

PYROLYSIS OF ORANGE PEEL: LIQUID PRODUCTS CHARACTERIZATION

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Abstract. Brazil is the main country processor of orange juice in the world, with 261,9 millions of box (1 box equaling 41 kg of fruit) 53,7 % in the world production. Since only about half of the fruit is juice, the remainder results in an abundant supply of "waste" material. In this work, there was a tentative of obtain and characterized pyrolysis liquids from orange peel. By this, pyrolysis of orange peel has been studied in a laboratory scale reactor. Three different temperatures and two different granulometries have been tested in order to assess their influence on product distribution and tar organic components. The products obtained from pyrolysis were gas, liquid fraction and char. The large amount of tar definitions and measurement methods, as well as the wide spectrum of organic compounds, makes it almost impossible to capture "tars" with a clear definition. Around 70 compounds have been detected in the liquid fraction obtained, most of them being present in very low percentages. In order to facilitate the study of the evolution of the liquid fraction composition with the temperature, the compounds detected have been grouped according to their chemical nature, but differently from other works, it was extended the range of compounds in order to better compare the influence of the reactor parameters in liquid fraction compositions. It can be observed that oxygenated compounds are the most significant group in all the temperature ranges, reaching about 80% of the liquid fraction produced in the 300-450 °C temperature range. An analysis of the results shows that under the operating temperature conditions studied (300-600 °C), the temperature has a greatest influence on the pyrolysis process. Gas and char are the main products of the process under all the conditions studied. There was not an optimum temperature for obtaining tar in the operating temperature conditions studied.

Keywords: Orange peel, tar characterization, pyrolysis

1. INTRODUCTION

Brazil is the main country processor of orange juice in the world, with 261,9 millions of box (1 box equaling 41 kg of fruit) 53,7 % in the world production (Gonçalves, 1996).

Since only about half of the fruit is juice, the remainder results in an abundant supply of "waste" material. The primary citrus by-products are cattle feed, essential oils and essences, d-limonene, pulp and pulpwash. There are other compounds of potential value present in small amounts such as naringin and hesperidin. Citrus by-product technology was driven by the concurrent need for disposing of processing waste as well as obtaining all possible value from the fruit. The peel of the citrus fruit has numerous glands that contain oil that is typically recovered as a major by-product. Each type of citrus fruit has its own characteristic set of compounds that comprise the oil and that are responsible for its flavor and aroma. In the Pinar del Río Province in central Cuba, a biomass residue of orange and grapefruit peel is generated by the juice production industry, processing annually about 150,000 tons of citrus fruits (orange and grapefruit), producing about 45,000 tons of peel residue (12,000 tons of dry solid). This residue is landfilled, causing an

unpleasant smell in the nearby city and wasting a potential source of renewable energy (Aguiar et al. 2006). This waste could be transformed into a valuable fuel, gas or liquid, by means of a pyrolysis process.

Because the decrease of the prize of the solid waste product, today several plants had been trying its energy utilization, by direct combustion or gasification. As orange peel is a form of biomass not commonly contemplated as a pyrolysis or gasification feedstock, there is few data available. There were previous experiments reported by Aguilar et al., 2006, relating to its behavior during gasification.

In pilot plants bio-oil typical yields are in the range of 60% to 65% wt (dry basis) and residual gas and char are used as an additional energy source in the process (Olivares-Gómez, 2002).

The liquids collection has long been a major difficulty for researchers. The capture of the pyrolysis vapors by almost all collection devices is very inefficient. The product vapors can be a combination of gas, micron sized droplets and polar molecules bonded with water vapor. The aerosols after cooling, need to be impinged onto a surface to be collected, and the most effective collector are the electrostatic precipitator (Bridgewater, 1999).

Tsai et al. (2006) used fast pyrolysis for producing valuable products from various biomasses. These products were characterized by gas chromatography/mass spectrometry and chemical characterization (CHNO). In view of the results presented, it can be seen that, as expected, the chemical compositions of pyrolysis bio-oils are very similar with aromatics and oxygenated compounds such as carboxylic acids, phenols, ketones, etc. It was noted that the pyrolysis liquid product contains a significant amount of water and fewer contents of complex compounds (aromatic and carbonyl structures), resulting in low pH and low heating values. The results therefore indicate that a large quantity of water evolves within a short time due to the water content of biomass feedstock and dehydration reaction in the fast pyrolysis process. GC-MS analyses have shown that carboxylic acids, phenols, alcohols and branched oxygenated hydrocarbons are the main compounds of the bio-oil. It is necessary that the resultant liquid product would need further processing to remove the condensed water for chemical feedstock and/or biofuel production.

Knowledge of various properties of biomass pyrolysis products is relevant for energy conversion, essential to identifying the utilization of each product. Experimental heating values of pyrolysis products were determined by Raveendran and Ganesh (1996). They concluded that heating values of biomass pyrolysis products are function of the initial composition of the biomass feed. Heating values of biomass pyrolysis liquid were comparable with those of ethanol.

The complex interaction of time and temperature on liquid product quality has not been properly explored, because there is no 'standard' pyrolysis liquid (Bridgewater, 1999).

Tar comprises a wide spectrum of organic components, generally consisting of several aromatic rings. Reported tar concentrations are strongly dependent on the tar definition used and the measurement method applied. The large amount of tar definitions and measurement methods, as well as the wide spectrum of organic compounds, makes it almost impossible to capture "tars" with a clear definition. According to the ECN definition, tar comprises all organic components having a higher molecular weight than to benzene (Bergman et al., 2002).

Ayllón et al. (2006), study meat and bone meal pyrolysis in a fixed bed reactor, analyzing the influence of the final pyrolysis temperature and heating rate on the product (char, liquid fraction and gas) distribution and composition and the char characterization. From the results obtained it is observed that the effect of the final pyrolysis temperature is more important than the effect of the heating rate. The liquid fraction obtained is mainly composed of more than 60% of nitrogenated aliphatic compounds (such as nitriles, amides and cyclic compounds), 15% of aliphatic hydrocarbons (such as alkanes and alkenes), 10% of oxygenated aliphatic compounds (mostly carboxylic acids) and about 8% of oxygenated aromatic compounds (mainly phenolics). Around 120 compounds have been detected in the liquid fraction obtained, most of them being present in very low percentages.

In this work, there was a tentative of obtain and characterize pyrolysis liquids from orange peel. By this, a pyrolysis of orange peel has been studied in a laboratory scale reactor. Three different temperatures and two different granulometries have been tested in order to assess their influence on product distribution and tar organic components.

2. EXPERIMENTAL

The material used in the experiments was orange peel with two particle sizes: smaller than 300 μm , and particles greater than 800 μm . The initial sample weight was 40 g in all the experiments performed.

The pyrolysis runs were performed in a bench scale plant, shown in Fig. 1, consisting of a 316L stainless steel fixed bed reactor of 90 mm in diameter and 320 mm in length, discontinuously feeder with the orange peel. The reactor is inside a tubular electric furnace of 325 mm in length, 355 mm in external diameter and 120 mm in internal diameter, connected to a temperature and heating control system. A datalogger provides a continuous record of carrier gas flow rate, time, temperature of the furnace and temperatures of thermocouples placed in the sample and in the furnace. A steel basket with a radius of 28.3 mm and height of 41 mm containing a sample weight of 40 g was placed in the reactor prior to the experiment and hung at a depth of between 201 and 245 mm from the top. This basket has two mesh screens, the external one having a diameter of 1000 μm and the internal one of 40 μm . A pair of thermocouples

monitored the temperature inside the sample. Once the reactor is closed, a nitrogen flow of 13 cm³ NTP/s (NTP: normal temperature and pressure, 0 °C and 1 atm) is set by means of a mass flow controller. After 30 min under nitrogen flow, when the air is purged from the reactor, heating of the sample starts at the selected heating rate from 30 °C until the final pyrolysis temperature is reached. The temperature of the reactor is then kept constant for 90 min to make sure that the pyrolysis process is complete. The exit gas passes through a tar condensation system that consists of two glass condenser vessels cooled with a mixture of ice and water and an electrostatic precipitator. Two different methods for collecting the gas were used. In the first, the whole gas produced is collected in Tedlar bags and analyzed. In order to follow the evolution of the gas composition with time for each experiment, a second method is used, consisting of taking gas samples every up 50 °C, after reached 200 °C, and analyzed them. The clean gas was analyzed partially by a GC-TCD HP5890, in a system equipped with a Porapak N column and a Molecular Sieve, and partially in a gas analyzer GC Agilent 3000 A. The compounds analyzed were H₂, N₂, CH₄, CO, CO₂, C₂H₆, C₂H₄, C₂H₂ and H₂S. Heavier compounds were not detected in the experimental conditions used in this study. Once the experiment is finished and the system is cooled down to room temperature, the char is removed from the basket and weighed. The liquid fraction collected by the tar condenser system is also weighed and subsequently extracted with 2-propanol. The diluted sample of liquid fraction is analyzed by GC-MS and GC-FID in order to identify and quantify the compounds present.

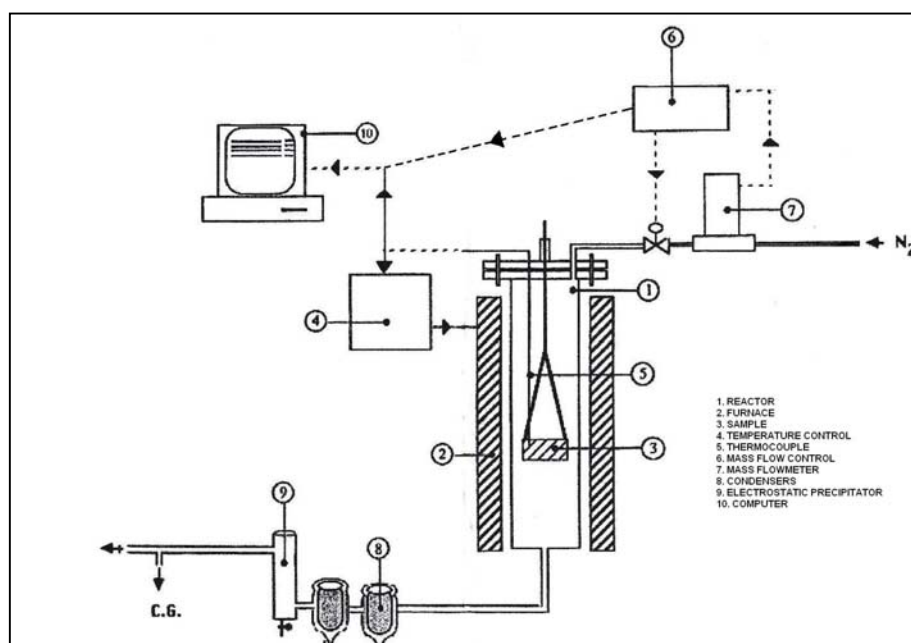


Fig.1. Bench scale plant.

3. RESULTS

3.1. Analysis of Orange Peel

The proximate and ultimate (dry basis) analyses of the sample used in the pyrolysis experiments are shown in Tab. 1 and Tab. 2. The lower heating value (LHV) of the orange peel used was 18.5 MJ/kg (dry basis).

Table 1. Proximate analysis of orange peel.

	Analytical Standard	%
Moisture	ISO 589-1981 - wet basis	8.62
Ash	ISO 1171-1976 – dry basis	3.6
Volatiles	ISO 5623-1974 – dry basis	75.8
Fixed Carbon	By difference – dry basis	20.6

Table 2. Ultimate analysis of orange peel.

Element	% (w/w) Dry basis
C	46.40
H	5.70
N	1.52
S	0.05
O*	46.33

* Calculated by difference

3.2. Product distribution

The products obtained from pyrolysis are gas, a liquid fraction (tar and water-solubles determined like water) and char. Figure 2, shows that the main products in the pyrolysis process, at any temperature studied, are water, gas and char.

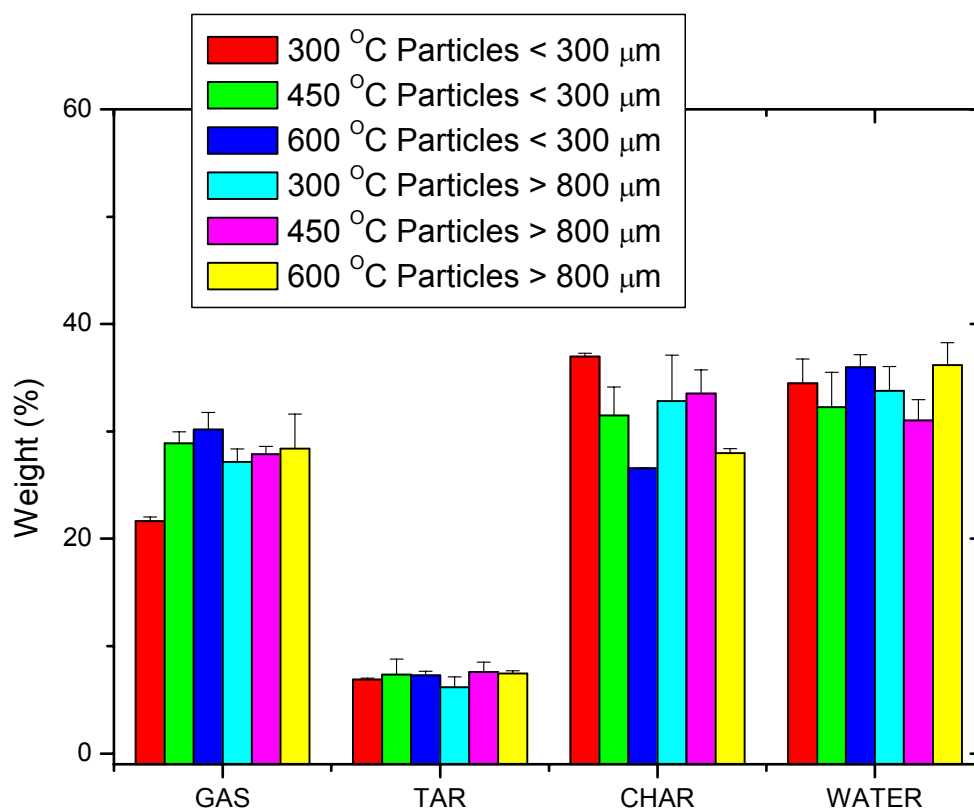


Figure 2. Product distribution.

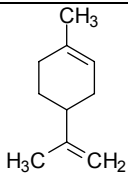

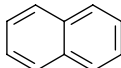

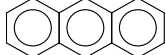
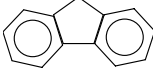
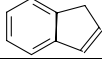
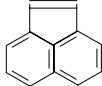
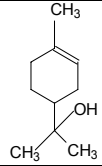
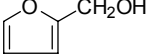
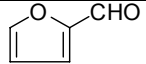
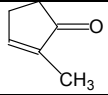


The gas yield increases a little bit with the increase of temperature. The char yield decreases with temperature like expected and the liquid fraction yield remains practically constant.

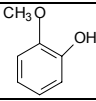

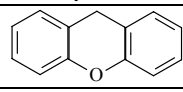
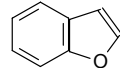
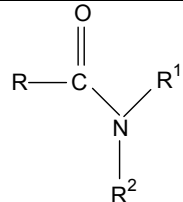
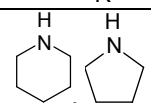
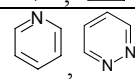
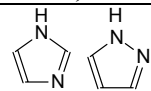
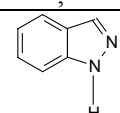
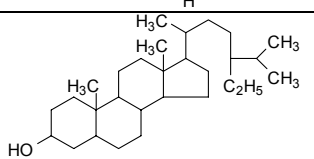
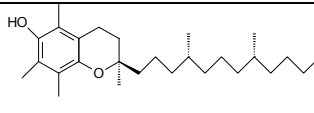
3.3. Liquid fraction composition

Around 70 compounds have been detected in the liquid fraction obtained, most of them being present in very low percentages, similar to results obtained by other researchers (Ayllón et al., 2006 and Garcia-Perez et al., 2007). In order to facilitate the study of the evolution of the liquid fraction composition with the temperature, the compounds detected have been grouped according to their chemical nature (see Table 3), but differently from other works, it was

extended the number of compounds in the classification table, in order to better compare the influence of the reactor parameters in liquid fraction compositions.

Table 3. Liquid fraction compound classification.

Class		Type	Examples	Principal Structure
Aliphatic hydrocarbons		Alkanes	Tridecane Eicosane Docosane Tricosane	> 10 C C_nH_{2n+2} $n > 20$
		Alkenes	Pentadecene	$CH_3(CH_2)_{11}CH_2CH=CH_2$
		Cyclic	Limonene	
Aromatic hydrocarbons	1 ring	Benzene Methyl benzenes	Benzene	
	Polycyclics (2 rings)	Naphthalene Methyl naphthalenes	Naphthalene	
	Polycyclics (3 rings)	Phenanthrene	Phenanthrene	
		Anthracene	Anthracene	
	Polycyclic (other rings)	Fluorene	Fluorene	
		Indene	Indene	
		Acenaphthylenes	Acenaphthylene	
Oxygenated	Oxygenated aliphatic	Carboxylic acids	Hexadecanoic acid	$CH_3(CH_2)_{14}COOH$
			Octadecanoic acid, Octadecanoic acid, methyl ester	$CH_3(CH_2)_{16}COOH$
	Oxygenated heterocycles	Alcohols	α -Terpineol	
	Oxygenated aromatics	Alcohols	Furfuril alcohol	
		Aldehydes	Furfural	
		Ketones	2-Methyl-2-cyclopenten-1-one	
			1-Indanone	
		Phenols	Phenol	

		Guaiacol	2-methoxyphenol	
		Cresols	o, m, p-cresol	
		Xanthenes	Xanthenoxanthene	
		Benzofuran	Benzofuran	
Nitrogenated compounds	Nitrogenated aliphatic	Nitriles	Hexadecanitrile	$RC \equiv N$
		Amides	Hexadecamide	
		Amines cyclics	Piperidine Pyrrolidine	
	Nitrogenated aromatics	Pyridines	Pyridine Pyridazine	
		Nitrogen heterocyclic series	Imidazole Pyrazole	
			Indazole	
Others	Steroid alcohols	Cholesterol	Stigmast	
		Tocopherol	Tocopherol	

The liquid fraction composition obtained at each temperature and particle size ranges considered is shown in Figure 3. It can be observed that oxygenated compounds are the most significant group in all the temperature ranges, reaching about 80% of the liquid fraction produced in the 300-450 °C temperature range. Can be note that with the increase of the temperature, the oxygenated compounds weight decrease. Between 300 and 600 °C aliphatic hydrocarbons represent 6–18% of the liquid fraction produced and with the increase of the temperature, this compounds weight decrease, whereas each of the other groups roughly represent less than 12% of the liquid fraction produced at each temperature range considered.

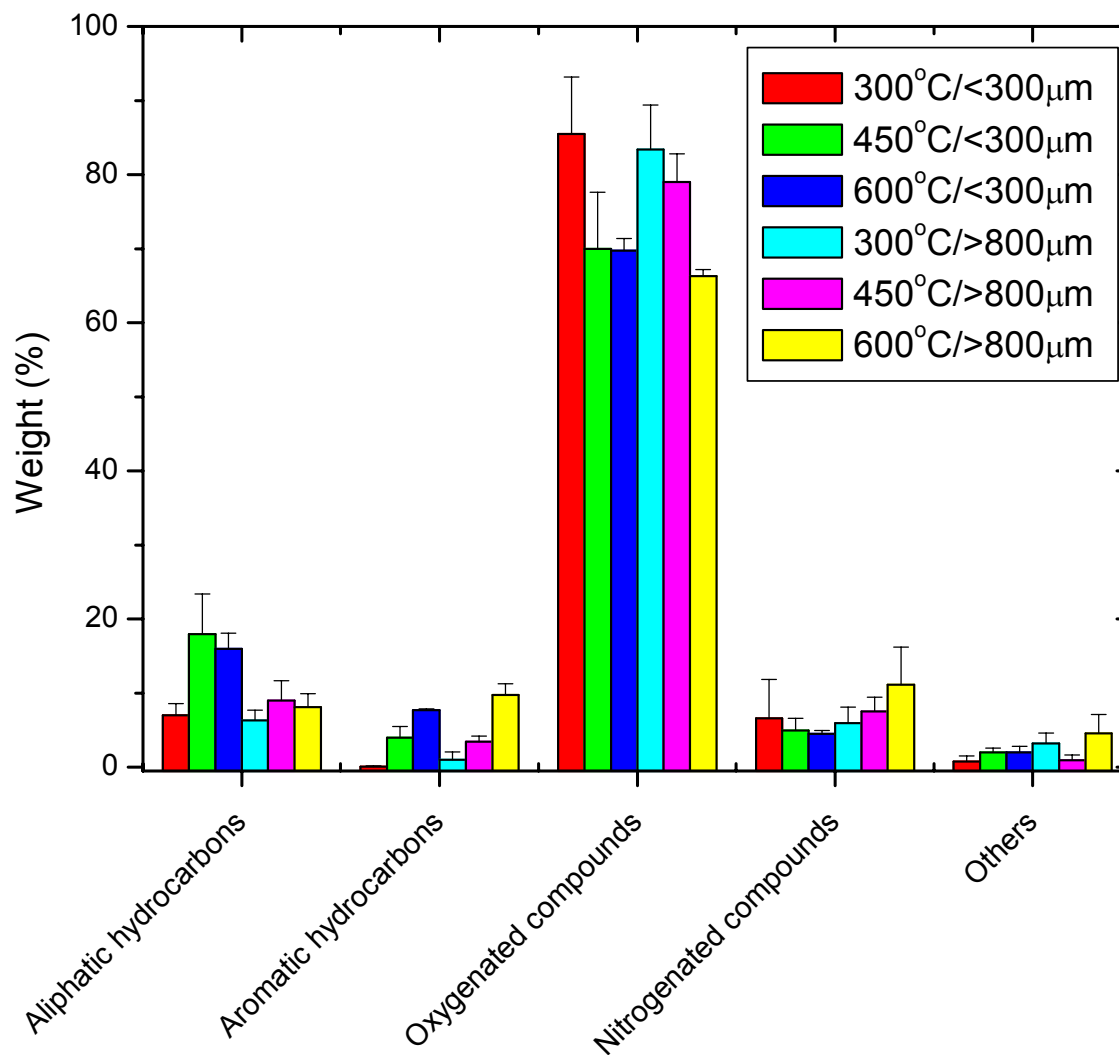


Figure 3. Liquid fraction composition obtained.

The liquid fraction obtained at 300 °C contains 83% of oxygenated compounds, mainly carboxylic acids, and practically none of aromatic hydrocarbons, but its weight increase with the temperature increasing, reaching about 10% at 600 °C.

It can be noted, too, that the weight of the compounds were affected by the particle size. With particles smaller than 300 µm, the nitrogenated compounds weight decrease with temperature increases, and with particles greater than 800 µm the nitrogenated compounds weight increase with temperature increase. With the increase of the particle size, it can be observed that the aliphatic hydrocarbons weight decrease and the nitrogenated compounds weight increase.

In figure 4 it can be observed the obtained compounds. The carboxylic acids are the most significant compound, reaching about 58 % in weight at 300 °C (<300 µm), decreasing with the increase of temperature or the increase of the particle size. Alcohols are the second group in weight, with about 15 % at 450 °C (>800 µm).

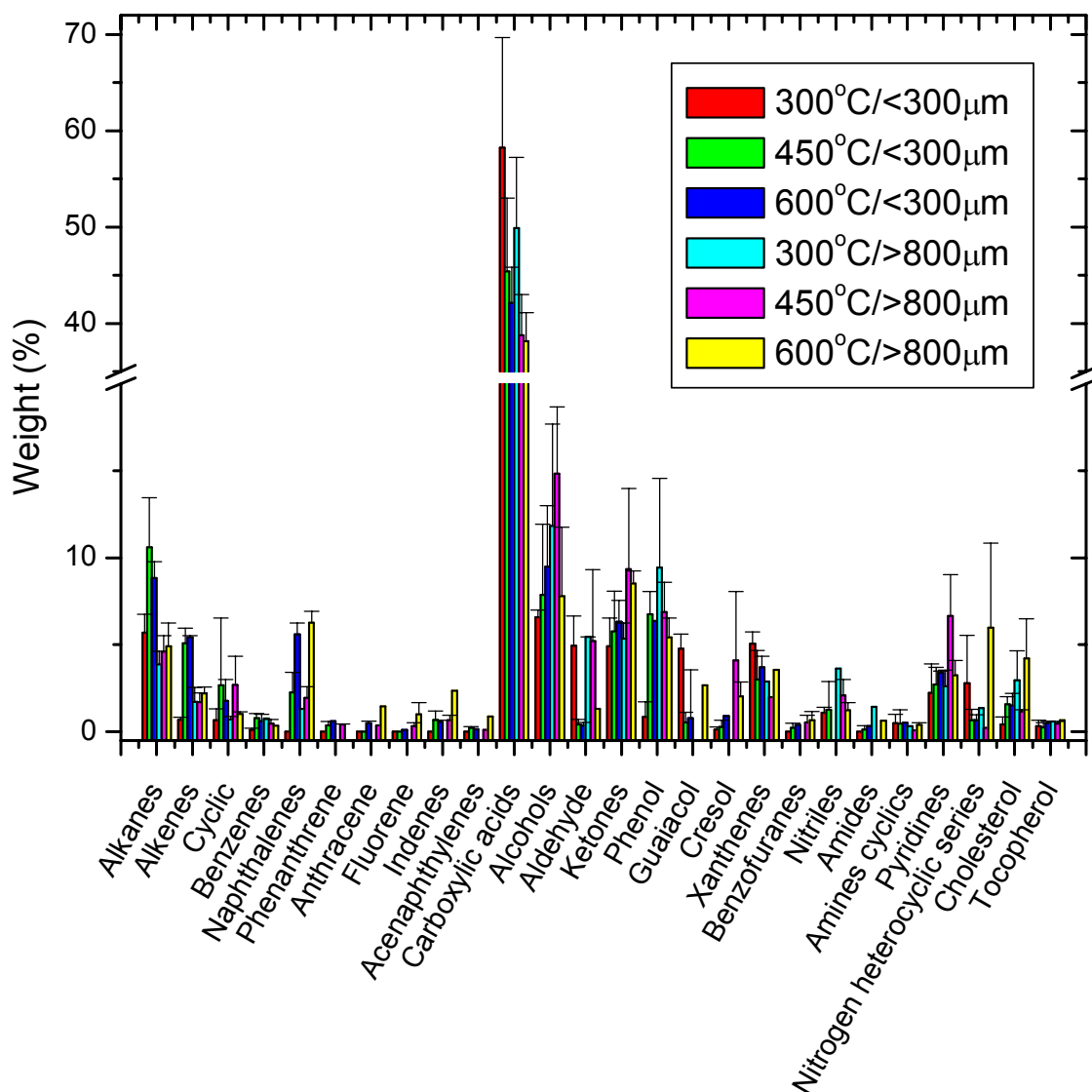


Figure 4. Obtained compounds.

4. CONCLUSIONS

An analysis of the results shows that under the operating temperature conditions studied (300–600 °C), the temperature has a greatest influence on the pyrolysis process. Water, gas and char are the main products of the process under all the conditions studied. There was not an optimum temperature for obtaining liquid fraction in the operating temperature conditions studied.

Liquid fraction is the product of greatest interest from the point of view of using pyrolysis as a thermal treatment of orange peel. On the other hand, since pyrolysis is an endothermic process, the gas fraction can also be important for sustaining the process from an energy point of view. Taking this into account the better temperature would be the higher, to increase the gas yield.

The suggestion that the compounds of the liquid fraction detected were grouped according to their chemical nature, showed the principal compound groups: oxygenated compounds, aliphatic hydrocarbons and nitrogenated compounds. The oxygenate compounds of the liquid fraction are the most significant group at all temperatures, and from an energy point of view, a fraction about 30% of hydrocarbons can be obtained under the operating conditions studied (300–600 °C and 300 & 800 µm).

5. ACKNOWLEDGEMENTS

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