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Study of Fast Pyrolysis Product Distribution of Commercial Pectin

Proyecto de Investigación

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Ingeniería Química

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DE TRABAJO DE TITULACIÓN**

Study of Fast Pyrolysis Product Distribution of Commercial Pectin

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Resumen

En este estudio se investigó experimentalmente la pirólisis rápida de pectina comercial por medio un reactor tubular de caída libre. La pectina fue caracterizada para obtener la composición y propiedades químicas y físicas. Los experimentos de pirólisis fueron realizados entre temperaturas de 600 a 800°C. La distribución de los productos fue obtenida por medio del balance de masa, los productos gaseosos se analizaron con un cromatógrafo de gases Thermo Fisher Scientific TRACE 1310, mientras que los sólidos fueron analizados con un espectrómetro FT-IR y con un microscopio LEICA. La caracterización determinó el grado de esterificación de la pectina comercial en 86.30%, La distribución de los productos de la pirólisis de las diferentes pectinas, presenta rendimientos entre 45 a 60 % de bio-oil, 4 a 15 % de bio-char, y 9 a 37 % de gases. El análisis con FT-IR de los sólidos presentó cambios en la composición química después de realizar los experimentos de pirólisis, reduciendo grupos de alcoholes, ésteres, éteres y los grupos con enlaces glicosídicos; por el contrario, mostró un incremento de los grupos carboxilatos en el bio-char obtenido. El análisis microscópico mostró un incremento en el tamaño de partícula después de realizar los experimentos de pirólisis que probablemente se debe a la aglomeración de sólidos y a presencia de azúcares.

Palabras claves: Pirólisis, pectina, grado de esterificación.

Abstract

In this study the fast pyrolysis of commercial pectin has been experimentally analyzed in a free fall tubular reactor. The pectin was characterized to find their chemical and physical composition and properties. Pyrolysis experiments were performed between 600 – 800°C. The products distribution was obtained from the mass balance, gaseous products were analyzed with a Thermo Fisher Scientific TRACE 1310 GC, and solids were analyzed using a FTIR spectrometer and a LEICA microscope. The characterization analyses defined ash, moisture, fat and anhydro galacturonic content. Additionally, the esterification degree was obtained with 86.30% The product distribution of the pyrolysis products of the different pectins present yields ranging between 40-60% of bio-oil, 4-15% of bio-char, and 9 to 37% of gas. FT-IR used for the solids' analysis presented chemical composition changes after pyrolysis by reducing alcohol, ester, ether and glycosidic functional groups, while carboxylate groups in the bio-char were increased. Microscopy analysis showed an increase on the particle size after the pyrolysis which can be due to agglomeration of the particles and sugar presence.

Key words: Fast pyrolysis, pectin, esterification degree

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1. Introduction

Nowadays, human progress activities require the development of new renewable products due to the increasing energy, fuels and chemicals consumption (Aburto, Moran, Galano, & Torres, 2015). Organic residues can be considered as abundant resources that allow the extraction of bio-based chemicals. These can be used as an alternative to the dependency on non-renewable fossil fuels (Wild, Reith, & Heeres, 2011). This is part of the circular economy concept which looks for valuable products that use waste materials to minimize the contamination produced from human activities (Morgano, 2018). The use of residual biomass as an industrial feedstock provides a reduction of the environmental impact by applying a sustainable method to obtain current demand commodities (Donate, & Oroian, 2014). However, biomass is not used in its complete potential due to the complexity in managing and transforming such heterogeneous material streams. For that reason, new technologies are being developed to find a complete economical valorization of residual organic material. Thermochemical procedures can represent an important technology for giving a solution to this difficult challenge (Wild, Reith, & Heeres, 2011).

Thermochemical conversion represents a promising technology for obtaining high valuable products as biofuels and green chemicals, using organic waste as the raw material (Canabarro et al., 2013). Processes as combustion, gasification and pyrolysis are some of the alternative procedures for obtaining bioenergy (Tanger et al., 2013). Some of the main differences between these thermochemical techniques are energy balance and efficiency, main products distribution, scale and cost. Combustion is a method in which the raw material reacts with oxygen at high temperatures obtaining heat and combustion gases as products. The heat can be energetically used by steam production as an alternative resource for electricity production (Kaa, Kamp, Rezaei 2017). On the other hand, gasification is a conversion method which uses high temperatures and partial oxidation reactions to produce gas (Canabarro et al., 2013). The

main product of this procedure is a gas mixture that is generally used as direct or intermediate fuels, and chemical precursor (Herng, 2019). Finally, pyrolysis is a complex process that consists on the conversion of organic matter through heating without the presence of oxygen to form solid, liquid and gaseous products. These substances obtained by pyrolysis can be used as biofuels, chemicals, charcoal and even for electricity production (Sharma, Pareek, & Zhang, 2016).

In general terms, pyrolysis is a thermal process that occurs in the absence of oxygen. It can be classified into conventional, fast, and flash pyrolysis. Each of them is performed at different operating conditions, obtaining a variety of final products (Demirbas, & Arin, 2002). At longer residence times and lower temperatures, charcoal production is favorable. While at longer residence times and higher temperature more gaseous products are obtained. Additionally, at a moderate temperature with a short residence time a higher percentage of liquid products are found (Bridgwater, 2012). For fast pyrolysis, a conversion of up to 75% of bio-oil can be obtained with 13% of gas, and 12% charcoal at a moderate to high temperatures and short residence times (Tumuluru, Sokhansanj, Hess, Wright, & Boardman 2011). Therefore, by applying fast pyrolysis to biomass, fuels or organic substances can be obtained.

Pectin is obtained from plants cell wall of different fruit peels (Fellah, Anjukandi, Waterland, & Williams, (2009). It is a heterogeneous polysaccharide composed of homogalacturonan, rhamnogalacturonan I and rhamnogalacturonan II, mainly formed of D-galacturonic acid with α -(1-4) glycosidic linkages from the homopolymer (Dranca, & Oroian, 2018). Pectin structural and macromolecular properties vary depending on the type of fruit from which it has been extracted. The galacturonic acid content, neutral sugar, galacturonan methoxylation and molecular weight may vary within a broad range of values. Pectin are classified as high or low methoxy content (Donald, 2001). Most of the carboxyl groups in pectin chain are presented as

methoxy groups that have been esterified with methanol (Lanza, 2003). In Figure 1 a typical pectin chain with a methoxy content of 60% is presented.

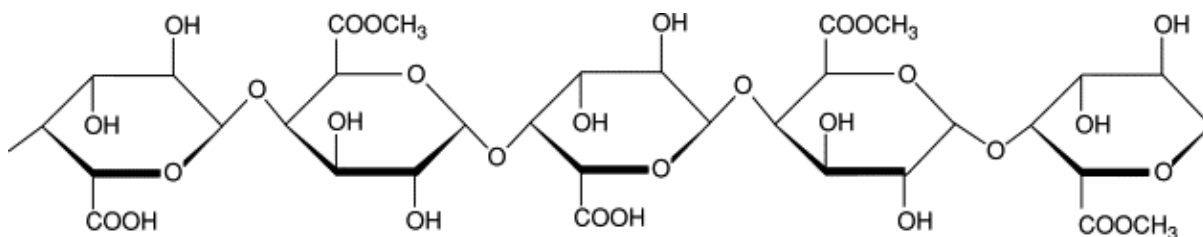


Figure 1. Acid galacturonic acid (Pectin chain) with some methoxy groups (Flutto, 2003)

Pectins are commonly used in the food industry and for commercial application as emulsifier, stabilizer, thickener and gelling agent (Tiwari et al., 2017). The importance of their investigation relies on the huge amount of citrus fruit waste with contents near 40% of pectin that can be used as classified biomass for pyrolysis experiments (Aburto, Moran, Galano, & Torres, 2015). The state of the art of the possible products obtained from pyrolysis of pectin is limited due to few articles published (Aburto, Moran, Galano, & Torres, 2015).

In this study the fast pyrolysis of pectin will be investigated. The research has the purpose to identify the thermochemical degradation products of pectin. The pyrolysis setup consists of a temperature controlled free fall reactor. The gas, liquid and solid distribution of pyrolysis of pectin is presented by a mass balance and the products obtained will be analyzed.

2. Materials and Methods

2.1. Materials

For the investigation of the pyrolysis of pectin, commercial pectin in analytical grade from LobaChemie was used. Pectin was characterized according to lipids, galacturonic acid content, esterification degree, ash and moisture content. During the extraction and characterization, the Fisher Scientific 98.5% pure hexane, 40% pure sodium hydroxide and hydrochloric acid with 37% . Gases used for the pyrolysis experiments and for the GC analyses were provided by

Linde Ecuador. Synthetic air (20% of oxygen), UHP Nitrogen and UHP Helium gases, both, grade 5.0 were used. Hydrogen needed by the GC chromatograph is obtained by a H₂ generator that used a solution of sodium hydroxide. Fisher Scientific 99.5.% pure ethyl acetate, 99% methanol, mixture of standard gases Scott Mini-mix and a mixture of methane and carbon dioxide gases were used as standards for the GC chromatograms.

2.2. Pectin characterization methods

The commercial pectin was characterized to determine moisture, ash, fat, and anhydro acid galacturonic content. For fat content 2 g were use, and for the ash and humidity 1 g was applied. All characterization methods were performed in triplicate.

Moisture contents were measured with AOAC official method and ash contents were determined with AOAC 942.05 official method (AOAC, 2012). Fat content was obtained using AOAC 2003.05 and 2003.06 official standards for Randall modified method with VELP Scientifica 148 solvent extractor equipment (AOAC, 2006).

The esterification degree was obtained using titration. For this process, 0.2 g of pectin were weighed, moistened with ethanol and dissolved with 20 mL of distilled water. The mixture was heated at 40°C and stirred until it was dissolved. A few drops of phenolphthalein indicator were added for the two titrations. At the first titration, sodium hydroxide 0.1 N was added until the solution change color to pink, which is the final point. Additionally, 10 mL of sodium hydroxide 0.1 N were added for 2 hours. After this 10 mL of hydrochloric acid 0.1 N were added and the sample was titrated with sodium hydroxide 0.1 N until it presents a pink color change. (Liew, Chin, & Yusof, 2014). Equivalent weight, free acidity, esterification degree (DE), methoxy content (Me) and anhydro galacturonic content (AGA) were obtained with the following equations.

$$\text{Equivalent weight} = \frac{\text{pectin sample weight}}{\text{meqA}} \quad \left[\frac{\text{mg}}{\text{meq}} \right] \quad (1)$$

$$\text{Free acidity} = \frac{\text{meqA}}{\text{pectin sample weight}} \times 100 \quad \left[\frac{\text{meq}}{\text{g}} \right] \quad (2)$$

$$\text{Me} = \frac{\text{meqB} \times 31}{\text{pectin sample weight [mg]}} \times 100 \quad [\%] \quad (3)$$

$$\text{DE} = \frac{\text{meqB}}{\text{meqA} + \text{meqB}} \times 100 \quad [\%] \quad (4)$$

$$\text{AGA} = \frac{176 - (\text{meqA} + \text{meqB})}{\text{sample weight [mg]}} \times 100 \quad [\%] \quad (5)$$

Where meqA is the milliequivalent of sodium hydroxide used for the first titration, meqB is the milliequivalent used for the second titration. The 176 number refers to the molecular weight (mg/meq) of anhydro galacturonic acid and 31 is the molecular weight of methoxy group (Vargas, Jiménez and Ramírez, 2017). All pectin characterizations are presented with its mean and standard deviation.

2.3. Pyrolysis equipment set up

The following pyrolysis system set up was used to pyrolyze the different types of pectins. It consists of a tubular vertical free-fall ceramic reactor with an inner diameter of 25 mm, a length of 750 mm and a volume of 368 mL. The reactor is heated in the inside with a Carbolite Gero Model VST 12/300 tubular heating jacket of 450 mm length with a temperature controller model Eurotherm 3508, which can reach temperatures up to 1200°C. Stainless steel 1/4" tubing is used to transport gases and products to the separation system. The separation system

consists of a cyclone for solid product separation, a trap for condensable liquids separation, and the gaseous products which are separated into a stainless steel tube of 1/8" into the Thermo Fisher Scientific Trace 1310 gas chromatograph and a purge.

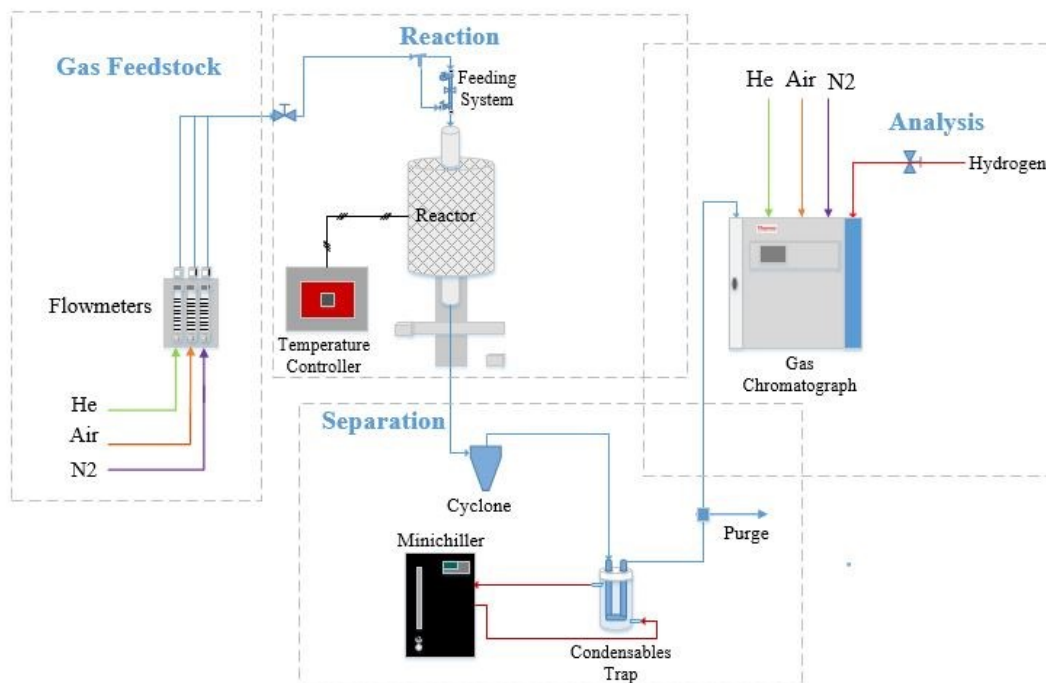


Figure 2. Scheme of pyrolysis system

The solid and inert gas feeding systems are made of Pyrex glass material which contains 3 Teflon ball valves to alternate between purging and feeding (Fig. 3a). The cyclone shown in Figure 3b is used to collect the solids after pyrolysis, and the trap in Figure 3c is used to collect the condensable liquids. The trap condenses the gases with the help of a minichiller set at -10 °C. The gaseous non-condensable products are separated into two gas streams, one is routed to the GC (Thermo Fisher Scientific Trace 1310) and the other is purged out of the system.

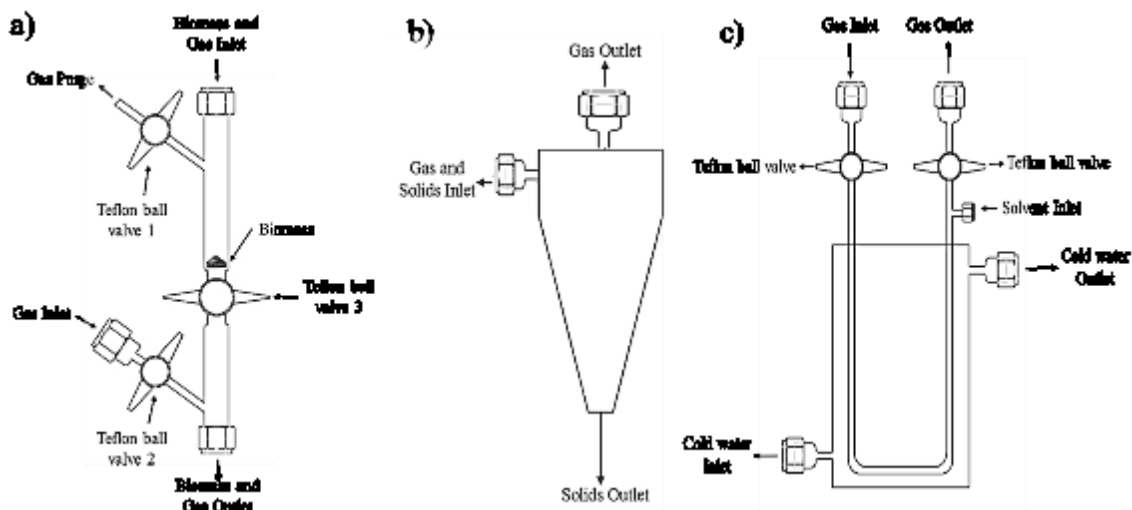


Figure 3. a) Feeding system, b) cyclone for solid products, and c) trap for liquids

2.4. Experimental design

The samples used for the pyrolysis were pure analytical grade pectin. For each pyrolysis, used $120 \text{ mg} \pm 0.5 \text{ mg}$ of pectin samples. Helium is the carrier and inert gas used with a flow rate of 2 L/min allowing the transportation of the feeding material and products through the system. The residence time of pyrolysis experiments was 0.15 s in the reaction zone at a temperature range between 600°C - 800°C with steps of 50°C . The solid product, biochar, was analyzed with FT-IR and microscope. The liquids were collected in the trap and only 0.3 gaseous fractions products were captured by the Thermo Scientific chromatograph GC-FID/TCD, while the rest is purged.

A mass balance presented in equation 6 has been calculated to obtain solids, liquids and gaseous fractions and yields.

$$\text{Accumulation} = \text{Input (Pectin fed)} - \text{Output (products)} \quad (6)$$

The mass balance was calculated with the weight difference of each element of the system before and after the reactor. The real mass into the reactor was estimated considering the weight difference of the feeding system before and after the experiments. The masses of solid and

liquids products were obtained from the cyclone and trap weight difference, respectively. Additionally, the mass loss is obtained from the weight difference of the additional parts from the system that are listed as: metal cylinders, packing rings and top cap. The accumulation from equation 6 is assumed to be zero, so the gaseous products mass was obtained from the difference between the real fed of pectin input and output are obtained from the sum of solids, liquids and losses. Mass yield of each product, $Y_{product}$, is calculated using equation 7.

$$Y_{product} = \frac{\text{mass of product}}{\text{real fed mass}} \times 100 \quad [\%] \quad (7)$$

The percentage of the mass losses is obtained from the sum of mass accumulation in the individual parts, as it is shown in the next equation.

$$\text{Mass losses} = \frac{\sum \text{mass lost from additional parts}}{\text{real fed mass}} \times 100 \quad [\%] \quad (8)$$

The gaseous products yield was calculated from the difference between the sum of the liquids, solids and losses percentage due to the dilution produced with the inert carrier gas.

2.5. Analytical methods

The gas chromatograph (Thermo Fisher Scientific TRACE 1310 GC) was used to analyze gas products. The equipment contains a 100% divinyl benzene phase nonpolar TG Bond QS column (Dimensions: 15 m x 0.53 mm x 20 μm). A Thermal Conductivity Detector (TCD) and a Flame Ionization Detector (FID) were used. For the experiments the conditions were 80°C as the inlet temperature, 200°C for both detectors, 200°C for the oven heated at a rate of 10 °C/min after been at 30°C the first 5 minutes. The column flow rate was set with a 2.1 mL/min and a 5 mL/min split flow.

The solid products were analyzed by a Cary 630 FTIR Spectrometer (Agilent Technologies) and a LEICA microscope. The microscope has the function of defining the particle size.

The Fourier Transform Infrared Spectroscopy (FTIR) analysis was used to determine the functional groups of feeding material and pyrolyzed products. It is also used to obtain the esterification degree taking into account peak areas from wavelength at 1639.4 cm^{-1} and 1747 cm^{-1} using the following equation (Sato et al., 2011).

$$Y_{Product} = \frac{A_{1747}}{A_{1747} + A_{1639}} \times 100 \quad [\%] \quad (9)$$

Where A_{1747} is the area of the peak at 1747 cm^{-1} wavelength, and A_{1639} is the area at 1639 cm^{-1} peak wavelength. These areas correspond to COO-asymmetric stretching of carboxylate groups and C=O esterified or ester functional groups.

3. Experimental Results and Discussion

3.1. Pectin Characterization

Commercial pectin was characterized to obtain their ash, water, fat, and anhydro galacturonic acid content as it is shown in table 1.

Table 1. Percentage of ash, water, fat, and anhydro galacturonic acid content

Characteristic	Content [%]
Fat	0.08 ± 0.01
Water	8.95 ± 0.15
Ash	1.80 ± 0.03
AAG	87.64 ± 0.35

The sum of all the components from table 1 is not equal to a 100%, the missing percentage corresponds to other carbohydrates or sugars and proteins that was washed out or not analyzed in this study. The pectin inorganic impurities are shown as ash content and, therefore, lower

ashes represent a better pectin quality (Girma & Worku, 2016). However, commercial pectin is below 10% limit of ash content that allows gels formation (Girma & Worku, 2016).

A higher moisture content leads to the growth of microorganisms and the formation of pectinase enzyme that have a negative effect on pectin quality (Igbokwe, Philomena, & Ogochukwu, 2018). For that reason, it is necessary to control moisture content for pectin storage (Igbokwe, Philomena, & Ogochukwu, 2018). However, even protein content was a missing characterization method, it is important to mention that protein content also is responsible of having an influence in the emulsifying property of the pectin (Igbokwe, Philomena, & Ogochukwu, 2018). While the ash content and anhydro galacturonic acid content determine the pectin purity.

Commercial pectin was also characterized to obtain the equivalent weight, free acidity, methoxy degree and esterification degree. The results are presented in table 2.

Table 2. Equivalent weight, free acidity, methoxy content and esterification degree

Characteristic	Value
Equivalent weight [mg/meq]	927.22 ± 25.36
Free acidity [meq/g]	1.08 ± 0.03
Methoxy content [%]	21.10 ± 0.74
Esterification degree [%]	86.30 ± 0.71

Esterification degree can represent an important influence on pectin properties as gelling formation (Igbokwe, Philomena, & Ogochukwu, 2018).

3.2. Pyrolysis of commercial pectin

Pyrolysis experiments of commercial pectin were performed using approximately 120 mg of sample in the feeding system. The reaction temperatures range between 600 to 800°C with 50°C step. Pyrolysis results show the product distribution using the mass balance and the GC analysis of the gaseous products.

3.2.1. Product distribution for commercial pectin pyrolysis

A mass balance was performed to obtain the yields of each product after pyrolysis experiments at 5 different temperatures for commercial pectin were performed.

Table 3. Product distribution of pure pectin at different temperatures

Temperatures	$Y_{Bio-oil}$ [%]	$Y_{Bio-char}$ [%]	Y_{Gases} [%]
600	60.23 ± 1.10	15.16 ± 1.24	9.44 ± 1.23
650	54.19 ± 2.35	11.22 ± 1.19	16.07 ± 0.77
700	50.51 ± 1.84	6.35 ± 1.88	29.62 ± 1.80
750	45.67 ± 2.44	4.92 ± 0.84	31.46 ± 2.10
800	40.60 ± 1.24	4.70 ± 1.08	37.01 ± 1.63

In table 2 the products distribution yield of pyrolysis of commercial pectin at different temperatures can be observed. The yields are obtained through the mass balance. The yields tend to increase or decrease as function of temperature. The bio-oil represents the content that was transformed into liquid. The tendency of its yield decreases from 60 to 40%, while the pyrolysis temperatures increases from 600°C to 800°C. The bio-char content and unreacted pectin has the highest yield value of 15.16% at 600°C with the tendency to decrease at higher temperatures. On the other hand, gas yield increases when temperature was elevated, the trend is the opposite from the other yields' products obtained. In Figure 4 the products yield tendency of the commercial pectin can be observed as function of pyrolysis temperature.

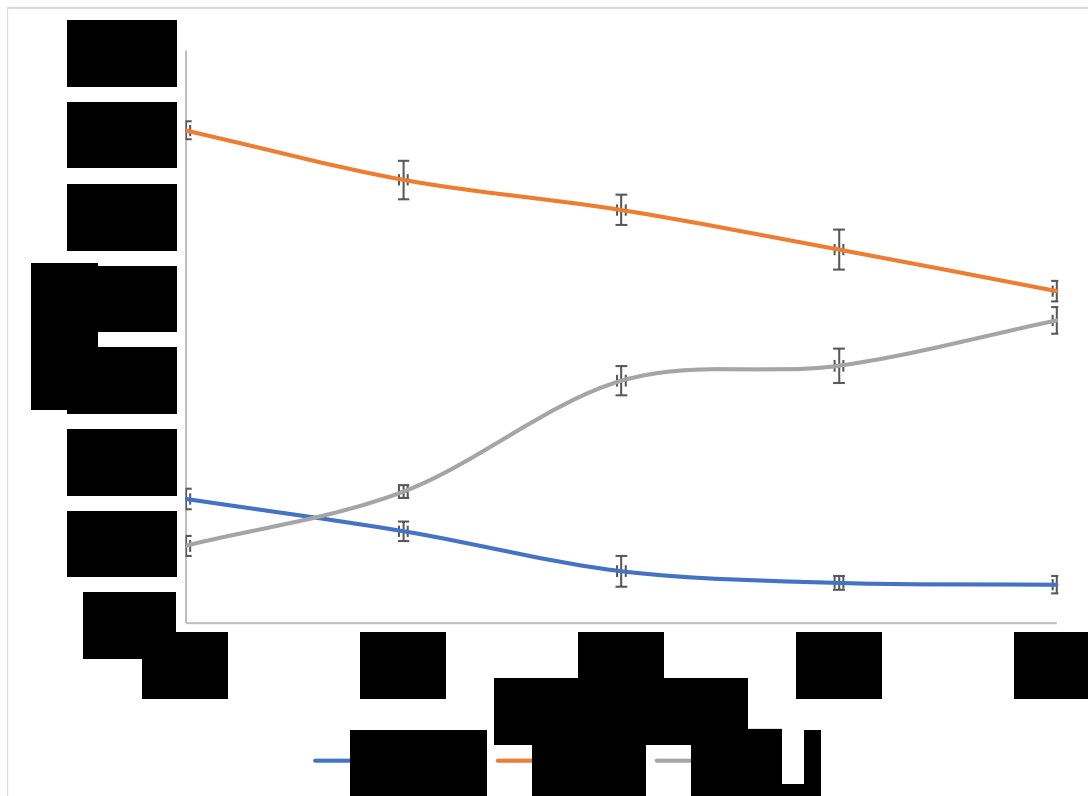


Figure 4. Product yield of pure pectin at different temperatures

As mentioned before, bio-char and bio-oil products tend to decrease while temperature is increasing. The opposite occurs with the gases, showing the highest gaseous yields at 800°C. Therefore, for fast pyrolysis experiments a 600°C is call to be the best temperature condition to obtain liquid products.

3.2.2. Gaseous products obtained of commercial pectin pyrolysis

Gas chromatography with FID/TCD detectors was used to analyze the gaseous products obtained from the pyrolysis of the commercial pectin. The results of pyrolysis experiments performed at different temperatures are presented in Figure 5.

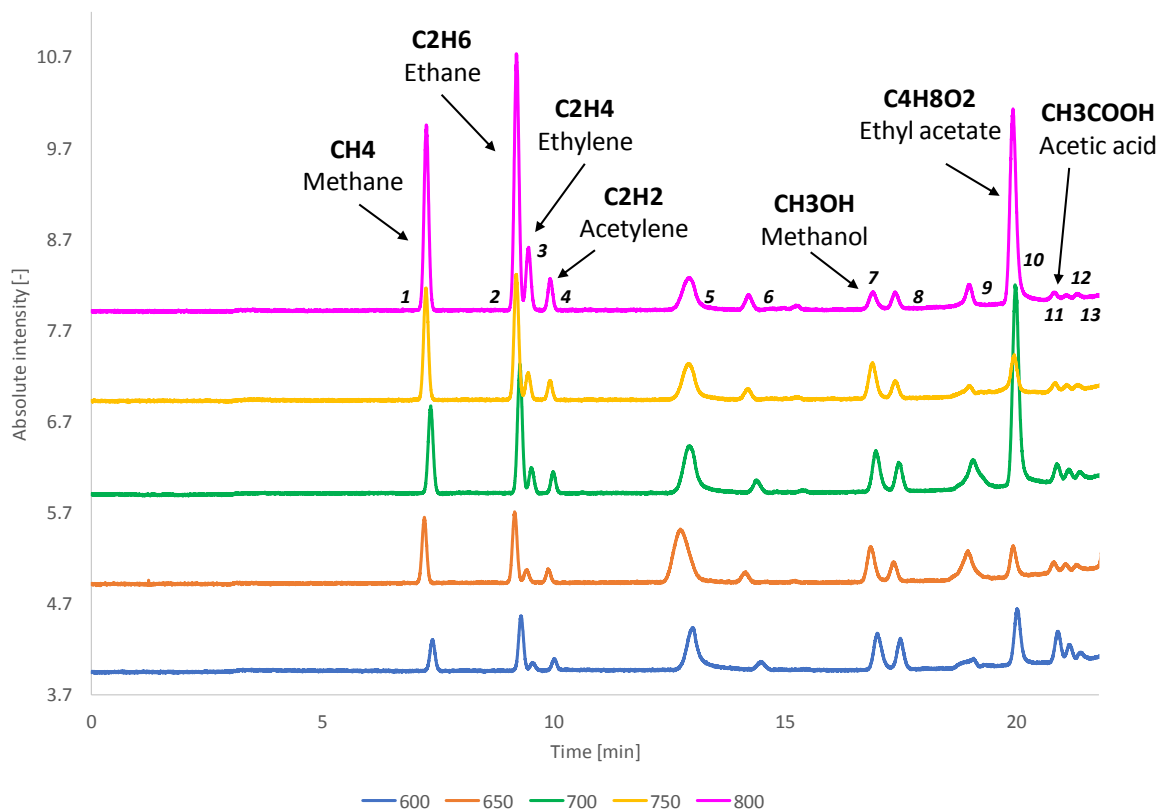


Figure 5. Gases chromatographs with FID detector and product components of commercial pectin at different temperatures

Figure 5 shows the chromatograms of the gaseous products obtained after performing the pyrolysis experiments at different temperature. The peaks tend to increase with temperature, which is in accordance with the increasing gas yield at higher temperatures. The higher gas fraction indicated the increase in the rate of the pyrolysis reactions.

The gaseous products of pyrolysis presented in Figure 5 were identified with standard liquids and gases as it is shown in figure 6.

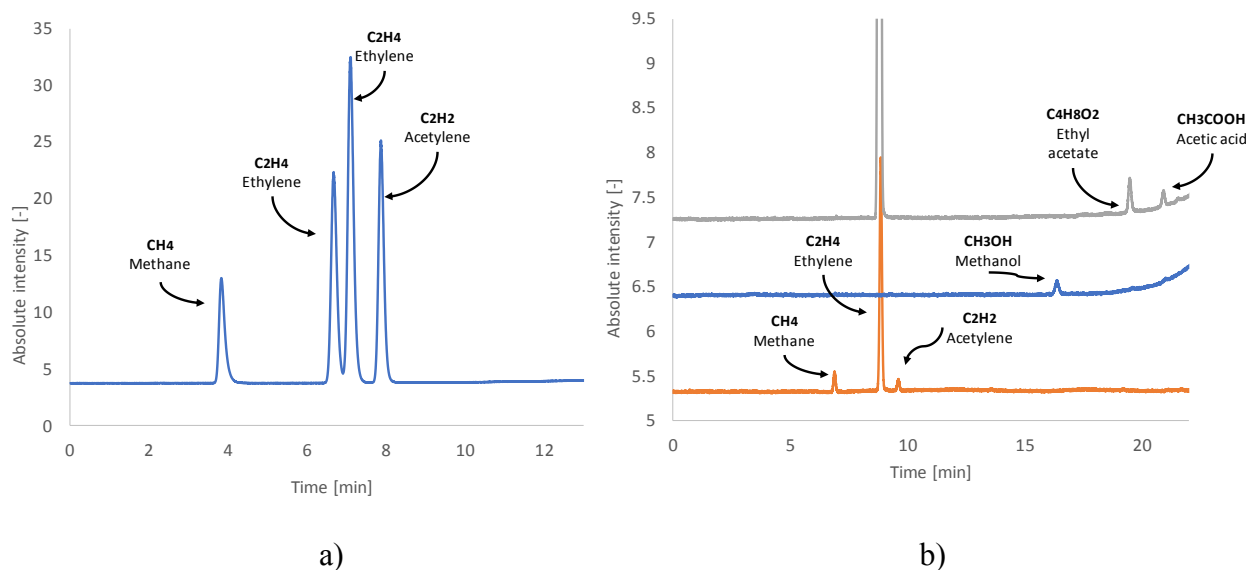


Figure 6. Chromatograms of standard gases a) for the standard mixture of gases b) standard liquids and gases

In figure 6 a standard gas mixture of methane, ethane, ethylene and acetylene are presented. These peaks can also be found in the gaseous products of biomass pyrolysis (Wijayanto & Ranoue, 2013). In figure 5, the time displacement is produced because the gases from pyrolysis pass through all the system before it gets to the GC, while the standards were injected directly to prevent them from being diluted by the helium used in the pyrolysis system. The standard gases were injected directly to the GC to observe the order of gases obtained by pyrolysis, the difference with the standard gases in Figure 5b is related with the valve time that has as a result the displaced the time in which gases appears in the chromatogram, but not its order.

With methanol, ethyl acetate, and acetic acid, some of the last peaks presented on the pectin chromatograms can be identified. Methanol is found approximately at minute 16.86, while ethyl acetate and acetic acid are shown at minutes 19.95 and 20.89, respectively.

Areas integration from the chromatograms using the FID detector were performed to observe the ratio of the different peak areas for all experiments at different temperatures of commercial pectin analyzed with respect the first peak of methane. This is presented next in table 4.

Table 4. Relative ratio with respect to the first peak area

	Fraction [-]												
Peak	1	2	3	4	5	6	7	8	9	10	11	12	13
Compound	CH ₄	C ₂ H ₆	C ₂ H ₄	C ₂ H ₂	-	-	CH ₃ OH	-	-	C ₄ H ₈ O ₂	-	CH ₃ COOH	-
Time	7.24	9.19	9.47	9.92	12.93	14.23	16.91	17.36	18.95	19.92	20.78	21.06	21.30
600°C	1.00	1.76	0.19	0.33	3.26	0.40	1.79	1.26	0.58	2.46	0.95	0.37	0.18
650°C	1.00	1.06	0.14	0.18	2.62	0.21	0.80	0.36	1.06	0.62	0.15	0.08	0.06
700°C	1.00	1.32	0.21	0.22	1.37	0.21	0.65	0.42	0.85	3.09	0.18	0.09	0.07
750°C	1.00	1.09	0.20	0.16	0.82	0.13	0.49	0.19	0.13	0.52	0.08	0.03	0.04
800°C	1.00	1.32	0.28	0.16	0.50	0.12	0.15	0.12	0.17	1.44	0.03	0.02	0.02

As it is observed in table 4, most of the area ratio of the peaks from 5 to 13, are decreasing while experiment temperature is increasing. While the ratio of the peaks from 2 to 4 tend to be more abundant when the temperature is increasing. It was observed from Figure 5 that methane area is bigger while the temperature increases. Taking that first peak as the reference, we can observe that at higher pyrolysis experiment temperatures, more methane, ethane, ethylene and acetylene gases are produced, while the gaseous products presented after the acetylene peak are reduced with temperature due to the bond breakage that will form the first gases. Aburto, Moran, Galano and Torres study mentioned that at temperatures higher than 600°C the rate limiting reaction step is dependent only in the temperature and heating rate (2015). This can be related with the Figure 5, where all the gaseous components are the same, but the areas from heavy gaseous components, from peak 5 in table 4, will reduced while the temperature is increasing.

3.2.3. Solid product analysis

The biochar samples obtained from the pyrolysis process have been analyzed by FT-IR analysis and with microscope imagines. FT-IR was performed to identify the different organic functional groups and changes in the esterification degree of pectins before and after the pyrolysis experiments.

Pectins were analyzed with FT-IR before and after the pyrolysis experiments. In Figure 7, the FT-IR analysis of commercial pectin and the biochar obtained at 600 to 800°C is presented.

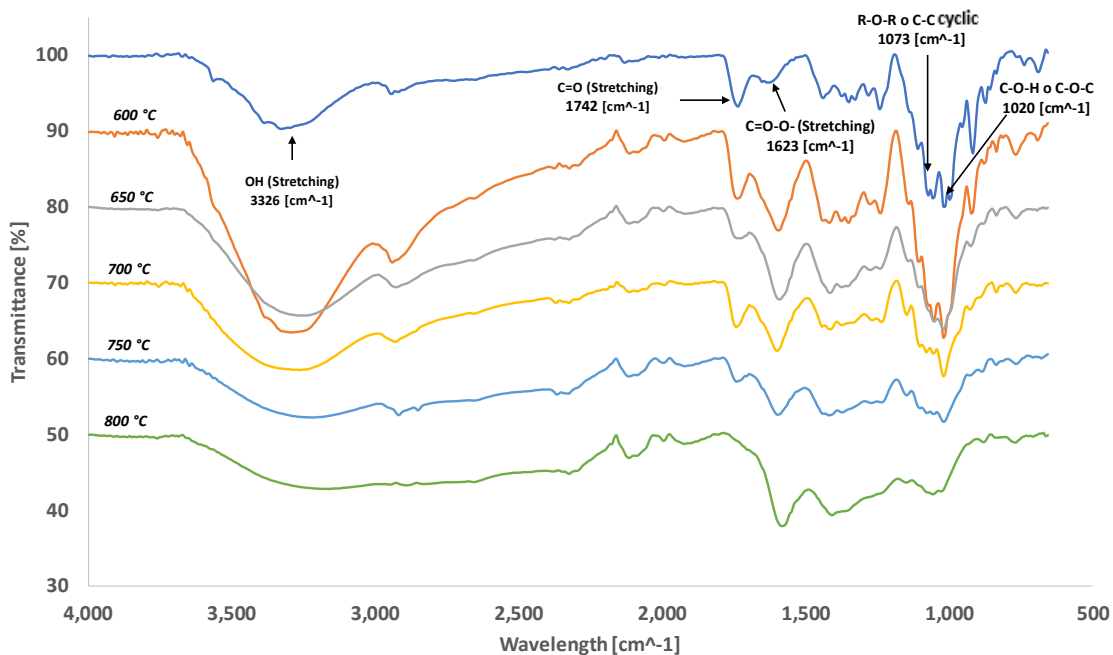


Figure 7. FT-IR spectra for commercial pectin and pyrolyzed pectin from 600°C to 800°C

Figure 7 presents the different spectra obtained before and after pyrolysis at different temperatures. Some of the common groups presented at the commercial pectin analyzed are alcohol (OH stretching) at the band 3326 cm^{-1} , esterified carboxyl (C=O, stretching) which is the ester groups of the pectin is at 1742 cm^{-1} , cyclic C-C bonds and ether (C-C, RCR) at 1073 cm^{-1} , 1020 cm^{-1} band correspond to C-OH groups and glycosidic bonds (C-O-C) and 1623 cm^{-1} band is from carboxylate. It is shown in Figure 7 that some functional are reduced groups are reduced as the esterified carboxyl, the cyclic C-C or ethers and the glycosidic bonds. Also, the alcohol functional groups are reduced, except from 600°C pyrolyzed char. However, the carboxylate groups presented in the band 1623 cm^{-1} are increasing, corresponding to a bond breakage of the esters groups. FT-IR spectroscopy is a reliable method for routine analysis of the degree of methylesterification of pectin in different fruit- and vegetable-based matrices. From this analysis, is expected that the esterification degree decreases while the temperature is higher, related with the less ester groups presented in the solid product.

Using FT-IR spectra it is possible to obtain the esterification degrees of pectin using a corrected peak area as it is shown in equation 9. Comparing the results of the analytical esterification degree with the estimation from the FT-IR, spectra the values are not the same.

Table 5. Esterification degree of commercial pectin before and after pyrolysis experiments using FT-IR method

Sample	FT-IR esterification degree [%]
Commercial pectin	71.63
600°C pyrolyzed pectin	27.05
650°C pyrolyzed pectin	15.13
700°C pyrolyzed pectin	14.29
750°C pyrolyzed pectin	12.71
800°C pyrolyzed pectin	-

In table 5 are presented the esterification degree obtained for the samples. The esterification degree obtained through the analytical method with 86.30 %, is not the same from the one of the FT-IR with 71.43 %. One possible reason is the integration areas were manually selected. However, it is possible to observed that while the temperature is increasing the char contains a less esterification degree. The 800°C pyrolyzed char was not calculated because the peak of ester functional group disappeared from the FT-IR spectra. The possible situation, as it was mentioned before, the ester bonds from the pectin are breaking and the sample have more carboxylates in their structure.

3.2.4. Solid particle image and size analysis

The commercial pectin used for different temperature pyrolysis analysis and the bio-char obtained were analyzed with a Leica microscope D500 to define the particle size differences. The following figures show the images 4x and 10x magnification. Figure 8 show the images for commercial pectin before and after pyrolysis experiments.

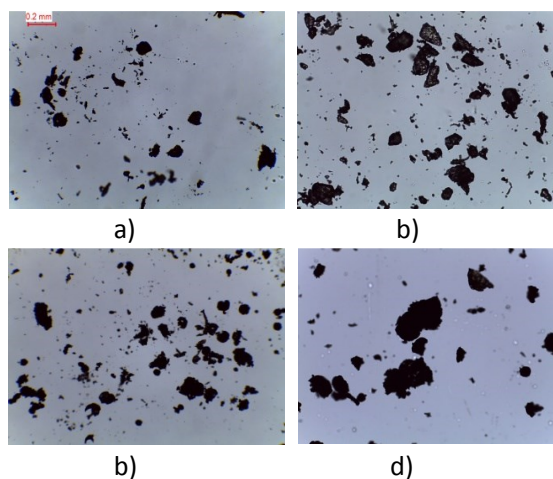


Figure 8. Microscopy images for commercial pectin at a) 4x, b) 10x, and for pyrolyzed commercial pectin c) 4x and d) 10x

In Figure 8 an increase of approximately a 50 % in the size of the particles after pyrolysis experiments can be observed. One of the reasons is the formation of different sugars when pectin structural bonds broke due to the heat reaction involved. Extracted fruits peels pectins contain carbohydrates and hexose sugar (Tyagi, Sharma, & Malviya, 2015). The other possible explanation is the increase of moisture content in the pyrolyzed pectin.

4. Conclusions

In this study the fast pyrolysis of commercial pectin has been investigated. Commercial pectin was characterized to find their composition and structural properties. Pectin presented small values for ash and fat content. While moisture and anhydro acid galacturonic content were the predominant composition elements. The pyrolysis experiments were performed in a free fall tubular reactor with a feeding and a products separation and collection system. The three main products are: bio-char, bio-oil and gases. The product distribution results were made from the mass balance. The different products distribution for each temperature used defined that the bio-oil obtained is dependent on the temperature of the pyrolysis experiments. The highest bio-oil content obtained is 60.23% from the 600°C experiment performed.

GC-FID chromatograph was used to analyze the gaseous products. The pyrolysis experiments performed presented that at different temperatures, methane, ethane, ethylene and acetylene

gaseous products increase, while the other products obtained decreases while temperature is higher.

Finally, bio-char obtained from pyrolysis was analyzed with FT-IR and Leica microscope. FT-IR shows a reduction in the peaks' areas of the spectra of the pyrolyzed pectin due to reduction of alcohol, ester, ether and glycosidic functional groups. It also presented that carboxylate groups increases in function of the temperature elevation. Microscope images present a morphological increase in the structure after pyrolysis, probably due to accumulation of particles and sugar presence.

The next steps in this study consist of the identification of the missing compounds in the analysis of the gases, also the chemical composition of bio-oils, and the analysis of the products obtained with different esterification degree pectins.

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