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Pectin Production from Tomato Seeds by Environment-Friendly Extraction: Simulation and Discussion

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The aim of this work is to model the extraction of pectin from tomato peels using different acids that could be more environmentally friendly. The AspenPlus® software is used to this end. Several cases, such as considering different extracting acids, the recycle of water and washing solvent streams are evaluated and compared. Tomato peels seasonally generated by factories in a local district, were considered as raw materials, as well as methanol and catalyst. Based on literature data and using Excel® worksheet, the mass and energy balances were set up for the extraction reactor and, hence, a pectin extraction yields up to 25 % and 17 %, for two different scenarios, was determined, while the washing and purification stages were simulated and optimized in AspenPlus®. The distillation tower for solvent recover was designed. The economic potential of these cases was calculated by considering utilities cost, product and by-product sales, wastewater treatment as well as raw material costs. Results show that tomato peels can be a feasible alternative for pectin production. Moreover, this work could be a basis for the development and design of a multi-product biorefinery based on tomato by-products produced by cannery industries in the frame of a circular economy approach.

1. Introduction

Pectin is a natural polysaccharide, composed by the union of several different monosaccharides, with galacturonic acid as the most occurring component. This natural polymer is an indigestible carbohydrate contained, mainly, in the cell walls of fruits and vegetables (Thakur et al., 1997). Pectin forms a gel when properly mixed with water and the right amount of sugar, for this reason it is used at an industrial level as gelling agent, in jams, as thickener and stabilizer, especially for proteins. Moreover, it is also widely used in the cosmetic, biotechnological, and pharmaceutical sectors, where it is exploited for drug trapping and in the formulation of medicines for the treatment of ulcers, intestinal problems, and cancer (Thakur et al., 1997). Recently, pectin has been proposed as a starting material for the preparation of edible films and coatings (Vanitha and Khan, 2019). Due to its wide application field, the health concerns and the increasing demand for natural and organic ingredients, the pectin global market is growing constantly so much that in 2015 the yearly income was estimated at about 964 Million $, but it is expected to increase even more in the next future (Koulouris and Petrides, 2020). Although, pectin is commonly present in most plant tissues, commercial pectins are almost exclusively derived from citrus peel or apple pomace, both by-products of juice production, due to higher quality standards, in terms of molecular weight and colour, and the possibility to have sufficient quantity to run a cost-effective production operation (Marić et al., 2018, Ruano et al., 2019).
The industrial process for pectin production is constituted by four main sections: an acid extraction in which the protopectin, contained in the raw material, is hydrolysed and transformed into a water-soluble molecule; the purification of the extract, which is separated from the solid matrix by filtration step; the repeated washing/precipitation of pectin by alcohol, a final pectin purification by drying and grinding (Marić et al., 2018).
The core of the process is therefore the extraction step that is conventionally carried out by treating the raw material in a reactor; batch operation under agitation is usually involved at industrial level, but recent research demonstrated that a continuous reactor could reach same pectin yield (Soemargono et al., 2016). The optimum temperature is usually in the range 70-100°C (Marić et al., 2018), while the pressure is kept at

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atmospheric in almost all the case (Morris and Binhamad, 2020). The residence time of the process may change from one producer to another, but in general it depends on the type of raw material (May, 1990). The extracting agent is usually a mineral acid, mainly hydrochloric acid, sulfuric acid, or phosphoric acid, at pH values ranging between 1-3. However, the main disadvantage of these mineral acids is their toxicity and the generation of environmentally harmful effluents (Yapo, 2009). Therefore, some organic acids, such as citric, tartaric, and maleic acid, have been tested for pectin extraction with results comparable to mineral ones (Yapo, 2009). Recently, autohydrolysis process has been proposed as a eco-friendly alternative to acid extraction, using only water and taking advantage of high pressure and temperature (Bassani et al, 2020), however it is still at lab-scale and not yet optimized for large scale pectin production.
Regarding alternative feedstocks, in 2006, Del Valle and coworkers were the first to report about the presence of pectin in tomato peels (Del Valle et al., 2006), an underused biowaste, that is generally sent to landfill, although it contains high value compounds (Cicognini et al., 2015; Lavecchia and Zuorro, 2008). Tomato peels are, together with tomato seeds, the main by-products in terms of amount and exploitability of tomato processing industry. Then, Grassino et al. (2016) developed a laboratory method to produce pectin from dried tomato peels, using ammonium oxalate and oxalic acid as extracting solvents. On another side, Alancay et al. (2017) optimized the pectin extraction from tomato processing waste by mineral acid extraction, i.e., with hydrochloric acid. According to their results, it can be concluded that tomato peels are a suitable source for pectin that can be used in food and pharmaceutical industry, and the extraction yields are between 20-30% when starting from dried peels and adopting acid extraction.
At the best of authors' knowledge, no studies or research were carried out to investigate the scalability as well as the technical and economic feasibility of a process plant producing pectin from tomato peels. Therefore, this work reports about the conceptual development and optimization of a plant based on tomato peels as feedstock and producing pectin for food industry. The use of two different acids was studied: a conventional mineral acid and a "green" alternative. Therefore, two alternative flowsheets are proposed, and in parallel the technical feasibility and the economic indexes of the two processes are discussed and evaluated. Aspen Plus® was utilized for simulation and optimization of processes.

2. Materials and methods

2.1 Feedstock characteristics

This work took in consideration the study and development of the section of a biorefinery plant, presented in a previous work (Casa et al., 2020) in which pectin is extracted from dried and dewaxed peels by two different acids, and then washed and purified with ethanol. Drying and dewaxing are carried out in different upstream sections of the biorefinery. As a basis for calculations, 465 ton/y, namely 83 kg/h, of treated tomato peels (TP) are considered, taking in account a plant working 350 days in a year for 16 hours per day. This is the amount of treated TP contained in tomato by-products produced by 5 medium-size companies during a two-month working season, located in Campania in small area with a diameter of 10 km. The pectin concentration in tomato peels was gathered by literature and considered around 30%wt, while the solid residue was considered as cellulose (Alancay et al., 2017), for the feedstock description in Aspen Plus®. The ethanol for the precipitation step was considered 86%wt pure.

2.2 Extraction process: parameters and yields

Two different scenarios for the extraction process were taken in account: the first one in which hydrochloric acid is used and the second one where the extraction is activated by citric acid obtained from waste lemons. The key parameters were inferred by an experimental research on the extraction of pectin from citrus by-products, assuming similar outcome for tomato peels. The conditions for the first scenario were gathered by the experimental research of Seggiani et al. (2009). A reactor temperature of 70°C, a solid to liquid ratio of 1/17 and a 0.2M of HCl were considered; moreover, with a residence time of 1 h, an extraction yield of 26 g/100g of tomato peels was assumed (Seggiani et al., 2009). In the 2nd scenario, an extraction temperature of 90°C, a solid to liquid ratio of 1/4.3 and pH of 1.5 were considered; moreover, with a residence time of 1.5 h, a reaction yield of 17g/100g of tomato peels was assumed (Casas-Orozco et al., 2015).

2.3 Process simulation

Process flowsheeting was carried out to assess the technical feasibility of the production of pectin from tomato peels, considering the recycle of the auxiliary streams, namely the ethanol for washing and the extracting acid, and, hence, enabling the comparison of the two scenarios. The simulation was performed with Aspen Plus®. The method selected to describe a solution was NRTL (Non-Random Two Liquid Model), which correlates the activity coefficients of a compound with its molar fractions. This is the mostly used model in the chemical engineering field for the calculation phase equilibria. The LEVOG-01 component is the one adopted to represent the pectin content. In fact, the brute formula of this compound is $(C_6H_{10}O_5)_n$, corresponding to the most representative building block of pectin. While DEXTR-1 ($C_6H_{12}O_6$) was used for representing the solid portion of the feed. The compounds' properties were imported in the simulation from APV88 PURE32, a primary component databank from Aspen Tech, allowing the process simulation in the absence of experimental data. Both schemes can be divided in 3 main sections (see Figure 1):

- Extraction: in this section the dried and dewaxed tomato peels are mixed with water and acid, then reaction mixture is brought to selected condition and sent to the extraction reactor.
- Pectin purification: in this section the reaction mixture is centrifuged to remove the spent solids, the extracted pectin is precipitated and washed with ethanol in a settling vessel, alcohol is removed by squeezing and successive drying and the final pectin is grounded to the desired fine size
- Reagent recovery: in this section the ethanol and the acid water solution are recovered by distillation and sent back to the extraction and purification stage.

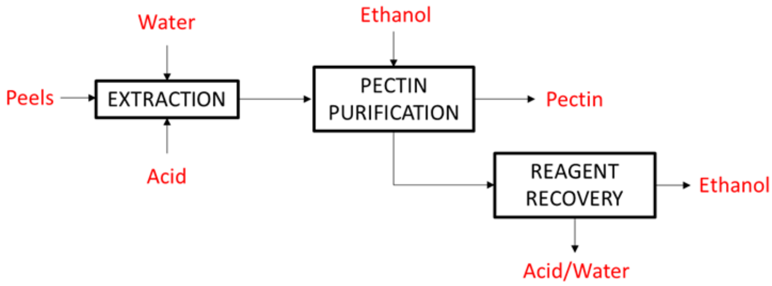

Figure 1 Simplified block diagram for pectin production from tomato peels

For the sake of clarity and readability, the two main flowsheets developed in Aspen Plus® software are not reported in the text but highlights of the main sections are shown and discussed in the following.

2.4 Economic Analysis

In order to assess the economic feasibility of the plant for pectin production, two categories of costs were considered: total capital cost for the construction and operating ones needed for the operations over time.
In this work the capital cost was evaluated as the sum of costs for unit equipment, establishment of services, production site and project design. Operating costs included raw materials, energy demand for operating equipment, labour and maintenance cost, patent cost and general expense. The net profit of the plant was evaluated as the revenues coming from the selling of the produced pectin (food additive grade) minus the operating costs, considering taxes and depreciation. Therefore, indexes as the return of investment (ROI) and the payback period (PBP) were calculated (Seider et al., 2008):

$$ROI = \frac{Net\ profit}{Total\ capital\ cost} \tag{1}$$

$$PBP = \frac{Total\ capital\ cost}{Net\ profit - Annual\ depreciation} \tag{2}$$

3. Results and discussion

Figure 2 shows the block diagram developed for the section in which extraction is carried out.

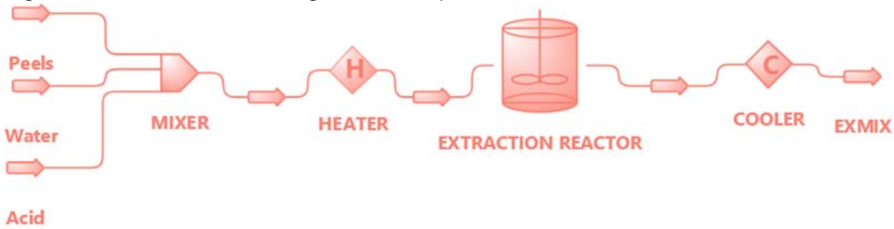

Figure 2 Flowsheet for pectin extraction section

In this section, 83 kg/h of tomato peels are mixed with 1400 kg/h of water and 10.3 kg/h of HCl in the first scenario. Vice versa, 249 kg/h of water and 107 kg/h of citric acids are used in the second one. The mixture is brought to reaction conditions and sent to the extraction reactor. The reactor cannot be designed by Aspen Plus®, due to lack in the software of a unit block that can simulate solid-liquid extraction. Therefore, the reactor was designed by an EXCEL worksheet, considering the residence time equal to the reaction time reported in literature (Casas-Orozco et al., 2015; Seggiani et al., 2009) and a loaded volume equal to 75% of the total reactor volume (Casas-Orozco et al., 2015). Under these conditions, the reactor geometry was:

Table 1: Design for extraction reactor in the two scenarios

	Volume [m3]	Height [m]	Diameter [m]	Impeller [No.]
1st scenario	2.12	0.55	1.1	3
2nd scenario	1	0.43	0.86	3

Due to the higher flows involved in the first scenario, the volume is bigger even if the residence time is smaller. After extraction, the mixture is cooled to ambient temperature and sent to the next section. EXMIX stream contains the extracted pectin dissolved in the acid mixture and the spent solid. The purification section was simulated in Aspen Plus® and the developed flowsheet is reported in the next figure.

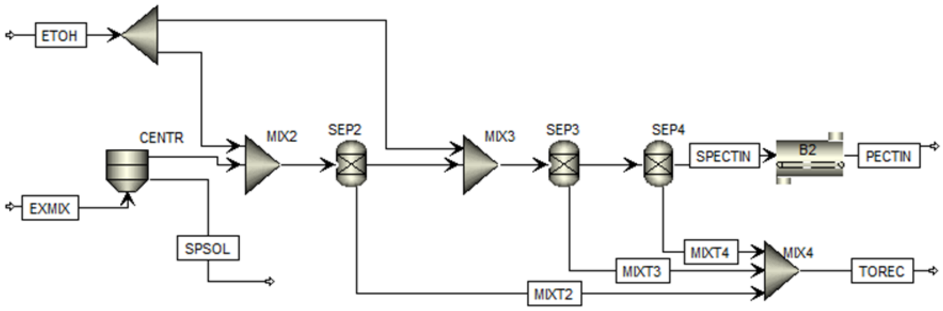

Figure 3 Flowsheet for purification section in Aspen Plus® software

In this section, the pectin is recovered from the extractor outlet and purified. In particular, the stream EXMIX is firstly centrifuged to remove the spent solid. In the simulation the separation efficiency for CENTR was set to 1, as suggested by literature (Casas-Orozco et al., 2015). Then the liquid mixture containing pectin is mixed (MIX2 and MIX3) with two ethanol flows (86%wt). In SEP2 and SEP3 blocks, in presence of ethanol, the pectin precipitates as a solid and is recollected at the bottom of the two settling vessels. The total mass flow of ethanol is 2890 kg/h for first scenario and 846 kg/h for the second scenario. The lower amount of ethanol is due to the reduced aqueous mixture coming out from the extractor. SEP4 simulates a press unit in which the solid pectin is squeezed to remove a part of adsorbed ethanol. The split fraction for the SEP unit of this block was extrapolated from a process simulation for pectin production by orange peels (Casas-Orozco et al., 2015), as mentioned above. In B2 unit block residues of ethanol and water are removed from solid pectin by hot air drying to 98%wt of purity (Casas-Orozco et al., 2015). In terms of mass flow, the plant productivity for pectin was 21.58 kg/h for the first scenario and 14.11 kg/h for the second one. For the energy demand of press and drying, commercial equipment suitable for this process yield was considered: Squeezing belt type filter press machine KZ1000 by Porvoo© and DW-series Belt Food Drying Machine by Food Drying Machine©. The PECTIN, MIXT2, MIXT3 and MIXT3 streams contain the spent ethanol with water and acid, therefore are collected in MIX4, and the TOREC output stream is sent to recycling section. In the final section, the TOREC stream, containing ethanol, the extraction water, and the extracting acid, are separated by distillation to obtain the ethanol rich stream to be recycled to purification section and an acid water stream to be recycled to the extraction section. The flowsheet section developed in Aspen Plus® is reported in Figure 4 while the operating conditions of the distillation tower for both scenarios are reported in the following table.

Table 2: Operating conditions of the distillation tower for reagents recovery

	Temperature	Pressure	Stage Number	Reflux ratio	Heat load at reboiler
1st scenario	25 °C	1 bar	10	0.65	1.8 MW
2nd scenario	30 °C	1 bar	10	7	2 MW

The inlet temperature for the distillation is set as the TOREC temperature, at it is around ambient temperature for both scenarios, the pressure is set as atmospheric. The stage number (N) and reflux ratio (R) were optimized by means of a series of sensitivity analyses to have ethanol recovery in the RECETOH stream higher than 0.9975 and its purity around 86%wt, which is the concentration of ethanol solution used for washing steps. The heat load is high in both cases due to the massive flow rate of the TOREC stream.

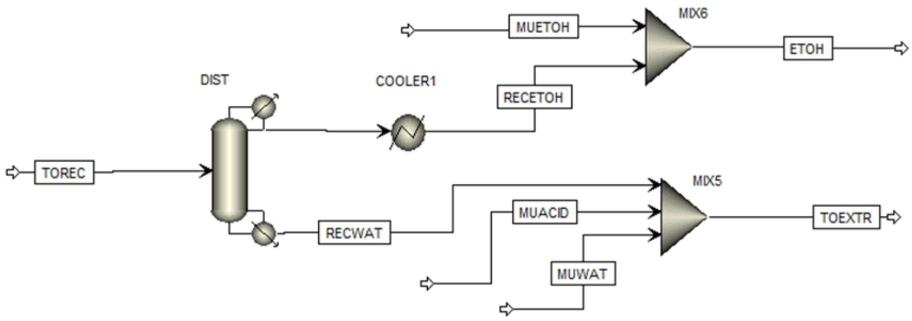

Figure 4 Flowsheet of distillation section for recovering and recycling.

After the distillation, the two streams are mixed with a make-up of ethanol, acid, and water respectively to recycle the ETOH stream at the purification section and TOEXTR to extraction section. The make-up flow rates were calculated by using the Calculator block of Aspen Plus®, which allows the evaluation of a variable stream (MUETOH, MUACID, MUWAT) depending on a fixed variable (RECTOH, RECWAT) to obtain a desired value of a third variable (ETOH, TOEXTR). The make-up flow rates of the fresh reagents for plant operation are reported in the next table:

Table 3: Make-up flows for both scenarios

Make-up [kg/h]	Ethanol	Water	Acid
1st scenario	105	46	0.510
2nd scenario	3.25	8.2	3.3

Make-up streams compared to the operating flows are consistently lower, they are less than 5% for all reagents and for both scenarios, meaning an optimal performance of the recycling section.
After the simulation of the two scenarios that assess the technical feasibility of the production of pectin from tomato peels, economic indexes were evaluated to assess the economic feasibility of the plant. For the calculation of Net Profit, ROI and PBP (reported in Table 4), the Energy and Economic Analyzer tool of Aspen Plus® were used. These tools allow the evaluation of capital and operative costs of the equipment involved in the process. For the equipment not included in Aspen Dataset, commercial options were selected and used to gather equipment cost and energy demand. Moreover, for the economic analysis, 4 workers, 5600 working hour per year and a tax index of 4% (Seider et al., 2008) were considered.

Table 4: Economic indexes for both scenarios

]	Net Profit	ROI	PBP
1st scenario	0.78 M$	0.25	1.75
2nd scenario	0.52 M$	0.3	2.3

Although both scenarios lead to a positive Net Profit of around 1M$, the second scenario, which represents a green alternative, has a higher ROI, meaning a better economic profitably; the corresponding PBP is higher mostly due to lower pectin yield. Anyway, it is worth noticing that both scenarios have ROI and PBP slightly better than standard chemical plants (0.15 ROI and 4y PBP), meaning that the production of pectin from tomato peels is both technical and economical feasible.

4. Conclusions

This work demonstrates the technical-economic feasibility of the production of pectin from tomato skins by two alternatives: the first one uses hydrochloric acid and the second involves extraction with citric acid. AspenPlus® was used to implement the work and generate the results, except for the solid-liquid extraction reactor, for which the pectin yield was calculated using the MS Excel® spreadsheet. The developed process schemes were composed of a pectin extraction section, a purification unit, and a recovery system for solvent. Literature data provided the basis for materials description and acid-assisted extraction yield and conditions.
A productivity of 22.58 kg/h of pectin for extraction with HCl, while in the case of citric acid the productivity was 14.11 kg/h. The economic potential was calculated considering the cost of utilities and raw materials, product sales, achieving a net profit of 0.78 M$/year for the conventional process and 0.52 M$/year in the "green" one. Even with lower net profit the ROI of the alternative “green” process is higher than the conventional one.

The results show that tomato peels may be a feasible alternative for pectin production and, furthermore, this work could be a basis for the development and design of a multi-product biorefinery, based on tomato by-products from the canning industries located in a reasonable small territorial area. To this end, a similar paper (Casa, Prizio and Miccio, 2020) reports about the biodiesel production in the same biorefinery framework.

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