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ORIGINAL PAPER

Techno-economic and Environmental Assessment of *p*-Cymene and Pectin Production from Orange Peel

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Abstract Citrus production generates a large quantities of residues which can be used in the production of intermediate compounds for the production of value added products which can be used in the synthesis of industrial fine chemicals, fragrances, flavorings, herbicides, pharmaceutical products among others. This work presents a study to increase the value added of essential oils obtained from orange peel producing *p*-cymene and pectin. Techno-economic and environmental assessments were developed demonstrating that computer-aided process engineering tools can be used to evaluate the feasibility of integrated processes. Two scenarios were evaluated (with and without electricity generation) obtaining 9.22 and 42.63 kg/h with purities of 97 and 81 % of *p*-cymene and pectin respectively. In the scenario with electricity generation, 99.81 kWh was obtained, covering all requirements in the process. The techno-economic analysis showed that the most appropriate scheme was that without electricity generation reaching a production cost of 5.27 and 3.53 USD/kg of *p*-cymene and pectin respectively. Environmental analysis reveals that the potential environmental impact was lowest for the scenario without electricity generation.

Keywords *p*-Cymene · Orange peel · D-Limonene · Pectin · Techno-economic analysis · Environmental analysis

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Introduction

Citrus are an important agroindustrial chain in Colombia producing juices, concentrates, nectar, purees, pastes, pulps, jellies and marmalades among others. More than 467,000 tonnes of citrus were produced in 2011 [1]. The Citrus production is typically composed of 71 % of oranges, 15 % of mandarins, 12 % of acid lime and 2 % of grapefruit and tangelo. In 2012, Colombia had a total production of 1,248,187 and 268,757 tonnes of general citrus and oranges respectively [2]. Despite that Colombia has approximately 553 plants dedicated to fruit processing, approximately 50 % of the citrus becomes in residues, which are used as animal food. Citrus wastes are represented by the peel (albedo and flavedo), segment membranes and all other residues from the citrus processing [3, 4].

In the case of orange, its peel has some important compounds, which have value added in the market; some of them are essential oils, polyphenols, flavonoids, cellulose and pectin [5–9]. These compounds are typically used in liquor, paint, rubber, food and pharmaceutical industries [10–12].

On the other hand, high value added products can be obtained from orange peel and its derivatives. Hesperidin can be recovered as a byproduct in large quantities after acid pretreatment of orange peel [7]. Biofuels and pectin have been obtained from orange peel using acid hydrolysis processes [13]. D-Limonene contained in orange peel can be used as an intermediate compound to obtain other high valuable products such as terpinolene, terpinene, *p*-menthene, *p*-menthane and *p*-cymene by means of dehydrogenation of D-limonene [14]. Allylic ethers have also been produced by oxidation of D-limonene with benzoquinone under alcohols solutions [15]. Perillic acid has also been produced from D-limonene by fermentative way using *Pseudomona putida* [16].

From the compounds mentioned above, *p*-cymene is one of the most important products with an annual production of approximately 4,000 tonnes per year [17]. *p*-Cymene is an excellent intermediate compound for industrial fine chemicals synthesis and it is used in fragrances, flavorings, herbicides, pharmaceutical products and synthesis of not nitrated musk as well as in *p*-cresol production among others. Besides, *p*-cymene can be produced in a cheaper, simpler and lower toxicity method with the additional production of hydrogen which becomes in bonus (or credits) for an integrated production of high valuable products from D-limonene [18].

Taking into account the large and available quantities of orange peel and its potential to be used as a renewable feedstock to produce important intermediate compounds such as D-limonene, this work presents a study to increase the value added of essential oils obtained from orange peel for the integrated production of *p*-cymene and pectin. This is made by means of techno-economic and environmental assessments suggesting that computer-aided process engineering tools can be used to evaluate the feasibility of integrated processes. Two scenarios are evaluated considering electricity generation from the remaining solid wastes in the integrated process and comparing them from economic and environmental points of view.

Materials and Methods

The methodology was carried out in three steps using different computational tools. The first step corresponds to the process simulation to obtain the energy and mass balances of the process using Aspen Plus V.8.0 (AspenTech: Cambridge, MA). The physicochemical properties of all compounds involved in the simulation step were obtained from the National Institute of Standards of Technology [19]. The Unifac Dortmund model was used for the properties calculation for all compounds.

The second step corresponds to the economic analysis which was made using Aspen Process Economic Analyzer (AspenTech: Cambridge, MA). Finally, the third step corresponds to the environmental analysis which was made using waste algorithm reduction developed by the US Environmental Protection Agency.

The techno-economic and environmental assessments were made for two scenarios, which correspond to that with and without electricity generation (scenarios 1 and 2 respectively) by mean of gasification of the remaining solid material at the end of the integrated process.

Model Calculation

Table 1 depicts the model calculation that was carried out according to the three steps described above. The model calculation scheme involves the mathematical models for the principal units used in the simulation as well as the algorithms for them, including the sequence of information obtained in each step.

Raw Material

The raw material used was orange peel and its characterization is shown in Table 2 [6]. The fiber of orange peel corresponds to 60.96, 32.97 and 6.07 % of cellulose, hemicellulose and lignin respectively. The ultimate analysis of orange peel corresponds to 46.4 % of C, 5.7 % of H, 1.52 % of N, 0.05 % of S and 46.33 % of O [20].

Process Simulation

Figure 1 shows the production scheme of *p*-cymene, hydrogen and pectin based on 1 tonne/h of orange peel, which corresponds to 2.97 % of the available wastes from orange processing (268,757 tonnes/year) in Colombia. Two plants compose the production scheme, the first one for *p*-cymene with an additional production of hydrogen (Plant A) and the second one for pectin production (Plant B).

The process begins with a stream of orange peel, which is milled to obtain particles less than 0.45 mm. After that, D-limonene and remaining oils are separated in an extractor using steam at 100 °C and 1 bar of pressure. Only 54 % of the D-limonene is separated [6] then, an additional decanter is used to obtain a stream of D-limonene at 96 % of purity to be used in the plant of *p*-cymene production (Plant A). The solid residue from extractor is employed in the pectin extraction (Plant B), it is send to a hydrolysis at 80 °C using citric acid to solubilize the pectin [21, 22].

After hydrolysis process, the liquid stream containing the solubilized pectin is precipitated using ethanol (90 % wt.) with which is possible precipitate and extract the pectin [21]. After pectin precipitation, a drying is made to purify the final pectin. Part of the citric acid and ethanol employed in pectin extraction is recovered and recycled to the process. The remaining solids (composed by cellulose, hemicellulose and lignin) from hydrolysis process are separated and used in electricity generation using a simple gas turbine after gasification at 850 °C. Finally, the gases produced from turbine are cooled at 120 °C.

On the other hand, *p*-cymene ($C_{10}H_{14}$) is produced in the plant A by means of dehydrogenation of D-limonene ($C_{10}H_{16}$) with an additional production of hydrogen (H_2) as it is shown in Eq. (1). This reaction is carried out using a mesoporous Silica-Alumina support at 165 °C obtaining 100 % of conversion and selectivity of *p*-cymene [17]. Finally, *p*-cymene and hydrogen are separated based on boiling point differences.

Table 1 Model calculation of the process simulation

First step: mass and energy balances

Introduction of compounds (from databases of Aspen plus and NIST)

Selection of the thermodynamic model (Unifac Dortmund)

$$Ln\gamma_i^c = Ln\left(\frac{\Phi_i'}{x_i}\right) + 1 - \frac{\Phi_i}{x_i} - \frac{z}{2}q_i\left(Ln\frac{\Phi_i}{\Theta_i} + 1 - \frac{\Phi_i}{\Theta_i}\right)$$

$$\frac{\Phi_i'}{x_i} = \frac{r_i^{3/4}}{\sum_j x_j r_j^{3/4}}; \Phi_i = \frac{x_i r_i}{\sum_j^{nc} x_j r_j}; \Theta_i = \frac{x_i \frac{z}{2} q_i}{\sum_j^{nc} x_j \frac{z}{2} q_j}$$

$$r_i = \sum_k^{ng} v_{ki} R_k; q_i = \sum_k^{ng} v_{ki} Q_k$$

where nc is the number of components, ng is the number of groups in the mixture, z is the coordination number set to 10, x is the molar composition, R and Q are the volume and area parameters, respectively, and v_{ki} is the number of groups of type k in molecule i

Definition of operational conditions (from the literature and described in "Process Simulation" section)

Models for units involved in the chemical process (Fig. 1)

Pumps (according to power consumption)

For power requirements: $P = m\left(\Delta\left(\frac{u^2}{2\alpha}\right) + g\Delta z + \int_{p1}^{p2} vdP + F\right)$

where P is the total work, m is the masic flow, u refers to the velocity, g is gravity, Δz is the static head, vdP is the pressure head, F is the dynamic head, α is a coefficient used to take into account the velocity profile inside the pipe (0.5 and 1 for laminar and turbulent flow respectively)

Crusher (cumulative analysis)

$$D_{P,n} = Particle\, diameter$$

$$A_{Solids} = \frac{6\lambda}{\rho_P}\int_0^1 \frac{d\phi}{D_{P,n}}$$

$$N_P = \frac{1}{a\rho_P}\int_0^1 \frac{d\phi}{D_{P,n}^3}$$

where Dp,n is the particle diameter, λ is the form factor, ϕ is cumulative fraction and ρ is the particle density.

Heat exchangers (heat and mass balances)

$$Q = UA\Delta T = \dot{m}C_P\Delta T$$

$$\frac{1}{U} = \frac{1}{h_0} + \frac{2.3D_0}{2K}\left(log\frac{D_1}{D_0}\right) + \frac{1}{h_1(D_1/D_0)}$$

where Q is heat, U is total coefficient of heat transfer, h_1 and h_2 are the convective heat transfer coefficients calculated for each of the fluids, respectively, D_0 and D_1 are the internal and external diameters of the tube in the heat exchanger, respectively, m is the mass flow and Cp corresponds to the heat capacity of the fluid

Flash (Radchford-Rice equation)

$$F = L + V, Fz_i = Lx_i + Vy_i, y_i = K_i x_i, \psi = V/F$$

$$z_i = (1-\psi)x_i + \psi K_i x_i, x_i = \frac{z_i K_i}{(1-\psi) + \psi K_i}, y_i = \frac{z_i K_i}{(1-\psi) + \psi K_i}$$

$$\sum_{i=1}^{M} x_i = 1, \sum_{i=1}^{M} y_i = 1, f(\psi) = \sum_{i=1}^{M}\left(\frac{z_i(1-K_i)}{1+\psi(K_i-1)}\right)$$

where F, L and V are feed, liquid and vapor, respectively, x_i, y_i, and z_i are the compositions for liquid, vapor and feed, respectively. Ψ is the vapor fraction

Distillation (Radfrac model using the MESH equations)

Mass and energy balances of component i around plate j

$$M_{i,j} = L_{j-1}x_{i,j-1} + V_{j+1}y_{i,j+1} + F_j z_{i,j} - (L_j + U_j)x_{i,j} - (V_j - W_j)y_{i,j} = 0$$

$$E_{i,j} = y_{i,j} - K_{i,j}x_{i,j} = 0$$

$$(S_y)_j = \sum_{i=0}^{c} y_{i,j} - 1 = 0$$

$$(S_x)_j = \sum_{i=0}^{c} x_{i,j} - 1 = 0$$

$$H_j = L_{j-1}h_{L,j-1} + V_{j+1}h_{V_{j+1}} + F_j h_{F_j} - (L_j + U_j)h_{L_j} - (V_j - W_j)h_{V_j} - Q_j = 0$$

where F, L, V, U and W are the flows for feed, liquid, vapor, lateral liquid and lateral vapor, respectively. x, y and z represent the mol compositions in the liquid, vapor and feed respectively. H and h are the enthalpies in the plate and flows, respectively. Finally, i and j represent the component and the plate, respectively

Table 1 continued

First step: mass and energy balances
Turbine (Mollier method)
$\eta\Delta h = \int_{p1}^{p2} VdP$
where η is the efficiency, h is the enthalpy, P_1 and P_2 are the pressure and V is the volume.
Units of hydrolysis, reactor and extractor (Yields from literature)
These units were simulated according to the yields found in the literature such are described in the "Process Simulation" section

Table 2 Characterization of orange peel

Compound	(%)
D-Limonene	1.50
Myrcene	2.14e−2
B-pinene	7.17e−3
A-pinene	5.36e−3
Terpinol	3.55e−3
G-terpin	4.48e−4
Octanal	8.48e−3
Decanal	3.07e−3
Dodecanal	4.11e−4
Undecanal	3.74e−4
Nonanol	4.86e−4
Linalol	1.83e−2
Octanol	8.59e−4
Nonanal	3.36e−4
Nerol	5.60e−4
Geraniol	2.62e−4
Sabine	8.75e−4
Water	79.91
Ascorbic acid	1.04e−5
Protein	3.94e−3
Lipid	9.90e−4
Pectin	6.15
Fiber	10
Ash	2.37

$$C_{10}H_{16} \rightarrow C_{10}H_{14} + H_2 \tag{1}$$

Economic Analysis

The economic analysis was made for the complete integrated process calculating the production cost per kg of *p*-cymene and pectin for plant A and plant B respectively. The electricity generated was taken as credits in the scenario 1 while the hydrogen produced was taken as credits in the *p*-cymene production for both scenarios. The total production cost considers the total raw material, utilities, operating, labor and maintenance costs as well as the operating charges, plant overhead and general and administrative costs. Additionally, tax rate was taken according to the laws in Colombia (25 %). The labor, utilities and feed costs are shown in Table 3.

Environmental Analysis

The environmental analysis evaluates eight environmental impact categories such as: human toxicity potential by ingestion (HTPI), human toxicity potential by dermal and inhalation exposure , terrestrial toxicity potential (TTP), aquatic toxicity potential, global warming potential, ozone depletion potential, photochemical oxidation potential (PCOP) and acidification potential. The potential environmental impact (PEI) of the process was calculated per kilogram of products (*p*-cymene, hydrogen and pectin). Natural Gas was used as fuel to cover the heat requirements for the integrated process.

Results and Discussion

Process Simulation

Table 4 shows the mass balance of the integrated process. *p*-Cymene, hydrogen and pectin were obtained with purities of 97, 98 and 81 % respectively. In scenario 1 (with electricity generation) was obtained 99.81 kWh and a final exhaust gases were obtained with 25 % of carbon monoxide, 19 % of carbon dioxide, 2.9 % of methane, 1 % of hydrogen and traces of sulfur dioxide. On the other hand, for scenario 2 (without electricity generation) residual solids with traces of ethanol, citric acid and pectin were obtained from hydrolysis process.

The *p*-cymene yield obtained was 1 % (0.01 kg/kg of extracted D-limonene), this yield is similar to other found with different techniques such as that obtained from industrial di-pentene dehydrogenation where a yield between 0.31 and 1.1 % was obtained [27]. Thus, *p*-cymene obtained from orange peel is an attractive alternative because it is a renewable and cheaper feedstock [18].

On the other hand, the hydrogen yield obtained was 0.01 NM3/kg of extracted D-limonene. This should be similar to

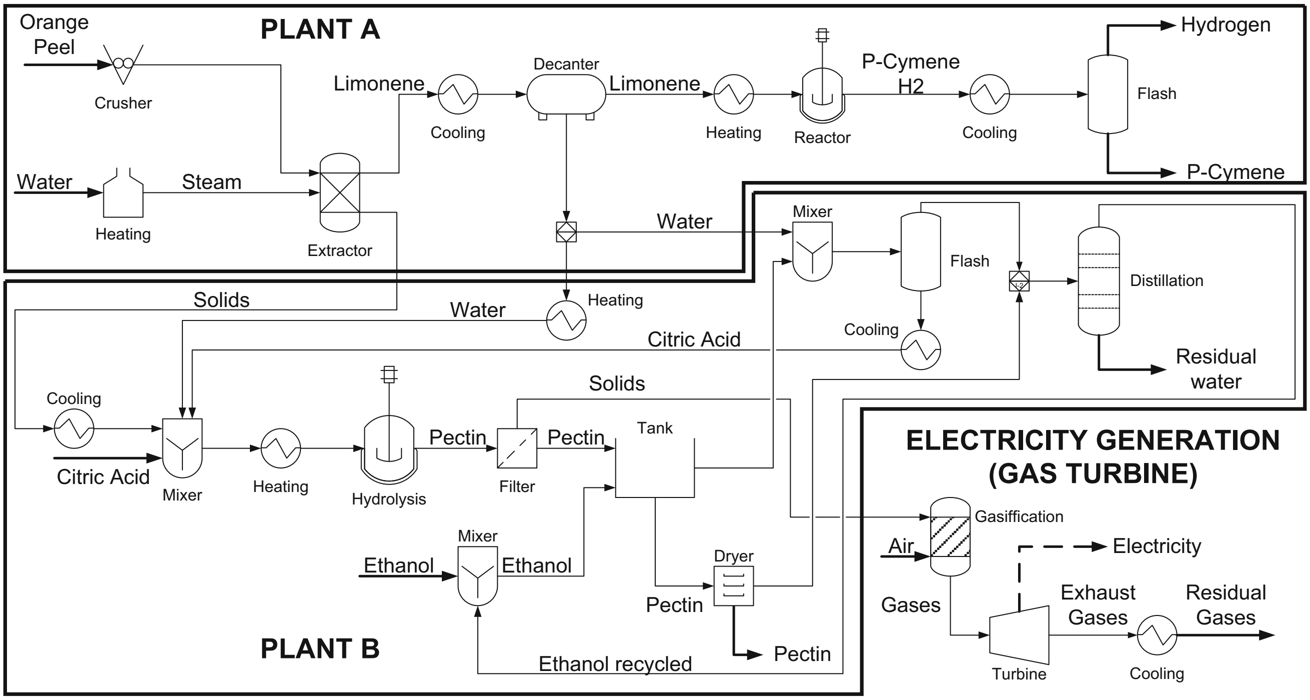


Fig. 1 Production scheme of *p*-cymene and pectin

Table 3 Operational costs to the *p*-cymene and pectin production

Item	Price	Unit
Operator[a]	2.14	(USD/h)
Supervisor[a]	4.29	(USD/h)
Electricity[a]	0.10	(USD/KWh)
Potable Water[a]	1.25	(USD/m^3)
Fuel[b]	7.21	(USD/MMBTU)
Raw material[c]	14	(USD/Ton)
Citric acid[d]	0.55	(USD/lb)
Ethanol[e]	0.8	(USD/kg)
p-Cymene[e]	7	(USD/kg)
Hydrogen[f]	0.07	(USD/NM3)
Pectin[e]	12	(USD/kg)

[a] Typical prices in Colombia

[b] Estimated cost of Gas to a period range of 2015–2035 [23]

[c] Calculated to a distance of 140 km with a truck of three axles

[d] Taken from ICIS Prices [24]

[e] Taken from Alibaba International prices [25]

[f] Taken from [26]

Table 4 Mass balance of *p*-cymene and pectin production

Stream	Amount	Unit
Orange peel (inlet)	1,000	kg/h
Water (inlet)	100	kg/h
Ethanol (inlet)	5.28	kg/h
Citric acid (inlet)	13.32	kg/h
Air (inlet)	280	kg/h
Hydrogen (outlet)[a]	8.76	NM3/h
p-Cymene (outlet)	9.22	kg/h
Residual water (outlet)	863.3	kg/h
Pectin (outlet)	42.63	kg/h
Electricity (outlet)[b]	99.81	KWh
Gases (outlet)[b]	483.28	kg/h
Residual solids (outlet)[c]	203.32	kg/h

[a] NM3 corresponds to normal m^3 (8.76 NM3/h is equivalent to 0.137 kg/h)

[b] For the scenario 1 (with electricity generation)

[c] For the scenario 2 (without electricity generation)

that obtained for *p*-cymene due to the fact that the process produces one mole of hydrogen per mole of *p*-cymene [18]. Finally, the pectin yield was 0.037 and 0.18 kg of pectin per kg of fresh orange peel and dry orange peel respectively. The yield on dry basis is similar to other obtained with other techniques such as 0.19 with microwave-assisted extraction and 0.18 with a high hydrostatic pressure treatment [28, 29]. These results suggests that orange peel can be used as raw material to obtain D-limonene as an intermediate compound and produce other important products reaching an integrated utilization of orange peel [30].

Economic Analysis

The distribution cost and shares for each economic factor considered in the economic assessment for the plants A and

Table 5 Cost distribution to Plant A (*p*-cymene production)

Item	Scenario 1 (with generation)		Scenario 2 (without generation)	
	Share (%)	Cost/year (1 × 10^3 USD)	Share (%)	Cost/year (1 × 10^3 USD)
Depreciation expense[a]	53.45	230.53	50.81	199.92
Total raw materials cost				
Orange peel	10.91	47.04	11.96	47.04
Citric acid	0.0	0.0	0.0	0.0
Ethanol	0.0	0.0	0.0	0.0
Total utilities cost				
Electricity[b]	0.0	0.0	3.43	13.50
Cooling water	5.76	24.82	6.31	24.82
Steam (low and medium pressure)	0.27	1.15	0.29	1.15
Operating labor cost	6.95	29.98	7.62	29.98
Maintenance cost	6.67	28.75	4.05	15.95
Operating charges	1.74	7.49	1.90	7.50
Plant overhead	6.81	29.36	5.84	22.96
G and A cost	7.46	32.16	7.78	30.62
Total project cost	100	431.29	100	393.46

[a] Calculated with the straight-line method

[b] The cost is zero due to all electricity requirements are cover by the electricity generated

Table 6 Cost distribution to Plant B (pectin production)

Item	Scenario 1 (with generation)		Scenario 2 (without generation)	
	Share (%)	Cost/year (1 × 10^3 USD)	Share (%)	Cost/year (1 × 10^3 USD)
Depreciation expense[a]	26.47	461.06	24.00	399.84
Total raw materials cost				
Orange peel	1.03	17.92	1.08	17.92
Citric acid	4.89	85.24	5.12	85.24
Ethanol	1.94	33.79	2.03	33.79
Total utilities cost				
Electricity	0.0	0.0	1.62	27.01
Cooling water	37.87	659.62	39.59	659.62
Steam (low and medium pressure)	13.14	228.82	13.73	228.82
Operating labor cost	3.44	59.96	3.60	59.96
Maintenance cost	3.30	57.50	1.91	31.90
Operating charges	0.86	14.99	0.90	14.99
Plant overhead	3.37	58.73	2.76	45.93
G and A cost	3.69	64.31	3.68	61.24
Total project cost	100	1,741.97	100	1,666.30

[a] Calculated with the straight-line method

[b] The cost is zero due to all electricity requirements are cover by the electricity generated

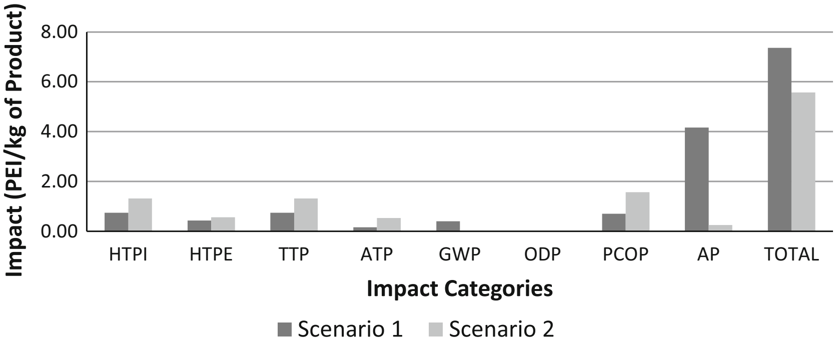
B in both scenarios are shown in Tables 5 and 6 respectively. The cost associated with the electricity generation was distributed between plants A and B in the scenario 1 (with electricity generation) according to the requirements of each plant.

The potential saving obtained (scenario 2 respect to scenario 1) for plants A and B was 8.77 and 4.34 % respectively. For the two plants, the scenario 2 (without electricity generation) showed the lowest costs despite of the 99.81 kWh generated in scenario 1 (0.55 kWh/kg of

Table 7 Production cost and profit margin to *p*-cymene and pectin

Product	Cost	Production cost (USD/Kg)		Profit margin (%)	
		Scenario 1	Scenario 2	Scenario 1	Scenario 2
p-Cymene	USD/kg	5.67	5.27	19.00	24.71
Pectin	USD/kg	3.76	3.53	68.66	70.58

Fig. 2 PEI leaving from the system



residual biomass gasified), which covers all requirements (67.55 kWh) in the integrated process. This happens because the gasification plant increases the capital cost associated with the integrated process for scenario 1.

This electricity generation is in agreement with other electricity production from gasification processes of biomass such as gasification processes in Africa using eucalyptus branches with a consumption of 0.84 kg/KWh (1.19 kWh/kg of biomass). Besides, this electricity generation is similar to that obtained with commercial gasifiers which produces 0.75 kWh/kg of biomass [31, 32].

In scenario 1, the remaining electricity is sold at the same price taken in the process (0.1 USD/KWh) and it was taken into account as credits in the same scenario for both plants. In the same way, the hydrogen produced was taken as credits in the *p*-cymene production cost [18]. The production cost and profit margins to *p*-cymene and pectin production in each scenario are showed in Table 7.

From these results, the pectin production has the highest profit margin; this indicates that the pectin should be integrated as a value added product in the orange peel utilization [6, 13]. To give an idea of the total profit margin of the complete integrated process (taken all products, *p*-cymene, hydrogen and pectin), the sale price to production cost ratio was calculated. This ratio is calculated as a sum of the sale prices divided for the sum of the production costs [33] obtaining 2.01 and 2.16 for scenarios 1 and 2 respectively. These values are higher than 1; therefore it suggests that the production of *p*-cymene, hydrogen and pectin is feasible in an integrated process using orange peel as raw material.

Finally, the internal rate of return is calculated to a period of 10 years from the cash flow of the project, obtaining 2 and 5 % for scenarios 1 and 2 respectively. This is in agreement with the results obtained for each plant and for the complete integrated process where the scenario 2 (without electricity generation) is more profitable. According to these results, the electricity produced in scenario 1 not compensates the additional capital cost of the units involved in the electricity generation, for this reason scenario 1 has the highest production cost in comparison with the scenario 2.

Environmental Analysis

The PEI was calculated to the complete integrated process and was calculated per kg of products (*p*-cymene, hydrogen and pectin) for the scenarios considered. In scenario 1 (with electricity generation) the residual water and gases were considered as wastes while for the scenario 2 (without electricity generation) the residual water and the remaining solids from hydrolysis process were considered as wastes. Figure 2 shows the leaving environmental impact for scenarios 1 and 2.

The total PEI is highest for scenario 1 because the leaving gases from gasification unit have 25 and 19 % of carbon dioxide and carbon monoxide respectively. Therefore, the AP is affected strongly in scenario 1 due to the composition of the leaving gases. On the other hand, the environmental categories HTPI, TTP and PCOP are the most affected in scenario 2 because the solid residues obtained after pectin extraction. This stream contains ethanol, citric acid, fiber (cellulose, hemicellulose and lignin), ash and the pectin that could not be recovered in the hydrolysis process. Thus, from an environmental point of view, the most appropriate scheme of production corresponds to scenario 2 (without electricity generation).

Finally according to both, techno-economic and environmental assessments, scenario 2 (without electricity generation) is the most appropriate and attractive scheme for the integrated process because this scenario permits the lowest production costs and it is more environmentally friendly. However, the PEI can be decreased if the concentrations of compounds such as ethanol, citric acid and pectin obtained in the leaving streams can be reduced or if an improvement of the purity in the products can be reached obtaining at the same time a high sale price for the products.

Conclusions

It is possible to increase the value added of essential oils from orange peel obtaining *p*-cymene and hydrogen in the same route of production. Besides, orange peel can be used as a cheaper and available feedstock for the production of D-limonene as an intermediate compound for the production of *p*-cymene and hydrogen.

The pectin production is an interesting and attractive compound, which should be integrated in the orange peel utilization. This fact permits to increase the profit margins and obtain a major profitability of the process.

The electricity generation is not suggested in an integrated process from an economic point of view because the electricity generated not compensates the additional capital cost despite that the electricity generated can cover all requirements in the process.

Environmental assessment suggests that electricity generation is not convenient due to the contamination from gases leaving from the process. However, it is necessary to improve the quality of the products to decrease the production cost or to decrease the contamination level of the leaving streams.

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