UPGRADING COFFEE GROUND WASTE AS ACTIVATED CARBON USING CHEMICAL ACTIVATION WITH ZINC CHLORIDE AND POTASSIUM CARBONATE

THANITTHA KHANTISUK

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF
THE REQUIREMENTS FOR
THE DEGREE OF MASTER OF SCIENCE
(APPROPRIATE TECHNOLOGY FOR RESOURCES
AND ENVIRONMENTAL DEVELOPMENT)
FACULTY OF GRADUATE STUDIES
MAHIDOL UNIVERSITY
2005

ISBN 974-04-5972-2

Thesis
Entitled

UPGRADING COFFEE GROUND WASTE AS ACTIVATED CARBON USING CHEMICAL ACTIVATION WITH ZINC CHLORIDE AND POTASSIUM CARBONATE

Thanittha Khantisuk
Miss Thanittha Khantisuk
Candidate

Asst. Prof. Aurapin Eamsiri,
Ph.D. (Fuel Chemistry)
Major-Advisor

Luepol P.
Asst. Prof. Luepol Punnakanta,
M.Sc. (Technology of Environmental Management)
Co-Advisor

Assoc. Prof. Rassmidara Hoonsawat,
Ph.D.
Dean
Faculty of Graduate Studies

C. yuwaree
Asst. Prof. Chumporn Yuwaree,
M.Sc. (Appropriate Technology for Resources Development)
Chair
Master of Science
Programme in Appropriate Technology for Resources and Environmental Development
Faculty of Environment and Resource studies

Thesis
Entitled

UPGRADING COFFEE GROUND WASTE AS ACTIVATED CARBON USING CHEMICAL ACTIVATION WITH ZINC CHLORIDE AND POTASSIUM CARBONATE

was submitted to the Faculty of Graduate Studies, Mahidol University
for the degree of Master of Science
(Appropriate Technology for Resources and Environmental Development)
on
21 March, 2005

Thanittha Khantisuk
....
Miss Thanittha Khantisuk
Candidate

....
Asst. Prof. Aurapin Eamsiri,
Ph.D. (Fuel Chemistry)
Chair

K. Sanguantrakul
....
Asst. Prof. Kanit Sanguantrakul,
M.Sc. (Technology of Environmental
Management)
Member

Luepol P.
....
Asst. Prof. Luepol Punnakanta.,
M.Sc. (Technology of Environmental
Management)
Member

....
Assoc. Prof. Rassmidara Hoonsawat,
Ph.D.
Dean
Faculty of Graduate Studies
Mahidol University

....
Assoc. Prof. Anuchat Poungsomlee,
Ph.D. (Human Ecology)
Dean
Faculty of Environment and Resource
Studies
Mahidol University

ACKNOWLEDGEMENT

The success of this thesis can be attributed to the extensive support and assistance from my major advisor, Asst. Prof. Aurapin Eamsiri, who gave the wonderful encouragement and useful advice and my co-advisor, Asst. Prof Luepol Punnakanta. I deeply thank them for their valuable advice and guidance in this research.

I am very grateful to Asst. Prof. Kanit Sanguantrakul, for kindness in examining the research paper and providing suggestions for improvement, and who was the external examiner of the thesis defence.

I gratefully thank Dr. Sirithan Jiemsirilers, Faculty of Science, Chulalongkorn University, for her kindly permission to supported S_{BET} equipment.

I wish to thank Mr. Witoon Sae-ngow, staff at Scientific and Technological Equipment centre, Silpakorn University for providing me with a kindness and supporting SEM equipment.

My special thank is also extended to the Khao Shong Insustry 1979 Co.Ltd., instant coffee plant in Samutprakarn, for raw material used in this thesis.

I would like to thank all staffs of the Faculty of Environment and Resource Studied, Mahidol University for their helpful, suggestion, especially laboratory staffs.

This research work is supported in part by the grant from the Post-Graduate Education, Training and Research Program in Environmental Science, Technology and Management under Higher Education Development Project of the Commission on Higher Education, Ministry of Education.

My special thank to all my friends, AT 15, for their helpful, grateful friendship, happiness and all enjoyable thing that we have ever done throughout my study, especially my best friends, Mr. Vasuwee Euanchita, Mr. Wanchai Tanglearkpipat, and Miss Petcharat Jekjuntut. . These would be in my memory forever.

Finally, I deeply appreciated my family, for their entirely care, infinite love, financial support, encouragement and understanding throughout my long period of study. I really could not achieve this success without them. The usefulness of this thesis, I dedicate to my family and all the teachers who have taught me since my childhood.

Thanittha Khantisuk

UPGRADING COFFEE GROUND WASTE AS ACTIVATED CARBON USING CHEMICAL ACTIVATION WITH ZINC CHLORIDE AND POTASSIUM CARBONATE

THANITTHA KHANTISUK 4337304 ENAT/M

M.Sc. (APPROPRIATE TECHNOLOGY FOR RESOURCES AND ENVIRONMENTAL DEVELOPMENT)

THESIS ADVISORS: AURAPIN EAMSIRI, Ph.D. (FUEL CHEMISTRY), LUEPOL PUNNAKANTA, M.Sc. (TECHNOLOGY OF ENVIRONMENTAL MANAGEMENT)

ABSTRACT

The main objective of this work was to utilize coffee ground waste as the precursor for activated carbon production using chemical activation with zinc chloride ($ZnCl_2$, widely used) and potassium carbonate (K_2CO_3, with less pollution). The effects of preparing parameters, namely the weight ratio of coffee ground waste to activating agent (WR), activation temperature and activation time, on iodine number, were studied in order to seek an optimum activation condition for producing activated carbon. The resulting activated carbons were classified by iodine number requirement of TISI (Thailand Industrial Standard Institute). In addition, all data were statistically analyzed by ANOVA and LSD at 95% confidence interval.

Based on the results of the experiment, it was concluded that coffee ground waste can be utilized as an alternative precursor for activated carbon production. The optimum condition of activation using $ZnCl_2$ was 1:3 of WR at a temperature of 800ºC with a retention time of 3 h, giving a yield of 44.8 % with an iodine number of 901 mg/g and S_{BET} of 1,088 m^2/g. In the case of K_2CO_3, the optimum activation condition was 1:2 of WR at a temperature of 800ºC with a retention time of 2 h, giving a yield of 18.4 % with an iodine number of 1,190 mg/g and S_{BET} of 943 m^2/g. In addition, these results show that the optimum WR and activation time for K_2CO_3 is lower than that of $ZnCl_2$, indicating less cost and energy consumption, and, it is a benign chemical. Therefore, it is reasonable to assume that K_2CO_3 is considerably better as an activating agent alternative.

KEY WORDS: ACTIVATED CARBON/ CHEMICAL ACTIVATION/ $ZnCl_2$/ K_2CO_3/ WASTE UTILIZATION/ COFFEE GROUND WASTE

87 pp. ISBN 974-04-5972-2

การปรับปรุงกากกาแฟเหลือทิ้งเป็นถ่านกัมมันต์โดยการกระตุ้นทางเคมีด้วยซิงค์คลอไรด์และโพแทสเซียมคาร์บอเนต (UPGRADING COFFEE GROUND WASTE AS ACTIVATED CARBON USING CHEMICAL ACTIVATION WITH ZINC CHLORIDE AND POTASSIUM CARBONATE)

ธนิษฐา ขันติสุข 4337304 ENAT/M

วท.ม. (เทคโนโลยีที่เหมาะสมเพื่อการพัฒนาทรัพยากรและสิ่งแวดล้อม)

คณะกรรมการควบคุมวิทยานิพนธ์: อรพินท์ เอี่ยมศิริ, Ph.D. (Fuel Chemistry), ลือพล ปุณณกันต์, วท.ม. (เทคโนโลยีการบริหารสิ่งแวดล้อม)

บทคัดย่อ

งานวิจัยนี้มีวัตถุประสงค์เพื่อนำกากกาแฟเหลือทิ้งมาใช้เป็นวัตถุดิบในการผลิตถ่านกัมมันต์โดยการกระตุ้นทางเคมีด้วยซิงค์คลอไรด์ซึ่งเป็นสารกระตุ้นที่นิยมใช้ในปัจจุบันและโพแทสเซียมคาร์บอเนตซึ่งเป็นสารเคมีที่มีความเป็นพิษน้อย งานวิจัยนี้จะศึกษาถึงสภาวะที่เหมาะสมในการผลิตถ่านกัมมันต์ทั้งอัตราส่วนโดยน้ำหนักของกากกาแฟต่อสารกระตุ้น อุณหภูมิ และระยะเวลาในการกระตุ้นที่มีต่อค่าการดูดซับไอโอดีนของถ่านกัมมันต์ โดยใช้มาตรฐานถ่านกัมมันต์ของสำนักงานมาตรฐานอุตสาหกรรมในการพิจารณาคัดเลือก สำหรับการวิเคราะห์ข้อมูลใช้ ANOVA และ LSD ที่ระดับความเชื่อมั่น ร้อยละ 95

จากผลการทดลองสรุปได้ว่ากากกาแฟสามารถใช้เป็นวัตถุดิบผลิตถ่านกัมมันต์ได้ โดยมีสภาวะที่เหมาะสมในการกระตุ้นด้วยซิงค์คลอไรด์ที่อัตราส่วนโดยน้ำหนัก 1:3 ที่อุณหภูมิ 800 องศาเซลเซียส เป็นเวลา 3 ชม ได้ปริมาณผลิตภัณฑ์ ร้อยละ 44.8 มีค่าการดูดซับไอโอดีน 901 มก/ก และพื้นที่ผิวจำเพาะ 1,088 ม^2/ก ในกรณีของสารกระตุ้นโพแทสเซียมคาร์บอเนต มีสภาวะที่เหมาะสมในการผลิตที่อัตราส่วนโดยน้ำหนัก 1:2 ที่อุณหภูมิ 800 องศาเซลเซียส เป็นเวลา 2 ชม ได้ปริมาณผลิตภัณฑ์ ร้อยละ 18.4 มีค่าการดูดซับไอโอดีน 1,190 มก/ก และพื้นที่ผิวจำเพาะ 943 ม^2/ก นอกจากนี้ยังพบว่าที่สภาวะที่เหมาะสมสำหรับสารกระตุ้นโพแทสเซียมคาร์บอเนตซึ่งเป็นสารเคมีที่มีความเป็นพิษน้อย ใช้อัตราส่วนโดยน้ำหนักและเวลาในการกระตุ้นน้อยกว่าซิงค์คลอไรด์ ดังนั้นโพแทสเซียมคาร์บอเนตจึงเป็นสารเคมีทางเลือกหนึ่งในการผลิตถ่านกัมมันต์

87 หน้า ISBN 974-04-5972-2

CONTENTS

Page

CHAPTER

1 INTRODUCTION

2 LITERATURE REVIEWS

3 MATERIALS AND METHODS

CONTENTS (CONTINUED)

Page

4 RESULTS AND DISCUSSION

5 CONCLUSION AND RECONNENDATION

LIST OF TABLES

LIST OF FIGURES

Figure **Page**

CHAPTER 1

INTRODUCTION

1.1. State of the Problem

Activated carbons are extremely versatile adsorbents of major industrial significance. They are used in a wide range of applications, which are concerned principally with the removal of species by adsorption from the liquid or gas phase, to effect purification or the recovery of chemicals and also find use as catalyst support. Basically, two methods are used to prepare activated carbon: physical and chemical activation. However, the advantages of chemical activation over physical activation include completion in only one step and at a relative low temperature, better development of a porous structure and also a yield of higher carbon content product [1].

For chemical activation, the effects of zinc chloride ($ZnCl_2$) and potassium carbonate (K_2CO_3) on activation of agricultural by-product precursors have been of particular interest. $ZnCl_2$ in particular is the widely used chemical agent for a long time [2-7]. However, the use of $ZnCl_2$ has been limited due to the problem of possible environmental contamination [8], thus a more benign chemical is desired. Recently, activated carbons with high specific surface area using K_2CO_3 as activating agent have been reported due to their less toxic properties and not deleterious as used for food additives [9-15]. Nerveless, the effects of these two chemicals on a single precursor have not been thoroughly investigated in the literature.

Activated carbons can be produced from virtually any carbonaceous source materials inclusive of coal (difference rank coal) and cellulosic biomasses as the two major resources [1]. Although coal was more widely used, agricultural waste might be a better choice in some places because of its availability and cheapness, for which the effective utilization has been desired [1,15-22]. Therefore the preparing of activated carbon from an agricultural by-product would be varying an interesting subject.

Coffee ground waste is an agricultural residue or by-product that was generated after extraction process within instant coffee industry. In Thailand, the expansion of coffee plantation was encouraged by the governmental policy. There were 455,00 rai of the coffee plantation in year 2001 and produced coffee bean amounted to 85,406 metric tons [23], with 35.7% of coffee bean production going to internal instant industry [24]. Thus, toalled 30,490 metric tons were used within instant coffee industry and coffee ground waste was generated amount 12,169 to 18,284 metric tons due to approximate 40 to 60% of coffee bean consumption [25]. It means that a large volume of coffee ground waste was generated and their disposal has become a matter of increasing concern. On the other hand, the techniques for giving additional value and reusing the by-products are need and the utilization of agricultural waste as raw material for the preparation of activated carbons has increased notably in recent year.

Moreover, it is interesting to confront the natural coffee ground waste i.e. high carbon content (53.8 to 59.5%) and low ash content (0.27 to 4.5%) [26-27]. In comparison to precursors for commercial activated carbon, the carbon content of coffee ground waste is higher than wood (40 to 45% [1]) and coconut shell (46.59%) [28], nearly to lignite (55 to 70%) [1] while lower than coal (85 to 95%) [1]. Therefore, coffee ground waste contained a large amount of carbon enough to make it a suitable precursor for activated carbon preparation.

The original goal of study was to upgrade an agricultural waste product into something useful, accordingly the present work was to study the effect of different parameters on the preparation of activated carbon from coffee ground waste by chemical activation with $ZnCl_2$ (widely use) and K_2CO_3 (with less pollution). Iodine number of the resulting activated carbon was analyzed and used to establish the appropriate operation condition including activation temperature, activation time and activating agent impregnation ratio.

1.2. Objectives

1.2.1 To study the possibility of producing activated carbon from coffee ground waste by chemical activation with zinc chloride and potassium carbonate.

1.2.2 To determine the suitable condition of activation carbon from coffee ground waste

1.3. Hypothesis

Various the weights of coffee ground waste and activating agent ratio, activation temperature and activation time were resulted different on iodine absorption efficiency.

1.4 Scope of the Study

1.4.1 This study had been carried out only on laboratory scale. The preparation of activated carbon was preformed by one-stage chemical activation combining carbonization with activation process.

1.4.2 Coffee ground wastes, an agricultural by-product after the extraction process from instant coffee industry was used as starting material for activated carbon, which collected by grab sampling. These coffee are Robusta coffee (*Coffea Canephora*).

1.4.3 Two chemical agents were used as activating agent due to zinc chloride ($ZnCl_2$) was the widely used activating agent and potassium carbonate (K_2CO_3) was the benign chemical agent.

1.4.4 This study had been focused on iodine number efficiency of activated carbon.

1.5. Conceptual Framework

In this study, coffee ground waste was utilized as the carbonaceous precursor for the production of activated carbon by chemical activation. The activating agents used were $ZnCl_2$ and K_2CO_3 and conditioning variables examined were the weight ratio of raw material to activating agent, temperature and time. Iodine number of the resulting activated carbon was analyzed and used to establish the suitable operation condition including activating agent impregnation ratio, activation temperature and activation time. To approach the subjects as mentioned in the state of the problem and hypothesis, the conceptual framework has carried out in following:

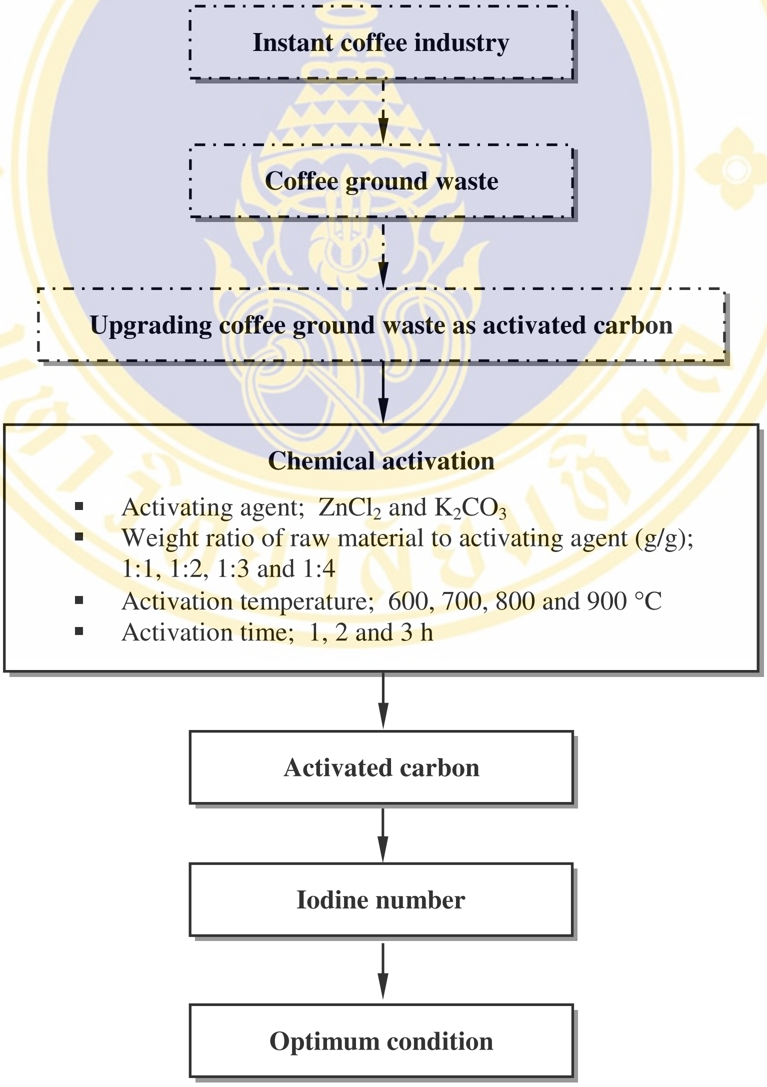


Figure 1-1: Conceptual framework for the study

1.6. Variables

1.6.1 Independent variables

The weight ratio of raw material to activating agent

Activation temperature

Activation time

1.6.2 Dependent variable

Iodine number

1.7. Expected Result

To be a guideline in producing activated carbon from coffee ground waste, a low cost alternative precursor substitute and increase efficientcy of utilization, value-addition of agricultural residues and on other side helps solving problem, which otherwise disposal cause.

CHAPTER 2
LITERATURE REVIEWS

2.1 Activated Carbon

Activated carbon is a microcrystalline, nongraphitic form of carbon that has been processed to develop internal porosity. This porosity yields the surface area that provides ability to adsorb gases and vapors from gases and to adsorb dissolved or dispersed substances from liquids. Activated carbon is characterized by a vast system of pores of molecular size within the carbon particles resulting in the formation of a material with extensive surface area. However, commercial grade of activated carbons generally have surface areas ranging from 600 to 1,200 m^2/g [21].

Activated carbon is widely used for a number of applications, such as separation of gases, recovery of solvents, and removal of organic pollutants from drinking water and as a catalyst support. Accordingly, among many other operations, activated carbon is important adsorbents in various industrial sectors such as the food, pharmaceutical and chemical industries. Further, as an environmental pollution is increasingly becoming a serious problem, the demand for activated carbon is growing.

2.1.1 Structure of Activated Carbon

Activated carbon is frequently termed amorphous carbon. X-rays studies have demonstrated that many so-called amorphous substances have crystalline characteristics, even though they may not show certain features such as crystal angles and faces, usually associated with the crystalline state. The X-ray diffraction pattern has shown that amorphous carbon consists of flat plates in which the carbon atoms are arranged in a hexagonal lattice, as Figure 2-1. The structure of activated carbon consists of elementary microcrystallites of graphite, but these microcrystallited are stacked upon another layer of graphite in random orientation and space between the adjacent layers provides micropores.

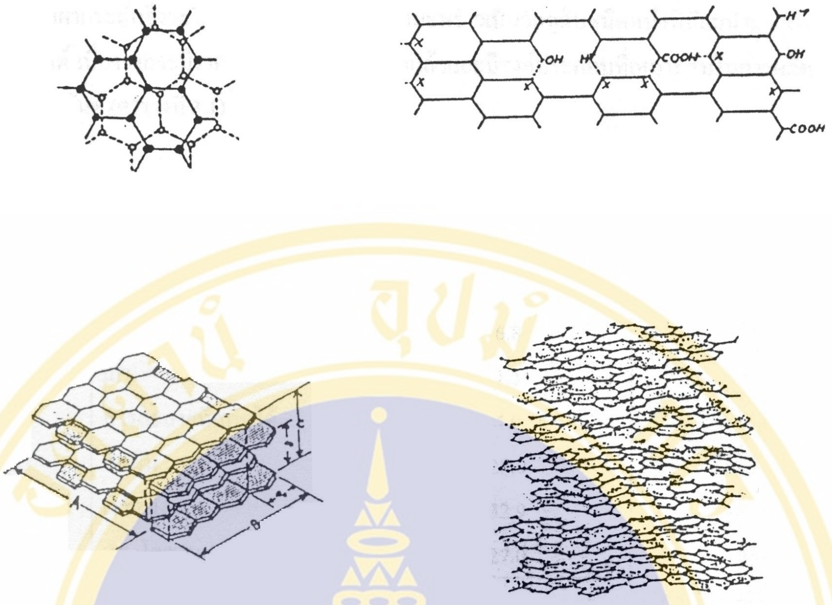


Figure 2-1: Structure of activated carbon [8]

Activated carbon is very porous materials with a highly varied texture. The pores range from micrometer size to those are so small as to be inaccessible even to the smallest of all molecules, the helium atom, whose diameter is approximately 0.23 nm (nanometer). The IUPAC classification of pores by size defines the following three class of pore [30]:

- Macropores with breadths greater than 50 nm (500 Aº (angstrom unit))
- Mesopores with breadths between 2 and 50 nm (20-500 Aº)
- Micropores with breadths less than 2 nm (20 Aº)

The composition and structure of an activated carbon depends on the raw material, the activating agent and the preparation procedure. These parameters condition the properties of the activated carbon and hence its applications.

2.1.2 Activated Carbon Adsorption

Activated carbons have several uses such as taste and odour control, chlorine reduction, organic reduction, and reduction of hazardous organic chemicals. These featured are sometimes combined in a single application, but they have distinctly different objectives. The fact that they are different is something, which must be kept in mind. While some activated carbons are excellent for one application, they may not be suited for another. Although there are different uses for activated carbon, the actual adsorption mechanism is the same.

Adsorption is the process in which matter adheres to the surfaces of an adsorbent (activated carbon). Activated carbon media can be produced from several materials. However, regardless of the base material, all activated carbons have surface whose texture is much like sponge.

Figure 2-2: Activated carbon adsorption [31]

Figure 2-2 illustrates this sponge-like nature of the carbon. Due to this texture, a teaspoon of activated carbon will have a total surface area equal to a football field. The atoms of carbon comprising the large internal surface area of activated carbon, present attractive forces outward from the surface. These forces, known as Van der Waals forces, attract the molecules of the surrounding gas or liquid. The combination of these attractive forces and those of molecules in the surrounding medium have resulted in adsorption of molecules at the surface of the activated carbon. Some molecules have structures that make them more easily adsorbed than others and it is due to this that separation of molecules is achieved.

2.1.3 Type and Selection of Activated Carbon

Physicochemical characteristics of activated carbon depend on the kind of raw material used and activation conditions. Activated carbon is classified in to one of two types, such as powder, granular its size and shape [1,4,30].

- Powder Activated Carbon is activated carbon in particle size predominantly smaller than 80 mesh.
- Granular Activated Carbon is activated carbon in particle size predominantly greater than 80 mesh.

Moreover, activated carbon is able to offer a range of different types of activated carbon media such as carbon briquettes, chemical impregnated granular activated carbon, and fibrous activated carbon.

Selection of the most appropriate activated carbon type is based either on known characteristics of the chemicals to be removed in the adsorption process or by a series of controlled laboratory tests. Powder carbons are mainly used in batch processes and removed by filtration after an appropriate contact time whereas granular carbons are used in fixing or moving filter beds. In the case of granular carbons, the smallest particle size is normally selected consistent with retention in the filter and acceptable flow resistance since this will provide the best adsorption kinetics. Activated carbon is sometimes chemically impregnated to enhance the performance by chemisorptions when adsorption affinity for particular contaminants is too weak to be effective.

2.2 Activated Carbon Manufacture

In principle, there are two procedures of the activated carbon manufactured: Carbonization and Activation.

- **Carbonization** is a process in which the material is turned into porous carbon structure through pyrolysis. In this process, most of the non-carbon organic matters are decomposed. The combination of carbon atoms-aromatic foliated structure is made with irregular split. Thus, the split will be developed into a structure with more pores during the process of activation.
- **Activation** is used the steaming or chemical methods to remove the tar, organic wastes and other rests. Its purpose to get more an absorption phase of activated carbon products.

However, the simple one-step method for the production of activated carbon has been developed to reduce the energy expenditure during the process. This method is a feasible alternative to the traditional two-step process for the production of activated carbons by consecutive carbonization of raw material and high temperature activation (900-1,000ºC) of the solid product from carbonization [18,32]. Nevertheless, the characteristic of the activated carbon varies with based on materials and condition of carbonization and activation steps.

2.2.1 Activation Methods

Basically, two methods are used to prepare activated carbons namely Physical and Chemical activation [1,13,16,33].

- **Physical activation**, the raw material is carbonized (carbonization step) at high temperature and prepared char is sequentially activated using steam or carbon dioxide (CO_2) (activation step). The porous structure is created due to the elimination of volatile matter during the carbonization step and the carbon on the char is removed by reaction with steam or CO_2 during the activation step.
- **Chemical activation**, the raw material is impregnated with an activating agent and heated in an inert atmosphere or absence of oxygen. Then carbonization step and the activation step process simultaneously. By dehydration and oxidation reactions of the chemical, the pores are developed.

In physical activation, elimination of a large amount of internal carbon mass is necessary to obtain a well developed carbon structure, whereas in the chemical activation process all the chemical agents used are dehydrating agents that influence pyrolytic decomposition and inhibit formation of tar, thus enhancing the yield of carbon [16]. The temperatures used in chemical activation are also lower than that used in the physical activation process, and therefore the development of a porous structure is better in the case of the chemical process.

Various works earlier studies dealing with conversion of several coals and lignocellulosic materials to activated carbon, using chemical activation have reported, an advantages and disadvantage of this process, as it has been point out [5,11,19,35]. Therefore, advantage and disadvantages of chemical activation process, mainly in comparison to physical activation can be summarized as follows [1,2,9,11,16,34]. Chemical activation use lower temperatures, for pyrolysis needs only one step. In addition, it produces a much higher yield than the physical activation and allows to obtain very high surface area. The microporosity can be well developed, controlled and maintained narrow, it desired. Significant important reduction of the mineral matter content is appeared. However, disadvantages of chemical activation process are few due to corrosiveness of the process and the washing stage in which.

2.2.2 Activating agent

The activating agents used in the chemical process are normally alkali and alkaline earth metal containing substances and some acid such as KOH, K_2CO_3, NaOH, Na_2CO_3, $AlCl_3$, $ZnCl_2$, MgCl and H_3PO_4 [1,16]. $ZnCl_2$ and H_3PO_4 have been commonly used as activating agents for a long time. However, the use of $ZnCl_2$ and H_3PO_4 has been recently limited due to problems of possible environmental contamination and eutrophication with zinc and phosphorus compounds [8,36].

Consequently, alkali hydroxide compounds such as KOH and NaOH have been used in order to prepare activated carbon with high specific surface area [13]. Activated carbon with high specific surface area is suitable for gas storage, gas purifications, recovery of solvent vapor and manufacture of electric double layer capacitors. However, KOH and NaOH are expensive and corrosive chemicals.

Thus a more benign chemical is desired. Recently, activated carbon with high specific areas using K_2CO_3 as activating agent has been reported due to their less toxic properties and not deleterious and used for food additives [9-15]. However, for chemical activation, the effects of $ZnCl_2$ and K_2CO_3 on activation of carbonaceous materials have been of particular interest due to $ZnCl_2$ is the widely used chemical agent whereas K_2CO_3 is the benign chemical agent. Also, the effects of these two chemicals on a single precursor have not been thoroughly investigated in the literature and the information published is limited.

2.2.3 The Methods of Activating Agent Mixing

Generally, three different methods are used to mixing raw material and activating agent [14,16], namely:

1) **Physical method**: dries precursor material was physically mixed with ground chemical agent and placed into reactor.

2) **Impregnation method**: dried precursor material was well mixed with a concentrated solution of chemical agent and then the resulting homogeneous slurry was dried at 110° C until constant weight.

3) **Acid pre-treat method**: dried precursor material was soaked in 1*N* solution of HCl: H_2SO_4 (1:1) for 2 days in order to reduce the ash content, then washed with distilled water and dried at 110° C for about 14 hours. The dried sample was further mixed with a solution of chemical agents according to impregnation method.

Physical method is a mixing methodology seldom used, although this is simpler and much less time consuming than impregnation with solution, due to the better distribution of chemical agents into the carbonaceous particle mass. While acid pre-treatment of the coal shows some advantages in some cases, but for the coal with low ash content the effect is negligible.

2.3 Raw Material for Activated Carbon

Activated carbon can be produced from virtually any carbonaceous solid precursors with a high carbon content and low level of inorganic compounds, both naturally occurring and synthetic. Common examples of commercial raw materials are materials of botanical origin (e.g. wood, coconut shell, fruit stones and nut kernels) and degraded or coalfield plant matter (e.g. peat, lignite and ranks of coal). The characteristics of raw materials for commercial activated carbon were shown in Table 2-1.

Table 2-1: Characteristics of commercial raw materials as activated carbon

Raw materials	Carbon (%)	Volatile (%)	Bulk Density (g/cc)	Ash (%)	Adsorption/ Application use
Hard wood	40–45	55–60	0.40–0.50	0.3–1.1	Liquid phase
Soft wood	40–42	55–60	0.55–0.80	0.3–1.2	Liquid phase
Lignin	35–40	58–60	0.30–0.40	-	Liquid phase
Nut shell	40–45	55–60	1.40	0.5–0.6	Vapour phase
Lignite	55–70	25–40	1.00–1.35	5.0–6.0	Waste water treatment
Peat	65–80	20–30	1.25–1.50	0.2–1.2	Liquid and vapour phase
Coke	75–85	15–20	1.35	0.5–0.7	Waste water treatment
Bituminous	70–75	10–15	1.45	5–15	Vapour phase
Coal	85–95	5–10	1.50–1.80	2–15	Vapour phase

***Source**: [1]*

The principal commercial carbon feed stocks and proportions in which they are used were summarized by Bansal et al. [1] as: wood 35%, coal 28%, lignite 14%, coconut shell 10%, peat 10% and others 3%. The most frequently used materials or precursors are coal (from different ranks), wood and coconut in the commercial products. Among them, coal is the most commonly used precursor due to activated carbon prepared from coal is superior to those derived from lignocellulosic materials in term of mechanical properties [1].

Process economics normally dictate the selection of readily available, low-cost feedstock. The price of the end product is dependent on the degree of processing required attaining the desired adsorptive properties.

2.3.1 The Selection of the Raw Materials

The selection of the precursor essentially determined range of adsorptive and physical properties that can be attained in the activated carbon products. Important considerations to be made in selecting a source of material include cost, availability and consistency of quality. Raw materials for activated carbon are chosen depending on there:

- Purity,
- Price,
- Potential extent of activation and
- Stability of supply.

Although coal was more widely used for commercial activated carbon, agricultural by-products may be better choice in some places because of its availability and cheapness [2-7]. Due to environmental considerations, agricultural by-products are gaining great importance as precursors to activated carbon production. Their importance arises from various aspects [12]:

1) They lost their role as major fuel and source of energy,
2) They are ever accumulating renewable source and
3) There are low-ash materials.

In the sense of environmental protection, the utilization of these wastes has awakened the interest for development of processes for production of carbon adsorbents based on agricultural waste. Both the nature of the precursors and the production process has a strong influence on porous structure and adsorption properties of the resulting activated carbon. Recent investigations have reported the utilization of various raw lignocellulosic materials, for example, various nutshell, fruit stones, sugarcane bagasse, coconut shell, corncob [2-7,9,11-13]. On the other hand, agricultural by-products, derived from natural resources are inexpensive, though there may be problems with the uniformity of quality, supply location and seasonal variability [10].

2.3.2 Agricultural By-product as Precursor for Activated Carbon

At present several researches on preparing activated carbon various agricultural by-product sources are under way from viewpoint of effective material utilization. The prospective demand of activated carbon had led to and increasing search toward plentiful, renewable supplies of low cost feedstock for activated carbon production. The suitability of several agricultural by-products has been investigated in the last years using different activation strategies. Table 2-2 summarizes characteristics of various agricultural by-products as precursor for activated carbon with their composition and adsorption capacity of produce activated carbon.

Table 2-2: Agricultural by-products as precursor for activated carbon

Authors	**Material**	**Composition (%)**				**Activated carbon**
		C	**H**	**N**	**Ash**	**S_{BET} (m^2/g)**
Tsai et al. (1998)	Corn cob	46.84	5.96	0.88	-	1,410
Palut (2000)	Coconut shell	46.59	5.45	0.27	-	975
Jim-WhaKim et al. (2001)	Walnut shell	46.64	6.05	0.73	-	1,297
Savova, D. et al. (2001)	Apricot stone	51.5	6.3	0.2	0.2	1,190
	Cherry stone	53.9	7.1	0.3	0.9	875
	Grape seed	55.4	7.0	1.5	2.5	497
	Almond shell	54.7	7.5	0.3	2.3	998
	Nut shell	53.6	7.5	0.3	3.8	743
Gyu Hwan Ho and Chong Rae Park (2002)	Rice straw	39.8	5.5	0.9	-	900
Venerson, T. et al. (2002)	*Arundo donax* cane	49.3	6.0	0.3	-	1,300
Aygüm et al. (2003)	Almond shell	50.3	6.05	-	-	736
	Walnut shell	50.5	6.03	-	-	783
	Hazelnut shell	51.4	5.95	-	-	793
	Apricot stone	49.0	5.75	-	-	774

Sources: *[2,4,7,17,18,20,28]*

It was interesting to point out; these precursors from agricultural by-product have high carbon content (around 50%) except rice straw (39.8%), and low ash content (0.2-3.8%), that important feature affect starting material for activated carbon [1]. Notably, the resulting products having surface area in range of 700 to 1,300 m^2/g, which is similar to commercial activated carbon (600 to 1,200 m^2/g [21]) in the market. Therefore, agricultural by-product has proved to be promising raw materials for the production of activated carbon because of their availability at a low price. They were used for the production of activated carbon with a high adsorption capacity, considerable mechanical strength, and low ash content [1-7,9-15,17-18]. Thus all the authors are in agreement on this aspect, confirming agricultural by-products suitable precursor for activated carbon.

2.4 Coffee Ground Waste

2.4.1 Coffee

Coffee (*Coffea* sp.) is one of the most important agricultural commodities in the world, belongs to the botanical family Rubiaceae, which has some 500 genera and over 6,000 species. Coffee has traditionally been grown under the canopy of the towering forest trees of inter-cropped fruit trees such as bananas, citrus, or leguminous pod trees, the produce other valuable food, timber, fuel wood and fodder crops. This shade canopy also sustainable supports the coffee plants themselves. However, since the 1970s, coffee plantation has dramatically changed with regard to crop pattern and practices, mainly to meet the high demand of coffee, and to tackle the leaf fungus. With the development of hybrid coffee varieties, “shade-coffee” has turned to “sun-coffee”. Current about one million tons of coffee is produced yearly in more the 50 countries [37-39].

1) Ecology of coffee

Coffee is an evergreen tree, which grows between the latitudes of 25 N and 25 S, an arrow subtropical belt around the world, but requires very specific environmental conditions for commercial cultivation. Temperature, rainfall, sunlight, wind and soils are all important, but requirements vary according to the varieties grown. All coffee needs good drainage, but it can grow on soils of different depths, pH and mineral content, given suitable applications of fertilizer. Wind-breaks are sometimes planted to protect coffee plantations; shade trees, which may be economic crops such as bananas, are a common feature and mimic the natural habitat of coffee. The two most important of coffee economically are Arabica coffee (*Coffea Arabica*) and Robusta coffee (*Coffea Canephora*). Some differences between Arabica and Robusta coffee are shown in Table 2-3.

Table 2-3: Ecology and botanical aspects of Arabica and Robusta coffee

Ecology/Botany Aspects	**Arabica**	**Robusta**
Date species described	1753	1895
Chromosomes (2n)	44	22
Time from flower to ripe cherry	9 months	10-11 months
Flowering	After rain	Irregular
Ripe Cherries	Fall	Stay
Yield (kg beans/ha)	1,500-3,000	2,300-4,000
Root system	Deep	Shallow
Optimum temperature (yearly average)	15-24° C	24-30° C
Optimum rainfall	1,500-2,000 mm	2,000-3,000 mm
Growth optimum	1,000-2,000 m	0-700 m
Caffeine content of beans	0.8-1.4%	17-4.0%
Shape of bean	Flat	Oval

Source: *[39]*

Ideal average temperatures in range between 15-24°C for Arabica coffee and 24-30°C for Robusta, which can take hotter, drier conditions but does not tolerate temperatures much below 15°C, as Arabica can for short periods. In general, coffee needs an annual rainfall of 1,500 to 3,000 mm, Arabica needing less than other species. The pattern of rainy and dry periods is important for growth, budding and flowering. Rainfall requirements depend on the retention properties of the soil, atmospheric humidity and cloud cover, as well as cultivation practices. Whereas Robusta coffee can be grown between sea level and about 700 meters, Arabica does best at higher altitudes and is often grown in hilly areas.

2) Red Cherry to Green Bean

The coffee plant first produces delicate clusters of white blossoms, resembling jasmine in shape and scent. These blossoms last only a few days. Small green coffee cherries that being to appear and ripen to yellow, red and finally almost black, within six to nine months. Coffee bean is actually the seeds of a cherry-like fruit. Coffee trees produce berries, called coffee cherries. The fruit is found in clusters along the branches of the tree. The skin of a coffee cherry (the exocarp) is thick and bitter. However, the fruit beneath it (the mesocarp) is intensely sweet and has the texture of a grape. Next comes the parenchyma, a slimy, honey-like layer, which helps protect the beans. A parchment-like envelope called the endocarp covers the beans themselves. This protects the two, bluish-green coffee beans, which are covered by yet another membrane, called the spermoderm or silver skin as shown in Figure 2-3. Once the coffee cherries are picked, they are transported for processing.

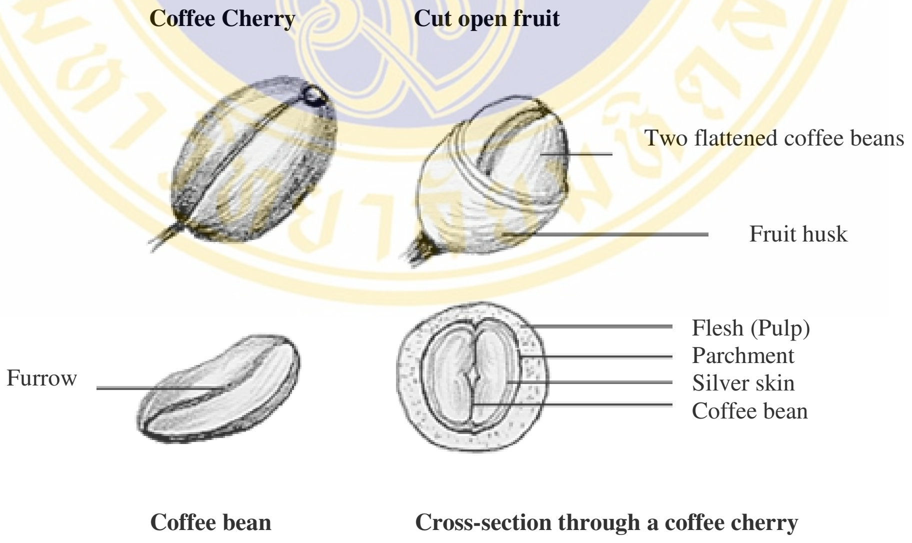


Figure 2-3: Coffee bean structure [37]

2.4.2 Coffee Ground Waste

Coffee ground waste, the residue obtained during the extraction process of raw coffee bean to prepare instant coffee. A scheme of the industrial production process of instant coffee is shown in Figure 2-4. The roasted and grinding coffee is introduced into the percolators in countercurrent with the steam, from where exits the "liquid coffee", which is introduced in the spray dryer; spent grounds from the percolators are introduced into cyclone to separate the exhaust vapors and then the liquid water is removed, using a press and dryer [25,27].

Usually, 40-60 kg of spent coffee grounds was produced for each 100 kg of coffee bean production, depending upon the processing mode of instant coffee factory [25]. Hence, a large volume of coffee ground waste was generate and their disposal has become a matter of increasing concern. Coffee ground waste also contains caffeine, tannin and polyphenols, although in lesser quantity. These compounds show that toxic nature and thus have not been utilized beneficially. This has also led to the problem of environmental pollution [37].

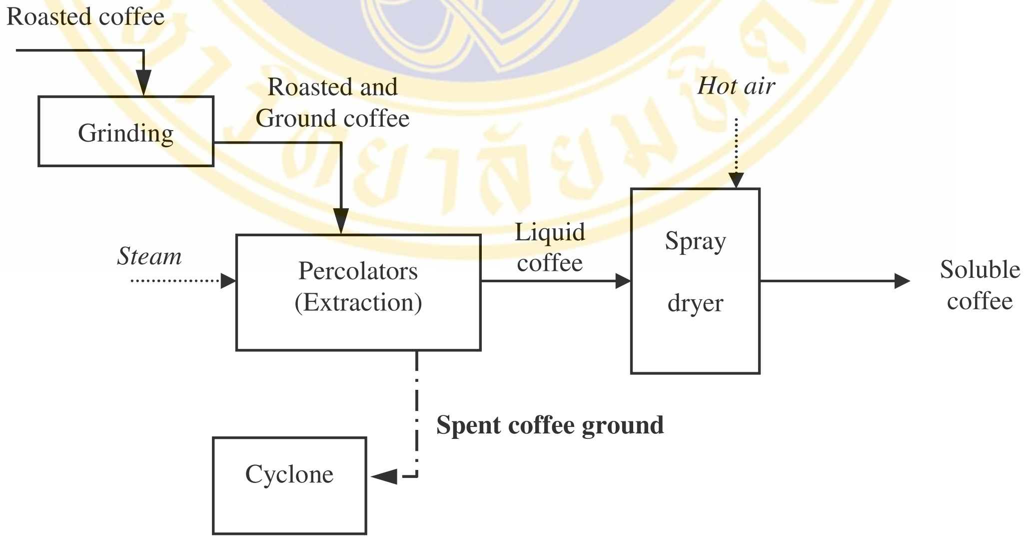


Figure 2-4: Instant coffee process flow sheet [25,27]

2.4.3 The Utilizations of Coffee Ground Waste

Coffee ground waste are highly pollutant due to the presence of organic material, caffeine, tannins and poly phenols, that demands a great quantity of oxygen in order to degrade [37]. Simply piled up, they can ferment and produce spontaneous combustion, as has occurred in some storage sites. They can thus not be thrown away untreated. With such a pollutant industrial residue being produced in great quantity, the identification of more rational uses has become necessary. The utilization of coffee ground waste were summarized by Silva, M.A. et al. [27] as follows;

1) Fertilizer
2) Animal feed
3) Substitute for wood powder
4) The production of methanol and acetone
5) The extraction of oil
6) Microprorous materials and adsorbents
7) Packing materials; exchangers of ions
8) Resins
9) Special lubricators
10) As a polisher for painting
11) A carrier for insecticides and herbicides
12) Fuel

2.4.4 Coffee Production and Coffee Ground Waste in Thailand

In Thailand, the expansion of plantation was encouraged by the governmental policy. The two major encouraging species of coffee economically are Robusta coffee and Arabica coffee, which suitability environmental conditions for cultivation [38].

- Robusta coffee is usually grown at lower elevation, between sea level and about 700 meters, average temperature 24 to 30ºC hotter than arabica coffee. An annual rainfall rang between 2,000 to 3,000 mm, higher than arabica coffee. Therefore, robusta coffee is encouraging planted in Southern Thailand such as Chum Porm, Surat Tani, Ranong, Krabi, Nakhin Sri Thammarat and Phangnga provinces.

- Arabica coffee grow best at altitudes 1,000 to 2,000 meters and often grown in hilly areas, average temperature range between 15 to 24ºC and annual rainfall 1,500 to 2,000 mm, less than other species. Thus, arabica coffee is encouraging planted in Northern Thailand such as Chiang Mai, Chiang Rai, Tak, Mae Hong Son and Phrae provinces.

The Office of Agricultural Economics of Thailand [23] had been reported that coffee planted area and coffee bean production in year 1993-2001 in Table 2-4. However, only 35.7% of coffee bean productions are going to internal instant coffee factory [24]. The coffee ground waste was produced after extraction process in coffee instant production with 40 to 60% of coffee bean production, depending upon the processing mode of instant coffee factory [25].

As can be seen in Table 2-4, coffee instant industry generated a large amount of coffee ground waste around 10,000 to 18,000 tons yearly and their disposal has become concern.

Table 2-4: Coffee planted area and production in year 1993-2001

Year	Planted Area (1,000 Rai)	Harvested Area (1,000 Rai)	Production (Tons)	Instant coffee factory* (Tons)	Coffee Ground** (Tons)
1993	468	420	70,426	25,142	10,057-15,085
1994	451	435	78,175	27,908	11,163-16,745
1995	445	445	86,450	30,863	12,345-18,518
1996	442	433	80,287	28,662	11,465-17,197
1997	439	422	83,810	29,920	11,968-17,954
1998	438	410	78,444	28,005	11,202-16,803
1999	440	407	54,923	19,680	7,843-11,765
2000	441	408	80,589	28,770	11,508-17,262
2001	455	411	85,406	30,490	12,196-18,294

Remark: ** Approximate with 35.7% of coffee bean production [24]*
*** Approximate 40-60% of coffee bean production in instant coffee factory [25]*
Source: *Adapted from data of the Office of Agricultural Economics of Thailand [23]*

2.4.5 Composition of coffee ground waste

To study the feasibility of uses it is necessary to know the composition of coffee ground waste, which was reported in Table 2-5. The reported composition varies from one author to another, such discrepancies being due to the different varieties of coffee used in production. Coffee ground waste has high carbon content (53.8 to 59.5%) and low ash content (0.25 to 4.5%) [26-27].

Table 2-5: Composition of coffee ground waste

Authors	**Carbon (%)**	**Hydrogen (%)**	**Nitrogen (%)**	**Ash (%)**
Silva M.A. et al	59.5	7.3	2.5	0.27 – 4.5
Mizuho Hirata et al	53.8	6.6	2.3	-

Source: *[26-27]*

In comparison to commercial precursors for commercial activated carbon, the carbon content of coffee ground waste is higher than wood (40 to 45% [1]) and coconut shell (46.59%) [28], but it is nearly close to lignite (55 to 70%) [1] while lower than high rank coal (85 to 95%) [1]. Particularly, it is similar to raw materials from agricultural by-product (app. 50%) such as various nutshells and fruit stones (see in Table 2-2). This fact indicated that coffee ground waste contained a large amount of carbon that enough to make them a suitable precursor for activated carbon preparing.

2.5 Activated Carbon from Agricultural By-product

Various works on conversion of several lignocellulosic material and coals to activated carbon, using chemical activation have been reported, including advantages and disadvantage in comparison to the physical process [5,11,19]. However, several research works on activated carbon preparation from various agricultural by-product sources are under way from viewpoint of effective material utilization. For chemical activation, the effects of $ZnCl_2$ and K_2CO_3 on activation of agricultural by-product precursors have been of particular interest. Due to $ZnCl_2$ is widely used as chemical agent whereas K_2CO_3 is the benign chemical agent. Table 2-6 and 2-7 are summarized various work using $ZnCl_2$ and K_2CO_3 as activating agent, with reference to the experimental condition, quality of product and their critical findings.

Table 2-6: Summary of earlier studies on activated carbon using $ZnCl_2$ activation

Authors	**Material**	**Experimental conditions**	**Quality of the product/ Key findings**
Tsai et al. (1998) [2]	Corn cob	Particle size; 1.44 mm A_temp; 400 – 800 °C A_time; 0.5, 1, 2, 3, 4 h IR; 20 – 200 wt%	S_{BET} 1,410 m^2/g A_temp; 500° C A_time; 0.5 h IR; 175 wt%
Tsai et al. (2001) [3]	Waste bagasse	A_temp; 500 °C A_time; 0.5 h IR; 25 – 100 wt%	S_L 790 m^2/g IR; 100%wt Total pore volume 0.288 cm^3/g Avg. pore diameter 14.6 A°
Jim-Wha Kim et al. (2001) [4]	Walnut shell	A_temp; 250 – 550 °C A_time; 0.5, 1, 2, 3, 4 h WR; 1:1, 1:3, 1:5, 1:7	Iodine number 1,100 – 1,297 mg/g Appropriate activation A_temp; 375° C, A_time; 0.5 h WR; 1:3
Kadirvelu et. al (2002) [5]	Parthenium (Stem and leaves)	A_temp; 700 °C A_time; 1 h WR; 0.25:1 (or 1:4)	-
Badie et al. (2002)[6]	Peanut hulls	Pyrolysis; 6 h at 300 °C Activation; 6 h at 750 °C IR; 50 wt%	S_{BET} 420 m^2/g Total pore volume 0.195 cm^3/g (Low adsorbing microporous carbons)
Aygün et al. (2003) [7]	Almond shell Walnut shell Hazelnut shell Apricot stone	Mixed with 30 wt% Pre-drying; 6 – 24 h A_temp; 750, 800, 850°C A_time; 2 h	S_{BET} 736 - 793 m^2/g Iodine number 638 – 965 mg/g A_temp; 750°C (for almond, hazenut and walnut shell) and A_temp; 800°C (for apricot stone)

Remark: *A_temp = Activation time, A_time = Activation time, IR = Impregnation ratio,*
WR = Weight ratio of raw material and activating agent, S_L *= Langmuir surface area,* S_{BET} *= BET surface area*
Sources: *[2-7]*

Table 2-7: Summary of earlier studies on activated carbon using K_2CO_3 activation

Authors	**Material**	**Experimental conditions**	**Quality of the product/ Key findings**
Tsai et al. (2001) [11]	Corn cob	Chemical/Physical activation Particle size; 1.19 – 1.68 mm A_temp; 500 – 800°C A_time; 1 h IR; up to 50 wt%	S_{BET} 1,541 m^2/g A_temp; 800°C IR; 37.5 wt% The maximum rate of increase in occurred between 650 – 700°C
Hayashi et al. (2002) [12]	Almond shell Coconut shell Oil palm shell Pistachio shell Walnut shell	Particle size less than 0.5 mm A_temp; 500 – 900°C A_time; 1 h	S_{BET} 1,200 – 1,800 m^2/g A-temp; 800°C In the temperature region below 500 ° C, cellulose and hemicellulose of nut shells changed on carbonization, rang above 600°C, chars removed as CO gas.
Hayashi et al. (2002) [13]	Chickpea husk	A_temp; 500 – 900°C A_time; 1 h IR; 1:1	S_{BET} 1,778 m^2/g A_temp; 800°C K_2CO_3 work effectively above a temperature of 700°C
Carvalho et al. (2004) [14]	Cork waste	Particle size; 0.297 – 0.42 mm A_temp; 500 – 800 °C A_time; 1 h WR; 1:1 to 1:5	S_{BET} 1,033 m^2/g A_temp; 700°C WR; 1:1

Remar:; *A_temp = Activation time, A_time = Activation time, IR = Impregnation ratio,*
WR = Weight ratio of raw material and activating agent, S_L *= Langmuir surface area,* S_{BET} *= BET surface area*
Sources: *[11-14]*

These researches results have shown that physicochemical characteristics of activated carbon depend on the kind of raw material used and activation condition. The degree of impregnation of the precursor, activation temperature and activation time are important parameters that govern the development of porous structure of the resulting activated carbon.

According to Table 2-6 and 2-7 the previous experimental condition in the earlier studies on activated carbon from different precursors of agricultural by-product using $ZnCl_2$ and K_2CO_3 as activation agent can be summarized as follows:

1) Activated carbon had been prepared in three stages in which pre-drying mixture of agricultural by-product and activation agent solution was firstly done then followed by activation at control temperature and time. Finally, the washing process of producing activated carbon had been carried out.

2) The mixture of precursor and activating agent was pre-dried at 100-110ºC, then the impregnated sample was activated at various temperatures and times.

3) Activation temperature had been varied from 400 to 850ºC for $ZnCl_2$ and 500 to 900ºC for K_2CO_3. However, the optimal temperature depend on the nature of precursor material as follows:

- In the case of $ZnCl_2$, the optimal activation temperature was 500ºC for corncob [2] whereas 750 to 800ºC for different nut shells [7]
- In the case of K_2CO_3, the optimal activation temperature was 800ºC for corncob [11], various nutshells [12] and chickpea husk [13] while 700ºC for cork waste.

4) Activation time condition had been varied from 0.5 to 4 hours, as well as the activation temperature, the proper activation time depend on the nature of precursor. However, 0.5 to 2 hours was the proper time of treatment of both $ZnCl_2$ and K_2CO_3, higher activation time was not preferable.

5) The proper ratio of agricultural by-product and activating agent for $ZnCl_2$ was varied from the ratio of 1:1 to 1:4, where as 1:2 was the proper ratio for K_2CO_3. However, those variation were also dependently on the precursor as well as temperature and time.

As mentioned above in item 1) and 2), they are leading to experimental procedure which has been conducted in preparation process. The impregnation method was used to mixing because it has better distribution of chemical agents into precursor particle mass, and gave an advantage over others method that was discussed by Ahmadpour A. and Do D.D. [16].

In addition, the experimental condition of chemical activation process is able to be changed largely, not only because of many variables that affect the activation process, but also the large variety of raw material precursors and chemical agents. Nevertheless, the stipulated various experimental conditions are used in this work as follows.

- The weight ratio of raw material to activation agent (w/w) are 1:1, 1:2, 1:3 and 1:4
- Activation Temperature are 600, 700, 800 and 900ºC
- Activation Time are 1, 2 and 3 hour(s)

2.6 Standard for Activated carbon

2.6.1 Characteristics of Activated Carbon

According to Bansal et al. [1], the effectiveness of activated carbon as an adsorbent is attributed to its unique properties, including large surface area, a high degree of surface reactivity, universal adsorption effect, and favorable pore size. Its extremely large surface area often characterizes activated carbon. For comparison, a given type or sample of activated carbon is usually quantified based on four primary criteria: total surface area, carbon density, particle size distribution, and adsorptive capacity. All of these factors influence adsorption rate and also capacity.

1) Total surface area

Total surface area is measured by the adsorption of nitrogen gas onto the carbon and is expressed in square meters of surface area per gram of carbon. Because the gas molecules used to measure adsorption are very small, it should be noted that this measurement of surface area might be misleading when considering the adsorptive capacity of a carbon for large organic macromolecules. Those types of compounds may have adsorption limited by pore size considerations. In fact, the surface area per gram of material ranging from 600 to 1,200 m^2/g, and as high as 2,500 m^2/g have been reported [21,29].

2) Carbon density

Carbon density is the weight of one milliliter of carbon in air. Bulk density is also sometimes used for carbon as it is for soil, and is expressed in pounds per cubic foot or in kilograms per liter.

3) Particle sizes

Particle sizes in carbons are measured using standard U.S. sieve sizes, as for soil constituents. Particle size distributions are important in carbon systems because they influence handling of the activated carbon material. For example, in granular carbon, the particle size affects hydraulic loading and backwash rates for a filter. On the other hand, particle size is often important because of its effect on adsorption rates as well.

4) Adsorptive capacity

Adsorptive capacity is characterized by the effectiveness of activated carbon in removing a given contaminant. For comparison, several standard compounds are used for these measurements. For example;

- ***Iodine number*** commonly used describes the carbon's capacity to adsorb low-molecular-weight substances. The iodine number indicates the porosity of activated carbon and defined as the milligrams of iodine adsorbed per gram of carbon. Iodine number represents the surface area contributed by the pores larger than 10ºA. Iodine number is commonly used in the industry, as a rough estimate of surface area of the activated carbon.
- ***Molasses number*** characterizes a carbon's capacity for more complex compounds. Molasses number represents the surface area contributed by the pores larger than 28ºA.

5) The structural properties

The structural properties of activated carbon are very important to its effectiveness as an adsorbent, though activated carbon's structure is not fully understood and is difficult to explain with text. In general, activated carbon is sometimes described as having a crumpled layered surface, in which flat sheets are broken and curved back upon them. This unique structure creates activated carbon's very large surface area. It can be more properly visualized with the attached images, which provide both electron microscope photos and conceptual diagrams of the surface structure.

There are several standard test methods were used to determine the characteristics of activated carbon. Among them, ASTM standard (The American

Society for Testing Material) and AWWA standard (American Water Works Association) have been recognized.

2.6.2 Specification of activated carbon

In Thailand, a physicochemical characteristic of commercial activated carbon was provided for by TISI 900-2532 (1989). As shown in Table 2-8, it is the specification of Thailand Industrial Standard Institute (TISI), Ministry of Industry.

Table 2-8: Physicochemical requirement of activated carbon

Characteristics	**Requirement**	
	Powder activated carbon	**Granular activated carbon**
Iodine number (mg/g)	No less than 600	No less than 600
Bulk density (g/cm^3)	0.20-0.75	No less than 0.37
Hardness (%)	-	70

Source: *Thailand Industrial Standard Institute (TISI) [41]*

It can be seen that the characteristics requirement focused on iodine number to represent the surface area due to it commonly used in the industry. Therefore Iodine number has been used to characterize activated carbon produced from this research work.

CHAPTER 3

MATERIALS AND METHODS

3.1 Experimental Procedure

This work has been performed in laboratory scale in order to prepare an activated carbon from coffee ground waste, residue from instant coffee, by chemical activation. The results from previous studied have shown that degree of the impregnation of precursor, activation temperature and activation time are important parameters that govern the development of porous structure of activated carbon. In order to obtain the previous studies information, this work had been conducted at various experimental conditions:

- The activating agents used are $ZnCl_2$ and K_2CO_3 that widely commercial used [1,2-7]) and interesting agent with less pollution [11-14].
- The weight ratio of coffee grounds waste to activating agent was orderly varied in range of 1:1, 1:2, 1:3 and 1:4 [4,5,13,14].
- The activation temperature was also varied in the range of 600, 700, 800 and 900 °C [7, 11-14] and
- The activation time was controlled at 1, 2 and 3 h [2,4].

Work had been carried out at Faculty of Environment and Resource Studies, Mahidol University, Salaya Campus, Nakornpathom Province. All experiments were repeated 3 times to ensure reproducibility. The Iodine number of the resulting activated carbon was analyzed and used to establish the appropriate operation condition including activation temperature, activation time and activating agent impregnation ratio. The general procedure of this work is described below and it's schematically outlined in Figure 3-1.

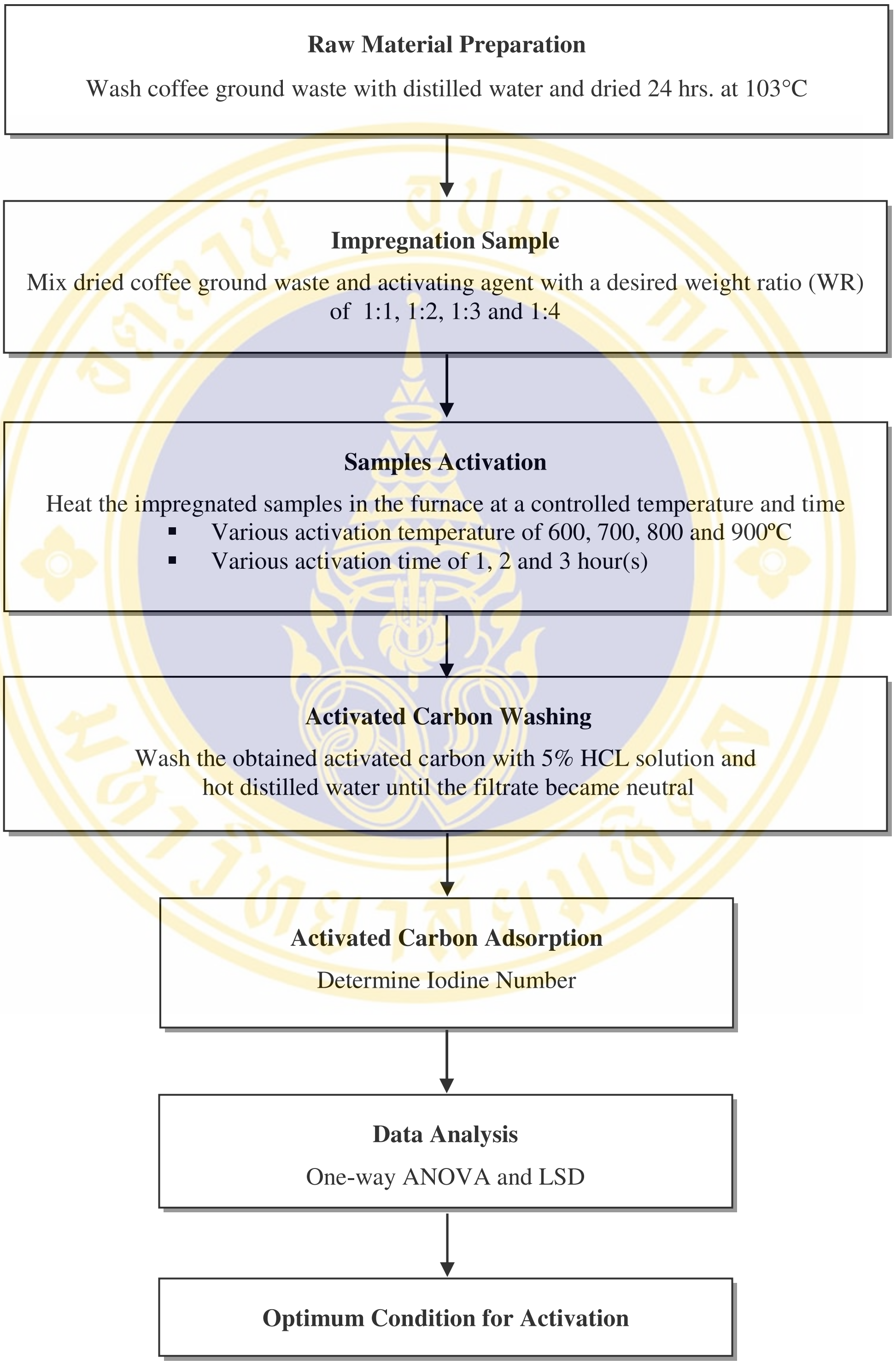


Figure 3-1: Flow diagram of experiment for this study procedure

3.2 Equipment and Chemical Reagents

3.2.1 Experimental Instruments

1) Hot air oven
2) Carbolite furnace
3) Analytical balance
4) Desiccator
5) Hot plate and stirrer
6) Magnetic stirrer
7) pH meter
8) Crucible and cover
9) Filter vacuum set
10) Sieve mesh

3.2.2 Chemical Reagents

1) Zinc chloride ($ZnCl_2$)
2) Potassium carbonate (K_2CO_3)
3) Hydrochloric acid (HCl)
4) Sodium thiosulfate ($Na_2S_2O_3 \cdot 5H_2O$)
5) Iodine
6) Potassium iodide (KI)
7) Potassium iodate (KIO_3)
8) Sodium carbonate (Na_2CO_3)
9) Distilled water

3.3 Experiments

3.3.1 Coffee ground waste preparation

The raw material used in this study was coffee ground waste, a residu product from instant coffee industry by grab sampling. The coffee ground waste thus treated was washed with distilled water in order to reduce the residue content and then dried at 103°C for 24 hours. The dried coffee ground waste was cooled and kept in desiccator before use in further experiments. Proximate analysis by using procedures prescribe in standard practice for proximate analysis of coal and coke, ASTM D 3172-89 (1994) and ultimate analysis with CHN-elemental analyzer had been performed.

3.3.2 Impregnation sample

1) Fifty grams of dried coffee ground waste were impregnated with activating agent solution (i.e. $ZnCl_2$ and K_2CO_3), which was carried out by mixing activating agent with 200 ml. distilled water resulting in desired weight ratio (decode as WR) of coffee ground waste to activating agent i.e. 1:1, 1:2, 1:3 and 1:4. Then it was left for 24 hrs. at room temperature, so that reagents are fully adsorbed into the coffee ground waste.

2) After removing the supernatant liquid, impregnated coffee ground waste was dried at 103° C 24 hours. The impregnation ratio (denote as IR) was defined as below.

$$\text{Impregnation ratio} = (m_1 - m_0)/m_0$$

When m_0 is mass of coffee ground prior to activating agent impregnation
m_1 is mass of impregnated coffee ground and

3) The dried impregnated coffee ground waste was kept in desiccator before use in activation step.

3.3.3 Sample activation

In this work, carbonization and activation had been carried out simultaneously in the absence of oxygen. All experiments were preformed as follows:

1) Twenty grams of dried impregnated coffee ground (w_1), in each set of experiments, was loaded on crucible with lid, and then place the crucible inside furnace.

2) The impregnated coffee ground samples were heated from an initial room temperature (app. 30° C) to final temperature of 600, 700, 800 and 900° C at heating rate of 15°C/min and maintained at activation time of 1, 2 or 3 h thereafter. Then it was cooled down in desiccator until constant weight.

3) In order to remove the remaining activating agent on the activated carbon, it was washed by 5% HCl solution, and followed with hot distilled water then filtered. The hot distilled water washing then filtration step were repeated until the filtrate become neutral. The washed activated carbon was dried at 103° C for 24 hours, then it was weighed (w_2) after cooling down to constant weight. The yield of resulting activated carbon (%Y) based on impregnated sample was calculated as follows:

$$\%Y = (w_2/w_1) \times 100$$

When w_1 is weight of impregnated coffee ground (g)

w_2 is weight of resulting carbon (g)

4) The resulting activated carbons were kept in desiccator in order to preserve the physical and chemical properties of sample, before characterization.

3.3.4 Analytical method

In this work, iodine number, absorption capacity of resulting activated carbon was examined. The method for analyzing of iodine absorption using ASTM standard test method (D 4607-94) and also characteristic of activated carbon were analyzed according to the methods as shown in Table 3-1.

Table 3-1: Analytical parameters and methods

Parameters	**Methods/Equipments**
Proximate analysis	
Moisture content	ASTM D 2867-95
Ash content	ASTM D 2866-94
Volatile matter	ASTM D 5832-95
Adsorption capacity	
Iodine number	ASTM D 4607-94
Specific surface area	ASTM D 4820-95
Surface image	Scanning Electron Microscope; SEM

3.3.5 Data analysis

The analysis of variance (ANOVA) to determine the difference of iodine absorption was also conducted at p-value at 0.05. Least Significant Difference Test (LSD) was used to perform a multiple comparison of the mean. All the data were analyzed by using the package program of SPSS version 10.0.

CHAPTER 4
RESULTS AND DISCUSSION

In this work, coffee ground waste, an agricultural by-product from instant coffee, was utilized as the precursor for activated carbon production using chemical activation, and its adsorption capacity as iodine number was evaluated. Two chemical agents such as zinc chloride ($ZnCl_2$) as a commercial activating agent and potassium carbonate (K_2CO_3), as an interesting with less pollution, were used as activating agents. The effect of parameters to preparation condition i.e. the weight ratio (WR) of raw material to activating agent, activation temperature and activation time were studied in order to seek an optimal condition to produce activated carbon. The resulting activated carbon was characterized the adsorption capacity as iodine number due to it indicates the porosity of the activated carbon, and also the amount of iodine that adsorbed to carbon as milligram per gram of carbon. Iodine number has represented the surface area that contributed to the pores larger than 10 Å, and was commonly used in the industry as a rough estimation of the activated carbon's surface area. In Thailand, TISI 900-2535 (1989) of Thailand Industrial Standard Institute (TISI) was the stipulation of standard of activated carbon which required iodine number no less than 600 mg/g. Therefore, the optimum activation condition was selected by considering TISI standard, iodine number development and economic process i.e. cost and energy saving. The experimental results are able to be explained as follows:

4.1 The Characteristics of the Coffee Ground Waste

The coffee ground wastes collected from an instant coffee factory in Samutprakarn province by using grab randomly sampling during the collection. Usually, coffee ground waste leaved the percolators with high moisture [27]. The sample used in this work has moisture content of 45.14% as received basis (see table A-1 in Appendix A).

However, after air-dried that took around seven days, the compositions of the coffee ground waste were analysed in weight percentage based on dry basis (wt.%db) and dry ash free basis (daf) in proximate and ultimate analysis as shown in Figure 4-1. and Table A-1 (see Appendix A).

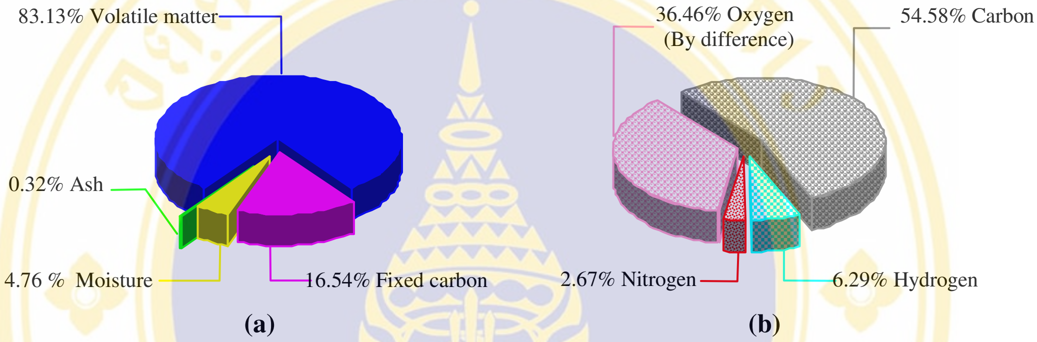


Figure 4-1: The compositions of coffee ground waste (a) Proximate analysis as wt.%db, and (b) Ultimate analysis as wt%daf

It was interesting to point out the nature of coffee ground waste affect as starting material for activated carbon in comparison with commercial precursors i.e. coal, lignite, peat, coke and coconut shell [1,28], and agricultural by-product precursors i.e. corncob, apricot stone, cherry stone, grape seed, almond shell, walnut and hazelnut shell [2,4,7,18,20,28], as follows;

- **Proximate analysis**

The results of proximate analysis of coffee ground waste as shown in Figure 4-1 (a), it can be seen that coffee ground waste was contained a very low moisture and ash content (4.76 wt.%db and 0.32 wt.%db) whereas high in volatile matter (83.13 wt.%db) and fixed carbon (16.54 wt.%db). However, the ash content of coffee ground waste is quite lower than lignite (5.0-6.0 wt.%db), peat (0.2-1.2 wt.%db) and coal (2-15 wt.%db) [1], but close together with coke (0.5-0.7 wt.%db) [1] and agricultural by products such as stones of apricot and cherry (0.2 wt.%db and 0.9 wt.%db) [18].

- **Ultimate analysis**

The ultimate analysis of coffee ground waste was conducted using elemental analyzer. The analytical results for C, H, N and O were shown in Figure 4-1 (b). It can seen that coffee ground waste is mainly composed of carbon (54.58%daf), which is the important property for starting material as activated carbon, but low in hydrogen (6.29%daf), nitrogen (2.67%daf) and oxygen content (36.46%daf ultimately by difference). The carbon content of coffee ground waste is similar to that reported (53.8 and 59.5% daf) by Mizuho Hirata et al. [26] and Silva et al. [27]. Although, the carbons content in both cases are largely similar, but there may be differences in its composition depending upon the processing mode and efficiency, crop variety, cultivation condition such as soil type, etc. [27].

In comparison to the other precursors, it is noted that carbon content in coffee ground waste (54.58%) is higher than wood (40-45%) [1], coconut shell (46.59%), corn cob (46.84%) [28], but similar to apricot stones (51.5%), cherry stones (53.9%), grape seeds (55.4%), almond shell (54.7%) [7], walnut shell (51.5%) and hazelnut (51.4%) [19]. However, it is lower than precursor materials from different coal rank in which they were mostly of >60% [6]. Although, these agricultural by-product materials are low in carbon content material (less than 60%), but their amount of carbon are highly enough to be produced as activated carbon. In addition, they are also sufficiently low in ash content to make them suitable precursor. Then, they are quite promising raw materials for production of activated carbon.

4.2 Impregnation Ratio

In this stage, impregnation method with a concentrated solution was used to mixing due to its better distribution of chemical agent into particle mass of the precursor that have the advantage of the other methods as discussed by Ahmadpour A and Do DD [16]. Incidentally, the obtainable preliminary experimental results indicated that impregnation ratio (IR) values between reflux and physical solution method were not significantly different. Hence, the impregnation with physical solution method was chosen for mixing coffee ground waste and activating agent, considering the simpler performance and the process economics.

The dried coffee ground waste was mixed with activating agent i.e. $ZnCl_2$ and K_2CO_3, the weight ratio of coffee ground waste to activating agent was varied in range of 1:1, 1:2, 1:3 and 1:4, followed by drying at 103ºC. Then, the impregnation ratio (see Table A-2 in Appendix A) was calculated based on the activating agent-free coffee ground waste precursor. And one-way ANOVA have been statistically applied in data analysis at 95% confidence of limit, and then Lest Significant Different Test (LSD) was used to perform a multiple comparison (see Appendix B). As shown in Figure 4-2, the results of impregnation ratio (IR) of coffee ground waste to activating agent obtained by $ZnCl_2$ agent and then those by K_2CO_3 agent were firstly discussed as follows;

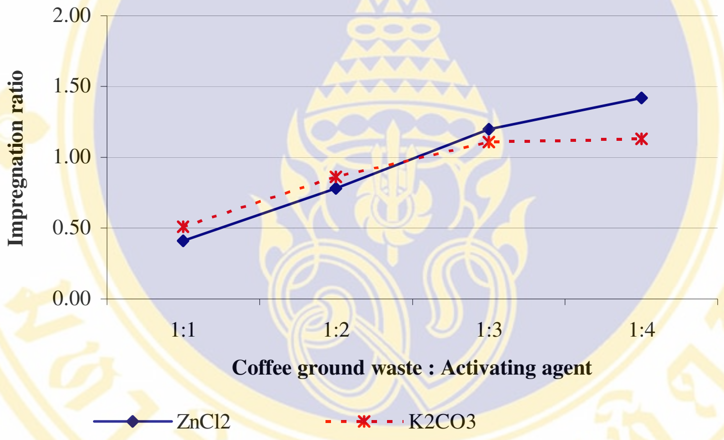


Figure 4-2: Impregnation ratio of $ZnCl_2$ and K_2CO_3 at different weight ratio of coffee ground waste to activating agent

4.2.1 Impregnation ratio in $ZnCl_2$ series

As shown in Figure 4-2, the results showed that the impregnation ratio in $ZnCl_2$ series were gradually increased from the weight ratio of 1:1 to 1:4 with an increasing of $ZnCl_2$ agent. They were 0.41, 0.78, 1.20 and 1.42 or 41%, 78%, 120% and 142%, respectively. In practice, increasing in weight ratio implies the increase in amount of activating agent, likewise the amount of activating agent that adsorbed into precursor material. In addition, the statistically analysis indicated that the impregnation ratio in $ZnCl_2$ series were significantly different. Thus, 1:1, 1:2, 1:3 and 1:4 weight ratio of $ZnCl_2$ were chosen for activated carbon preparation.

4.2.2 Impregnation ratio in K_2CO_3 series

As presented in Figure 4-2, the impregnation ratio in K_2CO_3 series were gradually increased from the ratio of 1:1 to 1:3, then it was rather stable after this point, as we can see the value of impregnation ratios of K_2CO_3 series were of 0.51, 0.86, 1.11 and 1.13 or 51%, 86%, 110% and 113%, respectively. Moreover, the result of LSD test indicated that the impregnation ratios of 1:1, 1:2 and 1:3 weight of coffee ground waste to K_2CO_3 were significantly different, while there were no significantly different at the ratio of 1:3 and 1:4. Therefore, it is deducible that K_2CO_3 are fully adsorbed into the coffee ground waste mass, the change of adding K_2CO_3 at the ratio of 1:3 up to 1:4 did not made any significant different to impregnation ratio. Hence, only the ratio of 1:1, 1:2 and 1:3 weight ratios of K_2CO_3 series were adopted.

4.3 Effect of the Weight Ratio of Coffee Ground Waste to Activating Agent

The weight ratio of coffee ground waste to activating agent used in this experiment were resulted from the foregoing impregnation ratio studies, they were 1:1, 1:2, 1:3, 1:4 (or 41%, 78%, 120% and 142% in impregnation ratio term) for $ZnCl_2$ agent and 1:1, 1:2, 1:3 (or 51%, 86% and 110% in impregnation ratio term) for K_2CO_3 agent. The effect of weight ratio on iodine number of resulting activated carbon was investigated. In Figure 4-3, it is the presentation of the variation of adsorption capacity as iodine number for activated carbon obtained from $ZnCl_2$ and K_2CO_3 versus the weight ratio of coffee ground waste to activating agent.

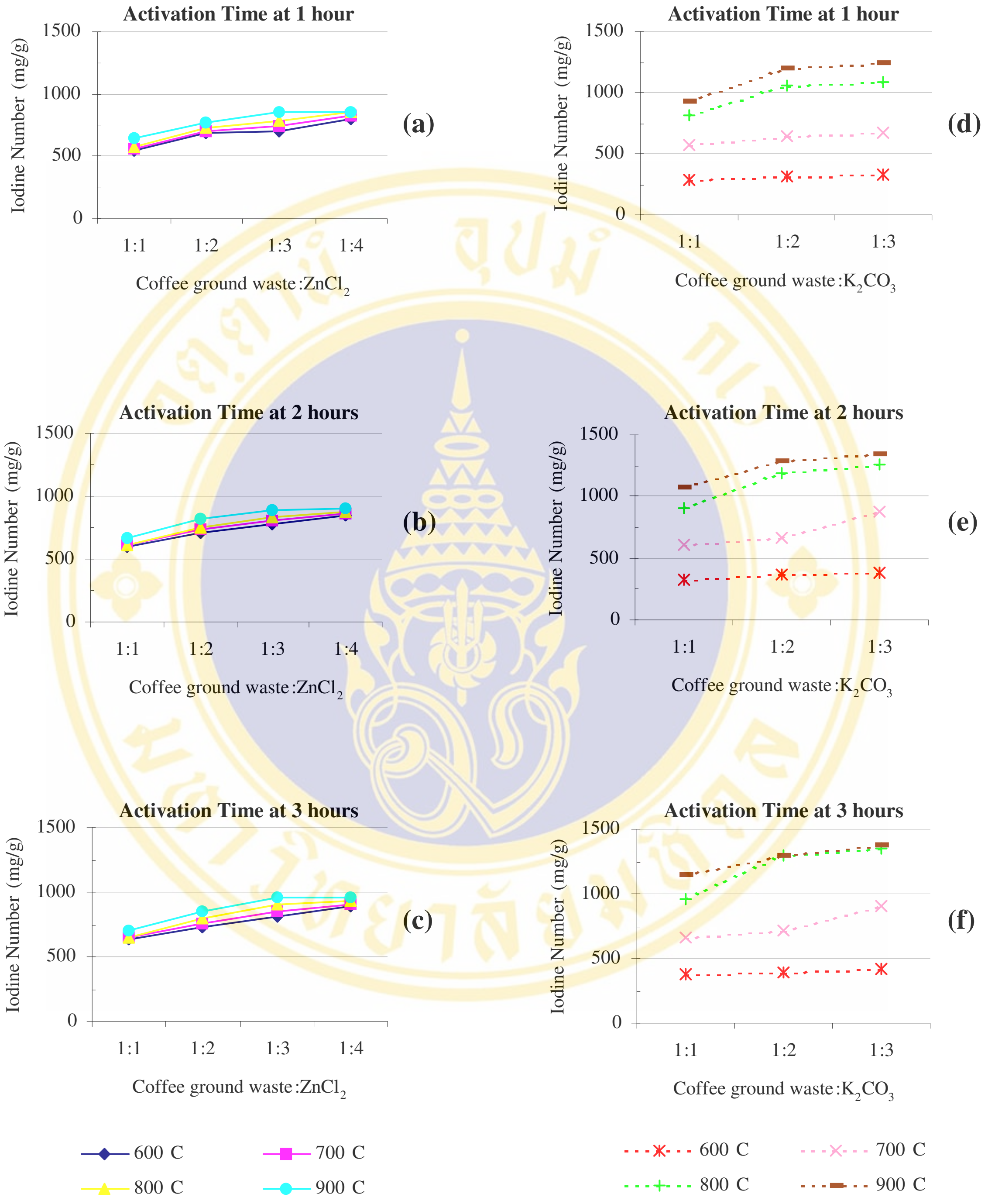


Figure 4-3: Effect of weight ratio of coffee ground waste to activating agent at various activation temperatures; (a)-(c) $ZnCl_2$ Series, (d)-(f) K_2CO_3 Series

4.3.1 Effect of the weight ratio in $ZnCl_2$ series

In Figure 4-3 (a), (b) and (c), the results showed that in all case of $ZnCl_2$, the values of the iodine number were gradually increased with increasing in weight ratio. These results demonstrated that high impregnation ratio or weight ratio was favorable for producing carbon adsorbents with high porosity and thus high iodine number, and also consistent to work done by Tsai et al. [2,3] and Jim-Wha Kim et al. [4]. As they reported that the more weight ratios/impregnation ratios are increased, the more surface areas are developed. Therefore, the activated carbons with higher surface area/or total pore volume were expected to be the excellent adsorbents.

As the TISI 900-2532 (1989) has recommended that iodine number of activated carbon should not be lesser than 600 mg/g [41]. In consideration to the results of iodine number at various weight ratio used in the experiment, it can be seen that at the ratio of 1:1, 1:2, 1:3 and 1:4 the iodine number are of 553-703 mg/g, 690-857 mg/g, 701-956 mg/g and 804-955 mg/g respectively. However, at the weight ratios of 1:1, the iodine number appeared to be closed to the standard level this possibly might be due to insufficient activation of time, and temperature. As we can see that only the iodine number of the weight ratio 1:1 at activation time of 1 and 2 hour were lower than TISI requirement while at the 3 hours were higher.

In order to find out an optimum of weight ratio, behavior of iodine number was observed in parallel with statistically consideration. It was observed that trend of iodine number at the ratio of 1:1 to 1:3 were gradually increased, then were dropped significantly after 1:3. Accordingly, the optimum weight ratio of $ZnCl_2$ was 1:3 or impregnation ratio of 120%, with respect to iodine number and economic cost. However, this result is consistent to work done by Jim-Wha Kim et al.[4] who indicated the optimum weight ratio of walnut shell was 1:3 , but rather different to other agricultural by-product which as Tsai, et al. [2] has reported that the impregnation ratio of corn cop and bagasses waste are 175% and 100%. By these reasons, it can be concluded that an optimum weight ratio/impregnation ratio, generally, depends on the nature of precursor material including activation method [1].

4.3.2 Effect of the weight ratio in K_2CO_3 series

As presented in Figure 4-3 (d), (e) and (f), the values of the iodine number were gradually increased with increasing in weight ratio. The values of iodine number were of 290-1,151 mg/g, 320-1,300 mg/g, and 330-1,380 mg/g at the weight ratio of 1:1, 1:2 and 1:3 respectively. However, at the weight ratios ranging from 1:2 to 1:3 the value iodine number were not significantly different. Therefore, it is reasonable to assume that the optimum weight ratio of 1:2, or impregnation ratio 86%, can be chosen for K_2CO_3 series. This resulting optimum ratio appeared to be higher than those obtained from weight ratio 1:1 of chickpea husk [13] and cork waste [14], including corn cob (impregnation ratio of 37.5%) [11]. Again, we can see that an optimum weight ratio depends on the nature of precursor materials.

In addition, the behavior of development of iodine number in ranging 1:1 to 1:3 of K_2CO_3 series are slightly different comparing among various temperature, at the low temperature condition, 600ºC and 700ºC, the values of iodine number were lower than those of high temperature, 800ºC and 900ºC. It implies also the strongly influence of activation temperature to the development of iodine number, leading to the higher adsorption capacity and also surface area (which discussed in further section).

It is interesting to see the iodine behavior at low activation temperature, 600°C and 700ºC, in which the value of iodine number were slightly changed by weight ratio. This result agreed with work done by Carvalho A. P. et al. [14] who attempted to prepare activated carbon from cork waste by chemical activation using K_2CO_3 at activation temperature of 700ºC, and they found the smallest amount of K_2CO_3 (1:1) that used in activation gave the textural characteristics of resulting activated carbon the same as activation with the highest (1:5) amounts of K_2CO_3.

4.4 Effect of the Activation Temperature

In this section, the effect of final activation temperature ranging from 600ºC to 900ºC on the resulting activated carbon was investigated. The heating rate was maintained at 15ºC/mim. In general, activation temperature was known to be very influential on micropore structures of activated carbon, leading to adsorption capacity [1,4], as well development of micropore can provide the adsorbent with a high specific surface area and absorbability [2]. As presented in Figure 4-4, the results showed the influence of activation temperature on iodine number of resulting activated carbon at various weight ratio of coffee ground to activating agent.

4.4.1 Effect of the activation temperature in $ZnCl_2$ series

As shown in Figure 4-4 (a), (b) and (c), it can be seen that iodine number has increased gradually with activation temperature which the values of iodine number were of 553-890 mg/g, 556-905 mg/g, 572-927 mg/g and 645-955 mg/g at activation temperature of 600ºC, 700ºC, 800ºC, and 900ºC respectively. The lowest iodine value at the activation temperature of 600ºC was shown, then it was rising up until the highest value was appeared at 900ºC. In consideration to the effect of activation temperature on characterization of the resulting activated carbon, it was revealed that in activation process using high temperature was greater than low temperature. It means that elevated heating temperature has improved the porosity and affected iodine absorption of the resulting activated carbon. It has been recognized, in general, that adsorption capacity is rising up with activation temperature [1]. This behavior is similar to that has been report by Tay, J H et al. [42].

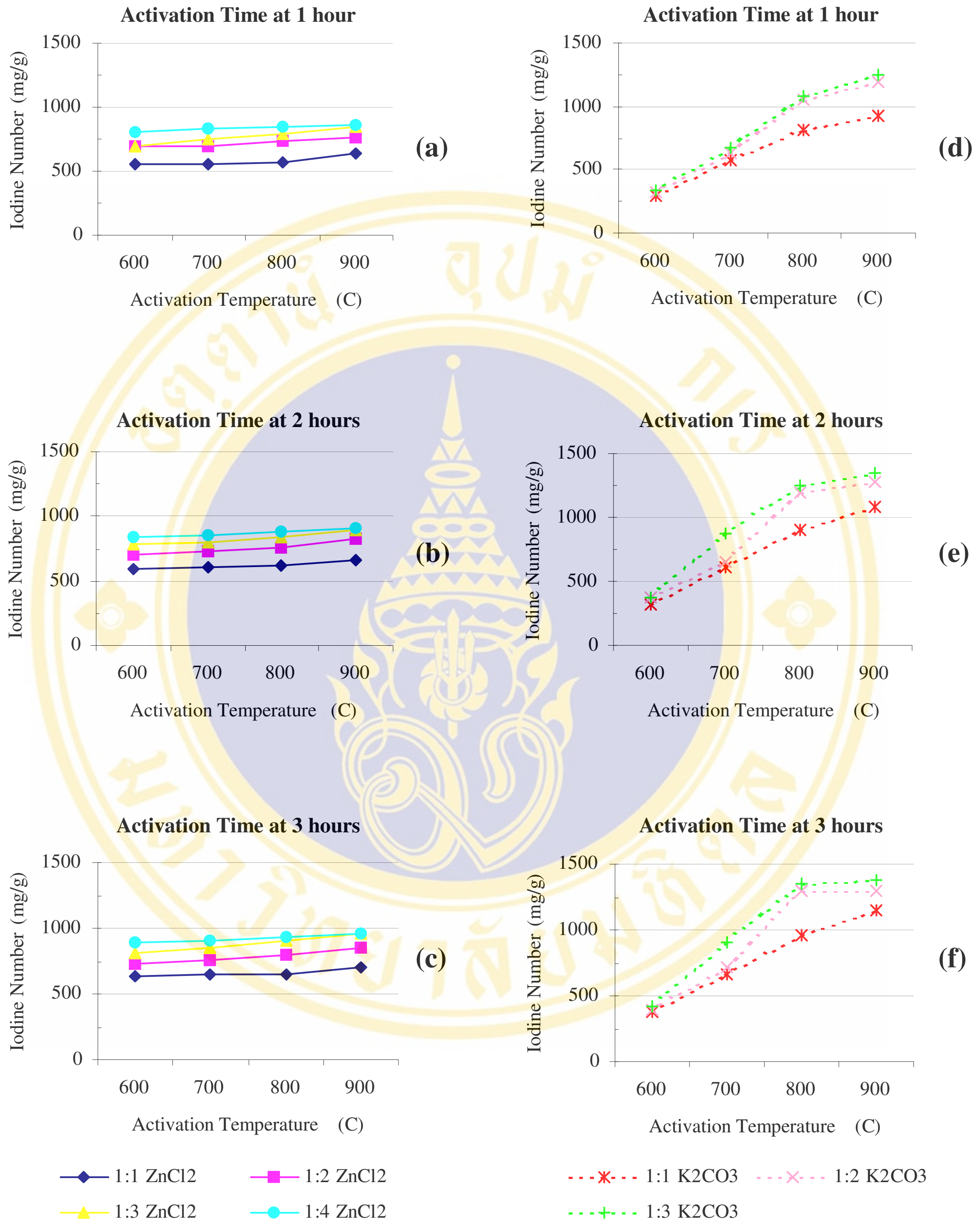


Figure 4-4: Effect of activation temperature at various weight ratio of coffee ground waste to activating agent; (a)-(c) $ZnCl_2$ Series, (d)-(f) K_2CO_3 Series

In consideration to changing of iodine numbers, it can be concluded that optimum activation temperature for $ZnCl_2$ series is approximately 800 ºC because there were no significantly change between the results obtained from the reaction of 800ºC and 900ºC. Although, this optimum temperature value, when compared with the reaction at 500ºC, was higher than that recommended for $ZnCl_2$ by other workers [2,3,16] in activation precursors with different conditions. But there has been a number of studies reported that at activation temperature above was suitable for $ZnCl_2$ [5-7]. However, we still found many works on agricultural by-product that was conducted at the temperature above 500ºC such as work done by Kadirvelu et al. [5] that activation temperature at 700ºC was applied for waste parthenium (stem and leaves). Beside, Aygün et al. [7] has also found that the highest surface area of activated carbon from almond, hazelnut and walnut shells were produced at 750ºC while apricot stone was at 800ºC.

4.4.2 Effect of the activation temperature in K_2CO_3 series

From Figure 4-4 (d), (e) and (f), it is appeared that iodine number value has rapidly increased with an increasing of activation temperature in range of 600ºC (290-418 mg/g), 700ºC (569-901 mg/g) and 800ºC (812-1,352 mg/g) then become slightly changed between 800ºC and 900ºC (928-1,382 mg/g). At the activation temperature of 600ºC, the resulting activated carbons have low in value of iodine number ranging from 300 to 400 mg/g, which is lower than the requirement of 600 mg/g of TISI 900-2535 (1989) [41]. This result indicated that at this temperature activated carbon could not be sufficiently promoted to meet the standard requirement. However, at the activation temperature of 700ºC, the resulting activated carbon property was able to meet TISI requirement and greater continuously when temperature rose up.

Clearly, working of K_2CO_3 at the temperature above 700ºC for producing activated carbon from agricultural by-product is recommended [9-17]. As generally known that coffee bean commonly consists of cellulose, hemi-cellulose and lignin [25-27], which could be decomposed at the temperature ranging from 300 to 430 and 250 to 550ºC. In case of hemi-cellulose, it could be decomposed at much lower temperature [12]. In addition, during impregnation with K_2CO_3, cellulose and hemi-cellulose in biomass material would have been modified [12]. Also, during activation/or carbonization at a temperature higher than 700ºC, metallic potassium is produced and they intercalated to the carbon matrix, which are responsible for further carbon gasification and release of gaseous products such as CO_2, CO and H_2 [11-13]. As Tsai et al. [11] have reported that the maximum rate of increasing of BET surface area (S_{BET}) occurred between temperature of 650ºC to 700ºC. Similarly, Hayashi et al. who prepared activated carbon from various nutshells [12] and chickpea husk [13] reported that K_2CO_3 work effectively above a temperature of 700ºC, however the specific surface area would be decreased because the combination of micropores takes place due to the collapse the wall of the micropore to mesopore by excess activation beyond 800ºC.

It is clear that the activation temperature had a significant influence on the iodine number development. The iodine number value was observed to be increased at higher activation temperature. However, at activation temperature ranging from 800ºC to 900ºC the value of iodine number was practically the same. Thus it is deduced that the optimum activation temperature is 800ºC for K_2CO_3 activation which is also considerable for energy saving. This chosen condition was similar to the suitable temperature for corn cob [11], various nutshells, coconut shell [12] and chickpea husk [13]. On the other hand, in working with cork waste by Carvalho et al. [14] the optimum temperature of 700ºC was considerably chosen in energy saving.

4.5 Effect of the Activation Time

In this section, activation time has been investigated to evaluate its effect on resulting activated carbon; the dried impregnated coffee ground waste were heated up to final activation temperature at heating rate of 15ºC/min then maintained the temperature for 1, 2 and 3 hour(s) thereafter. In general, adsorption capacity was increased with activation time [1], however, under extended activation, the micropores structure of produced activated carbon deteriorated and turns into macropores thus adsorption capacity was drop [4]. In Figure 4-5, the results of the effect of activation time on iodine number of resulting activated carbon are presented.

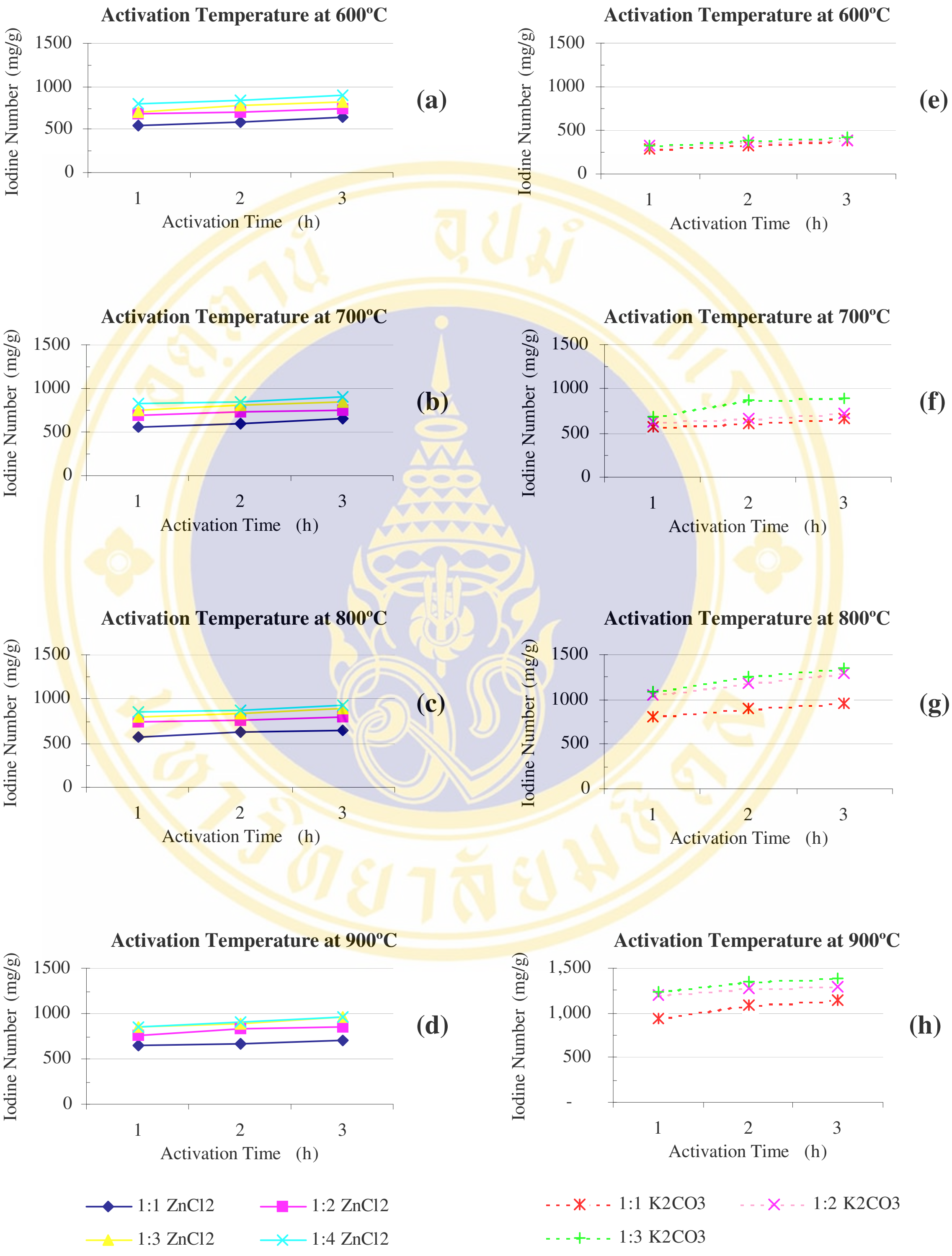


Figure 4-5: Effect of activation time at various weight ratio of coffee ground waste to activating agent; (a)-(d) $ZnCl_2$ Series, (e)-(h) K_2CO_3 Series

4.5.1 Effect of the activation time in $ZnCl_2$ series

As shown in Figure 4-5 (a), (b), (c) and (d), the iodine number has increased slightly with an increasing of activation time which the values of iodine number were of 553-860 mg/g, 591-905 mg/g, and 642-955 mg/g at activation time of 1 hour, 2 hours, and 3 hours respectively. However, these were no significantly difference of iodine number between 1 and 2 hours except for 3 hours which was clearly different. It is also noticed that whenever the harsher conditions, such as higher temperatures and higher $ZnCl_2$ ratio, are used the largest differences can be observed, meaning that the effect of activation time to iodine number was relatively minor in comparison with activation temperature and weight ratio. This result was similar to work done on the effect of dwell time to produced activated carbon by Tay et al. [42]. With regard to the iodine number at 3 hours of activation time, the best iodine number of the $ZnCl_2$ series was appeared and chosen.

4.5.2 Effect of the activation time in K_2CO_3 series

As presented in Figure 4-5 (e), (f), (g) and (h), it is the results of various iodine number versus with activation time. It can be seen that the value of iodine has slightly increased with increasing activation time which the values of iodine number were of 290-1,245 mg/g, 319-1,350 mg/g, and 381-1,382 mg/g at activation time of 1 hour, 2 hours, and 3 hours respectively. However, there were no statistically differences of iodine numbers at 1, 2 and 3 of activation time. Therefore, the impact of activation time on resulting activated carbon was not expected to be so significant in comparing with activation temperature.

Nevertheless, the different of iodine number between elevated activation times at each activation condition is possibly be used as an evidence in finding the optimum condition. As previously discussed (Item 4.4.2), the iodine numbers, at the activation temperature of 600ºC, were negligible as it is lower than TISI standard. In consideration to the results from the reaction with temperature above 600ºC, it can be seen that the differences of iodine number between activation time of 1 and 2 hour(s) was larger (>100 mg/g) than those of the differences between 2 and 3 hours (<50 mg/g except for at activation temperature of 800ºC), as see in Table A-7 (in Appendix A).

Therefore, it is deduced that the optimum activation time of 2 hours can be chosen for K_2CO_3 series, considering the iodine number development of resulting activated carbon and economic factor.

4.6 Conversion Yield of Activated Carbon

In term of assessing the feasibility of preparation of activated carbon from precursors, production yield was considerable important. It is usually calculated as a percentage of the product weight versus corresponding precursor weight. As the activated carbon, generally, was sold on weight basis, thus high conversion yield as much as possible, is expected. However, conversion yield are affected by various condition parameters as those has been investigated in this work such as weight ratio of coffee ground to activating agent, activation temperature and time. In Figure 4-6, the experimental results of conversion yield with various activation parameters, are presented as follows:

4.6.1 Conversion yield in $ZnCl_2$ series

The resulting yield of activated carbon for $ZnCl_2$ series was in range of 30.2-67.9 wt.%db (see Table A-3 in Appendix A). Basically, activation using $ZnCl_2$ at low temperature is rather not sufficiently accomplished and all elements such as H, O, N and S still are largely remaining with C after thermal treatment. Thus, as the activation temperature become higher, the product yield was expected to be decreased, depending on the kind of raw material.

As seen in Figure 4-6 (a), (b) and (d), the conversion yield was gradually decreased at higher activation temperature and time, including weight ratio which is possibly attributed to the volatilization of tar products derived from the lignocellulosic components of raw material [16]. As a result of shrinking in the carbon structure at higher activation temperature, it is reasonable that the true density and particle density of resulting activated carbons were increased with activation temperature [1].

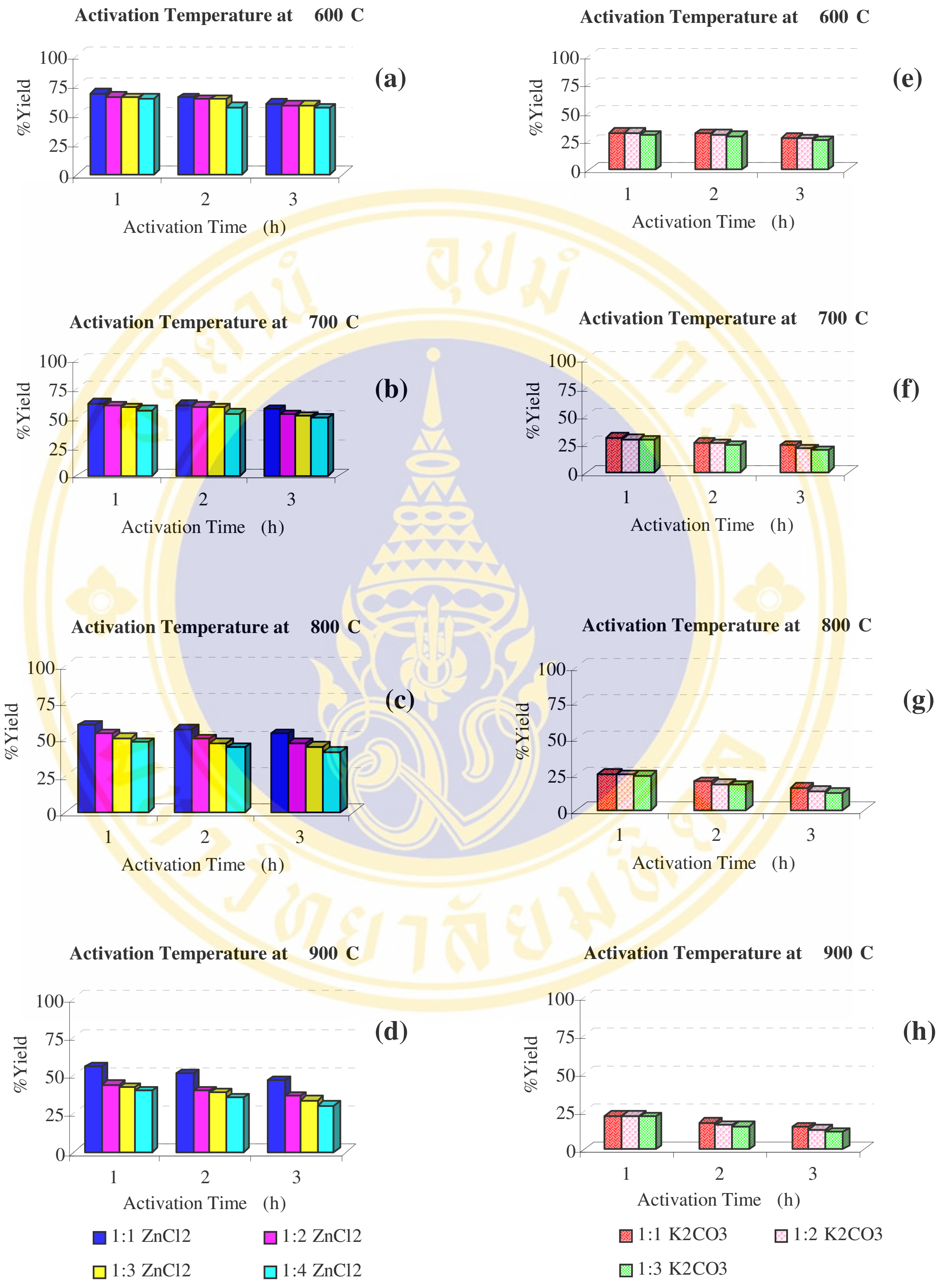


Figure 4-6: The conversion yield of activated carbon; (a)-(d) $ZnCl_2$ Series, (e)-(h) K_2CO_3 Series

4.6.2 Conversion yield in K_2CO_3 series

Difficulty arose and attempt has been made to recovering the entirely activated carbon from the surface of vessel as they were sticky to determine a yield, activated carbon had to scarp. As shown in Figure 4-6 (e), (f) and (h), it can be seen those conversion yields of activated carbons in K_2CO_3 series have been changed with temperature. They were in range of 11.2 to 32.6 wt.%db (see Table A-4 in Appendix A). However, they were reversely decreased with activation temperature, which was possibly attributed to the evolution of gaseous products and the volatilization of tar products from the carbonaceous structure at higher activation temperatures [1,2]. Therefore, the lower yields at high temperatures were expected.

Although, the conversion yields in K_2CO_3 series were lesser, but their adsorptive capacity were slightly higher than those from $ZnCl_2$ series. Thus, a compromise should considerably be made between the conversion yield and the adsorptive properties of product. Results from this work has shown that the highest activation temperature, time and the weight ratio of activating agent could be leading to the highest iodine number and also the adsorptive property, but the yield, in fact, was not satisfactory in K_2CO_3 series. However, the precursors used in this work are coffee ground waste from instant coffee factory which actually low cost but they are able to be produced as activated carbon with preferable adsorptive property.

4.7 The Optimum Condition for Coffee Ground Waste Activation

As this work aimed to optimize the activation condition for activated carbon preparation from coffee ground waste using $ZnCl_2$ and K_2CO_3. Experimental results that revealed the coffee ground waste can be utilized as an alternative precursor for activated carbon production and the chosen optimum and maximum condition were presented as follows:

In the case of $ZnCl_2$, the optimum activation condition was 1:3 weight ratio/or 120% impregnation ratio at temperature 800ºC with retention time of 3 hours. And the maximum condition that given highest value of iodine number was 1:4 weight ratio/or 142% impregnation ratio at temperature 900ºC with retention time of 3 hours.

For K_2CO_3 as activating agent, the optimum preparation condition was 1:2 weight ratio/or 86% impregnation ratio at temperature 800ºC for holding time 2 hours. The maximum condition was 1:3 weight ratio/or 110% impregnation ratio at temperature 900ºC for holding time 3 hours.

Typical Scanning Electron Microscope (SEM) image of the surface of coffee ground waste and representative activated carbons at optimum and maximum condition were illustrated in Figure 4-7 and their main characteristics were given in Table 4-1. As shown in Figure 4-7 (a), it is clearly seen that the surface of raw material was dense and plane without any cracks and crevices. This would account for its poor or negligible S_{BET} (2.73 m^2/g) as shown in Table 4-1. Also, the fiber could be seen clearly on the surface since the coffee bean is a typical type of lignocellulosic materials. In contrast, for the activated carbon, as shown in Figure 4-7 (b) and (c), there were no more lignocellulosic structures on the surface but many small cavities over the surface, forming a system of advanced pore network. Hence, the Activated carbon was expected to have S_{BET} and micropore surface area.

Generally, the porosity of the carbonaceous materials increases with an increasing of specific surface areas. Results in Table 4-1 showed that activated carbons have S_{BET} greater than coffee ground. In fact, this implies that activated carbons have many pores while coffee ground waste hardly have any. In comparison of this cellular structure, Figure 4-7 (a), with those of derived activated carbons, Figure 4-7 (b) and (c), attests substantial changes occasioned by activating agent, suggesting rearrangements of the constituent cellular structure of the precursor. It interesting to point out that the surface of the activated carbon with maximum condition, Figure 4-7 (b-2) and (c-2) appears to be friable and shows signs of structure weakness, as evidenced by rupture of walls and disintegrated particles, especially activated carbon from K_2CO_3.

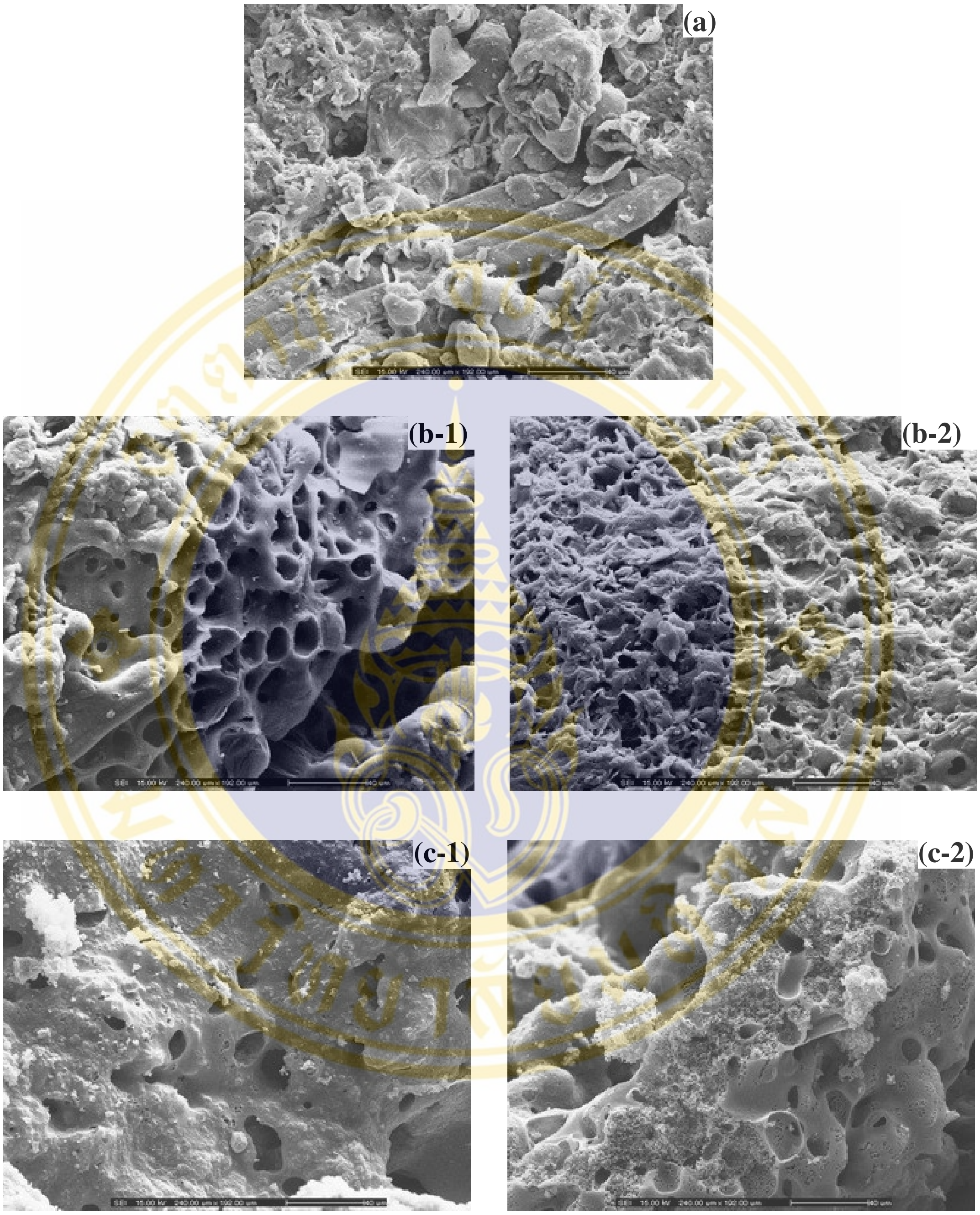


Figure 4-7: SEM image of coffee ground waste and derived activated carbon; (a) Untreated coffee ground waste, (b) Activated carbon with $ZnCl_2$, (b-1) at optimum condition, (b-2) at maximum condition; (c) Activated carbon with K_2CO_3, (c-1) at optimum condition, (c-2) at maximum condition

Remark: Magnification x 500. Scale bars are indicated on the photographs.

Table 4-1: The characteristics of raw material and derived activated carbon

Characteristics	Coffee ground waste precursor	Activated carbon from $ZnCl_2$*		Activated carbon form K_2CO_3**	
		Optimum condition	Maximum condition	Optimum condition	Maximum condition
Proximate analysis (wt.%db)					
Moisture	4.76	2.6	3.1	3.5	3.8
Ash	0.32	4.2	4.9	2.0	2.8
Volatile matter	83.18	17.5	14.7	18.7	16.5
Fixed carbon	16.54	78.3	80.4	79.3	70.7
Ultimate analysis (wt.%db)					
Carbon	54.58	79.52	84.60	80.64	72.69
Hydrogen	6.29	1.23	0.88	1.03	1.21
Nitrogen	2.67	1.49	2.88	1.88	1.89
Oxygen (by difference)	36.46	17.76	11.64	16.45	24.21
Production yield (wt.%db)	-	44.8	30.2	18.4	11.2
Adsorption capacity					
Iodine number (mg/g)	-	901	955	1,190	1,382
S_{BET} (m^2/g)	2.73	1,088	1,060	943	1,067

Remark: ** $ZnCl_2$ Series; Optimum condition was 1:3 weight ratio, 800ºC, with 3 h,*
Maximum condition was 1:4 weight ratio, 900ºC, with 3 h
*** K_2CO_3 Series; Optimum condition was 1:2 weight ratio, 800ºC, with 2 h,*
Maximum condition was 1:3 weight ratio, 900ºC, with 3 h

As presented in Table 4-1, it can be seen that the derived activated carbons contained a larger surface area and higher in weight of carbon (app.80%) than those of raw precursor (app.50%). Also the produced activated carbon from the optimum condition contain nearly 80 wt% of carbon content, showing the content of hydrogen and oxygen were mostly removed during the activation in a gaseous form (e.g. CO_2, H_2 and CO), resulting in low content of those elements [1,11].

However, derived activated carbon at optimum and maximum condition in $ZnCl_2$ series giving the value of iodine number (901 mg/g and 955 mg/g) lower than S_{BET} (1,088 m^2/g and 1,060 m^2/g) whereas in K_2CO_3 series giving the value of iodine number (1,190 mg/g and 1,382 mg/g) higher than S_{BET} (943 m^2/g and 1,067 m^2/g). This might be due to two reasons. Firstly, S_{BET} was measured by nitrogen gas adsorption, and the nitrogen molecule is so small that it can penetrate pores that are not available for larger molecules. Hence, S_{BET} could not exactly reflect the adsorption of larger molecules such as iodine. Secondly, it is well documented that, besides the pore structure of activated carbon, the surface chemistry structure, especially the oxygen-containing surface functional groups, is also an important factor influencing the adsorption performance, and to some aqueous adsorbents it may play the prominent role [1].

The most important property of the activated carbon is its adsorptive capacity that is related to the specific pore surface area. Generally, the higher the pore surface area of the activated carbon, the larger is its adsorptive capacity. Pore within porous materials are normally classified into micropores (<2 nm diameter), mesopores (2-50 nm) and macropores (>50nm) [30]. This classification is important because most molecules of gaseous pollutants vary from about 0.4 to 0.9 nm in diameter. Therefore, gas-phase activated carbons usually consist predominantly of micropores while liquid-phase activated carbons have significantly more mesopores because of the larger sizes of liquid molecules. However, the size distribution of micropores is governed by the method of activation and the shape of micropores is determined by raw material.

As a preliminary evaluation, comparing the two activating agents, the economic feasibility of the process proposed in the present study would depend greatly on the cost paid for the amount of activating agents used and energy consumption. The optimum activation temperature of the proposed process was 800ºC, for both cases. The optimum activation time of K_2CO_3 was 2 hours, which was evidently shorter than that of 3 hours of $ZnCl_2$, indicating less energy consumption. Further, the amount of chemical used in the process, the optimum weight ratio of K_2CO_3 was 1:2 of weight ratio, which was smaller than that of $ZnCl_2$ (1:3 of weight ratio). Moreover, it is also noted that the pollution control of $ZnCl_2$ is widely used in the industrial process causing additional cost in activated carbon production. On the other hand, growing of enforcement in environmental regulations that call for significantly lower level of pollution emissions can also increase additional cost of the production process [11]. Therefore, it is reasonable to be assumed that K_2CO_3 is considerably used as an activating agent alternative, as its lower contribution to pollution problem.

CHAPTER 5
CONCLUSION AND RECOMMENDATION

5.1 Conclusions

An upgrading of coffee ground waste to activated carbons using two chemical activation agents i.e. $ZnCl_2$ and K_2CO_3 have been conducted. The optimum activation condition was selected by considering TISI standard, iodine number development and economic factor i.e. cost and energy saving. Experimental results are based on the point of iodine number, and the following conclusions can be drawn from this work.

5.1.1 Activated carbon from coffee ground waste with $ZnCl_2$ agent

The optimum condition of activation using $ZnCl_2$ was 1:3 of weight ratio/or 120% of impregnation ratio at 800ºC with 3 hours of holding time, giving production yield of 44.8% with iodine number of 901 mg/g and S_{BET} of 1,088 m^2/g. However, at the maximum condition of activation which give rise the highest iodine number for $ZnCl_2$ was 1:4 weight ratio/or 142% of impregnation ratio at 900ºC with holding time 3 hours, the production yield of 30.2% with iodine number of 955 mg/g, and S_{BET} of 1,060 m^2/g are obtained.

5.1.2 Activated carbon from coffee ground waste with K_2CO_3 agent

In case of K_2CO_3, the temperature was expected to be very influential on activation due to it works effectively at temperature above 700ºC, at the temperature lower than this point could not be sufficient to produce activated carbon that meet the requirement of TISI. In addition, the difficulty arose due to the serious sintering that obtained entirely the activated carbon production, causing scrap out the products from the surface of vessel.

The optimum condition of activation for K_2CO_3 was 1:2 of weight ratio/or 86% of impregnation ratio at 800ºC heating temperature with holding time of 2 hours, giving production yield of 18.4% with iodine number of 1,190 mg/g and S_{BET} of 943 m^2/g. However, at the maximum condition for K_2CO_3 was 1:4 of weight ratio/or 110% of impregnation ratio at 900ºC heating temperature with holding time of 3 hours, the production yield of 11.2% with iodine number of 1,382 mg/g and S_{BET} of 1,067 m^2/g. are obtained.

5.1.3 In comparition of the two activating agent

From optimum condition of both activation process, these results revealed that the optimum values of the weight ratio/or impregnation ratio and activation time for K_2CO_3 was lower than that of $ZnCl_2$, indicating less cost and energy consumption. However, the conversion yield of activated carbon by K_2CO_3 was lower than that of $ZnCl_2$ while their adsorptive capacity were slightly higher. Thus, a compromise should considerably be made between the conversion yield and the adsorptive properties of the products. And it is reasonable to assume that K_2CO_3 is considerably better than $ZnCl_2$ and can be used as an activating agent alternative, considering less cost and energy consumption also it is a benign chemical.

5.2 Recommendations

As the results mentioned above, the recommendation can be given as follows:

5.2.1 In comparison, as K_2CO_3 is more preferable than $ZnCl_2$ because of the environmental disadvantage associated with $ZnCl_2$. Moreover, the activated carbon made from $ZnCl_2$ cannot be used in pharmaceutical and food industries as it may cause product contamination.

5.2.2 Due to their large adsorption capacity, large iodine number and S_{BET}, low cost coffee ground waste and cleaner production process with K_2CO_3 instead to $ZnCl_2$, the activated carbon from coffee ground waste may potentially be offered as substitutes for commercial activated carbon.

5.2.3 The usage activated carbon from coffee ground waste, this study suggest that $ZnCl_2$ make good granular activated carbon while K_2CO_3 may be suitable if activated carbon presented in the powder form, considering the physical derived activated carbon.

5.2.4 The other factors that are relevant to their further application as adsorbents, i.e. surface chemistry, density, mechanical resistance, should also be further examined to assess thoroughly the use of coffee ground waste as a reliable competitive option for activated carbon production.

5.2.5 In order to confirm whether these results would be commercially applicable, further studies on pilot scale including economical evaluation are recommended.

REFERENCES

1. Bansal R C, Donnet J B, Stoeckli F. Active carbon, New York: Marcel Dekker, 1988.

2. Tsai W T, Chang C Y and Lee S L. A low cost adsorbent from agricultural waste corn cob by zinc chloride activation. Bioresource Technology 1998; 64: 211-217.

3. Tsai W T, Chang C Y, Lin M C, Chien S F, Sun H F and Hsieh M F. Adsorption of acid dye onto activated carbons prepared from agricultural waste bagasse by $ZnCl_2$ activation. Chemosphere 2001; 45: 51-58.

4. Jin-Wha Kim, Myoung-Hoi Sohn, Dong-Su Kim, Seung-Man Sohn and Young-Shik Kwon. Production of granular activated carbon from waste walnut shell and its adsorption characteristics for Cu^{2+} ion. Journal of Hazardous Materials 2001; B85: 301-315.

5. Kadirvelu K, Senthilkumar P, Thamaraiselvi K and Subburam V. Activated carbon prepared from biomass as adsorbent: elimination of Ni (II) from aqueous solution. Bioresource Technology 2002; 81: 87-90.

6. Badie S Girgis, Samya S Yunis and Ashraf M Soliman. Characteristics of activated carbon from peanut hulls in relation to conditions of preparation. Materials Letters 2002; 57: 164-172.

7. Aygün A, Yenisoy-Karakaş S and Duman I. Production of granular activated carbon from fruit stones and nutshells and evaluation of their physical, chemical and adsorption properties. Microporous and Mesoporous Materials 2003; 66: 189-195.

8. Carolina R Loez, Mirta L Topalián and Alfredo Salibián. Effects of zinc on the structure and growth dynamics of a natural freshwater phytoplankton assemblage reared in the laboratory. Environmental Pollution 1995; 88: 275-281.

9. Tsai W T, Chang C Y, Wang S Y, Chang C F, Chien S F and Sun H F. Preparation of activated carbons from corn cob catalyzed by potassium salts and subsequent gasification with CO_2. Bioresource Technology 2001; 78: 203-208.

10. Jun'ichi Hayashi, Mikihito Uchibayashi, Toshihide Horilawa, Katsuhiko Muroyama and Vincent G Gomes. Synthesizing activated carbons from resins by chemical activation with K_2CO_3. Carbon 2002; 40: 2747-2752.

11. Tsai W T, Chang C Y, Wang S Y, Chang C F, Chien S F and Sun H F. Cleaner production of carbon adsorbents by utilizing agricultural waste corn cob. Resources, Conservation and Recycling 2001; 32: 43-53.

12. Jun'ichi Hayashi, Toshihide Horikawa, Isao Takeda, Katsuhiko Muroyama and Farid Nasir Ani. Preparing activated carbon from various nutshells by chemical activation with K_2CO_3. Carbon 2002; 40: 2381-2386.

13. Jun'ichi Hayashi, Toshihide Horikawa, Katsuhiko Muroyama and Vincent G Gomes. Activated carbon from chickpea husk by chemical activation with K_2CO_3: preparation and characterization. Microporous and Mesoporous Materials 2002; 55: 63-68.

14. Carvalho A P, Gomes M, Mestre AS, Pires J and Brotas de Carvalho M. Activated carbons from cork waste by chemical activation with K_2CO_3: Application to adsorption of natural gas components. Letters to the editor. Carbon 2004; 42: 667-691.

15. Addoun A, Dentzer J and Ehrburger P. Porosity of carbons obtained by chemical activation: effect of the nature of the alkaline carbonates. Letters to editor. Carbon 2002; 40: 1140-1143.

16. Ahmadpour A and Do D D. The preparation of active carbons from coal by chemical and physical activation. Carbon 1996; 34(4): 471-479.

17. Gyu Hwan Oh and Chong Rae Park. Preparation and characteristics of rice-straw-based porous carbons with high adsorption capacity. Fuel 2002; 81: 327-336.

18. Savova D, Apak E, Ekinci E, Yardim F, Petrov N, Budinova T Razvigorova M and Minkovo V. Biomass conversion to carbon adsorbents and gas. Biomass and Bioenergy 2001; 21: 133-142.

19. Rajeshwarisivaraj, Sivakumar S, Senthilkumar P and Subburam V. Carbon from Cassava peel, an agricultural waste, as an adsorbent in the removal of dyes and metal ions from aqueous solution. Bioresource Technology 2001; 80: 233-235.

20. Vernersson T, Bonelli P R, Cerrella E G and Cukierman A L. *Arundo donax* cane as a precursor for activated carbons preparation by phosphoric acid activation. Bioresource Technology 2002; 83: 95-104.

21. Chilton Ng, Jack N Losso, Wayne E, Marshall and Ramu M Rao. Physical and chemical properties of selected agricultural byproduct-based activated carbons and their ability to adsorb geosmin. Bioresource Technology 2002; 84: 177-185.

22. Hussein M Z, Tarmizi R S H, Zainal Z and Ibrahim R. Preparation and characterization of active carbons from oil palm shells. Letters to the editor. Carbon 1996; 34(11): 1447-1454.

23. Office of agricultural economics. Agricultural statistics of Thailand crop year 2002/2003 [online]. Available: http://oae.go.th/statistic/yearbool/2002-03/section6/sec6table78.xls. [2002, Dec. 10]

24. ศูนย์บริการวิชาการ คณะเศรษฐศาสตร์ มหาวิทยาลัยธรรมศาสตร์. รายงานการศึกษาผลกระทบจากการเปิดตลาดสินค้าเกษตร 23 รายการ ตามพันธะกรณีองค์การค้าโลก. 2544.

25. Sivetz M. Coffee processing technology. New York: The Avi Publishing Company; 1963.

26. Mizuho Hirata, Naohito Kawasaki, Takeo Nakamura, Kazuoki Matsumoto. Mineaki Kabayama Takamichi Tamura and Seiki Tanada. Adsorption of dyes onto carbonaceous materials produced from coffee grounds by microwave treatment. Journal of Colloid and Interface Science 2002; 254: 17-22.

27. Silva MA, Nebra SA, Machado Silva MJ and Sanchez CG. The use of biomass residues in the Brazilian soluble coffee industry. Biomass and Bioenergy 1998; 14: 457-467.

28. Palut Sopanakijlosol. Production of activated carbon from coconut shell for adsorption chromium (VI). Ms.E. [Thesis in Chemical Engineering]. Bangkok: Faculty of graduate studies, King Mong Kut University of Technology Thonburi; 2000.

29. Keller II G E, Anderson R A and Yon C M. Adsorption in Handbook of separation process technology. New York. John Wiley & Son. 1987:644-696.

30. IUPAC. Manual of symbols and terminology, App 2, Pt 1, Colloid and surface chemistry. Pure App Chem 1972; 31: 578.

31. Earth Resources. Water treatment [online]. Available: http://www.erwater.com/ENGLISH/WT/ filtration/pu.htm [2002, Dec. 10]

32. Minkova V, Razvigorova M, Goranova M, Ljutzkanov L and Angelova G. Effect of water vapour on the pyrolysis of solid fuels. Fuel 1991; 70: 713-719.

33. Srinivasakannan C and Mohamad Zailani Abu Bakar. Production of activated carbon from rubber wood sawdust. Biomass and Bioenergy 2004; 27: 89-96.

34. Philip C A and Girgis B S. Adsorption characteristics of microporous carbons from apricot atones activated by phosphoric acid. J Chem. Tech. Biotech nol 1996; 67:248-254.

35. Lillo-Ródenas M A, Cazorla-Amorós D and Linares-Solano. Understanding chemical reactions between carbons and NaOH and KOH. Carbon 2003; 41: 267-275.

36. Jankowska H, Swiatkowki A and Choma J. Active carbon. Ellis Horwood, Chichester, England. 1991.

37. Ashok Pandey, Carlos R Soccol, Poonam Nigam, Debora Brand, Radjiskumar Mohan and Sevastianos Roussos. Biotechnological potential of coffee pulp and coffee husk for bioprocesses. Biochemical Engineering Journal 2000; 6: 153-162.

38. Department of Agricultural Extension. Agricultural plantation [online]. Available: http://www.doae.go.th/ plant/ coffee.htm [2004, Sep. 8].

39. Clifford, M N and Willson, K C (Editors) - Coffee; botany, biochemistry and production of beans and beverage. London, Croom Helm, 1985 [online]. Available: http://www.allaboutcoffee.org/id20htm [2004, Sep. 8]

40. Coffee structure [online]. Available: http://www.tis-gddv.de/ tise/ ware/ genuss/ kaffee/abb4.htm [2004, Sep. 8]

41. Thailand Industrial Standard Institute. TISI 900-2532 (1989). Ministry of Industry, 1998.

42. Tay J H, Chen X G, Jeyaseelan S and Graham N. Optimising the preparation of activated carbon from digested sewage sludge and coconut husk. Chemosphere 2001; 44: 45-51.

43. American Society for Testing and Material. Annual book of ASTM Standard Sec. 5 Vol. 05.02 Petroleum Products, Lubricants, and Fossil Fuels. Easton, MD, U.S.A., 1996.

44. American Society for Testing and Material. Annual book of ASTM Standard Sec. 15 Vol. 15.01 Refractories; Carbon and Graphite Products; Activated carbon. Easton, MD, U.S.A., 1996.

APPENDIX

APPENDIX A
DATA RECORDED

Table A-1: Proximate analyzes of coffee ground waste

Compositions	**R#1**	**R#2**	**R#3**	**Average**
wt% receive basis				
Moisture content	45.19	45.47	44.76	45.14
wt% dry basis				
Moisture content	4.72	4.77	4.80	4.76
Ash content	0.33	0.30	0.34	0.32
Volatile matter	82.70	81.51	85.19	83.13
Fixed carbon	16.97	18.19	14.47	16.54

Table A-2: Impregnation ratio of coffee ground waste with activating agent

Activated reagent	**Impregnation Ratio**			
	R#1	**R#2**	**R#3**	**Average**
CG : $ZnCl_2$				
1:1	0.42	0.39	0.41	0.41
1:2	0.74	0.79	0.81	0.78
1:3	1.16	1.20	1.24	1.20
1:4	1.40	1.51	1.36	1.42
CG : K_2CO_3				
1:1	0.55	0.49	0.49	0.51
1:2	0.85	0.84	0.88	0.86
1:3	1.11	1.10	1.12	1.11
1:4	1.13	1.12	-	1.13

Table A-3: The yield of resulting activated carbon by Zinc Chloride ($ZnCl_2$)

CG:$ZnCl_2$ Ratio	Temp. (°C)	Time (h)	%Yield (impregnation basis) R#1	R#2	R#3	Avg.	%Yield (coffee ground basis)* R#1	R#2	R#3	Avg.
1:1	600	1	48.2	47.3	49.1	48.2	67.9	66.7	69.2	67.9
		2	46.9	45.7	44.6	45.8	66.2	64.4	62.9	64.5
		3	42.2	43.1	41.1	42.1	59.5	60.8	58.0	59.4
	700	1	43.9	45.2	44.3	44.5	61.9	63.7	62.5	62.7
		2	43.1	42.1	44.4	43.2	60.8	59.4	62.6	60.9
		3	41.7	39.8	41.6	41.0	58.8	56.1	58.6	57.8
	800	1	41.5	43.0	42.1	42.2	58.5	60.6	59.4	59.5
		2	40.1	38.3	41.8	40.1	56.5	54.0	58.9	56.5
		3	37.8	39.6	36.5	38.0	53.3	55.8	51.5	53.5
	900	1	39.7	40.9	38.4	39.7	56.0	57.7	54.1	55.9
		2	35.1	37.2	36.8	36.4	49.5	52.5	51.9	51.3
		3	34.5	32.5	32.7	33.2	48.6	45.8	46.1	46.9
1:2	600	1	37.2	36.5	36.2	36.6	66.2	65.0	64.4	65.2
		2	34.9	35.7	35.5	35.4	62.1	63.6	63.2	63.0
		3	32.6	33.3	32.2	32.7	58.1	59.3	57.3	58.2
	700	1	34.5	35.0	32.2	33.9	61.4	62.3	57.3	60.3
		2	33.7	34.2	32.3	33.4	60.0	60.9	57.6	59.5
		3	32.7	27.8	28.8	29.8	58.2	49.5	51.2	53.0
	800	1	28.8	30.7	31.0	30.2	51.3	54.6	55.2	53.7
		2	27.7	29.1	27.8	28.2	49.3	51.8	49.5	50.2
		3	25.6	26.4	27.3	26.4	45.6	47.0	48.6	47.1
	900	1	25.8	23.4	25.0	24.7	45.9	41.7	44.5	44.0
		2	23.0	21.7	22.9	22.5	40.9	38.6	40.8	40.1
		3	20.4	20.2	21.0	20.5	36.4	36.0	37.3	36.5
1:3	600	1	29.5	30.2	28.7	29.5	64.9	66.4	63.1	64.8
		2	28.7	27.9	29.1	28.6	63.1	61.4	64.0	62.8
		3	27.4	26.1	25.4	26.3	60.3	57.4	55.9	57.9
	700	1	26.0	26.9	27.7	26.8	57.2	59.1	60.9	59.1
		2	25.0	26.8	28.2	26.7	55.1	59.0	61.9	58.7
		3	24.7	19.1	26.4	23.4	54.2	42.1	58.1	51.5
	800	1	21.8	24.2	23.1	23.0	48.0	53.2	50.8	50.7
		2	22.4	20.9	21.1	21.5	49.3	46.0	46.4	47.2
		3	20.8	19.2	21.1	20.4	45.7	42.2	46.4	44.8
	900	1	20.3	19.6	17.9	19.3	44.7	43.1	39.4	42.4
		2	17.2	18.9	16.4	17.5	37.9	41.6	36.1	38.5
		3	16.2	14.5	15.2	15.3	35.6	31.9	33.4	33.7
1:4	600	1	23.2	28.0	28.1	26.4	56.0	67.7	68.0	63.9
		2	24.4	22.7	23.0	23.3	58.7	54.9	55.6	56.4
		3	23.2	23.3	22.5	23.0	56.0	56.5	54.5	55.6
	700	1	23.7	24.4	22.6	23.6	57.0	59.0	54.7	56.9
		2	22.8	22.8	21.2	22.3	54.9	55.2	51.3	53.8
		3	20.7	21.9	19.1	20.5	49.8	53.0	46.1	49.6
	800	1	19.2	19.4	20.4	19.6	46.2	46.9	49.4	47.5
		2	18.7	17.8	18.2	18.2	45.1	43.1	44.1	44.1
		3	16.3	17.8	16.9	17.0	39.2	43.1	41.0	41.1
	900	1	16.3	16.5	16.9	16.6	39.3	40.0	40.8	40.0
		2	14.8	13.6	15.4	14.6	35.7	32.9	37.3	35.3
		3	12.4	12.1	13.0	12.5	29.9	29.3	31.6	30.2

Remark: ** %Yield (coffee ground basis) test back by %Yield (impregnation basis) X % Impregnation ratio*

Table A-4: The yield of resulting activated carbon by Potassium Carbonate (K_2CO_3)

$CG:K_2CO_3$ Ratio	Temp. (^oC)	Time (h)	%Yield (impregnation basis)				%Yield (coffee ground basis)*			
			R#1	**R#2**	**R#3**	**Avg.**	**R#1**	**R#2**	**R#3**	**Avg.**
1:1	600	1	21.6	21.7	21.4	21.6	32.6	32.8	32.3	32.6
		2	20.9	21.0	20.8	20.9	31.6	31.7	31.4	31.6
		3	18.5	19.3	18.4	18.7	27.9	29.1	27.8	28.3
	700	1	20.7	19.6	20.6	20.3	31.3	29.6	31.1	30.7
		2	17.5	17.2	17.4	17.4	26.4	26.0	26.3	26.2
		3	15.2	16.7	15.5	15.8	22.9	25.2	23.4	23.8
	800	1	16.8	17.7	16.0	16.8	25.4	26.7	24.2	25.4
		2	12.8	13.7	13.0	13.2	19.3	20.7	16.6	19.9
		3	8.7	10.4	11.6	10.2	13.1	15.7	17.5	15.5
	900	1	14.5	14.7	14.5	14.6	21.9	22.2	21.7	22.0
		2	12.2	11.3	11.6	11.7	18.4	17.1	17.5	17.7
		3	8.3	10.3	10.8	9.8	12.5	15.6	16.3	14.8
1:2	600	1	17.8	18.2	16.2	17.4	33.1	33.9	30.1	32.4
		2	17.1	16.4	16.9	16.8	31.8	30.5	31.4	31.2
		3	14.7	15.2	13.9	14.6	27.3	28.3	25.9	27.2
	700	1	15.8	15.7	16.0	15.8	29.4	29.2	29.8	29.5
		2	14.2	13.8	13.5	13.9	26.4	25.7	25.1	25.7
		3	10.8	10.9	11.7	11.1	20.1	20.3	21.8	20.7
	800	1	13.6	12.8	13.8	13.4	25.3	23.8	25.7	24.9
		2	10.0	10.2	9.4	9.9	18.6	19.0	17.5	18.4
		3	7.3	6.3	8.0	7.2	13.6	11.7	14.9	13.4
	900	1	12.2	11.5	11.4	11.7	22.7	21.4	21.2	21.8
		2	8.4	8.1	9.3	8.6	15.6	15.1	17.3	16.6
		3	7.5	6.9	6.5	7.0	14.0	12.8	12.1	13.0
1:3	600	1	14.3	14.9	14.0	14.4	30.1	31.5	29.6	30.4
		2	13.6	14.3	13.8	13.9	28.7	30.3	29.2	29.4
		3	11.8	11.7	12.6	12.0	24.9	24.8	26.6	25.4
	700	1	13.5	14.0	13.4	13.6	28.5	29.6	28.2	28.7
		2	11.8	10.8	10.7	11.1	24.9	22.8	22.5	23.4
		3	8.5	9.5	9.9	9.3	18.0	20.0	20.9	19.6
	800	1	12.0	11.7	11.3	11.7	25.3	24.7	23.8	24.6
		2	8.0	8.5	8.6	8.4	16.9	17.9	18.1	17.7
		3	5.6	5.4	6.7	5.9	11.8	11.4	14.1	12.4
	900	1	9.4	10.3	10.6	10.1	19.8	21.7	22.4	21.3
		2	7.3	6.6	8.2	7.4	15.4	13.9	17.3	15.5
		3	5.2	5.9	4.8	5.3	11.0	12.4	10.1	11.2

Remark: ** %Yield (coffee ground basis) test back by %Yield (impregnation basis) X % Impregnation ratio*

Table A-5: Iodine Number of resulting activated carbon by Zinc Chloride

CG : $ZnCl_2$	Temp.	Time	Iodine Number (mg/g)			
Ratio	(°C)	(h)	R#1	R#2	R#3	Avg.
1:1	600	1	560	548	550	553
		2	600	584	590	591
		3	640	635	650	642
	700	1	550	558	560	556
		2	610	603	600	604
		3	650	652	660	654
	800	1	580	570	565	572
		2	610	622	620	617
		3	640	652	650	647
	900	1	647	638	640	642
		2	660	659	665	661
		3	700	699	710	703
1:2	600	1	690	700	680	690
		2	710	695	700	702
		3	740	725	730	732
	700	1	690	704	700	698
		2	730	728	738	732
		3	750	752	760	754
	800	1	726	740	735	734
		2	750	760	760	757
		3	810	798	800	803
	900	1	750	764	780	765
		2	825	822	830	826
		3	850	864	857	857
1:3	600	1	700	694	710	701
		2	790	775	780	782
		3	800	820	830	817
	700	1	740	750	755	748
		2	795	803	800	799
		3	849	852	850	850
	800	1	786	790	800	792
		2	850	838	830	839
		3	890	902	910	901
	900	1	851	848	850	850
		2	888	900	895	894
		3	963	954	952	956
1:4	600	1	802	810	800	804
		2	850	840	845	845
		3	880	900	890	890
	700	1	820	831	830	827
		2	852	852	860	855
		3	910	905	900	905
	800	1	847	852	850	850
		2	880	872	870	874
		3	920	932	930	927
	900	1	860	861	860	860
		2	900	902	914	905
		3	950	954	960	955

Table A-6: Iodine Number of resulting activated carbon by Potassium Carbonate

CG:K_2CO_3	Temp.	Time	Iodine Number (mg/g)			
Ratio	**(^oC)**	**(h)**	**R#1**	**R#2**	**R#3**	**Avg.**
1:1	600	1	293	288	290	290
		2	318	319	320	319
		3	380	378	385	381
	700	1	570	567	570	569
		2	605	607	610	607
		3	655	660	660	658
	800	1	810	815	810	812
		2	905	897	900	901
		3	959	962	965	962
	900	1	920	935	930	928
		2	1,050	1,087	1,100	1,079
		3	1,148	1,154	1,150	1,151
1:2	600	1	318	319	322	320
		2	375	369	370	371
		3	389	391	395	392
	700	1	630	638	640	636
		2	655	662	660	659
		3	675	784	680	713
	800	1	1,060	1,045	1,050	1,052
		2	1,200	1,180	1,190	1,190
		3	1,280	1,293	1,300	1,291
	900	1	1,186	1,203	1,200	1,196
		2	1,276	1,287	1,280	1,281
		3	1,295	1,304	1,300	1,300
1:3	600	1	330	330	330	330
		2	379	381	383	381
		3	412	422	420	418
	700	1	670	682	680	677
		2	870	875	870	872
		3	900	902	900	901
	800	1	1,090	1,074	1,080	1,081
		2	1,250	1,254	1,260	1,255
		3	1,340	1,357	1,360	1,352
	900	1	1,242	1,243	1,250	1,245
		2	1,340	1,350	1,360	1,350
		3	1,390	1,376	1,380	1,382

Table A-7: Iodine Number of resulting activated carbon by Zinc Chloride

CG : K_2CO_3	**Temp.**	**Time**	**Iodine Number (mg/g)**	
Ratio	**(^oC)**	**(h)**	**Avg.**	**Ranging increase**
1:1	600	1	290	
		2	319	29
		3	381	62
	700	1	569	
		2	607	38
		3	658	51
	800	1	812	
		2	901	89
		3	962	61
	900	1	928	
		2	1,079	151
		3	1,151	72
1:2	600	1	320	
		2	371	51
		3	392	21
	700	1	636	
		2	659	23
		3	713	54
	800	1	1,052	
		2	1,190	138
		3	1,291	131
	900	1	1,196	
		2	1,281	85
		3	1,300	19
1:3	600	1	330	
		2	381	51
		3	418	37
	700	1	677	
		2	872	195
		3	901	29
	800	1	1,081	
		2	1,255	174
		3	1,352	97
	900	1	1,245	
		2	1,350	105
		3	1,382	32

Remark: The values of ranging increase iodine number at the activation temperature of 600ºC were negligible as it lower than TISI requirement.

Table A-8: Proximate analyzes of activated carbon from coffee ground waste

Compositions	R#1	R#2	R#3	Average
Activated carbon by $ZnCl_2$				
• Optimum condition: WR=1:3, 800ºC,3 h				
Moisture content	3.15	2.51	2.14	2.60
Ash content	4.44	3.98	4.26	4.23
Volatile matter	18.63	17.17	16.76	17.52
Fixed carbon	79.43	69.83	78.51	78.26
• Maximum condition: WR=1:4, 900ºC,3 h				
Moisture content	2.86	3.23	3.31	3.13
Ash content	4.79	4.85	5.14	4.93
Volatile matter	15.34	14.82	13.97	14.71
Fixed carbon	81.22	79.94	80.12	80.43
Activated carbon by K_2CO_3				
• Optimum condition: WR=1:2, 800ºC,2 h				
Moisture content	3.62	3.47	3.58	3.56
Ash content	1.96	2.35	1.83	2.05
Volatile matter	19.02	18.67	18.45	18.71
Fixed carbon	80.14	78.73	79.08	79.32
• Maximum condition: WR=1:3, 900ºC,3 h				
Moisture content	3.74	4.01	3.63	3.79
Ash content	3.03	2.69	2.72	2.81
Volatile matter	17.57	16.78	15.02	16.48
Fixed carbon				

APPENDIX B

STATISTICAL RESULTS

Table B-1: Statistical analysis of impregnation ratio in $ZnCl_2$ series

ANOVA

ZnCl2 Impregnation Ratio

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	2.786	3	.929	393.739	.000
Within Groups	1.887E-02	8	2.358E-03		
Total	2.805	11			

Multiple Comparisons

Dependent Variable: ZnCl2 Impregnation Ratio

	(I) CG:Zinc chloride	(J) CG:Zinc chloride	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
						Lower Bound	Upper Bound
LSD	1:1	1:2	-.3733*	3.965E-02	.000	-.4648	-.2819
		1:3	-.7933*	3.965E-02	.000	-.8848	-.7019
		1:4	-1.2933*	3.965E-02	.000	-1.3848	-1.2019
	1:2	1:1	.3733*	3.965E-02	.000	.2819	.4648
		1:3	-.4200*	3.965E-02	.000	-.5114	-.3286
		1:4	-.9200*	3.965E-02	.000	-1.0114	-.8286
	1:3	1:1	.7933*	3.965E-02	.000	.7019	.8848
		1:2	.4200*	3.965E-02	.000	.3286	.5114
		1:4	-.5000*	3.965E-02	.000	-.5914	-.4086
	1:4	1:1	1.2933*	3.965E-02	.000	1.2019	1.3848
		1:2	.9200*	3.965E-02	.000	.8286	1.0114
		1:3	.5000*	3.965E-02	.000	.4086	.5914

*. The mean difference is significant at the .05 level.

Table B-2: Statistical analysis of impregnation ratio in K_2CO_3 series

ANOVA

Impregnation Ratio

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	.691	3	.230	458.539	.000
Within Groups	3.517E-03	7	5.024E-04		
Total	.695	10			

Multiple Comparisons

Dependent Variable: Impregnation Ratio

	(I) ratio	(J) ratio	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval Lower Bound	95% Confidence Interval Upper Bound
LSD	1:1	1:2	-.3467*	1.830E-02	.000	-.3899	-.3034
		1:3	-.6000*	1.830E-02	.000	-.6433	-.5567
		1:4	-.6150*	2.046E-02	.000	-.6634	-.5666
	1:2	1:1	.3467*	1.830E-02	.000	.3034	.3899
		1:3	-.2533*	1.830E-02	.000	-.2966	-.2101
		1:4	-.2683*	2.046E-02	.000	-.3167	-.2200
	1:3	1:1	.6000*	1.830E-02	.000	.5567	.6433
		1:2	.2533*	1.830E-02	.000	.2101	.2966
		1:4	-1.5000E-02	2.046E-02	.487	-6.3382E-02	3.338E-02
	1:4	1:1	.6150*	2.046E-02	.000	.5666	.6634
		1:2	.2683*	2.046E-02	.000	.2200	.3167
		1:3	1.500E-02	2.046E-02	.487	-3.3382E-02	6.338E-02

*. The mean difference is significant at the .05 level.

Table B-3: Statistical comparison of iodine number of activated carbon at various weight ratios in $ZnCl_2$ series

ANOVA

Iodine Number

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	1331071.076	3	443690.359	160.105	.000
Within Groups	387974.361	140	2771.245		
Total	1719045.438	143			

Multiple Comparisons

Dependent Variable: Iodine Number

	(I) ratio	(J) ratio	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval Lower Bound	95% Confidence Interval Upper Bound
LSD	1:1	1:2	-133.78*	12.41	.000	-158.31	-109.25
		1:3	-207.31*	12.41	.000	-231.84	-182.77
		1:4	-254.56*	12.41	.000	-279.09	-230.02
	1:2	1:1	133.78*	12.41	.000	109.25	158.31
		1:3	-73.53*	12.41	.000	-98.06	-49.00
		1:4	-120.78*	12.41	.000	-145.31	-96.25
	1:3	1:1	207.31*	12.41	.000	182.77	231.84
		1:2	73.53*	12.41	.000	49.00	98.06
		1:4	-47.25*	12.41	.000	-71.78	-22.72
	1:4	1:1	254.56*	12.41	.000	230.02	279.09
		1:2	120.78*	12.41	.000	96.25	145.31
		1:3	47.25*	12.41	.000	22.72	71.78

*. The mean difference is significant at the .05 level.

Table B-4: Statistical comparison of iodine number of activated carbon at various activation temperatures in $ZnCl_2$ series

ANOVA

Iodine Number

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	178791.743	3	59597.248	5.417	.001
Within Groups	1540253.694	140	11001.812		
Total	1719045.438	143			

Multiple Comparisons

Dependent Variable: Iodine Number

	(I) Temp.	(J) Temp.	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval Lower Bound	95% Confidence Interval Upper Bound
LSD	600 C	700 C	-19.61	24.72	.429	-68.49	29.27
		800 C	-47.06	24.72	.059	-95.93	1.82
		900 C	-93.86*	24.72	.000	-142.74	-44.98
	700 C	600 C	19.61	24.72	.429	-29.27	68.49
		800 C	-27.44	24.72	.269	-76.32	21.43
		900 C	-74.25*	24.72	.003	-123.13	-25.37
	800 C	600 C	47.06	24.72	.059	-1.82	95.93
		700 C	27.44	24.72	.269	-21.43	76.32
		900 C	-46.81	24.72	.060	-95.68	2.07
	900 C	600 C	93.86*	24.72	.000	44.98	142.74
		700 C	74.25*	24.72	.003	25.37	123.13
		800 C	46.81	24.72	.060	-2.07	95.68

*. The mean difference is significant at the .05 level.

Table B-5: Statistical comparison of iodine number of activated carbon at various activation times in $ZnCl_2$ series

ANOVA

Iodine Number

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	171413.542	2	85706.771	7.808	.001
Within Groups	1547631.896	141	10976.113		
Total	1719045.438	143			

Multiple Comparisons

Dependent Variable: Iodine Number

	(I) Time	(J) Time	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval Lower Bound	95% Confidence Interval Upper Bound
LSD	1 h	2 h	-40.21	21.39	.062	-82.49	2.07
		3 h	-84.48*	21.39	.000	-126.76	-42.20
	2 h	1 h	40.21	21.39	.062	-2.07	82.49
		3 h	-44.27*	21.39	.040	-86.55	-1.99
	3 h	1 h	84.48*	21.39	.000	42.20	126.76
		2 h	44.27*	21.39	.040	1.99	86.55

*. The mean difference is significant at the .05 level.

Table B-6: Statistical comparison of iodine number of activated carbon at various weight ratios in K_2CO_3 series

ANOVA

Iodine number

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	870055.574	2	435027.787	3.449	.035
Within Groups	13245368.528	105	126146.367		
Total	14115424.102	107			

Multiple Comparisons

Dependent Variable: Iodine number

						95% Confidence Interval	
	(I) Ratio	(J) Ratio	Mean Difference (I-J)	Std. Error	Sig.	Lower Bound	Upper Bound
LSD	1:1	1:2	-145.25	83.71	.086	-311.24	20.74
		1:3	-215.56*	83.71	.011	-381.55	-49.57
	1:2	1:1	145.25	83.71	.086	-20.74	311.24
		1:3	-70.31	83.71	.403	-236.30	95.68
	1:3	1:1	215.56*	83.71	.011	49.57	381.55
		1:2	70.31	83.71	.403	-95.68	236.30

*. The mean difference is significant at the .05 level.

Table B-7: Statistical comparison of iodine number of activated carbon at various temperatures in K_2CO_3 series

ANOVA

Iodine number

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	12429292.620	3	4143097.540	255.545	.000
Within Groups	1686131.481	104	16212.803		
Total	14115424.102	107			

Multiple Comparisons

Dependent Variable: Iodine number

						95% Confidence Interval	
	(I) Temperature	(J) Temperature	Mean Difference (I-J)	Std. Error	Sig.	Lower Bound	Upper Bound
LSD	600	700	-343.37*	34.65	.000	-412.09	-274.65
		800	-743.70*	34.65	.000	-812.43	-674.98
		900	-856.67*	34.65	.000	-925.39	-787.95
	700	600	343.37*	34.65	.000	274.65	412.09
		800	-400.33*	34.65	.000	-469.05	-331.61
		900	-513.30*	34.65	.000	-582.02	-444.57
	800	600	743.70*	34.65	.000	674.98	812.43
		700	400.33*	34.65	.000	331.61	469.05
		900	-112.96*	34.65	.002	-181.68	-44.24
	900	600	856.67*	34.65	.000	787.95	925.39
		700	513.30*	34.65	.000	444.57	582.02
		800	112.96*	34.65	.002	44.24	181.68

*. The mean difference is significant at the .05 level.

Table B-8: Statistical comparison of iodine number of activated carbon at various times in K_2CO_3 series

ANOVA

Iodine number

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	398914.685	2	199457.343	1.527	.222
Within Groups	13716509.417	105	130633.423		
Total	14115424.102	107			

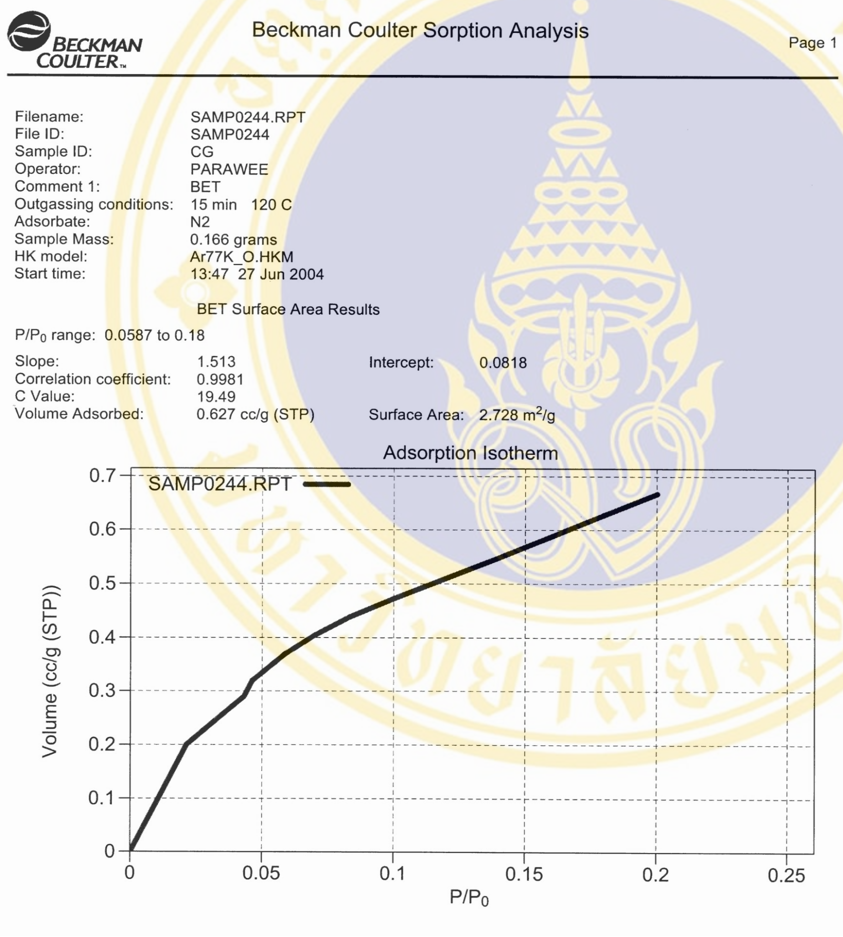
Multiple Comparisons

Dependent Variable: Iodine number

	(I) Time	(J) Time	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
						Lower Bound	Upper Bound
LSD	1 h	2 h	-94.00	85.19	.272	-262.92	74.92
		3 h	-146.97	85.19	.087	-315.89	21.94
	2 h	1 h	94.00	85.19	.272	-74.92	262.92
		3 h	-52.97	85.19	.535	-221.89	115.94
	3 h	1 h	146.97	85.19	.087	-21.94	315.89
		2 h	52.97	85.19	.535	-115.94	221.89

APPENDIX C
SPECIFIC SURFACE AREA RECORDED

C-1: BET Surface area result of coffee ground waste



BECKMAN COULTER

Beckman Coulter Sorption Analysis

Page 1

Filename: SAMP0244.RPT
File ID: SAMP0244
Sample ID: CG
Operator: PARAWEE
Comment 1: BET
Outgassing conditions: 15 min 120 C
Adsorbate: N2
Sample Mass: 0.166 grams
HK model: Ar77K_O.HKM
Start time: 13:47 27 Jun 2004

BET Surface Area Results

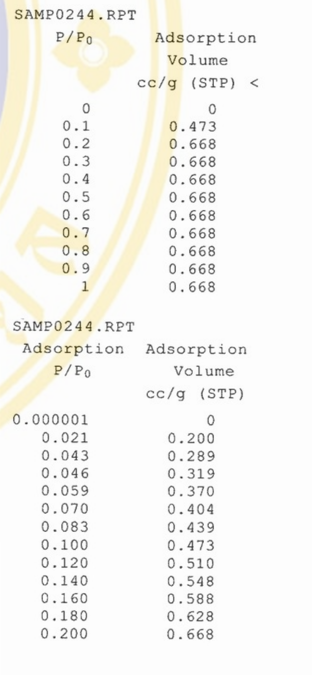
P/P_0 range: 0.0587 to 0.18

Slope: 1.513
Correlation coefficient: 0.9981
C Value: 19.49
Volume Adsorbed: 0.627 cc/g (STP)

Intercept: 0.0818

Surface Area: 2.728 m^2/g

Adsorption Isotherm



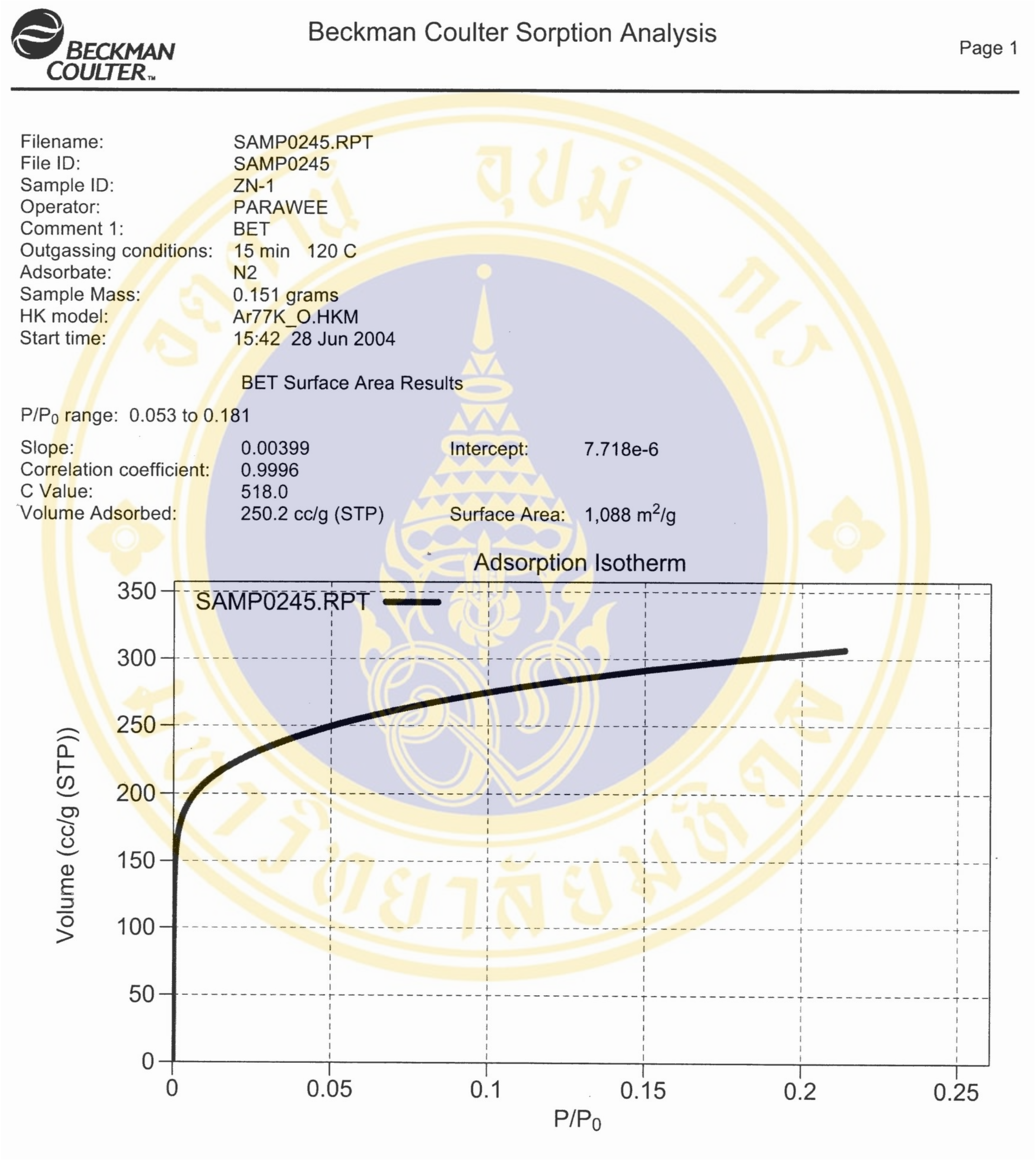
SAMP0244.RPT

P/P_0	Adsorption Volume cc/g (STP) <
0	0
0.1	0.473
0.2	0.668
0.3	0.668
0.4	0.668
0.5	0.668
0.6	0.668
0.7	0.668
0.8	0.668
0.9	0.668
1	0.668

SAMP0244.RPT

Adsorption P/P_0	Adsorption Volume cc/g (STP)
0.000001	0
0.021	0.200
0.043	0.289
0.046	0.319
0.059	0.370
0.070	0.404
0.083	0.439
0.100	0.473
0.120	0.510
0.140	0.548
0.160	0.588
0.180	0.628
0.200	0.668

C-2 a): BET Surface area result of activated carbon from optimum condition by $ZnCl_2$; WR= 1:3, 800ºC, 3 hours



BECKMAN COULTER™ Beckman Coulter Sorption Analysis Page 1

Filename: SAMP0245.RPT
File ID: SAMP0245
Sample ID: ZN-1
Operator: PARAWEE
Comment 1: BET
Outgassing conditions: 15 min 120 C
Adsorbate: N2
Sample Mass: 0.151 grams
HK model: Ar77K_O.HKM
Start time: 15:42 28 Jun 2004

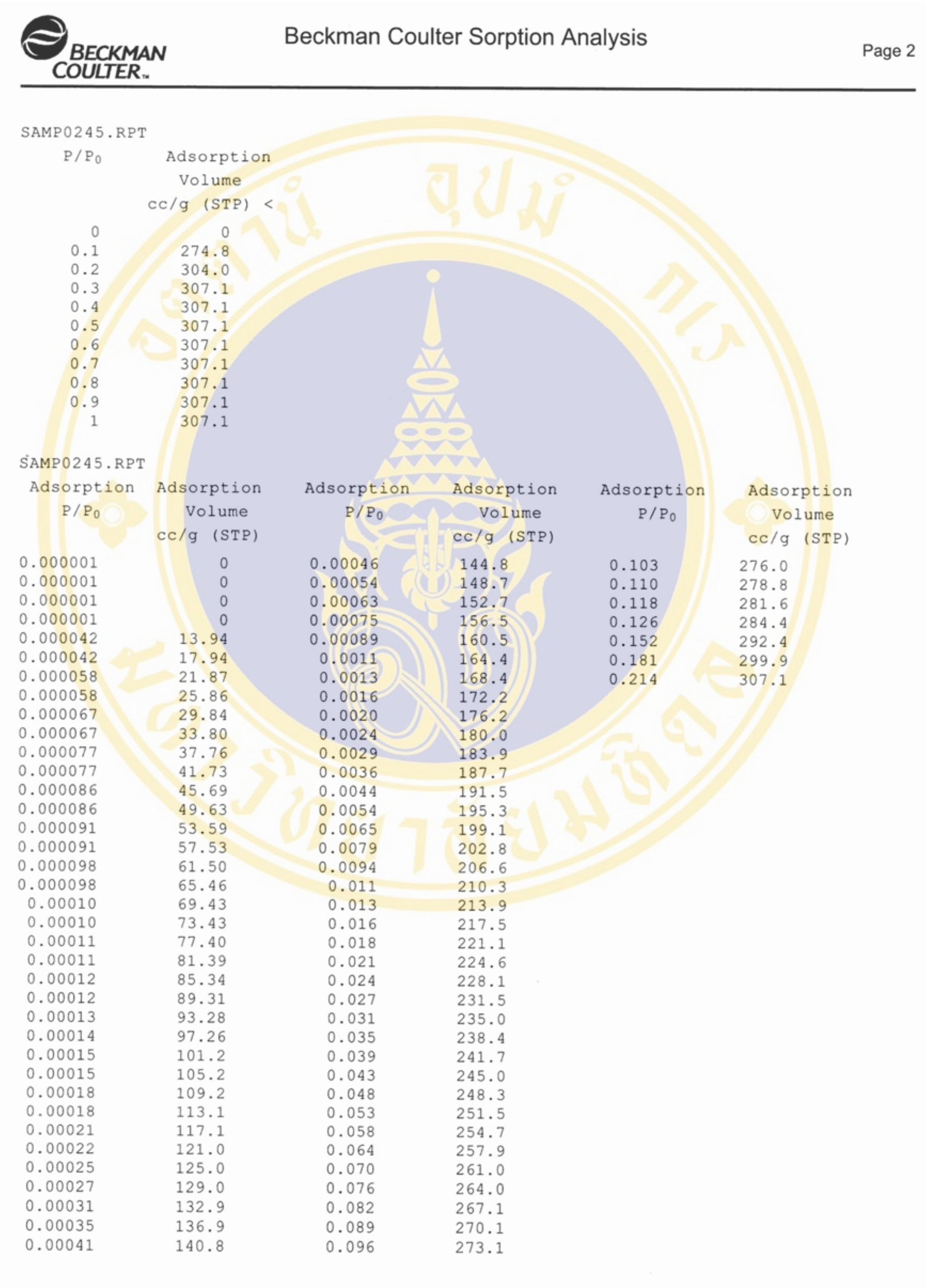
BET Surface Area Results

P/P_0 range: 0.053 to 0.181

Slope: 0.00399
Intercept: 7.718e-6
Correlation coefficient: 0.9996
C Value: 518.0
Volume Adsorbed: 250.2 cc/g (STP)
Surface Area: 1,088 m^2/g

Adsorption Isotherm

C-2 b): Adsorption data of BET Surface area of activated carbon from optimum condition by $ZnCl_2$; WR= 1:3, 800ºC, 3 hours



Beckman Coulter Sorption Analysis

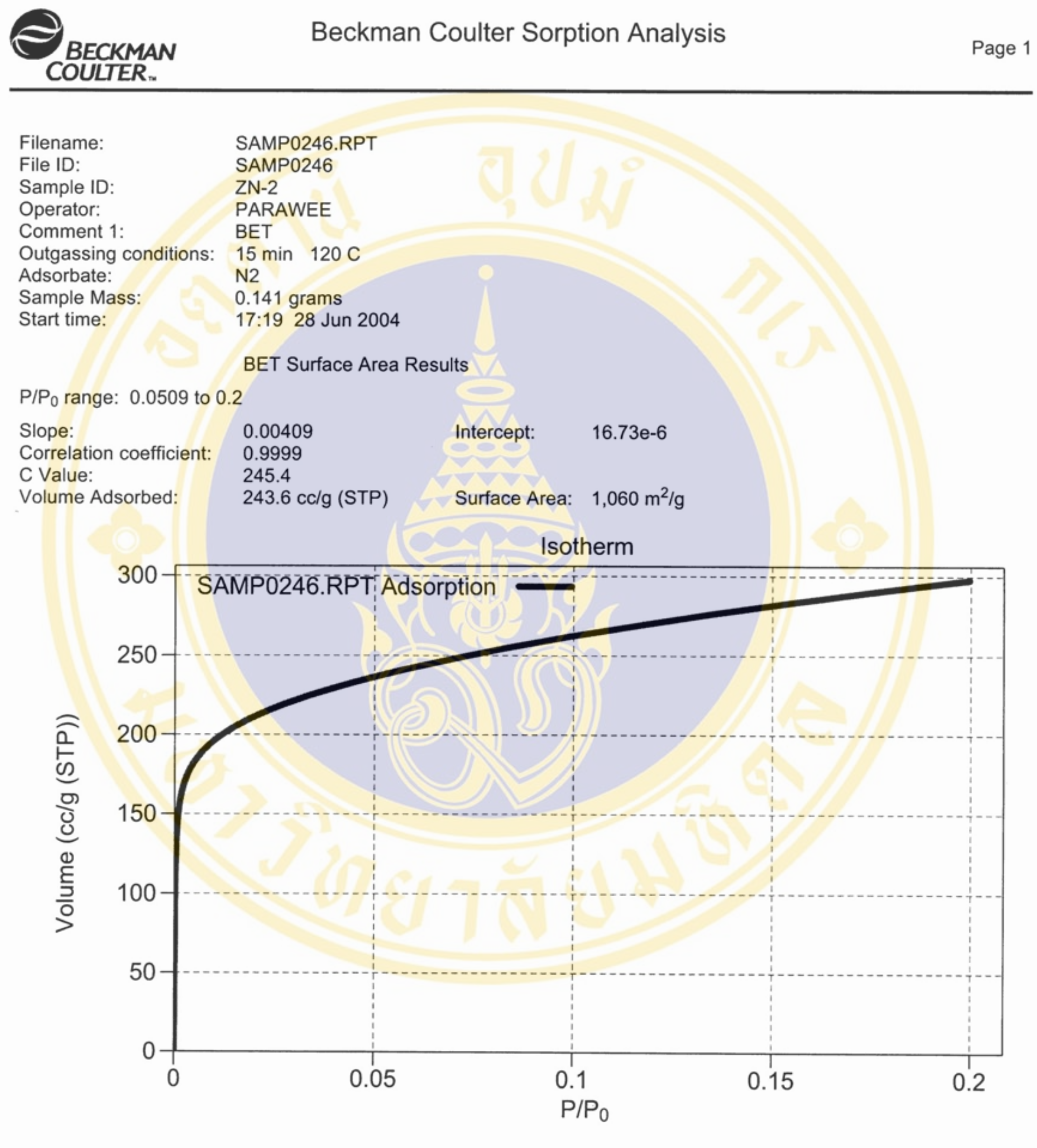
SAMP0245.RPT

P/P_0	Adsorption Volume cc/g (STP) <
0	0
0.1	274.8
0.2	304.0
0.3	307.1
0.4	307.1
0.5	307.1
0.6	307.1
0.7	307.1
0.8	307.1
0.9	307.1
1	307.1

SAMP0245.RPT

Adsorption P/P_0	Adsorption Volume cc/g (STP)	Adsorption P/P_0	Adsorption Volume cc/g (STP)	Adsorption P/P_0	Adsorption Volume cc/g (STP)
0.000001	0	0.00046	144.8	0.103	276.0
0.000001	0	0.00054	148.7	0.110	278.8
0.000001	0	0.00063	152.7	0.118	281.6
0.000001	0	0.00075	156.5	0.126	284.4
0.000042	13.94	0.00089	160.5	0.152	292.4
0.000042	17.94	0.0011	164.4	0.181	299.9
0.000058	21.87	0.0013	168.4	0.214	307.1
0.000058	25.86	0.0016	172.2		
0.000067	29.84	0.0020	176.2		
0.000067	33.80	0.0024	180.0		
0.000077	37.76	0.0029	183.9		
0.000077	41.73	0.0036	187.7		
0.000086	45.69	0.0044	191.5		
0.000086	49.63	0.0054	195.3		
0.000091	53.59	0.0065	199.1		
0.000091	57.53	0.0079	202.8		
0.000098	61.50	0.0094	206.6		
0.000098	65.46	0.011	210.3		
0.00010	69.43	0.013	213.9		
0.00010	73.43	0.016	217.5		
0.00011	77.40	0.018	221.1		
0.00011	81.39	0.021	224.6		
0.00012	85.34	0.024	228.1		
0.00012	89.31	0.027	231.5		
0.00013	93.28	0.031	235.0		
0.00014	97.26	0.035	238.4		
0.00015	101.2	0.039	241.7		
0.00015	105.2	0.043	245.0		
0.00018	109.2	0.048	248.3		
0.00018	113.1	0.053	251.5		
0.00021	117.1	0.058	254.7		
0.00022	121.0	0.064	257.9		
0.00025	125.0	0.070	261.0		
0.00027	129.0	0.076	264.0		
0.00031	132.9	0.082	267.1		
0.00035	136.9	0.089	270.1		
0.00041	140.8	0.096	273.1		

C-3 a): BET Surface area result of activated carbon from maximum condition by $ZnCl_2$; WR= 1:4, 900ºC, 3 hours



BECKMAN COULTER

Beckman Coulter Sorption Analysis

Page 1

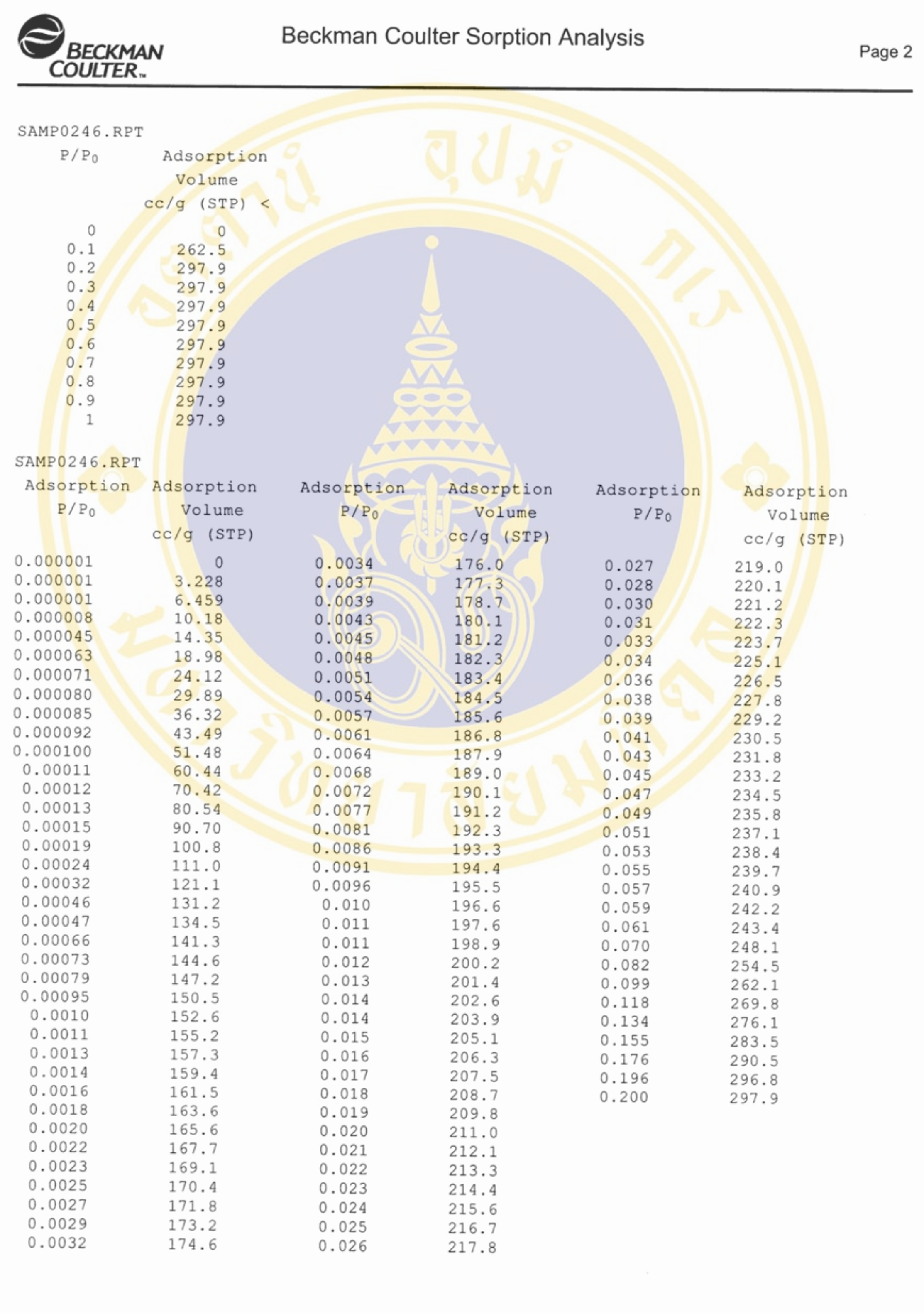
Filename:	SAMP0246.RPT
File ID:	SAMP0246
Sample ID:	ZN-2
Operator:	PARAWEE
Comment 1:	BET
Outgassing conditions:	15 min 120 C
Adsorbate:	N2
Sample Mass:	0.141 grams
Start time:	17:19 28 Jun 2004

BET Surface Area Results

P/P_0 range: 0.0509 to 0.2

Slope:	0.00409	Intercept:	16.73e-6
Correlation coefficient:	0.9999		
C Value:	245.4		
Volume Adsorbed:	243.6 cc/g (STP)	Surface Area:	1,060 m^2/g

C-3 b): Adsorption data of BET Surface area of activated carbon from maximum condition by $ZnCl_2$; WR= 1:4, 900ºC, 3 hours



Beckman Coulter Sorption Analysis

Page 2

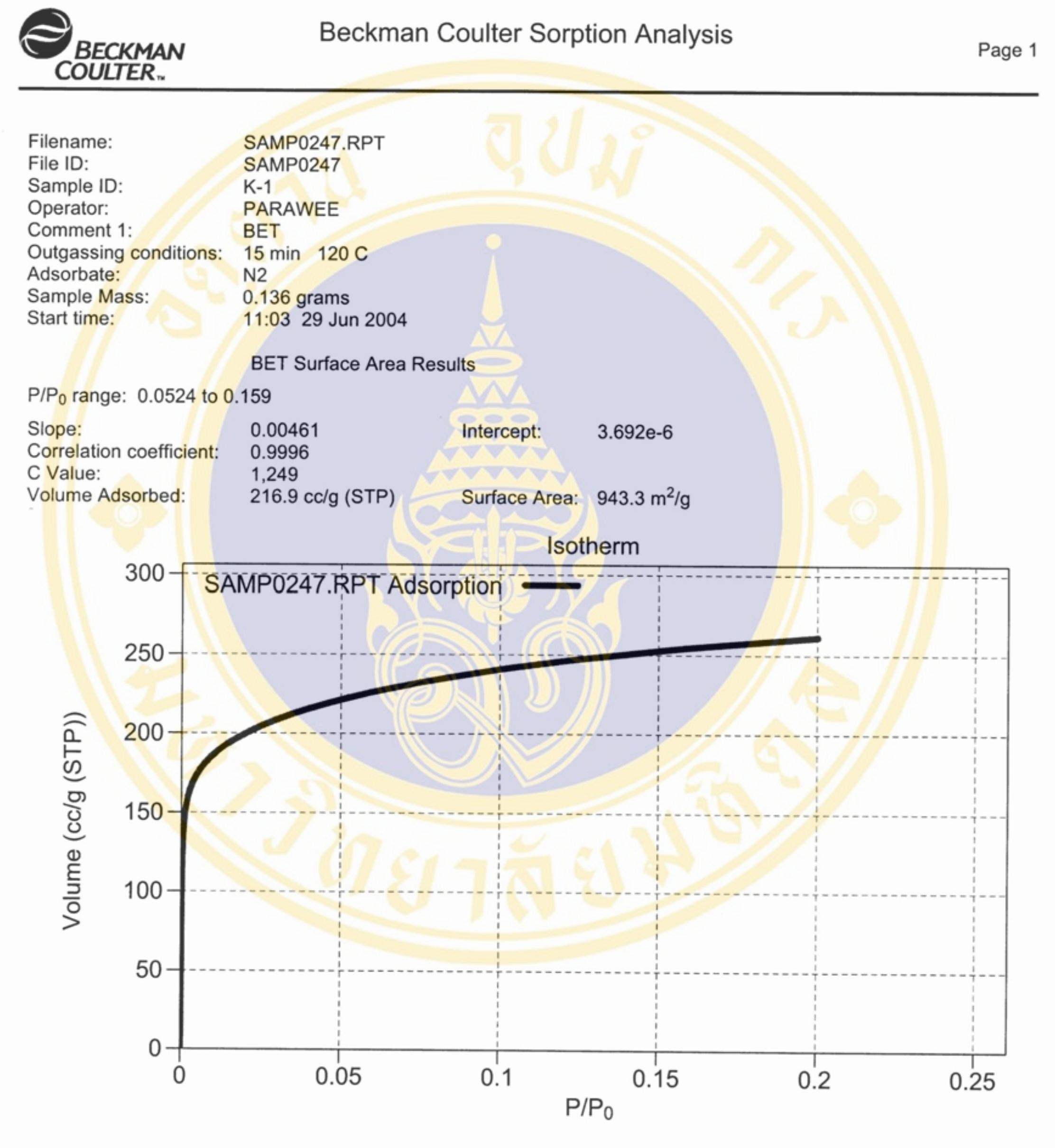
SAMP0246.RPT

P/P_0	Adsorption Volume cc/g (STP) <
0	0
0.1	262.5
0.2	297.9
0.3	297.9
0.4	297.9
0.5	297.9
0.6	297.9
0.7	297.9
0.8	297.9
0.9	297.9
1	297.9

SAMP0246.RPT

Adsorption P/P_0	Adsorption Volume cc/g (STP)	Adsorption P/P_0	Adsorption Volume cc/g (STP)	Adsorption P/P_0	Adsorption Volume cc/g (STP)
0.000001	0	0.0034	176.0	0.027	219.0
0.000001	3.228	0.0037	177.3	0.028	220.1
0.000001	6.459	0.0039	178.7	0.030	221.2
0.000008	10.18	0.0043	180.1	0.031	222.3
0.000045	14.35	0.0045	181.2	0.033	223.7
0.000063	18.98	0.0048	182.3	0.034	225.1
0.000071	24.12	0.0051	183.4	0.036	226.5
0.000080	29.89	0.0054	184.5	0.038	227.8
0.000085	36.32	0.0057	185.6	0.039	229.2
0.000092	43.49	0.0061	186.8	0.041	230.5
0.000100	51.48	0.0064	187.9	0.043	231.8
0.00011	60.44	0.0068	189.0	0.045	233.2
0.00012	70.42	0.0072	190.1	0.047	234.5
0.00013	80.54	0.0077	191.2	0.049	235.8
0.00015	90.70	0.0081	192.3	0.051	237.1
0.00019	100.8	0.0086	193.3	0.053	238.4
0.00024	111.0	0.0091	194.4	0.055	239.7
0.00032	121.1	0.0096	195.5	0.057	240.9
0.00046	131.2	0.010	196.6	0.059	242.2
0.00047	134.5	0.011	197.6	0.061	243.4
0.00066	141.3	0.011	198.9	0.070	248.1
0.00073	144.6	0.012	200.2	0.082	254.5
0.00079	147.2	0.013	201.4	0.099	262.1
0.00095	150.5	0.014	202.6	0.118	269.8
0.0010	152.6	0.014	203.9	0.134	276.1
0.0011	155.2	0.015	205.1	0.155	283.5
0.0013	157.3	0.016	206.3	0.176	290.5
0.0014	159.4	0.017	207.5	0.196	296.8
0.0016	161.5	0.018	208.7	0.200	297.9
0.0018	163.6	0.019	209.8		
0.0020	165.6	0.020	211.0		
0.0022	167.7	0.021	212.1		
0.0023	169.1	0.022	213.3		
0.0025	170.4	0.023	214.4		
0.0027	171.8	0.024	215.6		
0.0029	173.2	0.025	216.7		
0.0032	174.6	0.026	217.8		

C-4 a): BET Surface area result of activated carbon from optimum condition by K_2CO_3; WR= 1:2, 800ºC, 2 hours



Beckman Coulter Sorption Analysis

Page 1

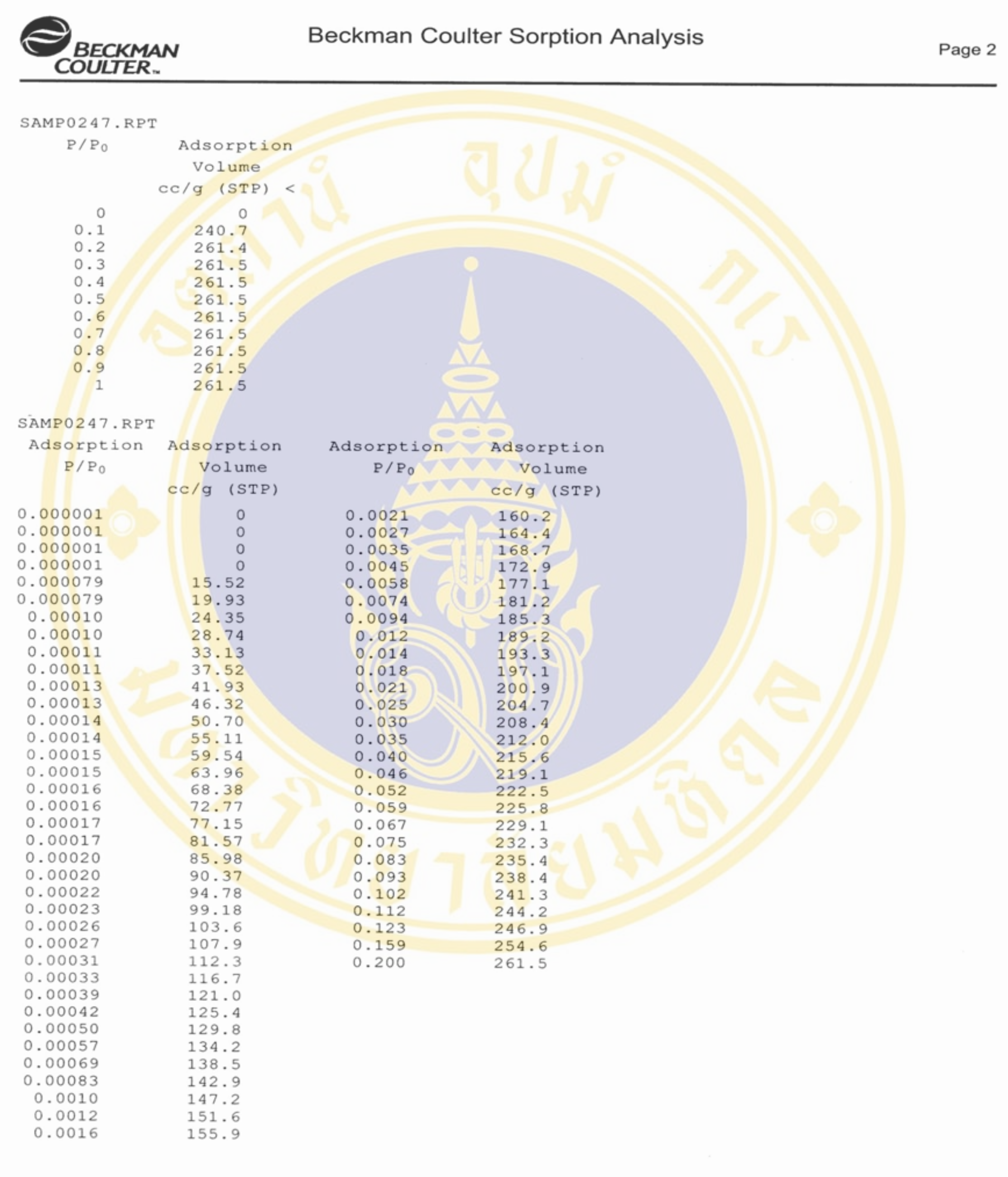
Filename:	SAMP0247.RPT
File ID:	SAMP0247
Sample ID:	K-1
Operator:	PARAWEE
Comment 1:	BET
Outgassing conditions:	15 min 120 C
Adsorbate:	N2
Sample Mass:	0.136 grams
Start time:	11:03 29 Jun 2004

BET Surface Area Results

P/P_0 range: 0.0524 to 0.159

Slope:	0.00461	Intercept:	3.692e-6
Correlation coefficient:	0.9996		
C Value:	1,249		
Volume Adsorbed:	216.9 cc/g (STP)	Surface Area:	943.3 m^2/g

C-4 b): Adsorption data of BET Surface area of activated carbon from optimum condition by K_2CO_3; WR= 1:2, 800ºC, 2 hours



BECKMAN COULTER™

Beckman Coulter Sorption Analysis

Page 2

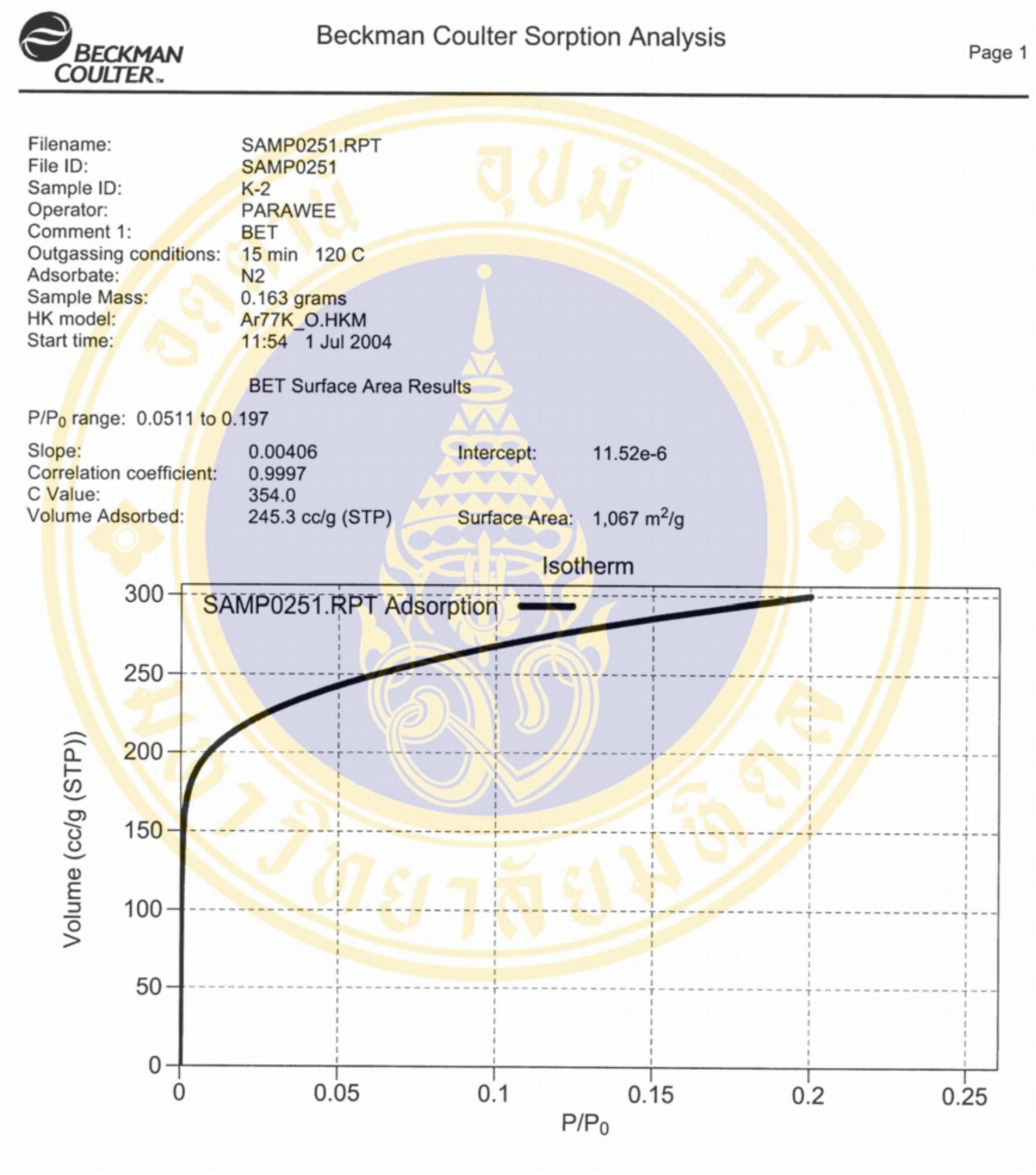
SAMP0247.RPT

P/P_0	Adsorption Volume cc/g (STP) <
0	0
0.1	240.7
0.2	261.4
0.3	261.5
0.4	261.5
0.5	261.5
0.6	261.5
0.7	261.5
0.8	261.5
0.9	261.5
1	261.5

SAMP0247.RPT

Adsorption P/P_0	Adsorption Volume cc/g (STP)
0.000001	0
0.000001	0
0.000001	0
0.000001	0
0.000079	15.52
0.000079	19.93
0.00010	24.35
0.00010	28.74
0.00011	33.13
0.00011	37.52
0.00013	41.93
0.00013	46.32
0.00014	50.70
0.00014	55.11
0.00015	59.54
0.00015	63.96
0.00016	68.38
0.00016	72.77
0.00017	77.15
0.00017	81.57
0.00020	85.98
0.00020	90.37
0.00022	94.78
0.00023	99.18
0.00026	103.6
0.00027	107.9
0.00031	112.3
0.00033	116.7
0.00039	121.0
0.00042	125.4
0.00050	129.8
0.00057	134.2
0.00069	138.5
0.00083	142.9
0.0010	147.2
0.0012	151.6
0.0016	155.9
0.0021	160.2
0.0027	164.4
0.0035	168.7
0.0045	172.9
0.0058	177.1
0.0074	181.2
0.0094	185.3
0.012	189.2
0.014	193.3
0.018	197.1
0.021	200.9
0.025	204.7
0.030	208.4
0.035	212.0
0.040	215.6
0.046	219.1
0.052	222.5
0.059	225.8
0.067	229.1
0.075	232.3
0.083	235.4
0.093	238.4
0.102	241.3
0.112	244.2
0.123	246.9
0.159	254.6
0.200	261.5

C-5 a): BET Surface area result of activated carbon from maximum condition by K_2CO_3; WR= 1:3, 900ºC, 3 hours



Beckman Coulter Sorption Analysis

Page 1

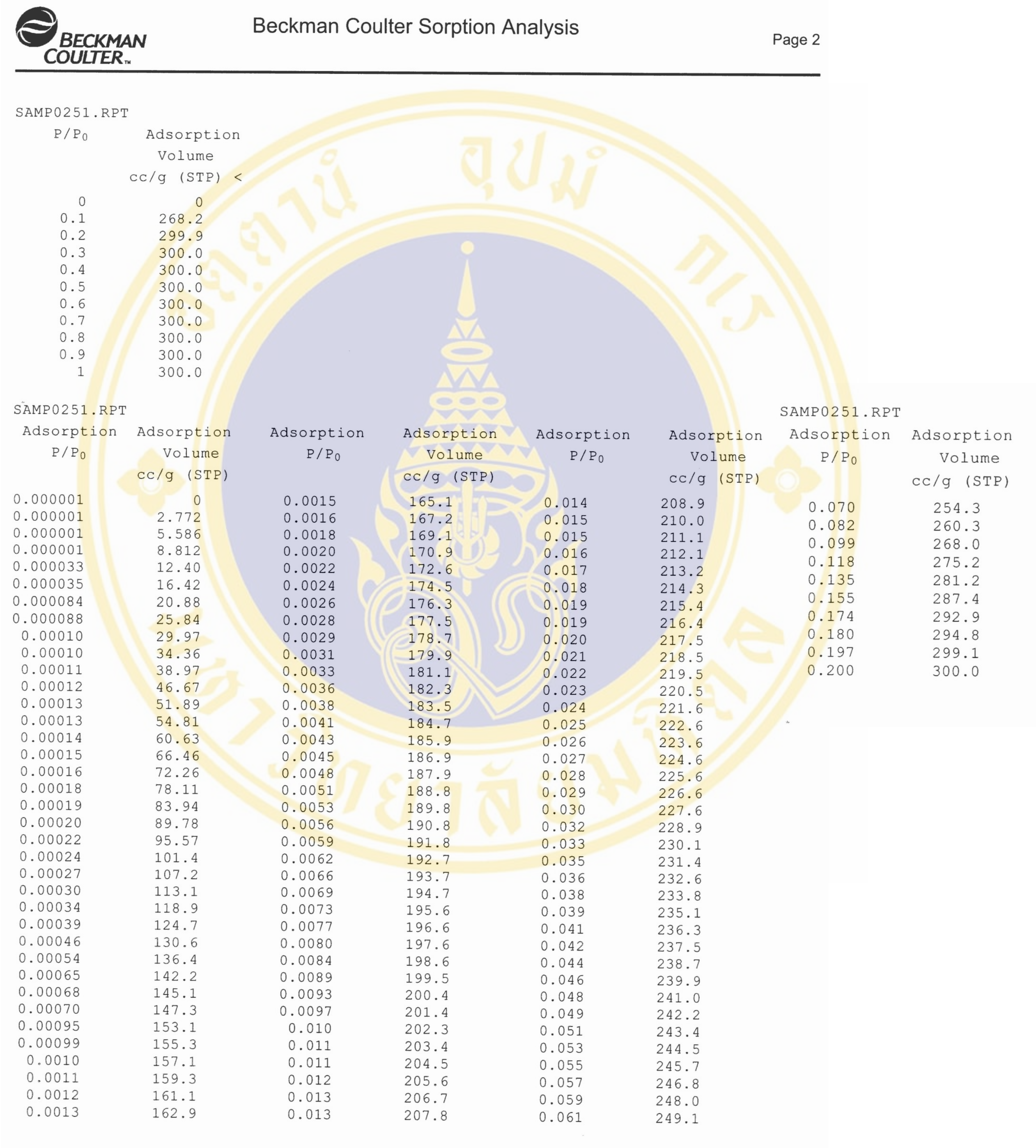
Filename: SAMP0251.RPT
File ID: SAMP0251
Sample ID: K-2
Operator: PARAWEE
Comment 1: BET
Outgassing conditions: 15 min 120 C
Adsorbate: N2
Sample Mass: 0.163 grams
HK model: Ar77K_O.HKM
Start time: 11:54 1 Jul 2004

BET Surface Area Results

P/P_0 range: 0.0511 to 0.197

Slope:	0.00406	Intercept:	11.52e-6
Correlation coefficient:	0.9997		
C Value:	354.0		
Volume Adsorbed:	245.3 cc/g (STP)	Surface Area:	1,067 m^2/g

C-5 b): Adsorption data of BET Surface area of activated carbon from maximum condition by K_2CO_3; WR= 1:3, 900ºC, 3 hours



BECKMAN COULTER

Beckman Coulter Sorption Analysis

Page 2

SAMP0251.RPT

P/P_0	Adsorption Volume cc/g (STP) <
0	0
0.1	268.2
0.2	299.9
0.3	300.0
0.4	300.0
0.5	300.0
0.6	300.0
0.7	300.0
0.8	300.0
0.9	300.0
1	300.0

SAMP0251.RPT

Adsorption P/P_0	Adsorption Volume cc/g (STP)	Adsorption P/P_0	Adsorption Volume cc/g (STP)	Adsorption P/P_0	Adsorption Volume cc/g (STP)
0.000001	0	0.0015	165.1	0.014	208.9
0.000001	2.772	0.0016	167.2	0.015	210.0
0.000001	5.586	0.0018	169.1	0.015	211.1
0.000001	8.812	0.0020	170.9	0.016	212.1
0.000033	12.40	0.0022	172.6	0.017	213.2
0.000035	16.42	0.0024	174.5	0.018	214.3
0.000084	20.88	0.0026	176.3	0.019	215.4
0.000088	25.84	0.0028	177.5	0.019	216.4
0.00010	29.97	0.0029	178.7	0.020	217.5
0.00010	34.36	0.0031	179.9	0.021	218.5
0.00011	38.97	0.0033	181.1	0.022	219.5
0.00012	46.67	0.0036	182.3	0.023	220.5
0.00013	51.89	0.0038	183.5	0.024	221.6
0.00013	54.81	0.0041	184.7	0.025	222.6
0.00014	60.63	0.0043	185.9	0.026	223.6
0.00015	66.46	0.0045	186.9	0.027	224.6
0.00016	72.26	0.0048	187.9	0.028	225.6
0.00018	78.11	0.0051	188.8	0.029	226.6
0.00019	83.94	0.0053	189.8	0.030	227.6
0.00020	89.78	0.0056	190.8	0.032	228.9
0.00022	95.57	0.0059	191.8	0.033	230.1
0.00024	101.4	0.0062	192.7	0.035	231.4
0.00027	107.2	0.0066	193.7	0.036	232.6
0.00030	113.1	0.0069	194.7	0.038	233.8
0.00034	118.9	0.0073	195.6	0.039	235.1
0.00039	124.7	0.0077	196.6	0.041	236.3
0.00046	130.6	0.0080	197.6	0.042	237.5
0.00054	136.4	0.0084	198.6	0.044	238.7
0.00065	142.2	0.0089	199.5	0.046	239.9
0.00068	145.1	0.0093	200.4	0.048	241.0
0.00070	147.3	0.0097	201.4	0.049	242.2
0.00095	153.1	0.010	202.3	0.051	243.4
0.00099	155.3	0.011	203.4	0.053	244.5
0.0010	157.1	0.011	204.5	0.055	245.7
0.0011	159.3	0.012	205.6	0.057	246.8
0.0012	161.1	0.013	206.7	0.059	248.0
0.0013	162.9	0.013	207.8	0.061	249.1

SAMP0251.RPT

Adsorption P/P_0	Adsorption Volume cc/g (STP)
0.070	254.3
0.082	260.3
0.099	268.0
0.118	275.2
0.135	281.2
0.155	287.4
0.174	292.9
0.180	294.8
0.197	299.1
0.200	300.0

APPENDIX C
EXPERIMENTAL PHOTOGRAPH

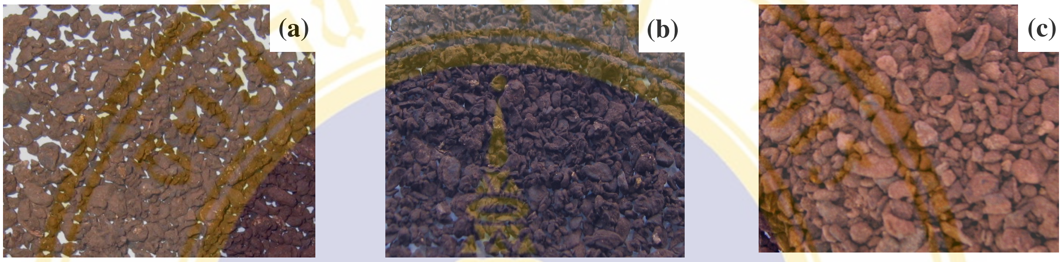


Figure C-1: Comparing coffee ground waste and impregnated coffee ground waste with activating agent; (a) Brown coffee ground waste, (b) Dark brown impregnated with $ZnCl_2$ and (c) Light brown impregnated with K_2CO_3

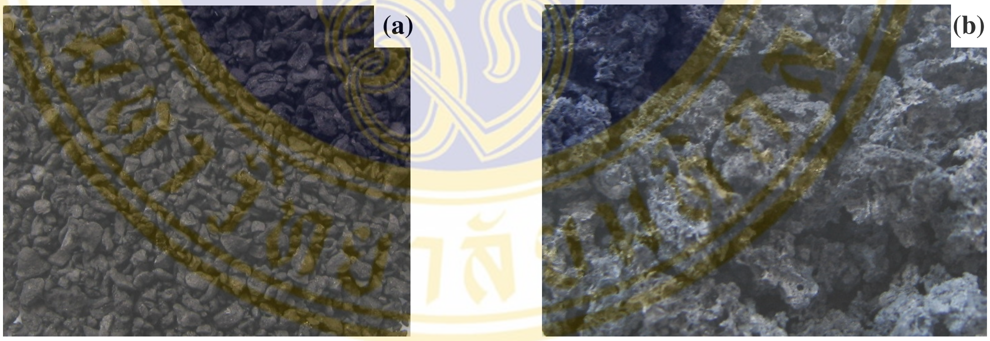


Figure C-2: Comparing derived activated carbon from coffee ground using two activating agent; (a) activated with $ZnCl_2$ and (c) activated with K_2CO_3

Figure C-2: Crucible with lid, the vessel contained impregnated sample

Figure C-3: Carbolite Furnace

BIOGRAPHY

NAME	Miss Thanittha Khantisuk
DATE OF BIRTH	12 April, 1972
PLACE OF BIRTH	Bangkok, Thailand
INSTITUTIONS ATTENDED	Silpakorn University, 1995: Bachelor of Science (Environmental Science) Mahidol University, 2005: Master of Science (Appropriate Technology for Resources and Environmental Development)
HOME ADDRESS	32/1 Moo 8 Tampol Bangpa Maung Rachaburi 70000 Tel. 0-6988-6131