PREPARATION OF ACTIVATED CARBONS FROM WASTE TYRES CHAR IMPREGNATED WITH POTASSIUM HYDROXIDE AND CARBON DIOXIDE GASIFICATION

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by

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LIST OF ABBREVIATIONS

AC	Activated carbon
BET	Brunuer, Emmet and Teller
BJH	Barrett-Joyner-Halenda
CH_4	Methane
CO_2	Carbon dioxide
DR	Dubinin-Radushkevich
DOE	Design of Experiment
EA	Elemental Analyzer
IR	Impregnation ratio
FTIR	Fourier Transform Infrared
HCL	Hydrocloric acid
IUPAC	International Union of Pure and Applied Chemistry
KOH	Potassium hydroxide
N_2	Nitrogen
rpm	Rotation per minute
SEM	Scanning Electron Microscopy
SSE	Sum of error squares
TEM	Tranmission Electron Microscopy
TGA	Thermogravimetric Analyzer

LIST OF SYMBOLS

C	Intercept	Dimensionless
C_e	Equilibrium concentration of adsorbate	mg/L
C_o	Initial concentration of adsorbate	mg/L
C_t	Concentration of adsorbate at time, t	mg/L
q_e	Amount of adsorbate adsorbed at equilibrium	mg/g
$q_{e,calc}$	Equilibrium adsorption capacity obtained from calculation of models	mg/g
$q_{e,\exp}$	Equilibrium adsorption capacity obtained from experiment data	mg/g
q_t	Amount of adsorbate adsorb per unit weight of adsorbent at time, t	mg/g
K_L	Langmuir isotherm constant	L/mg
K_F	Freundlich constant	$(mg/g)(L/mg)^{1/n}$
k_1	Rate constant of pseudo-first order sorption	1/h
k_2	Rate constant of pseudo-second order sorption	g/h.mg
k_i	Intraparticle diffusion rate parameter	$mg/g.\ h^{1/2}$
M_1	Concentration of initial adsorbate solution	mg/L
M_2	Concentration of final adsorbate solution	mg/L
N	Number of data points	Dimensionless
n	Freundlich heterogeneity factor	Dimensionless
p/p^o	Relative Pressure	Dimensionless
Q_o	Maximum adsorption capacity corresponding to complete monolayer coverage	mg/g
R_L	Langmuir separation factor	Dimensionless

R^2	Correlation coefficient	Dimensionless
S_{BET}	Total BET surface area	m^2/g
S_{mic}	Micropore area	m^2/g
S_{meso}	Mesopore area	m^2/g
$t^{1/2}$	Half adsorption time	g/h. mg
V	Volume of solution	L
V_1	Volume of initial adsorbate solution	mL
V_2	Volume of final adsorbate solution	mL
V_{mic}	Micropore volume	cm^3/g
V_{meso}	Mesopore volume	cm^3/g
V_{tot}	Total pore volume	cm^3/g
v	Stretching	Dimensionless
w	Weight of adsorbent	g
w_{ac}	Weight of activated carbons	g
w_c	Weight of chars	g
w_{KOH}	Weight of potassium hydroxide	g
w_{wt}	Weight of waste tyre	g

PENYEDIAAN KARBON TERAKTIF DARIPADA ARANG TAYAR TERBUANG DIJERAP ISI DENGAN KALIUM HIDROKSIDA DAN PENGGASAN KARBON DIOKSIDA.

ABSTRAK

Penghasilan karbon teraktif daripada bahan pepejal terbuang merupakan salah satu daripada penyelesaian masalah alam sekitar yang mesra alam dengan mengubah bahan terbuang yang bernilai negatif kepada bahan yang bernilai. Oleh itu, objektif utama penyelidikan ini ialah menyediakan karbon teraktif daripada tayar terbuang menggunakan kaedah fizikal kimia dua langkah. Proses pengkarbonan dijalankan pada suhu 800°C di bawah kadar aliran nitrogen 150 ml/min. Arang terhasil dijerap isi dengan kalium hidroksida (KOH) pada nisbah jerap isi yang berbeza (3, 4 dan 5). Arang yang telah dirawat secara kimia kemudiannya melalui proses pengaktifan pada pelbagai suhu pengaktifan (750°C, 800°C dan 850°C) di bawah masa penggasan karbon dioksida (CO_2) yang berbeza (1 dan 2 jam). Keadaan yang paling sesuai bagi penyediaan karbon teraktif ialah pada suhu 850°C, nisbah jerap isi 5 dan masa penggasan CO_2 selama 2 jam, dan ia dinamakan sebagai AC850(5)2. Melalui pemerhatian, AC850(5)2 memberikan luas permukaan yang tertinggi sebanyak 353.49 m^2/g dan isipadu liang keseluruhan sebanyak 0.64 cm^3/g dengan pecahan liang meso yang tinggi sehingga mencapai 90.55%. Diameter purata AC850(5)2 ialah di dalam lingkungan meso (4.92 nm). Prestasi kapasiti penjerapan bagi karbon teraktif yang disediakan di dalam penyelidikan ini dikaji dengan menggunakan 2 jenis bahan jerap yang berbeza iaitu metilena biru dan fenol. Penjerapan secara berkelompok dijalankan pada pelbagai kepekatan awal (100-500 mg/L) pada suhu

bilik (30ºC) selama 48 jam. Kapasiti penjerapan didapati telah meningkat dengan peningkatan kepekatan awal. Bahan penjerap AC850(5)2 telah menunjukkan kapasiti penjerapan maksimum bagi metilena biru dan fenol iaitu masing-masing sebanyak 200.00 mg/g dan 192.31 mg/g. Bagi penjerapan metilena biru kepada bahan penjerap AC850(5)2, data penjerapan adalah berpadanan dengan garis sesuhu model Langmuir dengan nilai R^2 sebanyak 0.9999. Manakala bagi penjerapan fenol kepada bahan penjerap AC850(5)2, data penjerapan dapat dihuraikan dengan baik oleh garis sesuhu model Freundlich dengan nilai R^2 sebanyak 0.9380. Kajian kinetik bagi kedua-dua sistem penjerapan mematuhi model kinetik pseudo tertib kedua. Keputusan penyelidikan ini menunjukkan bahawa karbon teraktif daripada tayar terbuang adalah bahan penjerap yang menarik untuk penyingkiran metilena biru dan fenol daripada larutan akuas.

PREPARATION OF ACTIVATED CARBONS FROM WASTE TYRES CHAR IMPREGNATED WITH POTASSIUM HYDROXIDE AND CARBON DIOXIDE GASIFICATION

ABSTRACT

The production of activated carbons from solid wastes is one of the most environment-friendly solutions by transforming negative–valued wastes to valuable materials. Thus, the main objective of this research was to prepare activated carbons from waste tyres using two-step physiochemical activation method. The carbonization process was carried out at 800°C for 1 hour under nitrogen flow rate of 150 ml/min. The char products were impregnated with potassium hydroxide (KOH) at different impregnation ratios (3, 4 and 5). The chemically treated chars were then proceed to the activation process at various activation temperatures (750°C, 800°C and 850°C) under different carbon dioxide (CO_2) gasification time (1 and 2 h). The most suitable conditions for the preparation of activated carbons were found at temperature of 850°C, impregnation ratio 5 and CO_2 gasification time 2 h, namely as AC850(5)2. It was observed that AC850(5)2 gives the highest surface area of 353.49 m^2/g and total pore volume of 0.64 cm^3/g with high mesopore fraction up to 90.55%. The average pore diameter of AC850(5)2 was in the meso range (4.92 nm). The adsorption capacity performances of prepared activated carbons in this work were investigated using two different adsorbates; methylene blue and phenol. The batch adsorption study was carried out at different initial concentrations of adsorbates (100-500 mg/L) at room temperature (30ºC) for 48 h. The adsorption capacity was found to increase with increasing of initial concentrations. AC850(5)2 adsorbent

presents the maximum adsorption capacities for methylene blue and phenol adsorption which are 200.00 mg/g and 192.31 mg/g respectively. For methylene blue adsorption onto AC850(5)2 adsorbent, the adsorption data were fitted to Langmuir isotherm with R^2 value of 0.9999. Whereas for phenol adsorption onto AC850(5)2 adsorbent, the adsorption data were described well by Freundlich isotherm with R^2 value of 0.9380. The kinetics studies on both adsorption systems obeyed the pseudo second order kinetic model. The result in this study indicated that activated carbon from waste tyres was an attractive adsorbent for removal of methylene blue and phenol from aqueous solutions.

CHAPTER ONE

INTRODUCTION

1.1 Waste tyre and problem disposal

The automobile has become an indispensable means of transportation for many households throughout the world. Thus, the disposal of vehicle tyres represents a major environmental issue throughout the world. Globally more than 330 million tyres are discarded every year and accumulated over the years in different countries (Cunliffe and Williams, 1999). In Malaysia, an estimated 150,000 tonnes of waste tyres per year are dumped mostly in an illegal process. The disposal and reprocessing tyres are difficult since they contain complex mixture of different materials such as rubber, carbon black, steel cord and other organic and inorganic minor components (Rodriguez *et. al*, 2001).

There are major aspects of tyre problems such as tyres stockpiles provide breeding ground for mosquitoes and vermin, this in turn, causing serious disease and affecting human health. Fire hazards in large stockpiles could consequently cause uncontrollable burning and air pollution where it will be emitting large amounts of thick black smoke and noxious gases including carcinogens. Other than that, the current "conservation of natural resources concept", i.e the reuse (retreat) first, then reuse the rubber prior disposal, does not accommodate the ever increased dumping of tyres. In fact, due to the high cost of legal disposal for tyres, illegal dumping may increase. The disposal of tyres is also becoming more expensive, while this trend is likely to continue as landfill space becomes more scarcer (Mui *et al.*, 2004).

Several attempts have been made to reduce the number of waste tyres, for example, by using them as a dock bumper, playground equipment, artificial reefs and others. Other than that, Jang *et al.*, (1998) also reported the used of discarded tyres as highway cash barrier which was studied in the late 1970s by the Texas Transportation Institute. However, no widespread use of tyres in this application has occurred. Therefore, from environmental and economical points of view, a much better solution is to convert such waste tyres into valuable products (Ariyadejwanich *et al.*, 2003).

A possible solution to overcome tyre problems would be recycling this cheap and plentiful resource as raw materials in alternative processes. In general, recycling is the economic reuse of materials from wastes like tyres to obtained improved products and energy. Their high volatile, carbon contents and higher heating value make them excellent material for energy recovery with the appropriate technology (Gonzalez *et al.*, 2001). Pyrolysis, incineration and gasification processes are considered to be more attractive and practical methods for recovering energy and by products such as carbon black, activated carbon and etc. from waste tyres.

Recently, much effort has been devoted to the thermal degradation of tyres into gaseous and liquid hydrocarbons and solid char residue, all of which have the potential to be processed into valuable products. The resulting hydrocarbons from thermal treatment can be used directly as fuel or added to petroleum refinery feedstocks. As for solid residue, the char can be used either as low–grade reinforcing filler or as activated carbon. However, reprocessing of the char from pyrolysis of

waste tyres into activated carbon has been considered to be a profitable way to convert this material into valuable product.

The activated carbons produced from tyre rubber could have commercial value in the (a) water purification (dissolved organics and toxic compounds, dechlorization, dye removal, municipal drinking water treatment, swimming pools etc.), (b) air purification (volatile inorganic and organic removal , solvent recovery, gas desulfurization, etc.), (c) special application such as batteries, fuel cells, nuclear power station, and (d) others such as cigarette filters and food industry (Zabaniotou and Stavropoulos, 2003).

Thus, the production of activated carbon adsorbents from waste tyre rubber can provide a two-fold environmental and economic benefit: A recycling path is created for waste vehicles tyres and new adsorbents are produced for commercial use in wastewater treatment.

1.2 Utilization of waste tyre using pyrolysis process

Many years back, incineration (without the recovery value) and landfill were the main and practical means for dealing with the problem of waste tyres. However, in light of the overall environmental impact along the drive toward energy and material conservation, more emphasise now has been given to the new disposal options having higher energy recovery values, and also being attractive environmentally.

From the comparison of different disposal available such as cryogenic pulverization, thermal destruction technologies (incineration with energy recovery), pyrolysis etc., it has been observed that pyrolysis appears to be the most viable means of waste tyres treatment and has a promising future (Fortuna *et al.*, 1997). Basically, pyrolysis involves the decomposition of organic wastes at high temperatures in an inert atmosphere or under vacuum. This process presents an alternative to scrap tyre disposal in landfill sites and can result in the recovery by a typical of useful products in an environmentally friendly manner. The products recovered by a typical pyrolysis process are usually, 33-38 wt% pyrolytic char, 38-55 wt% oil and 10-30 wt% gas fractions.

Pyrolysis offers an environmentally attractive method to decompose a wide range of wastes chemically (using system working at high temperature and oxygen-free environment), producing lower emission of nitrogen-oxide, sulphur-oxide and side by side valuable reusable products. For example, the oil and gas can be used as fuels within the pyrolysis system or for an adjacent plant such as combined heat and power system. The principle phases of pyrolysis process are given in Table 1.1 (Fortuna *et al.*, 1997).

Table 1.1: The principle phases of pyrolysis process (Fortuna *et al.*, 1997)

Temperature, (°C)	Phases of pyrolysis process
20-100	Mainly a dry phase meant for water removal and vapour formation
100-150	Starting of thermal degradation reaction
200-500	De-polymerisation, H_2S separation, formation of olefin, paraffin hydrocarbons and permanent gas.
500-600	Decomposition of long chain hydrocarbon into H_2, CO_2, CH_4 and olefin.
>600	Mainly aromatic radical reactions with the formation of aromatic compounds take place.

1.3 Activated carbon

Activated carbon can be defined as highly porous, carbonaceous materials. Commercial activated carbons have surface areas greater than 400 m^2/g and many have areas over 1000 m^2/g (Merchant and Petrich, 1993). Generally, the commercial activated carbon was produced using two step physical activation consist of carbonization and activation process using steam as activating agent and this process will be discussed later in Chapter 2. Plate 1.1 shows the process flow for preparation of powdered activated carbon from sawdust obtained from Century Chemical Works Sdn. Bhd., (2006) as one of the local activated carbons producer. Table 1.2 lists the local activated carbon producers in Malaysia.

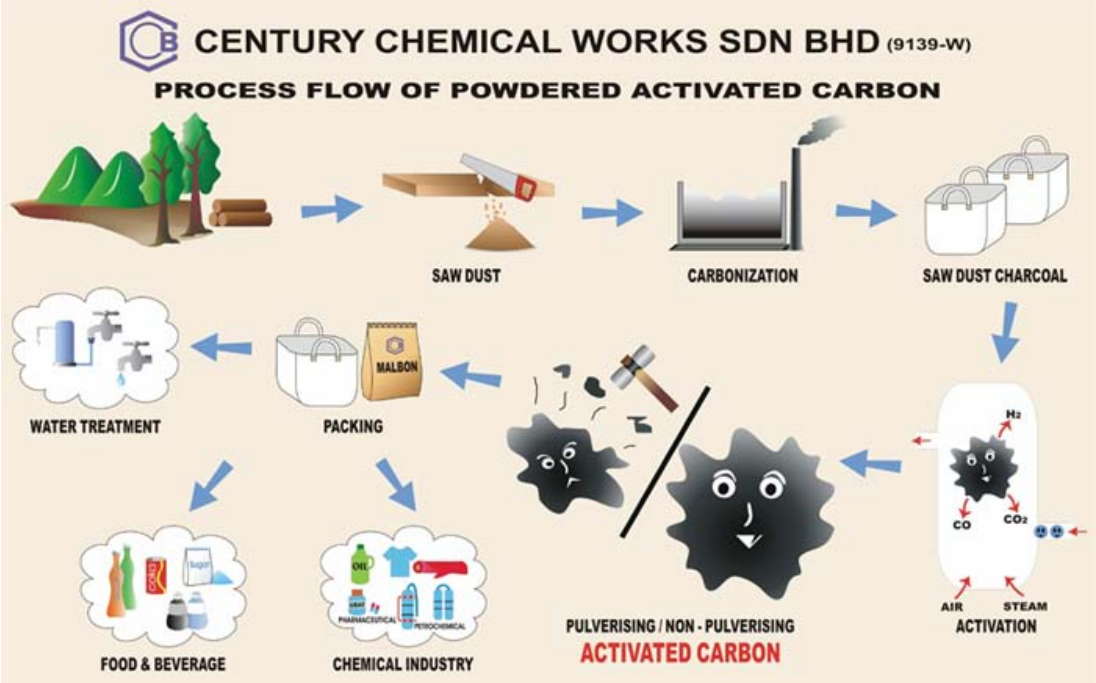


Figure 1.1: The process flow of powdered activated carbon (Century Chemical Works Sdn. Bhd., 2006)

Table 1.2: List of local producer commercial activated carbons in Malaysia

Name of producer	Raw material used	Type of activated carbon	Surface area (m^2/g)
Century Chemical Works, Penang	Sawdust charcoal	Powder form	800-1000
Effigen Sdn Bhd	Coconut shell	Granular and powder form	-
Laju Carbon Product Sdn. Bhd (LCP), Selangor.	Coconut shell	Granular, pellets and powder form	500-2500

1.4 Activated carbon adsorbents for waste water removal

Increasing demand for adsorption processes in the water treatment industry encourages research in the production of activated carbon from alternative precursors including industrial wastes and algricultural by-products. In wastewater treatment, activated carbon is a powerful adsorbent because it has a large surface area and pore volume, which allows the removal of liquid-phase contaminants, including organics pollutants, heavy metal ions and colors (Hsieh and Teng, 2000).

Generally, activated carbon is used for the tertiary treatment of wastewater in many industries, for example, food, textile, chemical and pharmaceutical. In some applications, molecules cannot easily penetrate into the micropores especially those involving large molecules to adsorb onto them, so the produced activated carbons should posses not only micropores but also interconnecting mesopores (Hsieh and Teng, 2000; Tamai *et al.*, 1999). Due to this reason, waste tyres give another important source of raw material because highly mesoporous activated carbons can be produced from waste tyres rubber (Ariyadejwanich *et al.*, 2003). Mesopores activated carbon is one of the most important characteristics in the liquid phase adsorption. Moreover, owing to the high surface areas (ranging from 164 to 1260

m^2/g) and pore volumes (up to 1.62 cm^3/g), tyre carbon are considered as a potential adsorbent in water treatment for the purpose of removing dye and organic pollutants such as phenol and chlorophenol (Mui *et al.*, 2004).

1.5 Problem statement

During the past 10 to 15 years, there are many fundamental studies reported on the production of activated carbon from pyrolysis of waste tyres using conventional method; physical and chemical activation process. The potential of these products as possible adsorbents for various pollutants has been assessed and found very successful, thus stimulating a serious research interest.

The latest approach in activated carbon production technology is physiochemical activation. This method is derived from combination of both physical and chemical activation method. From the literatures, it was found that this method could present a very high quality activated carbon in terms of surface area, pore volume and porosity (Hu *et al.*, 2003; Hu and Srinivasan, 2001; Tseng *et al.*, 2006; Wu and Tseng, 2006).

Since there is no research have been done yet using this physiochemical activation method in production of activated carbon from tyres, this study was carried out to investigate the performances of the prepared activated carbon using this method. The main purpose of the present work is to prepare highly mesoporous activated carbon from waste tyres which are suitable for adsorbing relatively large molecules.

1.6 Objectives

i. To prepare activated carbons from waste tyres through two-step physiochemical activation under different operating parameters and preparation variables such as activation temperature, impregnation ratio KOH/char and CO_2 gasification time.

ii. To establish the best conditions for producing activated carbons using waste tyres.

iii. To investigate the physical characteristics and surface chemistry of the prepared activated carbons.

iv. To study the equilibrium, isotherm and kinetics of methylene blue and phenol adsorption on the best activated carbon.

1.7 Scope of study

In this study, waste tyres were used as raw material in preparation of activated carbon adsorbent using two-step physiochemical activation method. The experiments were carried out in a batch muffle furnace which can heat up to a temperature of 1000°C. Potassium hydroxide (KOH) was selected as chemical agent in the impregnation procedure because it was found to be more effective than other chemical agents such as $ZnCl_2$ and H_3PO_4 in creating porosity in activated carbons derived from tyres (Teng *et al.*, 2000). Whereas, the activating agent used in the activation process was carbon dioxide gas.

The effects of various preparatory conditions including different activation temperature (750, 800 and 850ºC), impregnation ratio of KOH/char (3, 4 and 5) and CO_2 gasification time (1 and 2 h) was studied in order to establish the optimum

conditions for producing high surface area activated carbons using waste tyres. The prepared activated carbons were also characterized by using Micromeritics ASAP 2000, SEM, FTIR, TGA and EA to determine the physical characteristics and surface chemistry of the prepared activated carbons.

Two different adsorbates were used in the adsorption studies which are methylene blue and phenol to determine the performances of activated carbon adsorbent. The effect of initial concentration of adsorbate (100-500mg/L) and contact time (48 h) were carried out in the adsorption study. The experimental data are crucial in determination of the adsorption isotherm of the samples using Langmuir and Freundlich adsorption isotherm model followed by kinetic study. This kinetic study was carried out by using pseudo-first order, pseudo-second order and intraparticle diffusion models. The validity of each model was confirmed by judging the correlation coeffient, R^2 value and % SSE.

1.8 Organization of thesis

Chapter 1 includes a brief introduction on waste tyres problem and utilization waste tyres using pyrolysis process to produce the activated carbon. This chapter also enclosed with application of activated carbon in wastewater treatment. The problem statement of the research is stated to give clear objectives of the present study. The scope of the study covers the research work done to meet these objectives.

Chapter two covers the history of activated carbon and methods of preparation of activated carbons that have been applied by researchers. In addition, this chapter also gives a brief explanation on the physical and chemical properties of activated

carbon obtained from the characterization study. Finally, the last part discusses in details about the adsorption study including the adsorption isotherm and kinetic study used in this present work.

Chapter three provides list of materials and chemicals reagents used in the present research work. It also gives the general description of the equipment used in the activated carbon preparation system. It continues with the explanation on the methods and analysis required on preparation of activated carbon followed by adsorption studies. The description of equipments used for characterization of activated carbon is also included in this chapter.

Chapter four presents the result obtained from the experiments in the preparation of activated carbon, characterization of activated carbon and adsorption studies. Each of the results will be followed by the discussion and comparison between the present results and the results obtained by others researchers. This explanation clearly describes the performance of activated carbon from present study.

Chapter five gives the conclusions of the results obtained in the present study. Some recommendations for the future studies are also included in this chapter.

CHAPTER TWO

LITERATURE REVIEW

2.1 Definition of activated carbon

Activated carbon includes a wide range of amorphous carbon-based materials prepared to exhibit a high degree of porosity and an extended interparticulate surface area. It is also common term used for a group adsorbing substances of crystalline form, having large internal pore structures that make the carbon more adsorbent.

2.1.1 History of activated carbon and summary of its uses

The use of carbon extends far back into its history. Charcoal was used for drinking water filtration by ancient Hindus in India, and carbonized wood was used as a medical adsorbent and purifying agent by the Egyptians as early as 1500 B.C (Parker, I. and Hughes, D., 2008). In contrary, modern development and use has been documented more precisely. Activated carbon was first generated industrially in the first part of the twentieth century, when activated carbon from vegetable material was produced for use in sugar refining.

In the early 19^{th} century in Europe, powdered activated carbon was first produced commercially by using wood as a raw material. In the United States, the first production of activated carbon used black ash as the source, after it was accidentally discovered that the ash was very effective in decolorizing liquids. Activated carbon has been used extensively for this purpose in many industries such as textile industry for the removal of organic dyes.

The first documented use of activated carbon in a large scale water treatment application was in 19th century in England, where it was used to remove undesirable odors and tastes from drinking water. In recent years, the use of activated carbon for the removal of priority organic pollutants has become very common. Today, hundreds of brands of activated carbon are manufactured for a large variety of purposes. Generally, activated carbon is used in metal extraction (e.g. gold), water purification (especially in home aquariums), medicine, wastewater treatment, filters in gas and filter masks, filters in compressed air and gas purification, and many other applications.

The largest market for activated carbon is currently in the municipal water purification industry, where charcoal beds have been used for the dual purpose of physical filtration and sorption. In fact, activated carbon filters are used today in drinking water treatment to remove the natural organic compounds that produce carcinogenic chlorinated by-products during chlorine disinfection of water. In wastewater treatment, activated carbon is usually used as a filter medium in tertiary treatment processes. In these applications, carbon filters are usually quite effective in removing low concentrations of organic compounds, as well as some inorganic metals.

In addition to the drinking water and wastewater treatment applications, activated carbon also applicable in gas purification process. Filters with activated carbon are usually used in compressed air and gas purification to remove oil vapour, odor, and other hydrocarbons from compressed air and gas. The most common

designs use a 1 stage or 2 stage filtration principle where activated carbon is embedded inside the filter media.

Some other common uses included corn and cane sugar refining, gas adsorption, dry cleaning recovery processes, pharmaceuticals, fat and oil removal, electroplating, catalyst support, battery electrodes, alcoholic beverage production and supercapasitors.

2.1.2 Types of activated carbon

The types of activated carbon available in the current market are powder, granular and pellet. It is classified according to its particle sizes and shape, and each type has its specific application.

The size of powder activated carbon is less than 100μm in size with an average diameter between 15 and 25 μm. Thus, they present a large internal surface with a small diffusion distance. Powdered activated carbons are mainly used in liquid phase adsorption and flue gas treatment. In wastewater treatment, the most common used of powdered activated carbon is in the secondary treatment called powdered activated carbon treatment process (Norit Americas Inc., 2001).

Granulated activated carbon has a relatively larger particle size compared to powdered activated carbon and consequently, presents a smaller external surface. The size range is from 0.5 to 4.0 mm. This type of activated carbons is commonly used in water treatment facilities where the granular carbon bed to remove tastes,

colors, odors and dissolved organics. In addition, granular activated carbon can also be used for gas phase application.

Meanwhile, pellet activated carbon consists of extruded and cylindrical shaped activated carbon with diameters in the range of 4-7 mm and 8-15 mm length. Pellets activated carbon is mainly used for gas phase applications because of their low pressure drop, high mechanical strength and low dust content.

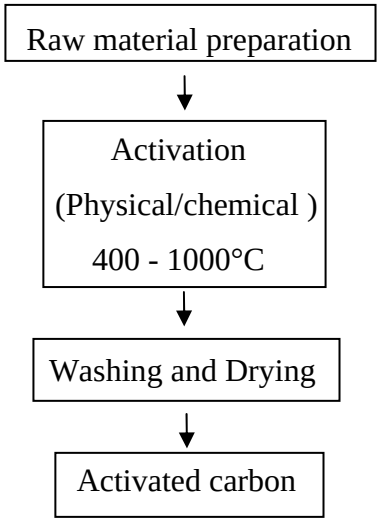
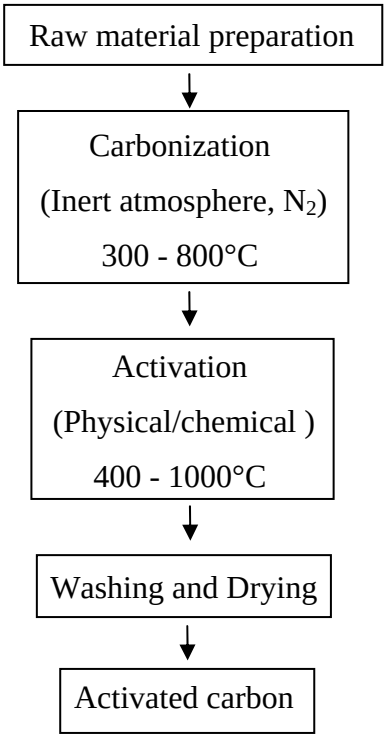
2.2 Activated carbon preparation

Activated carbon can be prepared from many carbonaceous materials including municipal and industrial wastes (Nakagawa *et al.*, 2004; Sainz-Diaz and Griffiths, 2000) and forest and agricultural by-products (Hu *et al.*, 2003; Hu and Srinivasan, 2001; Tseng, 2007; Tseng *et al.*, 2006; Wu and Tseng, 2006). Waste tyres are one of the interesting sources to prepare activated carbon because of their high carbon content. Several studies have reported on the production of activated carbon from waste tyres (Ariyadejwanich *et al.*, 2003; Gonzalez *et al.*, 2006; Helleur *et al.*, 2001; Laszlo *et al.*, 1997; Miguel *et al.*, 2003; Nakagawa *et al.*, 2004; Rozada *et al.*, 2005; Sainz-Diaz and Griffiths, 2000; Stavropoulos, 2005; Tanthapanichakoon *et al.*, 2005; Teng *et al.*, 2000)

Basically, there are 2 different methods in the preparation of activated carbon; single step pyrolysis and two step pyrolysis. Single step pyrolysis usually applied in the preparation of activated carbon using chemical activation method. However, the conventional preparation of activated carbon using physical activation method was based on two step pyrolysis where carbonization and activation process

takes place separately. The product quality of two step pyrolysis is better compared to the single step pyrolysis. Table 2.1 shows a block diagram and the summary of comparison for both procedures used in the preparation of activated carbon.

Table 2.1: Block diagram and comparison for both procedures used in the preparation of activated carbon (Din, 2005)

	Single Step Pyrolysis	Two Step Pyrolysis
Diagram		
Comparison	-Single stage process -Low energy consumption, cheap -Shorter process duration -Modest surface area and porosity	-Two stage process -High energy consumption and expensive -Longer process duration -High surface area and porosity

2.2.1 Carbonization

The terms carbonization means to convert organic matter to elemental carbon at high temperature in the absence of oxygen. This process drives off the volatiles matter to form char. The char obtained normally has low surface area and adsorption capacity since the porous structure is not well developed (Ahmad, 2006).

2.2.2 Activation

The activation process creates or increases porosity on the activated carbon surface as illustrated in Figure 2.1. There are three main activation process; physical activation, chemical activation and physiochemical activation.

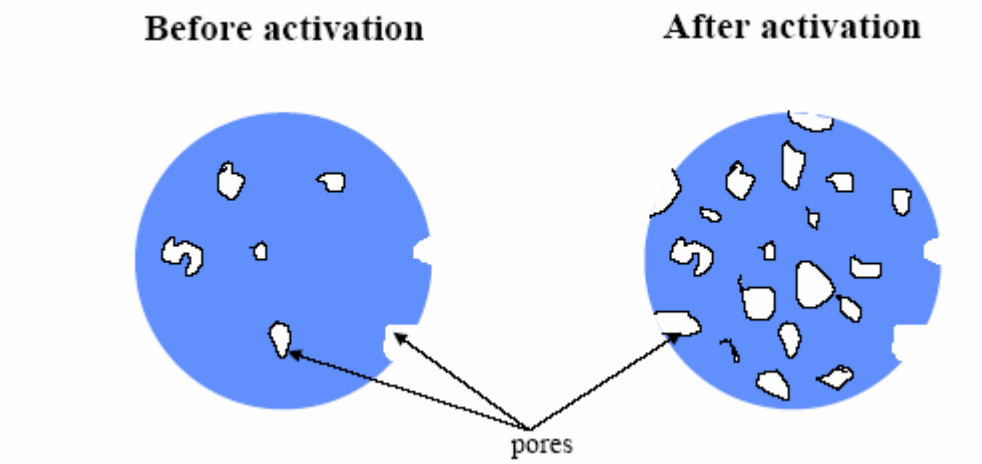


Figure 2.1: Two-dimensional representation of carbon activation (Lehmann, 1998)

2.2.2 (a) Physical activation

Physical activation using carbon dioxide or steam as oxidizing agents are the most commonly used processes in the production of tyre carbons. It is a conventional manufacturing process of activated carbon. The overall process usually consists of two steps: thermal pyrolysis at a relatively low temperature (typically 400-700^{o}C) in the presence of nitrogen or helium to break down the cross-linkage between carbon

atoms, and activation with activating gas at 800-1000^{o}C for further development of the porosity of tyre carbon (Mui *et al.*, 2004).

Carbon characteristics are greatly influenced by the degree of the activation but also by the nature of the activating agent (steam or carbon dioxide) and process temperature. For the purpose of elevating the degree of burn-off, the activation temperature is usually higher than 900^{o}C to maintain a sufficiently high reaction rate. A sharp increase in the surface area was observed when the activation took place at a temperature of 770^{o}C or above and based on current technologies and literature results (Mui *et al.*, 2004), tyre char activation below 700^{o}C is impractical. Previous studies have discover that steam is a better activating agent compare to CO_2 because the tyre char present higher reactivity with steam than with CO_2 (Miguel *et al.*, 2003; Zabaniotou and Stavropoulos, 2003). However, contradictory information has been published regarding the type of porosity generated by each activating agent.

Gonzalez *et al.*, (2006) studied the preparation of activated carbons from scrap tyres by gasification with both steam and carbon dioxide under different activation temperature and time. In the carbonization step, the temperature used was 800°C under nitrogen flow for 1 h and approximately a percentage of 43% chars were obtained from this process. Then the yielded chars proceed to the activation process under steam or carbon dioxide flow at different temperature and time ranging from 750 to 900°C and 1 to 3 h respectively. For burn-off higher than 50%, a slight increased in the average equivalent radius of micropores was observed, indicating a widening of the micropores. As the activation proceeds, this widening of the micropores can contribute to the strong increase of the mesoporosity detected in the

activated carbon. The highest BET surface area values of 1317 m^2/g and 496 m^2/g was obtained by activation with steam and carbon dioxide respectively. These results proved that steam is a better activating agent compare to CO_2. Figure 2.2 shows the thermal treatment scheme of two-step physical activation method applied in their work.

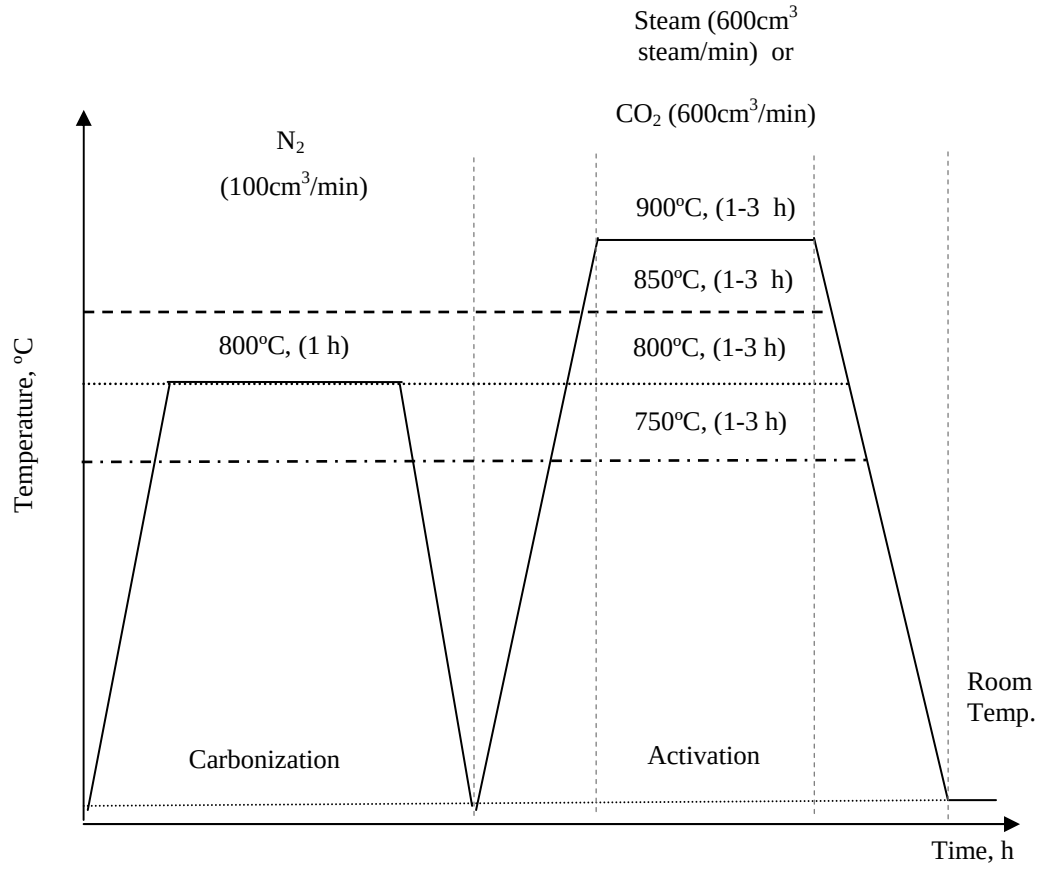


Figure 2.2: Thermal treatment scheme of two-step physical activation method (Gonzalez *et al.*, 2006)

In addition, the particle size of the tyre rubber was found to have influence on the porosity of the resultant carbon generated from steam activation. Both surface area and micropore volume of carbons produced from powdered tyre rubber (particle size < 0.42 mm) were 5% and 40% higher than those carbons prepared from particles in larger size (particle size < 2.0 mm) (Miguel *et al.*, 2003). It was believed that smaller particles allowed better diffusion of steam molecules into the structure,

leading to a more homogeneous activation of the carbonized precursor. However, it is worth noting that other research yielded a different point of view and suggested that particle size had not affected the surface area development in CO_2 activation (Teng *et al.*, 1995). Table 2.2 presents summary of previous works on preparation of activated carbons produced from waste tyres using physical activation method.

2.2.2 (b) Chemical activation

Chemical activation is another process for the production of activated carbon from tyres. It allows both pyrolysis and activation to be integrated into a single, relatively lower temperature process in the absence of oxygen. Chemical agents such as phosphoric acid, zinc chloride and potassium hydroxide act as dehydrating and stabilizing agents that enhance the development of porous structure in the activated carbon. Although wide varieties of activating agents are known, using potassium hydroxide (KOH) in making carbons has become popular in recent studies (Mui *et al.*, 2004). In addition, KOH also was found to be more effective than phosphoric acid and zinc chloride in creating porosity in activated carbons derived from tyres (Teng *et al.*, 2000).

Chemical activation offers several advantages since it is carried out in a single step which combining the carbonization and activation process, performed at lower temperatures, produced a much higher yield than the physical activation, and therefore resulting in the development of a better porous structure (Ioannidou and Zabaniotou, 2007; Lillo-Ródenas *et al.*, 2003). However, there are also some disadvantages of chemical activation process such as corrosiveness of the process and the washing stage (Teng and Lin, 1998).

Table 2.2: Summary of previous works on preparation of activated carbons produced by waste tyres using physical activation

References	Particle size of tyre rubber (mm)	Charring conditions (°C,h)	Activation conditions (°C,h)	Heating Rate ($°C\,min^{-1}$)	Activating Agent	Activating gas flow rate (ml/min)	BET surface Area (m^2/g)	Yield (g activated carbon/100g tyre rubber)	Equipment
Skodras *et al.*, (2007)		Temp=800 Time=0.75	Temp=900 Time= 2	-	Steam	-	358.5	-	Compact power pyrolysis plant
Gonzalez *et al.*, (2006)	0.5 - 1	Temp=800 Time=1	Temp=850 Time=3 Temp=900 Time=2	-	CO_2 Steam	600 600	496 1317	- -	Cylindrical refractory stainless steel reactor.
Ariyadejwanich *et al.*, (2003)	<0.595	Temp=500 Time=1	Temp=850 Time=4 Temp=850 Time=3	5 20	Steam	680	1119 1177	7.9 11.2	Quartz tube reactor
Lin and Teng *et al.*, (2002)	-	-	Temp=900 Time=1	-	Steam	-	602	-	Fixed bed reactor.
Helleur *et al.*, (2001)	~1	Temp=550 Time= 4	Temp=900 Time=3 Temp=875 Time= 7	20	Steam CO_2	135 342	272 270	-	Continuous ablative reactor (CAR), provided with a long coiled stainless steel tube

Table 2-2. Continued

Sainz-Diaz and Griffiths, (2000)	8	-	Temp=1000 Time=5 Temp=1000 Time=7	-	CO_2	-	431 284	33.0 -	Pilot-scale batch flaming pyrolyser
Cunliffe and Williams, (1999)	30	Temp=450 Time=1.5	Temp=935 Time= -	-	Steam	146	640	13.6	-
Allen *et al.*, (1999)	50	Temp=800 Time= - Temp=700 Time= -	Temp=877 Time= -	-	Steam	528 478	-	19.5 17.2	Steam saturated nitrogen atmosphere
Brady *et al.*, (1996)	2.5	Temp=600 Time=0.75	Temp=850 Time= 3	20	Steam	542	1031	10.0	Batch tubular (5.0cm OD) fixed bed reactor, (Lindberg, type 54232)
Streat *et al.*, (1995)	-	-	Temp=800 Time= 24 Temp=900 Time= 18	3	Steam	200 100	346 155	-	Tube furnace in a stream of oxygen free nitrogen

Teng *et al.*, (2000) prepared activated carbons from pyrolysis of waste tyres impregnated with KOH at impregnation ratio in the range of 0 to 8. Single step pyrolysis was applied at four different temperatures 600, 700, 800 and 900ºC under nitrogen flow at activation time 0, 1 and 2 h respectively. The carbon yield ranged from 11-26% where it was found to decrease with the increased pyrolysis temperature, holding time and impregnation ratio. In this work, the effect of mass ratio between KOH and tyre was proved to be an influencing factor to the pore development of carbon. The highest surface area performed at temperature 700ºC, impregnation ratio of 4 and zero holding time with a value of 474 m^2/g. Figure 2.3 shows the thermal treatment scheme of one-step chemical activation method utilized in their study.

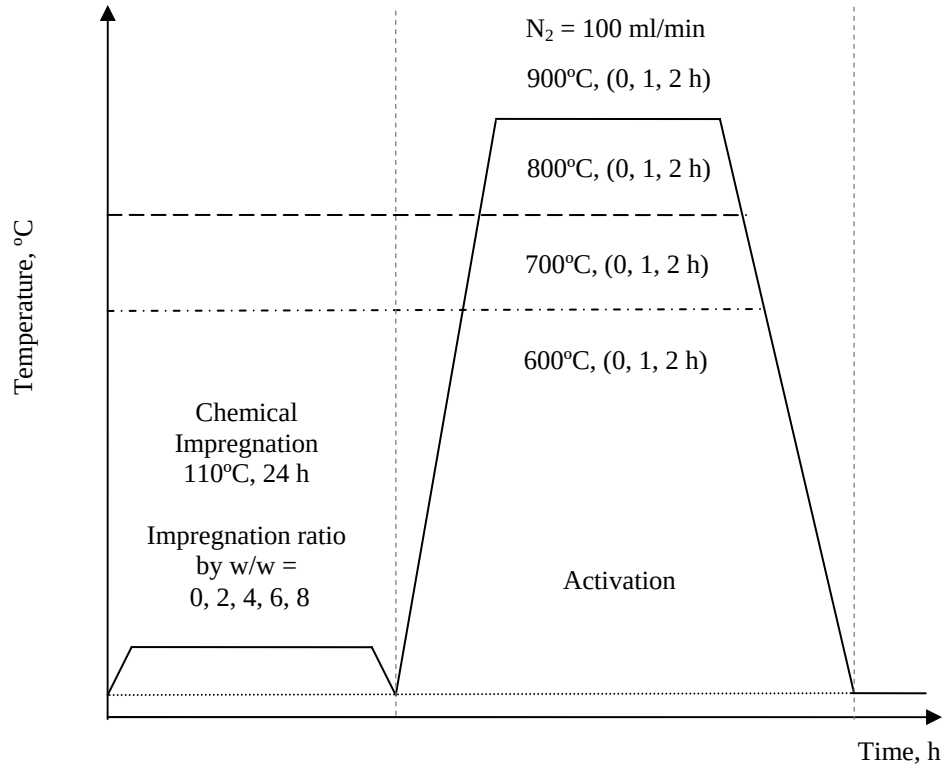


Figure 2.3: Thermal treatment scheme of one-step chemical activation method (Teng *et al.*, 2000)

In other finding, activated carbon were prepared from waste tyres through two-step chemical activation method (Stavropoulos, 2005). In this work, the waste tyres were carbonized first to produce char at temperature 800ºC for 1 h under nitrogen flow. Then, the chars were chemically treatment with KOH with KOH/char ratio 4:1 by weight. The mixture were activated in the furnace reactor system at 800ºC for three different activation times 1, 2 and 3 h. Carbon yield ranged from 55-63% which was slightly higher than that obtained by Teng *et al.*, (2000). The highest highest surface area up to 758 m^2/g was obtained at activation time 2 h. This literature proved that the product quality of two-step pyroysis is better compared to the single step pyrolysis. Figure 2.4 shows the thermal treatment scheme of two-step chemical activation method applied in this work. The summaries of previous works on preparation of activated carbons produced from waste tyres impregnated by KOH are shown in Table 2.3.

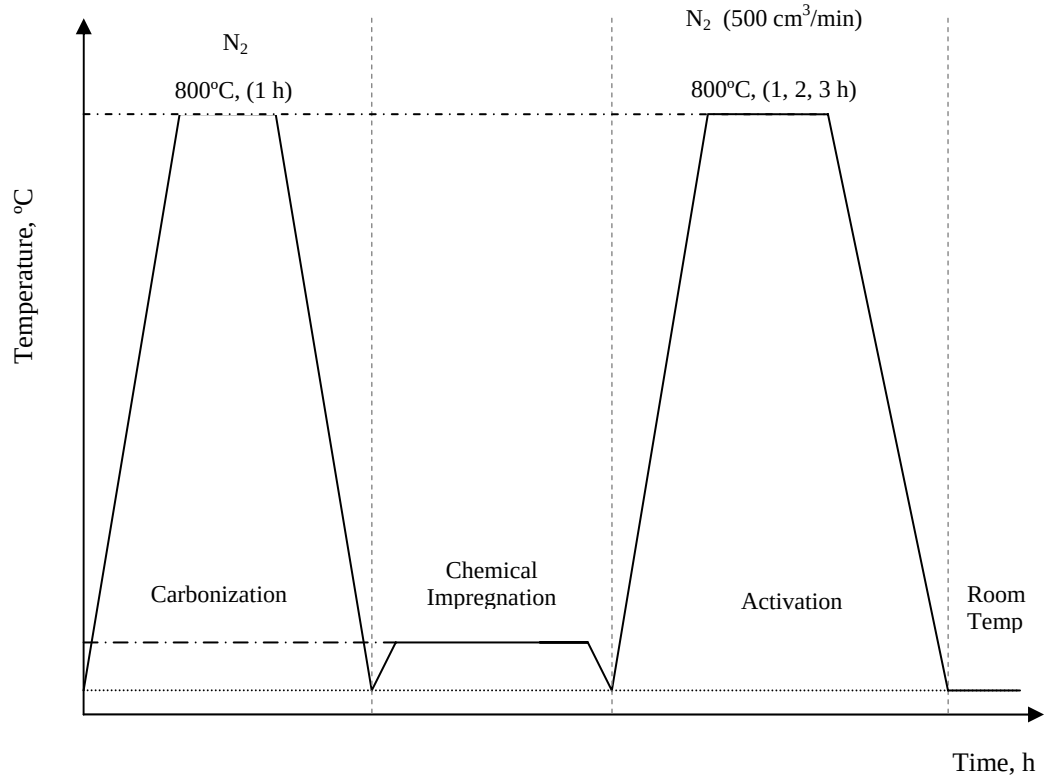


Figure 2.4: Thermal treatment scheme of two-step chemical activation method (Stavropoulos, 2005)

Table 2.3: Summary of previous works on preparation of activated carbons produced by waste tyres impregnated with KOH

References	Particle size of tyre rubber (mm)	Charring conditions (°C,h)	Activation conditions (°C,h)	Heating Rate ($°C\,min^{-1}$)	Chemical Treatment	Activating gas flow rate (ml/min)	BET surface Area (m^2/g)	Yield (g activated carbon/100g tyre rubber)	Equipment
Stavropoulos, (2005)	-	Temp=800 Time= 1	Temp=800 Time= 2	-	KOH/N_2 KOH = 4 Char	500	758	58	Furnace reactor system
Teng *et al*., (2000)	0.2-0.3	-	Temp=700 Time= 0 Temp=800 Time= 0	-	KOH/N_2 KOH = 4 Tyre	100	474 411	16.0 12.0	Horizontal cylindrical furnace
Sun *et al*., (1997)	3	- Temp=600 Time= 0.75	Temp=850 Time= 1.5 Temp=900 Time= 1 Temp=850 Time= 3	- -	KOH/N_2 KOH = 1 Tyre Steam	500 500	820 1031 888	- - -	Bench-scale tubular reactor with a horizontal tube furnace.