Development of a Sulfide-Free Unhairing Method Using High-Concentration Alkali for Food- Grade Gelatin Production

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Development of a Sulfide-Free Unhairing Method Using High-

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Abstract

Lime splits, a by-product of the splitting process following unhairing and liming, are utilized not only for split leather production but also as raw materials for food and cosmetics, such as collagen and gelatin. However, conventional unhairing agents like sodium sulfide and sodium hydrosulfide are not approved as food additives in Japan. Although these agents are highly water-soluble and do not remain in the washed pelts, many companies remain concerned about using raw materials processed with these chemicals for food production.

To address this, the Tokyo Metropolitan Leather Technology Center established an unhairing method using high-concentration alkali instead of sulfides, aiming to ensure food safety and expand applications. Given that certain high-concentration alkalis are approved as food additives, we prepared pelts using food-additive-grade high- concentration alkali and subsequently extracted gelatin from them. Furthermore, the extracted gelatin was processed into jellies, and their strength was measured to verify its potential for food applications.

Key Word: high-concentration alkali, unhairing, food safety, gelatin

Introduction

Pelt or lime splits generated in the leather manufacturing process are not merely by- products but are widely utilized as valuable raw materials for food products such as gelatin and collagen casings.

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However, conventional unhairing processes typically rely on sulfides, such as sodium sulfide, which are not approved as food additives in Japan. Although these agents are water-soluble and do not remain in the washed pelts, the use of such chemicals in the processing of raw materials for food creates significant apprehension among food manufacturers regarding safety. Furthermore, since sulfides lack degreasing properties, large amounts of surfactants are required in subsequent processes.

Therefore, this study aims primarily to ensure food safety and maximize the value of leather by-products for edible applications, in addition to reducing the environmental load. We investigated a sulfide-free unhairing method using food-additive-grade high-concentration alkali. This study verifies whether this method can achieve effective unhairing and degreasing while guaranteeing safety as a food raw material, and evaluates the properties of gelatin extracted from the resulting pelts.

2. Materials and Methods

2.1 Materials

Fresh or salted pigskins sourced in Tokyo were used as raw materials (hereinafter referred to as “raw skins”). The batch size was 10 skins, weighing approximately 50 kg per lot.

2.2 Chemicals

For the unhairing process, a 48% (w/w) potassium hydroxide solution (AGC Chemicals Company) was used as the main agent, and soda ash (sodium carbonate; Sumitomo

Shoji Chemicals Co., Ltd.) was used as a buffering agent. Calcium hydroxide (Chichibu Lime Industry Co., Ltd.) was used for liming, and ammonium sulfate (Yoneyama Chemical Industry Co., Ltd.) was used for deliming. All chemicals used in this study were of food additive grade.

2.3 Unhairing Process

The outline of the unhairing formulation is shown in Table 1. Raw skins were washed in a stainless steel drum,

Table 1 : Outline of Unhairing Formulation

Process Amount

□%□ Chemical Time (min) Remarks

Washing 5

3 Soda ash 10

Unhairing

50 48%NaOH

solution 30□40 Effective sodium hydroxide amount: 24%

Drainage

Washing 200 10 Batch rinsing

Liming 250 Water

4 Slaked lime Intermittent operation: 3 min rotation / 180 min rest ‘d’

Drainage

Washing 200 10 Batch rinsing

2.1 Gelatin Extraction and Yield Determination

Gelatin was extracted from the three types of samples obtained in Section 2.3 (unhaired pelts, limed pelts, and delimed pelts) by stirring in a water bath at approximately 70°C using a hot plate stirrer (Fig. 1).

The extract was separated via centrifugation into a supernatant and a precipitate containing undissolved residue and residual lime. The supernatant was freezedried to obtain gelatin powder. The dry weight of the precipitate was measured, and the gelatin yield was calculated by subtracting this value from the initial dry weight of the skin samples. Fig. 1. Gelatin extraction process

followed by the addition of soda ash and agitation. Subsequently, a 48% (w/w) potassium hydroxide solution was added at 50% based on the weight of the raw skins. Unhaired pelts were obtained by drumming for approximately 30 to 60 minutes while monitoring the condition of the skins. After washing, the unhaired pelts were limed overnight and delimed the following day to complete the preparatory process. During this process, samples for gelatin extraction were collected from the unhaired pelts, limed pelts, and delimed pelts, respectively.

2. Results and Discussion

2.1 Results of Unhairing

Unhairing was completed in approximately 30 to 40 minutes after adding the chemicals and rotating the drum gently at 6 rpm. No damage to the skin, such as grain coarseness, was observed. Conventionally, in unhairing methods using high-concentration alkali, sodium chloride (salt) is used as a buffer to suppress rapid swelling caused by the alkali. However, due to its weak buffering capacity,

Fig. 2 shows the washing process of the unhaired pelts to remove solubilized keratin and excess alkali. Fig. 3 shows the pelts after the completion of the preparatory process.

Fig. 2. Pelt after completion of unhairing reaction Fig. 3. Pelt after completion of beamhouse process

3.2 Gelatin Yield

All samples used for gelatin extraction (unhaired pelts, limed pelts, and delimed pelts) were completely dissolved by heating at approximately 70°C, losing their original shape. Table 2 shows the gelatin yields obtained from the samples at each process stage. As indicated, high yields of approximately 80% or more were achieved in all

Table 2. Gelatin yield at each process stage

Unhaired pelts (No liming) Limed pelts Delimed pelts

Yield□%□ 85□92 78□82 82□87

a large dosage—approximately 10% of the raw skin weight—is required, which leads to the issue of high salinity in the wastewater. In contrast, soda ash, used in this study, exhibits high buffering capacity. An addition of only

about 3% (see Table 1) was sufficient to effectively suppress excessive swelling and allow the unhairing reaction to proceed mildly. This result demonstrates that the proposed method achieves both a significant reduction in chemical usage and effective protection of the grain layer.

samples. Conventionally, the gelatin yield from scalded skins (skins unhaired by hot water treatment) heated at 70°C is considered to be around 30^ÿ40%. The proposed method demonstrated a significant improvement in yield compared to the conventional method, indicating that the high-concentration alkali treatment contributed to enhancing extraction efficiency.

3.3 Measurement of Jelly Strength

The results of jelly strength measurements for gelatin extracted from samples at each process stage are shown in Table 3. As indicated in the table, the jelly strength of gelatin extracted from unhaired pelts (without liming) was significantly low; the samples were classified as below 5th grade according to JIS standards, or in some cases, failed to form a gel. In contrast, samples processed after liming (limed pelts and delimed pelts) exhibited a marked

Table 3. Jelly strength measurement results

Unhaired pelts (No liming) Limed pelts Delimed pelts

Jelly strength□g□ 21□81 200□250 120□240

Gelatin quality (Grade) 5 □□ 2 2□3

4. Conclusion

In this study, with the aim of expanding the utility of domestic pigskins and ensuring food safety, we established a sulfide-free unhairing method using exclusively food additives and investigated gelatin extraction from the resulting lime splits. The key findings are summarized as follows:

(1) By combining soda ash, which exhibits high buffering

capacity, with high- concentration alkali, it was possible to produce unhaired pelts safely and effectively without skin damage, using only foodadditive-grade chemicals.

(2) The gelatin yield from samples processed by this

method was approximately 80% or higher, demonstrating significantly higher extraction

increase in strength, corresponding to 2nd or 3rd grade quality. Notably, even in the delimed pelts from which calcium had been removed, the jelly strength remained high and comparable to that of the limed pelts, although a slight decrease was observed in some samples. These findings suggest that the calcium hydroxide used in the liming process induces a structural change in collagen, and this modification significantly contributes to the development of jelly strength.

efficiency compared to conventional scalded skins (approx. 40%).

(3) Measurements of jelly strength revealed that the

action of calcium hydroxide during the liming process significantly enhances the gel-forming ability of gelatin. This improvement in strength was maintained even after the removal of calcium via deliming, suggesting that the calcium treatment induces irreversible structural modifications in collagen that contribute to jelly strength.

Future work will focus on analyzing the specific structural changes in collagen induced by calcium treatment and their correlation with jelly strength. This understanding is expected to open pathways for the controlled production of gelatin with desired strengths tailored to specific applications.