Characterization of activated carbon produced from coffee residues by chemical and physical activation

JAVIER SÁNCHEZ AZNAR

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Activated carbon

1.1 Introduction

Nowadays, there has been an increasing environmental concern around the world about emissions. Pollutants are constantly discharged to the environment –water, soils and air- and do also generate a lot of residues. Since years ago, there has been research going on to give value to wastes that had no value. In that sense the interest in utilization of several wastes has awaken the interest for the development of new processes where the production of adsorbents are gaining strength. Therefore, all-inexpensive residues with high carbon and low inorganic content can be considered as starting materials for the production of activated carbon, one of the most known and used adsorbent (1). That is why activated carbon produced from coffee residues could be used as efficient adsorbent with a lot of uses.

That specific residue could be treated appropriately to obtain activated carbons, and so far, there are few studies (2-5) about its use as raw material for its preparation. The aim of this study is to evaluate the possibility of using this waste to obtain activated carbon. The production could be of great interest because the coffee consumption was around 8,2 kg per capita per year in Sweden in 2008 according to the International Coffee Organization (ICO) (http://www.ico.org/historical.asp).

Activated carbon is largely used as versatile adsorbent with so many applications. Purification of water, air and many chemicals and natural products and it's also widely used for adsorption and removal of pollutants from gaseous and liquid phases. It has several applications in medical, industrial and pharmaceutical processes.

1.2. Characterization of activated carbons

1.2.1 Definition

Activated carbon has been explained in different ways by several authors. Marsh (1989) defined activated carbon as porous carbon, which have been treated by oxidizing gases during or after carbonization in order to increase porosity. Norlia Baharun (1999) defined activated carbon as an organic material constituted basically by a graphitic structure. While according to Benaddi (2000) stated that activated carbon is predominantly an adsorbent with a large internal pore volume and surface are. Activated carbon can also be defined as any porous material formed in the major part of carbon and characterized by a well-developed porosity (6).

Activated carbon is the generic term used to describe a family of amorphous carbonaceous adsorbents with a highly crystalline form and well developed internal pore structure.

In general terms, one can differentiate two types of carbon: graphitizable and non graphitizable. Carbon is converted into graphite when it is burned to 3000ºC in an inert atmosphere. Activated carbons belong to the second group –non-graphitizable carbon- and are prepared from rich carbon materials that do not pass through a fluid phase during carbonization.

A wide variety of commercial activated carbon products are available showing different characteristics depending on the starting material and activation method used in their production.

According to R.C. Bansal et al (7) wood, coal, lignite, coconut shell and peat are the most important raw materials for the production of activated carbons, although other materials such as synthetic polymers or petroleum residues can also be used. Coffee wastes are one of the lignocellulosic residues generated in large quantities all over the world because coffee is the second largest traded commodity in the world, after petroleum.

1.2.2 Characteristics of activated carbons

1.2.2.1 Adsorption process

Adsorption is a physicochemical phenomenon in which a solid, called adsorbent, retain in the walls a certain kind of molecules, called adsorbates, that are contained in a gas or liquid. Hence it is a separation and concentration process of one or more compounds of a system on a solid or liquid surface. The most employed adsorbents are silica, some synthetic resins and activated carbons.

Factors to be taken into consideration in an adsorption process regarding to the adsorbent – adsorbate are the following:

- ✓ Specific surface and porosity of the solid
- ✓ Particle size
- ✓ Pore size, structure and distribution.
- ✓ Affinity of the adsorbate, depending of the chemical properties of the adsorbent surface.
- ✓ Partial pressure or concentration of the adsorbate in the fluid phase, where may be equilibrium established between the adsorbate concentration in the solution and the mass adsorbed per mass unit of the adsorbent using i.e. the Freundlich equation.

There can be three types of adsorption attributed to the adsorbent-adsorbate attraction is electrical, Van der Waals or chemical. The first type is commonly called ion exchange because the ions of a substance are concentrated on the surface as a result of an electrostatic attraction. The Van der Waals adsorption also known as physical adsorption and takes place when the molecule is bound into the interphase usually at low temperatures. Most of organic compounds that are in water are adsorbed with activated carbons for this type of adsorption. The chemical adsorption is a reaction between the adsorbate and the adsorbent due to their chemistry and is characterized for being strong in the active point of the adsorbent.

In an adsorption process it is common to have a combination of all the three types. Actually, sometimes it is not easy to differentiate between a physical and chemical adsorption.

The union between the adsorbates in the surface of the carbon is mostly caused by the Van der Waals forces, which means, that the activated carbon of apolar nature, will adsorb all the apolar substances depending on the affinity of the chemical surface properties. However, when there are mixtures of gases or substances with different affinity, the concentration of one of the substances will increase in the activated carbon surface, decreasing it in the mixture, until the adsorption-desorption equilibrium is achieved.

In that sense, the process studied for evaluating an activated carbon is a term that explains the adhesion of ions, dissolved solids and all kind of molecules of gas and liquid including biomolecules to a solid surface. That process is explained by the force field created between the surface of the solid where the molecules fill in, the adsorption potentials are enhanced in micropores due to the overlap of the fields from the opposite pore walls and interactions between the adsorbed molecules.

Adsorption is a superficial phenomenon, as high surface area the active carbon could achieve means that higher adsorptive capacity it will have. The surface is an important characteristic of the activated carbon and their typical range is around 500-1000m^2/g (8). Besides achieving a high surface, it is also important to know the pore size distribution. The next picture is a representation of the structure of an activated carbon.

Fig 1.1 Representation of the structure of activated carbons (H. Fritzst Oeckli 1990) (47)

Adsorption is usually described through isotherms, which explains the relation of the amount of adsorbate on the adsorbent as a function of its pressure -gas- or concentration -liquid- at constant temperature. In other words, there is the connection between relative vapour pressure and amount of adsorbed gas at a constant temperature. Actually, one can get useful information from isotherms about the adsorption volume, pores size and its distribution and further more information.

There are lots of adsorption isotherm models, though those of Langmuir and Freundlich are the most used. Langmuir equation (9) is based on a theoretical model and assumes that the maximum adsorption corresponds to a saturated homogeneous monolayer with adsorbate molecules on the adsorbent surface. This is represented in the next equation:

$$Y/M = abC/1+aC \qquad \textbf{(1)}$$

Where:

- ✓ Y = concentration of pollutant adsorbed, mg/L
- ✓ M = PAC concentration, mg/L
- ✓ C = equilibrium concentration of pollutant, mg/L
- ✓ a = constant (determined graphically)

- ✓ b = constant (determined graphically)

The Freundlich equation (10) is an empirical model that considers heterogeneous adsorptive energies on the adsorbent surface.

$$Cs = Kf*c^{n} \qquad (2)$$

Where:

- ✓ c_s = concentration in solid phase
- ✓ c = concentration in fluid phase
- ✓ K_f = Freundlich adsorption constant
- ✓ n = Freundlich exponent

Brunauer, Deming, Deming and Teller (BDDT) have classified physical adsorption isotherms into five characteristic types but according to the International Union of Pure and Applied Chemistry (IUPAC) recommendations there are six physical adsorption isotherms shown in (Fig 1.2) (11).

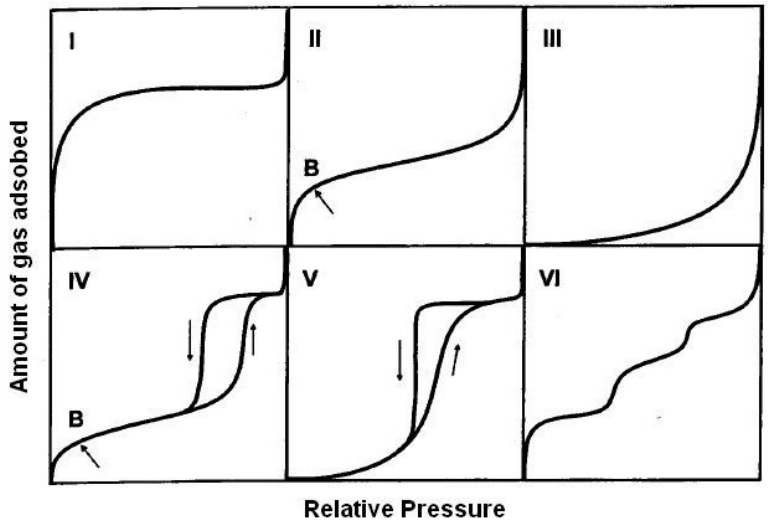

Fig 1.2 The six isotherm types according to IUPAC

Type I isotherms show a quick rise in adsorbed quantity with increasing pressure up to saturation. The isotherm is concave to the relative pressure axis and is typical of microporous materials. High energy adsorption in the micorpores makes the gas to be adsorbed at low pressure.

Type II isotherms show a concave tendency at low pressures and with creasing pressures it begins to be linear and finally convex. One interpretation is the formation of a layer which increases it thickness as the pressure increases. The B point shows the complete formation of the monolayer and starts the formation of the rest of the layer, also known as multilayers. That kind of adsorption is typical of non-porous materials or of macroporous adsorbents.

Type III is a convex isotherm for the pressure axis, which means a weak interaction between the adsorbent and the adsorbate the same as the type V isotherm. That kind of adsorption is not usually found. Otherwise type IV isotherm is typical of mesoporous materials.

Type VI is the least common and is associated to the layer-to-layer adsorption in homogenous surfaces.

Is important to notice that classification is a simplification of the reality where can be found more complex isotherms.

One can find different theories that explain the adsorptive phenomenon but the Brunauer Emmett and Teller (BET) is the most used.

The determination of specific surface area by the BET theory is based upon the phenomenon of physical adsorption of gases on the surfaces of a porous solid. Such a material that is surrounded by and in equilibrium with a certain gas adsorbs physically a certain amount of it at a relative vapour pressure (p/p_o) and temperature. The amount of adsorbed gas depends on its relative vapour pressure and is proportional to the total external and internal surface of the material.

The BET theory is based on the following assumptions:

- Homogeneous surface of the material.
- At a certain vapour pressure a varying number of molecules are adsorbed on any one site. They are stacked on top of each other to form a number of layers.

- The heat of adsorption and the constant condensation in all layers above the first are the same and equal to those of bulk liquid.
- The number of layers becomes infinite at saturation.
- A molecule covered by another molecule can not be evaporated.
- There is no horizontal interaction between molecules in different sites.
- Condensation constant is equal to evaporation constant, which means that the number of molecules evaporating from a layer is equal to the number of condensing on the layer below.

The common equation (12) is the following:

$$\frac{p}{n^a(p_0 - p)} = \frac{1}{n^a{}_m C} + \left(\frac{C-1}{n^a{}_m C}\right)\frac{p}{p_0} \qquad 3$$

Where:

- ✓ p = sample pressure,
- ✓ p_0 = Saturation vapor pressure,
- ✓ n^a = Amount of gas adsorbed at the relative pressure p/p0
- ✓ $n^a{}_m$ = monolayer capacity
- ✓ C = BET constant

The BET theory is from a theoretical point of view applicable if the isotherm is of type II or IV.

The most used adsorbent for the characterization of activated carbons is the liquid N_2 followed by the CO_2; both measured using an adsorption instrument. The N_2 adsorption is very slow because the diffusion trough the micropores is regulated by the low temperature of the analysis (77K). That is the reason to use the CO_2 as adsorbent because it can be used at higher temperatures (273 K or 298 K) where the diffusion takes place

easily and the equilibrium is reached before and also because the molecular size is quite similar.

1.2.2.2 Factors that affect adsorption

Adsorption is influenced by the properties of the carbon and the adsorbate as well as the conditions of the gas and liquid.

- ✓ Properties of the carbon

A correct pore size distribution is necessary to facilitate the adsorption process by providing adsorption sites and the appropriate channels to transport the adsorbate. A relevant parameter is the pore volume estimated as the liquid volume of adsorbate adsorbed (N_2) at a relative pressure. It is important to determine the micropore volume and microporous surface area due to the high relevance that have in the adsorption process.
The pore size distribution (PSD) was determined by using the Barrett–Joyner–Halenda (BJH) equation (13), though it can be calculated by the BET equation as well.
The ash content in a carbon has adverse effects that can be summarized in:

- It reduces overall activity of activated carbon
- It reduces efficiency of reactivation

Adsorption increases when the pore diameter is one to five times bigger than the adsorbate diameter.

- ✓ Properties of the adsorbate

Almost all kinds of organic molecules can be adsorbed. Otherwise, there is practically no adsorption of inorganic substances to the activated carbon surface, though there are some exceptions as silver salts or iodine.

Adsorption of organics compounds is stronger if its molecular weight is greater, provided that the size of the molecule is no greater than the pore size.
The n-polar organic molecules are well adsorbed than the polar ones, as well as, the major part of organic molecules that have bound chlorine, bromine or iodine atoms.
Adsorption increases in liquid medium where the solubility of the adsorbate decreases.

- ✓ Properties related with the gas or liquid temperature

In liquid phase when the pH decreases the adsorption increases generally. At high temperatures the solubility of the adsorbate is higher and the adsorption is more complicated, although, when the temperature goes up the viscosity is lower and the adsorbate is moved easily inside the pores. Summing up, as the temperature increases so does the adsorption.
Table 1.1 show the typical range of values for commercial activated carbons.

Specific surface area, BET (m^2/g)	**600 – 1500**
Total pore volume (m^3/g))	**0,6 – 1,8**
Apparent density (g/cm^3)	**0,3 – 0,7**
Granularity (mm) **a: dust** **b: granular**	**0,05 – 0,1 (a)** **0,1 – 2 (b)**
Ash percentage (%)	**2 - 10**
Uniformity coefficient (grain)	**1,1 – 12**

Table 1.1 Characteristics of activated carbons

1.2.3 Properties

The characterization of the active carbons requires information on both physical and chemical properties of the materials. On the physical side, one must obtain information such as moisture and ash content, as well as the pore structure and the size of the pores that determine how adsorption does take place. The chemical properties to have in consideration are the specific surface area and the surface chemistry.

1.2.3.1 Physical properties

1.2.3.1.1 Moisture content

Generally activated carbons are stored under dry conditions if not it might adsorb considerable moisture. Actually they may adsorb as much as 25 to 30% moisture and still appear dry. For many purposes, the moisture content does not affect the adsorptive power, but obviously it dilutes the carbon. However, an additional weight of moist carbon is needed to provide the required dry weight.

1.2.3.1.2 Ash content

The total amount of inorganic constituents will vary from one carbon to another depending on the source of materials and from activating agents added during manufacture.
Ash content can lead to increase hydrophilicity and can have catalytic effects, causing restructuring process during regeneration. The inorganic material contained in activated carbon is generally in the range between 2 and 10% as can be seen in table 1.

1.2.3.1.3 Pore structure

A pore is a kind of cavity which is linked to the surface of a solid and allows the connection of fluids into, out of, or through a material.
Basically, the pores are classified in three groups according to the International Union of Pure and Applied Chemistry (IUPAC) defining the diameter of the pore as:

- Micropores: D<2 nm
- Mesopores: 2<D< 50 nm
- Macropores: D >50 nm

Activated carbon is a mixture of the three size pores and each one has different functions. The micropores are the most important ones due to their high surface area which gives

them the higher adsorption capacity because of their smaller size; similar to the molecules that will be adsorbed. An activated carbon formed by numerous micropores in the same range of the pollutant is expected to be efficient due to the enhancement of the adsorption potential for such conditions. The adsorbent is filled completely because its behaviour is similar to a low pressure liquid ($P/P_0<0.01$). Microporous carbons are characterized by the presence of small voids having accessible widths in the range of 0,04 to 2 nm and representing the adsorptive capacity. Micropores have the appropriate size to retain molecules such as lot of solvents and volatiles, compounds that usually generate odour, flavour.

The mesopores have a double function, at sufficiently high pressures, in the range from $P/P_0=0.20$ till $P/P^o=0.95$, condensation take place forming a meniscus and, secondly, serve as a step towards the micropores. The typical molecules retained in these pores are those ones where the sizes are between the micropores and macropores range.

Macropores are the big size pores and can not be filled by capillary condensation. Their relative pressure is from $P/P_0=0.95$ till $P/P^o=1.00$ and their main function is to communicate the external surface of the activated carbon with the mesopores. Actually, the surface of the macroporous may be regarded as nonporous, though its importance lies in the liquid retention that may occur. For that reason one of the main functions of the macroporous is to ensure that the adsorbate arrives quickly to the smaller size pores located deeper in the activated carbon. Nevertheless, macropores can also retain big molecules such as humic acids, which are generated in decomposition of organic matter.

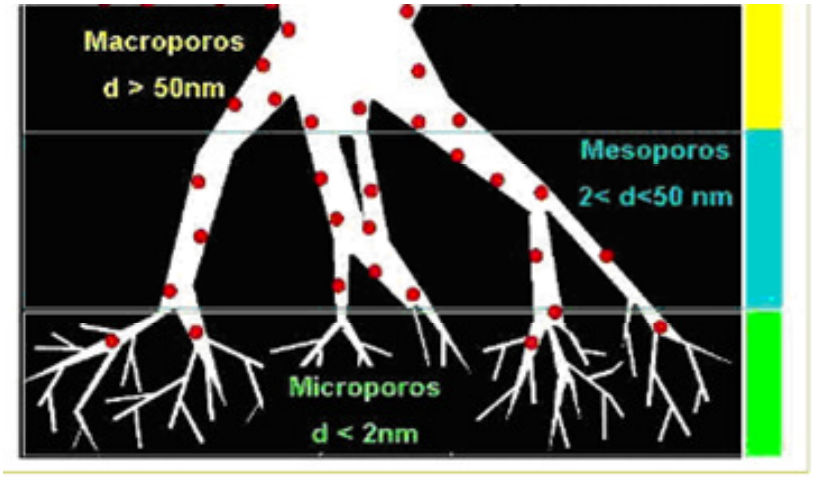

Fig 1.3 Representation of the three types of pores according to the IUPAC

Figure 1.3 is a representation of the transport of molecules being adsorbed at different points in relation to the pore diameter.
In that sense, activated carbons show different properties depending on the raw material employed and the conditions of the activation and it would undoubtedly determine the adsorption capacity that is usually attributed, besides to its surface area, for an appropriate internal pore volume that may be distributed in pores ranging in width from micropores to macropores (14).
The porous structure can be characterize by various techniques such as adsorption of gases as N_2, CO_2 or vapours as benzene, scanning electron microscopy (SEM) and transmission electron microscopy (TEM)

1.2.3.1.4 Surface area

Activated carbons are widely known for the high specific surface area, which provides a well developed porosity. The typical values ranged from 500 m^2/g to 3000m^2/g and can be explained by the micropore structure (2). One can think that for a higher surface area, the adsorption characteristics as adsorbent will be better because there will be more points where the adsorbates could be retained. However, depending on whether the adsorbate molecules size is bigger than some of the micropore size not all surfaces will be available for those molecules. At the same point the geometry of the adsorbate and the pore have to be taken into consideration as well.

1.2.3.2 Chemical properties

The physical properties and the chemical composition of the starting material, as well as the methods and process conditions employed for activation, determine the pore size distribution and the adsorption properties of the activated carbon (15). One of the parameters that differentiate one material from another is its composition, i.e. lignin, cellulose and halocellulose. Materials with a greater content of lignin as grape seeds or cherry stones develop activated carbon with a predominance of macroporous, while other

raw materials characterized by having a higher content of cellulose as apricot stones or almond shells produce activated carbons with a predominantly microporous structure (16). In the literature some results (7,17-20) suggested that it is easier to carry on with the preparation of activated carbons having more cellulosic content instead of having high lignin content.

Furthermore of the porosity properties, the chemical surface characteristics of the solid develop specific surface complex which are also important in the adsorptive process. Activated carbons show a lack of specificity in molecules retention but will retain easily apolar molecules, like hydrocarbons and dyes; while compounds like water, nitrogen and oxygen are not retained. a lack in a retention process.

The chemistry of the carbons takes places essentially on the edges of the graphitic sheets where a variety of oxygen groups or other induced chemically groups are found. One of the most important and studied is the oxygen complex; those ones are formed by the reaction between the carbon and the oxygen as well as reaction with oxidizing agents. Other compounds as hydrogen, nitrogen, phosphorous or sulphide could be mixed with carbon to form superficial complex but in a less quantity. The surface chemistry of an activated carbon is related to the presence of heteroatoms (oxygen, hydrogen, and nitrogen) within the carbon matrix resulting in superficial complex (21,22).

Polar molecules are adsorbed weakly on the surface of the carbon, where the fixation of heteratoms in the carbon create functional groups as carboxylic acids, lactones, etc which increases the affinity of polar molecules for the carbon surface.

These heteroatoms found on an activated carbon surface are directly attributed to three factors: the starting material, method of activation and treatment conditions; and are chemically bonded to the carbon surface during the carbonization and activation, forming carbon- heteroatom structures (7,21).

The surface chemistry of activated carbons determines their:

- Moisture content,
- Catalytic properties
- Acid-base character
- Adsorption capacity

The efficiency of a carbon for removing a given pollutant depends on both its adsorption capacity and its surface chemistry. Particularly, adsorption of substances with high polarity and low molecular weight will be very complicated and will take place easily if the carbon is impregnated with specific chemicals or are used properly the catalytic properties of the carbon.

1.2.4 Parameters to evaluate the properties of the adsorption

The following list enumerates the parameters that must be taken into consideration for the evaluation of adsorption:

1. Capacity and kinetics (rate). Capacity parameters determine the main characteristics of activated carbon and maximum adsorption capacity is achieved at equilibrium, while kinetic parameters determine the rate of adsorption.
2. Surface area is proportional to adsorption capacity and is calculated by degree of activation and pore structure.
3. Pore size
4. Particle Size. As smaller is one particle greater rates of adsorption are shown.
5. Temperature. Generally, lower temperatures increase adsorption capacity.
6. Concentration of adsorbate is proportional to adsorption capacity.
7. pH. Adsorption capacity increases normally under low pH.
8. Contact time is an important parameter due to reach adsorption equilibrium and to maximize adsorption efficiency.
9. Apparent density indicates the weight of carbon per unit of volume. Higher density shows better quality of an activated carbon because there is more available volume.
10. Ash content. Are undesirable inorganic residues that remain after carbonization.

1.2.5 Applications

At the moment the 60% of the production of activated carbons globally are obtained from coal (15). A part of that percentage is destined to the removal of pollutants from many different industries.

Activated carbons are versatile adsorbents with a wide range of uses in so many sectors basically due to the large surface area that confers a high capacity for holding chemicals from gases or liquids.

They can be used in powder or granular form and in liquid or gaseous media. The main application in liquids is related to water treatment and is commonly used to remove compounds that affect taste, odour, colour, chemicals and bacteria. The food industry is one of the big consumers to remove those kinds of compounds. Activated carbons can be applied for purification of proteins or in the separation of metallic compounds as gold and silver, but also have medical purposes as purification of blood plasma.

On the other hand, in gaseous medium their applications are the storage and separation of gases. They can be found in radioactive protection in nuclear plants, in food industries for deodorization and have perspectives as catalyst support and catalyst too.

Activated carbons are required in many industries for the treatment of waste water and gaseous effluents to meet environmental regulations and for material recovery purposes as well.

In general, the powder coal is used in liquid media while the granules can be applied in both media. The properties of the active carbon largely define their application.

1.2.6 Types

Relating to the particle size, activated carbon can be classified in dust carbons or granular carbon.

- ✓ Dust activated carbons: Those carbons are characterized for having a size lower than 100μm, being the common ones between 15 and 25μm. The most important physical properties are the filterability and global density. That kind of carbons

show some advantages, first of all is approximately twice cheaper than granular carbon and the adsorption kinetics is quick due to its surface is easily accessible. Otherwise, show some inconvenient in the recovery process.

Fig 1.4 Texture of dust activated carbon

- ✓ Granular activated carbon: Those carbons show an average particle size between 1 to 5 mm. Can be divided into two categories: chopped carbon (formless) and formed carbon with a specific form as cylindrical. The first type is obtained by milling and sieving while the second ones are a mixture of carbon and a binder. Furthermore, there also other forms of carbon adsorbents as activated carbon fibres, filters of activated carbon, monolithic structures, carbon membranes, etc.
  Those carbons are valuable for their hardness and particle size. Much of the operation cost is caused for the attrition during the regeneration and normal work.

Fig 1.5 Texture of granular activated carbon

1.2.7 Regeneration and recovery

Commercial activated carbons are expensive and valuable adsorbents and as such must be regenerated. There are different ways to reactivate them again. Activated carbons may be regenerated once their adsorption capacity is reached. The regeneration methods are the following:

1. Vapour through the bed at low pressure to evaporate and remove the solvents. It can be used to remove volatile compounds and it is useful for the surface recovery and it sterilization.
2. Removal of the adsorbate with a chemical (acid or alkali).
3. Thermal regeneration is the most used technique. There are lot of kinds of oven but the loss of activated carbon is about 10% for each regeneration, which means that in 10 or 12 regenerations it must be replaced.
4. Oxidising gases treatment

Thermal regeneration generally consists of the three following steps (23,24):

1. Drying at around 105 °C.

2. Pyrolysis under inert atmosphere. It is a complicated process consisting of thermal decomposition and cracking, desorption of decomposition products followed by polymerization of the residuals.

3. Gasification of residual organics by oxidizing gas, such as steam or carbon dioxide, resulting in the elimination of the charred residue formed in the pyrolysis and the exposure of the original carbon-pore structure.

1.3 Preparation of activated carbons

There are many activation methods that can basically be summarized in two: physical and chemical activation. In the same way, the manufacture of activated carbon involves two main stages, the carbonization of the starting material and the activation of the resulting char.

The physical activation involves carbonization of the raw material followed by activation at high temperature in a carbon dioxide or steam atmosphere. The chemical activation consists on the carbonization of the raw material previously impregnated with a chemical agent such as phosphoric acid (2-4,14,15,25-27), zinc chloride (3,26,27,28) and potassium hydroxide (8,26,29).

1.3.1 Factors affecting activated carbon production

The properties of activated carbons as adsorbent are influenced basically by the following factors:

- Properties of the starting materials. The most common raw materials come from coal, organic polymers and lignocellulosic materials.
- Activation method: physical, chemical or a mixture of both. Carbonization and activation conditions such as heating speed, time, temperature, etc
- Operation conditions such as impregnation ratio, impregnation time, and so on. Generally, operation conditions are influenced depending on the activation method.

1.3.1.1 Raw material

Activated carbons are manufactured from various carbonaceous substances of animal, vegetable or mineral provenience. Anthracite, petroleum coke, coal and waste products from lignocellulosic nature as wood, walnut shells, coconut or almond are frequently used as starting material. Anyway, any carbonaceous material can be suitable to be a good adsorbent but have to meet some requirements for being used commercially:

- ✓ Good availability
- ✓ Low cost
- ✓ The resulting activated carbon satisfies all kind of applications.

The starting material is amorphous and the porous structure is achieved during the activation. The composition of the material will longer define the properties of the

adsorbent. The literature shows differences between using coal or lignocellulosic materials as well as between lignocellulosic materials (16,17).
Bansal et al (7) showed that the porosity developed from vegetable as raw material using physical or chemical activation was more heterogeneous than the ones prepared from coal.
The carbon derived from coconut shells (17) have higher density and have a pore size distribution narrower, which makes these coals more suitable for the adsorption of small molecules, useful in gas purification applications.

The main properties of the activated carbons produced from lignocellulosic materials are:

- High temperature stability
- Resistance against acid attack
- Slightly hydrophilic
- Considerable mechanical strength
- Low economical cost due to the abundance of the raw material

Due to this reason, this project aims to study the viability of manufacturing activated carbon from coffee grounds, a lignocellulosic waste that comes from a coffee bean, which is the seed of a cherry-like fruit. Coffee trees produce coffee cherries, which are composed of an outer skin, the exocarp and an internal skin called mesocarp. The beans are covered in an envelope named endocarp.
The coffee tree plantations are located mainly in tropical countries, which export the coffee to other countries after a process called hulling, used to remove undesirable compounds as the exocarp. Before the roasting process it is necessary to remove the endorcarp, also used as precursor for preparation of activated carbons (30,31).
Once upon the coffee have been brewed, a residue is produced. It is commonly called, coffee grounds, which have a long content of carbon approximately around 50% (5) and thus it is a suitable precursor to obtain activated carbon. Elemental analysis of the original lignocellulosic materials showed a similar composition: 49% C, 6% H, 0,2% N (17) and during carbonization most of hydrogen and oxygen are lost.

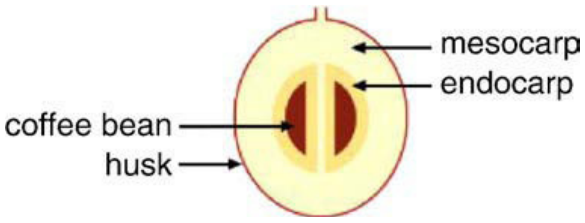

Fig 1.6 Structure of a coffee bean

Coffee is produced all over the world and in great quantities, which means that are generated a great amount of residues that must be treated properly. A part of the coffee grounds were recycled into soil remediation materials or adsorbents for odour removal after been carbonized (5).

1.3.2 Carbonization

The first step is a thermal treatment of the raw material that implies dehydration and where most of the non-carbon elements as dust and volatile substances are eliminated by heating the source in anaerobic conditions. The aim of the carbonization stage is to conserve the carbonaceous structure of the material which is achieved by burning off the material in a range of temperatures from 400ºC to 850ºC (6).

The char is constituted when carbon atoms regroup themselves into sheets forming rigid and dense clusters of microcrystals, each one consisting on several layers of graphitic planes. Each atom inside one stack is bonded to four adjacent carbon atoms. Thus, the carbon atoms on the edges of the planes have a high adsorption potential available.

The internal structure is not homogeneous neither regular; leaving free interstices that constitute the porosity of the char. These interstices may be filled or blocked by disorganized carbon resulting from deposition and decomposition of tars making them not always accessible and reducing the porosity (3).

Pyrolysis of lignocellulosic materials in an inert atmosphere produces a non-graphitizable char (29), because burning off polymeric cellulose or lignin, the typical composition of the raw materials used, during that step liberates most of the non-carbon elements mainly

hydrogen, oxygen, and nitrogen in the form of gases and tars, leaving behind a rigid carbon skeleton (32).

There are three stages in the carbonization process. First of all, is the loss of water in the 300-470K range. The second stage is the primary pyrolysis, takes place in the 470-770K temperature range and is characterized for the large generation of gases and tars due to the elimination of volatile matter and tars causing a remarkable reduction of weight and also for forming the basic structure of the char. The third step is the consolidation of char structure in the range of temperatures from 770 to 1120K, with a very small weight loss.

The small reduction in bulk density with increasing carbonization temperature, coupled with the large reduction in weight (especially in the second stage) implies a contraction of the precursor material; such contraction continues above 770K, since the density slightly increases in the third stage temperature range (33).

1.3.3 Physical activation

The objective of the activation process is to enhance the pore structure. The physical activation is the partial gasification of the char with steam, carbon dioxide and air, or a mixture of these, at temperatures around 1100- 1250K. Once the no desirable materials have been removed the char is accessible. The main change is an increase in pore volume making the crystallites become exposed to the action of the activating agent (oxidizing gases) for further development of porosity with increasing burn-off. The oxidizing gases employed, steam or CO_2, are reactive agents that reacts with the raw material and also remove volatile material from the solid.

The experimental information described in the literature on the gasification rate of different forms of carbon such as graphite (34), coke (35) and chars (13) show that, for a given temperature, the reactivity with steam is larger than with carbon dioxide. However, when the effect of the activating agent on the development of porosity is analyzed, the results do not show a clear tendency, for example for the graphite.

Many authors (7,21,36) have shown that the most important variables in the gasification process from the point of view of porosity development are:

- Activating agent

- The final bum-off reached
- The presence of inorganic impurities that catalyze or inhibit the gasification reaction

1.3.4 Chemical activation

The term, chemical activation is referred to the pyrolysis of the starting material which have been previously added some chemical as phosphoric acid or zinc chloride that restrict the formation of tar; in this way, a carbonized product with a well-developed porosity may be obtained in a single operation.

All the agents involved in the chemical activation have a common feature of being dehydrating agents that influence during the pyrolytic decomposition and inhibit the formation of tar increasing the yield of carbon.

The yield and properties of activated carbons depend on the impregnation conditions, such as impregnation ratio (weight of activating reagent/ weight of carbon precursor), time of predrying impregnated materials, as well as pyrolysis conditions, such as temperature, soaking time (period of time that the sample and chemical are in contact) and atmosphere. All these process variables vary with the type of carbon precursor and the activating agent.

The main impregnation condition is the chemical ratio, one of the most important parameter in the production of activated carbon by chemical activation. As said before, this parameter makes a relation between the agents as a function of the starting material involved. In the preparation of activated carbons, different ratios are studied in order to find out the effect on yield and other properties, though the typical ratios are 2:1 and 4:1.

There are two competing mechanisms of pore evolution in the carbon structure. The first one is the micropore formation, which starts with the addition of chemicals into the lignocellulosic structure that seems to be the cause of the creation of micropores, and the second one is the pore widening that is the result of the chemical effects inside the pores; therefore it starts acting when the chemical ratio is reasonably high (37). Several researchers (14,18,38) reported that activated carbons obtained at low impregnation ratios

were essentially microporous and when the amount of impregnation agent increases, the activated carbon becomes predominantly mesoporous.

The pyrolysis temperature is also an important factor that must be studied in detail, depending on the raw material the optimum temperature can vary taking into account the wide range of available temperatures. Activation is usually a one-step process and the temperature range is commonly around 450-900ºC. The optimum pyrolysis temperature for manufacturing activated carbon from lignocellulosic materials is 500ºC (39). In this temperature the maximum development of porosity is produced, though the carbonization of the material may be incomplete. Some studies (39-41) determined that by increasing the pyrolysis temperature, an increase in the mesopore volume corresponded to a decrease in microporosity and after a certain temperature, surface area decreased causing a contraction of the carbon porous structures.
Pyrolysis time is referred to the amount of time that the sample is going to be burning off and is a critical parameter that affects the quality of activated carbon. In most studies (2-5,15-17) related with the preparation of activated carbon by chemical activation the pyrolysis time more often used is 1 or 2 hours.
Generally, for a soaking time longer than 1 h led to a reduction in both surface area and total pore volume. The decrease in pore volume is referred essentially to a decrease in micropore volume, presumably due to collapse of the smaller pores.

There are many different activation agents, but the most studied ones are phosphoric acid, zinc chloride and potassium hydroxide.

1.3.4.1 Phosphoric acid

Phosphoric acid also known as orthophosphoric acid is a mineral acid having the chemical formula H_3PO_4. Phosphoric acid works in two ways (15): as an acidic catalyst in promoting bond cleavage reactions and formation of crosslink; and by being able to combine with organic species to form phosphate linkages, such as phosphate and polyphosphate esters, that can serve to connect biopolymer fragments.

As said before, it is one of the most used chemical agent, at temperatures around 450-500ºC producing the maximum development of porosity, even though the carbonization of the material can be incomplete, because the effect of the H_3PO_4 is to produce chemical changes and structural alterations at temperatures lower than in thermal treatment without impregnation (25,42).

1.3.4.2 Potassium hydroxide

This agent is an inorganic compound with the formula KOH. It is a strong base and is used in many industrial applications. Some of its characteristics are it high reactivity toward acids and its corrosive nature.

The activated carbons prepared with this chemical were developed during the 70´s to produce "super activated carbons" achieving specific surface areas of 3000 m^2/g.

The effects of KOH on carbonization of carbonaceous materials have been studied by several authors (8,26,29). Thus, the preparation of active carbons were made from starting materials poor in volatiles and a high content of carbon as petroleum cokes, metallurgical coke and charcoals from wood. The raw material and the chemical are mixed in an aqueous solution in ratios KOH: precursor between 2:1 and 4:1. After the reaction it is burned off at the range of 700–900ºC in an inert atmosphere. It can make the oxygen of the alkali remove cross-linking and stabilizing carbon atoms in crystallites whereas K metal may be intercalated. Removal of potassium salts, by washing, and carbon atoms from the internal volume of the carbon, by activation reaction, create the microporosity of the activated carbon in the new structure.

1.3.4.3 Zinc chloride

Zinc chloride is the name of chemical compound with the formula $ZnCl_2$.This product was employed in the 1970´s especially for wood wastes. However, it is no longer used due to the environmental problems that generate. Impregnation with $ZnCl_2$ produces a degradation of the cellulosic material, during the carbonization results in charring and aromatization of the carbon skeleton and creation of the pore structure (28).

PART 2

Experimental

2.1 Materials

Experiments were conducted to produce activated carbon from coffee residues and the equipment used is listed:

1. Oven
2. Beaker
3. Steam pump
4. Furnace.
5. ASAP 2000. Surface area and porosimetry system.

The chemicals involved in the preparation of activated carbons have been the following:

- ✓ Deionized water
- ✓ Phosphoric acid (H_3PO_4). Used in the chemical activation at different concentrations (30, 40 and 50%).

- ✓ HCl. Used to remove the ash contained in the sample after carbonization and the excess of dehydrating agent.

2.2 Experimental procedure

2.2.1. Samples characterization

In order to evaluate the adsorption properties of activated carbons produced from coffee grounds by the chemical and physical activation have been named as follows:

CA_3_500
CA_4_500
CA_5_500
CA_3_600
CA_4_600
CA_5_600
CA_3_700
CA_4_700
CA_5_700
TA _600
TA _700
TA _800

Table 2.1 List of samples

The abbreviation CA is referred to the chemical activation and TA to thermal activation, the next number corresponds to the concentration of the chemical used. Number 3 means 30%, 4 corresponds to the 40% and 5 to the samples impregnated by 50% of phosphoric acid. The last number is referred to the carbonization temperature. In the first example the sample CA_3_500 means that it has been treated with a 30% H_3PO_4 solution at 500ºC and a sample named CA_4_500 correspond to a sample burned off at 500ºC impregnated with a 40% of H_3PO_4 and so on. Totally, there have been 13 samples studied; three of them have been treated by physical activation at different temperatures while the rest of the samples have been treated by chemical activation at different H_3PO_4 concentrations and different carbonization temperatures.

2.2.2. Preparation of activated carbons from coffee grounds

The raw material selected for the study was coffee grounds collected in the coffeemaker at the Division of Chemical Technology, KTH.
The experimental procedures consist on evaluating the properties of the activated carbons prepared by the chemical activation using phosphoric acid and physical activation using steam. In both processes the preparation of the raw material was the same. First of all, the coffee grounds were dried in the oven at 110ºC during 24h, to remove moisture.

The experimental procedure used in the chemical activation process is as follows. The samples were prepared by putting 50g of the raw material on a beaker and adding the adequate volume, until the whole sample were completely covered, of an aqueous solution of H_3PO_4 at different concentrations: 30, 40 and 50%. After that, the samples were sonicated 1 h in an ultrasound bath (40 kHz) to allow the chemical agent to go inside. Afterwards, the samples were dried at 110ºC for 24 h.
The impregnated samples were pyrolysed in a furnace for 1 hour in an inert atmosphere. One studied parameter is the temperature of the activation; for the present work the selected temperatures were 500ºC, 600ºC and 700ºC by a continuous N_2 flow during the pyrolysis. The furnace was heated to the selected final temperature and in that moment the sample contained in a boat was introduced inside. At the end of the activation period, the sample was cooled by flow water in a cooling zone and under nitrogen atmosphere as well. The following picture shows the experimental system:

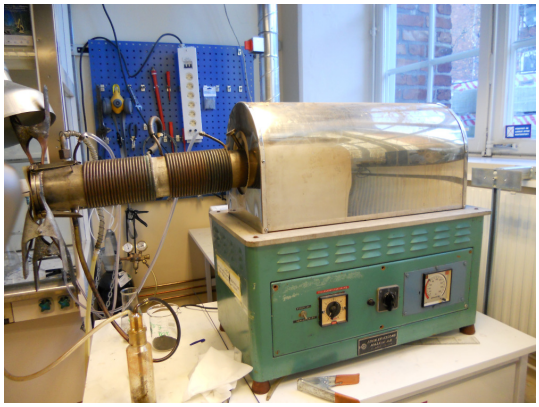

Fig 2.1 Furnace employed for carbonization

Afterwards, the obtained char was moved from the bed of the furnace to a beaker. The samples were washed by deionized water and filtered till the charred residue was completely removed. The samples were dried at 110ºC in an oven and moved to the beaker again to be washed with a 1M HCl solution in order to eliminate the excess of dehydrating agents and the fraction of soluble ash. A magnetic stirrer was used to blend the sample for 20 minutes. The picture illustrates this process:

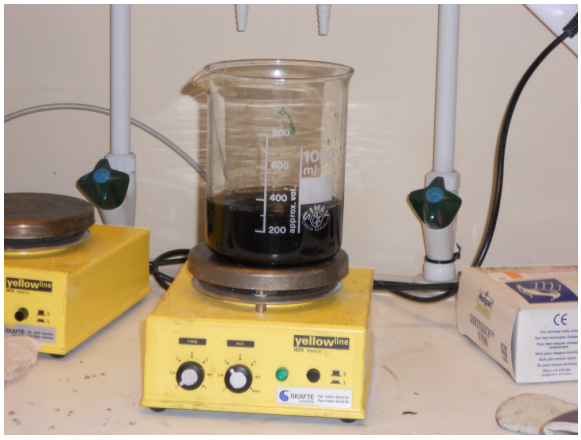

Fig 2.2 Magnetic stirrer during HCL washing

Then the sample was washed and filtered with deionized water to remove the residual organic and mineral impurities. The sample was dried at 110ºC for 24h.
Finally the carbon product was crushed and sieved to a uniform particle size and then was stored in closed bottles sealed with paraffin and aluminum paper until next analysis.

The physical activation is as follows. Once the coffee grounds, raw material, were dried it was put in a cylindrical tube to be pyrolyzed in the furnace. While the furnace was heating it was under an inert atmosphere by a continuous N_2 flow. In the physical activation the selected temperatures were 600, 700 and 800ºC. Once the activation temperature was reached the sample was introduced into the furnace. At this stage of the experiment the nitrogen flow was switched to steam. So the furnace temperature and the water vapor flow provided by injection of 20ml/h of liquid water were kept constant for 2 h. Totally were injected 40ml of steam during the activation The pictures show the experimental design:

Fig 2.3 Steam activation system

At the end of the activation period, the sample was cooled under nitrogen flow and in the cooling zone of the furnace. The cleaning steps are the same as in the chemical activation; firstly the samples were washed with deionized water followed by washing in 1M HCl solution. Finally, the samples were crushed and sieved to a uniform particle size and storage.

2.2.3. Procedure of analysis by N_2 adsorption- desorption

In order to characterize the activated carbons have been studied the isotherms of the activated carbons using an adsorption instrument (ASAP 2000) at liquid nitrogen temperature (77K) were conducted. The total surface area by the BET (Brunauer-Emmet-Teller), the pore diameter, the pore volume and the pore size distribution for each sample were analyzed and reported.

First of all, samples with a weight between 0,300 and 0,600g have been degased for at least 5 hours until the appropriate conditions of moisture removal are achieved. After this, were introduced into the analytical instrument choosing the *pyrolyserat bagasse* program. The next picture shows the sample being analyzed by the ASAP.

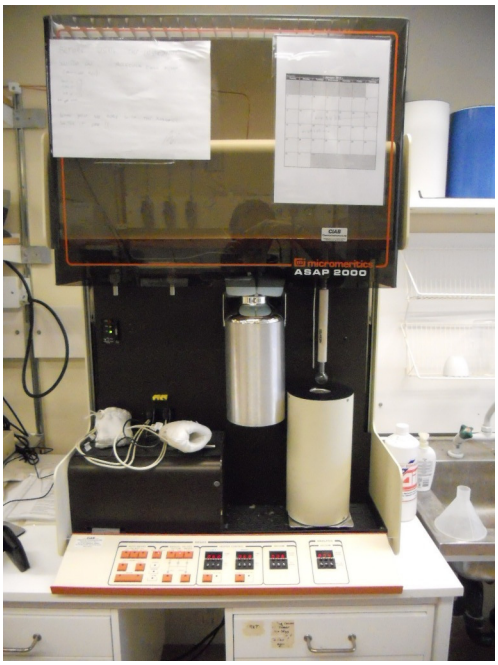

Fig 2.4 ASAP instrument

PART 3

Results and discussion

A physical characterization of the activated carbons produced from coffee residues was carried out. During the manufacturing step analyses have been made on the weight losses after activation process, after washing with HCl and finally after drying. After these steps surface area (BET), pore volume, pore diameter and pore distribution were analyzed.

- ✓ Carbon yield is defined by the weight of activated carbon after activation to the weight of dry coffee grounds. The weight of activation carbon is the one after carbonization, washing and drying. The burn off is the percentage of mass loss due to the whole activation step.
- ✓ Volatile content is defined by the weight loss during the carbonization step on the furnace.
- ✓ Ash content is defined as the weight loss after activation and washing with HCl.
- ✓ The chemical recovery (CR) is the relation between the chemical involved during the activation explained in the following equation:

$$CR = \frac{\text{(Weight of sample before washing – weight of sample after washing)}}{\text{Weight of impregnated chemical}}$$

The following table shows results about the yield of the weight of carbon based on the starting material as well as the chemical recovery for each sample.

	YIELD (%)	Burn off (%)	CR (%)
CA_3_500	38,97	61,03	31,63
CA_4_500	32,31	67,69	41,09
CA_5_500	36,60	63,40	48,18
CA_3_600	60,59	39,41	26,84
CA_4_600	34,92	65,08	40,49
CA_5_600	40,99	59,01	35,71
CA_3_700	48,07	51,93	29,36
CA_4_700	36,77	63,23	41,30
CA_5_700	53,57	46,43	35,76
TA _600	18,36	81,64	-
TA _700	13,43	86,57	-
TA _800	12,72	87,28	-

Table 3.1 Results of yield (%), burn off (%) and chemical recovery

The carbon yield (%) obtained by the chemical activation are around 35-50%, except the sample which was burned off at 600ºC showing an unusual high yield of 60,59%. On the other hand, the yields achieved by the physical activation (12-18%) are lower than the ones obtained by the chemical activation.

Carbon yields do not show a huge relevant increasing tendency, as the concentration of phosphoric acid gets higher. However, samples impregnated with 50% solution show higher yield compared to the values obtained of the samples at different concentrations at the same carbonization temperature, been very similar for the samples of 30% and 40%.

The second higher yield corresponds to the sample CA_5_700 one with highest concentration and activation temperature and sample CA_3_600 shows an unusual high yield for this concentration.

Table 3.2 shows the common values of yield of carbon, volatile content, density and percentage of ash for different starting materials used as precursors (43). It's useful in order to compare our experimental results with the typical ranges.

Raw materials	Carbon (%)	Volatile (%)	Density (Kg/m^3)	Ash (%)	Texture of AC
Softwood	40-45	55-60	0.4-0.5	0.3-1.1	Soft, large pore volume
Hardwood	40-42	55-60	0.55-0.8	0.3-1.2	Soft, large pore volume
Lignin	35-40	58-60	0.3-0.4	-	Soft, large pore volume
Nut shells	40-45	55-60	1.4	0.5-0.6	Hard, large multi pore volume
Lignite	55-70	25-40	1.0-1.35	5-6	Hard small pore volume
Soft coal	65-80	25-30	1.25-1.50	2.12	Medium hard, medium micropore volume
Petroleum coke	70-85	15-20	1.35	0.5-0.7	Medium hard,medium micropore volume
Semi hard coal	70-75	1-15	1.45	5-15	Hard large pore volume
Hard coal	85-95	5-10	1.5-2.0	2.15	Hard large volume

Table 3.2 Characteristics of common starting materials employed as activated carbon precursor (Manocha,2003)

As can be seen in table 3.2, values for carbon (%) for lignocellusic precursors as nut shells and also for lignin, hardwood and softwood are in the same range as the ones obtained experimentally in our study as shown in table 3.1. On the other hand, the carbon yields obtained are lower than the ones obtained by coal or petroleum coke.

3.1 Carbon yield and burn off

The yield must be studied in relation to the activation temperature for both activations and the concentration of the chemical (H_3PO_4) employed in the chemical activation samples.

In order to do a clear evaluation, Fig 3.1 shows visually the yields obtained for each sample at the 30%, 40% and 50% at different temperatures.

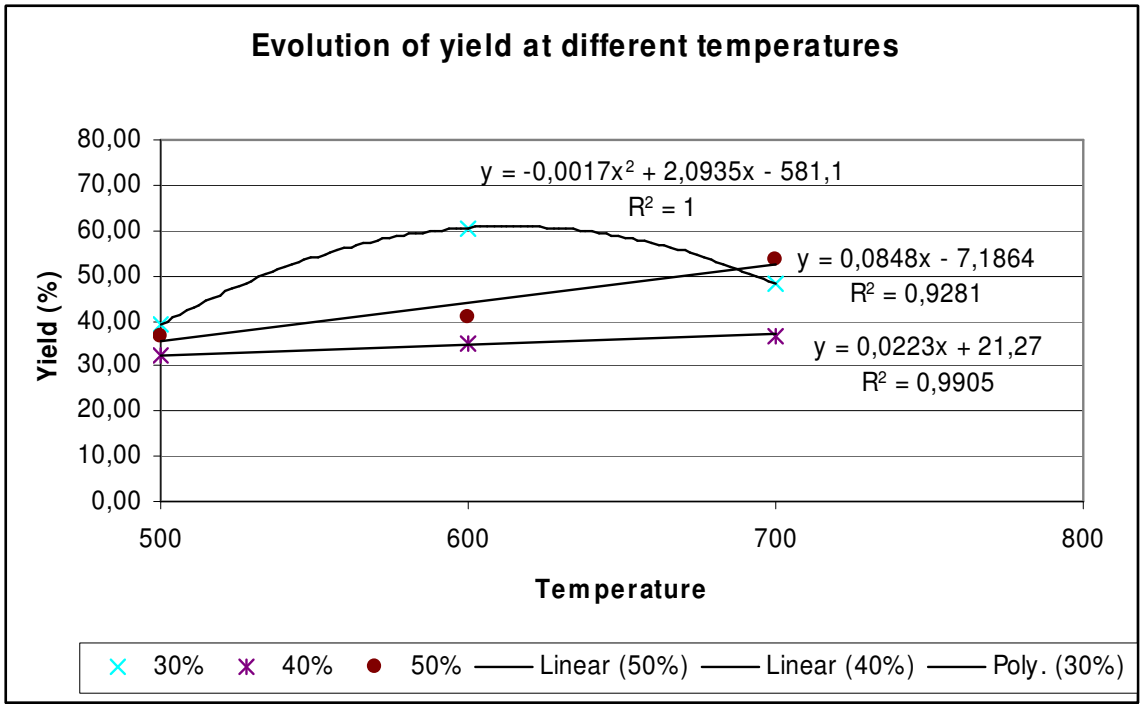

Fig 3.1 Results of yields for 30%, 40% and 50% samples by chemical activation at different temperatures

In fig 3.1 can be observed that for samples impregnated with 30% concentrations the carbon yield was the highest. There is an increasing yield from 500ºC to 600ºC about 20 % but decreases when the activation temperature is increased to 700ºC for the 30% samples. CA_3_600 show an unusual high value compared to the rest.

There is a progressive increase of yield as the temperature is getting higher. Samples impregnated with 40% show a slightly increasing yield as the temperature increases and show the lowest values being about 32%.

Samples impregnated with a concentration of 50% show higher yields as the temperature increases in a range from 36 to 53%. For this concentration there is a greater increase of the yield as temperature is increased compared with samples with 40%.

There is a decrease in the yield from concentrations for 30 to 40% for different activation temperatures. Moreover, there is an increase on carbon yields from samples impregnated with 40% to 50% solutions. Compared to other study (2) the yields and burn-off for the same raw material are quite similar but the tendency is a decrease in the yield as the impregnation rate (concentration) is higher. Thus, samples show the tendency for low

concentrations (30%) but, as the concentration reaches 50% increase may be due to increase in phosphates and other phosphate containing groups.

To sum up there are two points to be noted in the chemical activation. The first one, in relation to the yield obtained by the chemical activation, samples show that as the carbonization temperature is increased also does the yield. This can be observed more clearly for samples impregnated with 50% of H_3PO_4, the yield values were 36,60%, 40,99% and 53,57% for the 500ºC, 600ºC and 700ºC, respectively. Otherwise, this tendency is not so clear for the results obtained with 30% samples because of the result of the sample burned off at 600ºC is so high. The second one, show that increasing the chemical concentration also does the carbon yield probably due to the phosphates linkages formed that retain carbon and avoid the loss of volatile material. To confirm this assumption an elemental analysis of each sample as well as the analysis of functional groups should be made.

The next figure shows the obtained yields for samples prepared by physical activation.

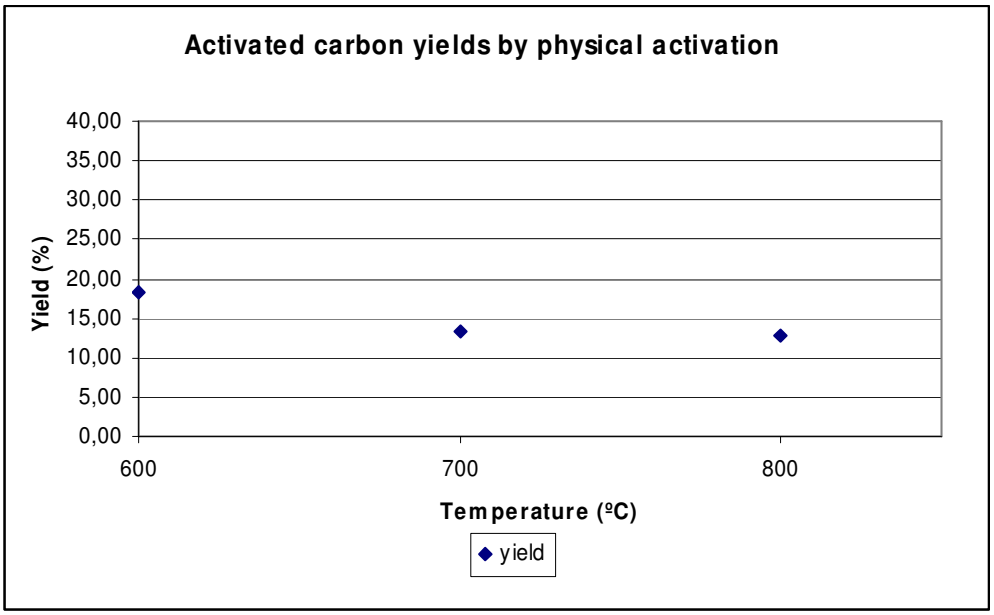

Fig 3. 2 Results of yields for samples activated by steam at different temperatures

Yield results are not really high compared to the ones obtained by chemical activation.

The samples prepared by the physical treatment show low yields of the order of 12-18%. In other literature (4) the carbon yields reported show the same order as with other lignocellulosic raw material as apricot stones and cherry stones. These values are

relatively very lower compared to the ones obtained by the chemical activation that can be explained for the ability of the phosphoric acid to retain the carbon material. The lower yield and the higher burn off (table 1) with steam activation can be related to the effect of the water to go inside of the material causing and efficient removal of volatile material and helping desorption (3).

So, carbon yield and burn off are affected by temperature and as is shown in Fig 3.2, as the temperature is increased in a physical activation treatment the yield is lower. The yield obtained by 700ºC and 800ºC treatment is practically the same.

Fig 3.3 shows the percentage of volatile compounds burned off during the pyrolysis by chemical and physical activation.

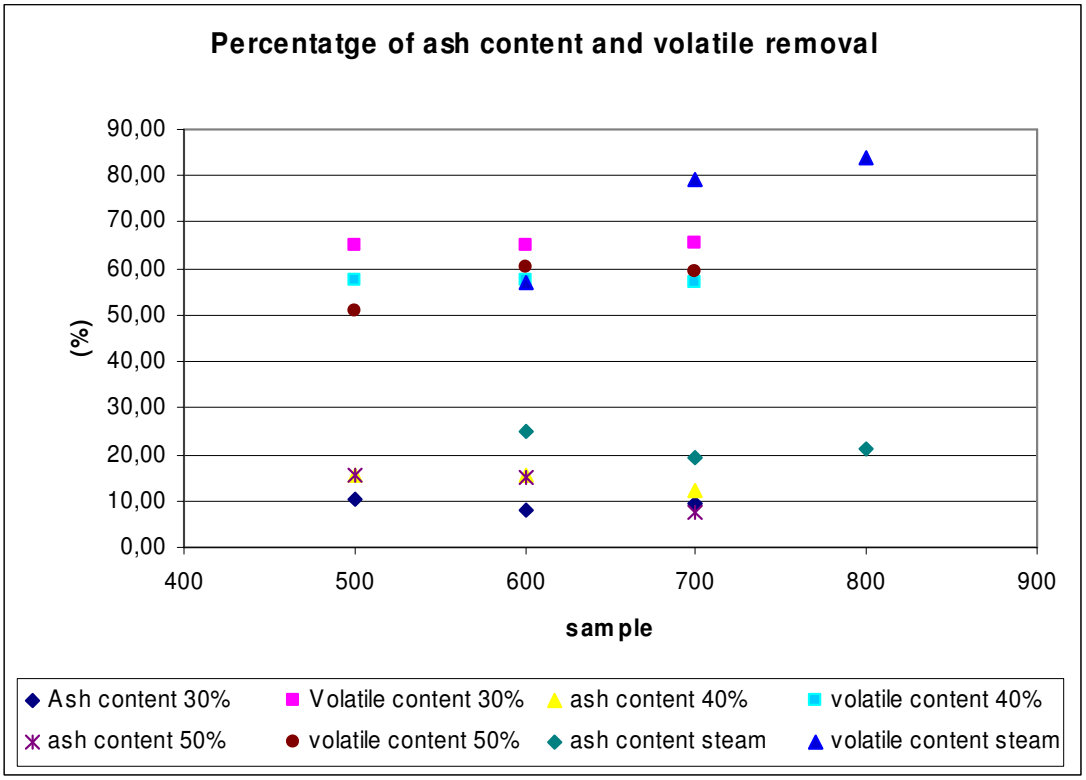

Fig 3.3 Results of volatile and ash content by chemical and steam activation

The volatile content is assumed to be the weight loss during the carbonization before washing with HCl while the ash content is the difference of weight after carbonization and washing with HCl.

Figure 3.3 shows a loss of biomass of around 50 to 65% in samples treated by the phosphoric acid while the results obtained by steam show a wide difference temperature range from 60 to 82%.

Samples with a 30% concentration show the highest loss of volatile material while the samples impregnated with a 50% show the lowest loss of volatile material. The loss of volatiles for 40% and 50% samples are very similar. The higher the concentration of the chemical, the lower is the loss of volatile material. That can be explained for the links created for the reaction of organic compounds and the phosphoric acid such as phosphate and polyphosphate esters. Obviously, a greater amount of phosphoric acid will create more of these compounds as can be noticed in higher yields.

For 30 and 40% samples loss of volatiles is constant independently of the temperature but for concentrations of 50% the loss is greater as the temperature increases. Considering the concentration of phosphoric acid, for samples of 50%, as the temperature increases further loss of volatiles takes place. So increasing the temperature, the burned volatile material is higher allowing easily the loss of those kinds of compounds.

On the physical treatment the loss of volatiles are greater than for the chemical treatment which indicates that phosphoric acid is bound and retains biomass and carbon whereas at high temperatures steam is a reactive agent. As activation temperature by steam is higher, the loss of volatile material is also higher due to the action of water. In that sense, water works in two ways, contributes to the extraction of volatile compounds from the tar and it is also an oxidizing gas with the raw material as can be observed in fig.3.3.

The volatile percentage obtained show results in the same range for lignocellulosic raw materials as can be seen in table 3.2.

The high range from 8 to 25% of ash is characteristic of the activation method. Samples treated with phosphoric acid have less ash content than the physical activation ones. By chemical activation ash content increases as the concentration of phosphoric acid is higher but is kept in constant values for higher or lower temperatures.

Generally, all samples show similar ash content compared to other studies (1) and also with the ones in table 1, but Bansal et al (7) found lower ahs contents from 0,2 to 6,2% for birch wood and straw pellets, respectively. As more removal of volatile compounds,

the resulting char is characterized for having low contents of organics obviously and high content of ash.

The ash content of activated carbons obtained depends on the atmosphere of the treatment. Thus, the treatment by steam yielded the highest ash content compared to the ones treated by chemical activation.

The ash content obtained from coffee wastes (fig. 3.3) show higher percentage compared to the other common precursors in table 3.2.

3.2 Adsorption properties

3.2.1 BET surface area

Figure 3.4 shows the surface area of activated carbons produced from coffee wastes by chemical and physical activation. The activation temperature and the activation time are factors that have a relevant role for the properties of the resulting carbon. In this study activated carbons have been produced at different temperatures keeping the time of two hours for steam activation and one hour for chemical activation.

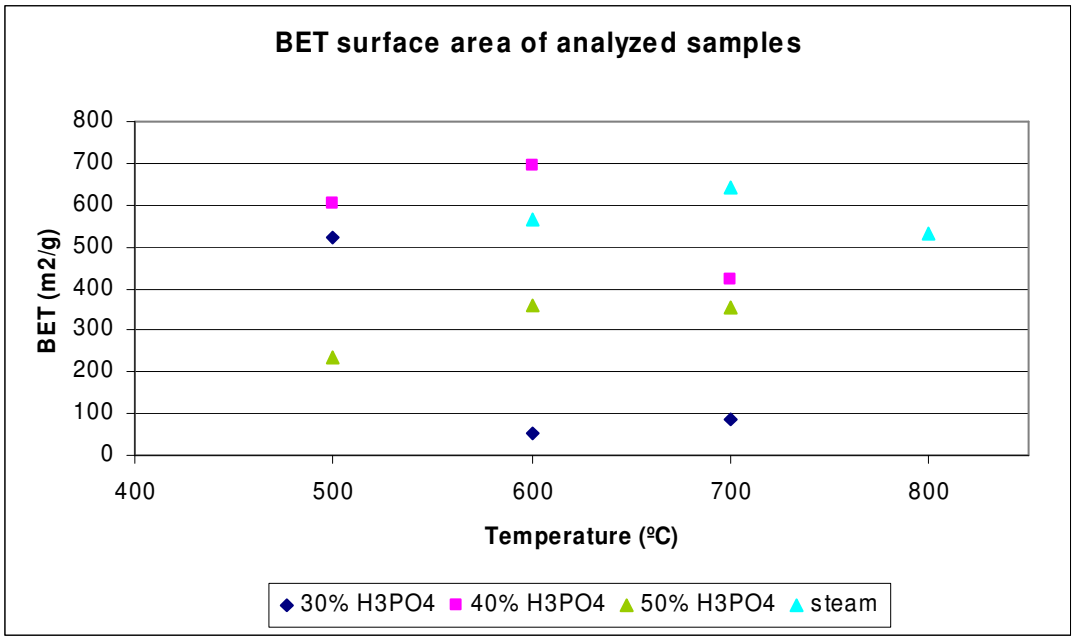

Fig 3.4 Results of BET surface area (m^2/g)

The experimental results show that samples prepared by chemical activation show a wide range of surfaces areas from 50 m^2/g to 695 m^2/g while samples prepared by steam show similar surface area values of around 550-650m^2/g.
Taking into account the samples prepared with phosphoric acid, 40% samples achieved the higher BET surface areas for the three activation temperatures. Actually, at 600ºC and at 40% H_3PO_4 (CA_4_600) the maximum surface area is reported. Rarely, there are two samples, CA_3_600 and CA_3_700, which show lower values of BET surface areas. Both samples were impregnated by a 30% solution.

As the concentration is increased from 30% to 40% there is an increase of the surface area but decreases again for 50% samples for all activation temperatures.
The effect of the temperature does not show a clear tendency for the different concentrations of phosphoric acid. Samples impregnated with 50% increase the BET surface area, as the temperature gets higher. However, 40% samples first increase the surface area until 600ºC and then decrease again, though the trend should be to increase a little or show around the same values as has been reported in other studies (2,27) hence the high outlier or the drastic decrease might be attributed to surface aggregation at higher temperature. In those studies, an increase in the BET surface area as the phosphoric concentration is higher is reported. However, N. Spahis et al (26) asserted that there is an increase in BET surface area as the concentration of chemicals increases but it decreases again as the concentration increases markedly.
Samples impregnated with a 30% H_3PO_4 aqueous solution show a loss surface area of 522 m^2/g to 53 m^2/g from 500ºC to 600ºC, respectively; due to the diluted concentration. Increasing the temperature till 700ºC there is a slightly increase in the BET surface area to 84 m^2/g.

Samples burned off at 700ºC by steam for 2 hours show the highest surface area which is lower than the one obtained with other lignocellulosic materials as apricot stones (1175 m^2/g) or cherry stones (835 m^2/g) in other study (44).
There is an improvement of the surface area from TA_600 to TA_700. But TA800 shows a decrease in the surface area compared to the TA_700 and also in the yield (fig 3.2) due

to the destruction of the micropores for the high reaction of the steam with the biomass. The low micropore volume from 0,232 cm^3/g to 0,184 cm^3/g for samples TA_700 to TA_800, as shown in table 3.3 is evident for the decrease of BET as well. This effect has been reported in other studies (45,46) with other lignocellulosic raw materials at the same temperature.

Surfaces area achieved by steam treatment seems to show an overall higher increase than the ones obtained by chemical treatment.

3.2.2 Pore characterization

The following figures show the isotherm obtained by the ASAP and give information of the adsorption capacity of the activated carbons.

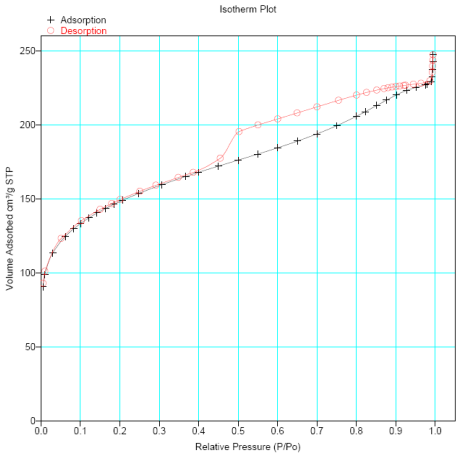

Fig 3. 5 Isotherm of the sample CA_3_500

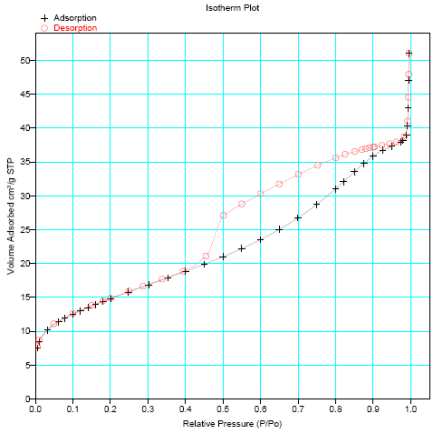

Fig 3.6 Isotherm of the sample CA_3_600

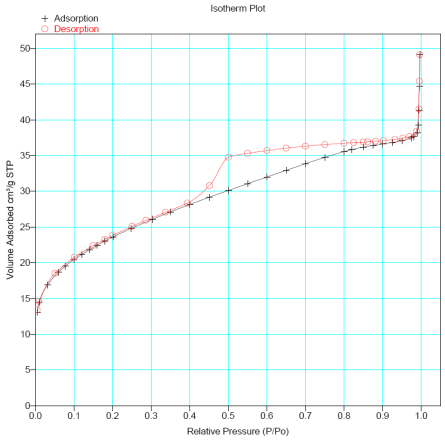

Fig 3.7 Isotherm of the sample CA_3_700

Samples impregnated with a 30% solution adsorb a low volume of gas as the temperature increases. There are predominantly mesopores and macropores and the isotherm is type II according to IUPAC.

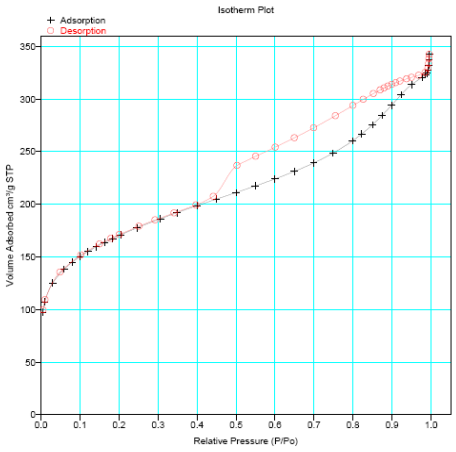

Fig 3.8 Isotherm of the sample CA_4_500

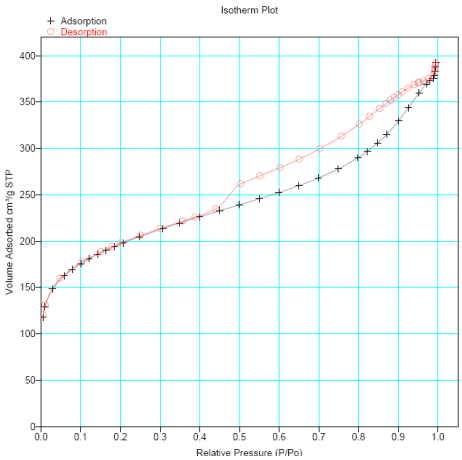

Fig 3.9 Isotherm of the sample CA_4_600

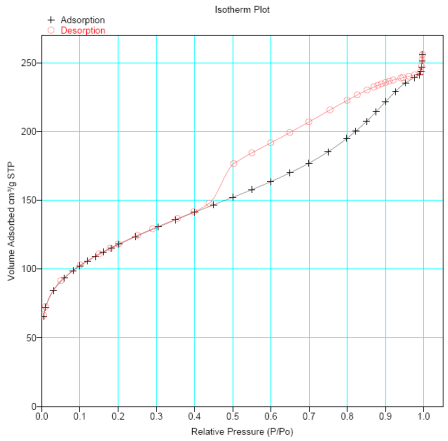

Fig 3.10 Isotherm of the sample CA_4_700

Samples impregnated with a 40% solution show a similar isotherm and CA_4_600 reported the maximum adsorption volume till 400 cm^3/g. In this case, isotherms are characteristic of type IV with a predominance of mesopores.

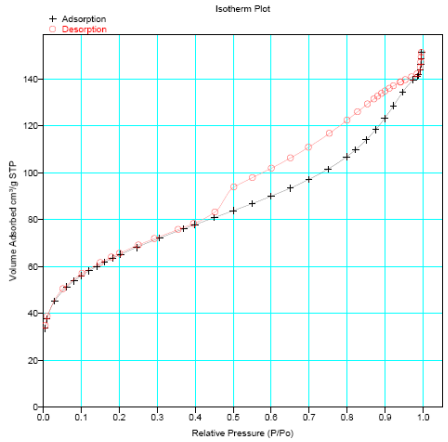

Fig 3.11 Isotherm of the sample CA_5_500

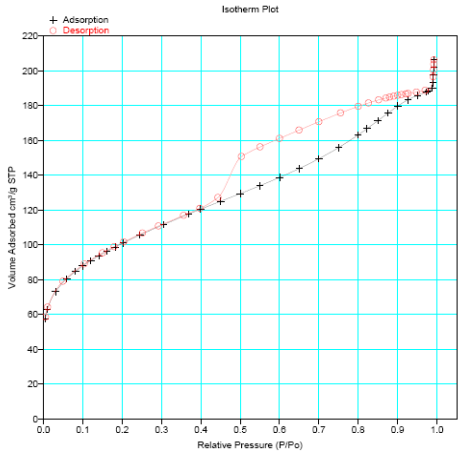

Fig 3.12 Isotherm of the sample CA_5_600

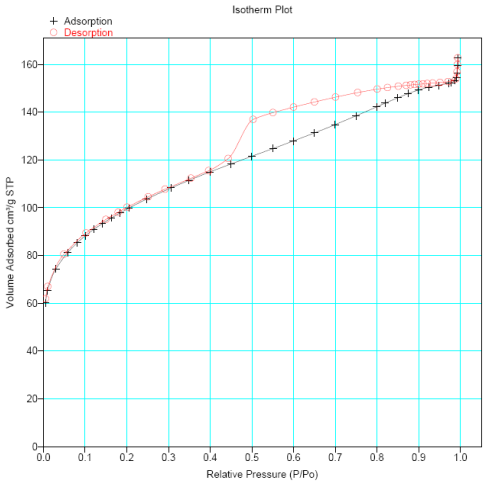

Fig 3.13 Isotherm of the sample CA_5_700

Samples impregnated with a 50 % solution show a predominance of mesoporous and can be assimilated to a type IV according to the IUPAC classification. At 600ºC (CA_5_600) the highest adsorption volume is reported for that concentration.

As the impregnation concentration is increased the mesoporous volume also increases instead of the microporous volume, as can be observed in table 3.3.

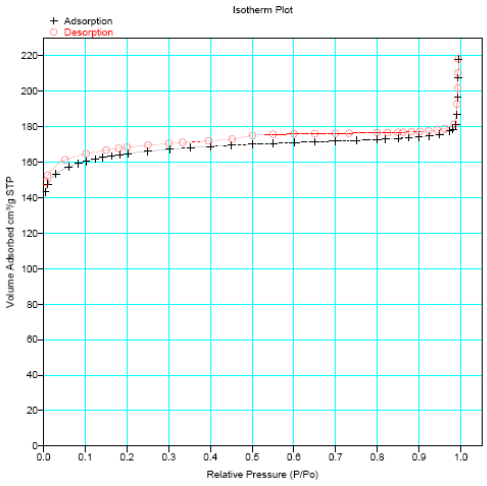

Fig 3.14 Isotherm of the sample TA_600

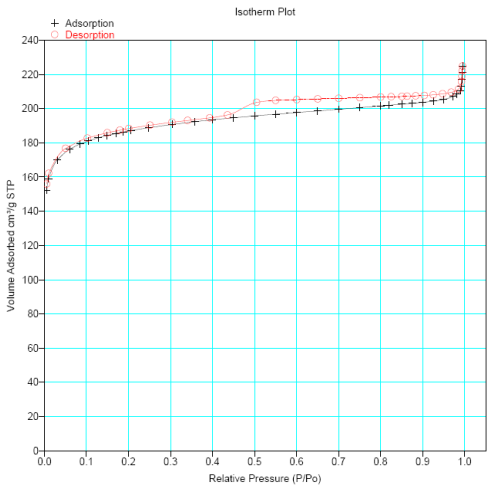

Fig 3.15 Isotherm of the sample TA_700

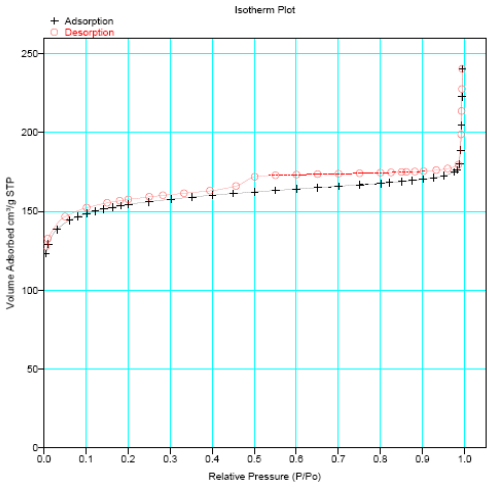

Fig 3.16 Isotherm of the sample TA_800

Samples activated by steam show a type I isotherm according with the IUPAC characterized for a well-developed microporosity. In these kinds of isotherm adsorption takes place at low pressure and there are essentially micropores. TA_700 show the highest adsorption volume for the physical activation (fig. 3.15)

Table 3.3 shows the total adsorption pore volume of pores less than 2500 Å diameter at P/P_0=0,99 compared to the micropore volume calculated by t-plot equation as well as the BET surface area and the pore diameter for each sample.

SAMPLE	H3PO4 (%)	Tª	BET (m2/g)	pore diameter (Å)	pore volume (cm3/g)	micropore volume (cm3/g)
CA_3_500	30	500	522,52	27,50	0,359	0,087
CA_4_500	30	600	53,41	46,76	0,062	0,0005
CA_5_500	30	700	84,44	28,77	0,061	0,007
CA_3_600	40	500	605,29	33,46	0,506	0,071
CA_4_600	40	600	695,59	33,67	0,585	0,101
CA_5_600	40	700	420,71	35,84	0,377	0,033
CA_3_700	50	500	233,17	38,13	0,222	0,015
CA_4_700	50	600	359,66	33,20	0,299	0,031
CA_5_700	50	700	352,43	27,10	0,239	0,046
TA_600	-	600	566,51	20,38	0,289	0,214
TA_700	-	700	641,27	20,55	0,329	0,232
TA_800	-	800	533,14	21,91	0,292	0,184

Table 3.3 Results of total pore volume, micropore volume, pore diameter and BET surface area of activated carbons with the concentration agent and temperature of activation

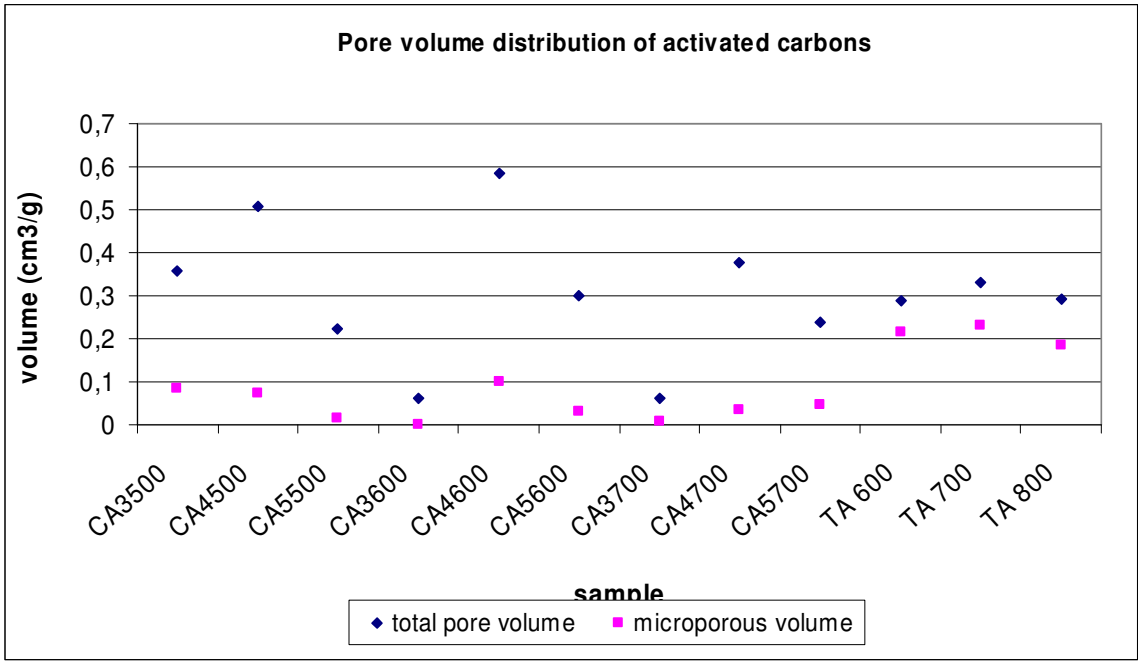

Fig 3.17 Total pore volume and micropore volume for both activations

As can be seen in figure 3.17, taking in consideration samples burned off at the same temperature there is an increase of the total pore volume for samples impregnated by 30% to 40% but decreases for 50% samples. A. Reffasa et al (2) reported that this increase in total pore volume might be associated to polyphosphates enhancing mesopores formation and widening microporous.

Activated carbons produced from coffee residues activated at 500ºC show that as the concentration is higher microporous volume decrease favouring the formation of mesoporous due to the increase in total pore volume; some researchers (2,25,27) reported similar results. On the other hand, this is not observed for the other activation temperatures, due to in 50% the results are similar for all activation temperatures and for 40% there is an increase in micropore volume from 500ºC to 600ºC but decreases increasing the temperature till 700ºC.

Taking into account the temperature as factor in the pore volume can be noticed that samples impregnated with 40% and 50% phosphoric acid solutions, activation increase with an increase in temperature from 500ºC to 600ºC and decrease with an increase in temperature to 700ºC this has been reported in other studies (6,43).

Activated carbons produced for 40% concentrations reported the highest total pore volume and the micropore volume show high results as well. However, samples impregnated with the 30% aqueous solution show an unusual very low total pore volume and micropore volume for samples burned off at 600ºC and 700ºC may be caused for using a diluted phosphoric acid solution, although CA_3500 show normal values.

On the other hand, activated carbons show a prevalence of micropores and a low mesopores volume treated by steam and is also observed narrower width where the average pore diameter (table 3.3) is significantly lower compared to the samples prepared by chemical activation.

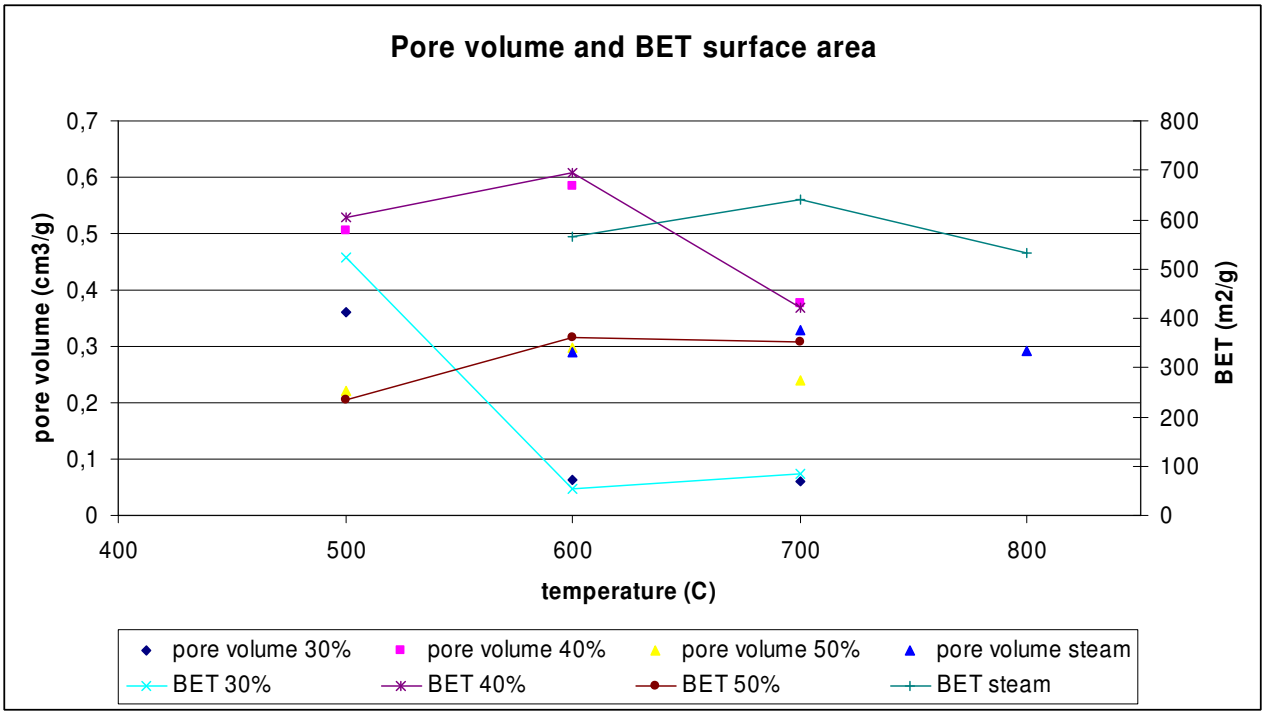

Fig 3.18 Results of total pore volume and BET surface area

As can be seen in table 3.3 and figure 3.18, there is a relation between the BET surface area and the pore volume, as the BET surface area increases or decreases also does the total pore volume for all samples of both activations. Also as the BET surface is higher also does the pore volume, hence for 40% are achieved the highest pore volume and greater BET surface areas.

Samples treated by steam and 40% show high surfaces areas but total pore volume is lower for the steam ones.

CONCLUSIONS

The use of coffee residues to produce activated carbon proves to be a good precursor but showed different results in order to the activation method employed. Activated carbons were prepared by physical activation using steam (oxidizing gas) and by chemical activation using phosphoric acid. Both activations were used to assess surface physical properties so that they serve as adsorbents. Steam activation works in the removal of all undesirable materials while the chemicals try to bond and create linkages between carbon and volatile materials as was shown in an increase in the carbon yield and a decrease in the burn off. This can be explained by the formation of phosphate linkages caused by the interaction of the phosphoric acid and the coffee residues compounds. It was also showed that there was a big loss of the percentage of volatile for samples treated by steam compared with the ones impregnated by chemical.

In this study the concentration of chemical, thermal and physical activation have been taken into consideration as main factors. Generally, increasing the activation temperature and the chemical concentration (from 40% to 50%) also did the carbon yield probably due to the phosphate linkages formed during the activation step. Samples treated by steam showed a decrease of the yield as the temperature was increased due to more reactivity of water at high temperatures.

All samples showed a relation between the BET surface area and the pore volume, as the BET surface area was increased or decreased also did the pore volume. Increasing the concentration from 30% to 40% there were an increase in the total pore volume and the BET surface area but decreased for 50% samples due to the action of phosphoric acid enhancing mesoporous and widening microporous.

Increasing the temperature from 500ºC to 600ºC BET surface area and pore volume were improved while increasing the temperature till 700ºC the results were slightly worse. So the best results are showed at 600ºC for all concentrations.

On the chemical activation were obtained different adsorption results considering the concentration of phosphoric acid; low concentrations (30%) showed the lowest surfaces areas as well as the adsorption volume and there were a predominance of macropores caused probably by the diluted concentration. On the other hand, samples impregnated

with a 40% phosphoric acid solution showed the best results leading to higher porosity and adsorption capacities. These samples showed the highest adsorption volume, especially at 600ºC, and highest BET surfaces areas, around 690 m^2/g, as well as higher total pore volume values. At this concentration and temperature with predominance of mesopores with appropriate values of micropore volume seems to be the most suitable conditions to produce activated carbon from coffee residues.

Samples treated by steam showed a large microporosity (high micropore volume), the narrowest pore diameter and also high surfaces areas so this treatment might also be a suitable choice to produce activated carbon. However, steam treatment also showed the lowest yields and the highest ash contents (20-25%).

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ABSTRACT

Activated carbons are one of the most used adsorbents with lots of applications in many sectors. Activated carbons can be produced from lignocellulosic materials with a large content of carbon. Coffee is the second trade most consumed all over the world; hence their residues can be treated in order to give a value.

In order to evaluate the viability of using coffee residues as precursor have been carried out experiments by chemical and physical activation. The chosen chemical was phosphoric acid, a dehydrating chemical widely used in production of activated carbons while steam was selected for a physical activation.

In this study have been studied the temperature activation and the concentration of chemical as the main factors. One of the advantages of using a chemical is the lower activation temperature; in this study were selected 500ºC, 600ºC and 700ºC while samples treated by steam were 600ºC, 700ºC and 800ºC. Water is a reactive agent that removes volatile compounds and makes wide pores whereas chemicals create linkages with the carbon and volatile compounds enhancing their porosity. Hence, have been studied the following impregnation concentrations 30%, 40% and 50% in order to evaluate their properties as adsorbents.

Isotherms were analysed to determine their surface area and pore size distribution. Also were determined the pore size and pore volume for all samples.

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CONTENTS

Characterization of activated carbon produced from coffee residues by chemical and physical activation

JAVIER SÁNCHEZ AZNAR

KTH Chemical Science and Engineering

Master Thesis in Chemical Engineering
Stockholm, Sweden, March 2011