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DISSERTATION

DEVELOPMENT OF BISCUITS TECHNOLOGY WITH THE ADDITION OF GRAPE POMACE POWDERS

Specialty 181– Food Technology
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The dissertation contains the results of own research. The use of ideas, results, and texts of other authors have references to the relevant source

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АНОТАЦІЯ

Луо Веньцзюань. Розробка технології печива із додаванням порошків з виноградних вичавків. – Кваліфікаційна наукова праця на правах рукопису.

Дисертація на здобуття ступеня доктора філософії за спеціальністю 181 – «Харчові технології» – Сумський національний аграрний університет, Суми, 2022.

Дисертаційну роботу присвячено науковому обґрунтуванню та розробці технології печива, збагаченого біологічно цінними речовинами за рахунок додавання порошків з виноградних вичавків, а також з кісточок та шкірочок, відокремлених з вичавків. Для виготовлення порошків використовували виноград сорту Каберне Совіньйон, вирощений у східній частині Китаю.

У роботі представлено результати аналітичного огляду літературних джерел, а саме напрямків переробки виноградних вичавків, особливостей формування їх хімічного складу, вплив властивості клейковини та крохмалю та на формування структури пшеничного тіста.

Дослідження хімічного складу виноградних порошків показало, що їх основним компонентом є харчові волокна, вміст яких становить від 59 до 68%. Лише 13% з них є розчинними. У кісточках переважає клітковина, у шкірочках – пектинові речовини. Крім харчових волокон вичавки містять білки (від 8,75% у кісточках до 16,31% у шкірочках), жири (до 20,92%), мінеральні речовини, у тому числі K, Na, Ca та Mg, Fe, Cu, Zn, Mn, Cr та Se. Відмічений низький вміст свинця та відсутність кадмію у виноградних порошках, хоча національними стандартами Китаю «Зелена їжа – сухофрукти» (NY/T 1041-2010) та «Зелена їжа – фрукти з помірного клімату» (NY/T 844-2010) дозволений вміст цих елементів у рослинних продуктах на рівні Pb ≤ 1 мг/кг, Cd ≤ 0,05 мг/кг. Вміст деяких елементів відрізняється від літературних значень, що пов’язано з особливостями сорту та походженням винограду, взятого для досліджень.

Якісний і кількісний поліфенольний склад виноградних порошків досліджено за допомогою методів рідинної хроматографія високого тиску –

тандемної мас-спектрометрії (HPLC-MS/MS). Показано, що у порошку з виноградних кісточок поліфеноли представлені в основному флавонолами (кверцетин, морін, мірицетин тощо) і похідними бензойної кислоти (ванілінова, сирінгова, галова кислоти тощо), тоді як кількість флаван-3-олу (катехін, епікатехін, епікатехін-галат, епігалокатехін-галат) і похідних коричної кислоти є невеликою. У порошку з виноградних кісточок приблизно 80% неантоціанових поліфенолів є флаван-3-олами, серед яких екстраговані метанолом значно більші за кількістю, ніж похідні бензойної кислоти та флавоноли. Виноградні кісточки також містять низьку кількість коричної кислоти. В основному одержані результати відповідають результатам інших досліджень, але відрізняються даними щодо вмісту кверцетину та ізокверцетину у порошку з кісточок. Вміст першого є набагато нижчим, а другого – набагато вищим, ніж відомо з літературних даних. Ймовірно, причина полягає в тому, що поліфенольний склад виноградних кісточок залежить від багатьох факторів, таких як сорт винограду, клімат місця вирощування, географічне середовище, час бродіння вичавків та зрілість ягід. Підтверджена висока антиоксидантна здатність поліфенольних сполук винограду. І той факт, що антиоксидантна активність поліфенольного екстракту виноградних вичавків значно перевершує активність вітаміну С.

Досліджено колір композитного борошна, одержаного змішуванням пшеничного борошна з виноградними порошками. Показано, що усі види порошків збільшують у суміші темно-рожевий спектр кольорової гами, а додавання порошку з шкірочок надає зразкам синього кольору.

За допомогою приладу Mixolab досліджено термомеханічні властивості тіста та окремих його компонентів – клейковини та крохмалю. Встановлено, що виноградні порошки мають значний вплив на водопоглинання композитного борошна, але напрямок впливу різний. Так, тісто з додаванням порошків з виноградних вичавків та кісточок характеризується нижчою здатністю до поглинання вологи порівняно з контрольним зразком. Даний результат суперечить іншим дослідженням, оскільки додавання харчових волокон зазвичай призводить до підвищення водопоглинання. Але його можна пояснити тим, що ліпіди, які містяться у цих порошках, можуть частково покривати гранули крохмалю та білкові молекули, знижуючи водопоглинання під час замішування. Порошок з виноградних шкірочок, навпаки, збільшує водопоглинання тіста. При додаванні 20% мас. цього порошку водопоглинання збільшується на 9,65%, що пов'язано з високим вмістом білка у добавці і відміною у складі харчових волокон. Білок порошку з виноградних шкірочок містить велику кількість аланіну та лізину, які відповідають за водопоглинання.

Вивчено результуючі ефекти додавання порошків на реологічні та мікроструктурні властивості тіста. Встановлено, що виноградні порошки збільшують час утворення та стабільність тіста, а також підвищують його міцність. Експеримент із динамічними коливаннями показав, що в усьому діапазоні частот додавання трьох виноградних порошків зменшило G' і G", але збільшило tanδ, що вказує на те, що поведінка борошняного тіста наближається до поведінки рідкої системи.

Дослідження мікроструктури зразків тіста показали, що додавання виноградного борошна порушує цілісність і безперервність клейковини в тісті.

Результати, отримані за допомогою швидкого віскоаналізатора (RVA) свідчать про те, що додавання виноградних порошків має обмежений вплив на температуру клейстеризації, незначно підвищуючи її. У всіх випадках час досягнення максимальної температури клейстеру зменшився через підвищення температури клейстеризації. Збільшення в'язкості при охолодженні крохмального клейстера свідчить про те, що порошки з виноградних вичавків можуть знизити термічну стабільність і стійкість крохмальних гранул до механічних пошкоджень. Результати диференціальної скануючої калориметрії (DSC) показали, що ентальпія, необхідна для клейстеризації, була значно нижчою через відносне зниження вмісту крохмалю, що узгоджувалося з результатами RVA.

Проведено оптимізацію рецептури печива з додаванням виноградних порошків. Виявлено, що найкращі показники якості має печиво із додаванням 15% порошку з виноградних кісточок, 5% порошку з виноградних шкірочок та 10% порошку з виноградних вичавків. Оптимальна кількість додавання цукрової пудри становила 35 %, пальмової олії – 9 %, а співвідношення розпушувачів харчова сода:глюколактон:бікарбонат амонію становило 0,6:0,8:1,0. За цих умов печиво мало шоколадний колір, сильний виноградний смак, загальне сприйняття печива було високим, а загальна кількість мікроорганізмів та коліформи були в межах безпечного діапазону.

Оцінено поживний склад та антиоксидантні властивості трьох видів печива за оптимальних умов процесу приготування. Результати показали, що твердість, жувальна здатність і крихкість печива зменшуються при збільшенні дозування виноградних порошків. Печиво з додаванням 10% порошку з виноградних вичавків показало зростання стійкості до окиснення.

Аналіз травних характеристик печива показав, що зі збільшенням додавання порошку з виноградних вичавків кількість швидкозасвоюваного крохмалю зменшується, а повільно засвоюваного крохмалю зростає.

Вивчення ароматичних компонентів у зразках печива дало змогу встановити, що на рівні 10% добавок печиво набуває змішаного смаку з присмаком гіркого мигдалю, банана, трав, підсмаженого і горіхового. У сукупності виноградні порошки мають багатообіцяючий потенціал як сировина для збагачення печива.

Згідно з кінетичною моделлю першого порядку прогірклості олії, термін придатності печива з додаванням порошку з виноградних вичавок, що зберігалося при 37°C, 47°C і 57°C, становив 198 днів, 105 днів і 77 днів відповідно, а подальша підгонка температури та терміну зберігання дала змогу одержати кінетичне рівняння $\ln(T) = -0{,}0024S + 4{,}2225$ ($R2 = 0{,}9412$). Результати підтверджувального експерименту показали, що відносна похибка прогнозованого значення терміну придатності печива, отриманого розрахунковим шляхом, становить менше 10%.

Ключові слова: печиво; порошки; вторинна сировина; виноградні вичавки; виноградні кісточки; виноградні шкірочки; пшеничне тісто; борошняні вироби; печиво; термомеханічні властивості; реологічні властивості; мікроструктурні властивості; органолептична оцінка; антиоксидантні властивості; харчова цінність; зберігання.

СПИСОК ПУБЛІКАЦІЙ ЗДОБУВАЧА ЗА ТЕМОЮ ДИСЕРТАЦІЇ

Публікації, що відображають основні наукові результати дисертації

1. Wenjuan Lou, Bo Li, Grevtseva Nataliya. The influence of Cabernet Sauvignon wine grape pomace powder addition on the rheological and microstructural properties of wheat dough. CyTA Journal of food, 2021, 19(1), 751-761. https://doi.org/10.1080/19476337.2021.1981458 (Scopus, Q2).
2. Wenjuan Lou, Haixu Zhou, Bo Li, Grevtseva Nataliya. Rheological, pasting and sensory properties of biscuits supplemented with grape pomace powder. Food science and technology, 2022, 42, 78421. https://doi.org/10.1590/fst.78421 (Scopus, Q2).
3. Wenjuan Lou, Bo Li & Grevtseva Nataliya. Preparation of grape pomace powders and analysis of their nutritive compositions. Acta innovations, 2021, 39(22), 22–31. https://doi.org/10.32933/ActaInnovations.39.3 (Scopus, Q3).

Тези доповідей

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ANNOTATION

Lou Wenjuan Development of technologies of tough biscuits based on wine grape pomace. Qualified scientific work as a manuscript.

Dissertation for the degree of Doctor of Philosophy in the specialty 181 – «Food technology» – Sumy National Agrarian University, Sumy, 2022.

The thesis is dedicated to the scientific substantiation and development of the technology of biscuits enriched with biologically valuable substances due to the addition of powders from grape pomace, as well as from seeds and skin separated from pomace. Cabernet Sauvignon grapes grown in the eastern part of China were used to make the powders.

The paper presents the results of an analytical review of literary sources, namely, the directions of grape pomace processing, the peculiarities of their chemical composition, the influence on the properties of gluten and starch, and on the formation of the structure of wheat dough.

A study of the chemical composition of grape powders showed that their main component is dietary fiber, the content of which ranges from 59 to 68%. Only 13% of them are soluble. In seeds, fiber prevails, in skin – pectin substances. In addition to dietary fiber, pomace contains proteins (from 8.75% in the seeds to 16.31% in the skin), fats (up to 20.92%), minerals, including K, Na, Ca, and Mg, Fe, Cu, Zn, Mn, Cr, and Se. Low lead content and absence of cadmium in grape powders were noted, although Chinese national standards "Green Food – Dried Fruits" (NY/T 1041-2010) and "Green Food – Temperate Fruits" (NY/T 844-2010) allow the content of these elements in plant products at the level of $Pb \leq 1$ mg/kg, $Cd \leq 0.05$ mg/kg. The content of some elements differs from the literary values, which is related to the characteristics of the variety and the origin of the grapes taken for research.

The qualitative and quantitative polyphenol composition of grape powders was investigated using high-pressure liquid chromatography-tandem mass spectrometry (HPLC-MS/MS) methods. It is shown that polyphenols in grape seeds powder are represented mainly by flavonols (quercetin, morin, myricetin, etc.) and benzoic acid derivatives (vanillic, syringic, gallic acid, etc.), while the amount of

flavan-3-ol (catechin, epicatechin, epicatechin- gallate, epigallocatechin-gallate) and cinnamic acid derivatives is small. In grape seeds powder, approximately 80% of the non-anthocyanin polyphenols are flavan-3-ols, of which the methanol-extracted ones are significantly more abundant than the benzoic acid derivatives and flavonols. Grape seeds also contain low amounts of cinnamic acid. In general, the obtained results correspond to the results of other studies, but differ from the data on the content of quercetin and isoquercetin in the seeds powder. The content of the quercetin is much lower, and of the isoquercetin is much higher, than is known from the literature. This is probably because the polyphenol composition of grape seeds depends on many factors, such as grape variety, growing climate, geographic environment, pomace fermentation time, and berry maturity. The high antioxidant capacity of grape polyphenolic compounds has been confirmed. We also confirmed that the antioxidant activity of their polyphenolic extract is significantly superior to that of vitamin C.

The color of the composite flour obtained by mixing wheat flour with grape powders was studied. It is shown that all types of powders increase the dark pink spectrum of the color gamut in the mixture, and the addition of skin powder gives the samples a blue color.

Thermomechanical properties of the dough and its individual components – gluten and starch – were investigated using the Mixolab. It was established that grape powders have a significant effect on the water absorption of composite flour, but the direction of the effect is different. Thus, the dough with the addition of powders from grape pomace and seeds is characterized by a lower ability to absorb moisture compared to the control sample. This result contradicts other studies, as the addition of dietary fiber usually leads to an increase in water absorption. But it can be explained by the fact that the lipids contained in these powders can partially cover starch granules and protein molecules, reducing water absorption during mixing. Grape skin powder, on the contrary, increases the water absorption of the dough. When adding 20% wt. of this powder, water absorption increases by 9.65%, which is due to the high protein content in the additive and the difference in the composition of dietary fibers. Grape skin powder protein contains a large amount of alanine and lysine, which are responsible for water absorption.

The resultant addition effects on the rheological and microstructural properties were studied. It has been established that grape powders increase the dough development time, stability time as well as increase its strength. The addition of the three grape powders reduced elastic modulus and viscous modulus.

The study of the microstructure of the dough samples showed that the addition of grape flour breaks the integrity and continuity of the gluten in the dough.

The results obtained using the rapid visco-analyzer (RVA) indicate that the addition of grape powders has a limited effect on the gelatinization temperature, slightly increasing it. In all cases, the attainment of the maximum paste temperature decreased due to an increase in gelatinization temperature. The increase in viscosity during cooling of the starch paste is due to the fact that powders from grape pomace can worsen the thermal stability and resistance of starch granules to mechanical damage. Differential scanning calorimetry (DSC) results showed that the enthalpy required for gelatinization was significantly reduced due to the relative decrease in starch content, which was consistent with the RVA results.

The biscuits recipe was optimized with the addition of grape powders. It was found that biscuits with the addition of 15% grape seeds powder, 5% grape skin powder, and 10% grape pomace powder have the best quality indicators. The optimal amount of added powdered sugar was 35%, palm oil – 9%, and the ratio of baking soda:gluconolactone:ammonium bicarbonate was 0.6:0.8:1.0. Under these conditions, the biscuits had a chocolate color, a strong grape flavor, the overall acceptability of the biscuits was high, and the total microorganism and coliform counts were within the safe range.

The nutritional composition and antioxidant properties of three types of biscuits under optimal conditions of the biscuits process were evaluated. The results showed that biscuits' hardness, chewability, and fragility decrease with increasing dosage of grape powders. Biscuits with the addition of 10% grape pomace powder showed increased resistance to oxidation.

Analysis of the biscuits' digestive characteristics showed that with increasing addition of grape pomace powder, the amount of rapidly digestible starch decreases, and the amount of fully digestible starch increases.

Research of aromatic components in the samples of biscuits can be established that at the level of 10% of additives biscuits have a mixed taste with a taste of bitter almond, banana, herbs, toasted and nutty. Collectively, grape powders have promising potential as raw materials for biscuits enrichment.

According to a first-order kinetic model of oil rancidity, the shelf life of biscuits with addition of grape pomace powders stored at 37°C, 47°C, and 57°C were 198 days, 105 days, and 77 days, respectively, and further adjusting the temperature and of the storage period made it possible to obtain the kinetic equation ln (T) = –0.0024S + 4.2225 (R2 = 0.9412). The results of the confirmatory experiment showed that the relative error of the predicted value of the expiration date of the biscuits, obtained by calculation, is less than 10%.

Keywords: biscuits; powders; secondary raw materials; grape pomace; grape seeds; grape skin; wheat dough; flour products; thermomechanical properties; rheological properties; microstructural properties; organoleptic evaluation; antioxidant properties; nutritional value; storage.

LIST OF PUBLICATIONS

Publications that reflect the main scientific results of the dissertation

1. Wenjuan Lou, Bo Li, Grevtseva Nataliya. The influence of Cabernet Sauvignon wine grape pomace powder addition on the rheological and microstructural properties of wheat dough. CyTA Journal of food, 2021, 19(1), 751-761. https://doi.org/10.1080/19476337.2021.1981458 (Scopus, Q2).
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CONTENT

THE LIST OF SYMBOLS

RVA – Rapid Visco-Analyzer

DSC – Differential Scanning Calorimetry

GSP – Grape Seeds Powder

GSKP – Grape Skin Powder

GPP – Grape Pomace Powder

GC-MS –Gas Chromatography-mass spectrometry

INTRODUCTION

Actuality of the Topic. Grapes are one of the most extensively cultivated crops in the world, and the vast majority of the total grape production (according to various statistics from 70% to 80%) is used to produce wine.

China ranks first in the world in terms of the amount of grapes grown – 10 million tons per year on average, second in terms of vineyard area, ninth in terms of wine production and fifth in terms of wine consumption. Winemaking in China has a thousand-year history, the first modern winery, Changyu Grape Wine Company, was opened there in 1892. The most popular red grape variety grown in China is Cabernet Sauvignon.

Approximately 20% of processed grapes remain at wineries every year as a secondary product of winemaking – grape pomace. In recent years, they have attracted the close attention of specialists, which is caused by two main reasons. On the one hand, large volumes of unprocessed pomace are a significant source of environmental pollution due to the long period of their decay. On the other hand, they contain dietary fibers, minerals, polyphenolic compounds with powerful antioxidant activity, due to which they have great potential for use in the medical, cosmetology, and food industries. Therefore, the investigation for ways of their effective application remains an urgent task both in China and around the world.

The works of scientists from all over the world, including those from Ukraine and China, are devoted to the study of the properties and composition of grape pomace and their processing products: Obolkina V.I., Lisyuk H.M., Grevtseva N.V., Chuyko A.M., Zhou T.., Zhou C., Zhang T., Liu, W, Liang Z., González-SanJosé, M. L., García-Lomillo, J.

Numerous scientific studies present the results of studying the composition of the products of grape pomace processing, obtained from individual grape varieties and their mixtures. Technologies for food products, including flour products, with the addition of grape extracts, pastes, and powders have been developed. A lot of researches on the influence of various components of grape pomace on the properties of gluten and starch of wheat flour, on the formation of the dough structure, are presented. However, studies of the composition and properties of powders obtained from the grape pomace of the Cabernet Sauvignon variety grown in the eastern part of China and their influence on the formation of the quality of wheat dough and biscuits have not been found in the literature.

Biscuits are one of the most popular products in both Ukraine and China. Traditionally, it contains a lot of fat and carbohydrates and is poor in biologically active substances. Adding of powders from grape pomace into biscuits may enrich it with dietary fibers, polyphenolic compounds, macro- and microelements, vitamins, as well as extend the shelf life of this fat-containing product due to the addition of substances with antioxidant properties. The development of biscuits technology using grape pomace powders will contribute to the reduction of certain nutritional problems identified in Western and Eastern societies, such as low average intake of antioxidants, fiber and minerals; as well as slowing down the rate of environmental pollution; reducing the amount of waste and increasing the economic value of the secondary product of winemaking.

Therefore, the development of biscuits technology with the addition of grape pomace powders is an actual task, the solution of which will ensure the creation of a product of high quality and nutritional value and allow rational and responsible processing of valuable food resources remaining at Chinese wineries.

Connection of work with scientific programs, plans, themes. Scientific research was carried out within the framework of the thematic plan of research works according to topic 0119U101237 "Innovative technological solutions in the production of food products", Department of Food Technology, Sumy National Agrarian University, Ukraine, and the School of Food Sciences of the Khyenan Institute of Science and Technology, China.

The purpose and objectives of the work. The aim of the dissertation is the scientific substantiation and development of biscuits technology using powders from pomace, as well as seeds and skin of Cabernet Sauvignon grapes grown in the eastern part of China, to improve quality, nutritional and biological value, as well as to expand the assortment and extend shelf life. of this product.

To achieve the main goal, it was necessary to solve a number of interrelated tasks:

– on the basis of the analysis and generalization of theoretical data, to substantiate the prospects of using grape powders in biscuits technology;

– to investigate the peculiarities of the chemical and polyphenolic composition of grape powders, to evaluate their antioxidant activity;

– to study the influence of grape powders on the rheological properties and microstructure of wheat dough, as well as on the color and granulometric composition of flour;

– evaluate the influence of grape powders on the thermomechanical properties of the dough and its components - gluten and starch; to investigate the process of starch gelatinization in dough with the addition of grape powders;

– to study the influence of grape powders on the quality indicators of biscuits – structural and mechanical properties, color, organoleptic characteristics; to optimize the recipe and technological parameters of making biscuits with the addition of grape powders;

– evaluate the chemical composition of biscuits with the addition of grape powders and its antioxidant properties;

– conduct research on digestibility of developed biscuits *in vitro*; to investigate the composition of substances that take part in the formation of the taste and aroma characteristics of biscuits with the addition of grape powders;

– to investigate and justify the shelf life of biscuits with the addition of grape powders.

The object of research is technology production fortified tough biscuits with grape pomace powders.

The subjects of research are grape pomace of Cabernet Sauvignon variety grown in eastern part of China, grape pomace powders, seeds and skin powders, dough and biscuits with the addition of grape powders.

Research methods – conventional, physical, chemical, microbiological, *in vitro* simulation experiment, experiment planning, processing of experimental data.

The scientific novelty of the obtained is that for the first time

– on the basis of theoretical and experimental research, a biscuits technology was developed using grape powders – from pomace, seeds and skin of Cabernet Sauvignon grapes grown in the eastern part of China, which allows to obtain products with an extended shelf life with high organoleptic and physico-chemical quality indicators and to ensure it has an increased content of biologically active substances, namely polyphenolic compounds, dietary fibers, minerals, vitamins;

– the influence of grape powders on the thermomechanical properties of the dough, the peculiarities of the formation of the gluten frame and the process of gelatinization of starch is substantiated;

– the in vitro digestion characteristics, antioxidant properties and aroma components of grape pomace biscuits were analyzed to provide reliable evidence for the application of by-product and its influence on blood glucose index;

– the influence of grape powders on the formation of flavor and aroma characteristics of biscuits during its preparation was studied; based on aroma component analysis, the biscuits are shown to have a mixed flavor that includes bitter almond, banana, herbal, toasty, and nutty flavors;

– the shelf life of grape pomace biscuits was predicted by peroxide value, and the temperature–shelf-life dynamic model based on peroxide value was obtained, and the reliability of this model was investigated.

The data on the chemical composition and functional-technological properties of powders from pomace, seeds and skin of Cabernet Sauvignon grapes grown in the eastern part of China, the discovery of the formation of quality and nutritional value of biscuits with grape powders have gained further development.

The practical significance of the obtained results. The treatment of wine grape pomace in China has been directly thrown away for a long time. In this study, this by-product was used to develop new edible products, which avoided the waste of by-products and improved its economic value. The project alleviates the environmental pollution caused by improper treatment of grape residue. The developed nutritional fortified biscuits met the health needs of both western and eastern countries due to insufficient intake of antioxidants and dietary fiber.

Biscuits’ recipes of with the addition of powders from the seeds, skin and pomace of the Cabernet Sauvignon grapes were optimized. A technological scheme of biscuits production and a project of technological documentation were developed.

The results of the dissertation can be used in the educational process when studying the disciplines "Theoretical foundations of food production", "Methods of control of food products", "General technologies of food production", as well as during the conduct of fundamental and applied research in the direction of the development of technologies of flour products or processing secondary plant raw materials.

Personal contribution of the applicant is in designing an experiment, organizing and conducting of analytical and experimental research in laboratory and production conditions, analyzing, processing and generalizing results. The author personally formulated conclusions and recommendations, prepared materials for publications, developed technological documentation.

Approbation of dissertation results.

Approbation of the scientific and practical results presented in the dissertation was carried out by the applicant personally with the methodical and scientific support of the scientific supervisor.

The main results of the work were reported at the of the Scientific and Practical Conference "Development of food production, restaurant and hotel industries and trade: problems, prospects, efficiency", Kharkiv. KhDUHT, 2019. Part 1. P. 44 (Kharkiv, May 15, 2019); X International Scientific and Practical Conference "Complex Quality Assurance of Technological Processes and Systems", Chernihiv Polytechnic National University (Chernihiv, April 29-30, 2020); at the scientific seminar "New trends and global trends in raw material storage and food production technologies", Poltava State Agrarian Academy (Poltava, March 30, 2021); International scientific and practical conference "Development of food production, restaurant and hotel industries and trade: problems, prospects, efficiency", Kharkiv State University of Food and Trade (Kharkiv, May 18, 2021); All-Ukrainian scientific and practical conference of young scientists and students "Innovative development technologies in the field of food production, hotel and restaurant business, economy and entrepreneurship: scientific research of youth", Kharkiv State University of Food and Trade (Kharkiv, April 8, 2021).

Publications. According to the results of this research, the applicant published 9 scientific papers, including 3 articles reflecting the main scientific results of the dissertation - in foreign publications of the 2nd and 3rd quartiles, the citations of which are tracked in Scopus and Web of Science; 2 – which additionally reflect the scientific results of the dissertation, of which 1 – in a foreign edition of the 1st quartile, 1 – in a scientific professional publication of Ukraine indexed in Scopus and Web of Science, 4 abstracts of Scientific Conference reports.

The structure and volume of the dissertation. The dissertation consists of an annotation, introduction, 5 sections, conclusions, list of references of 224 names, appendices. Main content dissertation is laid out on 110 pages of printed text, contains 34 tables, 27 figures.

SECTION 1

PREREQUISITES FOR THE APPLICATION OF GRAPE POMACE IN THE BISCUITS TECHNOLOGY

(Literature review)

1.1 Research and development status of wine grape pomace

Grapes are one of the most abundant fruits, and about 80% of them are used in the wine industry every year [1]. About 20% (by weight percentage) of them are converted into grape residue (GP), a by-product, which has been underestimated for a long time due to the lack of cost-effective alternative uses. GP traditionally produces "wine alcohol" through distillation, which is used to make highly liqueurs and acclaimed and value-added distilled spirits to fortify wines. Grape seed oil has been produced for decades, and which has rapidly won the market as a gourmet product. Other traditional applications for GP are as animal feed or fertilizer. However, it is estimated that one liter of wine can produce 17 kg of GP. Due to insufficient development, the disposal of GP and related environmental problems [2] is a considerable challenge.

Effective GP utilization accordingly has the potential to reduce waste and concomitantly rise profits, leading to a more sustainable economy.

Therefore, efficient use of GP has the potential to reduce waste and subsequently increase profits, leading to a more sustainable economy.

GP is rich in dietary fiber (DF) and polyphenols [3]. The DF content is typically 43-75% by dry weight [4]. Dietary fiber contained in fruits in general, especially grapes, provides a variety of useful physiological effects, and dietary fiber in fruits in general, especially grapes, exerts various beneficial physiological effects, including improving postprandial insulin response and gastric function, and reducing low-density lipoprotein cholesterol content and total cholesterol. The polyphenol content varies by grape source [5-6]. This diversity can be explained by intrinsic genetic variation as well as differences in maturity stage and agroclimatic conditions, as well as differences in extraction procedures and/or winemaking techniques. Polyphenols mainly include anthocyanins, flavonols, flavanols, phenolic acids and resveratrol, which have a variety of biological activities (such as antioxidant, antibacterial and anti-inflammatory effects) under the condition of rational utilization, and have potential health benefits [7-8]. Procyanidins derived from grape seeds, such as Endotelon, have been commercialized for medical use since 1970, but the use of similar products in the food industry is less common today. Until the late 1990s, almost all alternative methods involved an extraction process followed by a separation process and concentration to obtain products containing specific compounds such as proanthocyanidins or tartaric acid. Procyanidins derived from grape seeds, such as Endotelon, have been commercialized for medical use since 1970, but the use of similar products in the food industry is less common today. Until the late 1990s, almost all alternative methods involved an extraction process followed by a separation process and concentration to obtain products containing specific compounds such as proanthocyanidins or tartaric acid. However, over the past few decades, in order to avoid the extraction process and reduce the loss of valuable non-extractable components, other alternatives have been proposed to produce and use minimally processed distillers grains-derived products.

In food fortification, utilizing valuable ingredients with the potential to contribute to product-specific functionalities is a key objective in meeting diverse and escalating market demands. For example, mango peel powder has been used as an additive to wheat dough and to increase the content of dietary fiber and antioxidants [9]. Potato peel flour has been introduced into biscuits production to increase dietary fiber content [10]. Dietary fiber and antioxidant extracts in apple pomace have been shown to affect the physicochemical properties of cookies [11]. In order to improve the utilization rate of food processing by-products and meet consumers' demand for healthy food, people have paid more and more attention to the application of dietary fiber and natural antioxidants in baked goods [12-13, 1]. However, the effect of partial replacement of wheat flour with GPP in biscuits production is unclear.

The prospects for the use of grape pomace in the development of useful food products are determined by the peculiarities of their chemical composition. The most valuable components of pomace are phenolic compounds. Phenols are secondary metabolites of plants, which can be defined as substances with aromatic rings, with one or more hydroxyl groups, including their functional derivatives [14], and are usually divided into 4 groups: simple phenols (mainly C6- C1 and C6)-C3), flavonoids (C6-C3-C6 and oligomers), polymers (including hydrolyzable and condensable tannins, lignin, etc.) and creosote groups with very different structures (Xanthone, stilbene, beta-cyanines, etc.) [15].

The polyphenols in grape berries are mainly concentrated in the peel and seeds, accounting for 28-35% to 60-70% of the total extractable phenols in the grape [16]. Anthocyanin profiles were identified only in grape skin extracts, whereas procyanidin profiles, usually expressed as concentrations of flavan-3-ols, present in skin and seeds, were observed in both procyanidin and anthocyanin profiles of skin extracts Significant quantitative differences. Samples of different varieties, but not seeds. Malvidin-3-O-glucoside is the main pigment in all grape samples except Kotsifali skin extract [17].

Contents of phenolic compounds in grape seeds (2026 to 15,629mg of catechin equivalents (CE)/100g) are higher than that in skin (660 to 1839mg CE/100g) [18]. Grape seeds from GP contains a large amount of phenolic acid, flavonoids, proanthocyanidins and resveratrol, while grape skin is rich in anthocyanins, flavonols and soluble tannins [19]. Generally, the former is rich in gallic acid and protocatechuic acid [20], while the latter are richer in hydroxycinnamic acids, such as caftaric acid, coutaric acid and fertaric acid [21]. Regarding simple phenols, skin from red pomace is richer than that from white grapes. As for flavonoids, Anthocyanins and flavanols are the most abundant in GP. The most abundant phenolic substances isolated from grape seeds are catechins (catechin and epicatechin) collected from grape pomace and their polymer proanthocyanidins, all others are in a minority [22]. And flavanols are richer in seeds (range 56%-65%) than in skin (14%-21%).

Grape pomace contains a large amount of non-extractable polyphenols. Non-extractable polyphenols mainly include hydrolyzable polyphenols and non-extractable procyanidins, the former being monomeric phenols bound to proteins, polysaccharides or cells through hydrophilic/hydrophobic interactions, hydrogen bonds, or covalent bonds. The latter are mainly some phenols combined with the fibers in the grape pomace, and the low solubility of this fraction resulted in they are not extracted.

Grape pomace contains a certain amount of proteins. Li et al. (2018) [23] measured the hygienic index, nutrient content and amino acid composition of grape pomace by national standard methods, and analyzed the value of essential amino acids by international common methods. The results showed that the protein content of GP was 12.0% (dry matter), the total amount of amino acids was 10.78%, with the proportion of essential amino acids accounted for 34.88%, and the delicious amino acid accounted for 43.43%, depending on grape variety and harvesting Conditions. A grape seed protein extract has been reported to be proposed as a valuable wine fining agent [24]. The nutritional quality of grape seed protein has similar characteristics to other oilseeds and grains [25]. In addition, grape seed protein exhibits some functional properties such as good solubility and emulsifying activity [26]. Taking this into account, grape pomace with a well-balanced essential amino acid profile, with the exception of an insufficient amount of sulfur-containing amino acids, which are limiting, can be considered a valuable food resource worth developing.

The most commonly used methods for extracting protein from grape seeds are salt dissolution and alkali dissolution. Zhou et al. (2015) [27] studied the process of extracting grape seed protein by alkali-soluble acid precipitation. The best extraction conditions were as follows: grape seed crushed particle size 40 mesh, alkaline solution pH 9, material-liquid ratio 1:10, temperature 50 ℃, extraction time 45 min, the protein extraction efficiency is the highest.

Lipids are mainly found in grape seeds. It was reported that the grape seed in the GP contained oil range between 14% and 17% (dry matter) [28-29], depending on grape variety and growing conditions, of which the linoleic acid content is 64% to 74%, and the linoleic acid and VE content is higher than that of other vegetable oils. Linoleic acid is an essential fatty acid for human body, which can significantly inhibit the growth of tumor cells, and it can prevent and treat hypertension, arteriosclerosis, heart disease, and regulate autonomic dysfunction [30-33]. Studies have shown that grape seeds oil can reduce serum total cholesterol (TC), increase serum high density lipoprotein (HDL) and HDL/TC ratio, and long-term consumption has an auxiliary role in preventing and treating cardiovascular and cerebrovascular diseases and atherosclerosis [34].

Grape seeds oil is mainly prepared by pressing or solvent leaching method. The former is relatively simple, but the oil yield is low, the subsequent processing is complicated, and the quality of the pressed grape seed oil is not high [35]. The latter has a high oil yield and the active ingredients of the grape seed oil are retained, whereas the extraction process is more complicated, and it is easy to leave organic solvents, which poses a food safety hazard.

A more environmentally safe and highly efficient technology for extracting oil from grape seeds is CO2 extraction. Currently, it is widely used in food, medicine, chemical and other industries. The low extraction temperature allows maximum retention of biological activity of the oil and seeds.

Dietary fiber is very important for human health, including improving the intestinal environment, preventing intestinal diseases [36-37]. Insoluble dietary fiber (IDF) can stimulate the peristalsis of the intestine, some researchers have compared the functions of IDF and SDF in promoting fecal excretion, they found that IDF is better than SDF in promoting defecation, whereas the main function of SDF is to promote metabolism, such as affecting lipid and carbohydrate metabolism [38].

The content of DF in dried GP may range between 43% and 75%, which is the main component of GP. Grape seeds contain more DF than that in skin, and red pomace are richer than white. Generally, dietary fiber is divided into SDF and IDF, and the latter is the main component of DF in both red and white grape pomace. The extraction methods of DF mainly include enzymatic method, microbial fermentation method, membrane separation method, mechanical physical method, chemical separation method, etc. At present, the most commonly used methods are acid extraction method and enzymatic method. Liu et al. (2014) [39] prepared SDF from wild grape pomace using enzymatic method, based on Box-Behnken design, cellulase concentration, hemicellulase concentration, extraction time and extraction temperature were chosen as the four important factors with three levels. It was suggested that when the cellulase concentration was 93 IU/g, hemicellulase concentration was 121 IU/g, extraction time was 257 min and extraction temperature was 51 °C, the yield rate of SDF reached 152.13 mg/g. Qu et al. (2008) [40] researched the extraction technology of SDF from *Momordica. Charantia Var.* (MCV), and analyzed its main monosaccharide composition. Through response surface analysis, the factors such as solid-liquid ratio, enzyme addition amount, extraction temperature, extraction time, solution pH value and other factors were studied to obtain the optimized process of SDF, and the monosaccharide composition of neutral SDF was obtained by gas chromatography analysis.

The mineral composition of grape pomace is valuable. Potassium, phosphorus, sulfur and magnesium accumulate during grape ripening and are mainly distributed in grape skin. Therefore, the mineral content is higher in grape skinthan in grape seeds, mainly due to its high potassium content [41]. The most abundant potassium salts are tartrates, mainly potasium bitartrate (KC4H5O6). The tartrate content is between 4% and 14% on a dry matter basis. In contrast, seeds are the most powerful reservoirs of calcium, phosphorus, sulfur and magnesium due to the low mobility of these elements in the phloem.

Compared to other nutrients, the mineral content of grape pomace may vary more, due to the strong influence of the viticultural soil and climatic conditions. In addition, during the winemaking process, the duration of the maceration process also has a large impact on the residual mineral content in the lees.

1.2 Applications of grape pomace in the food industry

Over recent decades, a large amount of products has been developed from grape pomace. Among which extracts is the most widely approach, since 2000, the percentage of lees extract methods applied in the food industry is 62%, using water or organic solvents to produce concentrated extracts. The unextracted product, which accounts for 35%, is also recommended for use in the food industry. This method enables more thorough reuse of by-products and enables fortification with fiber, minerals, proteins, oils, and other components of the lees, such as phenols, including non-extractable phenolic compounds. In this way, nutritional value and potential health benefits can be enhanced. Furthermore, since no extraction is required, the process of obtaining these powder products is more economical and has a lower environmental impact, making it a sustainable method.

Grape seed oil that holds only 3% utilized by the food industry perhaps due to its high price [42]. Tartaric acid is used in a variety of food categories, including edible oils and fats, dairy products, fish and meat, fruits and vegetables, and soft and alcoholic beverages, due to its antioxidant, pH-adjusting and preservative activities. Additionally, it takes on a pleasant tartness and enhances some positive flavors. Potassium tartrates are also used in bakery products, where they can generate carbon dioxide without fermentation due to their ability to react with sodium bicarbonate [43-44].

Since GP contributes strong antioxidant and antibacterial activities to the food matrix, and does not affect the sensory quality and microbial stability of food, the development of seasonings is another application of GP in food industry [45]. Increasing consumer demand for alternatives of wheat flour, particularly flours with high fiber and mineral content, has driven the development of these products. Drying and processing grape skin residue into ultrafine powder or making grape seed tablets or capsules is easy to carry and rich in nutrition.

Ultrafine crushing technology and microencapsulation technology are becoming more and more mature. This is confirmed by recent studies of the dependence of polyphenol content and antioxidant activity in grape residues on temperature [46]. Compared with freeze-dried samples, the total polyphenol content of grape seeds decreased by 18.6% and 32.6% at 100 °C and 140 °C, respectively, and the antioxidant capacity of grape seed polyphenols also decreased with increasing temperature. The report by Khanal et al. (2010) [47] showed that high-temperature (125°C) treatment of grape residue can lose a large amount of proanthocyanidins, while low-temperature (40 °C) treatment of grape residue has no significant change in procyanidins. Different drying methods also have a certain effect on the stability of polyphenols in grape residue. However, recent research results have shown that heat treatment can promote the biological activity of grape residue. Kim et al. (2006) [48] found that compared with untreated grape seed, the heat-treated grape seed polyphenol extract has higher antioxidant activity *in vitro*.

In addition, the food industry offers products that naturally inhibit different microbial and chemical reactions, reducing the use of synthetic food preservatives and antioxidants, without compromising the food's ability to stabilize the final product. This fact helps increase the perceived value of consumers, thereby balancing the cost of developing new recipes and optimizing the food preparation process. Recent trends indicate potential interest in new research into non-extracted products such as flours and seasonings to take advantage of the wide range of nutrients in GPP, including fiber, minerals, phenolic compounds, and more. Of particular note, as a substitute for flour in bakery products, further research is required to optimize food formulations (other ingredients, food preparation and packaging) to achieve the highest possible quality, especially those related to sensory parameters. Furthermore, health-focused research is needed to demonstrate the true impact of by-products on different diseases and health modifications.

In recent years, fortified applications have seen the highest increase, followed by the antibacterial effect of GP. Food categories such as dairy, meat and cereals have been successfully enriched with phenols by incorporating grape pomace products. In fact, lees products are primarily used to enrich antioxidants in foods. The natural polyphenolic compounds present in grape pomace have various biological activities, and are found in oils, edible oils, fish [49], bread, ham, chocolate, instant noodles, fruits and vegetables, etc. However, the contribution of extractable phenols is often overestimated to the detriment of non-extractable polyphenols (NEPPs). NEPP reduces cholesterol absorption and increases fat excretion [50]. Furthermore, they are less affected by food and digestive processing conditions and are more stable than extractable polyphenols that degrade during processing. Other than the antioxidant activity, antimicrobial, anti-inflammatory and anti-cancer activities have been also reported, for example, the antioxidant activity of grape seed extract has been proven to inhibit spoilage and lipid peroxidation of foods, and to avoid the generation of spoilage odors [51]. Brannan et al. (2009) [52] compared the antioxidant effects of grape seed polyphenols on fresh and cooked chicken, and found that adding 0.1% grape seed polyphenols to frozen chicken breast can effectively inhibit chicken fat oxidation. Adding 0.1% grape seed polyphenols to cooked chicken breasts not only has a significant antioxidant effect, but also reduces the stale and musty smell of chicken refrigerated at 4°C for 12 days. Garrido et al. (2011) [53] pointed out that adding 0.6% grape seed polyphenols to fresh pork refrigerated can increase its antioxidant capacity and maintain meat color stability, but it has no significant inhibitory effect on microbial growth. However, Ahn et al. (2007) [54] found that during the cold storage of cooked beef, 1% of grape seed polyphenols can inhibit the growth of pathogenic microorganisms such as *Escherichia coli* and *Salmonella*, while reducing the oxidation of fatty acids in beef, thus to prevent browning reaction of beef. Such different results are due to the fact that different meat products have different lipid content, and different amounts of grape seed polyphenols need to be added to play an antioxidant role to ensure the freshness of the food and enhance extend the shelf life.

Therefore, the functions of the food industry are summarized as improving nutritional properties and possible health effects, preventing oxidative processes, interactions with microorganisms in food, effects on newly formed contaminants and natural food colors. For example, rich in polyphenols, fiber and minerals, improving fatty acid profile, preventing lipid oxidation, antibacterial action against food spoilage microorganisms and antibacterial action against foodborne pathogens, protection of probiotics.

Cereals and dairy products are the two major food categories for phenol enrichment using rosacea products [55]. However, the enrichment of flour products with powders from grape pomace requires consideration of many nuances to guarantee product quality. For example, adding grape pomace powder to bread and cookies has been found to produce better results than adding grape seeds powder [56].

Various works have noted modifications caused by these types of flours, such as an increase in alpha-amylase activity leading to a decrease in drop numbers (an indicator of enzymatic activity); and possible interactions of seed lipids with gluten, starch, and hydrophobic components This results in a weaker dough consistency, increased viscosity and delayed starch gelatinization. In contrast, Meral and Dogan (2013) [57] described opposite results, such as the enhanced activity of grape seed meal, attributed to covalent or non-covalent phenolics between gluten and protein, resulting in stronger flour dough, which is more malleable and resistant.

The second most successful application of GPP polyphenols is in the application of dairy varieties, such as the application of grape seed extract in cheese, due to the hydrophobic interaction of phenolic substances with casein, so as to maximize the retention of polyphenols content in the curd. And the study found that the addition of polyphenols has little effect on the growth of lactic acid bacteria [58], the application of GPP in candy, jam, salad dressing and tomato puree is also very successful.

Polyphenol oxidase (PPO) is a copper-containing enzyme distributed in various foods that catalyzes the oxidation of ortho-diphenols to ortho-quinones. O-quinones can polymerize and form brown pigments, which limit the shelf life of certain products. Soaking in 2.5 to 15 g/L solution of grape seed extract inhibited melanosis in shrimp [59-60].

Grape seed extract was able to reduce residual nitrite levels in dry-cured sausages after ripening, reduce the formation of nitrosamines, and inhibit the formation of N-nitrosodimethylamine [61]. It seems that polyphenols can remove residual nitrite by reduction or direct reaction [62-63]. Polyphenols can also alleviate nitrosamine formation by inhibiting microbial activity and scavenging free radicals involved in amine formation [64]. Polyphenols in rosacea may also affect the formation of pyrazine, a compound formed during cooking, such as pyrazine involved in the development of acceptable food flavors [65-67].

1.3 Effects of polyphenols and dietary fiber on the gluten structure

Glutenin is mainly divided into two types. One is the high molecular weight glutenin subunit (HMW-GS), which accounts for about 10% of wheat glutenin. β-helical structure, which has a significant influence on the elastic properties of the dough [68], another is the low molecular weight glutenin subunit (LMG-GS), which is the main component of glutenin, accounts for the overall 90% of the protein, its unique viscosity is the most important factor affecting the formation of the glutenin polymer structure, and it also determines the quality of wheat processing. The molecules interact through disulfide bonds to form a larger polymer than the monomer protein contains when LMG-GS interacts with HMW-GS, which further improves the strength and stability of the dough [69-70]. It can be seen from Fig. 1.1 that gluten protein is composed of linear polymer glutenin subunit and spherical melliadin.

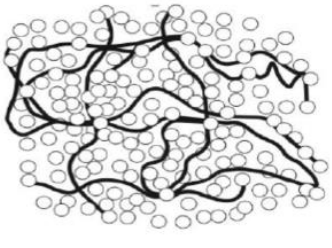


Figure 1.1 – Molecular structure model of wheat gluten protein. Lines represent high molecular weight glutenin subunits, other aggregates are represented by spherical structures

The molecular ends of linear glutenin subunits form reticular and annular structures through disulfide bonds. Under the conditions of disulfide bonds, hydrogen bonds, hydrophobic bonds and other forces, each subunit is intertwined to form a network structure [71]. The more the number of winding points is, the greater the molecular weight is, and the more stable the network structure is, which ultimately gives dough elasticity [72]. The gliadin forms a spherical structure under the action of disulfide bond, hydrogen bond and van der Waals force, and further stabilizes the network structure and gives dough viscosity through intermolecular hydrogen bond interaction with glutenin. There is no disulfide bond between melliadin molecules [73].

The introduction of polyphenols and dietary fibers into the dough affects the gluten structure. This effect depends on the properties and composition of additives. Girard (2016) [74] compared the effect of condensed sorghum tannins (degree of polymerization greater than 10) and grape seed tannins (degree of polymerization between 3-7) on dough strength. He found that although both types of tannins had the ability to enhance gluten, the gluten-enhancing ability of high degree of polymerization tannins was significantly stronger than that of low degree of polymerization tannins, without affecting the extensibility of the dough. Sorghum condensed tannins added to low-gluten flour doubled the amount of insoluble protein in the dough, increased the mixing time of 75%, an 82% increase in dough elasticity, and a 17^o increase in the rheological phase transition angle. After grape seed tannin was added, the content of insoluble protein in the dough increased by 75%, the mixing time increased by 36%, but the rheological phase transition angle decreased by 15^o, indicating that the mixing tolerance of the dough decreased. He believes that this difference may be due to the strong interaction between sorghum condensed tannins and gluten proteins counteracting the strong antioxidant effects of tannins themselves.

Zhang et al. (2010) [75] added tannins to the dough and found that the content of free sulfhydryl groups increased with the increase of the amount of tannins added, which indicated that the disulfide bonds between gluten molecules were reduced by tannins, this reduction destroys the gluten network structure. However, although the addition of tannins broke the most important disulfide bonds in the gluten protein network structure, the results of the rheological experiments showed that the tannins still enhanced the strength of the dough. The reason for the analysis may be due to the formation of new cross-links between tannins and gluten proteins, and this cross-linking effect increases gluten strength. On the other hand, due to the relatively small amount of tannins added, the weakening effect of tannins on the dough caused by the reducing properties of tannins is offset, and the addition of tannins generally shows a gluten-increasing effect.

Wang et al. (2021) [76] investigated the effects of insoluble dietary fiber (IDF), ferulic acid (FA) and their combination on the rheological properties of dough. When the IDF content increases, the water absorption of the dough increases. Due to the strong water absorption and filling effect, the elastic modulus and viscous modulus of the dough increase, but the creep strain decreases. In addition, IDF reduces the gelatinization properties of starch and the stability of thermoforming gels. In addition, it inhibits the aging of starch in the dough. However, when FA in the dough was in the range of 61.6% to 63.1%, the water absorption of the dough was lower than that of the control, which may be related to the rupture of the dough caused by FA. FA can reduce dough deformation due to cross-linking reaction with gluten. But the combination of insoluble produces an effect of dietary fiber and ferulic acid, which may be due to the cross-action of these substances and gluten, which increases the viscoelasticity of the dough and reduces the flowability of the dough.

According to Han (2011) [77], the addition of caffeic acid, ferulic acid, gallic acid and syringic acid significantly decreased the mixing tolerance, mixing time and maximum tensile resistance of the dough, while the ductility increased slightly. Among them, the effect of caffeic acid is the most significant. Caffeic and ferulic acids significantly reduced bread volume and increased the content of soluble high-molecular-weight subunits in the dough, suggesting that the structure of gluten proteins has undergone changes that are not conducive to their aggregation, changing the network structure of gluten, an effect that is related to phenolic acids. The antioxidant capacity was positively correlated.

According to Feng et al. (2020) [78], the effect of wheat bran and a mixture of ferulic acid (FA) and dietary fiber (DF) on gluten protein composition was investigated. Addition of wheat bran (100 and 150 g/kg) to gluten decreased the prolamin/gluten ratio and increased the disulfide bond (SS) content without significant changes in the glutenin macroaggregate (GMP) content, while the FA+DF addition group had the opposite effect, that is, the contents of GMP and SS were significantly reduced. After adding wheat bran and FA+DF, the GMP gel properties and microstructure were destroyed. FA+DF additives and wheat bran had different effects on the thermal properties and secondary structure of gliadin, glutenin and GMP. This suggests that the interaction mechanism of gluten and bran components is related to the interaction between additives and gluten components.

1.4 Effects of polyphenols and dietary fiber on nutritional and functional properties of baked foods

Medical studies have shown that a diet rich in natural antioxidants can significantly increase the antioxidant capacity of human organs and reduce many of the risk of the resulting disease. The intake of dietary antioxidants can significantly promote the occurrence of immune responses and enhance the defense capacity of cells [79]. Based on this, the use of natural extracts in food processing in the form of antioxidanbts or functional ingredients has become a new trend in food development and a new direction of research in recent years [80]. In western countries, bread can generally provide more than 50% of people's energy intake. Therefore, they have carried out a lot of research work on bread as a carrier for dietary supplementation of antioxidants. At present, research is mainly carried out in the form of changing the proportion of flour in the bread formula and developing mixed bread flour, which are mainly divided into the following two categories. One is to use grains rich in antioxidants to replace the high-gluten flour in the formula in a certain proportion. For example, the more popular whole-wheat bread today, the total phenolic content of whole-wheat flour is significantly higher than that of refined flour. The antioxidant capacity of the former is 3 times that of ordinary commercial flour baked bread [81]. For example, Slađana et al. (2010) [82] compared the total phenolic, total flavonoid and carotene content of 10 commercial wheat species and 10 durum wheat species, as well as the antioxidant capacity of bread. The results show that durum wheat is rich in Rutin, baked bread has a significant ability to scavenge DPPH free radicals, and both lipoxygenase and peroxidase activities are low. Another example is bran, Sairam et al. (2011) [83] found that the bread added with 15% rice bran was acceptable to the senses, and the addition of rice bran significantly improved the antioxidant and dietary fiber content of bread.

The second approach is to directly add antioxidants or plant extracts, fruits and vegetables, herbal dry powders containing a large amount of antioxidants, such as green tea catechins mentioned above, coriander leaf powder, turmeric powder, and dry onion skin powder [84] and grape seed extract [85]. Such substances have received extensive attention due to their high safety, rich nutrition and potential functional activities. Such additives have high content of polyphenols and a wide range of sources, and can significantly enhance the antioxidant capacity of bread even when the amount of addition is very low, and can also impart a special flavor to the bread.

In addition to antioxidant properties, numerous studies have supported grape phenolic compounds are associated with prevention of chronic degenerative diseases (atherosclerosis, cancer, cardiovascular disease and type 2 diabetes, among others). The ability of polyphenols to influence the postprandial blood glucose level is very important. This effect is mainly reflected in two aspects: inhibit the activity of digestive enzymes and increase the content of resistant starch. According to Barrett's research [86], tannins from four different sources (cocoa powder, pomegranate, cranberry, grape juice) can significantly inhibit the activities of α-amylase and glucose glucoamylase, and tannins may form protein-tannin complexes with enzyme proteins, thus to inhibit the hydrolyze ability of starch. He pointed out that the higher the molecular weight, the higher the degree of polymerization, the more complex the structure of tannins, such as pomegranate and cranberry tannin extracts. Lee et al. (2007) [87] also reported similar research results. He found that the inhibitory ability of polymeric tannins was significantly stronger than that of oligomeric tannins.

Barros et al. (2012) [88] studied the interaction between three different degrees of polymerization sorghum proanthocyanidins and starch, and their effect on starch in vitro digestibility. The results showed that the interaction between high polymerized tannin and oligomeric tannin and amylose was significantly stronger than that of amylopectin; the increase of resistant starch after the interaction between high polymerized tannin and ordinary starch was 2 times that of oligomeric tannin. The interaction between starch and high polymer tannin is stronger than that of oligomer tannin, and it is positively correlated with the content of amylose in starch.

The interaction between tannin and starch mainly exists in the form of hydrophobic bonds. Chai et al. (2013) [89] found that the interaction between tea polyphenols and high amylose starch promotes the aggregation of starch molecules, and tea polyphenols form complexes with starch in the form of hydrogen bonds, which significantly reduces the hydrolysis rate of starch and slows down the release of postprandial blood sugar.

Although the content of GP in a variety of compounds with different properties gives this by-product a wide range of potential functional and technological uses. Many of these choices are due to the content of phenolic compounds with high biological activity (antioxidant, antibacterial, vitamin P effect, etc.). Using products derived from GP can also cause a change in food color, which can have unusual effects. This fact may limit their application in certain food categories.

For example, the addition of grape products in a dose higher than 1% can cause redness in meat color, which after a Maillard reaction, meat products are further darkened and lightened [90]. For white meats such as chicken, a relevant color change was observed even at 0.1% addition [91].

In addition to changes in food appearance, grape pomace may also produce other types of changes in sensory properties, which are often associated with bitterness and astringency in the palate. Increased astringency may be beneficial for some products, such as soft drinks, chocolate, and wine [92]. According to some researchers, biscuits rich in grape pomace have higher sensory scores for fruity and tart flavors. However, increased astringency and bitterness in foods may limit the use of grape pomace on certain food substrates. Given this, the use of sweeteners, a protein complexed with polyphenols, can be considered to limit their interactions with taste receptors and salivary proteins, increase fat content to provide some lubricity, and address these negative effects [93]. Rosales Soto et al. (2012) [94] conducted an extensive study of the effect of grape seed extract on several parameters of three cereal products: cereal bars, pancakes and noodles. Of the three products, cereal bars with 5% grapeseed flour were considered the best choice for added flour. In this case, the grape seed extract improved appearance, taste, taste, mouthfeel, hand and texture attributes. 1% grape extract improved the acceptability of yogurt [95], and 1000 ppm of grape seed extract also improved the acceptability of overall dry sausage [96]. The potential nutritional value and natural origin of grape pomace products may help improve pipeline and consumer willingness to pay more for the product. But the creation of such a product requires careful large-scale research.

The purpose of this work is to study the most interesting proposals to re-evaluate the value of grape pomace and to develop healthy food products using grape pomace, conduct research to create a nutritionally fortified biscuits, which may help reduce the consumption of antioxidants, some of the nutritional problems identified in Western societies with lower average intakes of fiber and minerals.

However, the addition of grape flour requires adjustments to recipes and processing conditions to maintain the quality of the baked product. Various studies have noted modifications caused by these types of flours, e.g., increased alpha-amylase activity, resulting in decreased numbers of droplets, and possible interactions of seed lipids with gluten, starch, and hydrophobic components, resulting in softer dough and increased viscosity, starch gelatinization delay. Conversely, there have also been reports describing the opposite results, such as the enhanced activity of grapeseed flour, which is attributed to covalent or non-covalent bonds between gluten and phenolics, resulting in stronger dough and resistance.

In view of the above comments, it is particularly important and necessary to study the effect of grape pomace flour on wheat dough properties. For example, by studying the effects on thermomechanical properties, the addition amount of grape skin powder or grape seed powder can be determined according to the characteristics of the target product. The product formulation and processing technology can also be further adjusted.

Conclusions of section 1

1. Grape pomace has long been considered a low-value by-product, mainly used as an animal feed ingredient or fertilizer raw material by many small and medium-sized enterprises, greatly underestimating its expected value.

2. Grape pomace is currently receiving increasing attention due to its high content of phenolic compounds, with many studies supporting the role of grape phenolic compounds in the prevention of chronic degenerative diseases (atherosclerosis, cancer, cardiovascular disease and type 2 diabetes effect etc.) related.

3. Many researchers are developing food technologies to add processed grape pomace products, the most common of which are grape extracts and powders. Powders have advantages over extracts because they contain a wider range of unextracted nutrients, including dietary fiber, minerals, phenolic compounds, and more.

4. Grape pomace is added to products for a variety of purposes - extending product shelf life, improving physicochemical and organoleptic quality indicators, increasing nutritional value, and providing therapeutic and preventive properties. However, when developing such technologies, it should be taken into account that the components of grape pomace can interact with the raw ingredients of conventional products and change their properties. Therefore, in the case of adding grape flour to flour products, it is necessary to study its effect on the rheological properties and microstructure of wheat dough and the quality indicators of finished

products. In the future, this will provide a rationale for adjusting food formulations to ensure their nutritional value and sensory quality.

5. Importantly, using grape pomace to process products can not only improve the nutritional value of food, but also create economic benefits and solve the problem of environmental and resource waste cause.

SECTION 2

OBJECT, SUBJECTS, MATERIALS AND METHODS OF RESEARCH

2.1 Object, subjects and materials of research

The object of research in the dissertation was the technology of tough biscuits.

The subjects of research were: gluten properties of wheat flour, indicators of the quality of dough for tough biscuits and finished products with and without the addition of grape powders, including during storage.

The following research materials were used in the work.

Grape powders that were produced from fresh grapes (Cabernet Sauvignon, 2019 crop), obtained from Huailai city (Hebei, China).

Preparation of the various grape powders. The Cabernet Sauvignon grape, grown in Huailai city (2019, Hebei, China), was used as feedstock and fermented with 1 wt% Saccharomyces cerevisiae (Lalvin strain D-254) at 25°C for seven days. The grape pomace (GP) was collected under operating conditions of 25℃, 75 rpm by a laboratory-scale extruder (Shanghai Yulushiye Instrument Co., Ltd., Shanghai, China), and subsequently washed with water for 4-5 times. For grape skin (GSK) and grape seeds (GS), they were manually gathered. The GP, GSK, and GS were placed outside and dehydrated to around 65 wt%, and then transferred to an air-dry oven at 50 °C for 80 h. The dried GP, GSK, and GS were crushed by a laboratory-scale pulverizer (Shanghai Zhikai Powder Machinery Manufacturing Co., Ltd., Shanghai, China) and then screened to gather the powder with diameters less than 120 mesh (i.e., 0.125 mm) (Fig. 2.1).

Low gluten flour with 13.7% protein, 12.3% moisture, and 2.8% fat (Zhaoqing Fugard flour company, Guangdong, China) was purchased from COFCO Co., Ltd. (Beijing, China); eggs, pure milk, palm oil, pure water, sugar, purchased from local supermarkets, were used to make dough and biscuits.

All raw materials met the requirements of regulatory documentation.

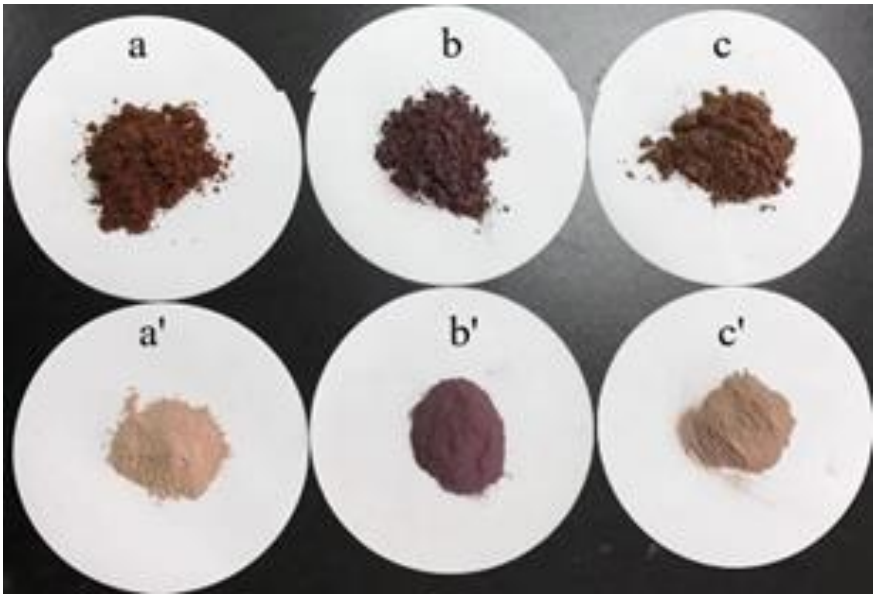


Figure 2.1 – (a) grape seeds powder (GSP); (b) grape skin powder (GSKP); (c) grape pomace powder (GPP); (a’) defatted wine grape seeds powder; (b’) defatted wine grape skin powder; (c’) defatted grape pomace powder

The following reagents were used for research.

2,2-dipheny-l-picrylhydrazyl(DPPH) and Folin-Denis (F-D) reagent (made up of 20 g of sodium tungstate, 4 g of phosphomolybdic acid, 10 mL of phosphoric acid (all purchased from Nanjing Chemical Reagent Co., Ltd., Jiangsu, China), and 150 mL of water, condense and reflux for 2 h, cooled, and dilute to 200 mL), potassium ferricyanide ($K_3Fe(CN)_6$), trichloroacetic acid, ferric chloride ($FeCl_3$), hydrogen peroxide (H_2O_2), petroleum ether, acetone, aluminum nitrate, ferrous sulfate ($FeSO_4$), high-temperature-resistant alpha-amylase solution (30 U/mg), and glycosylase solution (100 U/mg) were purchased from Shanghai Ruji Bio-technology Co., Ltd. (Shanghai, China). Alkaline protease solution (100 U/mg) was purchased from Shanghai Lanji Bio-technology Co., Ltd. (Shanghai, China). Tris-(hydroxymethyl)aminomethane (Tris) was bought from Sigma-Aldrich Chemical Co. (St Louis, MO, USA). Folin-Ciocalteu (FC) phenol reagent and tannic acid were purchased from Aladdin (Shanghai, China), gallic acid, Rutin were the products of Sigma (St. Louis, MO, USA). 2-(4-Morpholino) ethanesulfonic acid (MES).

Glucolactone, ammonium bicarbonate, baking soda, sodium chloride, 3,5-Dinitrosalicylic acid, glycerol, anhydrous ethanol, diethyl ether, petroleum ether; ascorbic acid, salicylic acid, methanol, butanol, ethanol, ammonium ferric sulfate, saturated solution of sodium carbonate, methyl red, nitric acid, hydrochloride, sodium hydroxide and other chemicals were of analytical grades.

The plan of theoretical and experimental research on the topic of the dissertation is shown in Fig. 2.2.

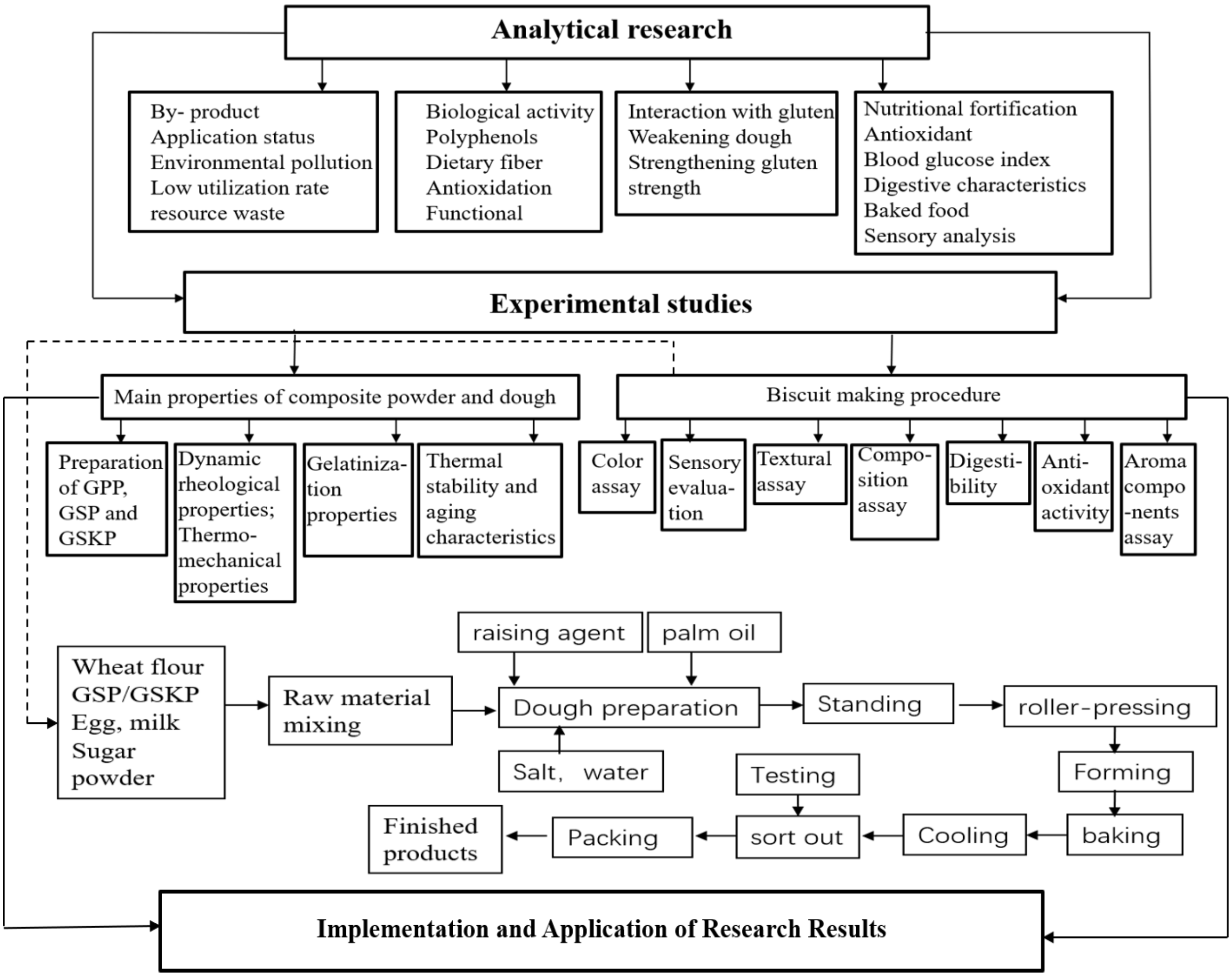


Figure 2.2 – The plan of theoretical and experimental research

2.2 Research methods

Chemical compositions of the various grape powders

General Composition: Moisture, ash, protein, and lipid content of GP, GS, and GSK powders were determined using AACCI-approved methods 44-15, 08-01, 46-11, and 30-10, respectively [97]. Total sugar content was determined using direct titration [98]. Total dietary fiber (TDF), insoluble dietary fiber, and soluble dietary fiber content were determined using an enzymatic gravimetric method [99].

Trace element analysis and minerals: The content of mineral elements was detected using inductively coupled plasma optical emission spectrometer (ICP-OES) according to AACCI approved method [100] (AACC International 2016).

Microwave digestion: Weigh different amounts of GSK (0.5015, 0.5019, 0.5023, 0.5029 and 0.5031 g), GS (0.5009, 0.5015, 0.5017, 0.5021 and 0.5028, g) and GP powder (0.5011, 0.5018, 0.5019, 0.5024 and 0.500 g) respectively g), and add it to the digestion tank together with 4 mL of concentrated nitric acid. Shake the mixture under the following microwave digestion procedure (Table 1.1): initial heating to 100 °C for 10 min, hold for 1 min, heating to 180 °C for 8 min, and hold at this temperature for 25 min.

Table 1.1

The digestion conditions

Steps	Heating-up time	Temperature	Holding time
1	5	120	10
2	5	150	10
3	5	170	10
4	5	180	15

After digestion, rinse the sample solution several times with ultrapure water in a 25 ml stoppered colorimetric tube, then dilute to volume. Reagent blanks were also tested.

Determination of polyphenol components in different grape powders: The tannin content of the three groups of grape powders was determined by sodium tungstate-phosphomolybdic acid colorimetry at 765 nm wavelength [101], while the total polyphenol and proanthocyanidin contents were determined by ultraviolet the spectrophotometric measurements were performed using FC phenol reagent and a molybdate-catalyzed colorimetric method, respectively [102]. The total flavonoid content was determined by the aluminum nitrate-sodium nitrite method [103]. The polyphenol components of various samples were analyzed by high performance liquid chromatography mass spectrometry-tandem mass spectrometry (HPLC-MS/MS) [104]. To obtain polyphenol extracts, GS, GSK, and GP samples were separately extracted in methanol in a shaking water bath (Shanghai, China, SHA-C) at 25 °C for 24 h in the dark. Then, the extract was centrifuged at 6000 rpm fo for 15 min, and the supernatant was concentrated in vacuo at 30 °C and made up to 25 ml with Crypt-grade methanol. The chromatographic conditions were: mobile phase A, 0.1% acetic acid aqueous solution (volume fraction); mobile phase B, acetonitrile; flow rate, 0.4 mL/min; column temperature, 30 °C; one-d injection volume, 5 μl. Gradient elution conditions were: 0–15 min, 10% B; 15–20 min, 10%–35% B; 20–23 min, 35%–90% B; 23–24 min, 90% B; 24–30 Minutes, 90%-10%B. The MS conditions were as follows: electrospray ion source; ion source temperature, 325°C; dry gas flow rate, 10 mL/min; sheath gas flow rate, 11 L/min; sheath gas temperature, 350°C; capillary voltage, 3000 V. Multiple reaction assay was used.

Preparation of a polyphenol extract from grape pomace for antioxidative activity assay

To extract the polyphenols, 10 g of GP powder was first degreased with petroleum ether for 12 hours. Then, the samples were mixed with 70% ethanol at a ratio of 1:5 (sample:ethanol, w/v), and six ultrasonic-assisted extractions (40 min each) were performed using an ultrasonic power of 250 W and an extraction temperature of 30 °C. . All extracts were then collected and filtered, and an equal volume of each filtrate (50 mL) was concentrated in vacuo.

Free radical scavenging test

The DPPH free radical scavenging activity of GP polyphenol extracts was determined using a previously published method [105]. Briefly, 2 mL of ethanol samples of different concentrations were each mixed with 2 mL of 2 mmol/L DPPH in ethanol and incubated at ambient temperature for 30 min. The absorbance of the DPPH-reactive samples (Ai) was then measured at 517 nm using a UNICO spectrometer (Shanghai, China). Under the same experimental conditions, controls (Ac) containing ethanol instead of samples were also measured. The absorbance of the original unreacted sample in ethanol was recorded as Aj. Finally, the DPPH radical scavenging activity of the sample was calculated using the following formula: DPPH scavenging activity (%) = [1–(Ai–Aj)/Ac] ×100%. A comparison of the antioxidant activity of vitamin C at the same concentration as the sample was also tested.

Hydroxyl radical scavenging assay

The hydroxyl radical scavenging activity of GP polyphenol extracts was determined using a previously reported method [106]. Briefly, 2 ml of sample solutions of different concentrations were mixed with 1 ml of 9 mmol/l FeSO4 and 1 ml of 9 mmol/l salicylic acid-ethanol, and the reaction was activated by adding 1 ml of 8.8 mol/l H2O2 solution. After 30 min incubation in a 37°C water bath, the absorbance of the sample (Ax) was measured at 510 nm using a UNICO spectrometer. Control 2 ml of deionized water instead of ferrous sulfate and salicylic acid-ethanol solution (Ax0) Under the same experimental conditions, 2 ml of deionized water was also measured instead of the sample solution (A0). When measuring A0, using the system without H2O2 addition as the reference solution and using deionized water as the reference sample for the determination of Ax and Ax0 The radical scavenging activity of the sample is calculated as follows: Hydroxyl radical scavenging rate (%) = [A0-(AX -AX0)/A0] ×100%. A comparison of the antioxidant activity of vitamin C at the same concentration as the sample was also tested.

Determination of reducing power

The reducing power of GP polyphenol extracts was determined according to a previously published method [107]. Briefly, 2.5 ml of samples at different concentrations were mixed with 2.5 ml of PBS (pH 6.6) and 2.5 ml of 10 mg/ml

K3Fe(CN)6 solution and incubated in a 50 °C water bath for 20 min. Then, after the solution had cooled, 2.5 ml of 100 mg/ml trichloroacetic acid was added, and the mixture was centrifuged at 3000 rpm for 10 min. Then, 2.5 ml of water and 0.5 ml of 0.1% ferric chloride were added to the supernatant, and the absorbance at 700 nm was measured using a UNICO spectrometer. A comparison of the antioxidant activity of vitamin C at the same concentration as the sample was also tested.

Determination of antioxidant properties of biscuits: add 0.5 g of sample powder to 10 ml of 80% methanol solution at 25 °C, and extract in the dark for 24 hours. The mixture was then centrifuged at 10,000 r/min to obtain the supernatant, which was used for subsequent measurements to evaluate its DPPH radical scavenging ability, hydroxyl radical scavenging activity, and iron ion reducing activity.

Dough Sample Preparation

For compound flour preparation, GPP, GSKP, or GSP were uniformly mixed with different additional levels of wheat flour (i.e., 5%, 10%, 12.5%, 15%, and 20%, according to the authors' previous studies). Using a laboratory scale kneader, a dough was prepared by adding water to the above well-mixed compound flour, the dough mixing time was 8 minutes, and the amount of water added was calculated from the water absorption measured by Mixolab.

Color measurement

The color of the composite flour was measured using an ADCI-60-C Hunter Colorimeter (Hunter Associates Laboratory Inc., Reston, USA) equipped with the CIE L*, a* and b* color systems. Where L* represents whiteness (100) or blackness (0), a* represents red (positive) or green (negative), and b* represents yellow (positive) or blue (negative). Colorimeters are calibrated using standards.

Particle size measurement

The particle size distribution of the composite flour was measured by a Malvern Laser Particle Size Analyzer (Malvern Mastersizer 3000, Malvern, UK). A 1.5 g sample is typically dispersed in absolute ethanol to form a suspension with a shadow coefficient of 9.80% and a refractive index of 1.333. Results are expressed as D90 and D50.

Rheological properties of dough

Thermomechanical properties. Thermomechanical properties of composite doughs with different percentages of GPP, GSKP or GSP were evaluated using Mixolab 2 (Villeneuve la Garenne Chopin Technologies, Paris, France). The analytical method is mainly based on the standard “Chopin+” protocol specified by ICC No. 173, while some operating parameters are slightly modified according to the published method [108]. Briefly, the mixing speed was 80 rpm, the target torque was 1.1 Nm, and the temperature profile was: hold at 30°C for 8 minutes, heat to 90°C at the hold rate, hold at 4°C/min for 7 min, then cooled to 50°C at 4°C/min (total time 45 min).

The Mixolab experiment mainly evaluates the following parameters: water absorption (WA, %), dough development time (DTT, min), stability (ST, min), minimum torque (C2, Nm), peak torque (C3, Nm), after heating the torque (C4, Nm. It is worth noting that the weakening rate, starch gelatinization rate, and enzymatic degradation rate of gluten protein can be derived from the torque curve, so α, β, and γ are used as markers, respectively.

Dynamic rheological properties. Dynamic viscoelasticity measurements of the samples were evaluated at a temperature of 25 ± 0.1 °C on a Haake MARS III controlled stress rheometer (Haake, Germany) equipped with a 1 mm gap parallel plate sensor system. The water absorption of the samples was determined after kneading with a KitchenAid flour kneader for 8 minutes, and then the samples were transferred to a rheometer plate where excess dough was scraped off. The exposed dough was specially covered with mineral oil to avoid moisture loss. The test parameters refer to a published method [109]. Frequency sweep testing is performed as a function of frequency from 0.1 to 10 Hz.

Microstructure of dough

The microstructure of the composite dough samples was observed using scanning electron microscopy (FEI, Hitachi, USA) according to the published method proposed by Nie et al. [110]. Briefly, samples added with different levels of GPP, GSP or GSKP were cut into slices less than 5 mm in diameter and 2–3 mm in thickness, and then freeze-dried. Dried dough slices with a natural fracture surface were passed through conductive resin, coated with gold, and then scanned under low vacuum and 20kV.

Determination of gelatinization properties

The RVA-TecMaster rapid viscosity analyzer was used for the determination according to the method of AACC 76-21 [97]. Accurately weigh 3.00 g of the sample in a RVA (Peron Scientific Instruments Co., Ltd., Sweden) graduated cylinder, add 25 mL of water, and after the flour is uniformly dispersed by stirring the slurry, then stick into the RVA rotating tower, and measure according to standard method 1 Gelatinization temperature, peak viscosity, minimum viscosity, final viscosity, breakdown value and receding value were recorded. The assay parameters are shown in Table 2.2, and each sample was repeated three times.

Table 2.2

Determination parameters of standard method 1 of RVA

Steps	Time	Types	Values
1	00:00:00	temperature	50 ℃
2	00:00:00	rotational speed	960 r/min
3	00:00:10	rotational speed	160 r/min
4	00:01:00	temperature	50 ℃
5	00:04:42	temperature	95 ℃
6	00:07:12	temperature	95 ℃
7	00:11:00	temperature	50 ℃
End of test	00:13:00	temperature	50 ℃
		Reading time interval	4 s

Determination of thermal stability and aging properties

Weigh 1.00 g of the dry powder of the sample and add 2 mL of water to uniformly stir the paste. A paste sample of 8-12 mg was then weighed in an aluminum crucible, and the aluminum lid was pressed and sealed. Taking the empty crucible as a control, it was measured by DSC (Q200 Differential Scanning Calorimeter, TA Company, USA). The scanning temperature range was 20–120°C, and the heating rate was 10°C/min. Onset temperature (To), peak temperature (Tp), end temperature (Tc) and enthalpy (ΔH) were recorded [111].

The thermodynamic curve

Mixolab Chopin+ converts the standard curve into six quality indicators, expressed on a scale of 0-9 (Mixolab-index): – Water absorption index (a function of flour constituents (protein, starch, fiber)). It affects dough yield. The higher the value, the more water is absorbed by the flour. – The mixing index represents the behavior of the dough during mixing (stability, development time and weakening). High values correspond to high gluten stability of the dough when mixed + index represents the behavior of the gluten when the dough is heated. High values correspond to high gluten resist heating angles. – The viscosity index indicates the increase in viscosity during heating. It depends on amylase activity and starch quality. High values correspond to the high viscosity starch breakdown index of the dough during heating, the ability of the starch to resist starch breakdown. High values correspond to reduced amylase activity. The retrogradation index represents the properties of the starch and its hydrolysis during the test period. A high value corresponds to a low shelf life of the final product.

Single factor experiment

Based on the basic process formula, biscuits were prepared according to the production process (Fig. 2.1) of tough biscuits. The effects of grape seed / grape skin powder addition (0%, 5%, 10%, 12.5%, 15%, 20%, calculated by grape powder weight/ composite powder weight) on texture, color and quality of biscuits, baking temperature (155℃, 160℃, 165℃, 170℃, 175℃), sugar powder addition (25%, 30%, 35%, 40%, 45%), palm oil addition (5%, 6%, 7%, 8%, 9%)

and compound additive (baking soda : glucolactone : ammonium bicarbonate) addition (0.4:0.6:0.8; 0.6:0.8:1.0; 0.8:1.0:1.2; 1.0:1.2:1.4; 1.2:1.4:1,6） on the quality of biscuits were investigated. Once the biscuits have cooled to room temperature, they are ready to pack. For GC-MS analysis, the biscuits were pulverized into a fine powder and stored in a refrigerator at –20 °C. For sensory evaluation, biscuits were made on the same day.

Sensory evaluation of tough biscuits

Biscuits containing different amounts of GPP were evaluated by quantitative descriptive sensory analysis using a hedonic 9-point scale as follows: 9, extremely like; 8, very like; 7, moderate; 6, slightly like; 5, neither like nor not disliked; 4. Slightly disliked; 3. Moderately disliked; 2. Very disliked; 1. Extremely disliked. 20 participants, aged 19-21 years. First, strength criteria and sensory attributes are established. These terms include color, appearance, taste and texture. Second, the participants received six sessions of training (one hour each) to allow for a reasonable assessment. Third, randomly coded biscuits were randomly placed and evaluated by each member after gargling. Sensory evaluation results are described as x (mean) ± SD (n=3).

Texture analysis

The hardness, crispness and chewiness of the biscuits were measured by a texture analyzer (TA-XT2i Texture Analyzer, Stable Micro System, UK). The measurement parameters are as follows: the probe type is P/36R, the speeds before, during, and after measurement are 1.0, 1.0, and 2.0 mm/s, respectively, and the compression ratio is 70%. 3 times in parallel. Results are expressed as x (mean) ± s (n=3).

Digestive properties measurement

The contents of rapidly digestible starch (RDS), slowly digestible starch (SDS) and resistant starch (RS) were determined according to the methods proposed by Mahasukhonthacat et al. [112] and Englyst et al. [113] and treated with 3,5-dinitro water The content of reducing sugar was determined by the salicylic acid colorimetric method. The equation is as follows:

$$\text{SDS (\%)} = \frac{(\text{G120} - \text{G20}) \times 0.9}{TS} \times 100\% \tag{1}$$

$$\text{RDS (\%)} = \frac{(\text{G20} - \text{G0}) \times 0.9}{TS} \times 100\% \tag{2}$$

$$\text{RS (\%)} = \frac{[TS - (\text{SDS} + \text{RDS})] \times 0.9}{TS} \times 100\%, \tag{3}$$

where G_{120}-Glucose content at 120 min, mg;

G_{20}-Glucose content at 20 min, mg;

G_0-glucose content at 0 min, mg;

0.9-transformation factor;

TS stands for sample weight, mg.

The hydrolysis rate (%) is the weight of the hydrolyzed glucose divided by the total sample weight. The hydrolysis index (HI) represents the area under the hydrolysis rate curve divided by the area under the hydrolysis rate curve of the control group. The glycemic index (GI) was determined according to the method of Goni et al. [114] using an in vitro simulation of the human intestinal digestive system. Biscuits' hydrolysis rates were fitted with first-order kinetics

$$C_t = C_\infty \times (1 - e^{-kt}), \tag{4}$$

where C_∞ – equilibrium concentration;

k – equilibrium coefficient.

The calculation of area under the sample hydrolysis curve was fitted as follow

$$AUC = C_\infty(t_f - t_0) - \left({C_\infty}/{k}\right)\left[1 - e^{-k(t_f - t_0)}\right] \tag{5}$$

where $C\infty$ – equilibrium concentration (t_{180});

t_f –final time (90min);

t_0 – initial time (0min);

k – equilibrium coefficient.

Aroma components analysis

Aroma components in biscuits were determined by headspace solid-phase microextraction combined with GC/MS analysis according mainly to the method documented by Pasqualone et al. [115] with some modifications. In brief, 4 g sample was placed into a sealed sample bottle, and then transferred to a magnetic stirring heating table operated at 60 ℃ for 10 min. Subsequently, an activated extraction head (75 μm, CAR/PDMA) was inserted into its upper void space, which was 1.5 cm above the sample powder. After heating at 50 ℃ for 1h, gas-solid and gas-liquid equilibrium were reached, and then the extraction head was inserted into the GC inlet and suffered from thermal desorption at 230 ℃ for 3 min. GC was equipped with a HP-5 column (30 m×0.25 mm×0.25 μm), and the following temperature profile was used: starting at 25 ℃ and maintaining for 3 min, heating to 130 ℃ at a rate of 2 ℃/min and holding for 1 min, and then ramping up to 210 ℃ at a rate of 5.5 ℃/min and lasting for 3 min. MS was equipped with an electron ionization source working under electron energy of 70 eV, and interface temperature and ion source temperature were both 230 ℃. Mass scanning was in the range of 33 to 260 U. Each sample was tested for 3 times. The compounds were identified mainly by searching the NIST library. Semi-quantitative analysis was carried out by the the peak area normalization method.

Determination of peroxide value of biscuits during storage

The grape pomace biscuits were prepared according to the optimal process and stored at 37 °C, 47 °C and 57 °C for 6 weeks, respectively, and sampled every other week. 100 g grape pomace biscuits were weighed and placed in a 500 mL conical flask with plug, and 100 mL petroleum ether was added. After mixing, the biscuits were placed for 12 h, and the oil was filtered and recovered by decompression, and the peroxide value was determined. The peroxide value of biscuits should not exceed 0.25g / 100g and acid value should not exceed 5mg / g according to GB5009.56-2003 “Analysis method of cake hygienic standard" the results were expressed as mean ± standard deviation.

Kinetic study on oxidative rancidity of oil

According to the previous reports, the oxidative rancidity of edible oils follows the first-order kinetic equation [116-117], and the mathematical relationship between oxidative rancidity of edible oils and storage time [118] is as follows:

$$ln[POV] = bt + ln[POV_0], \tag{6}$$

where POV – measured peroxide value, g/g;

b – rate constant of food oxidation, day^{-1};

t – storage time, day;

POV_0 – initial peroxide value, g/g.

Grape pomace biscuits were stored at a constant temperature. The peroxide value of grape pomace biscuits at different storage time was measured. The *ln [POV] - t* graph was drawn with the peroxide value *ln [POV]* as Y axis and the time t as X axis, and the *b* value was calculated by linear fitting.

Prediction of shelf life of grape pomace biscuits at different temperatures

According to the national standard, the maximum limit value of *[POV]* is 0.25 g/100g, and the initial peroxide value and the upper limit value of *[POV]* are inserted into the equation (6) to predict the shelf life of grape pomace biscuits at constant temperature.

The shelf life of food and its storage temperature fit the following equation:

$$\ln T = mS + n, \qquad (7),$$

where S – shelf life, day;

T – storage temperature, °C;

m and n – equation constants, which are obtained by linear fitting.

Validation of shelf-life model

Grape pomace biscuits were stored at 37 °C, 47 °C, 57 °C. The peroxide value was measured at different storage time until the indicators exceeded the specified value. Paralleled three times, the results are expressed as average. The experimental measurement results were compared with the predicted values of the model, and the credibility of the model was verified according to the standard deviation.

Statistical analysis

All experiments were conducted in triplicate, and the results were expressed as the mean ± standard deviation. Dunnett's T3 test was applied for multiple comparisons and differences were statistically significant at $p < 0.05$. SPSS version 17.0 (SPSS Inc., Chicago, IL, USA) was used for all statistical evaluations, and OriginPro 8.6.0 was used for the construction of the graphs.

SECTION 3

DETERMINATION OF CHEMICAL COMPOSITION OF GRAPE POMACE POWDERS AND ITS EFFECT ON PROPERTIES OF WHEAT DOUGH

3.1 Chemical compositions and antioxidant properties of the grape powders

3.1.1 General compositions

According to the review of the scientific literature, the chemical composition of grape powders largely depends on the grape variety, growing conditions, and other factors. Therefore, it was important to study the chemical composition of exactly those powders that were used in the work. The results of the research are presented in the Table. 3.1.

Table 3.1

Chemical compositions of the various grape powders (%, on dry weight)

(n=3, P≥0,95)

Component	Grape seeds powder	Grape skin powder	Grape pomace powder
Crude protein	8.75	16.31	13.62
Crude fat	20.92	10.66	17.46
Ash	2.98	3.95	6.02
Moisture	3.69	4.51	5.86
Total dietary fiber	68.53	59.38	65.20
Total carbohydrate	57.04	50.25	51.66

It can be seen that the main component of dried grape pomace is dietary fiber. Their content ranges from 59% to 68%, which positively influence on maintaining normal gastrointestinal function and lowering blood pressure. Powder from grape seeds contains much more dietary fiber than from skin.

The low moisture content of grape powders will affect the formation of the gluten matrix during dough kneading and the stability of its structure. The highest amount of ash is contained in the powder from grape pomace, while the smallest – in the powder from grape seeds, which correlates with the data [119].

The protein content of raw materials in grape seed, skin and fruit residue powder is 8.75%, 16.31% and 13.62% respectively, which is also consistent with the research results [120]. In general, the protein content of raw materials in grape dregs, seeds and pericarp is higher than that in some grain seeds (for example, the protein content in corn seed meal is 8.60%).

The content of raw fat in grape seed was the highest (20.92%). This corresponds to the information that the energy of grape seed is 22.64 MJ/kg due to the high fat content [121].

The mineral composition of grape powder was studied. The obtained data of main mineral element content in various powders are shown in the Table 3.2.

Table 3.2

Contents of minerals and trace elements in grape powder (mg/g)

(n=3, P≥0,95)

Element	Grape seeds powder	Grape skin powder	Grape pomace powder
K	7.36	22.74	18.67
Na	0.27	0.36	0.31
Ca	5.57	2.27	3.78
Mg	1.28	0.77	1.12
Fe	0.025	0.079	0.061
Zn	not detected	not detected	0.001
Cu	0.019	0.092	0.078
Mn	0.002	not detected	not detected
Cr	not detected	not detected	not detected
Se	0.002	not detected	not detected

Grape residue powder is characterized by high potassium, sodium, calcium, magnesium and other major physiological useful elements, as well as iron, copper, zinc, manganese, chromium and other essential trace elements for human body.

Selenium, known as an anti-cancer element, also exists in grape seed powder.

The lead content of all samples does not exceed the national standard of Green Food – Dry Fruits (NY/T 1041-2010) and Green Food – Temperate Fruits (NY/T 844-2010): lead content ≤ 1 mg/kg, cadmium content ≤ 0.05 mg/kg. Cadmium was not detected in samples of grape powders.

All samples of grape powders differ from each other in the content of mineral elements.

The contents of K, Na, Fe, Cu and Cr in grape skin powder were significantly higher than those in grape seed powder, especially K and Na, which reached 22.75 and 0.365 mg/g respectively. Grape seed powder is characterized by high content of calcium and magnesium, and its content (5.576 and 1.287 mg/g respectively) is significantly higher than grape skin powder.

In addition, the contents of selenium, manganese and zinc in grape seed powder are 2, 2 and 1 mg/kg respectively.

These results differ significantly with respect to the content of Se in grapes, which is described in the literature [122-125]. This may be due to the varieties of studied grape samples and their diverse origins.

3.1.2 Polyphenolic compositions of three types of grape powders

The polyphenol composition of grape powders was studied using HPLC-MS/MS (high-pressure liquid chromatography-tandem mass spectrometry) methods. The resulting chromatograms are shown in Fig. 3.1.

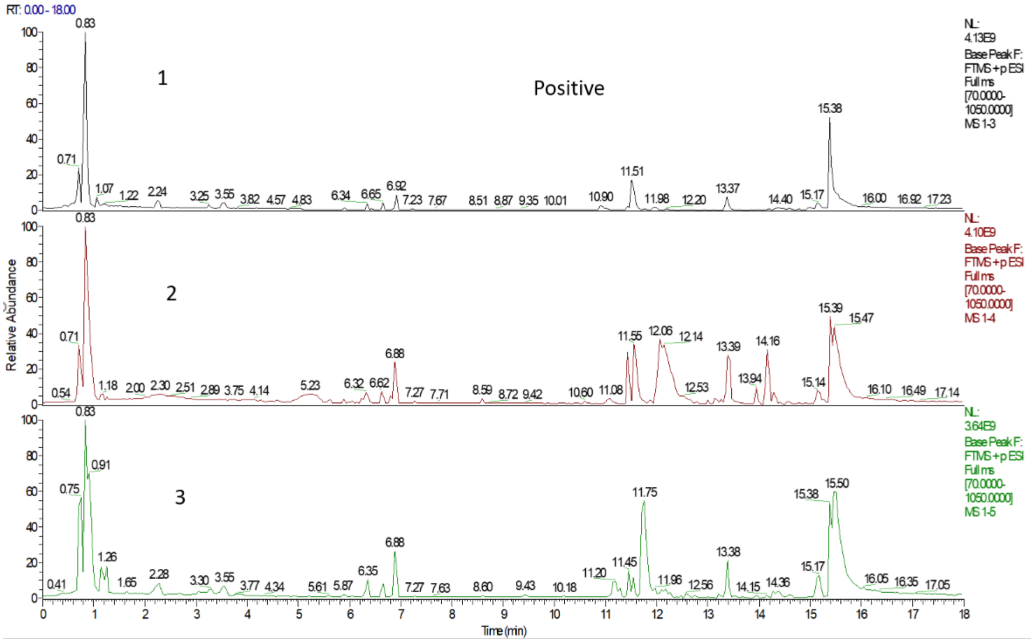


Figure 3.1 – HPLC-MS/MS chromatograms of polyphenols in various grape powder samples. 1: Grape seeds; 2: Grape skin; 3: Grape pomace

Quantitative analysis results of polyphenols in grape seed and peel powder are shown in the Table 3.3.

Table 3.3

Polyphenolic compositions of grape powders (mg/kg)

(n=3, P≥0,95)

Component	Grape seeds powder	Grape skin powder
1	2	3
Epicatechin	405.51	87.70
Epicatechin gallate	7.85	2.99
Epigallocatechin gallate	2.00	1.84
Gallic acid	152.57	65.53
Coumaric acid	1.24	0.50
Vanillic acid	93.65	125.00
Syringic acid	3.56	40.89
Catechin	316.80	69.62
Myricetin	59.98	250.40
Morin	10.92	33.64

Table 3.3 Continued

1	2	3
Quercetin	1.64	33.17
Isorhamnetin	0.89	11.24
6-Gingerol	0.15	0.04
Kaempferol	1.13	3.21
Luteolin	0.28	0.73
Isoquercitrin	10.74	0.02

It can be seen that both powders are rich in polyphenols, but the contents are different. Therefore, about 80% of the non-anthocyanidin polyphenols in grape seed powder are flavan-3-ol polyphenols, and the polyphenols extracted by methanol reach 707.48 mg/kg, which is significantly higher than benzoic acid and flavonol.

Grape skin mainly contains flavonol alcohols (quercetin, mulberry, myricetin, etc.) and benzoic acid derivatives (vanillic acid, syringic acid, gallic acid, etc.), while flavan-3-ol (catechin, epicatechin, epicatechin gallate, epicatechin gallate) and cinnamic acid (i.e., only 0.5 mg/kg coumaric acid) are insignificant.

Grape seeds also contain low concentrations of cinnamic acid. The results obtained are consistent with those of other studies [104, 126-127].

GS and GSK contain large amounts of polyphenols. GSK has the highest content of flavonol (quercetin, mulberry, myricetin, etc.) and benzoic acid polyphenols (vanillic acid, syringic acid, gallic acid, etc.), while flavanol (catechin, epicatechin, epicatechin gallate, epicatechin gallate) and cinnamic acid polyphenols (i.e., only 0.5 mg/kg coumaric acid). In the GS sample, about 80% of the non anthocyanin polyphenols are flavan-3-ol polyphenols, of which the methanol extraction reaches 707.48 mg/kg, significantly higher than flavonol polyphenols and benzoic acid. GS also contains low concentrations of cinnamic acid. These data are consistent with the results of other studies [104126-127]. It should be noted that the content of quercetin in GS sample is much lower than that reported in the past [104128], while the content of isoquercitrin is much higher than that reported in the past [104128]. This may be because the polyphenol composition in GP depends on many factors, such as grape variety, growth climate, geographical environment, fermentation time and maturity [129-130]. Among various polyphenols of GSK, the content of benzoic acid and flavonol is the highest, followed by flavane-3-ol, cinnamic acid and stilbene. In contrast, GS sample has the highest content of non anthocyanin polyphenols, especially flavan-3-ol polyphenols. The content of flavonol polyphenols and benzoic acid in GS sample is lower than that of flavan-3-ol polyphenols, which is similar to GSK sample. GS only contains trace stilbene and cinnamic acid. In GP samples, myricetin has the highest flavonol content, followed by morin, quercetin, isorhamnetin and kaempferol, and its flavonol content is higher than GS. Epicatechins and catechins are dominant in GS samples and GSK samples, accounting for 96% - 100% of total flavan-3-ol polyphenols. In addition, the content of epicatechin and catechin in GS sample is significantly higher than that in GSK sample ($p<0.05$), which is consistent with other studies [104]. Research shows that GS and GSK contain a certain amount of resveratrol, and resveratrol in red GSK is 1.11-12.3 mg/100 g [104], this is inconsistent with the results of this study. This is closely related to the solvent used for extracting GP and the pretreatment method. In addition to resveratrol, GP also contains a certain amount of stilbene compounds, while the content of other stilbene compounds is very low.

These phenolic substances endow wine with a variety of flavor characteristics and colors, and constitute an important factor of wine quality [131-132]. The content of total phenols, total flavonoids, tannins and procyanidins in GS powder is higher than that in GSK and GP powder (Table 3.4).

All data are expressed as mean ± standard deviation (n=3) in mg/g DW. DW, dry weight; GS, grape skin; GSK, grape skin; GP, grape residue; GAE, gallic acid equivalent; RE, rutin equivalent; TAE, tannic acid equivalent; CE, anthocyanin equivalent.

The total phenol content in GS, GSK and GP powders was the highest, 92.68 mg/g, 56.43 mg/g and 87.21 mg/g respectively, followed by tannin and procyanidins.

Table 3.4

The amounts of the main phenolics in various grape samples

(n=3, P≥0,95)

Items	Standard Equation	Standard Plasmids	GSP	GSKP	GPP
Total polyphenol (mg GAE·g^{-1}DW)	Y=0.0133x-0.0045 R^2=0.9995	Gallic acid	92.68	56.43	87.21
Flavonoid mg (RE·g^{-1}DW)	Y=0.0827x+0.0006 R^2=0.9994	Rutin	9.86	2.50	7.20
Tannins (mg TAE·g^{-1}DW)	Y=0.057x+0.0256 R^2=0.9911	Tannic acid	19.28	13.49	17.91
Procyanidine (mg CE·g^{-1}DW)	Y=0.0048x+0.0226 R^2=0.9956	Procyanidine	84.50	37.21	71.08

Proanthocyanidins endow wine with astringency and bitterness, and are the key quality components and important taste substances of wine [133]. They can also combine with anthocyanins to form a stable condensate during wine aging, thus ensuring the stability of wine color [134]. In addition, proanthocyanidins are strong antioxidants with the ability to absorb oxygen free radicals. Their antioxidant activity has been found to be 50 times of vitamin E and 20 times of vitamin C [135]. On tannin, Zhang et al. [136] Studied their effects on gluten structure, dough properties and bread quality, and found that they can not only destroy disulfide bonds, but also have a positive impact on bread quality and dough properties. These authors then used this property to study new, safe and efficient flour additives. To sum up, the content of flavonol and benzoic acid polyphenol in wine grape skin is the highest, followed by flavane-3-ol polyphenol, and the content of cinnamic acid polyphenol and stilbene in wine grape skin is almost minimal. The highest content of non anthocyanidin polyphenols in wine grape seeds is flavan-3-ol polyphenols, accounting for about 80% of non anthocyanidin polyphenols in grape seeds. Among them, flavan-3-ol polyphenols extracted with methanol reached 707.66 mg/kg.

Among them, flavan-3-ol polyphenols that was extracted by methanol reached 707.66 mg/kg. The contents of flavonol polyphenols and benzoic acid in wine grape seeds were lower than those of flavan-3-ol polyphenols, and were similar to those of grape skin. Grape seeds also contained only a small amount of stilbene polyphenols and cinnamic acid.

3.1.3 Antioxidative activity of the polyphenol extract from grape pomace

At present, three authoritative methods are used to determine antioxidants in herbal ingredients; Namely, DPPH and hydroxyl radical scavenging test and reduction capacity test.

As shown in Fig. 3.2, GP polyphenol extract has a strong DPPH radical scavenging capacity, and it also shows higher antioxidant activity than vitamin C even at low mass concentration, and the activity increases with the increase of mass concentration. At a mass concentration of 2 µ At g/mL, the DPPH free radical scavenging activity of the extract was 85.80%, 54.3 times that of vitamin C (1.58%). The determination of hydroxyl radical scavenging (testing the H donor capacity of the sample) showed that polyphenol extract was more active than vitamin C in capturing free radicals. In addition, according to the determination of iron ion reduction capacity, the electron donor effect of polyphenol extract is also significantly higher than that of vitamin C.

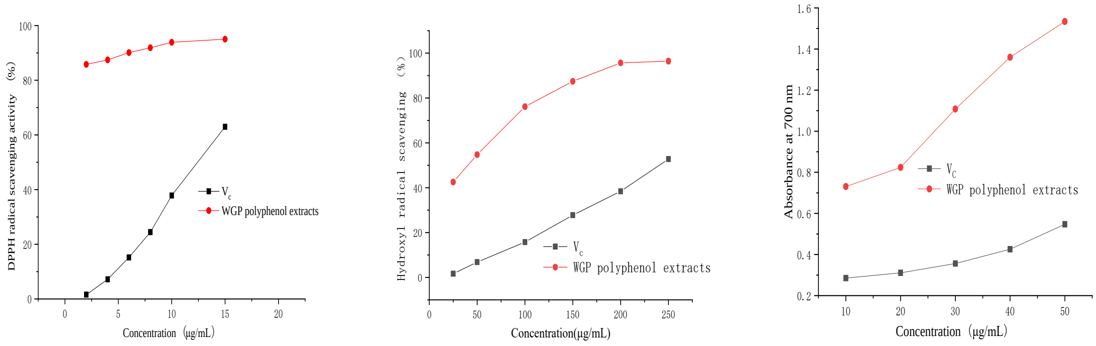


Figure 3.2 – Antioxidant activity of polyphenol extract and vitamin C (Vc) from grape wine residue (WGP). (a) DPPH radical scavenging activity; (b) Hydroxyl radical scavenging activity; (c) Reduce power

Three authoritative antioxidant tests have been carried out, which are usually used for antioxidant evaluation of plant ingredients [137]. It can be seen from Fig. 3.2 that WGP polyphenol extract has a strong scavenging effect on DPPH free radicals, showing a higher scavenging effect at a lower mass concentration, and continues to increase with the increase of mass concentration. Mass concentration is 2 μ At g/mL, the free radical scavenging rate of DPPH was 85.80%, 54.3 times that of vitamin C (1.58%). The elimination of hydroxyl radicals determined is related to the H donor capacity of the sample. It was found that the scavenging capacity of WGP polyphenol extract to hydroxyl radical was much higher than that of vitamin C. Iron ion power reduction test can reflect the electron feeding ability of the sample. The performance of WGP polyphenol extract is obviously better than that of vitamin C.

3.2 The influence of Cabernet Sauvignon wine grape pomace powder addition on the rheological and microstructural properties of wheat dough

3.2.1 Color measurement

The flour color plays an important role in final products (e.g., bread, cookie, etc.), as it has non-negligible impact on product acceptability for consumers. As shown in Table 3.5, GPP, GSP, and GSKP addition had a significant influence on wheat flour color.

Wheat flour added with GPP, GSP or GSKP showed a decrease in L * value and an increase in a * value, indicating that these additives can reduce brightness and increase dark rose color compared with the control group without any additives (i.e., 0 wt% addition level). GSKP generally had a higher degree of influence on both L* and a* values than GSP. For 10 wt% GSKP and 10 wt% GSP addition, L* values decreased 23.06% and 6.38%, respectively, while the a* values increased 87.95% and 48.77%, respectively, which could be attributed to the larger amounts of pigments in GSKP. Besides, the more GPP powder was added, the smaller the L* value and the larger the a* value. GSKP addition resulted in a decreased b* value, thus rendering a blue color of the samples.

Table 3.5

Effect of GSKP on the color of wheat flour

(n=3, P≥0,95)

Samples	Addition level (wt%)	L*	a*	b*
WF[*]	0	92.44	0.83	12.27
GSP[*]	5	87.80	1.53	10.30
	10	86.54	1.62	9.33
	12.5	83.77	2.62	9.27
	15	82.09	3.95	10.42
	20	80.87	4.37	10.68
GSKP[*]	5	77.01	4.98	7.48
	10	71.12	6.89	6.57
	12.5	69.19	7.41	6.39
	15	66.37	8.21	6.23
	20	64.89	8.62	6.19
GPP[*]	5	82.45	4.45	9.51
	10	77.27	5.85	10.01
	12.5	74.75	6.49	10.24
	15	73.08	6.74	10.32
	20	70.57	7.47	10.97

In addition, GPP and GSP addition could also decrease the b* values, which decreased at lower addition level and then increased, but still lower than that of control group. GSKP had a larger impact on the L*, a*, and b* values than that of GPP and GSP.

3.2.2 Particle size

As shown in Table 3.6, the average grain size of wheat flour at D90 and D50 is 242.50 respectively μ M and 96.52 μ m.

Table 3.6

Particle size distribution of partial substitution of wheat flour with GPP/GSP/GSKP

Samples	D50 (μm)	D90 (μm)
WF*	96.52	242.50
10 wt% GPP*	29.66	126.40
10 wt% GSKP*	35.49	151.66
10 wt% GSP*	26.48	117.60

* WF: wheat flour; GSP: grape seeds powder; GSKP: grape skin powder; GPP: grape pomace powder

These values are the mean ± SD of three independent measurements. The mean values of superscripts followed by different letters in the columns were significantly different ($p<0.05$).

Compared with WF, the addition of 10 wt% GPP resulted in a significant reduction of D90 (i.e., 126.40 μ M and 242.50 μ m). The average particle size of 10 wt% GSKP sample is the largest among the three composite samples (35.49 μ m) But still lower than that of the control group ($p<0.05$). It is reported that fine flour is characterized by higher flour content, longer stability and lower dough softening [138-139]. This is consistent with our results (Table 3.7). C2 torque decreases with the decrease of particle size, which may be related to the release of water molecules or the presence of secondary activity in the dough.

The particle size has a significant negative effect on WA, indicating that with the decrease of particle size, WA increases, which is due to the larger surface area of particles, which adsorbs more water. These results are consistent with the observations reported by Ahmed (2019) et al. [140] and Drakos (2017) [141] et al. For rye, barley flour and quinoa. When the amount of GPP added was 10 wt%, DDT suddenly increased (about 2-3 times), which was related to the particle size. DDT increased significantly in large grain composite flour, indicating that it took a long time from the amount of water added to the dough to achieve the best viscosity and elasticity.

Table 3.7

Effects of different particle sizes of WF incorporated with GSP/GSKP/GPP on Mixolab parameters

(n=3, P≥0,95)

Samples	Addition level (wt%)	Parameters				
		D50 (μm)	C2（Nm）	DDT* (min)	ST* (min)	WA* (%)
WF*	0	96.52	0.436	4.207	6.367	64.0
GSKP*	10	86.73	0.338	4.053	5.407	61.5
GPP*	10	75.25	0.361	3.230	5.677	62.0
GSP*	10	62.86	0.385	1.353	6.603	62.5

* WF: wheat flour; GSP: grape seed powders; GSKP: grape skin powders; GPP: grape pomace powders; DDT: dough development time; ST: dough stability; WA: water absorption.

The increase of DDT can be explained by the addition of gluten free flour, which affects the quality of gluten. The negative correlation effect of grain size on ST indicates that the increase of gluten network is due to the fact that the composite dough with smaller grain size can maintain longer machining time during bread making. Because tannin can interact with gluten through disulfide bond to increase the ST. of dough, this increase may be related to some components in grain size composition.

3.2.3 Thermo-mechanical properties

To predict the behavior of the dough during the processing, forming, and baking of biscuits, the effect of grape powders on the thermomechanical properties of the dough was investigated using the Mixolab device.

The obtained thermomechanical curves are presented in Fig. 3.3.

Compared with the control group, the curve trend of dough at the cooling stage changes with grape residue powder's addition, while the shape trend on the curve is similar to that of the control group. Each index's eigenvalues could still be detected. Mixolab can measure the starch properties and protein of sample under the dual influence of mechanical shear temperature and stress.

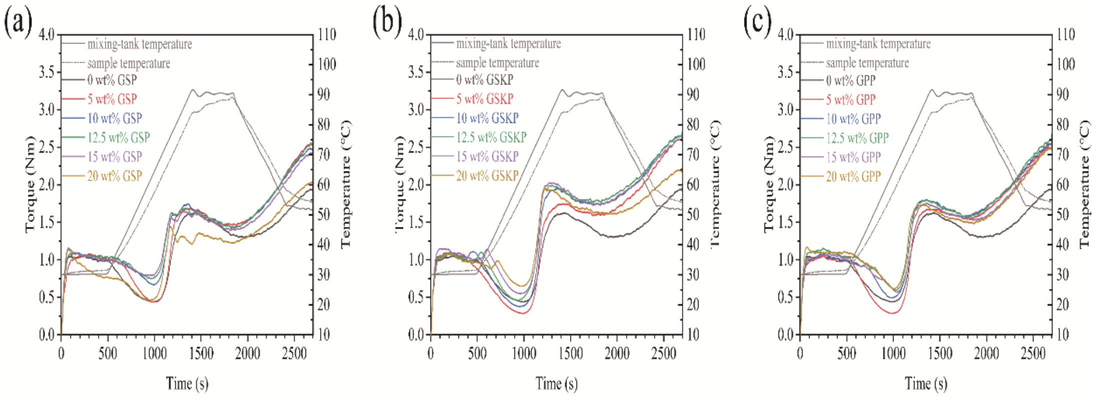


Figure 3.3 – The typical thermo-mechanical curves of doughs (1-a: curves of doughs with different GSKP addition levels; 1-b: curves of doughs with different GSP addition levels; and 1-c: curves of doughs with different GPP addition levels)

C1, C2, and slope-α can be used to characterize the thermo-mechanical properties of the sample protein (Table 3.8), and C3, C4, C5 to delineate the starch component's thermo-mechanical properties (Table 3.9).

Table 3.8

Effect of different addition levels of GSP/GSKP/GPP on protein thermomechanical properties

(n=3, P≥0,95)

Samples	Addition level	WA (%)	DT (min)	ST (min)	C1-C2 (Nm)	α	C2 (Nm)
1	2	3	4	5	6	7	8
WF*	0 wt%	67.5	3.17	6.20	0.726	-0.078	0.413
GSP*	5 wt%	66.5	4.85	9.70	0.640	-0.148	0.438
	10 wt%	63.6	2.60	10.40	0.430	-0.068	0.667
	12.5 wt%	62.3	2.18	11.00	0.368	-0.010	0.749
	15 wt%	62.0	1.35	6.60	0.347	-0.038	0.789
	20 wt%	62.0	1.30	1.90	0.677	-0.058	0.462

Table 3.8 Continued

1	2	3	4	5	6	7	8
GSKP*	5 wt%	68.4	3.13	6.10	0.809	-0.114	0.286
	10 wt%	69.2	7.57	8.10	0.731	-0.108	0.377
	12.5 wt%	70.1	9.03	9.40	0.641	-0.128	0.460
	15 wt%	70.6	1.75	7.60	0.598	-0.138	0.551
	20 wt%	75.0	3.03	8.70	0.429	-0.026	0.648
GPP*	5 wt%	67.3	4.22	8.60	0.769	-0.134	0.287
	10 wt%	65.5	4.23	9.30	0.592	-0.148	0.493
	12.5 wt%	65.3	4.08	9.60	0.560	-0.042	0.594
	15 wt%	65.4	5.17	8.50	0.516	-0.096	0.570
	20 wt%	65.4	1.17	10.00	0.554	-0.066	0.613

* WF: wheat flour; GSP: grape seeds powder; GSKP: grape skin powder; GPP: grape pomace powder; DDT: dough development time; ST: dough stability; WA: water absorption

Table 3.9

Effect of different addition levels of GSP/GSKP/GPP on starch thermomechanical properties

(n=3, P≥0,95)

Samples	Addition level	C3 (Nm)	C5-C4 (Nm)	C4/C3	T-C3 (°C)	T-C4 (°C)
1	2	3	4	5	6	7
WF*	0 wt%	1.615	1.151	0.909	84.2	87.7
GSP*	5 wt%	1.681	1.204	0.869	78.9	86.7
	10 wt%	1.747	1.177	0.813	79.4	88.1
	12.5 wt%	1.687	1.078	0.934	77.6	82.2
	15 wt%	1.557	1.002	0.971	67.5	72.0
	20 wt%	1.440	0.882	0.856	66.8	71.9

Table 3.9 Continued

1	2	3	4	5	6	7
GSKP*	5 wt%	1.746	1.123	0.909	83.0	87.7
	10 wt%	1.951	1.044	0.888	80.4	89.0
	12.5 wt%	1.992	0.982	0.887	76.4	88.5
	15 wt%	2.027	0.991	0.850	73.4	88.0
	20 wt%	1.959	0.677	0.821	70.1	82.5
GPP*	5 wt%	1.675	1.086	0.920	79.6	87.7
	10 wt%	1.805	1.095	0.870	79.4	87.5
	12.5 wt%	1.799	1.132	0.867	80.1	88.3
	15 wt%	1.758	1.046	0.870	79.6	87.5
	20 wt%	1.734	1.085	0.854	78.7	87.3

* WF: wheat flour; GSP: grape seeds powder; GSKP: grape skin powder; GPP: grape pomace powder

The results showed that GSKP, GSP and GPP had significant effects on the WA of the corresponding composite samples. At the level studied, the WA of the GSP-added dough was lower than that of the control group ($p<0.05$), and the WA of the GPP-added sample was also slightly lower. This result is in contrast to other studies, as the addition of extracts or fibers resulted in higher WA [142-144]. On the one hand, this phenomenon can be attributed to the lack of gluten and polysaccharides in GSP and GPP, which is attributed to the higher WA. On the other hand, lipids in GSP and GPP may partially cover gluten and starch granules, thereby reducing WA during mixing [145]. However, the addition of GSKP increased the WA of the composite samples by 9.65% when 20 wt% GSKP was added, due to the high protein content in GSKP and the inherent properties of dietary fiber. Furthermore, the proteins in GSKP are rich in alanine and lysine, which are responsible for WA [146].

Dough Formation Time (DDT) is the interval between the initial time point and the point at which the dough exhibits maximum torque. The stabilization time (ST) is the duration to maintain a constant torque of 1.1 Nm during kneading. These two parameters are indicators of dough strength and are positively correlated [147]. Furthermore, this hardness is often used as an indicator of product quality, and Hoye and Ross (2011) [148] reported that bread hardness increased with the addition of GSP. In this study, GPP, GSP, and GSKP had strong effects on ST and DDT, as shown in Table 3.8. The dough to which GSKP was added showed the longest DDT, followed by GSP and GPP. For GSKP, DDT was increased from 3.17 minutes to 9.03 minutes with an addition of 12.5 wt%, indicating that the appropriate addition of dried grape pomace could improve the dough strength and increase the mixing resistance of the composite dough, thereby improving its processability and imparting a good gaseous state maintain ability. Among the GSKP addition levels and the investigated GSPs, the maximum DDT was shown to be 12.5 wt%. The increase in dough strength may be due to phenolics in grape flour, and Anil (2017) [149] has reported a positive correlation between total phenolics and ST. However, the dilution of gluten protein in the presence of GPP leads to a decrease in dough strength, which becomes the dominant factor when the addition exceeds 12.5 wt%, leading to deterioration of ST.

In terms of gluten weakening, C2 (Nm) is the minimum torque value of samples (such as dough) under heat treatment and mechanical mixing. C1-C2 (Nm) represents the degree of weakening, estimated as the difference between the torque at the end of C2 stability period and 30 ℃. It reflects the ability of dough to withstand mechanical mixing, and is negatively correlated with C2. Low value corresponds to high gluten strength [150]. Many studies have shown that the C2 value can be used to predict the volume, external shape and internal pore structure of biscuits [151-152]. As shown in Table 3.8, compared with the control group, the C2 value of the samples added with GPP and GSKP first decreased and then increased with the increase of the addition level. The C2 value of GSKP and GPP was lower. If the addition level was lower than 10 wt%, the dough showed a higher protein weakening, while the pure wheat dough showed a higher C2 value, indicating a lower egg white matter weakening. This can be explained by the destruction of gluten network and the reduced gluten content [153]. However, when the addition amount exceeds 10 wt%, the opposite situation will occur, which may be due to the high content of phenolic substances [149]. There is a trade-off between their weakening effects related to gluten strength enhancement and cracking through disulfide bonds interacting with gluten [154-155]. The effect of polyphenols on the final baked food depends on their relative content, antioxidant capacity and hydroxyl content. A similar trend can be observed in the case of the difference between the peak C1 and C2 values (C1-C2), which represents the degree of protein weakening due to heat [156]. For the composite dough containing 20 wt% GSKP, the lowest C1-C2 value was determined, which was highly consistent with the C2 value. This phenomenon can also be attributed to the high phenol content [149].

Mixolab evaluated the physicochemical properties of starch in composite wheat dough, including peak torque (C3), cooking stability (C4/C3) and shrinkage (C5-C4), and recorded them at a heating temperature above 60 °C. The peak torque (C3) value is related to the starch gelatinization process [150]. With the increase of GSKP addition, C3 value increased (Table 3.9) and was very significant ($p<0.05$). This indicates that the viscosity of the dough after adding GSKP increases, which may be due to the rapid cracking of starch granules, which leads to lower gelatinization temperature and higher paste consistency [157]. In the dough samples added with GPP and GSP, when the added amount was higher than 10 wt% ($p>0.05$), the C3 value decreased slightly ($p>0.05$), indicating that the gelatinization ability of the composite dough samples was reduced, which may be due to the slightly increased amount of free water in the dough, thus intensifying the starch hydrolysis, because the activity of amylase in the flour mixture increased [157, 108]. The formation of amylase lipid complex, the amount of extracted amylose and the free water competition between unglued particles and extracted amylose are the three main factors affecting the starch gelatinization process [158]. Compared with the control group, the difference between C5 and C4 values representing starch degradation [159] showed a significant downward trend with the increase of all three additive levels. The low value (C5-C4) obtained by GSKP indicates high degradation resistance [160]. The results show that the rheological properties of dough play an important role in the production of biscuits, because they determine the attributes and characteristics used to evaluate their quality [157]. Compared with the control group, a decrease in C4/C3 value was observed (see Table 3.5), indicating that GSP may reduce the cooking stability of composite flour, which has been determined by our previous use of composite flour to make noodles and cooking characteristics. However, the level of GSKP addition or the difference between different GPPs was not significant. In terms of dough temperature during starch gelatinization, the addition of GSP, GSKP or GPP reduced the T-C3 value and reached the minimum when the GSP addition amount was 20 wt%. The existence of GSP, GSKP or GPP promotes starch gelatinization, which is highly consistent with the existing reports of Silvia Mironeasa (2012) et al. [108]. Because the addition of GPP to wheat flour exacerbates the deterioration of starch (starch decomposition), increases the amount of fermentable sugar in the dough, reduces the maximum viscosity gelatinization temperature, and increases the viscosity of the formed dough gel, the α- Starch decomposition increased. The activity resulted in the highest T-C3 value [161]. Regarding the dough temperature (T-C4) at the active stage of starch decomposition, it was observed that this value decreased with the increase of GSP addition level.

3.2.4 Dynamic rheological properties of dough

It is well known that the viscoelasticity of dough depends on its three-dimensional network, which originates from the interaction between starch and gluten or non-starch polysaccharides [162]. The dynamic rheological properties of dough can not only characterize its physical properties, such as anti-kneading and adhesiveness, but also determine its elasticity, hardness, volume and color. Oscillation frequency, storage modulus (G ‘), loss modulus (G’ ‘) and loss tangent angle (tan) through scanning mode δ = G ‘’/G ‘) is described as a function of frequency, as shown in Fig. 3.4.

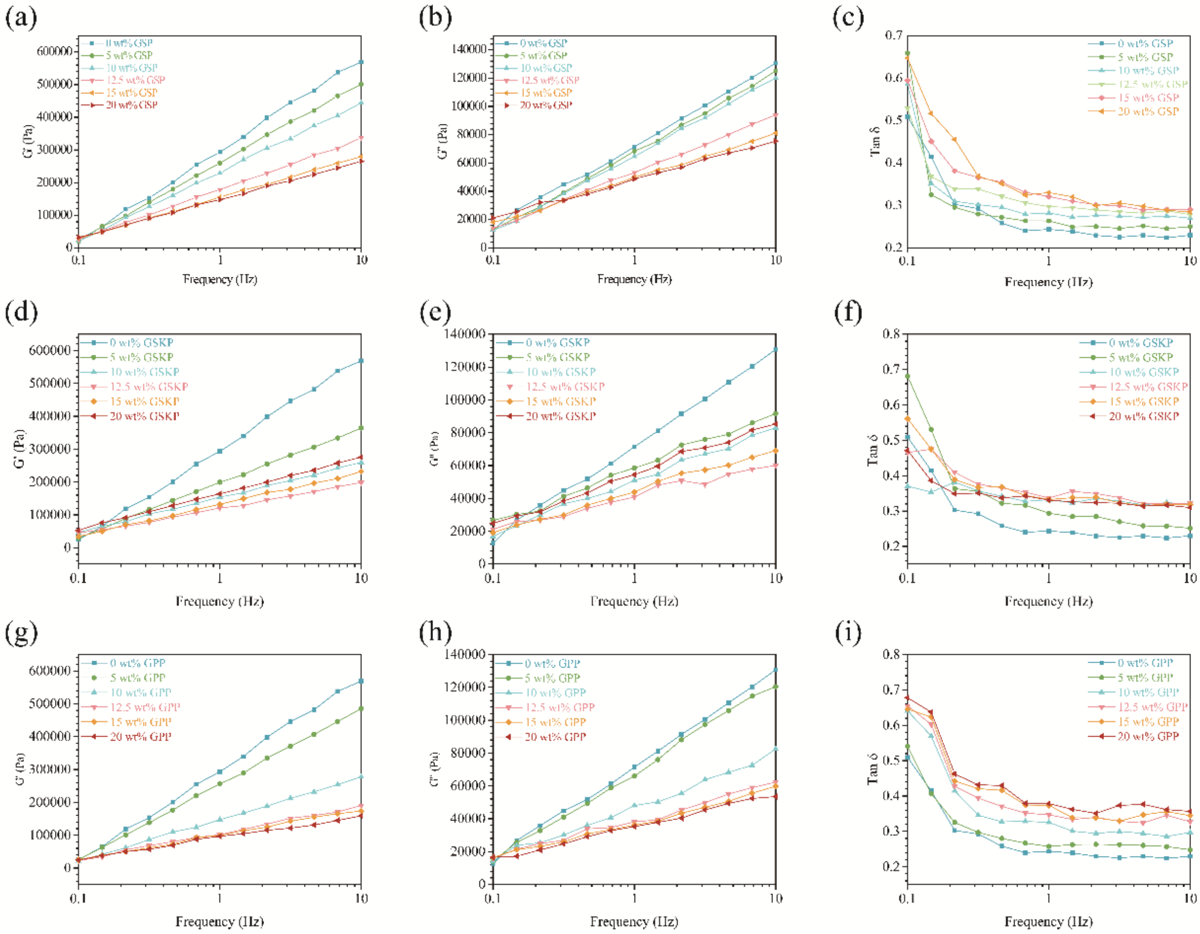


Figure 3.4 – Effects of different GSP/GSKP/GPP additions on dynamic rheological properties of wheat dough (a, b, c: G‘, G’‘and tan of wheat dough with different GSP additions δ; d. E, f: tan of wheat dough with G‘, G’‘and different GSKP additions δ; g. H, i: G‘, G’‘and tan of wheat dough with different amounts of GPP

Both G ‘and G’ ‘show an increasing trend, and the frequency increases in the range of 1 to 10 Hz. It can be observed for all samples. The report emphasizes that the results of this behavior are the same, because there is a dominant attraction between adhesive and starch particles in the mixed flour dough. The G value of all samples is higher than the G value, indicating that the elastic property of the dough dominates its viscosity [164], and all the tangent tans are lost δ the values are all less than 1, indicating that the typical dynamic rheological characteristics of dough are weak gel with significant elasticity [165]. Compared with the control group, G and G ‘’ showed a downward trend with the increase of GPP addition or GSP, as shown in Fig. 3.4-a, 3.4-b, 3.4-g and 3.4-h. This was contrary to the experimental results.

Nie et al. (2019) [61] reported the wheat dough added with *Flammulina Velutipes* powder. The reduction of modulus may be attributed to the different interactions between starch particles and GSPs with different particle sizes [166].

For the samples added with GSKP, the elastic modulus (G ‘) of all samples is higher than the viscous modulus (G’ ‘), which results in $\tan \delta < 1$。 G and G ‘’ increase in the whole range of frequency, depending on particle size and GSKP concentration, indicating that the composite flour dough formula has solid elastic sample behavior. Compared with the control group, the values of GSKP and G ‘’ composite samples decreased significantly with the increase of GSKP addition amount, and reached the lowest value when the addition amount was 12.5 wt%, then gradually increased, and reached the maximum value when the addition amount reached the maximum. The addition amount was 20 wt%, which was still lower than that of the control group. This fluctuation could be explained by the difference in the hydration capacity between flour mixtures. In addition, the different interactions between GSP particle size and starch particles also have an impact, and the chemical composition and structure of GSP particle size may be related to this change [163]. As shown in Fig. 3.4-c, 3.4-f and 3.4-I, all dough samples added with grape flour behave more like liquid than pure wheat dough because their tan δ It is higher than the control. This may be due to the dietary fiber in grape flour can enhance the WA capacity of dough. The significantly increased water promoted the expansion of protein and wheat flour starch, thus increasing the viscosity of the dough. These results showed that the addition of grape flour weakened the gluten network structure of the dough. This may be due to the easy formation of hydrogen bond between polysaccharide and water molecules in grape flour [167], which destroys the formation of gluten network in dough [168]. In addition, the antioxidation of polyphenols in grape residue is not conducive to flour processing. Its reduction destroys the formation of disulfide bonds in gluten molecules, hinders the cross-linking and aggregation of gluten proteins, and brings adverse effects to the gluten network structure [169]. However, although the addition of grape residue polyphenols destroyed the most important disulfide bond in the gluten network structure, Mixolab experiment showed that the dough strength was still enhanced (C2 value increased). The reason may be that some phenolic substances, such as tannic acid in GPP, form a new cross link with gluten protein, thus increasing gluten strength [170].

3.2.5 Microstructure of dough

The microstructure of pure wheat dough and composite dough with different GSP, GSKP or GPP addition levels were observed by scanning electron microscope (Fig. 3.5, 3.6, 3.7).

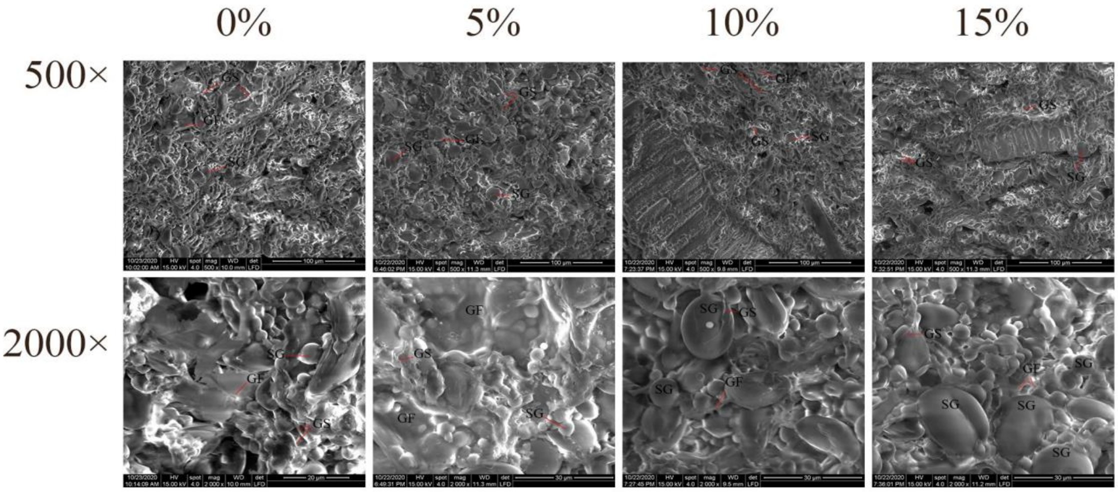


Figure 3.5 – Scanning electron micrograph of composite dough with different levels of GSP added. SG: starch granules; GS: gluten chain; GF: gluten film

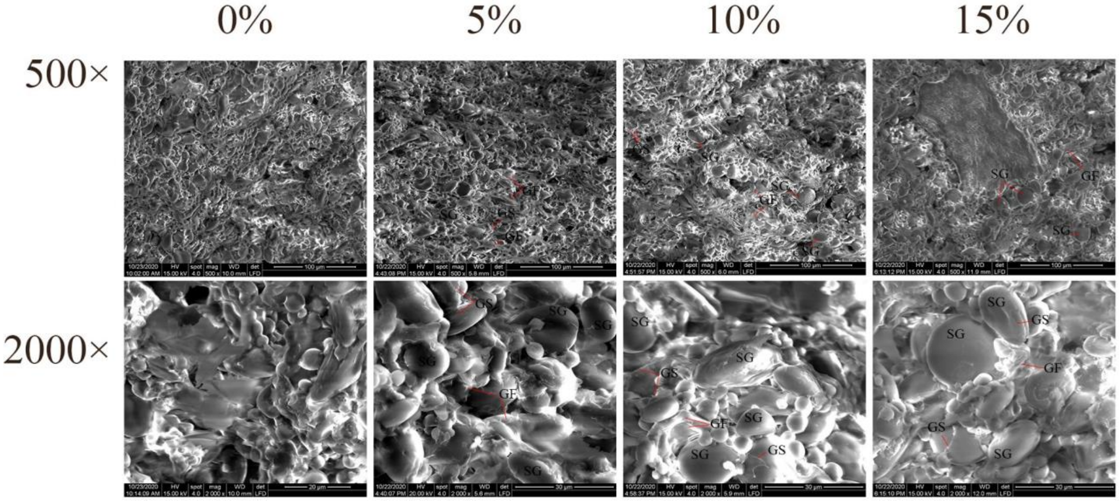


Figure 3.6 – Scanning electron micrograph of composite dough with different levels of GSKP added

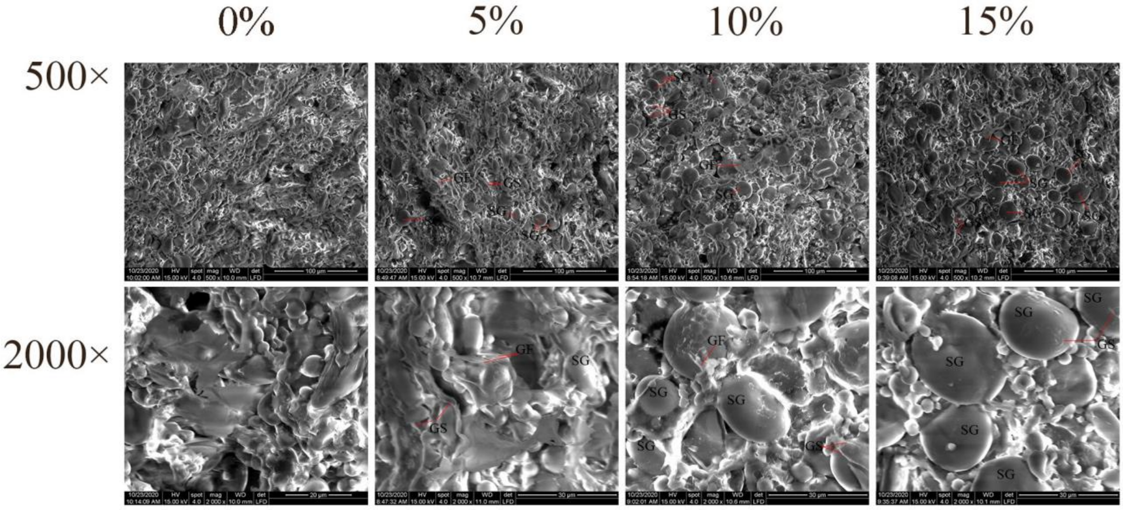


Figure 3.7 – Scanning electron micrograph of composite dough with different levels of GPP added

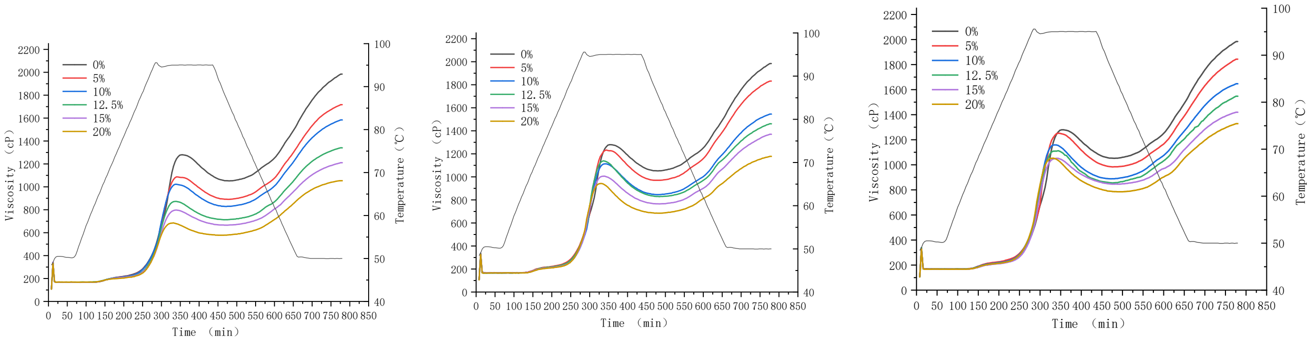
Starch granules (SG) were tightly wrapped and uniformly distributed in the continuous and complete gluten network composed of gluten membrane (GF) and gluten chain (GS), as shown in the micrograph of the control group (0 wt% added) [171]. According to the report of Jekle and Becker (2011) [172], proteins form cross-linked networks during kneading and water addition, mainly through ionic bonds, hydrogen bonds, covalent bond interactions and hydrophobic bonds. Higher magnification (2000 ×), which is clearly shown that the surface reinforcement forms a sheet network structure or a continuous filament structure. With the increase of GSP, GSKP or GPP, the continuity and integrity of the protein network structure are damaged to varying degrees by macropores. When the GSP/GSKP/GPP dosage was 5 wt%, the amount of GF found at high magnification was significantly reduced, and GS became thinner than the control group. In addition, at 15 wt% addition, more SG was exposed, and some fiber or bone structures were clearly visible, while the network structure of filamentous or layered gluten protein in all composite samples was further damaged. Although some GF can be observed in the dough added with high level of grape flour, they cannot completely wrap SG. Compared with the control sample, SG is less embedded in the gluten network, indicating that the addition of GSP/GSKP/GPP destroys the network structure of wheat gluten protein, and increasing the amount of addition leads to more deterioration, which is consistent with the results of dynamic rheological dough analysis. However, Mixolab results show that adding a certain amount can increase the dough strength. Considering the dilution effect of additives and the weakening effect related to the reduction of phenolic compounds, these phenomena may be due to the formation of a new cross link between polyphenols and gluten protein, This dominates the increase in gluten strength. Therefore, more efforts are needed to clarify potential mechanisms.

From the change of dough microstructure, it can be seen that the dilution of wheat protein with flour substitution>15wt% is too high to effectively blend grape flour into wheat dough. Because gluten is limited by phenolic substances and fibers, the extensibility and elasticity of the dough become poor, which will lead to a decline in air retention, thus reducing the volume of bread.

3.3 The influence of Cabernet Sauvignon wine grape pomace powders addition on the gelatinization, aging properties of wheat dough

3.3.1 Gelatinization properties

The gelatinization properties of composite flours were assayed by RVA. The gelatinization curves of flours supplemented with grape pomace powders were shown in Fig. 3.8(a-c), and parameters of RVA pasting characteristics are presented in Table 3.10-3.12.



a b c

Figure 3.8 – Examples of pasting curves of grape pomace – starch systems (n = 3) (a, b, c: curves of flours with varying GSP, GPP and GSKP addition levels, respectively)

Table 3.10

The effect of adding GSP on gelatinization properties of wheat flour

(n=3, P≥0,95)

GSP addition level, %	Peak viscosity, cP	Trough viscosity, cP	Breakdown, cP	Final viscosity, cP	Setback, cP	Peak time, min	Pasting temperature, °C
0.0	1280	1052	228	1984	932	5.93	89.05
5	1087	891	196	1717	826	5.67	89.95
10	1022	828	194	1584	756	5.6	89.95
12.5	811	679±13	132	1284	605	5.67	89.95
15	798	666	132	1211	545	5.67	91.65
20	685	578	107	1054	476	5.53	90.75

Table 3.11

The effect of adding GSKP on gelatinization properties of wheat flour

(n=3, P≥0,95)

GSKP addition level, %	Peak viscosity, cP	Trough viscosity, cP	Breakdown, cP	Final viscosity, cP	Setback, cP	Peak time, min	Pasting temperature, °C
0.0	1280	1052	228	1984	932	5.93	89.05
5	1252	983	269	1843	860	5.73	89.00
10	1159	888	271	1647	759	5.60	89.10
12.5	1142	934	208	1570	636	5.67	90.00
15	1052	846	206	1420	574	5.67	90.10
20	1053	785	268	1329	544	5.53	89.05

Table 3.12

The effect of adding GPP on gelatinization properties of wheat flour

(n=3, P≥0,95)

GPP addition level, %	Peak viscosity, cP	Trough viscosity, cP	Breakdown, cP	Final viscosity, cP	Setback, cP	Peak time, min	Pasting temperature, ℃
0.0	1280	1052	228	1984	932	5.93	89.05
5	1233	970	263	1832	862	5.73	89.00
10	1113	846	267	1545	699	5.67	90.00
12.5	1006	765	241	1370	605	5.60	89.90
15	1036	775	261	1372	597	5.60	87.80
20	942	685	257	1178	493	5.47	89.90

The essence of gelatinization is the process of breaking intermolecular and intramolecular hydrogen bonds between ordered and disordered starch molecules and dispersing in water (forming hydrogen bonds between starch and water molecules). Heating promotes this process, and a certain temperature is a necessary condition for gelatinization. Generally, the temperature at which the polarization cross disappears is called gelatinization temperature [173]. According to literatures [174-175], both protein and lipid can increase the gelatinization temperature of starch by forming complex with starch, resulting in slow expansion of starch granules. Therefore, the fluctuation of gelatinization temperature of composite powder in a small range is attributed to the protein and lipid contained in grape dregs However, no significant differences were observed between the control and GSKP groups. The peak time is the time required to reach the peak viscosity. In all cases, the peak time is shortened due to the increase of gelatinization temperature.

At the initial stage of determination when the temperature is lower than 50 ℃, starch granules are usually insoluble in water. However, when the temperature gradually rises and reaches the critical temperature, starch granules absorb a lot of water and expand to the multiple of the original volume, resulting in a sudden rise in viscosity and reaching the maximum viscosity before cooling, that is. For example, peak viscosity [176]. The viscosity of the tank is obtained by stirring at 95 °C. At this time, the starch granules are broken into small molecules and rearranged in the solution. The final viscosity is measured at 50 °C after cooling. In the cooling stage, due to the increase of hydrogen bond at low temperature [177], the viscosity of the slurry rises rapidly. With the increase of GPP, the three viscosities decreased significantly ($p<0.05$), mainly due to the dilution effect of starch in GPP paste, resulting in the decline of dough stability [178].

The breakdown viscosity refers to the difference between the trough viscosity and the peak viscosity. Since the decomposition value reflects the stability of starch granules, a lower value will lead to higher thermal stability of paste and better shear and mixing resistance [179]. The retrogradation parameter is the difference between the tank viscosity and the final viscosity, indicating the retrogradation of starch in the cooling stage (i.e., the degree of aging). The higher setback value is related to the high degree of recombination of amylose molecules in the size [180]. The starch pastes with GPP/GSKP concentration studied have a higher degree of cracking than the control, because their breaking viscosity values are also higher (Tables 3.11 and 3.12), which may reduce the resistance of GPP paste to mechanical and thermal damage [181]. Since the slurry is measured under the same conditions, it is assumed that the difference in the degree of fragmentation depends on the nature of the particles. However, for GSP starch (Table 3.10), the decomposition viscosity shows a reverse trend, which is again attributed to the fact that the lipids in grape seeds can form complexes with starch. Compared with the control group, the setback value of all grape residue groups decreased significantly, and decreased with the increase of GPP level. Because starch granules have similar proportion of amylose/amylopectin, the short-term retrogradation trend of GPP paste is low, which may be due to the interaction of polyphenols, lipids and GPP in starch granules, so the spatial steric hindrance reduces the tendency of dispersion and linear fragment rearrangement [182, 183-187].

The results showed that GSP's addition affected starch granules' decomposition ability in flour after cooking. With starch's decrease content, the decomposition ability after cooking was also reduced, while the thermal stability was enhanced.

3.3.2 Thermal properties

Thermal properties of the GP- fortification flours are shown in Table 3.5, gelatinization is a process of starch molecular diffusion due to intermolecular and intramolecular hydrogen bond breaking due to the swelling of starch in water, and the energy changes in this process are characterized by endothermic peaks in differenlial scanning calorimetry (DSC) analysis. The pasting initial temperature (To), peak pasting temperature (Tp) and pasting termination temperature (Tc) of gelatinization can be obtained from the formation to the end of the peak on the DSC spectrum. The peak area represents the enthalpy (ΔH) required for gelatinization. The thermal stability and aging characteristics of the composite powder of grape pomace powder and wheat flour were measured by DSC, the DSC parameters were shown in Table 3.13 and the DSC parameter variation curves were shown in Fig. 3.9.

Table 3.13

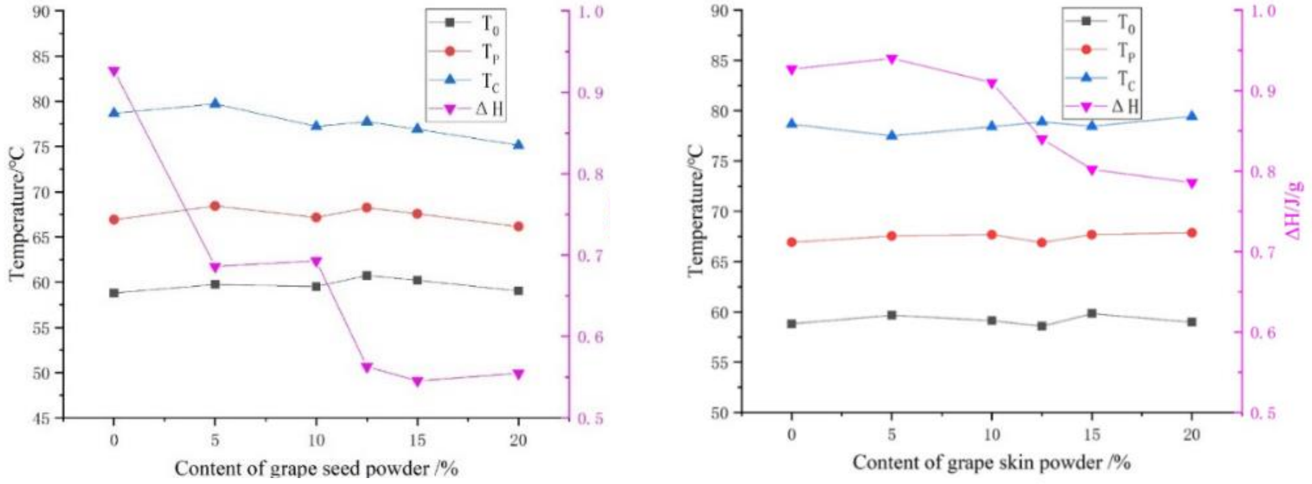
Thermal analysis of gelatinization of wheat flour supplemented with different grape powders

(n=3, P≥0,95)

Addition level, %	Pasting initial temperature To/℃	Peak pasting temperature Tp/ ℃	Pasting termination temperature Tc/ ℃	Enthalpy change/(ΔH)/ J/g
1	2	3	4	5
0	58.81	66.92	78.67	0.9269
GSP5%	59.76	68.43	79.72	0.6860
10%	59.53	67.16	77.21	0.6930
12.50%	60.74	68.24	77.72	0.5628
15%	60.20	67.56	76.92	0.5456
20%	59.05	66.15	75.13	0.5548

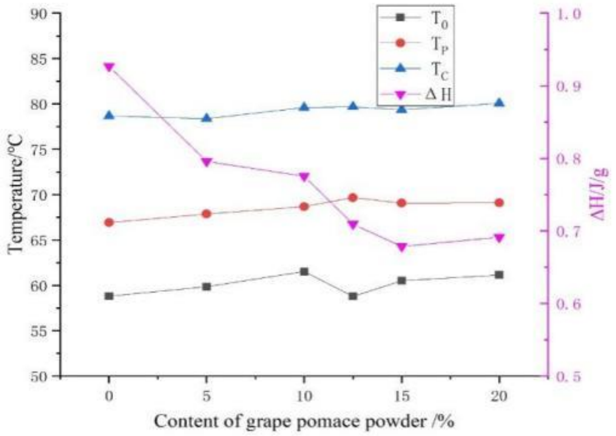
Table 3.13 Continued

1	2	3	4	5
GSKP5%	59.67	67.54	77.48	0.9405
10%	59.12	67.68	78.42	0.9124
12.50%	58.56	66.89	78.88	0.8405
15%	59.84	67.68	78.46	0.8074
20%	58.96	67.86	79.43	0.7825
GPP5%	59.86	67.87	78.36	0.7957
10%	61.53	68.68	79.59	0.7754
13%	58.79	69.67	79.68	0.7094
15%	60.50	69.07	79.34	0.6487
20%	61.15	69.09	80.06	0.6914



a

b



c

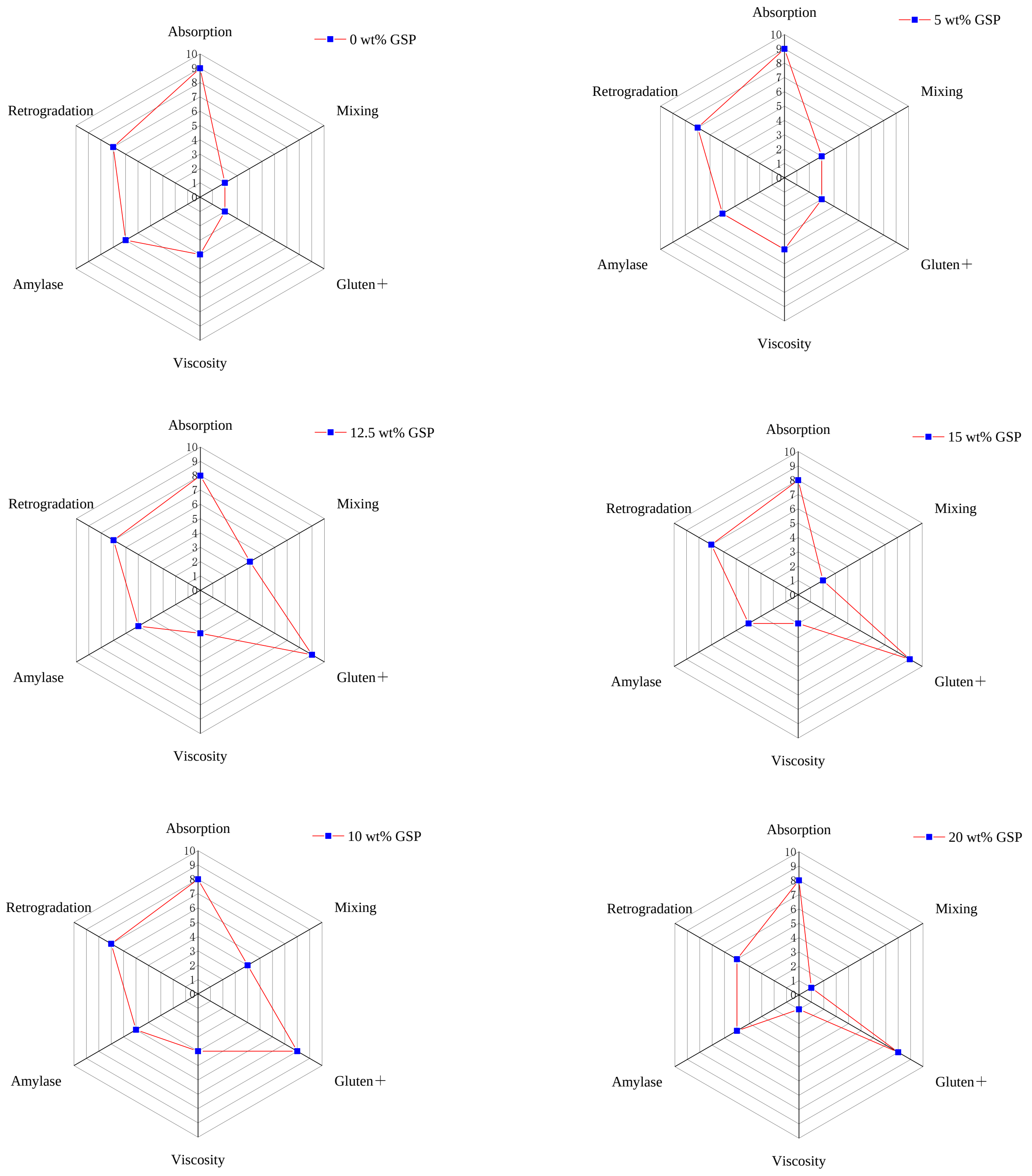
Figure 3.9 – Effects of GPP(a)/GSP(b)/GSKP(c) with different addition levels on thermal stability and aging characteristics of wheat flour

Compared with the control group with zero addition, the To, Tp and Tc values of all samples were slightly increased when the addition amount above 5 %. However, the ΔH values showed a significant downward trend, indicating that grape pomace powders had influence on the thermal stability and aging characteristics of flour at a lower amount of addition. However, with the increasing GPP addition level, the enthalpy required for gelatinization was significantly reduced due to the relative decrease of starch content, which was due to the relative starch content reduction resulted in decreased energy demand. In addition, there were certain amounts of dietary fiber and protein content in GPP, relatively large amount addition slightly increased T_o, T_p, and T_c, suggesting that when the amount reached a certain value, improved the thermal stability and aging resistance were delivered. In addition, due to the higher content of polysaccharide in GPP, the gelatinization temperatures of the composite flours were affected at the addition levels ranging from 5% to 20%, resulting in a slight increase in the gelatinization To, Tp and Tc, indicating that the addition of grape pomace powder improved the thermal stability and aging characteristics of flour to a certain extent, which was consistent with the previous RVA determination results.

3.3.3 Analysis of Mixolab Profile Test Mode

The results of Mixolab profile experimental protocol of grape powders with different addition levels were shown in Fig. 3.10-3.12.

Influence of partial wheat flour substitution by GSP, GSKP or GPP on dough absorption, mixing, gluten, viscosity, amylase and retrogradation can be seen from Fig. 3.10-3.12. The water absorption index of dough is mainly determined by the composition of flour such as protein, starch and fiber, which is mainly affects the production of dough, for producers, the higher water absorption leads to more dough obtained. It can be seen from Fig. 3.10 and Fig. 3.12 that the water absorption index decreased with the increase of GSP content but remains unchanged with the increase of GSKP content (Fig. 3.11). Which was consistent with the Mixolab results.



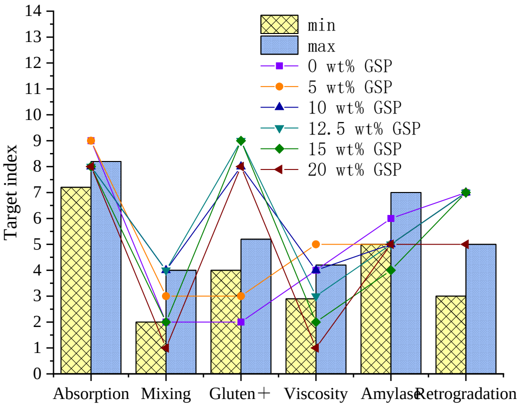
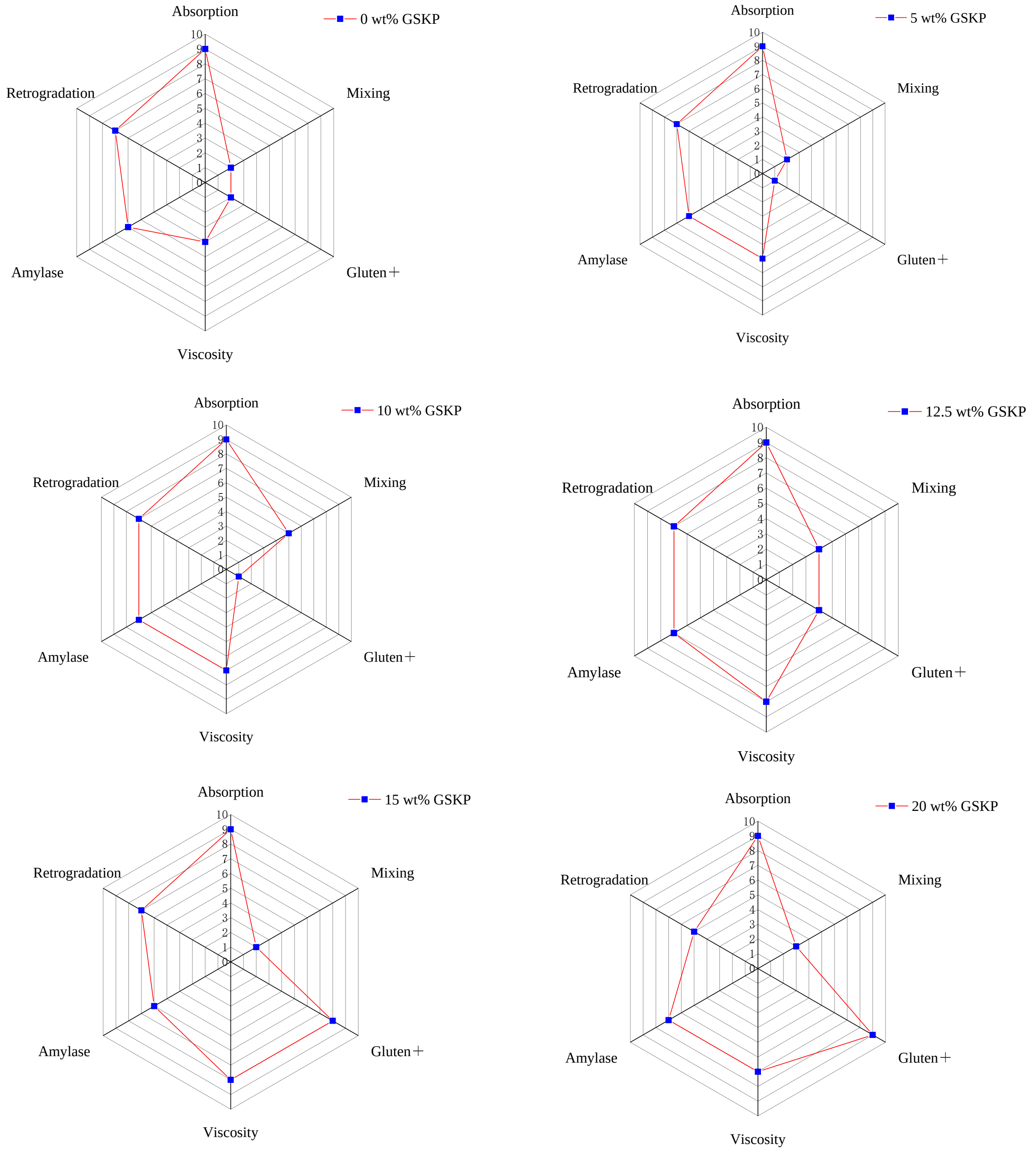


Figure 3.10 – Results of Mixolab profile experimental protocol and Mixolab target index of grape seeds powder with varying addition levels



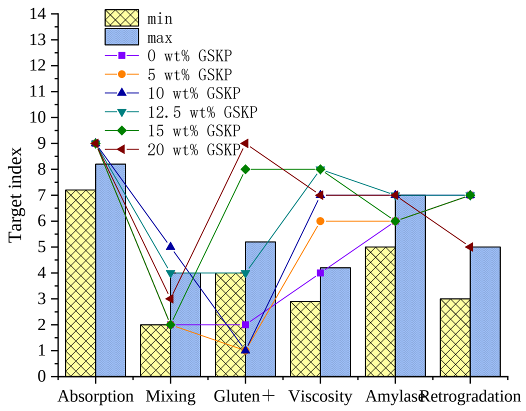


Figure 3.11 – Results of Mixolab profile experimental protocol and Mixolab target index of grape skin powder with varying addition levels

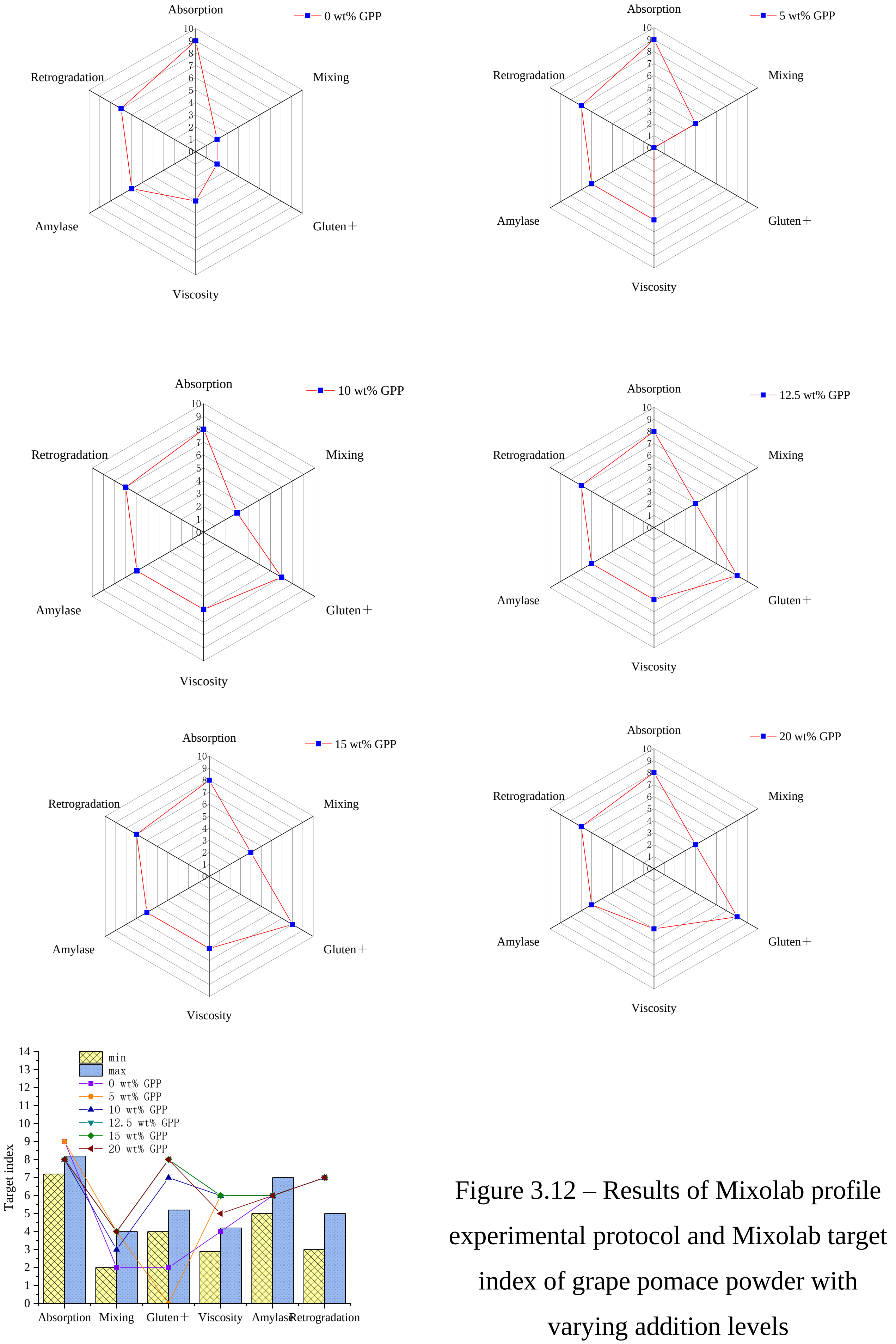


Figure 3.12 – Results of Mixolab profile experimental protocol and Mixolab target index of grape pomace powder with varying addition levels

The mixing index represents the characteristics of flour at constant temperature kneading stage, which was related to the concepts of stability time, formation time and protein weakening. The larger of the value leads to the longer dough stability time. The mixing index of all grape powder samples increased first and then decreased and the maximum mixing index showed at 10% or 12.5% GSP/GSKP addition levels. The gluten strength index represents the characteristics of the gluten in the heating stage. The greater the value is, the stronger the heat resistance of the gluten network is. After adding GSP/GPP/GSKP, the gluten strength indexes of flours were all significantly improved, which was again attributed to the interaction between polyphenols and starch granules. Viscosity index is defined as the viscosity of pasted starch increases during continuous heating, which depends on amylase activity and starch content in flour. It can be seen from the Fig. 3.10 that with the addition of grape seeds powder, the viscosity index decreased but increased with GSKP and GPP addition. Amylase activity index refers to the ability of starch to resist amylase hydrolysis. The greater value leads to the lower the amylase activity. The results showed that the amylase activity increased after adding GSKP but decreased with GSP, the discrepancy was due to the different chemical composition of grape skin and grape seeds. The retrogradation index is mainly determined by the characteristics of starch in flour and the hydrolysis characteristics of gelatinized starch. The retrogradation value is too high means it will have a great influence on the flavor and texture structure of the product over time. The addition of grape powders does not affect the retrogradation value, until the addition amount was higher than 15%.

After the sample was determined by the instrument, the index results of the dough would be shown on the target index profile. The more the number of test indexes of the tested sample falling into the target index profile (shadow part), the more satisfied the requirements of flour for this purpose. As shown in Fig. 3.10-3.12, our target product was biscuit, the maximum number of rheological indices measured by 12.5 % GSP/GSKP incorporation fell between the target indices, and for GPP, 10% addition was the most suitable addition for biscuits.

Conclusions of section 3

1. Compared with ordinary cereal seeds and skin, GP is rich in nutrients (protein, fat, carbohydrates, etc.) and mineral and trace elements (K, Ca, etc.), and its total phenolic content is high. We have also verified that the antioxidative activity of its polyphenol extract was far superior to that of vitamin C.

2. Systematical investigation was carried out by a combination of thermo-mechanical property characterization, dynamic viscoelastic measurement, and scanning electron microscope observation, along with color measurement. The results indicated that GPP and GSP significantly reduced the water absorption of the corresponding dough, while three types of grape powders could increase the development time and dough stability. Furthermore, all kinds of grape powders with various incorporations could significantly enhance the strength of dough systems. GPP significantly increased protein weakening at 5 wt%, and maximized the stability time at 12.5 wt%. For GSKP, it substantially increased the viscosity. In addition, Grape powders decreased the storage (G′) and loss (G″) moduli, while the tan δ increased with the increasing of GSP/GSKP/GPP addition levels. In terms of the viscoelastic characteristic, the dough with GSKP addition displayed slightly difference compared to that with GSP or GPP.

3. The microstructure observation of these dough suggested that the integrity and continuity of gluten networks were destroyed in the presence of grape powders. Combined with rheological parameters (the dough strength is weaker when <10% GSKP / GPP was added; >10%, stronger doughs. For GSP, <15%, stronger doughs; >15%, weaker doughs) and microstructure results, and relatively high addition levels of 10% to 15% for GSP, 5% to 10% for GSKP/GPP seem promising to be successfully applied to wheat flour foods.

4. GPP/GSP/GSKP addition had limited effect on pasting temperature, the minor increase of gelatinization temperature of flours incorporated with GSP/GPP is attributed to the protein and lipid contained in grape seeds and pomace. In all cases, peak time decreased due to gelatinization temperature increased. However, three types of grape powders significantly decreased the setback value of the paste

system, which indicated that active polyphenol fraction in grape pomace can effectively prevent amylose association in starch paste upon cooling stage. However, an increase of breakdown viscosity suggested that GPP could reduce the thermal stability and mechanical damage resistance of starch granules. These three viscosities decreased significantly ($p < 0.05$) as GPP increased, majorly due to the starch dilution effect in GPP pastes, which leads to a decrease in dough stability.

5. The Differential Scanning Calorimetry (DSC) results showed that enthalpy required for gelatinization was significantly reduced due to the relative decrease of starch content, which was consistent with the RVA results.

SECTION 4

DEVELOPMENT OF TECHNOLOGY OF BISCUITS

This section presents the results of research on biscuits quality indicators, which made it possible to determine the best dosage of grape powders. First, the data obtained for the samples of biscuits with the addition of grape seeds and skin are given, below – with the addition of grape pomace.

4.1 Textural assay of biscuits incorporation of grape powders

In order to create high-quality biscuits, research was conducted on the effect of grape powders on its texture. The results of the research are given in Table. 4.1.

Table 4.1

Effect of GSP addition on texture of biscuits

(n=3, P≥0,95)

GSP* addition level (%)	Texture quality of biscuits		
	Hardness（g）	Fracturability（g）	Chewiness（g）
0	2810.24	451.28	25.80
5	3951.58	1068.36	128.12
10	3905.79	1497.51	204.58
12.5	8156.58	6514.30	586.34
15	3868.13	2859.31	100.68
20	4696.01	2757.19	85.20

*GSP: grape seeds powder

It can be seen from Table 4.1 that with the increase of GSP addition, the hardness of biscuits first increased and then decreased. When the addition amount of GSP was 12.5%, the hardness reached the maximum. Further increasing the addition amount of grape seeds, the hardness decreased rapidly, but it was still higher than that of the control group. The fracturability and chewiness of biscuits showed a similar trend, showing the highest fracturability and chewiness when the addition amount was 12.5%. When the addition of GSP was 15%, compared with the control group, the hardness, fracturability and chewiness of biscuits increased by 1.38 times, 55.76 times and 3.90 times, respectively. Therefore, combined with the sensory evaluation index of biscuits, in the actual production, the addition amount of GSP was mainly considered as 15%. Under this condition, biscuits showed certain crispness, moderate hardness, no chewing effort and difficulty in swallowing. When the addition of GSP was more than 20 %, the biscuits displayed a bad taste, which was due to the hard shell of grape seeds, resulting in the overall acceptance of grape seeds biscuits decreased. It is well known that there are abundant polyphenols in grape seeds, and the water absorption of the composite powder of GSP and wheat flour shows that grape seeds powder can reduce the water absorption. There is a certain cross-link between phenols and protein and starch granules in flour. However, when phenols increase to a certain extent, the dilution effect of gluten protein in the composite powder occupies the dominant position, which is the reason for the above results.

The values are mean ±SD of three independent determinations. Means followed by different alphabetic superscripts within a column are significantly ($p<0.05$) different. The effects of GSKP on the texture characteristics of biscuits are shown in Table 4.2.

Table 4.2

Effect of GSKP addition on texture of biscuits

(n=3, P≥0,95)

GSKP addition level (%)	Texture quality of biscuits		
	Hardness（g）	Fracturability（g）	Chewiness（g）
0	2810.24	451.28	25.80
5	4519.33	1941.46	217.58
10	13823.79	3930.25	1916.50
12.5	8754.37	2359.44	1458.42
15	9097.16	1594.43	1537.15

For biscuits with grape skin powder, the hardness, fracturability and chewiness of biscuits still show similar trends as those of grape seeds powder. However, it is interesting that when the addition amount of grape skin powder is 10%, the above three indexes show the maximum value, which is due to the differences in the contents of polyphenols, dietary fiber and amino acids in grape skin and grape seeds. At the same time, different treatment methods will lead to further increase in the difference in the content of nutrients. For example, the grape skin is treated by washing separation, which will cause the loss of some water-soluble substances. When the addition amount was more than 10%, the three indexes began to decline again. Considering the overall acceptance of grape skin biscuits, the grape skin addition amount of 5% was considered to substitute wheat flour. At this addition level, the grape skin biscuits had a certain fermented grape flavor and with a strong flavor. However, when the GSKP addition amount was more than 5%, the biscuits showed a strong astringent and bitter taste, which brought uncomfortable experience to consumers.

4.2 Color assay of biscuits incorporation of grape seeds or grape skin powder

The values are mean ±SD of three independent determinations. Means followed by different alphabetic superscripts within a column are significantly ($p<0.05$) different.

The effects of GSP on the color of biscuits are shown in Table 4.3.

Table 4.3

Effect of GSP addition on color of biscuits

GSP addition Level (%)	L*	a*	b*
0	68.38	6.24	29.85
5	62.23	6.40	20.69
10	57.86	7.25	20.01
12.5	56.13	10.55	18.16
15	53.54	7.42	17.05
20	50.86	7.54	14.67

Compared with the control group, the L* value and b* value of biscuits showed a significant downward trend ($p < 0.05$), indicating that the addition of GSP darkened the color of biscuits, and the yellowness value also decreased significantly ($p < 0.05$). Interestingly, the redness of biscuits first increased and then decreased with the increase of GSP. When the addition amount of GSP was 12.5 %, the color of biscuits was the reddest, and then decreased, but it was still higher than that of the control group. When the amount of grape seeds is more than 10 %, the biscuits show a red-brown color that similar to chocolate, which greatly increases the acceptance of grape seeds biscuits. However, when the addition of GSP was more than 20 %, the yellow color of biscuits decreased significantly ($p < 0.05$), which meant that the blue color of biscuits increased. Studies showed that there was a positive correlation between b* value and food acceptance. It is well known that the color of food is the first factor for consumers to accept the food, and the factors affecting the color of the food in addition to raw materials, Maillard reaction in the baking process is also an important factor affecting the color of the food, so it is particularly important to improve the overall acceptance of grape seeds biscuits by changing the amount of grape seeds and controlling the baking conditions.

The effects of GSP on the color of biscuits are shown in Table 4.4.

Table 4.4

Effect of GSKP addition on color of biscuits

(n=3, P≥0,95)

GSKP addition level (%)	L*	a*	b*
0	68.38	6.24	29.85
5	46.5	6.97	20.10
10	44.80	7.00	12.39
12.5	38.10	7.77	9.61
15	34.35	7.87	6.82

The Table shows that the L * and b * values of grape skin biscuits decrease significantly with the increase of grape skin powder addition ($p < 0.05$), and the decrease is much greater than that of grape seeds powder. Thus, the influence of grape skin powder on the brightness of biscuits is greater than that of grape seeds powder, which means that even a small amount of grape skin powder can make the color of biscuits darker, and the yellow of biscuits begins to become not obvious, and the blue deepens, which will greatly reduce the attractiveness of biscuits to consumers.

4.3 Sensory evaluation of biscuits incorporation of grape seeds or grape skin powder

The results of the organoleptic evaluation of biscuits with the addition of grape seeds powder are presented in the Table 4.5.

Table 4.5

Effect of GSP addition on sensory scores of biscuits

($n=3$, $P\geq0,95$)

GSP addition level(%)	Sensory scores				
	color	appearance	flavor	texture	acceptability
0	8.25	8.05	7.75	7.85	8.00
5	7.95	7.55	7.85	7.65	7.55
10	8.10	7.80	7.85	7.60	8.15
12.5	8.75	8.35	8.05	8.05	8.75
15	8.90	8.30	8.45	7.90	8.35
20	8.00	7.90	7.95	7.45	7.45

As shown in Table 4.5, the scores of biscuits with 12.5 % addition in color (8.75) were significantly different from those in the control group (8.25) ($p< 0.05$). The scores of biscuits in appearance were consistent with the trend of color (decreased first and then increased), which may be due to the influence of color on appearance to some extent. This is similar to the research results of Sudha and Devinder [188-189]. In this study, when the proportion of grape seeds powder was 12.5 %, the increase in color score may be related to the color of biscuits tending to chocolate color. When the proportion of grape seeds powder was more than 12.5 %, biscuits would have a sense of pellet feeling and a slight sense of bitterness, which was also the reason for the gradual decrease in the score of texture structure. In terms of flavor, the score (8.45) was the highest when the addition ratio was 15 %, followed by 12.5 % (8.05), and the score (7.75) of the control group was the lowest. This is due to the addition of grape seeds powder can contribute to grape aroma. This result could also be consistent with the results of GC-MS. The addition of GSP can bring more rich baking fragrance for biscuits, and increase the consumer's preference for its flavor. In terms of overall acceptance, the addition of grape seeds powder content is too low or too high (<5% or >15%) will lead to a decrease in the score, which showed that the addition amount within 15 % can be accepted by consumers.

The results of the organoleptic evaluation of biscuits with the addition of grape skin powder are presented in the Table. 4.6.

Table 4.6

Effect of GSKP addition on sensory scores of biscuits

(n=3, P≥0,95)

GSKP addition level(%)	Sensory scores				
	color	appearance	flavor	texture	acceptability
0	8.25	8.05	7.75	7.85	8.00
5	7.85	7.75	7.85	7.50	7.45
10	5.75	6.30	6.45	6.45	6.55
12.5	5.10	5.25	5.05	5.35	5.45
15	4.25	4.35	4.85	5.25	5.20

As shown in Table 4.6, the addition of GSKP resulted in a significant decrease in the color score of the biscuits ($p<0.05$). This result is different from GSP, which is related to the fact that the grape skin makes the color of the biscuits too dark. When the addition amount is 5%, The biscuits' flavor score (7.85) was slightly higher than that of the control group (7.75), the difference was not significant ($p>0.05$), which may be caused by the grape skin imparting a certain fruity aroma to the biscuits. When the addition ratio is 10%, the biscuits taste is obviously grainy, and the bitterness is prominent, so the flavor score is significantly reduced ($p <0.05$). At the same time, the volume of the biscuits decreases with the increase in the amount of grape skin. This result has also been reported by other literatures that the addition of any gluten-free raw material will result in a reduction in the volume of the final product [190]. In addition, we observed that when the added amount exceeds 5%, bubbling will appear on the surface of the biscuits product, and the higher the added amount, the more serious the bubbling. This phenomenon has not been observed in grape seeds biscuits. This is also the reason why the score of biscuits in terms of texture structure has dropped significantly （$p < 0.05$）. In terms of acceptability, only 5% of grape skin added has no significant difference with the control group ($p> 0.05$), higher than this addition ratio leads to a significant decrease in the overall acceptability of biscuits ($p < 0.05$). Therefore, 5 % addition is suitable.

4.4 Effect of auxiliary material addition amount on sensory evaluation of biscuits

4.4.1 Single factor experiment

Baking temperature and time are two important technical indicators in the process of biscuits production, which are directly related to the acceptability of the product. Other studies have shown that in the process of biscuits baking, with the increase of temperature, the microbial content in the biscuits shows a downward trend, and the total plate count, molds, *aerobic Bacillus*, *Bacillus cereus* and baking time in the biscuits are significantly negatively correlated. In our study, when the baking temperature was 165 °C, 155 °C, baking time was 11 min, the sensory score of biscuits reached the maximum (89.14) (Table 4.7).

Table 4.7

The effect of baking temperature and time on the sensory score of biscuits

Number	Baking temperature (℃)	Baking time (min)	Sensory score
1	155，145	9	53.45
2	155，145	11	65.60
3	155，145	13	76.84
4	180，160	9	75.23
5	165，155	11	89.14
6	180，155	13	77.57
7	175，165	9	84.20
8	175，165	11	63.95
9	175，165	13	41.97

From the sensory score side, the biscuits baked at 155 °C were immature or sticky, and the biscuits baked at 180 °C had a burnt taste.

The effects of sugar powder addition, palm oil addition, and the addition ratio of expansion agent (baking soda : glucolactone : ammonium bicarbonate) on the sensory score of biscuits are shown in Fig. 4.1.

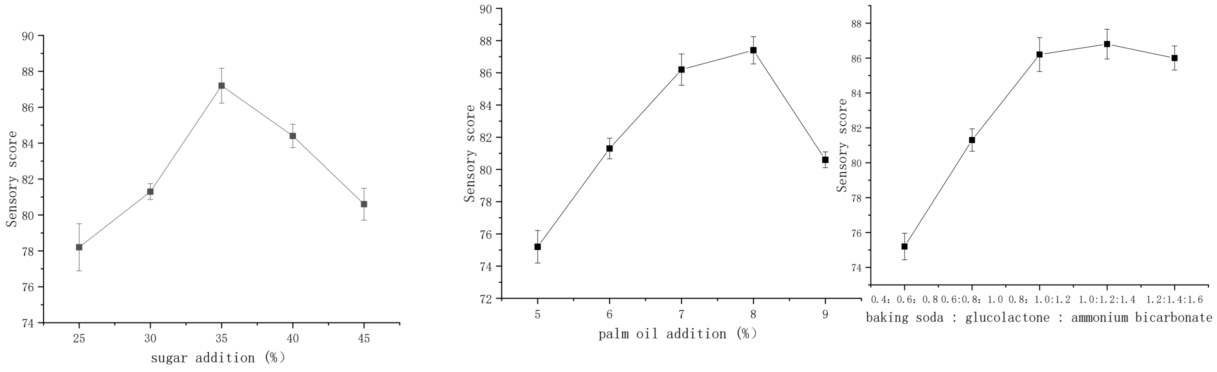


Figure 4.1 – Results of single factor experiment

It can be seen from Fig. 4.1 that with the increase of sugar powder and palm oil addition, the sensory score of biscuits increased first and then decreased. This was because the content of sugar powder and oil is too high or too low, which would cause the decrease of consumer acceptance. The expansion agent is heated and decomposed in the baking process, producing gas to make the dough rising, and the volume expands, forming uniform and dense porous tissue inside, giving biscuits a crisp taste. Sodium bicarbonate, commonly known as baking soda, is the most widely used swelling agent at present. It is heated to produce carbon dioxide, but sodium carbonate remains in food and is alkaline. Ammonium bicarbonate can be decomposed at lower temperature (30–60 °C) to produce carbon dioxide, water and ammonia. Because both of them are alkaline, it is necessary to add gluconic acid-δ-lactone for neutralization and react with sodium bicarbonate to produce carbon dioxide. The effect of bulking agent addition ratio on the sensory score of biscuits is shown in Fig. 4.1. It can be seen that when the amount of bulking agent was too low, the biscuits surface was rough and taste was not good. When the addition was too high, the biscuits was loose and not brittle, the internal foaming was uneven, the hole was too large, and the formability was not good. When the dosages of baking soda, ammonium bicarbonate and lactone were 0.8, 1.0 and 1.2 g, the biscuits had the best quality, uniform internal structure and good brittleness.

4.4.2 Orthogonal experiment results

As shown in Table 4.8, according to the results of single factor experiment, the three levels of orthogonal experiment were selected as follows: GSP addition amount of 10 %, 15 % and 20 %, sugar powder addition amount of 30 %, 35 % and 40 %, palm oil addition amount of 7 %, 8 % and 9 %, and the proportion of compound additives : baking soda : glucolactone : ammonium bicarbonate of 0.6 : 0.8 : 1.0, 0.8 : 1.0 : 1.2, 1.0 : 1.2 : 1.4.

The results of Table 4.9 extreme difference analysis showed that the order of the influence of various factors on the sensory score was B (sugar powder addition) > C (palm oil addition) > A (grape seeds powder addition) > D (composite additive).

Table 4.8

Design of Orthogonal test level

Level	A	B	C	D
	GSP addition (%)	Sugar addition (%)	Palm oil addition (%)	baking soda : glucolactone : ammonium bicarbonate
1	10	30	7	0.6:0.8:1.0
2	15	35	8	0.8:1.0:1.2
3	20	40	9	1.0:1.2:1.4

Table 4.9

Orthogonal experiment results

Number	Factors				Results
	GSP addition	Sugar addition	Palm oil addition	baking soda : glucolactone : ammonium bicarbonate	Sensory score
1	1	1	1	1	58.75
2	1	2	2	2	85.56
3	1	3	3	3	82.27
4	2	1	2	3	73.14
5	2	2	3	1	81.86
6	2	3	1	2	87.44
7	3	1	3	2	75.62
8	3	2	1	3	80.05
9	3	3	2	1	82.64
k1	1.7968	2.359	2.3054	2.5367	
k2	2.6542	2.476	2.2086	2.0162	
k3	2.5977	2.183	2.5347	2.3958	
k1/3	0.5989	0.7863	0.7685	0.7122	
k2/3	0.8847	0.7920	0.8362	0.8387	
k3/3	0.8659	0.7712	0.7449	0.7986	
R	0.1045	0.2858	0.1265	0.0916	

Among the four influencing factors, the extreme difference of sugar powder addition is the largest, and the extreme difference of composite additive is the smallest. According to extreme difference analysis, $A_2B_2C_3D_1$ was selected as the best combination of biscuits processing technology, GSP addition was 15 %, sugar powder addition was 35 %, palm oil addition was 9 %, baking soda : glucolactone : bicarbonate was 0.6 : 0.8 : 1.0. The optimal level of $A_2B_2C_3D_1$ in the extreme difference analysis of this experiment was inconsistent with the highest score combination of biscuits in the nine groups of orthogonal experiments. Therefore, it is necessary to do three parallel experiments according to $A_2B_2C_3D_1$ combination, and the results showed that the biscuits score reached 87.65 under this combination condition, which is slightly higher than that of $A_2B_3C_1D_2$ combination. Under this combination condition, the biscuits had certain brittleness, moderate hardness and rich grape flavor. Fig. 4.2 shows the biscuits product.

Figure 4.2 – Biscuits with different GSP/GSKP addition levels

4.5 Development of biscuits recipes and technological scheme with the addition of grape powders

The conducted complex of researches made it possible to scientifically substantiate the biscuits technology and recipes with the addition of grape powders.

According to the results of previous studies, it was established that the optimal dosage of grape powders is: seeds powder – 15.0%, skins powder – 5.0%, pomace powder – 10.0%. The technological scheme for the production of biscuits with the addition of grape powders is presented in Fig. 4.3.

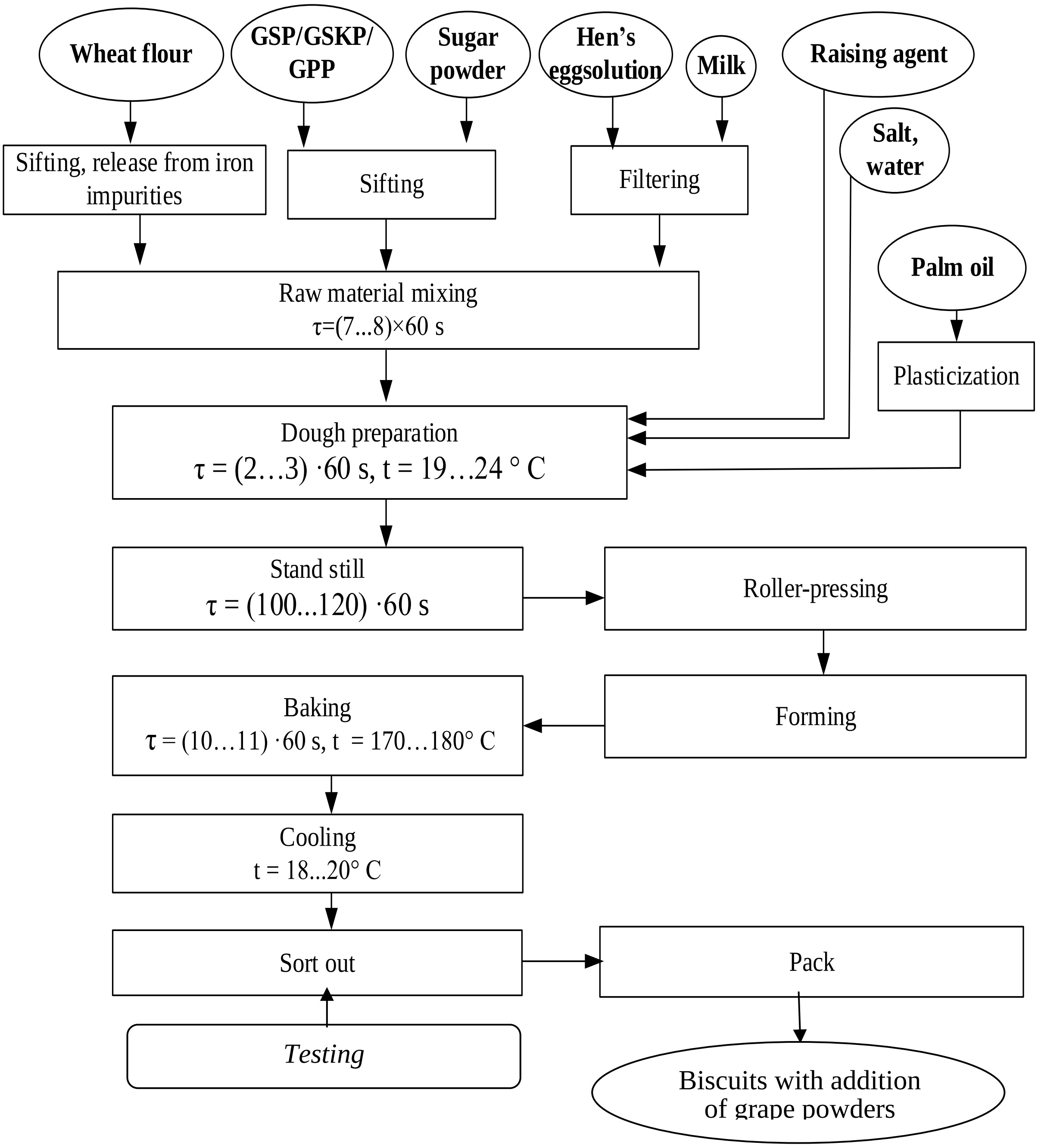


Figure 4.3 – Technological scheme of making biscuits with the addition of grape powders

The developed technology differs from the traditional biscuits technology by replacing the flour fraction at the stage of mixing raw grape powders with a high content of polyphenolic compounds, dietary fibers, micro- and macroelements, which allows to obtain products of increased quality and nutritional value.

To implement this technology, it is necessary to provide additional containers and dispensers for powders in the biscuits production line.

Based on the results of the research, recipes for biscuits with the addition of grape powders were developed, which are presented in the Table 4.10.

Table 4.10

Biscuits recipe with the addition of grape powders

Raw materials	Dry matter content, %	Consumption of raw materials for 100.0 kg of biscuits with the addition, kg					
		GSP		GSKP		GPP	
		in kind	in dry matter	in kind	in dry matter	in kind	in dry matter
Wheat flour	85.50	56.67	48.45	61.58	52.65	60.00	51.30
Grape seeds powder (GSP)	96.30	10.00	9.63	0.00	0.00	0.00	0.00
Grape skin powder (GSKP)	95.50	0.00	0.00	3.24	3.10	0.00	0.00
Grape pomace powder (GPP)	94.10	0.00	0.00	0.00	0.00	6.67	6.27
Sugar powder	99.85	23.33	23.30	25.93	25.89	23.33	23.30
Palm oil	84.00	6.00	5.04	5.83	4.90	6.00	5.04
Hen's eggsolution	27.00	9.33	2.52	9.07	2.45	9.33	2.52
Water	0.00	6.27	0.00	6.09	0.00	6.27	0.00
Milk	12.50	3.33	0.42	3.24	0.41	3.33	0.42
Salt	96.50	0.47	0.45	0.45	0.44	0.47	0.45
Ammonium Bicarbonate	99.00	0.40	0.40	0.39	0.39	0.40	0.40
Sodium Bicarbonate	50.00	0.53	0.27	0.52	0.26	0.53	0.27
Glucolactone	99.60	0.67	0.66	0.65	0.65	0.67	0.66
Total		117.00	91.13	117.00	91.12	117.00	90.63
Yield		100.00	90.00	100.00	90.00	100.00	90.00

The organoleptic indicators of biscuits with the addition of grape powders are shown in Table. 4.11.

Table 4.11

Organoleptic indicators of biscuits

Indicator	Characteristics of the indicator for biscuits			
	without additives (control)	with GSP	with GSKP	with GPP
Form	Round, smooth edges, no damage			
Surface	Unburned, without swelling, burst bubbles and scattered crumbs, with uniform puncture marks over the entire plane			
Color	Creamy, homogeneous	Brown, homogeneous	Dark brown, homogeneous	Light brown, homogeneous
Taste and smell	Biscuits' characteristic of this type, without extraneous odors and flavors			
Structure	It is baked with uniform porosity without voids and traces of non-mixing			

The physico-chemical indicators of biscuits with the addition of grape powders are shown in the table. 4.12.

Table 4.12

Physico-chemical indicators of biscuits

(n=5, $p \leq 0,05$)

Indicator	Requirements of DSTU 3781	Indicator value for biscuits			
		without additives (control)	without additives (control)	without additives (control)	without additives (control)
Mass fraction of moisture, %	no more than 15.5	10,00	10,00	10,00	10,00
Mass fraction of total sugar, %	not less than 2.0	20,0	23,3	25,8	23,3
Mass fraction of fat, %	not less than 1.5	4,5	5,1	5,0	5,1
Alkalinity, degree	no more than 2.0	1,4	1,3	1,2	1,3
Wetting ability, %	not less than 110.0	140,0	150,0	145,0	148,0

As can be seen from the table, biscuits with the addition of grape powder correspond to the physicochemical indicators of DSTU for butter biscuits.

A project of technological instructions has been developed for the new biscuits, which is presented in the Appendix A,

4.6 Analysis of the composition and antioxidant properties of biscuits incorporation of grape seeds or grape skin powder

The results of the analysis of the chemical composition of biscuits with the addition of grape powders are presented in the Table 4.13.

It can be seen from Table 4.10 that carbohydrates are still the main component of biscuits. However, compared with the control group biscuits, the addition of GS/GSK significantly increased the contents of polyphenols and TDF in biscuits. Since the lipid content in grape seeds powder and grape skin powder was higher than that in wheat flour, the lipid content in grape pomace biscuits was also significantly higher than that in the control group biscuits. In summary, after the addition of grape seeds or grape skin, the dietary fiber and polyphenols in biscuits increased significantly, which met the needs of modern food. Therefore, GSP or GSKP was a kind of high-quality biscuits processing raw material.

Table 4.13

General composition of biscuits with 10% GS/ GSK addition

(n=3, P≥0,95)

Component (%)	Biscuits		
	Control group	GS biscuits	GSK biscuits
Crude protein	8.99	9.00	9.00
Crude fat	9.48	12.75	6.32
Ash	2.08	2.40	3.38
Moisture	1.85	1.48	1.69
TDF	0.72	6.14	6.89
Total carbohydrate	68.45	66.32	71.74
Total polyphenols	0.74	1.16	1.23

Fig. 4.3 shows the scavenging capacity of biscuits with different GSP / GSKP additions on DPPH radical and hydroxyl radical, as well as the reducing power of biscuits.

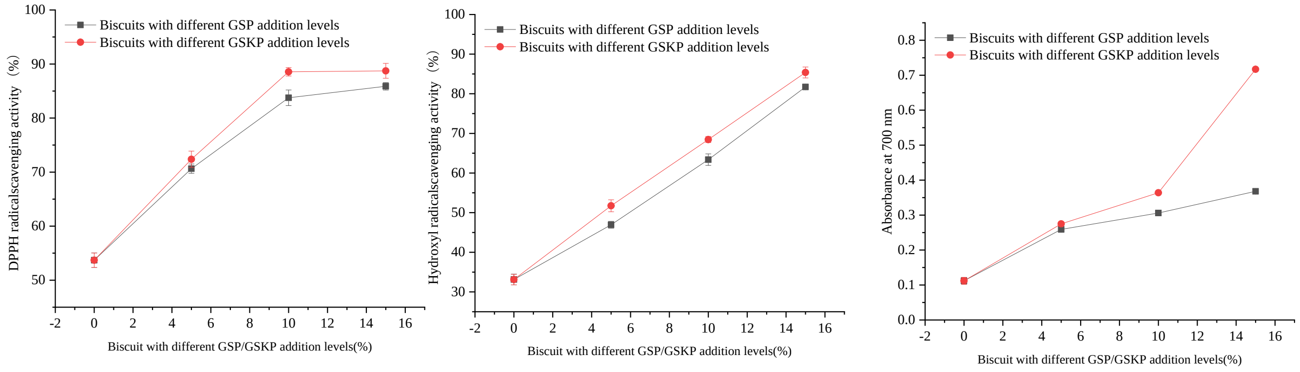


Figure 4.4 – Antioxidant properties of biscuits with different GSP/GSKP addition levels

It can be seen from the Fig. 4.3 that compared with the control group biscuits; the antioxidant properties of biscuits increased with the increase of GSP / GSKP addition. Among them, the antioxidant effect of grape skin biscuits was stronger than that of grape seeds at the same addition level. When the GSP / GSKP addition was 10 %, the scavenging capacity of biscuits on DPPH radical reached more than 80 %, which was more than 30 % higher than that of the control group biscuits. Therefore, the antioxidant effect of biscuits with GPP / GSKP addition is greatly enhanced, which provides a certain reference value for the study of the shelf life of grape pomace biscuits.

4.7 Antioxidant, digestive and sensory properties of grape residue biscuits

4.7.1 Sensory evaluation

A sensory evaluation of biscuits with various GPP contents is summarized in Table 4.14.

Table 4.14

Sensory evaluation results of biscuits with varying GPP addition levels

(n=3, P≥0,95)

GPP addition level, wt%	Evaluation score				
	color	appearance	flavor	texture	acceptability
0	8.25	8.05	7.75	7.85	8.00
5	7.85	7.65	7.65	7.60	7.45
10	7.30	7.70	7.45	7.66^{a}	7.55
12.5	7.75	7.85	8.05	7.35	7.75
15	6.25	7.35	5.85	6.65	7.25
20	4.20	7.20	4.45	6.35	6.10

There were no significant differences in appearance and texture between the GPP group and the control group. In terms of color, the scores between the 5 wt% group and the control group were significantly different ($p<0.05$), 7.85 and 8.25, respectively, while 10 wt% (7.30) or 12.5 wt% (7.75) were compared with 5 wt% (7.75). Appearance score and color score showed a similar trend, which may be explained to some extent by the influence of the latter on the former. This is consistent with the previous study [191]. In this study, when the GPP level reached 12.5 wt%, the color score increased slightly, reflecting favorable chocolate color. When the GPP exceeds 12.5 wt%, the rough particle surface and astringency can be clearly observed, resulting in a decrease in the fraction. In terms of flavor, at 10 wt%, the score was the highest (8.05), while the increase of GPP led to the decrease of the score. Therefore, 10 wt% of GPP gives sufficient grape flavor and is beneficial to consumers. This is similar to the previous results [192], in which apple pomace is used to improve the flavor of cookies. As for texture, increasing GPP will result in lower scores, which may be caused by smaller size and higher surface roughness. When the GPP is lower than 12.5 wt%, there is no significant difference between the acceptability and that of the control group, indicating that biscuits can be accepted by consumers. In general, when 10 wt% GPP is used, the corresponding biscuits show the characteristics of chocolate color, regular appearance, relatively smooth surface, rich aroma, moderate grape taste, crisp, obvious cross section structure, small pores and even distribution.

4.7.2 Color measurement

Table 4.15 shows the results of color measurements of biscuits made with different levels of GPP preparations.

Table 4.15

The effect of different GPP additions on the color of biscuits

(n=3, P≥0,95)

GPP addition level, %	L^*	a^*	b^*
0	68.58	6.22	29.84
5	57.40	6.38	19.59
10	49.08	8.38	17.15
12.5	48.73	8.67	16.80
15	47.82	8.99	16.48
20	43.60	9.87	14.14

Compared with the control group, the L* and b* values of the GPP group decreased significantly ($p<0.05$) and decreased with the increase of GPP ($p<0.05$). This effect is mainly due to natural pigments, such as anthocyanins in GPP [193]. Conversely, the values of a* show the opposite trend, indicating an increase in redness. Combining the color analysis results with the color sensory evaluation can achieve a reasonable quality evaluation.

4.7.3 Textural assay

Hardness is the force required to deform a sample [194]. Brittleness refers to the breaking force of the sample during the first compression and is negatively correlated with the brittle character in sensory evaluation [195]. Chewability describes the force required to transform a sample from a chewed to a swallowed state. These parameters are closely related to human perception of freshness, so they are of great interest in the evaluation of bakery products [196]. As shown in Fig. 4.4, the hardness shows a maximum value at 15 wt% GPP, which is significantly higher than that of the control group.

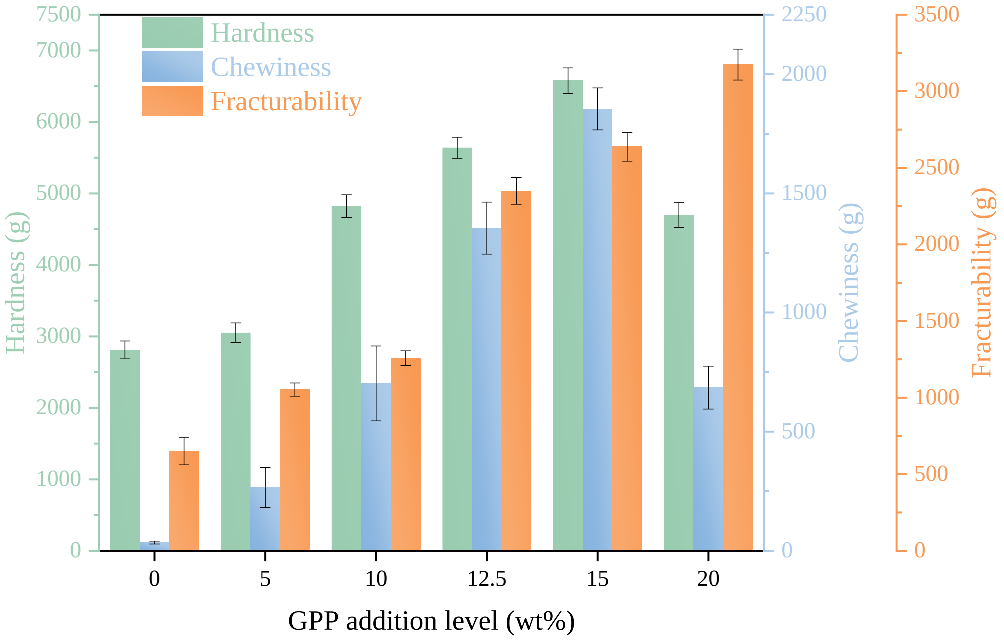


Figure 4.5 – Effect of different GPP addition levels on dough texture

The author’s results differ from those reported by Kuchtová (2018) et al. [197]. This phenomenon may be related to the relationship between polyphenols in GPP and protein or starch, resulting in increased gluten network strength and dough strength [198], which Consistent with previous rheological results. A further increase in GPP results in a decrease in relative gluten protein content and thus a decrease in firmness. Chewability showed the same trend as firmness. Brittleness increases with increasing GPP. In general, lower hardness is more acceptable to consumers [199]. For this reason, the addition of grape pomace should be minimized to ensure acceptable biscuits firmness.

4.7.4 General composition

Table 4.16 summarizes the general composition of biscuits with different GPP addition levels.

In contrast to the control group, the crude protein, crude fat and total polyphenols contents were significantly increased in the GPP group. When 12.5 wt% GPP was used, the contents of these three components increased by 14.01%, 24.79% and 44.59%, respectively; for 20 wt%, these contents increased by 25.14%, 31.96% and 71.62%, respectively.

Table 4.16

General composition of biscuits

(n=3, P≥0,95)

Component (%)	GPP addition level (wt%)					
	0	5	10	12.5	15	20
Moisture	1.85	2.14	1.36	2.01	1.47	1.33
Ash	2.08	2.21	2.38	1.67	1.83	2.02
Crude fat	9.48	9.43	10.24	11.83	11.96	12.51
Crude protein	8.99	9.00	9.58	10.25	10.63	11.25
Total carbohydrate	68.45	65.32	61.74	61.80	56.21	53.47
Total polyphenols	0.74	0.82	0.99	1.07	1.23	1.27
TDF	0.92	4.12	6.53	7.98	9.05	11.21

Total dietary fiber content was positively correlated with GPP content. According to the statement, food products with high fibre content can only be served if they contain at least 6 grams of fibre per 100 grams of product [Regulation EC No 1924/2006], as indicated in the Regulation of the European Parliament (EC). There were no significant differences in ash and moisture content between the GPP group and the control group. In conclusion, biscuits containing GPP content ≥ 10wt% can be considered as high-fiber foods.

4.7.5 Antioxidant activities

The antioxidant activity of biscuits containing GPP is shown in Fig. 4.6.

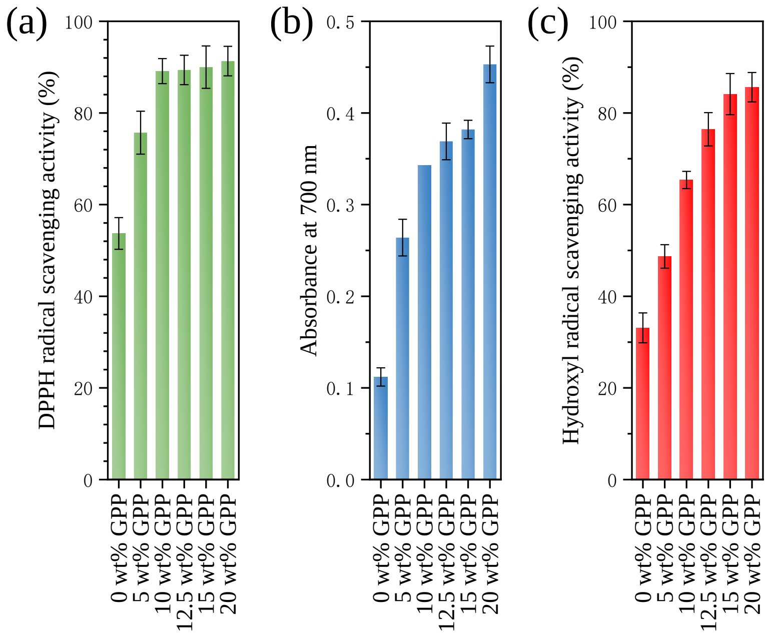


Figure 4.6 – Chemical antioxidant activity of biscuits with different levels of GPP addition. (a) DPPH radical scavenging activity, (b) reducing capacity, and (c) hydroxyl radical scavenging capacity

Compared with the control group, DPPH and hydroxyl radical scavenging activities were significantly increased ($p < 0.05$) and increased with the increase of GPP content. The scavenging activities of 5 wt% GPP on DPPH and hydroxyl radicals were increased by 40.95% and 47.01%, respectively, compared with the control group. Furthermore, the observed antioxidant effects increased with increasing GPP levels, suggesting that GPP has a good antioxidant effect in vitro. These results are consistent with those of Santa et al. (2020) [200]. The reducing activity (Fig. 4.5-b) increased with increasing GPP, and the polyphenol content increased. Therefore, GPP may be a promising natural antioxidant to improve the shelf life and quality of biscuits products.

4.7.6 *In vitro* digestion characteristics

Fig. 4.7-4.9 shows the in vitro digestibility curves of biscuits with and without added GPP.

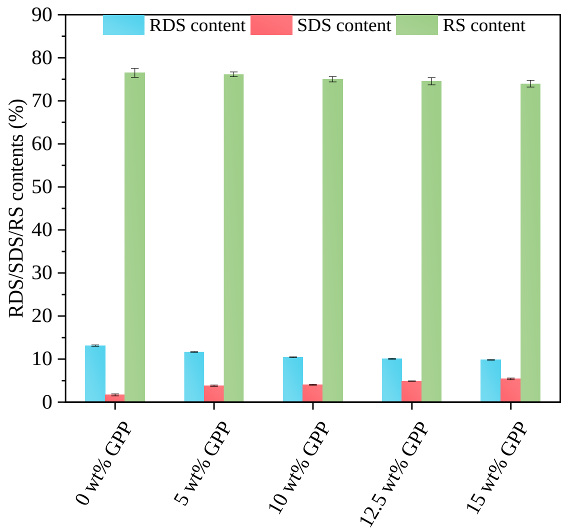


Figure 4.7– Starch content in biscuits

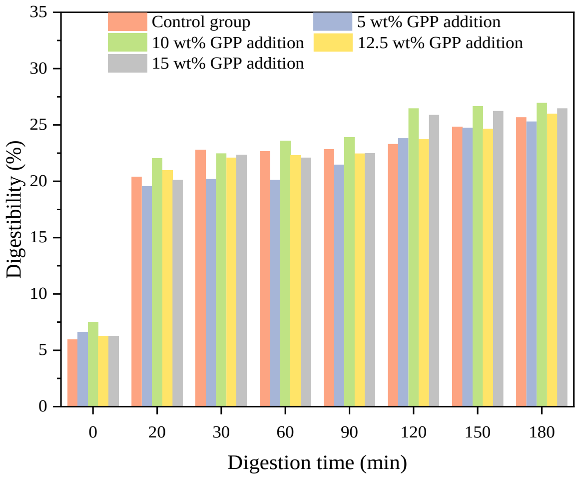


Figure 4.8 – The in vitro digestion rate of biscuits

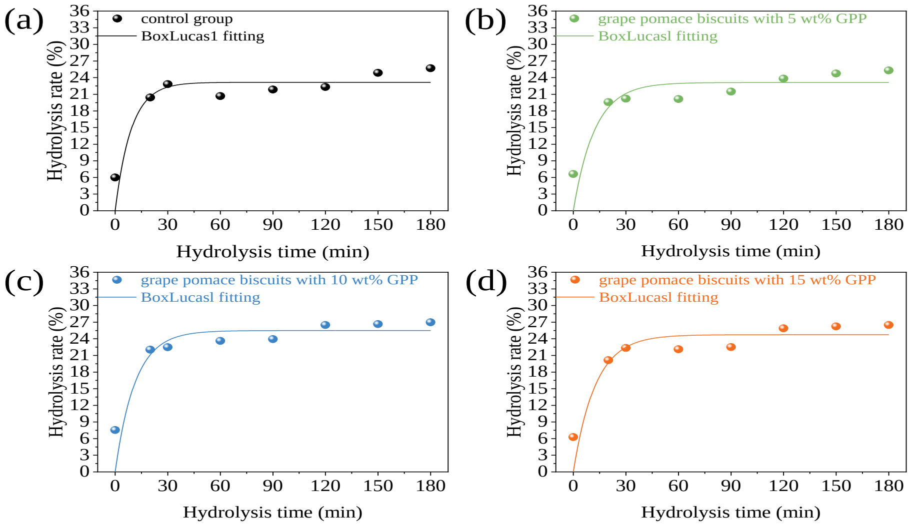


Figure 4.9 – First order kinetics fit curve of in-vitro digestion

No significant differences were observed in samples supplemented with different GPPs compared to the control group. In all cases, the hydrolysis rate increased rapidly and continuously during the first 45 min of the reaction, then decreased until 120 min, where the hydrolysis rate decreased further. However, the predicted glycemic index was calculated (r=0.96) using the empirical equation pGI=39.71+0.549 (HI90). It was found that all biscuits, including controls, were surprisingly high (≥90). However, the reason was not clarified, thus further in vivo studies are needed to elucidate the actual postprandial glycemic response of biscuits. The corresponding characteristic parameters are listed in Table 4.17, where the equilibrium concentration C∞ relates to the hydrolysis coefficient k.

Table 4.17

The characteristic parameters and hydrolysis index of different biscuits

Sample	C_∞	k	Kinetic formula of hydrolysis rate
0% GPP addition level	23.16	0.11	$C_t = 23.16 \times (1 - e^{-0.11t})$
5% GPP addition level	23.13	0.08	$C_t = 23.13 \times (1 - e^{-0.08t})$
10% GPP addition level	25.49	0.09	$C_t = 25.49 \times (1 - e^{-0.09t})$
15% GPP addition level	24.74	0.08	$C_t = 24.74 \times (1 - e^{-0.08t})$

The results showed that C∞ was not significantly different (p>0.05) between different GPP additions within the time window of 0-180 minutes, and k was also not significantly different, about 0.1 h-1. In this In this case, GPP addition did not significantly affect the hydrolysis rate, indicating that GPP addition does not affect the hydrolysis rate ld and does not result in significant differences in blood glucose concentrations between these samples.

4.7.7 Aroma components analysis

The fragrance of baked food primarily originates from raw materials, fermentation, and baking process. For biscuits, it mainly comes from raw materials and baking process, in which Maillard reaction of amino acids and sugars was mediated to produce heterocyclic compounds with specific color and volatility

[205]. Determination of aroma components in grape pomace powder and biscuits with different grape pomace addition amount by HPLC-MS / MS (Fig. 4.10).

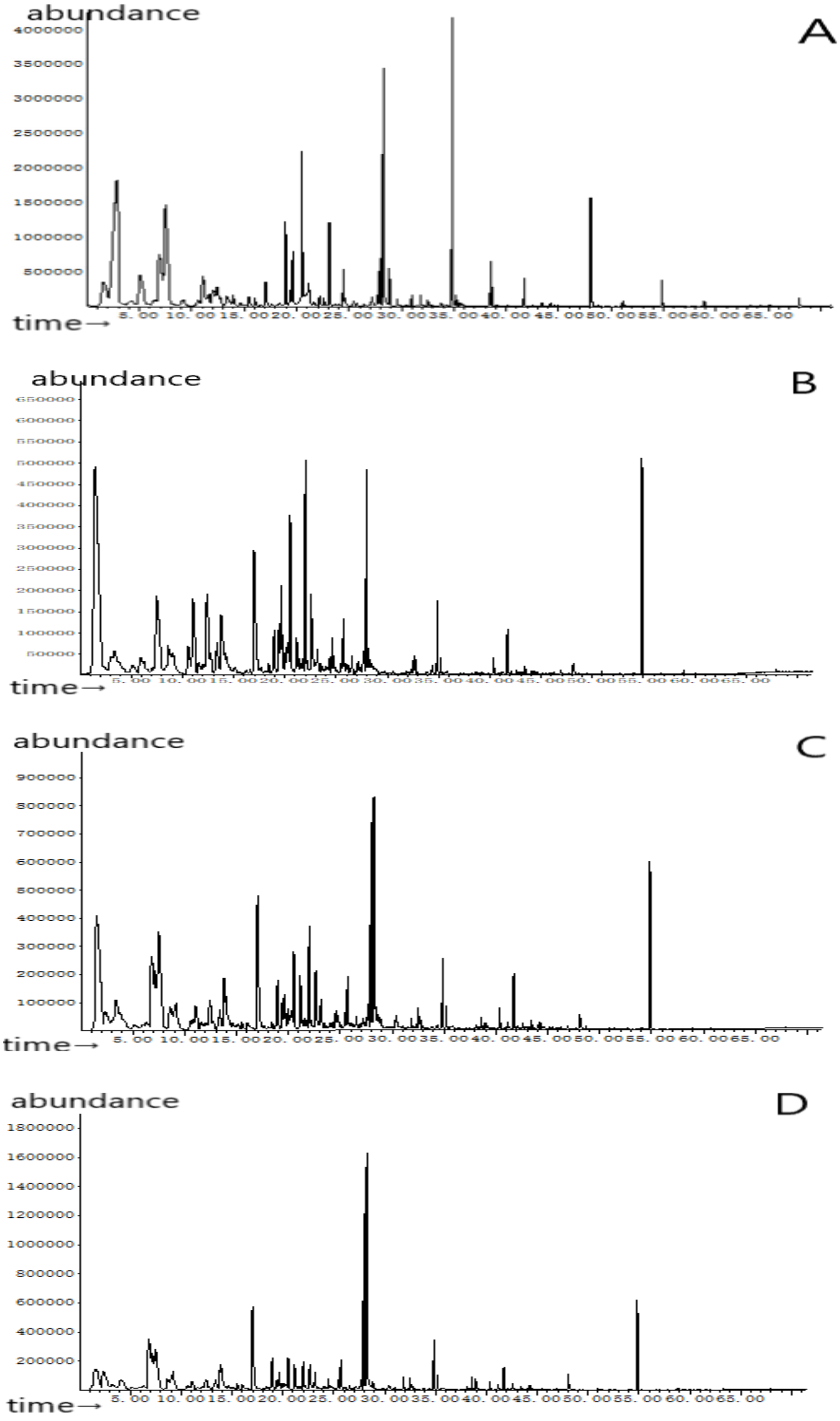


Figure 4.10 – HPLC-MS/MS chromatograms of grape pomace powder and biscuits（A. grape pomace powder B. biscuits with 0% grape pomace addition C. biscuits with 5% grape pomace addition D. biscuits with 10% grape pomace addition）

The aroma components of three biscuits were listed in Appendix B. With respect to GPP, 49 compounds were detected and identified by GC/MS, which consisted of alcohols (9), acids (5), aldehydes (9), ketones (3), organic acids (5), esters (11), furans (2), and others (5). With regard to the control group, 37 compounds were identified, including alcohols (4), aldehydes (7), ketones (2), esters (5), furans (1), pyrazines (4), and others (14). In terms of biscuits with 5 wt% GPP, 47 compounds were identified, which were comprised of alcohols (12), aldehydes (6), organic acids (2), esters (6), ketones (1), furans (3), pyrazines (6), and others (11). As for biscuits with 10 wt% addition, 41 compounds were identified, including alcohols (9), aldehydes (7), organic acids (3), esters (1), furans (3), pyrazines (5), ketones (1), and others (12).

Compared with GPP, the contents of alcohols, organic acids, and esters derived from biscuits with GPP were significantly reduced, while furans, pyrazines, and pyrans were considerably increased, which were common aroma compounds in baked food. As for alcohols, 2, 3-butanediol was not detected in the control group, but its relative content in biscuits increased with increasing GPP addition levels; the relative contents of 3-methyl-1-butyl alcohol and phenylethyl alcohol were positively correlated to GPP addition levels; and the remaining 6 alcohols (i.e., 1-pentanol, 1-hexanol, 1-octene-3-ol, 1-heptanol, 2-ethyl-1-hexanol, and benzyl alcohol) had the highest relative contents in the control group. The above differences may be attributed to the high content of 3-methyl-1-butanol in GPP. Previous studies have suggested that 3-methyl-1-butanol is positively correlated to the flavor score of (fermented) bread in sensory evaluation [206], Phenylethyl alcohol could deliver honey fragrance to baked food. Therefore, GPP could potentially offer malt and honey flavor to biscuits product. In terms of aldehydes, acetaldehyde, heptyl aldehyde, benzaldehyde, and nonyl aldehyde were detected in all three biscuits. Heptyl aldehyde mainly presented fat and oil flavor, benzaldehyde mainly delivered bitter almond flavor, and nonyl aldehyde mainly offers fresh rose fragrance. Strecker aldehyde may originated from the oxidative deamination and decarboxylation of any α-amino acid compound containing dicarbonyl, which pre-existed in primary materials, under heating. 3-Methylbutyraldehyde, benzaldehyde, and phenylacetaldehyde might be derived from leucine, methionine, and phenylalanine, respectively. 3-Methylbutyraldehyde features a mixture of malt, lipid, and chocolate fragrances, and phenylacetaldehyde provides honey and rose fragrances. For all three biscuits, the relative contents of benzaldehyde were higher than nonyl aldehyde. Phenylacetaldehyde was detected in these two biscuits with 5 wt% and 10 wt% GPP addition, and their relative contents were also lower than benzaldehyde.

Acetic acid could be derived either from sugar degradation in Maillard reaction [207], or from microbial metabolism, which took place in both material mixing and dough formation processes, and could be facilitated by introducing certain amount of water [208]. As ethanol compound in GPP could be oxidized to acetic acid [115], it might contribute to the increased relative content in biscuits with GPP addition in comparison to the control group. Acetic acid was identified as an important flavor compound in wheat bread and rye bread, and also a flavor enhancer. Short-chain organic acids (C2~C5) account for only 1% of titratable acids, while they can play a decisive role in the flavor of bread. In addition, more of them could be generated in fermentation, which would intensify the specific flavor. In contrast, short-chain isoacids have a negative effect on the flavor of bread [209].

Given the high volatility of esters, they could probably be released under thermal treatment in baking process [210]. Butyrolactone is the most widely distributed γ-lactone, and has a sweet caramel flavor. It was only detected in GPP. Ethyl acetate and 2, 3-butyl dimethylpropionate featuring fruity and candy flavor were not detected in biscuits when GPP addition level reached 10%, which was similar to the results of Sobhym et al. [211]. In their study, soybean protein was isolated and used as additive in biscuits production, and the content of lactone compounds decreased significantly when the addition levels in the range of 10%~20%.

Diketones could be originated from carbohydrate degradation, and would offer positive flavor characteristics to final product (e.g., biscuits) [209]. Three ketones, which were comprised of 6-methyl-5-hept-2-one with lemon flavor, 3-

octyl-2-one with mushroom flavor, and acetophenone with almond flavor, were identified in biscuits with GPP addition, of which the relative contents were reduced with increasing addition level. Sobhym et al. [211] reported that when 5% isolated soybean protein was added to biscuits, the contents of lipid-derived volatile components (e.g., aldehydes, ketones and alcohols) significantly increased. However, when more than 10% was used, obvious decreasing took place, which might be ascribed to the free radical scavenging activity of the intermediates derived from Maillard reaction, thus hindering the spread of free radical reaction. In addition, proanthocyanidins in GPP are also capable of scavenging free radicals [212].

Furans could be derived from carbohydrates thermal degradation and rearrangement [213]. 2-Pentyl furan and 2, 3-dihydrooctafuran could offer fruit and herbal flavor to final product. As for 2-pentylfuran, it is a product of oxidation and/or thermal degradation of unsaturated fatty acids, which is universally existed in cooking oils, rice, bread, cakes, and other foods [214-215].

Pyrazines are typical products in Maillard reaction, which have attracted considerable attention focusing on their contribution to presenting roasting flavor and nutty flavor in heat-processed cereals [195]. These compounds could have intensive impacts on the flavor of bread, cakes, and biscuits [216]. In biscuits analysis, 7 kinds of pyrazine compounds were identified. Compared with the control group, the relative contents of 2, 6-dimethyl pyrazine and 2, 5-dimethyl pyrazine were increased by the GPP addition, while 2 -acyl pyrazine, 1-methyl-2-alkenyl pyrazine, 2-ethyl-6-methyl pyrazine were decreased with increasing GPP addition levels. In addition, other alkylpyrazines displayed no significant change. It is worth to note that GPP does not have detectable pyrazines. However, GPP addition complicated the system by introducing dietary fiber, protein, and procyanidins, among others, whereby Maillard reaction was possibly affected to deliver different product slate, such as by the interference of protein on the amino acids hydrolysis or deamination [195]. In spite of all pyrazine compounds can provide roasting flavor, 2, 6-dimethylpyrazine, trimethylpyrazine, and 6-methyl-2-ethyl pyrazine are probably playing the major role [217].

Conclusions of section 4

1. The processing technology of grape seeds and grape skin biscuits was optimized by single factor and orthogonal experiments. The effect of grape powder addition on the sensory score of biscuits was investigated by nine-point hedonic method. At the same time, the single factor and orthogonal experiments were used to optimize the processing technology of biscuits.

2. Finally, the nutritional composition and antioxidant properties of biscuits under the optimal process conditions were evaluated. The results showed that with the increase of grape powder addition, the hardness, chewiness and brittleness of the two biscuits increased first and then decreased. When the grape skin powder addition was 5 % and the grape seeds powder addition was 15 %, the biscuits were most likely to be accepted by consumers.

3. When the grape seeds powder / grape skin powder addition was 10 %, compared with the control group, the polyphenols and dietary fiber of the former increased by 5.42 % and 0.41 %, and the latter increased by 6.17 % and 0.49 %, respectively.

4. As for the DPPH and hydroxyl radical scavenging ability of biscuits, the former increased by 30.0 % and 31.2 %, and the latter increased by 35.1 % and 34.3 %, respectively.

5. The tough grape pomace biscuits met the market demand of modern biscuits, and the optimal addition amount of sugar powder in the processing technology of grape pomace biscuits was 35 %, the optimal addition amount of palm oil was 9 %, and the ratio of grape pomace: glucolactone : grape pomace was 0.6 : 0.8 : 1.0. Under these conditions, the biscuits had chocolate color, strong grape flavor, high overall acceptance of biscuits, and the total plate count and coliforms were within the safe range. In addition, after the addition of grape seeds or grape skin, the content of polyphenols and dietary fiber in biscuits increased greatly, and the scavenging ability of biscuits on DPPH and hydroxyl radicals and the reducing power of biscuits were greatly enhanced, indicating that grape pomace was an excellent raw material for biscuits.

6 .The influence of varying GPP addition levels on the qualities of resulting biscuits were systematically investigated. The results suggested that, GPP significantly improved the antioxidant activity of biscuits, that RDS decreased with increasing GPP addition while SDS increased, and that at the level of 10%, biscuits delivered mixed flavor featuring bitter almond flavor, banana flavor, herbal flavor, toasty and nutty. As for sensory analysis, the results indicated that at the level of 12.5%

7. GPP addition, the score of biscuits fragrance was relatively high, and that the biscuits gained considerable acceptability with GPP addition less than 15%. In addition, GPP addition enhanced contents of dietary fiber and polyphenol in the final biscuits. Taken together, GPP holds a promising potential as fortification material for biscuits, and this work advances the progress towards its effective utilization.

SECTION 5

STUDY ON SHELF LIFE PREDICTION OF GRAPE POMACE BISCUITS

Self-life is one of the important indicators of food quality and safety, which is crucial for producers and consumers. The shelf life of food is a period of time when it is safe to eat under recommended storage conditions and has ideal quality characteristics, including sensory properties, physicochemical properties and microbial properties, while retaining any nutritional value declared by the nutritional label. Accelerated Shelf-Life Testing (ASLT) can accelerate the quality response of foods in order to quickly predict the shelf life of foods [218]: ASLT has been successfully applied to predict the shelf life of compressed biscuits [219], cookies [220] and crisp biscuits [221]. Food is greatly affected by temperature, humidity, gas and other environmental factors during storage. In which oil rancidity or oxidation reaction occurs, resulting in the destruction of nutrients, adverse flavor or toxic and harmful substances, resulting in increased acid value and peroxide value. Therefore, the peroxide value was used as the evaluation index of the shelf life prediction model in this paper. Through accelerated test, the influence of different storage time on the peroxide value of grape pomace ductile biscuits was studied, and the relevant dynamic models were established to predict the shelf life of products, so as to provide the basic theoretical basis for the storage management of grape pomace ductile biscuits.

5.1 Peroxidation value of grape pomace biscuits at different storage temperatures

The change of peroxide value of grape pomace biscuits at different storage temperatures is shown in Fig. 5.1. The results showed that at the same storage temperature, the peroxide value of biscuits increased with the extension of storage time, when they were stored until the sixth week, the peroxide value of grape pomace biscuits stored at 37 °C, 47 °C and 57 °C increased by 0.041, 0.052 and 0.065, respectively, compared with that stored at 0 week. At the same storage time, the peroxide value of grape pomace biscuits increased with the increase of storage temperature. Which showed that high temperature could accelerate the deterioration of product quality.

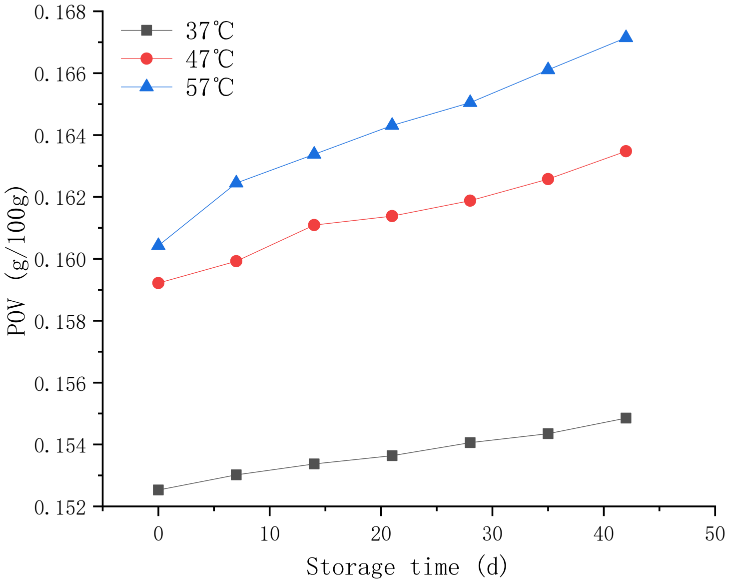


Figure 5.1 – The POV changes of grape pomace biscuits at different temperature

5.2 Kinetic analysis of peroxide value of grape pomace biscuits

The change of peroxide value of grape pomace biscuits measured at different temperatures (37, 47 and 57 °C) is shown in Fig. 5.2.

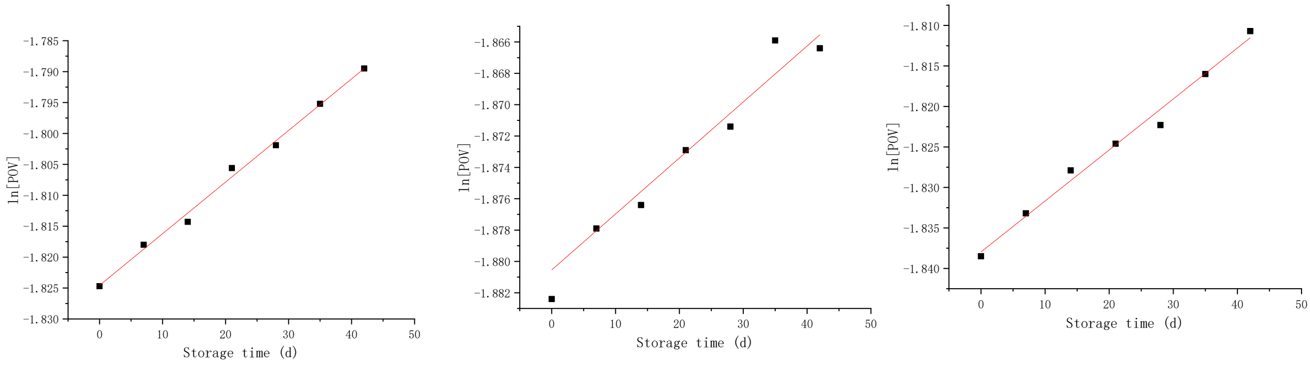


Figure 5.2 – The POV changes of grape pomace biscuits at 37℃, 47℃ and 57℃

It can be seen from the figure that the higher the storage temperature is, the faster the peroxide value of grape pomace biscuits increases. The changes of peroxide value of grape pomace biscuits during storage at different temperatures were fitted and the equation was shown in Table 5.1.

Table 5.1

Regression equation of POV changes with time under different temperatures

Temperature (°C)	Regression equation	R^2	Shelf life (d)
37	Ln [POV]=0.0025t-1.8804	0.987	198
47	Ln [POV]=0.0043t-1.8375	0.981	105
57	Ln [POV]=0.0057t-1.8237	0.976	77

Table 5.1 showed that the correlation coefficient (R^2) of the regression equation of peroxide value at all storage temperatures was > 0.9, indicating that the equation has good fitting effect. The change rate constant（b）of peroxide value increased with the increase of temperature, suggesting that the increase of temperature can promote the lipid oxidation. The maximum allowable peroxide value of 0.25 g / 100 g was substituted into each regression equation, and the shelf life of grape pomace biscuits stored at 37, 47 and 57 °C was 198 days, 105 days and 77 days, respectively.

The temperature and shelf life were analyzed and fitted, and the shelf life prediction model equation was $\ln (T) = -0.0024S + 4.2225$ ($R^2 = 0.9412$). This equation can be used to predict the shelf life of grape pomace ductile biscuits at any temperature.

5.3 Validation of shelf life model

In order to verify the accuracy of the shelf life model, the predicted value and the real value of the shelf life prediction model of grape pomace biscuits were compared and analyzed at 25, 35 and 45 °C with peroxide value as the index.

From Table 5.2, the shelf-life prediction model established in this study was used to predict and analyze the shelf-life, and the relative error of the predicted shelf-life was less than 10 %, indicating that the peroxide value prediction model had a good fitting effect, which could quickly and reliably predict the shelf-life of grape pomace ductile biscuits under different temperature storage conditions.

Table 5.2

Prediction and measurement values of shelf life of grape pomace biscuits stored at various temperatures

Storage temperature (℃)	Peroxide value model		
	Shelf life value prediction (d)	Real value of shelf life (d)	Relative error* (%)
25	294	281	4.6
35	195	183	6.5
45	122	119	2.5

Note：relative error = [Prediction value - Real value] / Real value

Conclusions of section 5

By detecting the peroxide value of 37, 47 and 57°C in different periods of storage, according to the first-order kinetic model of oil rancidity, the shelf life of grape pomace tough biscuits was 198 days, 105 days and 77 days, respectively, and further fitting the temperature and shelf life, the kinetic equation is ln (T) = -0.0024S + 4.2225 (R^2 = 0.9412). And the confirmatory experiment results show that the relative error of the shelf life prediction value obtained by applying the grape pomace tough biscuits shelf life prediction model established in this study is less than 10%, and it can predict the shelf life of products at different temperatures well.

CONCLUSIONS

1. Based on the analysis and generalization of theoretical data, the perspective of using the processing products of grape pomace of Cabernet Sauvignon grown in the eastern parts of China, namely powders from pomace, seeds and skin in biscuits technology, was established.

2. Dietary fiber is the main component of dried wine pomace, with concentrations ranging between 59% and 68%. Generally, seeds are richer in fiber than skin. The hydrolyzable polyphenols in seeds are richer than skin (92 mg GAE$\cdot$g^{-1}DW VS 56 mg GAE$\cdot$g^{-1}DW), among which Epicatechin and Catechin exhibited the highest content in grape seeds and skin. Furthermore, the antioxidant activity of its polyphenol extract was far superior to that of vitamin C.

3. GPP and GSP significantly ($p<0.05$) reduced the water absorption but three types of grape powders could increase the development time and dough stability. Furthermore, all kinds of grape powders with various incorporations could significantly ($p<0.05$) enhance the strength of dough systems. The dynamic oscillation experiment showed that in the whole frequency range, the addition of three grape powders reduced G' and G", but increased tanδ, suggesting a more liquid-like behaviour of the composite flour dough formulations. The microstructure of dough samples showed that the addition of grape flour decreased the integrity and continuity of gluten network in dough. Overall, the addition of grape seeds and grape skin powder had a significant effect on the quality of dough, furthermore, the particle size also has a significant effect on the rheological properties of the dough.

4. RVA results suggested that GPP/GSP/GSKP addition had limited effect on pasting temperature, the minor increase of gelatinization temperature of flours incorporated with GSP/GPP is attributed to the protein and lipid contained in grape seeds and pomace. In all cases, peak time decreased due to gelatinization temperature increased. However, three types of grape powders significantly decreased the setback value of the paste system, which indicated that active polyphenol fraction in grape pomace can effectively prevent amylose association in

starch paste upon cooling stage. However, an increase of breakdown viscosity suggested that GPP could reduce the thermal stability and mechanical damage resistance of starch granules. These three viscosities decreased significantly ($p < 0.05$) as GPP increased, majorly due to the starch dilution effect in GPP pastes, which leads to a decrease in dough stability. The Differential Scanning Calorimetry (DSC) results showed that enthalpy required for gelatinization was significantly reduced due to the relative decrease of starch content.

5. The incorporation of grape seeds, grape skin and grape pomace powder was 15 %, 5 % and 10 %, respectively. The optimal addition amount of sugar powder in the processing technology of grape pomace biscuits was 35 %, the optimal addition amount of palm oil was 9 %, and the ratio of grape pomace : glucolactone : grape pomace was 0.6 : 0.8 : 1.0. Under these conditions, the biscuits had chocolate color, strong grape flavor, high overall acceptance of biscuits, and the total plate and coliforms were within the safe range.

6. The nutritional composition and antioxidant properties of three biscuits under the optimal process conditions were evaluated. The results showed that the hardness, chewiness and brittleness of the biscuits increased with lower grape powders addition, and then decreased at higher addition amount. When the grape skin powder addition was 5 % and the grape seeds powder addition was 15 %, the biscuits were most likely to be accepted by consumers. When the grape seeds powder / grape skin powder addition was 10 %, compared with the control group, the polyphenols and dietary fiber of the former increased by 5.42 % and 0.41 %, and the latter increased by 6.17 % and 0.49 %, respectively. Additionally, biscuits incorporated with an addition amount of 10% GPP exhibited nailing oxidation resistance and can be considered as a food with a high fiber content, which is a good option for people to pursue modern healthy foods.

7. The digestive characteristics of biscuits results showed that the rapidly digestible starch (RDS) decreased with increasing GPP addition while slowly digestible starch (SDS) increased, and the analysis of biscuits aroma components suggested that at the level of 10%, biscuits delivered mixed flavor featuring bitter

almond flavor, banana flavor, herbal flavor, toasty and nutty. As for sensory analysis, the results indicated that at the level of 12.5% GPP addition, the score of biscuits fragrance was relatively high. Taken together, GPP holds a promising potential as fortification material for biscuits.

8. According to the first-order kinetic model of oil rancidity, the shelf life of grape pomace tough biscuits was 198 days, 105 days and 77 days, respectively, and further fitting the temperature and shelf life, the kinetic equation is $\ln(T) = -0.0024S + 4.2225$ ($R^2 = 0.9412$). The relative error between the predicted value and the actual value is less than 10%, therefore, the shelf life of the product at different temperatures can be well predicted.

The main scientific results of the dissertation were published in a scientific articles [222-224], at scientific conferences and seminar (Appendix C).

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APPENDICES

APPENDIX A

РЕЦЕПТУРА
І ТЕХНОЛОГІЧНА ІНСТРУКЦІЯ
на печиво з додаванням порошків з вичавків винограду Каберне Совіньйон

Підстава: ДСТУ 3781:2014 «Печиво. Загальні технічні умови ».

1. Технічні вимоги.

Печиво з додаванням порошків з вичавків винограду Каберне Совіньйон – здобне формове печиво з борошна вищого гатунку з додаванням порошку з виноградних кісточок або з виноградних шкірочок або з виноградних вичавків. Має круглу форму.

В 1 кг міститься не менше 80 штук.

Вологість 10,0±1,5%.

За органолептичними показниками печиво з додаванням порошків з вичавків винограду Каберне Совіньйон має відповідати вимогам, зазначеним у таблиці 1.

Таблиця 1.

Найменування показника	Характеристика
Форма	Кругла, без пошкоджень. Допускається надламане печиво не більше 7% від маси нетто пакувальної одиниці
Поверхня	Непідгоріла, без здутин, пухирців, що лопнули й вкраплень крихт, з рівномірними слідами від проколів по всій площині, шорстка
Колір	Від світло- до темнокоричневого, рівномірний
Смак і запах	Властиві, без стороннього присмаку і запаху
Вид в розломі	Пропечене з рівномірною пористістю без пустот і слідів непромішення

За фізико-хімічними показниками печиво з додаванням порошків з вичавків винограду Каберне Совіньйон повинно відповідати вимогам, зазначеним в таблиці 2.

Таблиця 2.

Найменування показників	Норма	Метод аналізу
Вологість, %	10,0 ± 1,5	ДСТУ 4910
Масова частка загального цукру (за сахарозою) в перерахунку на суху речовину, %	22,0 ± 2,5	ДСТУ 5059
Масова частка жиру в перерахунку на суху речовину, %	5,0 ± 1,0	ДСТУ 5060
Лужність, град не більше	2,0	ДСТУ 4672
Масова частка золи, нерозчинної в розчині соляної кислоти з м.ч. 10%, %, не більше	0,1	ДСТУ 4672
Здатність до намокання, %, не менше	110	ДСТУ 5023

Вміст токсичних елементів в печиві не повинен перевищувати гранично допустимих концентрацій, передбачених Сан ПіН 42-123-4089 та приведених в таблиці 3.

Таблиця 3.

Найменування токсичного елементу	Гранично допустима концентрація, мг/кг, не більше	Метод аналізу
Ртуть	0,02	ГОСТ 26927
Миш'як	0,3	ГОСТ 26930
Свинець	0,5	ГОСТ 26932
Кадмій	0,1	ГОСТ 26933

За мікробіологічними показниками печиво повинно відповідати вимогам, наведених в таблиці 4.

Таблиця 4.

Найменування показників	Норма
Кількість мезофільних аеробних і факультативно-анаеробних мікроорганізмів, КУО в 1,0 г продукту, не більше	$1x10^4$
Бактерії групи кишкових паличок (коліформи), в 0,1 г продукту	не допускаются
Патогенні мікроорганізми, в т.ч. бактерії роду Сальмонела, в 25 г	не допускаются
Плісеневі гриби, КУО в 1 г, не більше ніж	100
Дріжджі, КУО в 1 г, не більше ніж	50

Вміст мікотоксинів в печиві не повинен перевищувати рівні, передбачені «Медико-біологічними вимогами та санітарними нормами якості продовольчої сировини та харчових продуктів» №5061, а **вміст пестицідів** не повинен перевищуватит рівнів, зазначених у ДСанПіН 8.8.1.2.3.4.-000 і їх регламентують у сировині.

2. Вимоги до сировини

Сировина, що застосовується при виготовленні печива, повинна бути дозволена до застосування МОЗ України. Якість її повинна відповідати вимогам чинної нормативної документації; за вмістом токсичних елементів, мікотоксинів, пестицидів, нітратів має відповідати «Медико-біологічним вимогам і санітарним нормам якості продовольчої сировини і харчових продуктів № 5061».

Рецептура на печиво з додаванням порошків з вичавків винограду Каберне Совіньйон наведена в таблиці 5.

Таблиця 5.

Сировина	Вміст сухих речовин, %	Витрата сировини на 100,0 кг печива з додаванням порошку, кг					
		з кісточок		зі шкірочок		з вичавків	
		у натурі	у сухих речовинах	у натурі	у сухих речовинах	у натурі	у сухих речовинах
Борошно пшеничне	85,50	56,67	48,45	61,58	52,65	60,00	51,30
Порошок з виноградних кісточок	96,30	10,00	9,63	0,00	0,00	0,00	0,00
Порошок з виноградних шкірочок	95,50	0,00	0,00	3,24	3,10	0,00	0,00
Порошок з виноградних вичавків	94,10	0,00	0,00	0,00	0,00	6,67	6,27
Пудра цукрова	99,85	23,33	23,30	25,93	25,89	23,33	23,30
Олія пальмова	84,00	6,00	5,04	5,83	4,90	6,00	5,04
Меланж	27,00	9,33	2,52	9,07	2,45	9,33	2,52
Вода	0,00	6,27	0,00	6,09	0,00	6,27	0,00
Молоко	12,50	3,33	0,42	3,24	0,41	3,33	0,42
Сіль	96,50	0,47	0,45	0,45	0,44	0,47	0,45
Амонію бікарбонат	99,00	0,40	0,40	0,39	0,39	0,40	0,40
Натрію бікарбонат	50,00	0,53	0,27	0,52	0,26	0,53	0,27
Глюколактон	99,60	0,67	0,66	0,65	0,65	0,67	0,66
Разом		117,00	91,13	117,00	91,12	117,00	90,63
Вихід		100,00	90,00	100,00	90,00	100,00	90,00

Технологічна інструкція з приготування печива з додаванням порошків з вичавків винограду Каберне Совіньйон

Приготування печива складається з наступних стадій:

- підготовка сировини до виробництва;
- приготування тіста;
- формування тіста, випікання;
- упаковка, маркування, транспортування і зберігання.

Підготовка сировини до виробництва

Підготовка сировини до виробництва здійснюється відповідно до Технологічних інструкцій по виробництву борошняних кондитерських виробів. Допускається взаємозамінність сировини відповідно до Вказівок до рецептур на печиво.

Приготування тіста

В місильній машині протягом 7-8 хвилин змішують молоко, меланж, борошно пшеничне та порошок виноградний, потім додають пластифіковану олію пальмову, розпушувачі, воду та сіль і перемішують 2-3 хв. Тісто має бути рівномірно перемішаним, незатягнутим.

Формування тіста, випікання

Готове тісто розкочують у пласт завтовшки 2-3 мм і круглою формою з гострими краями формують печиво, на його поверхню наносять рівномірні проколи. Випікають відформовані заготовки на поду печі протягом 10-11 хвилин за температури 170-180°С.

Випечене печиво надходить на стрічковий транспортер, де під обдувом холодного повітря охолоджується до температури 18-20°С.

Упаковка, маркування, транспортування і зберігання.

Упаковка, маркування, транспортування і зберігання печива проводяться відповідно до вимог ДСТУ 3781:2014.

Допустимі відхилення маси нетто пакувальної одиниці печива складають, не більше:

мінус 9,0 % — від 5 г до 50 г включно,
мінус 4,5 г - понад 50 до 100 г,
мінус 4,5 % - «100 до 200 г,
мінус 9,0 г - «200 до 300 г,
мінус 3,0 % - «300 до 500 г
мінус 15,0 г - «500 до 1000 г,
мінус 1,5 % - «1000 до 10000 г,
мінус 150,0 г - «10000 до 15000 г,

Відхилення маси нетто за верхньою межею не обмежується.

Печиво зберігають у сухих, чистих, добре вентильованих приміщеннях, що не мають стороннього запаху, не заражених шкідниками хлібних запасів, при температурі (18±5) °С і відносній вологості повітря не більше 75%.

Строк придатності печива з додаванням порошків з вичавків винограду Каберне Совіньйон до споживання :

- вагового з подальшим обтягуванням короба полімерною плівкою — 4 міс.

Харчова (поживна) та енергетична цінність (калорійність) 100 г печива з додаванням порошків з вичавків винограду Каберне Совіньйон»:

Білки, г	Жири, г	Вуглеводи, г	Калорійність, ккал Енергетична цінність, кДж
6,8	8,2	64,9	360 ккал/1507 кДж

РОЗРОБЛЕНО:

аспірантка кафедри технологій та безпечності харчових продуктів Сумського національного аграрного університету спеціальності 181 «Харчові технології»

Луо ВЕНЬЦЗЮАНЬ

SUMMARY OF AROMA COMPONENTS OF GPP AND BISCUITS

Compound		Retention Time (min)	Area percentage（%）				Odour description*
			GPP	Control group	5% GPP addition	10% GPP addition	
Total alcohol							
1	Ethanol	1.53	5.93	16.35	16.87	1.52	alcoholic ethereal medical
2	3-methyl-1-Butanol	6.52	2.04	ND	ND	ND	Fusel, alcoholic, pungent, etherial, cognac, fruity, banana and molasses
3	1-Pentanol	6.57	0.018	ND	ND	ND	Pungent, fermented, bready, yeasty, fusel, winey and solvent-like
4	Pentaethylene glycol	19.14	0.17	ND	ND	0.54	ND
5	3,5-Octadien-2-ol	31.94	2.66	ND	ND	ND	ND
6	2-ethyl-1-Hexanol	31.12	0.31	ND	ND	ND	citrus fresh floral oily sweet
7	1-methoxy-2-Propanol	3.38	ND	ND	3.18	ND	ND
8	2,3-Butanediol	6.79	7.11	ND	5.11	13.32	fruity creamy buttery
9	2,4-Butanediol	6.81	ND	ND	2.48	ND	ND
10	2,5-Butanediol	7.19	ND	ND	1.94	ND	ND
11	2-Furanmethanol	10.76	ND	ND	0.34	ND	Cooked Sugar, Burnt
12	Benzyl alcohol	22.62	ND	1.48	2.51	1.72	Sweet, floral, fruity with chemical nuances
13	1-Octanol	25.68	ND	1.37	1.43	ND	Waxy, green, citrus, aldehydic and floral with a sweet, fatty, coconut nuance
14	(Z)-9-Methyl-10-pentadecen-1-ol	26.53	ND	ND	0.26	ND	ND
15	Phenylethyl Alcohol	28.39	8.71	ND	5.96	ND	Sweet, floral, fresh and bready with a rosey honey nuance
16	1-Octen-3-ol	18.95	2.96	1.40	ND	1.99	Earthy, green, oily, vegetative and fungal
17	3,6,9,12-Tetraoxahexadecan-1-ol	16.02	0.69	ND	ND	0.40	ND
18	(Z)-2-Dodecenol	25.41	ND	ND	ND	0.81	A pleasant, fatty odor

19	Phenylethyl Alcohol	28.23	ND	ND	ND	12.19	Sweet, floral, fresh and bready with a rosey honey nuance
Total acid							
20	Acetic acid	2.34	24.07	ND	1.30	1.87	Pungent acidic and dairy-like
21	3-methyl-Butanoic acid	13.34	0.06	ND	ND	ND	Dairy products with sour, mature fat and fruit aroma
22	3-Methyl-hexanoic acid	13.86	0.45	ND	ND	ND	Mild sour
23	2-methyl-Butanoic acid	14.78	0.05	ND	ND	ND	sour, fruity
24	Hexanoic acid	29.42	0.07	ND	ND	ND	Mild sour, cheese
Total aldehydes							
25	Hexanal	7.49		7.16	9.85	0.16	Green, fatty, leafy, vegetative, fruity and clean with a woody nuance
26	Hexanal	7.93	13.18	ND	ND	ND	grassy taste
27	(E)-2-Heptenal	21.52	1.10	ND	ND	ND	Intense green, fatty, oily, with fruity overtones
28	(E,E)-2,4-Nonadienal	55.13	0.12	ND	ND	ND	in dipropylene glycol. fatty melon waxy green violet leaf cucumber tropical fruit chicken fat
29	Heptanal	13.37	0.58	1.46	1.18	1.14	green aldehydic oily cortex grassy clover cilantro
30	Benzaldehyde	17.02	0.17	6.92	7.27	8.98	almond, fruity, powdery, nutty and benzaldehyde-like
31	Benzeneacetaldehyde	23.15	ND	ND	0.92	0.20	Honey, floral rose, sweet, powdery, fermented, chocolate with a slight earthy nuance
32	Nonanal	27.94	1．53	4.33	4.78	8.63	Waxy, aldehydic, citrus, with a fresh slightly green lemon peel like nuance, and a cucumber fattiness
33	Benzaldehyde dimethyl acetal	28.13	ND	0.41	0.35	ND	Green, winey, fruity and sharp with a floral nuance
34	2-Nonenal	32.52	0.30	ND	0.38	ND	Fatty, green, waxy and vegetative with cucumber-melon, cereal notes and a chicken fat nuance
35	Decanal	35.19	0.37	0.38	0.54	ND	Sweet, aldehydic, orange, waxy and citrus rind
36	3-methyl-Butanal	24.33	ND	0.43	ND	ND	ethereal aldehydic chocolate peach fatty
37	2-Octenal	24.46	1．12	ND	0.30	ND	fatty green herbal
38	2-Dodecenal	38.96	ND	ND	ND	0.47	waxy, mandarin orange
39	(E,E)-2,4-Decadienal	42.57	ND	ND	ND	0.35	oily cucumber melon citrus pumpkin nut meat

40	Octanal	20.51	ND	ND	ND	2.08	Aldehydic, waxy, citrus orange with a green peely nuance
41	Decanal	35.19	ND	ND	ND	0.67	Sweet, aldehydic, orange, waxy and citrus rind
Total ester							
42	1,3,5,7-Cyclooctatetraene	12.41	ND	2.39	0.87	ND	ND
43	3-methyl-1-Butanol acetate	13.91	0.11	ND	ND	ND	Sweet, banana, fruity with a ripe estry nuance
44	2-ethyl -Allyl butyrate	39.43	0.42	ND	ND	ND	ND
45	Butyrolactone	16.75	0.37	ND	ND	ND	Creamy, oily with fatty nuances
46	Methyl nonanoic acid ester	43.98	0.16	ND	ND	ND	Sweet, fruity, pear-like, waxy, winey, with a slight tropical nuance
47	Ethyl octanoic acid ester	54.05	7.89	ND	ND	ND	Waxy, sweet, musty, pineapple and fruity with a creamy, dairy nuance
48	Methyl decanoic acid ester	70.60	0.12	ND	ND	ND	oily wine fruity floral
49	3-methylbutyl octanoic acid ester	85.65	0.13	ND	ND	ND	Sweet, fruity, waxy, green, fatty, pineapple and coconut-like
50	3-ethoxyacrylate ethyl	34.68	0.28	ND	ND	ND	ND
51	Ethyl hexanoic acid ester	20.51	4.62	4.54	2.41	ND	Mild fruity, sweet
52	2,3-methyl-propanoic acid butyl ester	24.58	ND	0.95	0.41	ND	Sweet, fruity, estry and green with a waxy nuance
53	(Z)-2-Dodecenol	25.42	ND	ND	0.59	ND	ND
54	Ethyl decanoic acid ester	48.04	3.30	ND	0.34	ND	Sweet, bacon,fruity
55	Carbamic acid,1-methylethyl ester	3.33	ND	0.65	ND	ND	ND
56	Hexanoic acid,2-propenyl ester	26.54	ND	0.62	ND	ND	ND

57	Acetic acid, 2-phenylethyl ester	38.57	1.42	ND	ND	0.64	Sweet, honey, floral rosy, with a slight yeasty honey note with a cocoa and balsamic nuance
Total ketone							
58	6-methyl-5-Hepten-2-one	19.42	ND	ND	1.23	0.89	Fruity, apple, musty, ketonic and creamy with slight cheesy and banana nuances
59	3-Octen-2-one	23.16	ND	0.70	ND	ND	Earthy, oily, ketonic, sweet, with hay and mushroom nuances
60	Acetophenone	24.76	ND	1.42	ND	ND	sweet, cherry pit, marzipan and coumarinic. It has a slight almond nutty and heliotropin-like vanilla nuance
61	3,5-Octadien-2-one	36.23	0.17	ND	ND	ND	fruity fatty mushroom
62	3,5,5-trimethylcyclopent-2-en-1-one	40.58	0.24	ND	ND	ND	ND
63	2-methyl-1-Hepten-6-one	25.56	0.42	ND	ND	ND	ND
Total Furan							
64	2-pentyl-Furan	19.64	1．61	2.96	1.30	1.21	Fruity, grassy
65	2,3'-Bifuran, octahydro-	27.22	ND	ND	0.24	ND	ND
Total pyrazine							
66	Methyl Pyrazine	8.58	ND	0.58	0.53	0.53	A nutty, cocoa, roasted meat aroma
67	2,5-dimethyl Pyrazine	13.73	ND	ND	0.33	3.18	Nutty, peanut, musty, earthy, powdery and slightly roasted with a cocoa powder nuance
68	2,6-dimethyl Pyrazine	13.79	ND	2.50	2.76	2.78	Meaty, nutty, coffee
69	2-ethyl-6-methyl Pyrazine	19.95	ND	0.35	0.82	0.66	roasted potato
70	1-methylethenyl Pyrazine	21.33	ND	ND	0.12	ND	caramellic chocolate nutty roasted
71	Acetylpyrazine	21.60	ND	ND	0.56	ND	Musty, roasted, corn chip, popcorn, nutty and potato-like
72	trimethyl Pyrazine	20.32	ND	0.33	ND	ND	Nutty, musty, powdery cocoa, potato and musty
Others							

73	2,3,4-tri-O-methyl-β-D-Ribopyranoside	46.52	0.31	ND	ND	ND	ND
74	2,3,4-tri-O-methyl-β-D-Xylopyranoside	30.35	ND	ND	ND	0.28	ND
75	2,3-dihydro-3,5-dihydroxy-6-methyl-4H-Pyran-4-one	30.35	ND	ND	ND	0.13	ND
76	Ethylbenzene	10.56	ND	0.98	0.46	0.08	ND
77	p-Xylene	11.02	ND	ND	1.79	0.03	ND
78	Toluene	5.94	ND	0.23	ND	ND	phenolic narcissus animal mimosa
79	1,3-dimethyl-Benzene	11.02	ND	4.88	ND	ND	ND
80	1,2,4-trimethyl-Benzene	19.42	ND	1.83	ND	ND	ND
81	Butylated Hydroxytoluene	54.85	ND	4.54	4.02	4.39	mild phenolic camphor
82	O-Xylene	11.04	ND	ND	ND	0.16	ND
83	Styrene	12.44	ND	2.07	0.70	0.67	sweet balsam floral plastic
84	Anethole	38.59	ND	0.44	0.28	0.39	Sweet, anise, licorice and medicinal
85	D-Limonene	22.01	ND	5.79	2.89	1.57	Sweet, citrus and peely
86	Decane	20.32	0.08	0.62	0.55	ND	ND
87	Undecane	27.68	0.20	0.69	0.75	0.54	Waxy, fruity, ketonic with fatty pineapple nuances
88	Dodecane	34.85	ND	1.59	1.77	2.71	ND
89	Tridecane	40.35	0.78	1.03	0.56	1.11	ND
90	3-Ethyl-3-methylheptane	41.71	ND	ND	1.33	ND	ND
91	Tetradecane	48.19	ND	ND	0.29	0.31	mild waxy
92	Nonane	13.21	ND	0.15	ND	ND	ND
93	Cyclooctane	25.68	ND	ND	ND	1.62	ND
94	4,5-dimethyl-2-cyclohexyl-1,3-Dioxolane	42.57	0.93	ND	ND	ND	ND
95	4-Heptafluorobutyroxytridecane	54.79	0.15	ND	ND	ND	ND

96	Bicyclo[4.2.0]octa-1,3,5-triene	12.46	ND	ND	ND	0.44	ND
97	Naphthalene	32.68	ND	0.51	0.39	0.32	Medical, musty, tobacco with a pyridine and leather nuance
98	4,6-dimethyl Pyrimidine	13.78	ND	ND	0.55	ND	ND

*Odour description were obtained from http://www.thegoodscentscompany.com/. ND indicates not detected or value below the detection threshold.

Poltava State Agrarian Academy

Educational and Scientific Institute of Information and Educational Innovation Technology

CERTIFICATE

CC00493014/000519-21

of authenticates participation

Wenjuan Lou

in the scientific seminar of the Department of Food Technologies

New Tendencies and Global Trends in Technologies for Raw Material Storage and Food Production.

the topic of the report

BISCUITS TECHNOLOGY WITH THE ADDITION OF GRAPE POWDERS

(3.5 hours)

30 March, 2021,
Poltava, Ukraine

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First Vice-Rector
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signature

CERTIFICATE OF PARTICIPATION

This is certify that **Wenjuan Lou**

has participated in the annual scientific and practical conference of lecturers, postgraduates and students of the SNAU, April 17-20, 2019

Dean of Food Technology Faculty **Radchuk O. V.**

Food Technology Faculty

April 18, 2019