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Pectin Extraction in the Presence of Alcohols

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ABSTRACT

A theoretical discussion of the extraction process and especially of the factors influencing extractant penetration in pectin-containing raw materials is presented. The necessity of adding surfactant in the pectin extraction is proved. Experiments were carried out with two types of apple pressings differing in anhydrouronic acid content and quantity of extractable pectin.

The addition of low molecular alcohols in concentrations from 1% to 3% to the acid extragent resulted in an acceleration of extraction and increase in the pectin yield by 55–90%. Ethylene glycol, glycerol and diethylene glycol had a better effect than monohydric alcohols. The effect of the process duration on the pectin yield during acid extraction was studied. A 25-min extraction was sufficient for taking out the extractable pectin. It was shown that the addition of alcohols resulted in a measurable increase in the pectin gel strength.

INTRODUCTION

Pectin extraction is a complex physicochemical process in which hydrolysis and extraction of pectin macromolecules from plant tissue and their solubilization take place under the influence of different factors (Kertesz, 1951). The main aim of the extraction is maximum pectin yield with preserved pectin quality — especially concerning its high gel strength.

The first stage of the process is extractant penetration into the rigid cell micropores. The presence of an acid and the action of temperature

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help cell wall disruption, 'protopectin' hydrolysis and solubilization of pectic substances. Simultaneously a degradation process of pectin macromolecules takes place (Kaneko *et al.*, 1983; Thibault & Rombouts, 1985). This undesired process limits the extraction under severe conditions (high acidity and high temperature), so it is very important to search for other factors intensifying pectin extraction. One possibility is the application of surfactants as extractant components which stimulate its penetration in the capillary pore structure of the fruit tissue. Experiments with the addition of quaternary ammonium salts in concentration 0·01–1% to the extractant and with other similar surfactants have been carried out (Konicy Hikaru, 1983). The application of such extraction process stimulators is problematic because they are toxic and difficult to separate from the end product. The addition of organic solvents (mainly different alcohols) is an alternative in this direction. They act as surfactants and reduce surface tension, thus contributing to the more subtle pectin extraction. They also improve the extractant wetting ability thus facilitating extractant penetration in the plant tissue. This has a favorable effect on the 'protopectin' hydrolysis rate. Our preliminary studies on ethanol addition to apple pectin extraction in acidic medium have shown encouraging results. We have made it our aim to carry out a systematic investigation on pectin extraction from apple pressings in the presence of different monohydric and polyhydric alcohols.

THEORETICAL CONSIDERATIONS

Considering the capillary pressure Δp which is the main reason for extractant capillary penetration, we must also have in mind the factors influencing its value. In accordance with Adamson (1979) the value of Δp can be calculated according to one of the following expressions:

$$\Delta p = \frac{2 . \sigma_{LG} . \cos \theta^0}{r} \tag{1}$$

or

$$\Delta p = \frac{2(\sigma_{SG} - \sigma_{SL})}{r} \tag{2}$$

where σ_{LG} is the surface tension between extractant phase and gas phase; σ_{SG} is the surface tension between solid phase and gas phase; σ_{SL} is the surface tension between solid phase and liquid phase; θ^0 is the solid/extractant contact wetting angle; and r is the capillary radius.

It can be seen from eqns (1) and (2) that when θ decreases, the value of Δp increases, other conditions being equal; this consequently leads to an increase in capillary penetration value (H), which can be calculated for any capillary pressure according to eqn (2) (Summ & Goriunov, 1976):

$$H = \frac{\sigma_{LG} . S_0 . \cos \theta}{\rho_L . g . \varepsilon}$$

where S_0 is the specific capillary surface (inner capillary surface area/total structural volume); ε is porosity (pore volume/total structural volume); ρ_L is extractant density; and g is gravitational acceleration.

Because of the plant waxes and resins, fruit tissue surface (especially that of apple pressings) has very pronounced hydrophobic properties ($\theta^0 > 90$). The choice of a suitable surfactant as an extractant component considerably reducing plant tissue wetting angle will lead to an increase of Δp, and hence to an increase in penetration rate, stimulating the extraction process as a whole.

The regulation of plant tissue wetting by means of surfactants will improve plant tissue drainage properties. It is almost impossible to model and analyse theoretically the role of a certain surfactant. The choice of a surfactant should be made by estimating the quality of pectin obtained.

MATERIALS AND METHODS

Materials and reagents

Two types of apple pressings were used: pressings A, produced by the 'Pectin' Plant in Pernik in 1986 — anhydrouronic acid (AUA) = 16·8%, degree of esterification (DE) = 74·1% — and pressings B, produced by 'Vitamina' Canning Factory in Stamboliiski in 1986 (AUA = 14·2%, DE = 83·1%).

Ethanol (95%) was redistilled and all other alcohols, conc. nitric acid, conc. hydrochloric acid and sodium hydroxide were of AR grade. Technical ethanol (95%) was used for coagulation.

Extraction

A determined quantity of the chosen alcohol was added to the distilled water heated up to 87–90°C in such a way that the final volume was 2000 cm^3. Concentrated nitric acid (10 ml) was then added and

100 g apple pressings were added, continuously stirring the mixture with a mechanical stirrer. The extraction was carried out at 80°C for a chosen period of time, continuously stirring the mixture. The mass was filtered when hot, the filtrate was cooled down to room temperature, its volume was measured and it was coagulated by the addition of an equal volume of 95% ethanol. After staying for 2 h at room temperature the precipitate was filtered, washed twice by 70% ethanol containing hydrochloric acid, successively washed with 70% ethanol to neutral reaction and washed twice more with 95% ethanol. Then it was dried *in vacuo* at 40°C to a constant weight.

Analytical methods

The method of Gee *et al.* (1958) was used to determine the AUA content and DE in the initial apple pressings. The DE of the pectin samples was determined by the method of Owens *et al.* (1952). The gel strength was determined by the Tarr–Baker method using standard 65% sugar jellies (Bender, 1949).

RESULTS AND DISCUSSION

First we studied the influence of the type of alcohol on the pectin yield at a 25-min pectin extraction with 0·5% nitric acid. The results given in Table 1 show an acceleration of extraction in all cases, represented by a significant increase in yield for the various alcohols — from 60% to 80%. Monohydric alcohols give slightly lower yields than polyhydric ones.

Data from experiments with a different type of apple pressings poorer in extractable pectin are presented in Table 2. These data show that the addition of alcohol in this case has a more pronounced favorable effect (70–90%).

In another series of experiments we studied the effect of alcohol concentration on extraction acceleration. We carried out the experiments with ethanol, glycerol and diethylene glycol which happened to be the most characteristic examples from Table 1. We chose four concentrations — from 1% to 5% — since the higher concentrations were practically and theoretically inconvenient and lower concentrations did not seem effective. The results are presented in Table 3. It can be seen that the pectin yields have increased in all cases when the concentration is increased from 1% to 2·5%. Above 3·5% there is a decrease in yield. The presence of an optimal alcohol concentration concerning the pectin yield could be explained by assuming that alcohol accelerates not only the extraction but also the degradation, making the pectin more accessible to

TABLE 1
Effect of Type of Alcohol (2·5% v/v) on the Yield and Quality of Obtained Pectin[a]

Type of alcohol	*Pectin yield (%)*	*AUA (%)*	*Degree of esterification (%)*	*Gel strength (°TB)*
K control	6·7	59·3	76·4	210
1. Ethanol	11·1	57·6	74·2	227
2. 1-Propanol	11·0	58·4	74·1	228
3. 2-Propanol	11·5	58·0	73·9	230
4. 1-Butanol	10·7	57·4	74·1	220
5. 2-Butanol	10·9	56·7	73·4	220
6. 2-Methyl-1-propanol	11·2	58·1	73·4	218
7. 2-Methyl-2-propanol	10·8	57·4	74·4	216
8. 1-Pentanol	11·1	58·0	74·8	220
9. 1-Hexanol	11·3	58·9	74·8	220
10. Cyclohexanol	10·9	58·1	75·4	225
11. Ethylene glycol	11·7	57·3	73·6	230
12. Glycerol	11·8	57·6	74·5	227
13. Diethylene glycol	12·1	58·0	74·8	230

[a]Conditions: 0·5% nitric acid extraction; hydromodule, 1:20; temperature, 80°C; duration, 25 min; apple pressings with AUA, 16·8%; DE, 74·1%.

TABLE 2
Effect of Type of Alcohol (2·5% v/v) on the Yield and Properties of Obtained Pectin[a]

Type of alcohol	*Pectin yield (%)*	*AUA (%)*	*Degree of esterification (%)*	*Gel strength (°TB)*
1. Control	4·7	79·4	84·2	225
2. Ethanol	8·0	71·6	76·6	225
3. 1-Propanol	8·7	72·0	75·6	232
4. 2-Propanol	8·8	72·0	75·9	230
5. 1-Butanol	8·2	72·9	76·6	225
6. Ethylene glycol	8·8	72·4	76·7	227
7. Glycerol	8·6	70·4	76·1	222
8. Diethylene glycol	8·9	71·8	77·0	227

[a]Conditions: 0·5% nitric acid extraction; hydromodule, 1:20; temperature, 80°C; duration, 25 min; apple pressings with AUA, 14·1%, DE, 83·1%.

the dilute nitric acid. On the other hand, it is possible that the increase in alcohol concentration could change in a specific way the different physical and chemical processes (wetting of the apple pressings, extractant diffusion into the interior of the particles, transport of the pectin

TABLE 3
Effect of Alcohol Concentration on Pectin Yield and Characteristics[a]

Type of alcohol	*Concentration (% v/v)*	*Pectin yield (%)*	*AUA (%)*	*Degree of esterification (%)*	*Gel strength (°TB)*
K control	—	6·7	59·3	76·4	210
1. Ethanol	1·0	10·4	57·7	74·1	220
2. Ethanol	2·5	11·1	57·6	74·2	227
3. Ethanol	3·5	10·7	57·4	73·6	225
4. Ethanol	5·0	10·6	58·0	73·8	220
5. Glycerol	1·0	10·9	57·4	74·4	227
6. Glycerol	2·5	11·8	57·6	74·5	227
7. Glycerol	3·5	11·6	57·3	74·6	225
8. Glycerol	5·0	11·3	57·6	73·1	225
9. Diethylene glycol	1·0	10·8	58·4	74·1	220
10. Diethylene glycol	2·5	12·1	58·0	74·8	230
11. Diethylene glycol	3·5	11·9	58·1	74·4	230
12. Diethylene glycol	5·0	11·6	57·8	73·8	230

[a]Conditions: 0·5% nitric acid extraction; hydromodule, 1:20; temperature, 80°C; duration, 25 min; apple pressings with AUA, 16·8%, DE, 74·1%.

TABLE 4
Effect of Extraction Time on Pectin Yield and Characteristics[a]

Extraction time (min)	*Pectin yield (%)*	*AUA (%)*	*Degree of esterification (%)*	*Gel strength (°TB)*
1. Control 15 min	4·8	58·9	77·4	200
2. Control 25 min	6·7	59·3	76·4	210
3. Control 45 min	10·0	57·2	74·1	225
4. 15[b]	7·6	58·0	75·2	200
5. 20[b]	10·7	57·9	74·8	227
6. 25[b]	12·1	58·4	74·6	230
7. 30[b]	12·0	58·3	74·1	230
8. 45[b]	12·1	58·0	74·0	230

[a]Conditions: 0·5% nitric acid; hydromodule, 1:20; temperature, 80°C; apple pressings with AUA, 16·8%; DE, 74·1%.
[b]Diethylene glycol, 2·5% (v/v).

macromolecules up to the surface, etc.) which determine the extraction efficiency.

In the last series of experiments we studied the influence of extraction duration on pectin yield. The results obtained are presented in Table 4.

Pectin yield in the control experiments was significantly improved — from 4·8% to 10% — with an increase in duration from 15 to 45 min, as expected. The changes in AUA were insignificant. The esterification degree was slightly altered. The gel strength was simultaneously increased. The experiments with diethylene glycol resulted in quite a different situation. Pectin yield was increased with time up to 25 min and then remained constant.

In addition, data from Tables 3 and 4 show that the chosen extraction parameters for experiments in Tables 1 and 2 are optimal, and the results obtained correctly reflect the effect of alcohol on the extraction processes.

CONCLUSION

It was established that the addition of alcohols with a low molecular weight to the acidic extractant in the concentration range from 1% to 3% leads to an acceleration of extraction and to an increase in pectin yield by 55% to 90%. It was established that a 25-min extraction is sufficient for taking out the extractable pectin. Ethylene glycol, glycerol and diethylene glycol had a better effect than monohydric alcohols. The addition of alcohols to the extractant resulted in a measurable increase in the gel strength of the obtained pectin.

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