

Optimization of method for extraction of pectin from apple pomace

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Method for extraction of pectin from apple pomace-waste generated from apple juice processing industries for commercial adoption was optimized. Fresh pomace yielded 13.3% pectin on dry weight basis (dwb). Blanching of pomace (boiling at 95°C for 5 minutes followed by cooling) and drying (at 50±2°C) was found to be a necessary pretreatment before pectin extraction. Among different methods of pectin extraction and precipitation, extraction of apple pomace by using 0.05N HCl at 95°C for one hour followed by precipitation in 95% ethanol was found optimum with pectin yield of 10.5% on dry weight basis. The resultant pectin was characterized by 59.1% anhydrogalacturonic acid content, 71.2% degree of esterification (DE) and 110 jelly grade. Water and Ammonium Oxalate-oxalic acid extractions on the other hand yielded very low 3.4 and 8.0% pectin, respectively. Sequential combination extractions, viz. water and acid or water and ammonium oxalate-oxalic acid though yielded slightly higher amount of pectin yet the addition of a unit operation along with comparatively low increase in pectin yield was found to limit their use for pectin extraction. Among precipitation methods, precipitation of extract in 95% ethanol resulted in higher pectin yield with comparable quality of the pectin obtained by using aluminium chloride precipitation. The cost of production of pectin calculated on the basis of input used and after adding labour and processing charges worked out to be Rs. 808.30 per kg. The standardized method of pectin extraction and precipitation can be used commercially by the processing industries for utilization of apple pomace.

Keywords: Apple pomace, Blanching, Pectin extraction, Waste utilization.

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Introduction

Apple (*Malus x domestica* Borkh.) is an important fruit crop of the world. In India, it is predominantly grown in Jammu and Kashmir, Himachal Pradesh and Uttarakhand and has a large contribution towards the economy of these hill states. A substantial quantity of the apple produce is processed into juice, pulp, concentrate and other processed products and apple pomace is the major by-product left after extraction of apple juice. It is estimated that more than 10,000 tonnes of apple pomace is being generated as a waste in India. Since apple pomace is highly biodegradable, its disposal near the processing units leads to environmental pollution besides causing a huge economic loss to the processing industry. Although efforts have been made to utilize apple pomace for making edible products, but have not yet proven fruitful for its commercial utilization. Apple pomace is a rich source of sugars (17.35%), pectin (16.95%)

and crude fibre (16.16%)¹ with a very high biological oxygen demand i.e. 240-19000 mg/L². Apple pomace reported to contain about 18-19% pectin on moisture free basis³. Pectin extraction from apple pomace is considered a reasonable way of utilizing it in the technologically developed countries of the world^{3,4}. Pectin is a plant polysaccharide present in the middle lamella of all plant primary cell walls including apple. It is used as a gelling agent, thickener, emulsifier and stabilizer in a large number of food products such as jams, jellies, fruit conserves, bakery and confectionary products, beverages, etc^{5,6} as well as in pharmaceuticals and cosmetics besides possessing some medicinal benefits⁷. Various studies conducted on extraction of pectin from apple pomace^{3,4,8,10,11} mainly focused on fresh apples as the raw material which are also suitable for table purpose. While in India very small, deformed and pitoo sized fruits (not otherwise fit for fresh market) are used for processing. A huge quantity of pomace produced during processing goes waste due to non availability of literature on feasibility of such raw material (pomace)

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for pectin extraction. Further, the pectin extraction methods^{12,13} are quite generalized for direct application in apple pomace utilization. The huge demand for pectin in the processed food industry in developing countries including India is met mainly by importing it from Europe and USA. Although substantial amount of raw material is available in India, industries for production of pectin from apple pomace have not yet been established mainly due to lack of proper technology in this direction.

The present study was therefore, conducted to investigate the effect of various extraction variables, viz. pretreatment of raw material, extraction and precipitation methods on the yield and quality of pectin in order to develop a method for the commercial extraction of pectin from apple pomace.

Materials and Methods

Fresh pomace left after extraction of apple juice from processable grade fruits at HPMC (Himachal Pradesh Horticultural Produce Marketing and Processing Corporation Ltd) Fruit Processing Plant, Parwanoo, Dist. Solan (H.P.) was utilized to carry out these studies. Apple pomace after different pretreatments such as blanching (boiling at 95°C for 5 minutes followed by cooling) and drying (in mechanical dehydrator at 50±2°C) was used for extraction of pectin using different extraction and precipitation methods. Method for extraction of pectin consisted of boiling the apple pomace in distilled water, 0.05N HCl (acid extraction) and 0.75% ammonium oxalate-oxalic acid (1:1) for one hour at 95°C^(Ref. 3). On the basis of preliminary observations it was found that the ratio of 1:2 of fresh apple pomace to extraction medium was the most suitable and was followed in all the extraction methods. After extraction, the extract was separated from the solid residue by filtration through a muslin cloth prior to its use for pectin precipitation. Sequential combination extractions such as two-stage sequential water-acid and water-oxalate extraction were carried out in which the pomace was extracted first with boiling water for one hour to separate the water soluble fraction, and the remaining residue was again extracted for one hour with the corresponding extractant. The pectin extract obtained from different extractions after cooling to room temperature was used for precipitation of pectin either with 95% ethanol (alcoholic precipitation)³ or precipitating by using aluminium chloride¹⁴. The precipitates were then separated, washed successively with 70 and 95%

ethanol and dried in an oven at 50°C. The dried pectin from both the methods of precipitation was packed in polythene pouches and stored in a cool dry place until further analysis. For optimization of pretreatment of apple pomace, acid extraction followed by alcoholic precipitation method was followed.

Physico-chemical analysis

Apple pomace was analyzed for different physico-chemical attributes such as moisture, ash, total soluble solids (TSS), titratable acidity, sugars, ascorbic acid, crude fibre and pectin content (as calcium pectate) as per method described by Ranganna¹⁵. The extracted pectin was analyzed for moisture, ash, acid insoluble ash, equivalent weight, methoxyl content, anhydrogalacturonic acid content, acetyl value and jelly grade¹⁵. Equivalent weight of the pectin was determined by titrating a known weight of pectin against standardized 0.1N NaOH solution to a faint pink end point and expressed as under:

$$\text{Equivalent Weight} = \frac{\text{Weight of Sample} \times 1000}{\text{Titre} \times \text{Normality of alkali}}$$

Methoxyl content was determined by saponification of extracted pectin and titrating the liberated carboxyl group against standardized 0.1 N NaOH solution using phenol red as indicator to a faint pink end point. Methoxyl content was calculated as per expression:

$$\text{Methoxyl content, \%} = \frac{\text{Titre} \times \text{Normality of alkali} \times 3.1}{\text{Weight of sample}}$$

Degree of esterification was calculated from the observed value of methoxyl content and anhydrogalacturonic acid content as per the following expression given by Schultz¹⁶:

$$\text{Degree of esterification, \% (DE)} = \frac{176 \times \text{methoxyl content} \times 100}{31 \times \text{Anhydrogalacturonic acid content}}$$

Jelly grade of extracted pectin was measured by making test jellies with assumed jelly grade and comparing them with a standard jelly of 150 grade pectin. Each attribute was determined in triplicate. Alkalinity of ash of pectin was determined for the subsequent calculation of acid insoluble ash and anhydro-galacturonic acid contents¹⁵. The ash obtained after determination of ash contents was dissolved in standardized 0.1N HCl solution, heated to boiling and cooled and titrated against standardized 0.1N NaOH solution using phenolphthalein as

indicator to a faint pink end point. Alkalinity of ash was calculated as per the following expression:

$$\text{Alkalinity of ash, \% (as carbonate)} = \frac{\text{Titre} \times \text{Normality of alkali} \times 60 \times 100}{\text{Weight of ash} \times 1000}$$

Cost of production

The cost of production of pectin was calculated by taking into consideration various input costs such as cost of raw material, labour and electricity, processing costs, packaging and other charges. The cost of recovered raw material like alcohol was subtracted from cost of production for calculation of cost of pectin per kg.

Statistical analysis: The data were analyzed statistically by following Completely Randomized Design (CRD)¹⁶.

Results and Discussion

Physico-chemical composition of apple pomace

The pomace was found to contain 8.87 % total soluble solids consisted of sugars (6.18%), acid (0.29% as malic acid) and ascorbic acid (3.45 mg/100g); while insoluble material constituted about 2.33% pectin (as calcium pectate) and 5.39% crude fibre (Table 1). The mineral matter, represented by total ash content amounted to 0.87%. Thus, the pomace besides being a rich source of sugars, acid and minerals, also contained appreciable amount of pectin, which can be utilized in the food industry.

Table 1—Physico-chemical composition of apple pomace

Attributes	Mean \pm S.E.	
	Fresh weight basis	Dry weight basis
Moisture, %	84.07 \pm 0.16	—
Total solids, %	15.93 \pm 0.16	—
TSS, °Brix	8.87 \pm 0.20	—
Titrateable acidity/% malic acid	0.29 \pm 0.01	1.84 \pm 0.08
Total sugars, %	6.18 \pm 0.40	38.78 \pm 2.05
Reducing sugars, %	2.20 \pm 0.05	13.85 \pm 0.30
Non reducing sugars, %	3.77 \pm 0.29	23.68 \pm 1.81
Ascorbic acid, mg/100g	3.45 \pm 0.28	21.87 \pm 1.80
Crude fibre, %	5.39 \pm 0.29	33.86 \pm 1.81
pH ^c	4.17 \pm 0.12	—
Ash content, %	0.87 \pm 0.03	5.48 \pm .19
Pectin, % calcium pectate	2.33 \pm 0.19	14.66 \pm 1.21

^c dilution 1:3

Optimization of pre-treatments of pomace

Fresh pomace (13.3% pectin on dry weight basis) (Table 2) was found to be a good source of pectin followed by blanched pomace (13.0%) with a jelly grade of 120-125. Substantial losses in yield as well as quality of pectin were observed during drying of pomace. However, these losses were reduced when drying was preceded by blanching. Since drying is necessary to facilitate raw material handling, blanching of pomace prior to drying was optimized as pretreatment before pectin extraction. The yield and jelly grade of pectin obtained from dried pomace after blanching and drying was recorded as 10.5% and 110 respectively. The likely causes of lower pectin yield from unblanched dried pomace are degradation of pectin by the action of inherent or added pectinolytic enzymes¹⁸ which are inactivated by blanching, non-enzymatic degradation at high temperature¹⁹, and insolubilization of pectin due to enzymatic browning²⁰. Thus, drying of pomace after blanching has been optimized for extraction of pectin.

Standardization of extraction and precipitation methods

Single acid extraction resulted in higher pectin yield (6.3-10.5%) than single oxalate (4.0-8.0%) or water extraction (1.8-3.4%) methods (Table 3). Sequential extractions in which the water soluble fraction removed before extraction with either acid or oxalate, were found to improve yields by 13.1 and 20.7%, respectively when the collective yield from water and extractant soluble fractions was considered. Thus two-stage sequential water-acid extraction yielded the highest amount of pectin. The pectin yield from apple pomace after precipitation by using 95% ethanol was found to range between 3.4 to 10.5% which was significantly higher than the yield obtained

Table 2—Effect of various pre-treatments of apple pomace on the yield and quality of pectin

Pre-treatment	Pectin			
	Yield, % (dwb)	AGA, %	DE, %	Jelly Grade
Unblanched fresh	13.3	59.9	74.9	125
Blanched fresh	13.0	59.7	72.1	120
Unblanched dried	7.3	57.9	61.0	100
Blanched dried	10.5	59.1	71.2	110
CD(0.05)	0.74	1.57	1.82	9.41

AGA= Anhydrogalacturonic acid content, DE= Degree of esterification, dwb= dry weight basis

Table 3— Effect of different extraction and precipitation methods on the yield and quality characteristics of pectin from blanched dried pomace

Extraction method	Precipitation method	Pectin yield, % dwb	Moisture, %	Ash, %	AIA, %	EW	AGA, %	DE, %	Acetyl value, %	Jelly grade
Boiling water, 1 h	E	3.4	8.5	0.70	0.61	1271.4	51.7	60.8	0.46	40
	A	1.8	9.0	0.70	0.60	1000.3	57.8	60.5	0.44	40
Boiling with 0.05N HCl, 1 h	E	10.5	10.0	0.63	0.55	1239.8	59.1	71.2	0.37	110
	A	6.3	11.7	0.67	0.57	872.2	64.4	69.0	0.45	120
Boiling with 0.75% ammonium oxalate-oxalic acid (1:1), 1 h	E	8.0	11.2	0.73	0.64	1316.4	56.3	74.9	0.44	100
	A	4.0	11.6	0.67	0.58	1035.2	61.5	70.7	0.48	105
Boiling water, 1 h + boiling with 0.05N HCl, 1h*	E	9.8	10.0	0.60	0.52	1111.5	60.3	71.7	0.34	120
	A	4.1	11.5	0.63	0.54	877.4	64.9	69.8	0.39	130
Boiling water, 1h + boiling with 0.75% ammonium oxalate-oxalic acid (1:1), 1h*	E	6.1	9.5	0.70	0.60	1230.7	57.9	69.7	0.4	80
	A	3.8	10.2	0.67	0.57	961.8	61.3	68.7	0.41	90
CD(0.05)										
Precipitation method (P)		0.58	0.43	0.172	0.148	19.80	0.48	0.69	0.047	3.61
Extraction method (E)		0.91	0.68	0.272	0.235	31.31	0.75	1.08	0.074	5.71
P x E		1.29	0.96	0.385	0.332	44.28	1.06	1.53	0.105	8.08

AIA= Acid insoluble ash, EW= Equivalent weight, AGA= Anhydrogalacturonic acid content, DE= Degree of esterification

E = Alcoholic precipitation, A = Aluminium chloride precipitation;

* Data given for extractant soluble fraction

from aluminium chloride precipitation method (1.8-6.3%). This could be due to precipitation of pectin with high degree of esterification in alcoholic precipitation²¹ and/or purification of pectin by elimination of neutral polysaccharides and further removal of neutral sugar side chains during acid alcohol washing process²².

The level of moisture in the pectin extracted from apple pomace ranged from 8.5-11.7% with the highest amount of moisture recorded in pectin obtained after oxalate extraction (Table 3). The difference in moisture content of various pectin samples could be due to the difference in hygroscopic nature of pectin with different degrees of esterification²³. The total ash content in the pectin extracted from apple pomace by using different extraction and precipitation methods ranged from 0.63 to 0.73%, while the values of acid insoluble ash ranged from 0.52 to 0.64%. The ash content of the pectin extracted in the present study was well below the Food and Agriculture Organization (FAO) specifications of not more than 1% acid insoluble ash for commercial pectins²⁴. The anhydrogalacturonic acid (AGA) contents ranged from 51.7-64.9% with the highest value recorded in pectin obtained from two-stage sequential water-acid

extraction (60.3-64.9%) which was higher than that of pectin from single oxalate extraction. Further, the pectin obtained from water extraction was found to have the lowest value of anhydrogalacturonic acid content. Precipitation of pectin by the use of aluminium chloride resulted in a purer pectin with higher anhydrogalacturonic acid content as compared to the precipitation by using ethanol. A minimum value of 65% AGA for commercial pectins has been specified by FAO²⁴. Thus the pectin obtained from apple pomace by using different extraction and precipitation methods, was found close to the range of anhydrogalacturonic acid content for standard pectin. The pectin was also found of high methoxyl type with degree of esterification ranging between 60.5-74.9%.

Among the extraction methods, pectin produced by single oxalate extraction has highest degree of esterification, which was closely followed by single acid extraction. Lower degree of esterification was obtained in the pectin precipitated by aluminium chloride as compare to pectin precipitated with ethanol. The acetyl value was found to range between 0.34-0.48% in pectin extracted from apple pomace. High degree of acetyl esterification of about 21 to 25 moles per 100 moles of galacturonic acid in sugar

beet pectin has been considered to inhibit jelly formation²⁵. In apple pectin acetyl esterification value is reported to range between 4.0-8.7mol/100 moles of galacturonic acid⁴ but is too low to inhibit jelly formation. With respect to the extraction and precipitation methods, the pattern of degradation of acetyl and methyl esters (degree of esterification) was found to be similar with high acetyl value in pectin obtained from oxalate and water extractions and lower values in the pectin from acid extraction and sequential water-acid as well as water-oxalate extractions. Jelly grade of pectin was found to range from 40 to 130. The jelly grade of the pectin extracted

by two-stage sequential water-acid extraction was highest followed by acid extraction. Aluminium chloride precipitation resulted in pectin with higher jelly grade in comparison to alcoholic precipitation.

Thus two-stage sequential water-acid extraction is found to give high yield of pectin with best quality characteristics. However, the use of single acid extraction was found more appropriate as two-stage sequential water-acid extraction add one extra unit operation for pectin extraction without increasing the yield in equivalent proportion,. The optimized method for extraction of pectin from apple pomace is presented in Figure-1.

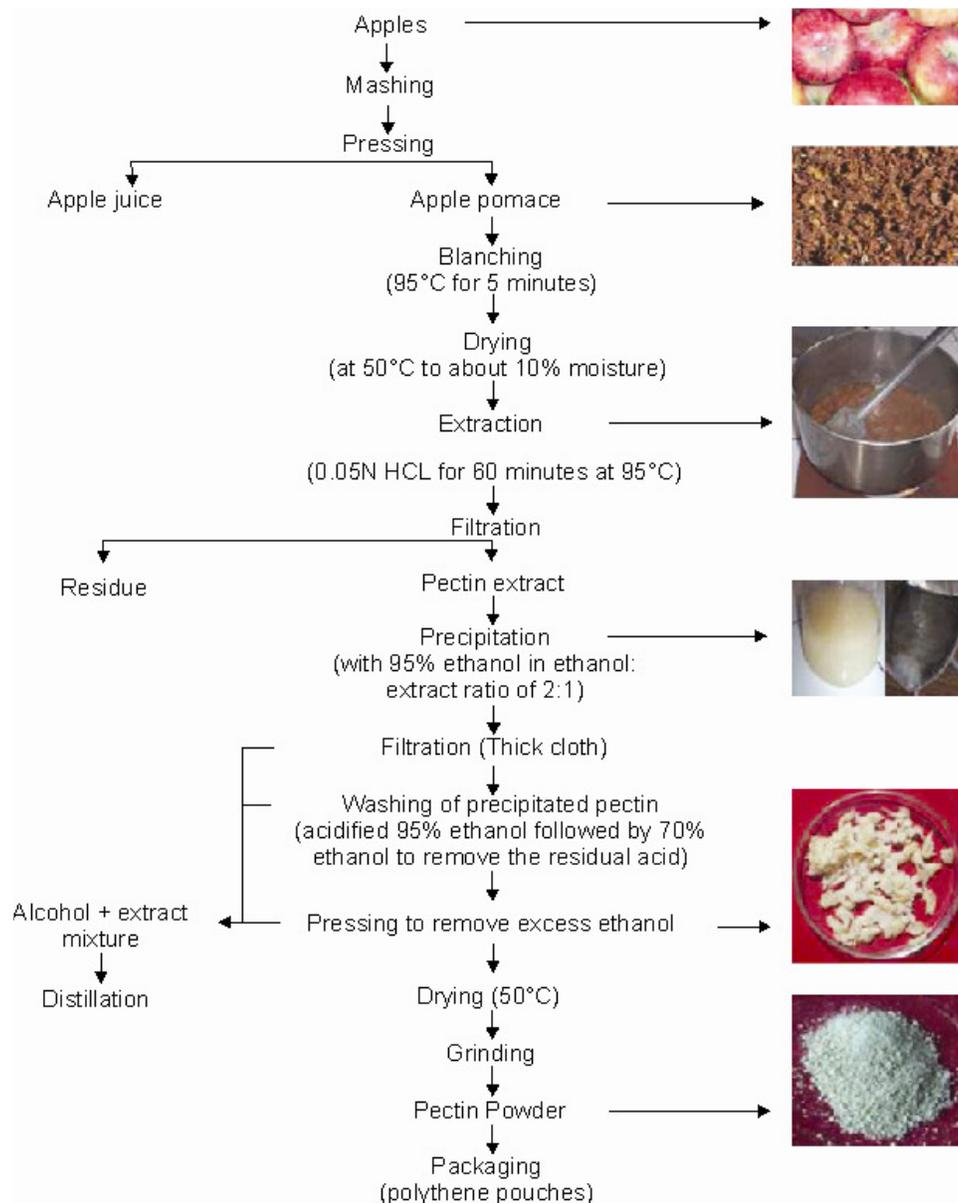


Fig. 1–Flow sheet for extraction of pectin from apple pomace

Cost of production

The cost of production of pectin per kg has been calculated assuming handling of 10kg fresh apple pomace in a single extraction process. This pomace would yield about 195g of pectin. The cost of production of pectin has been worked out to be Rs 808.30 per kg which is slightly more than the market price for pectin i.e. about 10 US\$ per kg²⁶. High cost of precipitation medium is the main factor which contributes to high cost of production. At commercial scale however, the use of recovered ethanol for precipitation of successive batches of pectin can reduce this cost. Besides handling of larger quantities of pomace during the same extraction period would possibly further reduce the operating costs.

Conclusion

Thus, dried pomace after blanching in hot water for 5 minutes can be used as a suitable raw material for extracting pectin. The optimized method for pectin extraction consisted of treating apple pomace with 0.05N HCl at 95°C for 60 minutes followed by precipitation using 95% ethanol in the ratio of 1:2 (extract: ethanol) prior to drying to a moisture content of about 10%. The extracted pectin having 110 jelly grade can be used in the food industry for manufacture of different products.

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