using the iodine value is an important factor affecting oxidative stability. The

fatliquors with more double bonds are easier to be oxidized. Oxidation induction time, Δ IV, and Δ AV can be used in quantifying the difficulty level of fatliquor oxidation when the oxidation induction time is less than 13 h.

3.2 Effect of modification method on the oxidative stability of fatliquors

The water solubility of natural oils that mainly exist in the form of triglycerides can be improved, and active groups that can react with collagen fibers [26, 27] can be introduced through modification using sulfation, sulfonation, oxidation–sulfitation, and phosphorylation reactions before the natural oils are used as leather fatliquors. These modification processes consume the double bonds of oils and reduce unsaturation, as shown in Scheme 2, which should be helpful in improving the oxidative stability of fatliquors. In this section, we investigated the effect of modification method on the oxidative stability of fatliquors by comparing the oxidative induction time, Δ IV, and Δ AV of sulfated, sulfonated, oxidized–sulfited, and phosphated rape oils that were all produced by modifying the same rape oil. We hope to provide a guide for improving the design of the



Scheme 2 Diagram of modification mechanism of rape oil

molecular structures of fatliquors and selecting appropriate modified fatliquors that do not cause unpleasant odor and produce Cr(VI) and VOCs.

Figure 5 shows the ATR-FTIR spectra of rape oil and modified rape oils. Compared with rape oil, sulfated rape oil had a new absorption peak at 1198 cm^{-1}, which was attributed to the sulfate ester group [28]. Sulfonated and oxidized-sulfurized rape oils showed a new absorption peak at 1042 cm^{-1}, which was assigned to the sulfonic group [29, 30]. Phosphated rape oil showed a new absorption peak at 1068 cm^{-1}, which was ascribed to the phosphate ester group [31]. The above results indicated that the target active groups were successfully introduced into the rape oil. Moreover, the iodine value of rape oil (111.5 g/100 g, Fig. 2) was reduced to less than 98.0 g/100 g after modification (Additional file 1: Fig. S4[a]), indicating that these modifications did consume the double bonds of the oil.

As shown in Fig. 6a and Additional file 1: Fig. S3, the oxidation induction times of the modified rape oils were longer than that of the rape oil, indicating that the modifications that decreased the double bonds of the rape oil improved the oxidative stability of the fatliquors. The order of oxidation induction time was sulfation > sulfonation > oxidation–sulfitation > phosphorylation, which was consistent with the Δ IV and Δ AV results in Fig. 6b and c. These results showed that the improvement of the oxidative stability of rape oils by modification followed the order: sulfation > sulfonation > oxidation–sulfitation > phosphorylation. Sulfation modification changed most of the double bonds of rape oil to sulfate ester bonds through an addition reaction [28]. Sulfonation and oxidation–sulfitation modifications partially consumed the double bonds of rape oil [29, 30]. Phosphorylation modification basically reserved the double bonds of rape oil because the esterification reaction occurred between P_2O_5 and the hydroxyl group of rape oil [31]. Therefore, the sulfated rape oil had the lowest iodine value and highest oxidative stability among the four modified rape oils, whereas the phosphated rape oil had the highest iodine value and lowest oxidative stability. Notably, the Δ AV of the phosphated rape oil was similar to that of rape oil

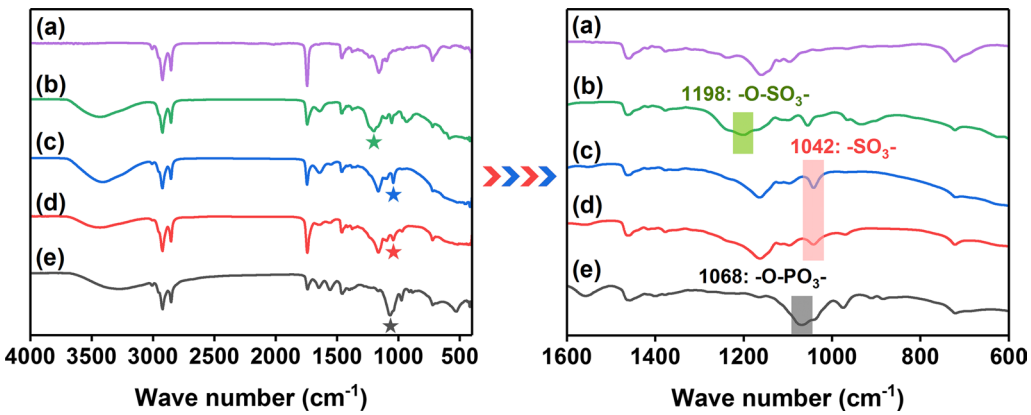


Fig. 5 ATR-FTIR spectra of rape oil (**a**), sulfated rape oil (**b**), sulfonated rape oil (**c**), oxidized–sulfited rape oil (**d**), and phosphated rape oil (**e**)

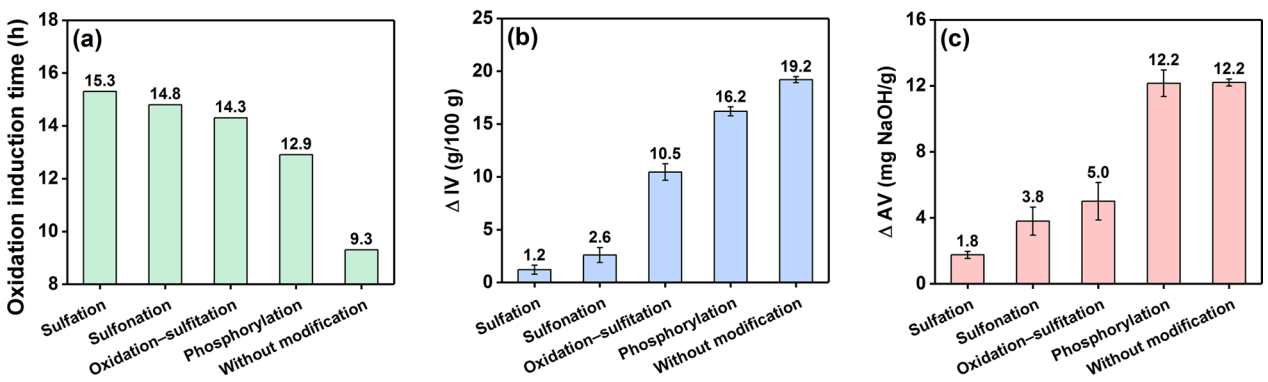


Fig. 6 Effect of modification of rape oil on its oxidation induction time (**a**), Δ IV (**b**), and Δ AV (**c**)

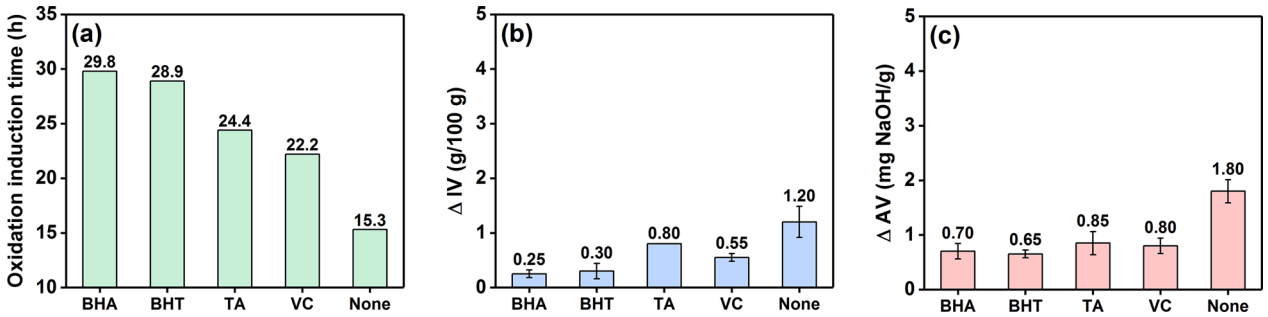


Fig. 7 Effect of antioxidant on oxidation induction time (**a**), Δ IV (**b**), and Δ AV (**c**) of sulfated rape oil

(Fig. 6c). This result was inconsistent with the results of oxidation induction time (Fig. 6a) and Δ IV (Fig. 6b). This phenomenon suggested that the sensitivity of Δ AV in evaluating the oxidative stability of fatliquors was lower than that of oxidation induction time or Δ IV.

3.3 Effect of antioxidant on the oxidative stability of fatliquors

Adding antioxidants is regarded as one of the most effective and convenient methods for improving the oxidative stability of natural oils used in food and pharmaceutical fields [32, 33]. In this section, the effects of typical synthetic antioxidants (BHA and BHT) [34] and natural antioxidants (TA and VC) [35] on the oxidative stability of fatliquors were investigated by analyzing changes in the oxidative induction time, Δ IV, and Δ AV of sulfated rape oil. Figure 7a and Additional file 1: Fig. S5 provide the oxidation induction time of sulfated rape oil after the addition of various antioxidants, which clearly showed that the introduction of antioxidants greatly improved the oxidative stability of the fatliquor, and synthetic antioxidants exhibited better antioxidant effects than natural antioxidants. The reason for this phenomenon should be the fact that the solubility, the thermal stability, and the purity of synthetic antioxidants were higher than those of natural antioxidants [36].

The Δ IV and the Δ AV of sulfated rape oil after the addition of various antioxidants did not show significant differences (Fig. 7b and c, and Additional file 1: Fig. S6) possibly because the antioxidants significantly improved the oxidative stability of sulfated rape oil, making the iodine and acid values of fatliquor nearly unchanged after oxidation. The results also indicated that Δ IV and Δ AV did not accurately reflect difference in the oxidative stability of fatliquors when the oxidation induction time of the fatliquor was more than 22 h. Therefore, the sensitivity of Δ IV or Δ AV for the evaluation of oxidative stability was inferior to that of oxidation induction time.

4 Conclusions

Oxidation induction time, Δ IV, and Δ AV can be used for evaluating the oxidative stability of leather fatliquors. Oxidation induction time has the highest sensitivity and widest scope of application. The evaluation of the oxidative stability of fatliquors with Δ IV and Δ AV has low cost and easy operation, but Δ IV and Δ AV are unsuitable for distinguishing difference of the fatliquors with relatively high oxidative stability. Modification processes that can reduce the double bonds of natural oils, especially sulfation modification, improve the oxidative stability of fatliquors. Moreover, the addition of antioxidants is a convenient method for improving oxidative stability, and synthetic antioxidants BHA and BHT showed excellent effects.

Abbreviations

Δ AV: Change in acid value; BHA: Butylated hydroxyanisole; BHT: Butylated hydroxytoluene; Δ IV: Change in iodine value; Δ PV: Change in peroxide value; TA: Tannic acid; VC: Vitamin C; VOCs: Volatile organic compounds.

Supplementary Information

The online version contains supplementary material available at https://doi.org/10.1186/s42825-021-00070-3.

Additional file 1. Fig. S1. Research process of this study. **Fig. S2**. Iodine value (a), acid value (b), and peroxide value (c) of synthetic and natural oils before and after accelerated oxidation (100 °C, 12 h, 10 L/h air). **Fig. S3**. Conductivity–time curves of sulfated (a), sulfonated (b), oxidized–sulfited (c), and phosphated (d) rape oils under accelerated oxidation conditions (100 °C, 10 L/h air). **Fig. S4**. Iodine value (a) and acid value (b) of modified rape oils before and after accelerated oxidation (100 °C, 12 h, 10 L/h air). **Fig. S5**. Conductivity–time curves of sulfated rape oil with BHA (a), BHT (b), TA (c), and VC (d) under accelerated oxidation conditions (100 °C, 10 L/h air). **Fig. S6**. Iodine value (a) and acid value (b) of sulfated rape oil with antioxidants before and after accelerated oxidation (100 °C, 12 h, 10 L/h air).

Acknowledgements
This work was financially supported by the Fundamental Research Funds for the Central Universities and the College Students Innovation and Entrepreneurship Training Program.

Authors' contributions
YY developed the methodology, performed the experiments, analyzed the data, and wrote the initial draft. MH performed the experiments and analyzed the data. JL performed the experiments. YZ formulated the research goals and aims, supervised the project, and revised the manuscript. QS provided the fatliquor samples and developed the methodology. BS revised the manuscript. The authors read and approved the final manuscript.

Funding
This work was financially supported by the Fundamental Research Funds for the Central Universities (2021SCU12094) and the College Students Innovation and Entrepreneurship Training Program (C2021117946).

Availability of data and materials
All data generated or analyzed during this study are included in this manuscript and the additional file. The authors declare that the data in this article are reliable.

Declarations

Competing interests
The authors declare that they have no competing interests.

Author details
[1]National Engineering Laboratory for Clean Technology of Leather Manufacture, Sichuan University, Chengdu 610065, China. [2]Sichuan Decision Chemical Co., Ltd, Deyang 618000, China. [3]Key Laboratory of Leather Chemistry and Engineering, Ministry of Education, Sichuan University, Chengdu 610065, China.

Received: 30 July 2021 Accepted: 22 September 2021
Published online: 15 November 2021

References

1. Ma JZ, Wang TT, Yu S, Zhang YH, Lyu B. Preparation and application of dialdehyde nanocellulose reinforced jatropha oil based polymer emulsions as leather fatliquors. Cellulose. 2021;28(1):331–46. https://doi.org/10.1007/s10570-020-03494-y.
2. Hao DY, Wang XC, Liu XH, Zhu X, Sun SW, Li J, Yue O. A novel eco-friendly imidazole ionic liquids based amphoteric polymers for high performance fatliquoring in chromium-free tanned leather production. J Hazard Mater. 2020;339: 123048. https://doi.org/10.1016/j.jhazmat.2020.123048.
3. Sahu B, Selvi AT, Aravindhan R. Fungus-resistant fatliquor from blended natural oils-a sustainable lubricating product. J Am Leather Chem Assoc. 2020;115(9):324–9.
4. Kamely N. "Fatliquors" for leathers: an application of microemulsion-a review. Polym Bull. 2021. https://doi.org/10.1007/s00289-021-03579-z.
5. Adachukwu NN, Pius OU, Ikhazuagbe HI. Synthesis of sulfonated Sesamum indicum L. seed oil and its application as a fatliquor in leather processing. J Leather Sci Eng. 2020;3:16. https://doi.org/10.1186/s42825-021-00053-4.
6. Saranya R, Selvi AT, Jayapriya J, Aravindhan R. Synthesis of fat liquor through fish waste valorization, characterization and applications in tannery industry. Waste Biomass Valori. 2020;11(12):6637–47. https://doi.org/10.1007/s12649-020-00944-3.
7. Yu Y, Zeng WC, Wang YN, Shi B. Inhibitory effect of protein filling agent from boveine hair on the oxidation of Cr(III). J Am Leather Chem Assoc. 2015;110(12):385–91.
8. Rabe V, Graupner-von Wolf R, Kleban M. Minimizing emissions of automotive leather. Germany: XXXV IULTCS Congress, Jun. 25–28, 2019.
9. Xu T, Jiang XF, Tang YL, Zeng YH, Zhang WH, Shi B. Oxidation of trivalent chromium induced by unsaturated oils: a pathway for hexavalent chromium formation in soil. J Hazard Mater. 2021;405: 124699. https://doi.org/10.1016/j.jhazmat.2020.124699.
10. Cao J, Deng L, Zhu XM, Fan YW, Hu JN, Li J, Deng ZY. Novel approach to evaluate the oxidation state of vegetable oils using characteristic oxidation indicators. J Agr Food Chem. 2014;62(52):12545–52. https://doi.org/10.1021/jf5047656.
11. Karrar E, Sheth S, Wei W, Wang XG. Effect of microwave heating on lipid composition, oxidative stability, color value, chemical properties, and antioxidant activity of gurum (Citrulluslanatus var. Colocynthoide) seed oil. Biocatal Agric Biotechnol. 2020;23:101504. https://doi.org/10.1016/j.bcab.2020.101504.
12. Nadeem M, Imran M, Taj I, Ajmal M, Junaid M. Omega-3 fatty acids, phenolic compounds and antioxidant characteristics of chia oil supplemented margarine. Lipids Health Dis. 2017;16:102. https://doi.org/10.1186/s12944-017-0490-x.
13. Xu N, Wu XL, Zhu YQ, Miao JY, Gao Y, Cheng C, Peng SF, Zou LQ, McClements David JL, Liu W. Enhancing the oxidative stability of algal oil emulsions by adding sweet orange oil: Effect of essential oil concentration. Food Chem. 2021;355: 129508. https://doi.org/10.1016/j.foodchem.2021.129508.
14. Linke A, Teichmann H, Kohlus R. Simulation of the oxidation of microencapsulated oil based on oxygen distribution-Model setup and validation. J Food Eng. 2021;298: 110486. https://doi.org/10.1016/j.jfoodeng.2021.110486.
15. Takhar M, Li YC, Chan AWH. Characterization of secondary organic aerosol from heated-cooking-oil emissions: evolution in composition and volatility. Atmos Chem Phys. 2021;21(6):5137–49. https://doi.org/10.5194/acp-21-5137-2021.
16. Aydin S, Sayin U, Sezer MO, Sayar S. Antioxidant efficiency of citrus peels on oxidative stability during repetitive deep-fat frying: evaluation with EPR and conventional methods. J Food Process Pres. 2021:e15584. https://doi.org/10.1111/jfpp.15584.
17. Gaikwad NN, Kalal AY, Suryavanshi SK, Patil PG, Sharma D, Sharma J. Process optimization by response surface methodology for microencapsulation of pomegranate seed oil. J Food Process Pres. 2021:e15561. https://doi.org/10.1111/jfpp.15561.
18. Dodoo D, Tulashie SK, Dodoo T, Kwaw F. Assessing the effects of sunlight on the photooxidation of tropical oils with experimental and computational approaches. J Am Oil Chem Soc. 2021;98(4):439–53. https://doi.org/10.1002/aocs.12478.
19. ISO 6886. Animal and vegetable fats and oils–Determination of oxidative stability (accelerated oxidation test). Geneva, Switzerland, 2016.
20. ISO 3961. Animal and vegetable fats and oils–Determination of iodine value. Geneva, Switzerland, 2018.
21. ISO 660. Animal and vegetable fats and oils–Determination of acid value and acidity. Geneva, Switzerland, 2009.
22. ISO 3960. Animal and vegetable fats and oils–Determination of peroxide value–Iodometric (visual) endpoint determination. Geneva, Switzerland, 2017.
23. Taylan O, Cebi N, Sagdic O. Rapid screening of mentha spicata essential oil and L-menthol in mentha piperita essential oil by ATR-FTIR spectroscopy coupled with multivariate analyses. Foods. 2021;10(2):202. https://doi.org/10.3390/foods10020202.
24. Wang CX, Sun CX, Lu W, Gul K, Mata A, Fang YP. Emulsion structure design for improving the oxidative stability of polyunsaturated fatty acids. Compr Rev Food Sci F. 2020;19(6):2955–71. https://doi.org/10.1111/1541-4337.12621.
25. Choe E, Min DB. Mechanisms and factors for edible oil oxidation. Compr Rev Food Sci Food Saf. 2006;5(4):169–86. https://doi.org/10.1111/j.1541-4337.2006.00009.x.
26. Luo ZY, Yao J, Fan HJ, Xia CC, Wang SS. The biodegradabilities of rape oilbased fatliquors prepared from different methods. J Am Leather Chem Assoc. 2010;105(4):121–8.
27. Luo ZY, Xia CC, Fan HJ, Chen X, Peng BY. The biodegradabilities of different oil-based fatliquors. China Leather. 2011;88(7):1029–36.
28. Duan WN, Li WM, Ren PF. Synthesis of sulfuric fatty acid methyl ester. China Oils And Fats. 2012;37(3):56–9.
29. Huo WK, Zhou JB, Liao XP, Shi B. Synthesis of leather fatliquor using two-step esterification reaction and its application properties. Leather Science and Engineering. 2020;30(3):7–14. https://doi.org/10.19677/j.issn.1004-7964.2020.03.002.

30. Fan GC, Zhang Z, Qiang XH, Guo R, Zhang GH. Study on properties and preparation of oxidized-sulfited cottonseed oil for fatliquoring. China Leather. 2007;36(11):37–40.
31. Lan YJ, Bao LH, Qian ZD, Zhou ZP. The development of POV series phosphate vegetable oil. China Leather. 2002;31(1):32–4.
32. Xu N, Wu XL, Zhu YQ, Miao JY, Gao Y, Cheng C, Peng SF, Zou LQ, McClements DJ, Liu W. Enhancing the oxidative stability of algal oil emulsions by adding sweet orange oil: effect of essential oil concentration. Food Chem. 2021;355: 129508. https://doi.org/10.1016/j.foodchem.2021.129508.
33. Juliano C, Cossu M, Alamanni MC, Piu L. Antioxidant activity of gamma-oryzanol: mechanism of action and its effect on oxidative stability of pharmaceutical oils. Int J Pharmaceut. 2005;299:146–54. https://doi.org/10.1016/j.ijpharm.2005.05.018.
34. Zhang FH, L J, Yang SP, Bi YL. Inhibitory effect of antioxidants on biodiesel crystallization: Revealing the role of antioxidants. Fuel. 2021;297:120782. https://doi.org/10.1016/j.fuel.2021.120782.
35. Saez MI, Suarez MD, Martinez TF. Effects of alginate coating enriched with tannins on shelf life of cultured rainbow trout (Oncorhynchus mykiss) fillets. LWT-Food Sci Technol. 2020;118: 108767. https://doi.org/10.1016/j.lwt.2019.108767.
36. Zhang M, Wei W, Zhang LY, Lu XD, Liang P, Cheng WJ, Chen LJ. Evaluation of the antioxidant effect of several kinds of food antioxidants on large yellow croaker roe oil. Farm Products Processing. 2019;1:40–43. https://doi.org/10.16693/j.cnki.1671-9646(X).2019.01.012.

Publisher's Note