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PREPARATION, CHARACTERIZATION AND CONTINUOUS PROCESS DESIGN OF ACTIVATED CARBON FROM WASTE TIRES

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ในงานวิจัยนี้ ถ่านกัมมันต์ถูกเตรียมขึ้นจากยางรถยนต์ใช้แล้ว โดยวิธีที่นิยมกันโดยทั่วไปและวิธีที่เน้นในทางปฏิบัติได้ง่ายในการผลิตในอุตสาหกรรม เพื่อลดค่าใช้จ่ายในการผลิต อันมาจากค่าแก๊สเฉื่อย ซึ่งใช้เป็นแก๊สตัวกลางในกระบวนการคาร์บอไนเซชัน และการกระตุ้น แก๊สที่นำมาใช้แทนแก๊สเฉื่อยในกระบวนการคาร์บอไนเซชันนั้นคือ อากาศ ส่วนในกระบวนการกระตุ้นนั้นใช้แก๊สผสมระหว่าง ไอน้ำ คาร์บอนไดออกไซด์ ออกซิเจน และไนโตรเจน ซึ่งเป็นองค์ประกอบส่วนใหญ่ของแก๊สที่ออกมาจากปล่องเตาเผา นอกจากนี้ ได้ทำการศึกษาถึงผลกระทบของอุณหภูมิและเวลาในการคาร์บอไนเซชันและการกระตุ้นต่อคุณสมบัติทางกายภาพ และคุณสมบัติทางความพรุนของถ่านกัมมันต์ จากนั้นถ่านกัมมันต์ที่ได้จากการเตรียมทั้งสองวิธีนี้จะถูกนำไปใช้เป็นตัวดูดซับในระบบการดูดซับสารอินทรีย์เหลว เช่น ฟีนอลและ สีย้อมเรด31 เปรียบเทียบกับถ่านกัมมันต์เกรดการค้า พบว่าถ่านกัมมันต์ที่เตรียมได้นั้นสามารถดูดซับฟีนอลได้ดีเทียบเท่ากับถ่านกัมมันต์เกรดการค้า แต่สามารถดูดซับสีย้อมเรด31 ได้ดีกว่าถ่านกัมมันต์เกรดการค้า เนื่องจากมีรูพรุนระดับเมโซพอร์มาก ถ่านกัมมันต์ที่เตรียมได้จากงานวิจัยนี้ น่ามีความเหมาะสมในการใช้บำบัดน้ำเสีย ของประกอบที่ไม่ย่อยสลายทางชีวภาพ

โดยการอาศัยข้อมูลที่ได้จากการทดลองในระดับห้องห้องปฏิบัติการ และงานวิจัยที่เกี่ยวข้อง นำไปสู่การคำนวณออกแบบแผนผังการไหลและดุลมวลและพลังงานของระบบ ซึ่งมีกำลังการผลิต 720 ตันต่อปี จากนั้นจึงทำการกำหนดขนาดของอุปกรณ์หลักทุกตัวของกระบวนการ รวมทั้งการศึกษาถึงความเป็นไปได้ทางด้านเศรษฐศาสตร์ พบว่ามีระยะเวลาคืนทุน 6 ปี โรงงานนี้นี้มีค่าอัตราการคืนทุนถึง 29% นอกจากนี้มีค่าดัชนีกำไรมากกว่าหนึ่ง ซึ่งบ่งชี้ว่าโครงการนี้เป็นไปได้ที่จะได้กำไร มีอัตราผลตอบแทน 20.58% นอกจากนี้ได้ทำการวิเคราะห์ตัวแปรที่มีผลต่อผลกำไรของโรงงาน ซึ่งตัวแปรเหล่านั้นประกอบด้วย ราคาวัตถุดิบ ราคาขายของถ่านกัมมันต์ กำลังการผลิต ราคาแก๊ส LPG อัตราดอกเบี้ย และเงินลงทุนคงที่

ภาควิชา วิศวกรรมเคมี	ลายมือชื่อนิสิต..
สาขาวิชา วิศวกรรมเคมี	ลายมือชื่ออาจารย์ที่ปรึกษา..................................
ปีการศึกษา 2548	ลายมือชื่ออาจารย์ที่ปรึกษาร่วม.............................

4670281121 MAJOR ENGINEERING
KEY WORD: ACTIVATED CARBON / WASTE TIRES / CONTINUOUS PROCESS DESIGN

CHALIDA KLAYSOM: THESIS TITLE. (PREPARATION, CHARACTERIZATION AND CONTINUOUS PROCESS DESIGN OF ACTIVATED CARBON FROM WASTE TIRES) THESIS ADVISOR: ASSOC. PROF. TAWATCHAI CHARINPANITKUL, D.Eng., THESIS CO-ADVISOR : PROF. WIWUT TANTHAPANICHAKOON, Ph.D., 118 pp. ISBN 974-53-1261-4

In this work, activated carbon was prepared form waste tires by conventional and practical methods. The practical method was adopted to reduce the operating cost of inert N_2 gas which was continuously used as carrier gas in the carbonization and activation steps. The practical gas used in the carbonization was air and that used in the activation was a mixture gas of steam, CO_2, O_2, and N_2. Furthermore, the effects of carbonization temperature, activation temperature, and holding times of the carbonization and activation steps on the physical and porous properties of chars and activated carbons were investigated. Next, the obtained conventional and practical activated carbons were used as absorbent in water-phase adsorption of organic compounds such as phenol and Red 31. In comparison with a commercial activated carbon, the results indicated that the obtained activated carbons show comparable phenol adsorption capacity as the commercial one. However, the obtained activated carbons show superior Red 31 adsorption capacities to the commercial one. Because of their highly mesoporous properties, the obtained activated carbons should be suitable for tertiary waste water treatment of bulky non-biodegradable compounds.

Based on the lab-scale experimental and relevant published data, chemical engineering design of a continuous production process for activated carbon from waste tires was carried out. Process flow diagram and overall mass and energy balances were developed for a 720 ton/year plant. Then sizing of the major equipment and an economic evaluation of the activated carbon investment and production costs were determined. Having a payback period of 6.42 years, the proposed plant is generated should yield an ROI up to 29%. Moreover, the cumulative cash ratio of this project is greater than unity indicating that this project is potentially profitable. The rate of return in this project is 20.58%. And analysis on the major factors affecting the profitability of the proposed plant is carried out. These factors include: (1) raw material price; (2) AC selling price; (3) production capacity; (4) LPG price; (4) interest rate; and (6) fixed capital investment.

Department Chemical Engineering Student's signature....................................
Field of study Chemical Engineering Advisor's signature...................................
Academic year 2004 Co-advisor's signature..............................

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NOMENCLATURES

C_e	Equilibrium concentration [mg/l]
C_{OL}	Cost of operating labor (US$)
C_{RM}	Cost of raw materials (US$)
C_{UT}	Cost of utility (US$)
COM	Cost of manufacturing (US$)
CCP	Cumulative cash position (US$)
CCR	Cumulative cash ratio
$COMd$	Manufacturing cost exclude depreciation (US$/year)
$DCFROR$	Discount cash flow of return (%)
$dV_p/dlog(R_p)$	Pore size distribution [cm^3/g]
FCI	Fixed capital investment (US$)
Nnp	Number of non particulate processing steps handing step and including compression, heating and cooling, mixing, and reaction
N_{OL}	Number of operating per shift
NPV	Net present value (US$)
P	number of processing steps involving the handling of particulate solid
P/P^o	Relative pressure [-]
PBP	Pay back period (year)
PVR	Present value ratio
q	The amount of N_2 adsorbed [cm^3 (STP)/g]
Q	The amount of adsorbate adsorbed [g/g AC]
R_p	Pore radius [nm]
ROI	Rate of return on investment (%)
S_{BET}	BET surface area [m^2/g]
V_{meso}	Mesopore volume [cm^3/g]
V_{micro}	Micropore volume [cm^3/g]

CHAPTER I

INTRODUCTION

1.1 Background

Disposal of waste tire has produced serious environmental problems. Because of their characteristics that make tires are long life and durability, waste tire becomes one of wastes that are difficult to handle. Most of waste tires are disposed in landfill site. However, land filling of waste tires is declining, because waste tire do not degrade easily, they are bulky, taking up valuable landfill space and preventing waste compaction. Moreover, waste tire presents hazards to human health and the environment. Tires stored in the open quickly accumulate rainwater, providing stagnant water for mosquito breeding which can transmit a number of diseases to humans. Other pests such as rats are attracted to tire piles by the water and shelter they provide. Alternative waste management options to land filling and open dumping have included, tire retreating, crumbing to produce rubber for applications such as carpets, sports surfaces and children’s playgrounds.

There are several reports on the production of activated carbon from municipal and industrial waste including waste tires. The production of activated carbon form waste tires has a number of advantages as a treatment option, since it utilizes the high calorific value of tires. Derived oils from pyrolysis step may be used directly as fuels or added to petroleum refinery feed stocks, they may also be an important source for refined chemical. The derived gases are also useful as fuel.

D. C.K. Ko et at. [1] carried out the process design and economical analysis for the production of activated carbon from waste tire. Tire crumbs are carbonized at 500 ^{o}C under nitrogen atmosphere; then obtained char is activated at 850 ^{o}C with steam. Gas produced from carbonization step is condensed as pyrolytic oil that will be sold. The light fraction of gas product (pyrolytic gas) is mixed with the exhaust form the activation furnace and fed to the combustion chamber to remove combustible components in excess air. Moreover, it is expected that by putting tire processing and cement production into an integrated production scheme the total capital investment will be significantly lowered as both units will share the single gas emission treatment facility, which is already installed.

In the present work, preparation and characterization of activated carbon from waste tires as well as continuous process design and economical feasibility study of the production of activated carbon from waste tires are investigated. The concept of process design is to produce the activated carbon by using the utility generated from the process such as pyrolytic gas as fuel in the process. Waste tires are to be carbonized in air atmosphere to reduce the operating cost of nitrogen, a carrier gas, which is expensive. Up to 80% of the total thermal energy required by the process will be produced from combustion of waste tires and char. Pyrolytic gas form the carbonization process is fed to the afterburner to remove combustible gas, smoke and foul smell in a high-temperature furnace. Exhaust gas rich in CO_2 and N_2 is recirculated to the process and mixed with steam for use in the activation step.

1.2 Objectives of Research

1.2.1 To investigate the effect of practical preparation condition on the properties of activated carbon from waste tires.

1.2.2 To characterize the obtained activated carbon and to investigate its potential in wastewater treatment

1.2.3 To carry out process design of the activated carbon production plant and its economical analysis.

1.3 Scope of Research

1.3.1 Preparation and characterization of activated carbon

1.3.1.1 Carbonization (in air atmosphere)

- Air flow rate 20 – 80 ml/min
- Carbonization temperature 750 – 900 ^oC
- Holding time 30 and 60 minutes

1.3.1.2 Activation (in gas mixture atmosphere: CO_2, N_2, and O_2 ; activating agent: steam)

- Temperature 850 and 900 ^oC
- Holding time 3 and 4 hr

1.3.1.3 Characterization of the prepared activated carbon:

- Micropore and mesopore volumes
- BET surface area
- Pore size distribution
- Standard adsorption tests, for instance, Iodine Number and Methylene Blue Number
- Physico-chemical properties such as volatile matter, ash content, moisture content, and bulk density

1.3.2 To explore potential application of the obtained activated carbon, carry out batch liquid-phase adsorption equilibrium of phenol and dyes in wastewater by determining adsorption-desorption characteristics.

1.3.3 Chemical engineering process design

- Design a continuous process for producing activated carbon from waste tires at the design capacity of 2.4 ton/day of activated carbon
- Flow chart diagram
- Overall mass and energy balances
- Design and sizing main reactor of the process such as activator, carbonizer, after burner, heat exchanger and waste heat boiler

1.3.4 Feasible study of the production

- Plant equipment cost
- Total capital investment
- Total production cost
- Payback period
- Sensitivity analysis

1.4 Expected Benefits

1.4.1 Understand in the effect of practical preparation condition on the properties of activated carbon from waste tires.

1.4.2 Gain insight and fundamental knowledge on how to modify the batch production to become continuous production.

1.4.3 Get more reliable estimation on the production cost of the continuous process.

CHAPTER II

LITERATURE REVIEW

2.1 Preparation of Activated Carbon from waste tires

S. Ogasawara, M. Kuroda, and N. Wakao [2] used automotive tires to produce activated carbon in a flow reactor. The results showed that H_2 and CO were the prime components of gaseous product, and aliphatic hydrocarbons and alkylbenzenes were the major components of oil product. The surface area of carbon residue was found to increase whereas the yield of carbon residue to decrease as water feed and reaction temperature increased.

P.T. Williams, S. Besler, and D.T. Taylor [3] pyrolyzed shredded automotive tires in N_2 atmosphere at the pyrolysis temperature up to 720^{o}C and at heating rates between 5 and 80^{o}C/min. The %yield of char decreased as the pyrolysis temperature increased, while gas and oil products increased until 600^{o}C, after that there was a small change in product yield. There was no significant effect of heating rate on the product yield. The products consisted of 55% oil, 10% gas and 35% char. There was a small effect of heating rate on the product yield. The gases were identified as H_2, CO, CO_2, C_4H_6, CH_4, and C_2H_6. The surface area of the derived char showed a significant increase with increasing temperature and heating rate.

H. Teng, M.A. Serio, M.A. Wojtowicz, R. Bassilakis, and P.R. Solomon [4] prepared activated carbon from used tires by pyrolysis in He or a mildly oxidizing atmosphere with temperature up to 900^{o}C and then activated with CO_2 at the same temperature. There were two rubber samples used in this investigation: granulated and non-granulated rubber. The char yield increased with decreasing pyrolysis temperature and increasing heating rate. Both the gas and char yields of tire pyrolysis were increased by oxygen pretreatment, whereas the oil yield was reduced. The sulfur in tires was preferentially retained in the char product after pyrolysis. From SEM micrographs of tire char, the zinc and sulfur grains were widely spread in tire char and existed at the same location, which suggested that they occurred in the form of zinc sulfide. The total surface area of activated carbon increased with carbon burn-off for the nongranulated sample, while no significant increase was observed for the granulated sample.

A.M. Cunliffe and P.T. Wailliams [5] used a nitrogen purged static-bed batch reactor to paralyze shredded scrap tires at 450-600°C. Subsequently, tire char was activated in a steam/nitrogen or carbon dioxide/nitrogen mixture at 835-935°C and then the prepared activated carbons were demineralized by acid. The oils were trapped in a series of condensers and the derived gases analyzed off-line by packed column gas chromatography. The result showed that the derived tire oils had fuel properties similar to those of a light petroleum fuel oil. The influence of pyrolysis temperature showed an increase in the aromatic content of the oils with increasing temperature, with a consequent decrease in aliphatic content. All the obtained activated carbon had a greater mesopore volume than micropore volume, which was due to the predominantly mesoporous structure of the initial tire char. Tire char activation proceeded via the standard carbon gasification mechanism of micropore formation, pore widening and finally pore wall destruction. Carbon dioxide activation produced carbons with a lower BET surface area, micropore volume, and total pore volume, but narrower size distribution than when steam was the activating agent. There was no obvious link between the activation temperature and the surface area and porosity of tire derived activated carbon over the investigated range.

S. Galvagno, S. Casu, T. Casbianca, A. Calabrese, and G. Cornacchia [6] evaluated performance of a pilot scale of scrap tire pyrolysis process. A series of tests were carried out by varying process temperatures between 550-680°C, while other parameter such as residence time, pressure, etc. were act equal. Pyrolysis plant process data were collected by an acquisition system. Scrap tire samples used for the treatment, solid, and liquid by-products and produced syngas were analyzed through both on-line monitoring (for gas) and laboratory instrumentation. Results showed that process temperature, in the explored range, did not provide significant influence on the volatilization reaction yield, at least from a quantitative point of view, while it observably influenced the distribution of the volatile fraction (liquid and gas) and by-products characteristics. The obtained products had a high calorific value therefore they could be used to support process costs. With respect to the solid residue and to the liquid fraction, they could be stored in view of the next valorization. To reduce plant management costs, it seems an interesting solution to using the gas in situ. The oil, if used as a fuel after purification, apart from the high calorific value, has the advantage of a practically ash-free combustion, since the most part of the inorganic components in the scrap tires is retained in the solid residue.

Yu-Run Lin and Hsisheng Teng [7] carbonized waste tire char with steam. Carbons with different porosities were obtained by activating the char to different extents of burn-off. Unlike commercial grade carbons that are generally microporous, the pores of the tire-char carbons are mainly composed of mesopores that have a mean size of 500 A. Both the surface area and pore volume of the carbons increase with the extent of activation and pass through a maximum at a burn-off of 43%, above which the porosity decreases with further activation. Adsorption of methylene blue capacity of the carbons was found to increase with the adsorption temperature. Langmuir analysis shows that this increase in capacity with temperature can be attributed to an increase in the number of the adsorption site as well as the endothermic nature of this specific adsorption.

G. San Miguel, G.D. Fowler, and C.J. Sollars [8] studied the effect of different activation conditions on the porosity and adsorption characteristics of carbon adsorpbents produced from waste tire rubber. For the purpose of this work, three carbon series were produced using different activation temperatures (between 925 and 1100^{o}C) and oxidizing agents (steam or carbon). Carbons produced to different degrees of burn off were characterized using gas (nitrogen) and liquid phase (phenol, methylene blue and Procion Red H-E2B) adsorption. Total micropore volumes and BET surface areas increased almost linearly with the degree of activation to 0.554 ml/g and 1070 m2/g, respectively, while the development of external surface area was particularly rapid at degrees of activation above 50wt% burn-off. Steam was observed to generate a narrower but more extensive microporosity than carbon dioxide.

However, carbon dioxide produced carbons of slightly larger external surface areas. Activation at higher temperatures resulted in pores of slightly larger dimensions, although this was only evident in highly activated samples.

P. Ariyadejwanich, W. Tanthapanichakoon, K. Nakagawa, S.R. Mukai, and H. Tamon (2003) prepared activated carbon form waste tire and investigated their characteristics. Waste tires were carbonized at 500°C in N_2 atmosphere, and then the obtained chars were activated with steam at 850°C. The results presented that mesoporous activated carbon with mesopore volumes and BET surface area up to 1.09 cm^3/g and 737 m^2/g, respectively was obtained. To further improve the porous properties of the activated carbons, the char was treated with 1 M HCL at room temperature for 1 day prior to steam activation. This treatment increased mesopore volumes and BET surface areas of the activated carbons up to1.62 cm^3/g and 1119 m^2/g, respectively. Furthermore, adsorption characteristics of phenol and a dye, Black 5, on the activated carbon prepared via acid treatment were compared with those of a commercial activated carbon in the liquid phase. Although the prepared carbon had a larger micropore volume than the commercial carbon, it showed a slightly lower phenol adsorption capacity than the commercial carbon due to its larger mesopore volume.

E. L.K. Mui, D. C.K. Ko, and G. Mckay [10] review the current status of research into the production of activated carbon from waste tires. The effects of various process parameters, particularly, temperature and heating rate, on the pyrolysis stage are presented. In general, those activated carbons produced by using steam activation occupied BET surface areas over 1000 m^2/g. Although several studies report the activation step by using carbon dioxide, these generally have surface areas in the range of 270-980 m^2/g. A number of studies have performed to investigate the pyrolysis of waste tire to char.

2.2 Adsorption of organic compound on activated carbon

H. Tamai, T. Yoshida, M. Sasaki, and H. Yasuda [11] investigated the adsorption of acid dyes, direct dyes, and basic dyes on a highly mesoporous activated carbon fiber (Y-ACF) obtained from pitch containing yttrium acetylacetonate. They concluded that small size acid dyes and basic dyes showed high adsorption on microporous activated carbon fiber of high BET surface area as well as mesoporous activated carbon fiber obtained from pitch containing yttrium acetylacetonate. On the other hand, the adsorption of dyes with large one or two dimensions in molecular structures was dependent on large pore size of activated carbon fiber and electrostatic attractive interaction between dye molecules and the surface of activated carbon fiber.

M. Sankar, G. Sekaran, S. Sadulla, and T. Ramasami [12] studied the removal of Direct Red 31, Acid Black 1, and Acid Green 16 using Rice Bran-based Activated Carbon (RBAC). They reported that the molecular weight of the dye chemicals, the mass of RBAC and the diameter of RBAC particle had positive effects on the rate of adsorption, in contrast, the initial concentration of dye chemicals, pH of the dye solution, and temperature of adsorption showed a negative impact on adsorption. It was concluded that the adsorption phenomenon is a physical process, so that regeneration of the adsorbent becomes easier.

C. Hsieh and H. Teng [13] conducted the liquid-phase adsorption of phenol, iodine and tannic acid on commercial grade granular activated carbons and fabric activated carbon. On the basis of the adsorption isotherms and the analysis using the Langmuir and the Dubinin-Radushdevich models, they elucidated that the adsorption capacity of carbons with similar surface areas and micropore volumes increased with the increasing mesopore volume of the carbons. Furthermore, it was found that the influence of mesopore volume on the capacity was enhanced by the increase in the adsorbate size.

Yu-Run Lin and H. Teng [7] employed waste tire char as the precursor for the production of activated carbons with steam activation carbons with different porosities were obtained by activating the char to different extents of burn-off. Unlike commercial grade carbons that are generally microporous, the pores of the tire-char carbons are mainly composed of mesopores that have a mean size of 50 nm. Both the surface area and pore volume of the carbons increase with the extent of activation and pass through a maximum at a burn-off of 43%, above with the porosity decreases with further activation. Adsorption of methylene blue from aqueous solutions shows monolayer coverage of the adsorpbate on the carbon surface and a full access of the adsorbate to all the pores, which renders a high discoloration capability per unit area of the carbons. The methylene blue capacity of the carbons was found to increase with the adsorption temperature. Langmuir analysis shows that this increase in capacity with temperature can be attributed to and increase in the number of the adsorption sites as well as the endothermic nature of this specific adsorption.

Manuel Fernando R. Pereira, S.F. Soares, Jose J.M. Orfao, and J.L. Figueiredo(2003) studied the surface chemistry of a commercial activated carbon in dye adsorption performance. The resultant samples were characterized in terms of their surface chemistry and textural properties, and subsequently tested in the removal of different classes of dyes. It was shown that the surface chemistry of the activated carbon plays a key role in dye adsorption performance.

K. Nakagawa, A. Namba, S. R. Mukai, H. Tamon, P. Ariyadejwanich, and W. Tanthapanichakoon(2004) prepared activated carbon from several solid wastes such as waste PET, waste tires, refuse derived fuel and waste generated during lactic acid fermentation from garbage. Activated carbon having various pore size distributions was obtained by the conventional steam-activation method and via the pre-treatment method (i.e., mixture of raw materials with a metal salt, carbonization and acid treatment prior to steam-activation). The liquid-phase adsorption characteristics of organic compounds from aqueous solution on the activated carbons were determined to confirm the applicability of these carbons, where phenol and a reactive dye, Black5, were employed as representative adsorbates. The hydrophobic surface of the carbons prepared was also confirmed by water vapor adsorption. The characteristics of a typical commercial activated carbon were also measured and compared. It was found that the activated carbons with plentiful mesopores prepared from PET and waste tires had quite high adsorption capacity for large molecules. Therefore they are useful for wastewater treatment, especially, for removal of bulky adsorbates.

2.3 Process design of activated carbon

C. Ng, W.E. Marshall, R.M. Rao, R.R. Bansode, and J.N. Losso [16] developed process flow diagrams for the large-scale production of pecan shell-based carbons derived from steam or phosphoric acid activation and carried out an economic evaluation.

C.K. Ko, E. L.K. Mui, K. S.T. Lau, and G. Mckay [1] preformed the process design and economic analysis of plants for producing activated carbons from waste tires and coal. The potential range of products from each process had been considered. Sensitivity analyses had been carried out by considering the main process factors, which were product price, production capacity, total production cost, capital investment and the tipping fee. The internal rates of return were 27.4% and 18.9% for the waste tire plant and the coal plant, respectively. It was reported that there was a possibility of yielding a higher ROI if tire processing facility was designed as an integral part of a cement manufacturing facility or power generating plant which can effectively use the energy produced, even though the revenue from the selling price of activated carbon was significantly decreased.

CHAPTER III

THEORY

3.1 Activated Carbon

Activated carbon is a processed carbon material with a highly developed porous structure and a large internal specific surface area, and it is capable of collecting gases, liquids, or dissolved species on the surface of its pores. Figures 3.1.1-3.1.2 illustrates the structures of graphite and turbostratic carbon, respectively. Activated carbon is similar to the latter type, having microcrystallites only a few layers in thickness and less than 10 nm in width The level of structural imperfections in activated carbon microcrystallites is very high, which results in many possibilities for reactions of the edge carbons with their surroundings.

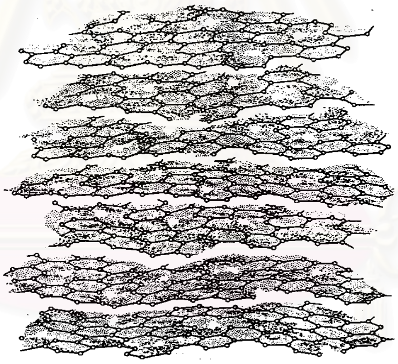


Figure 3.1.1 Graphite Lattice

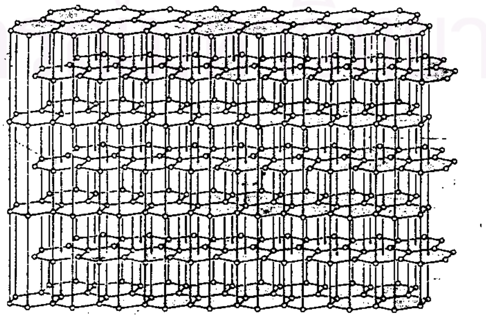


Figure 3.1.2 Turbostratic Structure

3.1.1 Production of activated carbon

Almost any carbonaceous raw materials can be used for the manufacture of activated carbon. The activated carbon can be produced in one of two ways:

- By carbonizing material with the addition of activating agent such as $ZnCl_2$, $CaCl_2$, and H_3PO_4 which influences the course of pyrolysis. This method is generally called as "chemical activation".
- By carbonizing raw material and then reacting with suitable gaseous substances (steam, carbon dioxide, or oxygen). This method is generally known as "physical activation".

Chemical activation

In chemical activation process the starting material is mixed with chemicals, and then kneaded, carbonized and washed to produce the final activated carbon. The most widely used activation agents are

Aluminum chloride
Ammonium chloride
Boric acid
Calcium chloride
Calcium hydroxide
Hydrogen chloride
Iron salt
Nickel salt
Nitric acid
Phosphoric acid
Potassium hydroxide
Potassium sulfide
Potassium permanganate
Sodium hydroxide
Sodium oxide
Sulfuric acid
Sulfur dioxide
Zinc chloride

The chemicals incorporated to the interior of precursor particles react to form products resulting from the thermal decomposition of the precursor, reducing the evolution of volatile matter and inhibiting the shrinkage of the particle. In this way, the conversion of the precursor to carbon is high, and once the chemicals are eliminated after the heat treatment, there is the porous product. Chemical activation offers several advantages: (1) it is performed in one stage that consists of carbonization and activation, (2) it yields higher carbon products, (3) it uses lower temperature, and (4) in most cases part of the added chemicals is easily recovered. However, chemical activation involves hazardous chemicals and the recovery of these chemicals from the products or off gas results in multiple operations. Non-recovery of chemicals not only makes the process uneconomical but also contributes to environmental pollution.

Physical activation

Carbonization

Carbonization is one of the most important steps in the production process of activated carbons since it is in this course which the initial porous structure is formed. During carbonization most of the non-carbon elements, hydrogen and oxygen are first removed in gaseous form by thermal decomposition of the starting material, and the freed atoms of elementary carbon are grouped into organized crystallographic formations known as elementary graphitic crystallites. The mutual arrangement of the crystallites is irregular.

The important parameters that determine the quality and the yield of the carbonized product are the rate of heating, the final temperature, the soaking time at the final temperature, and the nature of the raw material.

The final temperature is the most important parameter in the process; this is associated with the amounts of energy needed to split of the weaker chemical bonds and to enable migration of the volatile products of thermal decomposition of the raw material to the granule or grain environment. As the carbonization temperature is increased, the condensation processes in the material are enhanced and the greater the mechanical strength of the resulting granules becomes.

The soaking time of the carbonaceous material at the final carbonization temperature has an effect on the ordering of the compact structure of the carbon material.

The next important parameter of the carbonization process is the heating rate at which the final temperature is achieved. When the temperature is raised rapidly, the particular stages of the thermal decomposition of coal and the secondary reactions of the pyrolysis products with each other overlap, so control of the establishment of the porous structure in the carbonizate is more difficult. If the temperature is raised rapidly, a large quantity of volatile matter evolves within a short time, and as a result pores of greater sizes are usually formed. The reactivity of the carbonizate obtained in this way is greater than that of the products heated at a slow rate. This is due to the greater porosity and reduced ordering of the compact carbon material as compared with carbonizates obtained from the same raw material but at a low rate of heating.

The thermal decomposition of carbonaceous material, the course of the secondary mutual reactions of the pyrolysis products and the reactions of the latter with the solid carbonizate are also affected by the atmosphere in which the carbonization process is conducted. If the gases and vapors evolving during pyrolysis are rapidly removed by a neutral gas or combustion gases, then the quantity of the carbonizate obtained is smaller but its reactivity is greater.

The main aim of the carbonization process is to generate in the granules and grains the required porosity and ordering of structure of the compact carbon material. Both these factors have a crucial effect on the reactivity of the carbonizate in its reaction with the gaseous activating agent. This reactivity increases (1) with the degree of porosity generated and (2) with reduction in the ordering of the compact carbon matter. A large volume of pores in the carbonizate facilitates the diffusion of the gaseous activator into the granules and ensures a large surface area on which chemical reactions may take place.

Activation

The oxidizing agents most often used are steam, carbon dioxide, oxygen (air). During the activation of the carbonized product, first the disorganized carbon is removed, and the surface of the carbon crystallites becomes exposed to the action of the oxidizing agent. Details of the mechanism of this process, however, are not yet reliably understood.

The removal of unorganized carbon and the non-uniform burnout of elementary crystallites lead in the first phase of activation to the formation of new pores and the development of the microporous structure. In the subsequent phases, however, the effect that becomes increasingly significant is the widening of existing pores or the formation of larger size pores by the complete burnout of walls between adjacent micropores. This leads to an increase in the volume of transitional and macropores, whereas the volume of micropores diminishes. As a measure of the degree of activation the so-called burn-off is usually used, which is the percentage weight decrease of the material during activation, compared to the original carbonized product. Sometimes the so-called activation yield is used, which is the weight of the resulting activated carbon expressed as a percentage of the carbonized intermediate product prior to activation. The burn-off (B) and the activation yield (A) are related thus:

$$B = 100 - A$$

The carbon atoms, which form the structure of the carbonized product, differ markedly from one another in their affinity towards the activation agent. Those at the edges and corners of elementary crystallites, and those situated at defective places of the crystal lattice, are more reactive, because their valencies are incompletely saturated by interaction with neighboring carbon atoms. These places are the so called "active sites" on which reaction with the activation agent occurs; these sites represent only a small part, at the most only a few percent of the total surface exposed to the reaction. In the reaction of a gaseous activation agent with carbon, complex surface compounds are temporarily formed on the active sites, and on their decomposition the oxidized carbon is removed from the surface as gaseous oxides (carbon monoxide or dioxide). As a result of this, new incompletely saturated carbon atoms become exposed on the surface of the crystallites and the active sites are thus again prepared to react with further molecules of the activation agent. Details of the mechanism by which carbon reacts with steam, carbon dioxide and oxygen are shown below:

- **Activation with steam**

The reaction of steam with carbon is endothermic and a stoichiometric equation has the form:

$$C + H_2O \longrightarrow H_2 + CO \qquad \Delta H = +130 \text{ kJ/mol}$$

The rate of gasification of carbon by a mixture of steam and hydrogen is given by the formula:

$$v = \frac{k_1 P_{H2O}}{1 + k_2 P_{H2O} + k_3 P_{H2}} \ldots\ldots\ldots.(1)$$

where: P_{H2O} and P_{H2} are the partial pressures of steam and hydrogen, respectively, k_1, k_2, k_3 are the experimentally determined rate constants. The following reaction scheme is accepted as highly probable:

$$C + H_2O \leftrightarrow C(H_2O)$$
$$C(H_2O) \rightarrow H_2 + C(O)$$
$$C(O) \rightarrow CO$$

The inhibiting effect of hydrogen can be ascribed to its occupying active centers on which it becomes absorbed:

$$C + H_2 \leftrightarrow C(H_2)$$

It was assumed that the first step of the reaction is the dissociated adsorption of water molecules according to the scheme:

$$2C + H_2O \rightarrow C(H) + C(OH)$$
$$C(H) + C(OH) \rightarrow C(H_2) + C(O)$$

Hydrogen and oxygen are adsorbed at neighboring active sites, which account for about 2 percent of the surface area.

The reaction of steam with carbon is accompanied by the secondary reaction of water-gas formation, which is catalyzed by the carbon surface:

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad \Delta H = -42 \text{ kJ/mol}$$

Activation with steam is carried out at temperatures from 750 to 950^{O}C with the exclusion of oxygen, which at these temperatures aggressively attacks carbon and decreases the yield by surface burn-off. It is catalyzed by the oxides and carbonates of alkali metals, iron, copper and other metals; the activation catalysts usually employed in practice are carbonates of alkali metals, which are added in small amounts to the material to be activated.

- Activation with Carbon Dioxide

For the rate of gasification of carbon by carbon dioxide an equation analogous to that for the reaction with steam has been derived:

$$v = \frac{k_1 P_{CO2}}{1 + k_2 P_{CO} + k_3 P_{CO2}} \text{..........(2)}$$

where: P_{CO2} and P_{CO} are the partial pressures, and k_1, k_2, k_3 are the experimentally determined rate constants. Although the quantitative validity of this equation has been subject to criticism, it is taken as a basis for consideration of the mechanism of the reaction of carbon dioxide with carbon.

The rate of this reaction is retarded not only by carbon monoxide, but also by the presence of hydrogen in the reaction mixture. When from the possible hypothetical schemes, which satisfy Equation 2, those are eliminated which include stages that have been experimentally shown to be improbable; two basic variants of the reaction mechanism remain:

Variant A $C + CO_2 \rightarrow C(O) + CO$

$C(O) \rightarrow CO$

$CO + C \rightarrow C(CO)$

Variant B $C + CO_2 \rightarrow C(O) + CO$

$C(O) \rightarrow CO$

The basic difference between the two schemes lies in the explanation of the inhibiting effect of carbon monoxide. The rate of the reaction depends on the number of free active sites. In variant A, the rate of the reverse reaction is considered to be negligible and the inhibiting effect of carbon monoxide is supposed to be due to the blocking of active sites by their being covered by the adsorbed carbon monoxide. According to variant B the rate of the reverse reaction is considered to be significant, and the effect of carbon monoxide is explained as being due to a displacement of the reaction equilibrium in the latter equation.

Activation with carbon dioxide involves a less energetic reaction than that with steam and requires a higher temperature 850-1000^{O}C. The activation agent used in technical practice is flue gas to which a certain amount of steam is usually added, so that actually this is a case of combined activation. The catalysts for the reaction with carbon dioxide are carbonates of alkali metals.

- **Activation with Oxygen (air)**

In the reaction of oxygen with carbon both carbon monoxide and carbon dioxide are formed according to the equations:

$$C + O_2 \rightarrow CO_2 \qquad \Delta H = -387 \text{ kJ/mol}$$

$$2C + O_2 \rightarrow 2CO \qquad \Delta H = -226 \text{ kJ/mol}$$

Both reactions are exothermic. The mechanism of the reaction of carbon with oxygen is not yet fully understood; the most discussed point is whether carbon dioxide is a primary product of carbon oxidation or the monoxide is formed first and the dioxide is the product of secondary reaction. According to the present state of knowledge it may be assumed that both oxides are primary products. The value of the ratio CO/CO_2 increases with the increase of temperature.

The reactions with oxygen being exothermic, it is not easy to maintain the correct temperature conditions in the oven; it is especially difficult to avoid local overheating which prevents the product from being uniformly activated. Furthermore, because of the very aggressive action of oxygen, burn-out is not limited to the pores but also occurs on the surface of the grains, causing great loss. Carbons activated with oxygen have a large amount of surface oxides.

3.1.2 Porosity

During the process of activation the spaces between the elementary crystallites become cleared of various carbonaceous compounds and disorganized carbon, and carbon is also removed partially from the layers of the elementary crystallites. The resulting voids are called pores. A suitable activation process causes a large number of pores to be formed so that the total surface area of their walls, i.e. the internal surface of the activated carbon is very large, and this is the main reason for its large adsorptive capacity. Activated carbon usually has several groups of pores, each group having a certain range of values of the effective diameter. Formerly pores can be classified into three groups: micropores, mesopores, and macropores.

Micropores have small sizes comparable with those of adsorbed molecules. Their effective diameters are usually smaller than 2 nm, and average pore volumes of activated carbons usually fall in the range of 0.15-0.5 cm^3/g. In general, the surface area of microporous activated carbons lies between 100-1,000 m^2/g. The energy of adsorption in micropores is substantially greater than that for adsorption in mesopores or at the non-porous surface. In micropores, adsorption proceeds via the mechanism of volume filling.

Mesopores, also known as transitional pores, have effective diameter falling in the range of 2-50 nm. The process of filling their volume with adsorbate takes place via the mechanism of capillary condensation. For average activated carbons, the volumes of mesopores lie between the limits 0.02-0.1 cm^3/g. The peak of the distribution curve of their pore volume versus their radius is mostly in the range of 4-20 nm. For adsorption in liquid phase, activated carbon should have pores size larger than 3 nm in diameter, which falls in the range of mesopores. Besides their significant contribution to adsorption, mesopores also perform as the main transport arteries for the adsorbate.

Macropores are those having effective diameter >50 nm and their volumes are not entirely filled with adsorbate via the mechanism of capillary condensation. The values of their specific surface area are negligibly small when compared with the surface of the remaining types of pore. Consequently macropores are not important in the process of adsorption as they merely act as transport arteries rendering the internal parts of the carbon grains accessible to the molecules of the adsorbate.

3.1.3 Determination of the properties of activated carbon

The properties of activated carbon that usually should be determined are following:

Surface Area:

BET surface area is the surface area that is measured using liquid nitrogen and calculated by BET theory. Several assumptions are used in BET theory, such as that the heat of adsorption is constant over the entire surface coverage of the monolayer and that the monolayer is achieved despite the fact that exactly one monomolecular layer is never actually formed.

Porosity:

Pore size distribution can be determined by applying the Dollimore-Heal method to the measured desorption isotherms, and the microporosity is evaluated by t-plot method. Then the mesopore and micropore volumes are determined to evaluate the potential adsorption capacities of the obtained activated carbon.

Adsorption Test:

The adsorption properties of activated carbon are generally estimated by determining the isotherms of adsorption in liquid phase. The test substances that usually used as adsorbates are iodine and methylene blue. Iodine adsorption is an indicator of the capability to remove the taste and odor from water. On the other hand, methylene blue adsorption test evaluates the adsorption capacity for the color in water.

Physico-chemical properties, which generally are determined, are:

Volatile matter, which is the percentage of gaseous products, exclusive of moisture vapor. Volatile matter is determined by establishing the loss in mass resulting from heating an activated carbon sample under rigidly controlled conditions.

Ash content, which consists mainly of oxides, sulfates and carbonates of iron aluminum, calcium and sodium. In specific end uses the amount and composition of ash content may influence the capability and certain desired properties of activated carbon.

Moisture content, which is the water content in activated carbon and it is often required to define and express the water content in relation to the net weight of activated carbon.

Bulk density, which is defined as the mass per unit volume of the activated carbon including both the pore system and the external void space between the particles.

3.2 Adsorption Theory

When two phases are in contact, there is a region at their interface the composition of which is different from that of the bulk of either phase. The increase in the concentration of a substance at the interface as compared with the bulk concentration is known as adsorption. On the surface of a solid, substances can be adsorbed from a gaseous or liquid phase. The solid is known as the adsorbent and the gas or liquid is called the adsorbate.

Adsorption is brought about by the intereactions between the solid and the molecules in the fluid phase. Two kinds of forces are involved, which give rise to either physical adsorption or chemisorption. Physical adsorption forces are the same as those responsible for the condensation of vapors and the deviations from ideal gas behaviour, whereas chemisorption interactions are essentially those responsible for the formation of chemical compounds. The most important distinguishing features may be summarized as follows:

1. Physical adsorption is a general phenomenon with a relatively low degree of specificity, whereas chemisorption is dependent on the reactivity of the adsorbent and adsorbate.
2. Chemisorbed molecules are linked to reactive parts of the surface and the adsorption is necessarily confined to a monolayer. At high relative pressures, physical adsorption generally occurs as a multilayer.
3. A physisorbed molecule keeps its indentity and on desorption returns to the fluid phase in its original form. If a chemisorbed molecule undergoes reaction or dissociation, it loses its identity and cannot be recovered by desorption.
4. The energy of chemisorption is the same order of magnitude as the energy change in a comoparable chemical reaction. Physical adsorption is always exothermic, but the energy involved is generally not much larger than the energy of condensation of the adsorbate. However, it is appreciably enhanced when physical adsorption takes place in very narrow pores.
5. Activation energy is often involved in chemisorption and at low temperature the system may not have sufficient thermal energy to attain equilibrium fairly rapidly, but equilibration may be slow if the transport process is rate-determining.

The variation of extents of adsorption with relative pressure of the adsorate at constant temperature is the adsorption isotherm. Next, the variation of extents of adsorption with temperature of adsorption, at constant relative pressure, is the adsorption isobar. Finally, the variation of relative pressure of the adsorbate, with adsorption temperature, to maintain a constant amount adsorbed on the adsorbent is the adsorption isostere.

Adsorption isotherm

The adsorption isotherm provides essential information about the porosity in solids and there are significant variations in isotherm shape. According to IUPAC classification, the shapes of adsorption isotherm are shown in Figure 3.2.1. Type I isotherm is concave to the relative pressure (p/p^o) axis. It rises sharply at low relative pressures and reaches a plateau: the amount adsorbed by the unit mass of solid approaches a limiting value as $p/p^o \rightarrow 1$. The narrow range of relative pressure necessary to attain the plateau is an indication of a limited range of pore size and the appearance of a nearly horizontal plateau indicates a very small external surface area. The limiting adsorption is dependent on the available micropore volume.

Type II isotherm is concave to the p/p^o axis, then almost linear and finally convex to the p/p^o axis. It indicates the formation of an adsorbed layer whose thickness increases progressively with increasing relative pressure until $p/p^o \rightarrow 1$. If the knee of the isotherm is sharp, the uptake at Point B is usually considered to represent the completion of the monomolecular layer and the beginning of the formation of the multimolecular layer.

In Type III, the isotherm is convex to the p/p^o axis over the complete range and therefore has no Point B. This feature is indicative of weak adsorbent-adsorbate interactions.

Type IV isotherm, whose initial region is closely related to the Type II isotherm, tends to level off at high relative pressures. It exhibits a hysteresis loop, the lower branch of which represents measurements obtained by progressive addition of gas of adsorbent, and the upper branch by progressive withdrawal. The hysteresis loop is usually associated with the filling and emptying of the mesopores by capillary condensation.

Type V isotherm is initially convex to the p/p^o axis and also levels off at high relative pressures. As in the case of the Type III isotherm, this is indicative of weak adsorbent-adsorbate interactions. A Type V isotherm exhibits a hysteresis loop which is associated with the mechanism of pore filling and emptying.

Eventually, Type VI isotherm, or stepped isotherm, is associated with layer-by-layer adsorption on a highly uniform surface such as graphite. The sharpness of the steps is dependent on the system and the temperature.

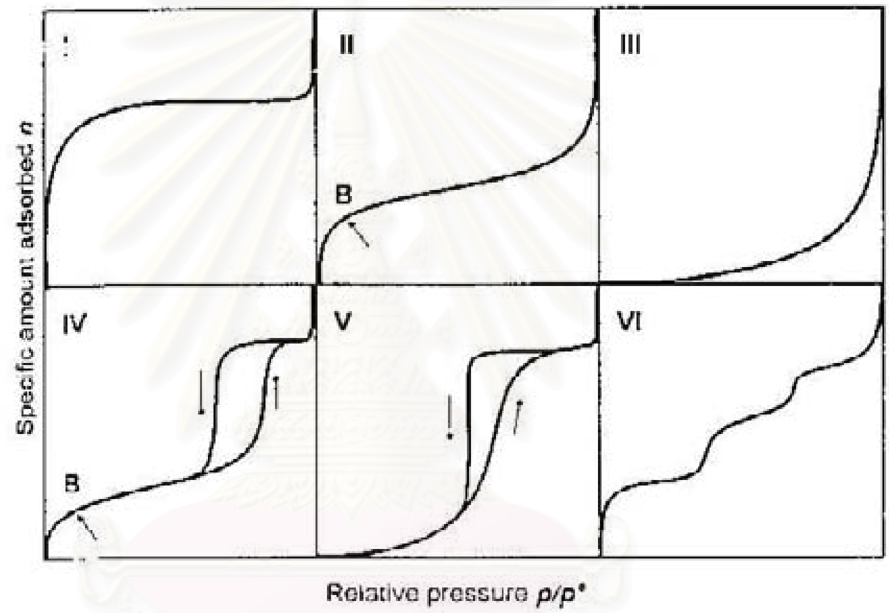


Figure 3.2.1 Shapes of adsorption isotherm

3.3 Chemical engineering process design

3.3.1 Process design

Process design establishes the sequence of chemical and physical operations; operating conditions; the duties, major specifications, and materials of construction (where critical) of all process equipment (as distinguished from utilities and building auxiliaries); the general arrangement of equipment needed to ensure proper functioning of the plant; line sizes; and principal instrumentation. The process design is summarized by a process flowsheet, a material and energy balance, and a set of individual equipment specification.

3.3.2 Equipment

Two main categories of process equipment are proprietary and custom-designed. Proprietary equipment is designed by the manufacturer to meet performance specifications made by the user. These specifications may be regarded as the process design of the equipment. This category includes equipment with moving parts such as pumps, compressors, and drivers as well as cooling towers, dryers, filters, mixers, agitators, piping equipment, and valves, and even the structural aspects of heat exchangers, furnaces, and other equipment. Custom design is needed for many aspects of chemical reactors, most vessels, multistage separators such as fractionators, and other special equipment not amenable to complete standardization.

3.3.3 Material and energy balances

Material and energy balances are based on a conservations law which is stated generally in the form

input + source = output + sink + accumulation.

The individual terms can be plural and can be rates as well as absolute quantities. Balances of particular entities are made around a bounded region called a system. Input and output quantities of an entity cross the boundaries. A source is an increase in the amount of the entity that occurs without a crossing of the boundary, for example, an increase in the sensible enthalpy or in the amount of a substance as a consequence of chemical reaction. Analogously, sinks are decreases without a boundary crossing, as the disappearance of water from a fluid stream by adsorption onto a solid phase within the boundary.

Accumulations are time rates of change of the amount of the entities within the boundary. For example, in the absence of sources and skins, an accumulation occurs when the input and output rates are different. In the steady state, the accumulation is zero.

3.3.4 Design basis

Before a chemical process design can be properly embarked on, a certain body of information must be agreed upon by all concerned persons, in addition to the obvious what is to be made and what it is to be made from. Distinctions may be drawn between plant expansions and wholly independent ones, so-called grassroots types. The needed data can be classified into specific design data and basic design data for which separate check lists will be described. Specific design data include:

1. Required products: their compositions, amounts, purities, toxicities, temperatures, pressures, and monetary values.
2. Available raw materials: their compositions, amounts, toxicities, temperature, pressures, monetary values, and all pertinent physical properties unless they are standard and can be established from correlation. This information about properties applies also to products of item1).
3. Daily and seasonal variations of any data of items 1) and 2) and subsequent items of these lists.
4. All available laboratory and pilot plant data on reaction and phase equilibrium behaviors, catalyst degradation, and life and corrosion of equipment.
5. Any available existing plant data of similar processes.
6. Local restrictions on means of disposal of wastes.

Basic engineering data include:

7) Characteristics and values of gaseous and liquid fuels that are to be used.
8) Characteristics of raw makeup and cooling tower waters, temperatures, maximum allowable temperature, flow rates available, and unit costs.
9) Steam and condensate: mean pressures and temperatures and their fluctuations at each level, amount available, extent of recovery of condensate, and unit costs.

10) Electrical power: Voltages allowed for instruments, lighting and various driver sizes, transformer capacities, need for emergency generator, unit costs.
11) Compressed air: capacities and pressures of plant and instrument air, instrument air dryer.
12) Plant site elevation.
13) Soil bearing value, frost depth, ground water depth, piling requirements, available soil test data.
14) Climatic data. Winter and summer temperature extreme, cooling tower dry bulb temperature, air cooler design temperature, strength and direction of prevailing winds, rain and snowfall maxima in 1 hr and in 12 hr, earthquake provision.
15) Blowdown and flare: What may or may not be vented to the atmosphere or to ponds or to natural waters, nature of required liquid, and vapor relief systems.
16) Drainage and sewers: rainwater, oil, sanitary.
17) Buildings: process, pump, control instruments, special equipment.
18) Paving types required in different areas.
19) Pipe racks: elevations, grouping, coding.
20) Battery limits; pressures and temperatures of individual feed stocks and products.
21) Codes: those governing pressure vessels, other equipment, buildings, electrical, safety, sanitation, and others.
22) Miscellaneous: includes heater stacks, winterizing, insulation, steam or electrical tracing of lines, heat exchanger tubing size standardization, instrument locations.

Utilities

These provide motive power and heating and cooling of process streams, and include electricity, steam, fuels, and various fluids whose changes in sensible and latent heats provide the necessary energy transfers. In every plant, the conditions of the utilities are maintained at only a few specific levels, for instance, steam at certain pressures, cooling water over certain temperature ranges, and electricity at certain voltages. At some stages of some design established.

3.3.5 Process flowsheets

Process flowsheets embody the material and energy balances between and the sizing of the major equipment of the plant. They include all vessels such as reactors, separators, and drums; special processing equipment, heat exchangers, pumps, and so on. Numerical data include flow quantities, compositions, pressures, temperatures, and so on. Inclusion of major instrumentation that is essential to process control and to complete understanding of the flowsheet without reference to other information is required particularly during the early stages of a job, since the process flowsheet is drawn first and is for some time the only diagram representing the process. As the design develops and a mechanical flowsheet gets underway, instrumentation that is essential to process control and to complete understanding of the flowsheet without reference to other information is required particularly during the early stages of a job, since the process flowsheet is drawn first and is for some time the only diagram representing the process. As the design develops and a mechanical flowsheet gets underway, instrumentation may be taken off the process diagram to reduce the clutter.

3.4 Engineering economics

Cost estimation is a specialized subject and a profession in its own right. The design engineer, however, needs to be able to make quick, rough, cost estimates to decide between alternative designs and for project evaluation. Chemical plants are built to make a profit, and an estimate of the investment required and the cost of production are needed before the profitability of a project can be assessed.

The economic evaluation of a process proceeds in several steps. These are:

1. preparing a process flow diagram
2. calculating mass and energy flows
3. sizing major equipment
4. estimating the capital cost
5. estimating the production cost
6. forecasting the product sales price
7. estimating the return on investment

Total capital investment and total production costs

There are numerous costs required to build and operate a chemical plant other than the operating costs and the installed equipment costs. Some of these costs add to the capital investment, whereas others are operating expenses.

It is common practice in the development of a design first to calculate the sizes of all the equipment and to estimate the amounts of utilities required. Next, the equipment costs are determined, and the utility costs are calculated. Then the other cost factors are added, and finally a profitability analysis is undertaken. However, for preliminary process design, we prefer to look for process alternatives as soon as a design appears to be unprofitable. Therefore, we would like to develop simplified cost models for total investment, total processing costs, and process profitability. We develop a simple model of this type as we discuss the individual cost items.

Total capital investment

The total capital investment(Tot. Inv.) is the sum of the fixed capital investment (Fixed Cap.) and the working capital (Work. Cap.):

Tot. Inv. = Fixed Cap. + Work. Cap.

I Fixed capital investment

Fixed capital investment (FCI) is the costs required to build the process, equal to the sum of the direct costs and the indirect costs.

A. Direct costs equal the sum of the material and labor costs required to build the complete facility; about 70-85% FCI.

1. Onsite costs or ISBL (inside of battery limits) are the costs of installing the equipment shown on the process flowsheet in a specific geographical location (the battery limits); about 50-60% of FCI.
    - a. Purchased equipment includes all equipment listed on a complete flowsheet; spare parts and uninstalled equipment spare; surplus equipment, supplies, and equipment allowances; inflation cost allowance; freight charges; taxes, insurance, and duties; allowance for modification during start-up; about 20-40% of FCI.
    - b. Purchased-equipment installation includes installation of all equipment listed on a complete flowsheet including structural supports, insulation, and paint; about 7.3-26% of FCI or 35-45% of purchased equipment cost.
    - c. Instrumentation and control includes purchase, installation, and calibration; about 2.5-7% of FCI or 6-30% of purchased equipment cost.

   d. Piping includes cost of pipe, pipe hangers, fittings, valves, insulation, and equipment; about 3-15% of FCI or 10-18% of purchased equipment cost.
   e. Electrical equipment and materials include the purchase and installation of the required electrical equipment including switches, motors, conduit, wire, fitting, feeders, grounding, instrument and control wiring, lighting panels, and associated labor costs; about 2.5-9% of FCI or 8-20% of purchased equipment cost.

2. Offsite costs or OSBL cost (outside of battery limits) include costs directly related to the process but built in separate locations from the main processing equipment.
   a. Buildings (including services); about 6-20% of FCI or 10-70% of purchased equipment cost.
      1) Process building include substructures, superstructures, stairways, ladders, access way, cranes, monorails, hoists, elevator. (Some companies include these factors as part of the ISBL costs, and not the OSBL costs.)
      2) Auxiliary buildings include administration and office, medical or dispensary, cafeteria, garage, product warehouse, parts warehouse, guard and safety, fire station, change house, personnel building, shipping office and platform research laboratory, control laboratory.
      3) Maintenance shops include electrical, piping, sheet metal, machine, welding, carpentry, instruments.
      4) Building service include plumbing, heating, ventilation, dust collection, air conditioning, building lighting, elevators, escalators, telephones, intercommunication system, painting, sprinkler systems, fire alarm.
   b. Yard improvements involve site development includeing site clearing, grading, roads, walkways, railroads, fences, parking areas, wharves and piers, recreational facilities, landscaping; about 1.5-5.0% of FCI.
   c. Service facilities (installed); about 8.0-35% of FCI
      1) Utilities include steam, water, power, refrigeration, compressed air, fuel, waste disposal.

        2) Facilities include boiler plant, incinerator, wells, river intake, water treatment, cooling tower, water storage, electric substation, refrigeration plant, air plant, fuel storage, waste disposal plant, fire protection.
        3) Nonprocess equipment composed of office furniture and equipment, safety and medical equipment, shop equipment, automotive equipment, yard material-handling equipment, laboratory equipment, shelves, bins, pallets, hand trucks, fire extinguishers, hoses, fire engines, loading equipment.
        4) Distribution and packaging include raw-material and product storage and handling equipment, product packaging equipment, blending facilities, loading stations.
    d. Land; about 1-2% of FCI or 4-8% of purchased equipment costs.
        1) Surveys and fees.
        2) Property costs.

B. Indirect costs are expenses not directly involved with material and labor of actual installation; about 15-30% of FCI.

1. Engineering and supervision; about 4-21% of FCI or 5-15% of direct costs.
    a. Engineering costs include administrative, process design and general engineering, drafting cost engineering, processing, expediting, reproduction, communications, scale models, consultant fees, and travel.
    b. Engineering supervision and inspection.
2. Construction expenses; about 4.8-22.0% of FCI
    a. Temporary facilities composed of construction, operation, and maintenance of temporary facilities; offices, roads, parking lots, railroads, electrical, piping, communications, fencing.
    b. Construction tools and equipment.
    c. Construction supervision involving accounting, timekeeping, purchasing, expediting.
    d. Warehouse personnel and guards.
    e. Safety, medical, and fringe benefits.
    f. Permits, field tests, special license.
    g. Taxes, insurance, and interest.
3. Contractor's fee; about 1.5-5.0% of FCI.

4. Contingency-to compensate for unpredictable events such as storms, floods, strikes, price changes, small design changes, errors in estimates, etc.; about 5-20% of FCI.

C. Alternate breakdown of FCI.

II. Working capital

Working capital is the capital required to actually operate the plant; about 10-20% of the total capital in vestment.

A. Raw material for a one month supply.

B. Finished products in stock and semifinished products; approximate production costs for one month.

C. Accounts receivable-to give customers 30 days to pay for goods; about the production costs for one month.

D. Cash on hand to meet operating expenses-salaries and wages, raw-material purchases.

E. Accounts payable and taxes payable.

Total production cost

Total production cost is the sum of manufacturing costs (Manu. Cost) and the general expenses (or SARE)

Total. Prod. Cost = Manu. Cost + SARE

I. Manufacturing cost

Manufacturing cost = direct production costs + fixed charges + plant overhead

A. Direct production cost (about 60% of the total product cost).

1. Raw materials (about 10-50% of total product cost).
2. Utilities (about 10-20% of total product cost).
3. Maintenance and repairs (about 2-10% of FCI).
4. Operating supplies (about 10-20% of cost for maintenance and repairs or 0.5-1% of FCI).
5. Operating labor (about 10-20% of total product cost).
6. Direct supervision and clerical labor (about 10-50% of total product cost).
7. Laboratory charges (about 10-20% of operating labor).

8. Patents and royalties (about 0-6% of total product cost).

B. Fixed charge (about 10-20% of total product cost).

1. Depreciation (about 10% of FCI).
2. Local taxes (about 1-4% of FCI).
3. Insurance (about 0.4-1% of FCI).
4. Rent (about 10% of value of rented land and buildings).
5. Interest (about 0-7% of total capital investment).

C. Plant overhead (about 50-70% of the costs for operating labor, supervision, and maintenance or 5-15% of total product cost); costs include general plant upkeep and overhead, payroll overhead, packaging, medical services, safety and protection, restaurants, recreation, salvage, laboratories, and storage facilities.

II. General expenses

General expenses = administrative costs + distribution and selling costs + research and development costs [also called SARE (sales, administration, research, and engineering)].

A. Administrative cost (about 15% of the costs for operating labor, supervision, and maintenance or 2-5% of total product cost); include cost for executive salaries, clerical wages, legal fees, office supplies, and communications.

B. Distribution and selling costs (about 2-20% of total product cost); includes costs for sales offices, sales staff, shipping, and advertising.

C. Research and development costs (about 2-5% of every sales dollar or about 5% of total product cost).

Sensitivity analysis

An economic study should pinpoint the areas most susceptible to change. It is easier to predict expenses than either sales or profits. Fairly accurate estimates of capital costs and processing costs can be made. However, for the most part errors in these estimates have a correspondingly smaller effect than changes in sales price, sales volume, and the costs of raw materials and distribution.

Sales and raw-materials prices may be affected by any of the following: discounts regulations, quality and form of the materials, and competition. Sales volume may be affected by any of the following: new uses for the product, new markets, advertising, quality, overcapacity agreements, wage rates, transportation systems, storage systems, quality, losses, and seasonal effects.

Distribution costs depend on plant location, physical state of the material (whether corrosive, explosive, flammable, perishable, or toxic), freight rates, and labor costs. Distribution costs may be affected by any of the following: new methods of materials handling, safety regulations, productivity agreements, wage rates, transportation systems, storage systems, quality, losses, and seasonal effects.

It is worthwhile to make tables or plot curves that show the effect of variations in costs and prices on profitability. This procedure is called **sensitivity analysis**. Its purpose is to determine to which factors the profitability of a project is most sensitive. Sensitivity analysis should always be carried out to observe the effect to departures from expected values.

CHAPTER IV

RESEARCH PROCEDURE

4.1 Preparation of activated carbon

4.1.1 Conventional preparation method

Activated carbons were produced from waste tires through the process of carbonization followed by steam activation. In the carbonization step, waste tire rubber will be carbonized in N_2 atmosphere The reactor was electric heat from room temperature to carbonization temperature varied in the range of 500-900^oC at a constant heating rate of 5^oC/min. Normally, the carbonization temperature will be maintained 30 to 60 minutes, and finally left to naturally cool down. In the activation step, the product obtained from the carbonization step will be activated with steam in a quartz tube reactor by heating the reactor to activation at 850 and 900^oC with a heating rate of 10^oC/min. The steam used for activation is generally generated from a heating pot at a constant rate of 0.5 g/min, and mixed with N_2 gas with a flow of 200 cm^3/min. Therefore, the partial pressure of water vapor was around 0.46 and the activation time was 2 and 3 hours. Figure 4.1.1 illustrates the quartz tube reactor which can be used for both carbonization and steam activation in this work.

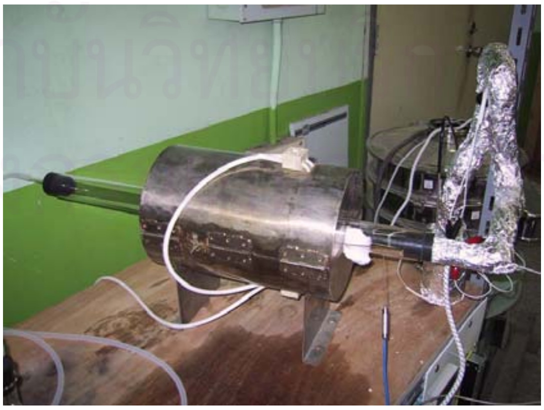


Figure 4.1.1 Quartz tube reactor

4.1.2 Practical preparation method

Like conventional method, the practical preparation method consists of two steps: carbonization and activation. In the carbonization step, waste tire rubber was carbonized in air atmosphere (instead of in an inert gas such as N_2) at 600-900°C at a constant heating rate of 10°C/min, then held at the carbonization temperature for 30 and 60 minutes. In the activation step, char from the carbonization step was activated with steam by heating the reactor to activation at 850 and 900°C with a heating rate of 10°C/min. The steam was introduced to the reactor with a 100 cm^3/min flow of gas mixture of 83% N_2, 2.45% O_2 and 14.5 %CO_2. The components and the percentage of this gas mixture were estimated from flue gas from afterburner which was used as the carrier gas instead of an inert gas such as N_2. The partial pressure of water vapor was around 0.46 and the activation time was 3 and 4 hours.

4.2 Characterization of waste tires

The waste tires were supplied from Union Commercial Development, Thailand. The particle size of the rubber sample obtained through this process was around 3 mm. Physical properties of used tires such as the proximate analysis and bulk density were characterized. The results of elemental analysis of used waste tires are summarized in Table 4.2

Table 4.2 Elemental and proximate analysis of waste tires

Elemental analysis		**Proximate analysis**	
Component	**%wt**	**Component**	**%wt**
Carbon	85.19	Rubber+organic components	54.4
Hydrogen	5.39	Carbon black	30.9
Nitrogen	0.82	Ash	14.7
Oxigen	1.05		
Sulfur	0.79		
Other	6.76		
Density			525 kg/m^3

4.3 Characterization of char and activated carbon

4.3.1 Physical properties

Physical properties of obtained char and activated carbon such as the proximate analysis generally were characterized.

4.3.2 Porous properties

The BET surface area S_{BET}, mesopore volume V_{meso}, micropore volume V_{micro}, and pore size distribution, of each samples were determined from N_2 adsorption-desorption isotherms measured at 77 K using the adsorption apparatus. Pore size distribution and V_{meso} were evaluated by applying the Dollimore-Heal method to the desorption isotherm, whereas the t-plot method was used to estimate V_{micro}.

4.4 Liquid-Phase Adsorption-Desorption equilibrium

The prepared activated carbons were used as adsorbent in the liquid-phase adsorption-desorption experiments. Phenol and reactive dyes, Red 31, were used as adsorbates. 200-250 mg of activated carbons was contacted with the aqueous solutions of various initial concentration prepared. These mixtures were put in a shaking water bath which was kept at 30°C to maintain well-mixed conditions. After equilibrium was achieved, which normally took 10, 15 days for phenol and Red 31, respectively, the solutions were filtered and their residual concentrations were measured using the UV-visible spectrophotometer (UV-6405, Jenway, England). The amounts adsorbed on the activated carbons were calculated from the measured concentrations, and the adsorption isotherms were obtained. To determine the desorption isotherms, after filtration, the spent activated carbons were put in distilled water and left for the same times used in adsorption step. The desorption isotherms were obtained by calculating from the amounts adsorbed and finally measured concentrations.

4.5 Process design and economic analysis

The process design and economic analysis was carried out step by step as shown in figure 4.5.

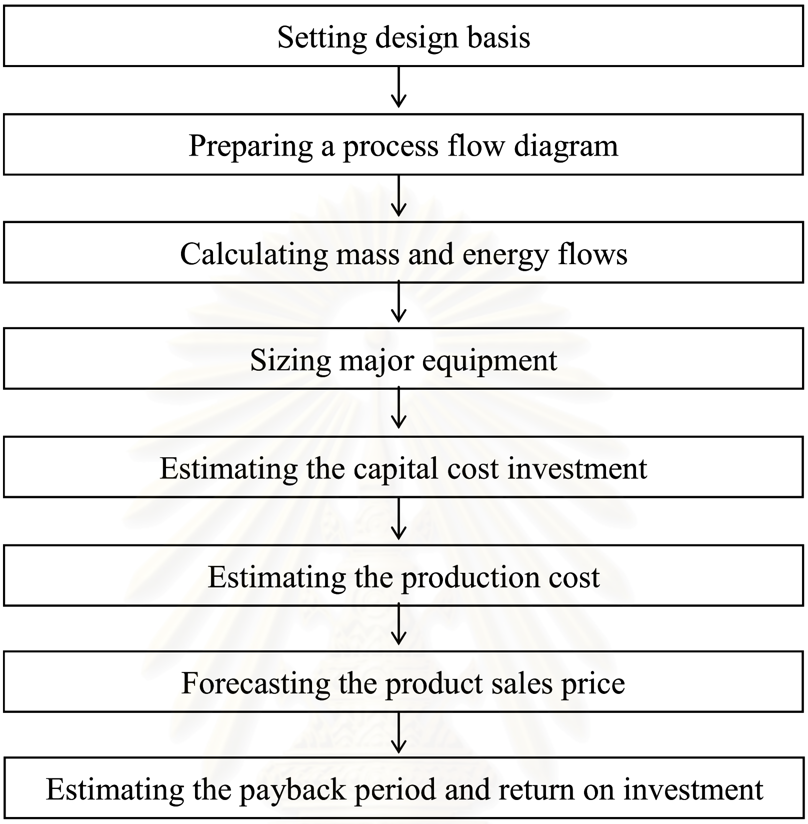


Figure 4.5 Diagram for estimating the process design and economic analysis

CHAPTER V

RESULTS AND DISCUSSION

5.1 Conventional preparation

Before investigating alternative for preparing mesoporous activated carbon, a conventional preparation procedure was conducted to ensure that the system employed in this work is applicable. Moreover, some parameters were also taken into account for confirming their effects on the characteristics of the obtained product.

5.1.1 Properties of prepared char by conventional method

As shown in Table 5.1.1.1, char yields obtained through the carbonization at 500-900^{o}C were around 40 wt%, and the prepared chars had ash content about 11%. It was observed that the volatile matter (VM) content in the char carbonized at 500-600^{o}C was higher than the char carbonized at a temperature above 600^{o}C because the tire rubber started to decompose at 450^{o}C and this phase was essentially completed at 500-600^{o}C [5]. So, at a carbonization temperature below 600^{o}C the volatile matter content was quiet high. In contrast, the fixed carbon content was quite low. Moreover it can be noticed that varying the temperature in the range of 750-900^{o}C and increasing the holding time had no significant effect on the physical properties of the prepared chars.

Table 5.1.1.1 Physical properties of chars prepared by conventional method

Temp. (^{o}C)	Holding time (min)	% Burn-off	%M	Dry basis		
				%Ash	%VM	%FC
500	30	53	1.9	11.0	20.5	68.5
	60	58	1.2	11.7	18.0	70.3
600	30	58	1.9	11.8	14.3	73.8
	60	60	1.1	10.4	10.0	79.6
750	30	58	0.8	11.0	7.8	81.2
	60	61	0.7	11.6	7.9	80.6
850	30	59	0.8	11.8	6.0	82.2
	60	59	0.7	12.0	6.2	81.8
900	30	59	0.8	11.3	7.2	81.5
	60	60	0.1	10.1	8.3	81.7

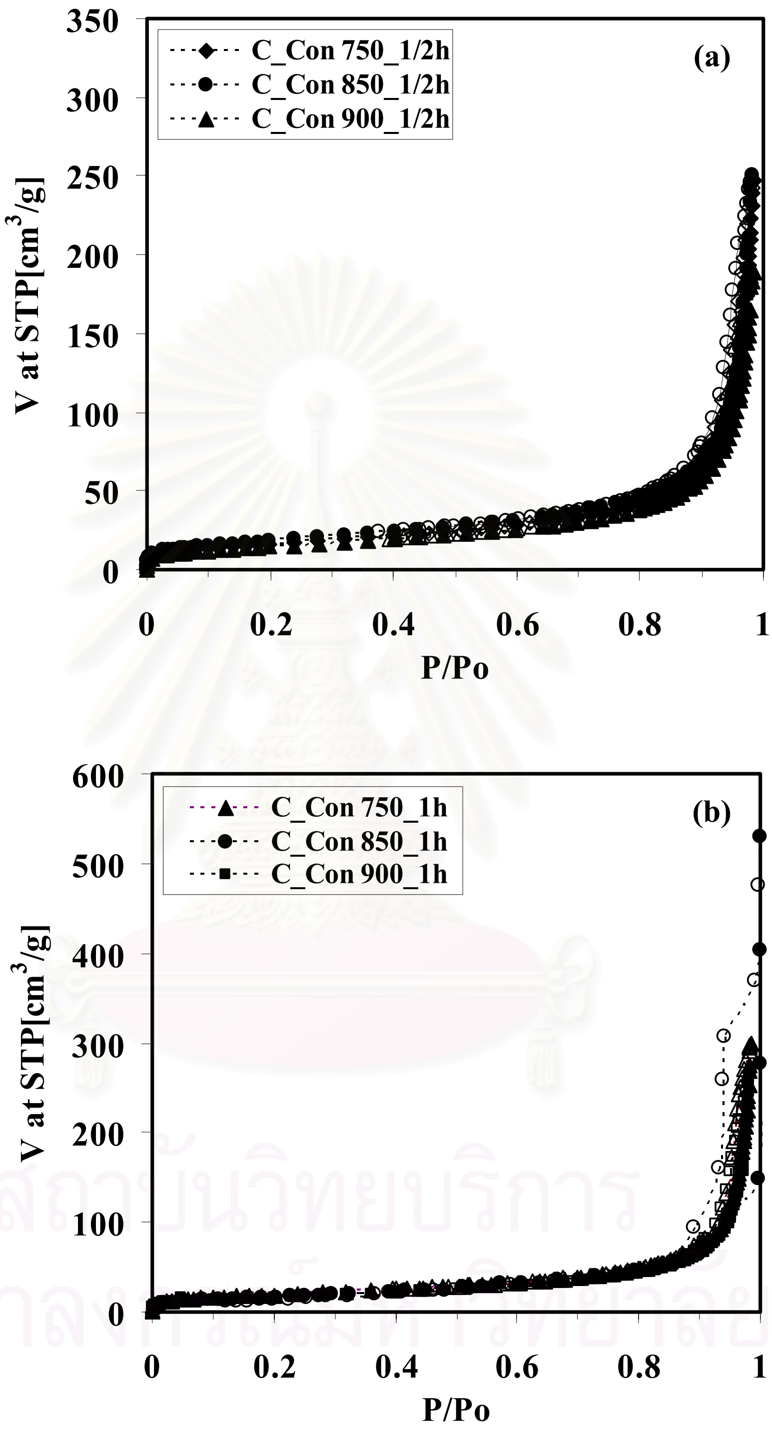


Figure 5.1.1.1 N_2 adsorption-desorption isotherms on chars from waste tires carbonized in N_2 atmosphere at 750, 850 and 900°C for (a) 30 min (b) 60 min; closed symbols: adsorption, open symbols: desorption

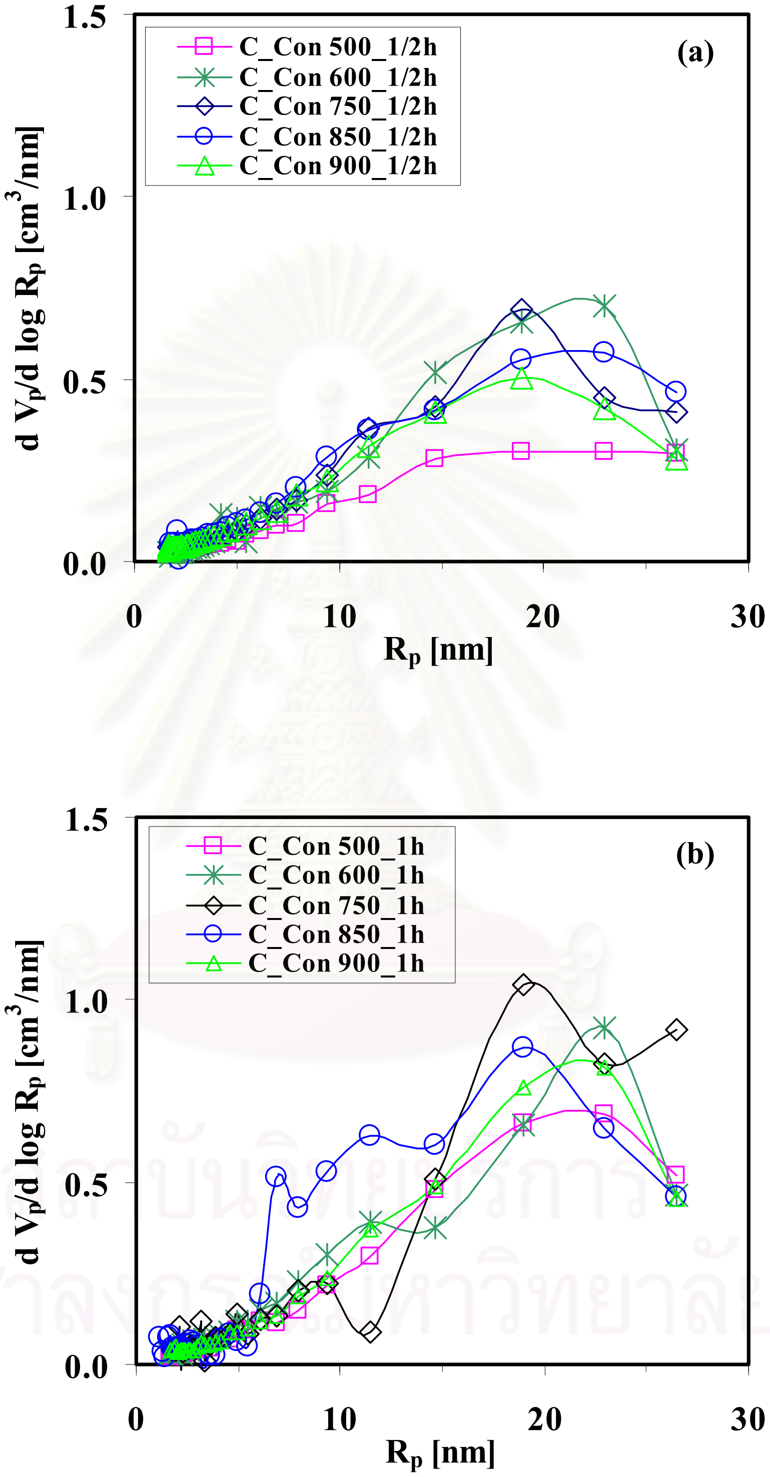


Figure 5.1.1.2 Pore size distribution of char from waste tires carbonized in N_2 atmosphere at 500-900^{o}C for (a) 30 min (b) 60 min

Figure 5.1.1.1 shows the N_2 adsorption-desorption isotherms of the chars obtained at different carbonization temperature. Here q and P/P^o are the amount of N_2 adsorbed and relative pressure, respectively. Obviously, a slight hysteresis was noticed in the isotherms, suggesting the existence of mesoporous structure in the obtained chars. The pore size distributions of the obtained chars were shown in Figure 5.1.1.2 indicating that the chars obtained from waste tires carbonized by the conventional contained method mainly mesopores of which nominal radius are quite large size.

Table 5.1.1.2 Porous properties of chars prepared by conventional method

Temp. (°C)	**Holding time (min)**	**%Burn-off**	**BET (m^2/g)**	**V_{micro} (cm^3/g)**	**V_{meso} (cm^3/g)**	**V_{total} (cm^3/g)**
500	30	53	38	0.03	0.15	0.18
	60	58	51	0.06	0.27	0.32
600	30	58	53	0.07	0.27	0.34
	60	60	63	0.06	0.61	0.67
750	30	58	59	0.09	0.26	0.35
	60	61	68	0.08	0.62	0.70
850	30	59	66	0.08	0.27	0.35
	60	59	62	0.03	0.41	0.43
900	30	59	53	0.06	0.24	0.29
	60	60	60	0.06	0.30	0.36

The porous properties determined from the isotherms in Figure 5.1.1.1 are also summarized in Table 5.1.1.2. The existence of mesoporous structure in these chars can be confirmed from their V_{meso} values. The small V_{micro} values in the obtained chars were detected by applying the t-plot method to the N_2 adsorption isotherms. As shown in figure 5.1.1.3, the S_{BET} values of the obtained chars slightly increased with the increase in the carbonization temperature and the holding time. However, the S_{BET} reached its peak at 850°C and 750°C for 30 and 60 minutes of holding time, respectively. The carbonization temperature is associated with amounts of energy needed to supply to the macromolecule of raw material in order to split of the weaker chemical bonds and to enable migration of the volatile products to the grain environment [2]. At high temperature, it can start burning off walls between the adjacent pore and turning more small pore into large pore leading to decrease in BET surface area. The peak of S_{BET} of chars carbonized for 60 minutes occurred at higher temperature than that of char carbonized for 30 minutes.

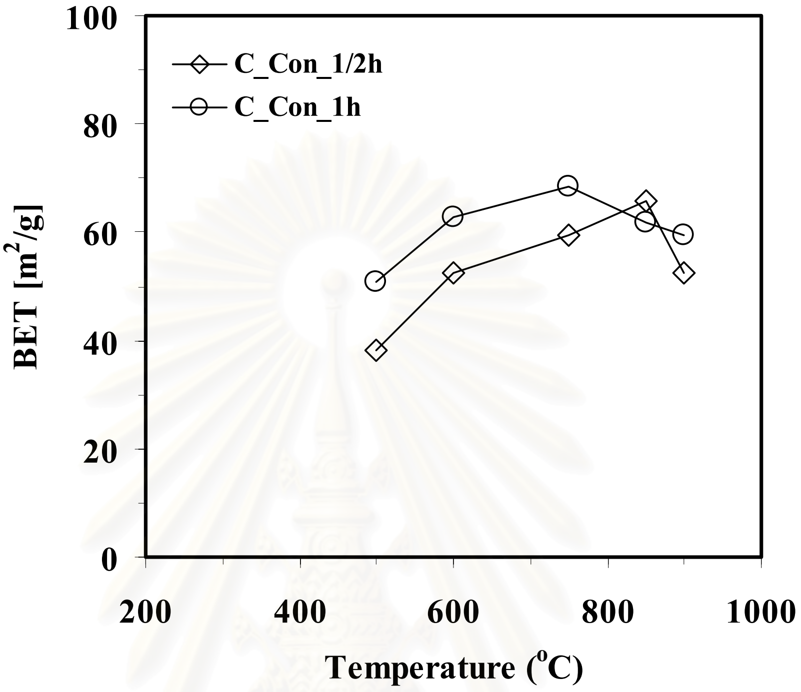


Figure 5.1.1.3 Effect of temperature on BET surface area at different time

Carbonization is one of the most important steps in the production process of activated carbon because the initial porous structure is formed and activation develops this structure further. From the above results, the carbonization condition suitable for producing desirable char was carbonization temperature of 850°C and 30 minutes of holding time. With these conditions the obtained char contained low content of volatile matter, high content of elemental carbon and sufficient specific surface area. Moreover it should be noted that sufficiently short resident time is one of the most important parameters required for the industrial production process.

5.1.2 Properties of prepared activated carbon by conventional method

The char carbonized at 850°C for 30 minutes was first activated solely with steam at 850 and 900°C for 2-3 hours. As expected in Table 5.1.2.1, % burn-off during activation increased with the increase in activation temperature and activation time. Obviously, the increasing activation temperature and holding time had no effect on the volatile matter content. It was known that steam, activating agent, oxidized with carbon element in char. With an increase of the oxidation temperature, the rate of the chemical reaction increased exponentially. At high temperatures the oxidation reaction rate became so high that significant losses of the carbon material occurred, thereby resulting in quite high ash content. Moreover, table 5.1.2.1 indicates that iodine adsorption increased with the increase of the activation temperature and holding time because of the formation of small porous structure. Surprisingly a longer holding time led to a reduction in the adsorption of methylene blue.

Table 5.1.2.1 Physical properties of activated carbon prepared by conventional method

Temp. (°C)	**Holding time (hr)**	**% Burn-off**	**%M**	**Dry basis**			**IA (mg/g)**	**MB (mg/g)**
				%Ash	**%VM**	**%FC**		
850	2	36	2.5	15.2	11.6	73.2	509	513
	3	48	2.9	17.6	11.5	70.9	561	360
900	2	60	1.9	18.0	10.3	71.7	710	549
	3	83	3.0	33.9	12.5	53.6	561	260

Figure 5.1.2.1 shows the N_2 adsorption-desorption isotherms on the activated carbons obtained through the steam activation at various temperatures. Considering the shape of the isotherm and the N_2 adsorption capacity, the development of micropores and mesopores during activation could clearly be observed.

From these isotherms, the pore size distributions of the obtained activated carbons are shown in Figures 5.1.2.2. It was found that both mesoporosity and microporosity could be improved by steam activation. It was believed that the pore development mechanism consists of micropore creation followed by pore widening into mesopore [9,10].

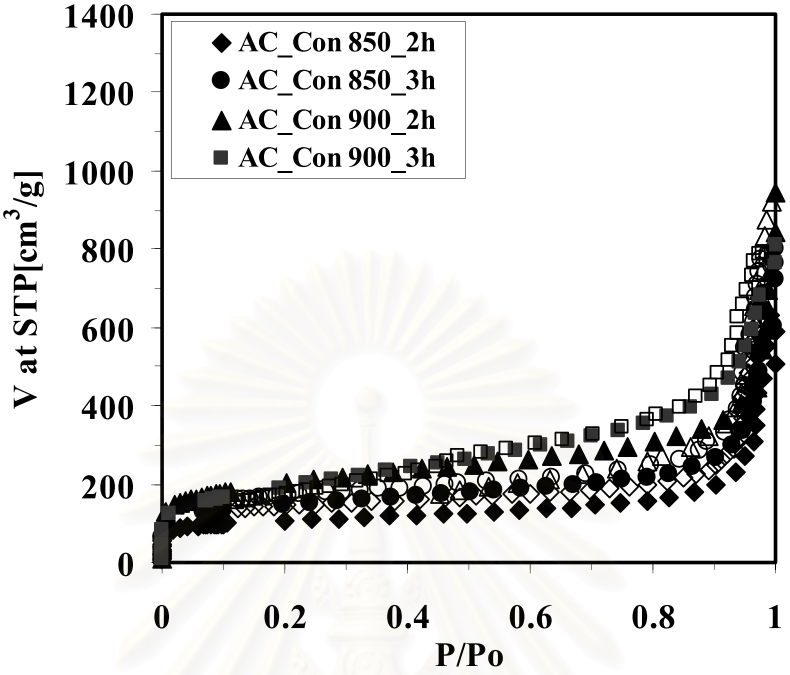


Figure 5.1.2.1 N_2 adsorption-desorption isotherms on activated carbon prepared by conventional method; closed symbols: adsorption, open symbols: desorption

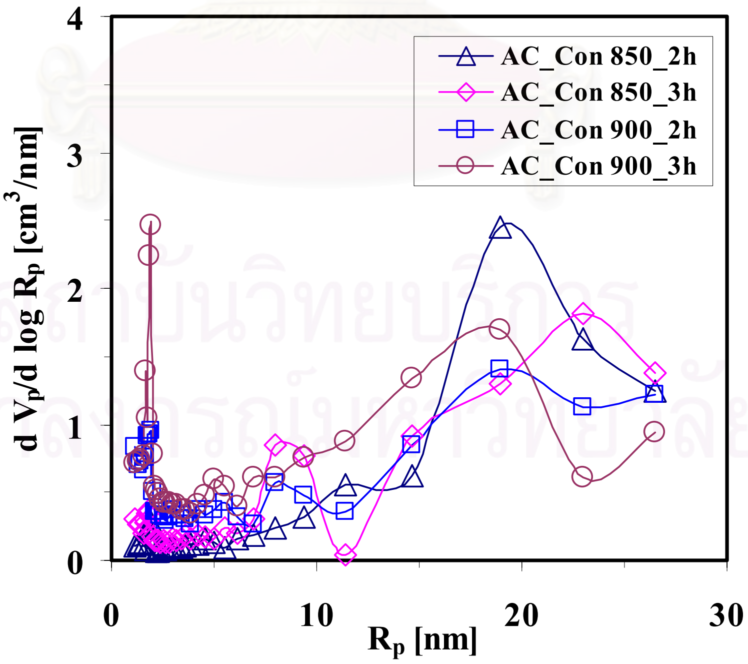


Figure 5.1.2.2 Pore size distribution of activated carbon prepared by conventional method

Table 5.1.2.2 Porous properties of activated carbon prepared by conventional method

Temp. (^{o}C)	**Holding time(h)**	**% Burn-off**	**B.E.T. (m^2/g)**	**V_{micro} (cm^3/g)**	**V_{meso} (cm^3/g)**	**V_{total} (cm^3/g)**
850	2	36	389	0.20	0.64	0.84
	3	48	543	0.21	0.66	0.87
900	2	60	691	0.26	0.82	1.08
	3	83	668	0.23	1.09	1.32

Table 5.1.2.2 also provides the porous properties of the obtained activated carbons calculated from above isotherms. The prepared activated carbons had the V_{meso} and V_{micro} values up to 1.09 and 0.23 cm^3/g, respectively. It was found that the prepared activated carbons with higher V_{meso} value can be obtained at higher % burn-off, while the V_{micro} and S_{BET} values increased with burn-off up to 60 % and then tend to decrease. A similar phenomenon reported in the literature, pore developed on highly activated sample, were mainly mesoporous and macroporous since steam activation both widened existing pores and created new porosity [10]

Conclusion for section 5.1

- Carbonization temperature below 600^{o}C looks impractical.
- The varying temperature in the range of 750-900^{o}C and the increasing holding time had no significant effect on the physical properties of prepared chars.
- The carbonization condition suitable for producing desirable char was carbonization temperature of 850^{o}C and holding time of 30 minutes.
- Both mesoporosity and microporosity could be improved by steam activation.

5.2 Practical preparation

5.2.1 Properties of prepared activated carbon by practical method

Similar to the combustion process, there are three parameters playing important roles in carbonization in air. These parameters, amount of oxygen in the reaction, raw material (fuel) and energy supply, could affect the reaction rate and yield. Table 5.2.1.1 shows the relation ship between air flow rate and %burn-off of chars prepared by carbonization in air. It is assumable that at high temperature (850°C) air flow rate has no significant effect on the carbonization yield because at high temperature the reaction rate is controlled by diffusion of oxygen into raw material. From this preliminary test, the air flow rate is kept constant at 30 ml/min for carbonization step.

Table 5.2.1.1 Effect of air flow rate on %burn-off of char carbonized in air at 850°C for 30 minutes

Air flow rate (ml/min)	%Burn-off
20	54
30	55
50	55
80	56

Table 5.2.1.2 Physical properties of char prepared by practical method

Temp. (°C)	Holding time (min)	% Burn-off	%M	Dry basis		
				%Ash	%VM	%FC
750	30	57	1.4	11.0	7.7	81.3
	60	56	1.5	12.0	7.3	80.7
850	30	55	1.0	10.6	7.0	82.4
	60	54	0.5	27.5	3.5	69.0
900	30	55	0.7	10.5	5.9	83.7
	60	55	0.3	31.4	6.3	62.3

Table 5.2.1.1 shows the physical properties of char carbonized at various temperatures and holding time. It was found that carbonization yields were around 45 wt%. At the carbonization temperature in range of 750-900°C, increasing the holding time had no significant effect on char yield. Interestingly, by increase carbonization

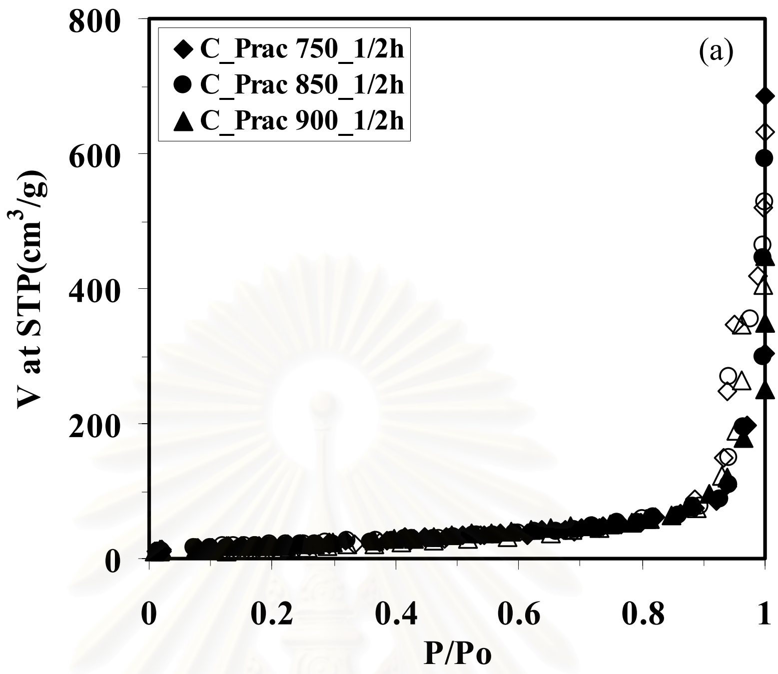
temperature and holding time, % burn-offs had no noticeable changes while ash content had dramatically increase. It suggests that some metallic components in ash occurred. From the above result, with occurrence of quite heavy ash, %burn-off which normally related to reaction rate had no significant changes. It was found that at carbonization temperature in the range of 850-900°C chars prepared by practical method had higher ash content than that char prepared by conventional method.

Figure 5.2.1.1 shows the N_2 adsorption-desorption isotherms of chars obtained at different carbonization temperature. Similar to conventional method, a slight hysteresis was observed in these isotherms which suggest the existence of mesoporous structure in the chars. The pore size distributions of the obtained chars were shown in Figure 5.2.1.2 which indicate that the chars prepared by practical method mainly mesopores whose pore radius are mainly larger than 5 nm.

The porous properties calculated by using the isotherms in Figure 5.1.1 are also summarized in Table 5.2.1.3. The S_{BET} values of the obtained chars were around 52-77 m^2/g and exhibited a decreasing trend with the increase in carbonization temperature and holding time. The existence of mesoporous structure in the chars can be confirmed from their V_{meso} values. Moreover, the small V_{micro} values in chars could be slight detected by applying the t-plot method to the N_2 adsorption isotherms.

Table 5.2.1.3 Porous properties of char prepared by practical method

Temp. (°C)	Holding time (min)	%Burn-off	BET. (m^2/g)	V_{micro} (cm^3/g)	V_{meso} (cm^3/g)	V_{total} (cm^3/g)
750	30	57	77	0.07	0.36	0.43
	60	56	64	0.03	0.43	0.46
850	30	55	69	0.06	0.32	0.39
	60	54	60	0.02	0.31	0.33
900	30	55	73	0.05	0.41	0.46
	60	55	52	0.03	0.36	0.38



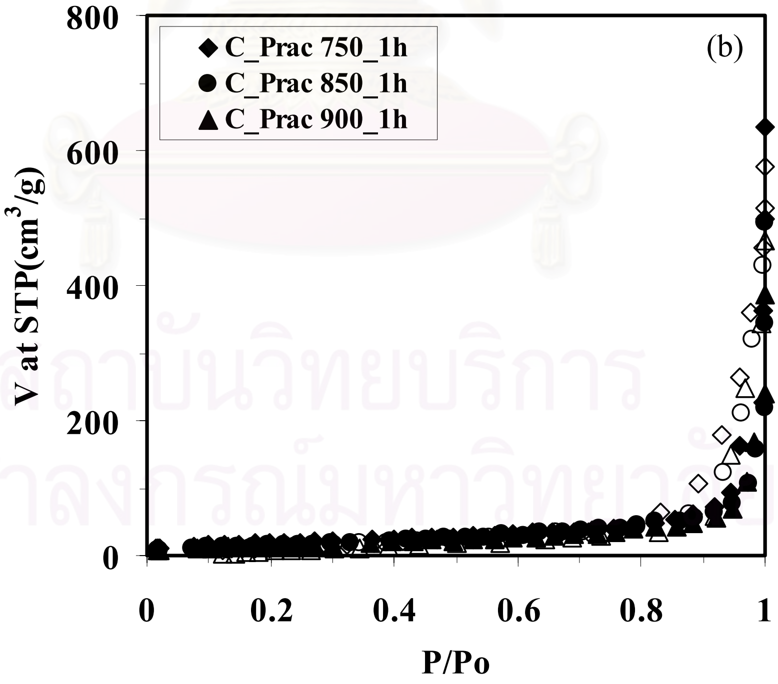


Figure 5.2.1.1 N_2 adsorption-desorption isotherms on chars from waste tires carbonized in air at 750, 850 and 900°C for (a) 30 min (b) 60 min; closed symbols: adsorption, open symbols: desorption

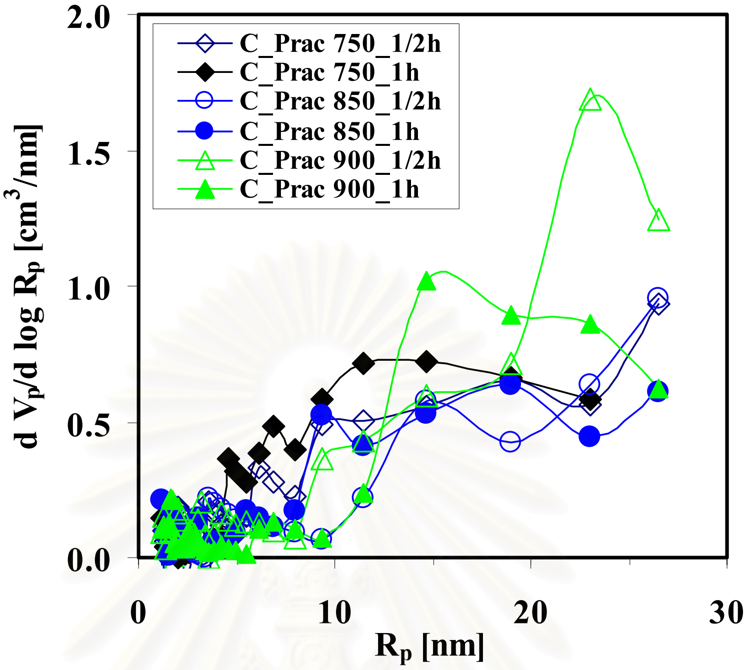


Figure 5.2.1.2 Pore size distribution of char from waste tires carbonized in air atmosphere at 500-900°C

From the above result, practical carbonization condition which is suitable for producing desirable char was carbonization temperature of 750°C and holding time of 30 minutes.

5.2.2 Properties of prepared activated carbon by practical method

Table 5.2.2.1 Physical properties of activated carbon prepared by practical method

Temp. (°C)	Holding time (hr)	% Burn-off	%M	Dry basis			IA (mg/g)	MB (mg/g)
				%Ash	%VM	%FC		
850	3	47	2.1	14.4	5.3	80.3	260	186
	4	62	0.9	24.5	7.5	68.0	436	221
900	3	64	1.1	20.4	7.8	71.9	478	258
	4	85	0.6	37.4	7.3	55.8	498	271

Char carbonized at 750°C for 30 minutes was activated with the gaseous mixture of steam, CO_2 and O_2 at 850 and 900°C for 3-4 hours. As shown in Table 5.2.2.1, % burn-off during activation increased with the increase in activation temperature and activation time. From the preliminary adsorption standard test of iodine and methylene blue, it is expectable that the increase in activation temperature and holding time will led to an increase in micropore and mesopore structure.

From the shape of isotherm in figure 5.2.2.1, activated carbons prepared by practical method exhibited mesoporous structure. As expected, the N_2 adsorption capacity of the obtained activated carbon increased with an increase in activation temperature and holding time.

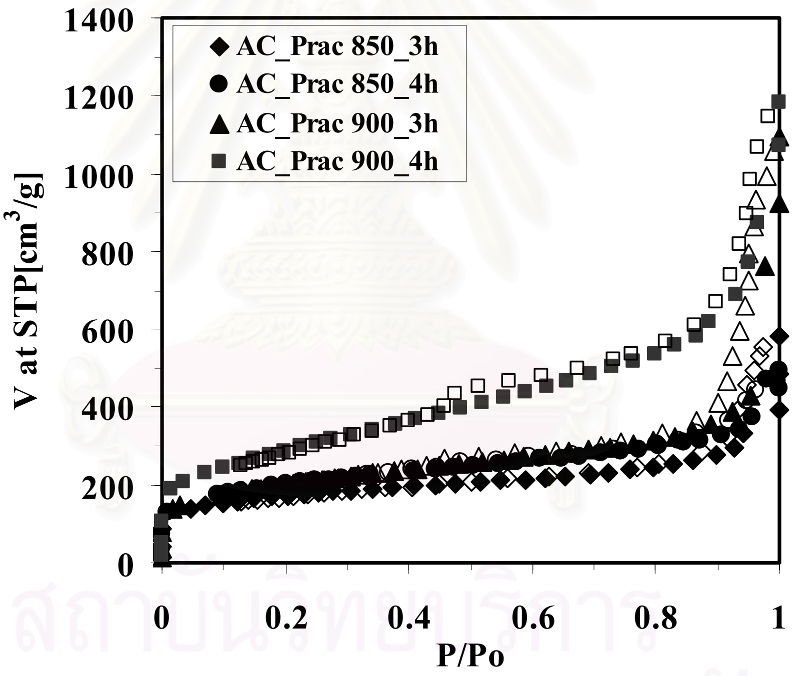


Figure 5.2.2.1 N_2 adsorption-desorption isotherms on activated carbon prepared by practical method; closed symbols: adsorption, open symbols: desorption

By applying the Dollimore-Heal method, the pore size distribution of obtained activated carbons was shown in the figure 5.2.2.2. It was clear that the development of micropores and mesoproes took place during activation step. A peak in pore size distribution at the radius of around 2 nm was observed.

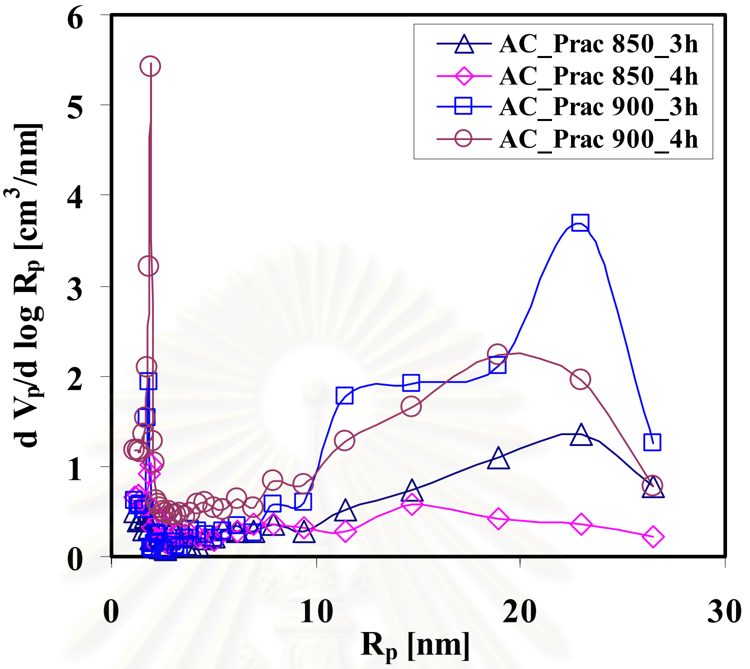


Figure 5.2.2.2 Pore size distribution of activated carbon prepared by practical method

The porous properties of these activated carbons were given in Table 5.2.2.2. The S_{BET} value of activated carbon increased with the increasing activation temperature. It was assumed that the increase in S_{BET} value of the obtained activated carbon with the increasing activation temperature was due to the existence of the small mesopores (pore radius around 2 nm) and micropores. It was clear that both preparation methods, conventional and practical method, could produce the activated carbon which had the same trend of the properties.

Table 5.2.2.2 Porous properties of activated carbon prepared by practical method

Temp. (°C)	Holding time(h)	% Burn-off	BET. (m^2/g)	V_{micro} (cm^3/g)	V_{meso} (cm^3/g)	V_{total} (cm^3/g)
850	3	47	611	0.26	0.61	0.87
	4	62	690	0.28	0.52	0.80
900	3	64	702	0.28	1.24	1.52
	4	85	1008	0.33	1.57	1.90

Conclusion for section 5.2

- At high temperature air flow rate had no significant effect on the carbonization yield because the reaction rate had been control by diffusion of oxygen into raw material.
- By increasing carbonization temperature and holding time, % burn-offs had no noticeable changes while ash content dramatically increased of existence of because some metallic components in ash.
- The practical carbonization condition suitable to produce the desirable char was 750^{o}C of carbonization temperature and 30 minutes of holding time.
- Both preparation methods, conventional and practical method, could produce the activated carbon which had the same trend of the properties.

5.3 Liquid-phase adsorption

5.3.1 Properties of absorbents

For comparison, the prepared conditions and properties of the present activated carbons, a commercial one (Calgon Co. Ltd., USA) and those obtained from waste tire with HCl treatment prior to steam activation was summarized in table 5.3.1.1. It was observed that activated carbon prepared by the practical method obtained from this study had the highest mesoporosity and had exceptionally high microporosity.

Considering practical activated carbon and conventional activated carbon, it was found that activated carbon prepared by practical method had higher mesopore volume than that obtained from the conventional method. It was suggested that the presence of CO_2 in the activation step produced larger pore size than that activated by steam because CO_2 have larger molecular size than that steam [17]. However, activated carbon prepared by practical method had higher ash content than that one from the conventional method because of the combustion in the carbonization step and the longer holding time in the activation step. Moreover, from the standard adsorption test of iodine and methylene blue, it was found that activated carbon obtained from the conventional method had the iodine and methylene blue number higher than that of activated carbon from the pracitcal method. It implies that the conventional activated carbon is more suitable for adsorption of small and large molecules than practical activated carbon.

By comparing non-acid treated activated carbon (practical and conventional activated carbon) and acid treated activated carbon, it found that acid treated activated carbon had higher S_{BET} surface area and micropore volume than that of non-acid treated activated carbon. It can clearly observe that V_{meso}, V_{micro} and S_{BET} are improve by HCl treatment prior to steam activation.

By comparison of granular activated carbon with powder activated carbon, the size of raw materials has strong affect the porous properties of the obtained activated carbon.

Table 5.3.1.1 Comparison of prepared condition and properties of activated carbons obtained in this work, a commercial activated carbon and reported HCl treated activated carbon in the reference [9, 18]

	AC_Prac 900_3h	AC_Con 900_2h	AC_Cal	AC_HCl_granular	AC_HCl_powder
Raw material	waste tire	waste tire	coal	waste tire	waste tire
Size of raw material	3 mm	3 mm	NA	3 mm	<0.567 μm
Carbonization	750(5 °C/min) for30 min with air	850(5 °C/min) for 30 min in N_2 atmosphere	NA	500(5 °C/min) for 1.5 hr in N_2 atmosphere	500(5 °C/min) for 1 hr in N_2 atmosphere
Activation	900(20 °C/min) for 3 hr in N_2 atmosphere	900(20 °C/min) for 2 hr in N_2 atmosphere	NA	850(20 °C/min) for 4.5 hr in N_2 atmosphere	850(20 °C/min) for 4 hr in N_2 atmosphere
Activating agent	steam, CO_2, O_2	steam	NA	steam	steam
Treatment	None	None	NA	acid treated	acid treated
% burn off	64	60	NA	65	65
% Moisure	1.1	1.9	7.0	NA	2.2
% Ash (dry basis)	20.4	18.0	9.1	NA	18.7
%Volatile matter (dry basis)	7.8	10.3	7.7	NA	4.7
% Fixed carbon (dry basis)	71.9	71.7	83.2	NA	76.6
IA (mg/g AC)	478	710	746	NA	659
MB (mg/g AC)	258	549	221	NA	356
Surface area BET (m^2/g)	702	691	988	701	985
V_{micro} (cm^3/g)	0.28	0.26	0.31	0.28	0.37
V_{meso} (cm^3/g)	1.24	0.82	0.27	0.46	1.07

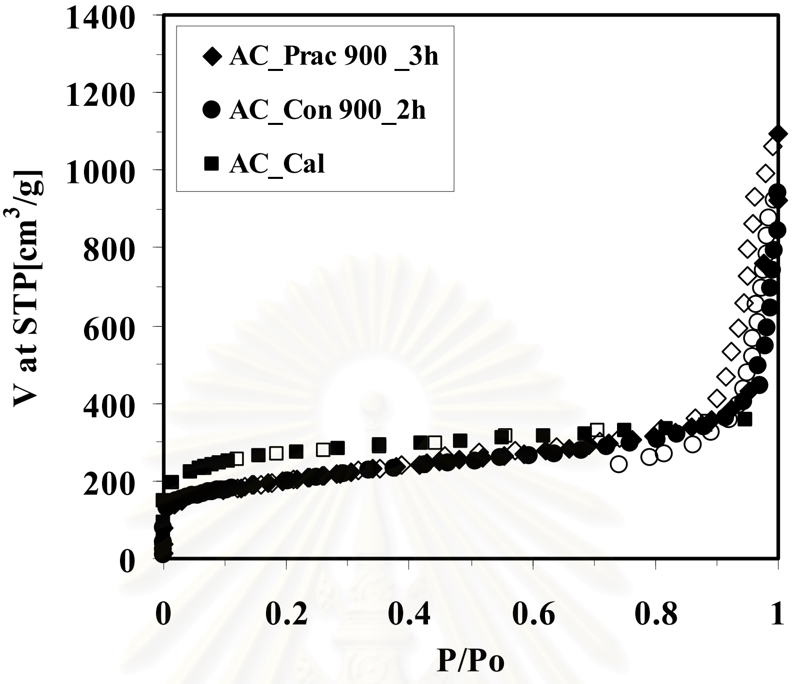


Figure 5.3.1.1 N_2 adsorption-desorption isotherms on activated carbon used as absorbent in liquid-phase adsorption; closed symbols: adsorption, open symbols: desorption

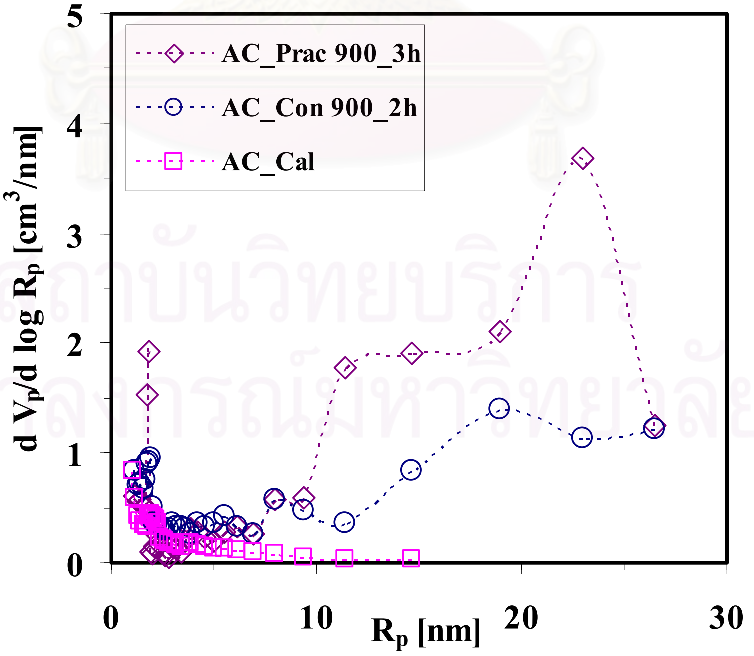


Figure 5.3.1.2 Pore size distribution of activated carbons as absorbent in liquid-phase adsorption

It was found that powder activated carbon had higher S_{BET}, V_{micro}, and V_{meso} value than that granular activated carbon. It was known that small particle allowed better diffusion of steam molecules in to the structure, leading to a more homogeneous activation of the carbonized precursor [10].

Figures 5.3.1.1 and 5.3.1.2 present the N_2 adsorption/desorption isotherms and the pore size distributions of activated carbon used as absorbent in this work, respectively. It was found that commercial activated carbon had only small mesopores (around 2 nm) which different from the others.

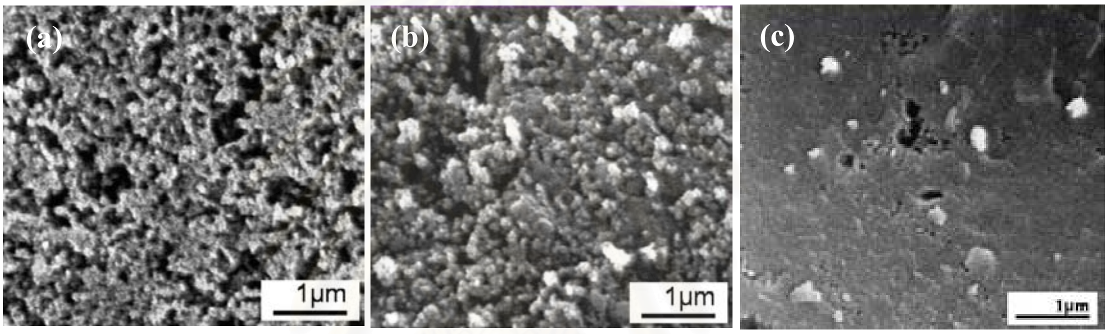


Figure 5.3.1.3 SEM image of the (a) conventional activated carbon, (b) practical activated carbon and (c) commercial activated carbon

The exterior surfaces of these adsorbents are characterized with scanning electron microscopy (SEM) as shown in figure 5.3.1.3. The surface of both activated carbons from waste tire seems to result from the loose agglomeration of small particles. Both, macropores and mesopores can be observed in the figure 5.3.1.3. In contrast, the surface of commercial activated carbon appears quite smooth with fewer opening of macropores and mesopores. However, the surface of conventional activated carbon appears looser than that of practical activated carbon.

5.3.2 Adsorption/desorption equilibrium

The adsorption isotherms of phenol and Red 31 on those activated carbons are shown in Figures 5.3.3 and 5.3.4, respectively. The q and C_e are the amount of adsorbates adsorbed and equilibrium concentration, respectively. From figure 5.3.3, it was found that the obtained activated carbons show a slightly lower phenol adsorption capacity than the commercial one due to the lower V_{mircor} and S_{BET} value.

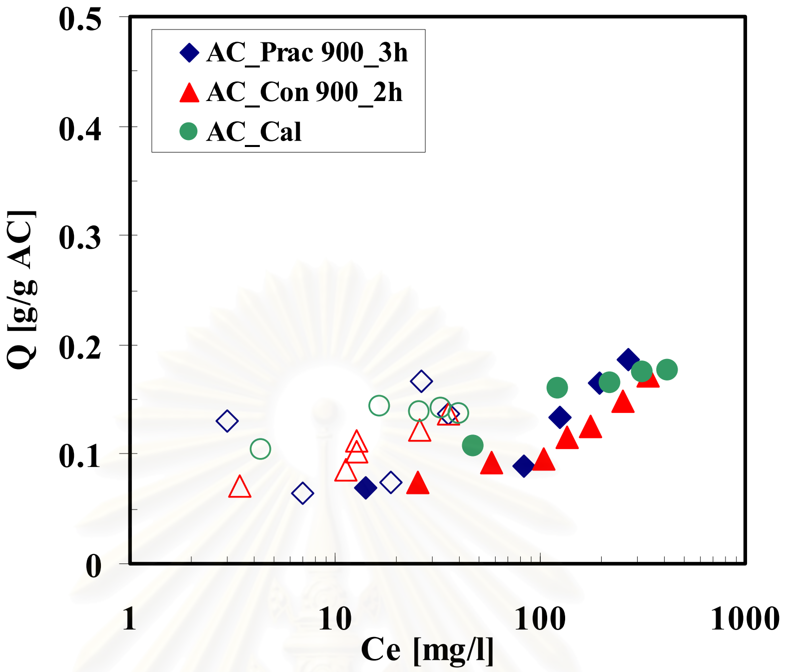


Figure 5.3.2.1 Phenol adsorption equilibrium on activated carbons; closed symbols: adsorption, open symbols: desorption

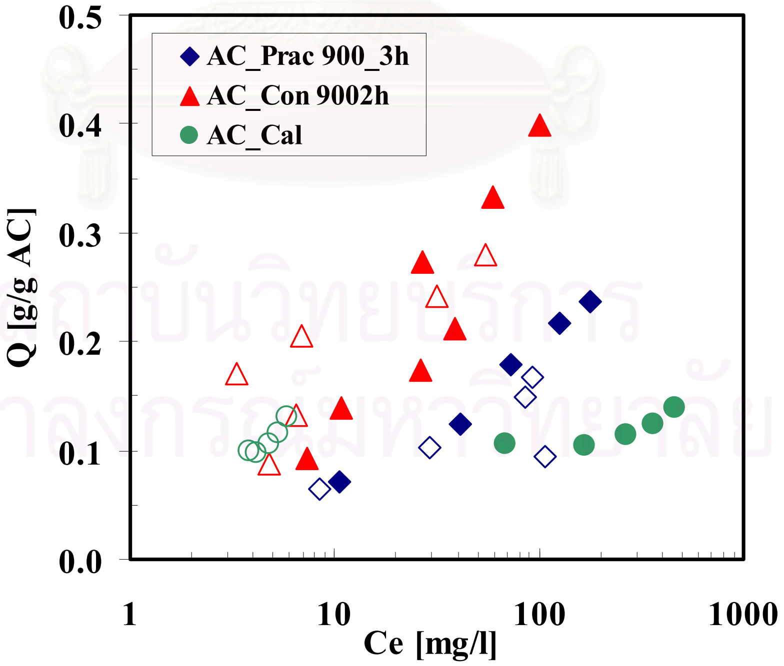


Figure 5.3.2.2 Red31 adsorption equilibrium on activated carbons; closed symbols: adsorption, open symbols: desorption

From red31 adsorption equilibrium as shown in figure 5.3.2.2, interestingly it was obviously noticed that the prepared activated carbons show higher dye adsorption capacity than the commercial activated carbon.

The obtained practical and conventional activated carbons had 70% and 160% higher capacity for red31 adsorption than the commercial one. The usual relation between the pore volumes or specific surface area and the adsorption capacities is not observed because the chemical nature of the surface simultaneously influences the adsorption capacities. Although V_{meso} value of the practical activated carbon is higher than that of the conventional one, the latter shows a double higher red31 adsorption capacity than the former. Refer to the review paper [15], it is reported that the surface nature of activated carbon from waste tires activated with steam is hydrophobic as commercial activated carbon (Calgon Co. Ltd., USA). So, the obtained activated carbons from waste tires have the higher red31 adsorption capacity than commercial one because of the influence of pore structure (V_{meso} of activated carbons from waste tires > V_{meso} of commercial activated carbon). Comparing the practical with convention activated carbon, the appearance of CO_2 and O_2 in the practical method may affect the chemical nature of the surface making it less hydrophobic. In this case it may suggest that the chemical nature of surface has a much stronger effect than that of the pore structure.

As for the desorption characteristics, as shown in figures 5.3.2.1 and 5.3.2.1, the hysteresis of adsorption and desorption of both phenol and red 31 was observed except the adsorption and desorption of red31 on the activated carbon prepared by practical method. It had been reported that the hysteresis of adsorption and desorption characteristics, indicated that irreversible adsorption occurred. On the other hand, non-hysteresis suggested the occurrence of reversible adsorption [4, 19] . Normally, the desorption process greatly depends on the substituted groups of the adsorbed aromatic compounds. For aromatic compounds substituted by electron-donating groups such as the hydroxyl group (-OH) in phenol and red31, hysteresis of adsorption and desorption was observed. For hysteresis of adsorption and desorption of red31 on the practical activated carbon was not observed, it is reasonable to assert that the appearance of CO_2 and O_2 in the practical activation may affect the chemical nature of the surface, thereby influencing the desorption characteristics [4]. It is well known that if irreversible adsorption occurs, regeneration of the spent adsorbent is quite difficult. Based on the above result, the practical preparation may produce surface oxides on the activated carbon which improved the desorption characteristics of the red31 [4].

Conclusion for section 5.3

- Activated carbon prepared by practical method obtained from this study had the highest mesoporosity and had exceptionally high microporosity.
- The obtained activated carbons show a slightly lower phenol adsorption capacity than the commercial one due to the lower V_{mircor} and S_{BET} value.
- The obtained practical and conventional activated carbons had 70% and 160% higher capacity for red31 adsorption than the commercial one. It suggests that the different chemical nature of these two carbons influences their liquid-phase adsorption characteristics.
- Highly mesoporous activated carbons prepared by the practical and conventional method have large adsorption capacities for red31. It is confirmed that these activated carbons are good adsorbents for bulky molecules in aqueous solutions.

5.4 Continuous process design

5.4.1 Design basis of the activated carbon production from waste tires

Production rate	100 kg AC./hr (2.4 tons A.C./day).
Activated carbon properties	- BET surface area > 700 m^2/g. - Mesopore volume > 0.50 cm^3/g.
Raw material	Waste tires, which are already crushed with pieces of metal/wire and cords already removed.
Ultimate yield of AC.	Activated carbon 1 kg per 6.8 kg waste tires (not including rubber used as energy source of the process).
Energy supply (target)	80% of the total thermal energy required in carbonization step is produced from combustion of waste tires.
Carbonization temperature	750°C
Activation temperature	900°C
Measures to eliminate smoke and foul smell	Reburning (after burning) in a high temperature (900°C for 1 sec) furnace.
The design approach	Continuous process
Raw material feeding process	- particle size of 3 mm in diameter. - feeding rate 840 kg waste tires/hr.
Discharge process of activated carbon	Continuous discharge after reduction of A.C. temperature by passing through the moving-bed heat exchanger
Exhaust gas recycle process	Combustion gas rich in N_2, CO_2 and O_2 is recirculated to the activation step mixing with the steam to use as activating agent and medium gas.
Waste heat boiler	Saturated steam at 3 bars is produced (with pressure reduced to 1 bar g) for use in the activation step.

5.4.2 Process flow diagram and process description

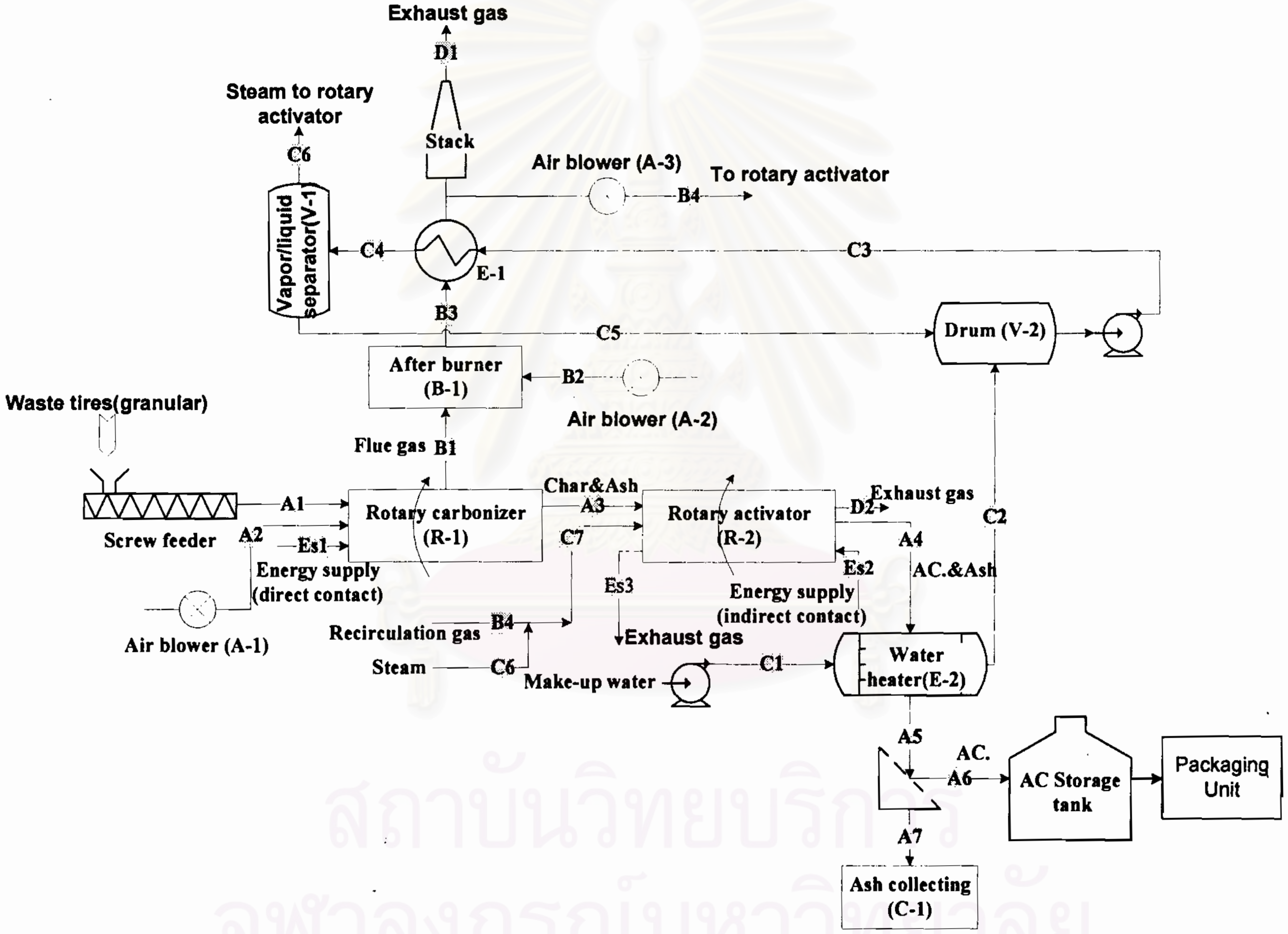


Figure 5.4.2.1 Process flow diagram of the production of the activated carbon from waste tires

Process description

As shown in figure 5.4.2.1, process flow diagram of the production of the activated carbon from waste tires was presented. The production of the activated carbon was a continuous process and can be simply described as written below.

Raw material

Raw material was the waste tires, which was already crushed with pieces of metal/wire and cords already removed.

Process

The waste tire in the size of 3 mm was fed as a raw material of the process at the rate of 850 kg/hr into the feeder to produce high porous activated carbon 100 kg/hr (2.4 tons/day). The feeder was designed to be a screw-type to eliminate the unnecessary air input with raw material thus leads to more accurate prediction of the reaction.

The reactor was the key unit of this production process where the waste tire was converted into valuable activated carbon. The reactor (Carbonizer and Activator) was rotary kiln, in which the raw material or waste tire was conveyed through all the length continuously.

- Carbonizer

  The first reactor was the place where the carbonization process occurred at 750°C. The heat used in the carbonization was 70-80% supplied by combustion of some raw material (15% of raw material). Char is produced from this process with 303.22 kg/hr (42% yields). Flue gas from the carbonizer was sent to the after burner for treatment before releasing to the atmosphere and recycling to the activator as the carrier gas.

- Activator

  Char from carbonizer was flown through the second part where the activation process with gas mixture from the after burner and steam was carried on with 900^{0}C. Saturated steam and carrier gas were fed to the activator for the activation process. The reactions of steam, CO_2, and O_2 with carbon are endothermic and stoichiometric equations have the form:

$$C + H_2O \rightarrow H_2 + CO \qquad \Delta H = +130\ \text{KJ/mole}$$

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad \Delta H = -42\ \text{kJ/mol}$$

$$C + CO_2 \rightarrow 2CO \qquad \Delta H = +159\ \text{kJ/mol}$$

$$C + O_2 \rightarrow CO_2 \qquad \Delta H = -387\ \text{kJ/mol}$$

The heat used in the activation was 100% supplied by the external heat from the combustion of fuel gas with indirect contact. It was obtained 65 % burn off from char. Flue gas from the activator was sent to the cyclone before releasing to the atmosphere while the activated carbon was being passed to the cooling unit (to preheat water) to reduce its temperature to the suitable temperature for storage.

The after burner was added as an air treatment unit to get rid of the bad-odor gas. Flue gas from the reactor was predicted to be a mixture of N_2, O_2, H_2O, CO, H_2, SO_2, NH_3, CH_4, C_2H_4 and tar. The reaction occurred is the combustion reaction of some gas. Gas from the after burner was sent to the steam generator as a hot stream of the heat exchanger to produce steam fed back to the reactor in the activation step. The smokeless product gas had no foul smell and was released to the atmosphere without causing air pollution and some of this gas was circulated to the activator as medium gas mixed with steam.

Preheated water unit was used to remove excess heat from the activated carbon before direct contact with ambient air since the contact with the air when the activated carbon has a high temperature (900 ^{0}C) could lead to burn. The preheated water unit worked as a moving bed heat exchanger using water at room temperature as a heat exchanger fluid. A group of tubes was installed across the column. When operated, water flew through the tubes while the activated carbon was fed through the column. Hot water from this unit was fed to the steam generator. The temperature of the activated carbon reduced from 900^{o}C to around 300^{o}C.

After the cooling process, activated carbon was screened in the screening to remove ash and then was kept in a storage unit waiting for the customer order.

5.4.3 Overall mass and energy balance

Overall mass and energy balance of the plant are summarized in this section. Table 5.4.3.1 and 5.4.3.2 show summary of mass and energy balance of the process.

Table 5.4.3.1 Summary of mass balance for PFD in figure 5.4.2.1

	Unit	A1	A2	A3	A4	A5	A6	A7	B1	B2	B3	B4	C1	C2	C3	C4	C5	C6	C7	D1	D2	Es1	Es2	Es3
Temperature	°C	25	25	750	900	300	200	200	750	25	900	850	35	100	100	135	135	135	800	800	900	25	25	25
Pressure	bar	1	1	1	1	1	1	1	1	1	1	2	3	2.999	3	2.999	1.000	2.999	3	1	1	1.000	1.000	
Air	kg/h		3,281.75							5292.96													2,551.08	
Waste tire	kg/h	850.00																						
Char	kg/h			303.22																				
Activated carbor	kg/h				106.13	106.13	106.13																	
Ash	kg/h			20.40	41.86	41.86		41.86																
C_3H_8	kg/h																					51.73	103.53	
C_4H_{10}	kg/h																					29.22	58.49	
H_2O	kg/h								289.41		692.51	59.78	850	850	1107	1107	256	311.20	370.98	632.73	129.80			295.39
CO_2	kg/h								645.96		1820.98	157.20							157.20	1,663.78	157.20			488.07
CO	kg/h								9.10												403.41			
CH_4	kg/h								2.26															
C_2H_4	kg/h								0.49															
SO_2	kg/h								4.42		18.75	0.20							0.20	18.54	1.62			
NH_3	kg/h								2.40		2.40	0.03							0.03	2.37	0.21			
N_2	kg/h								2,482.82		6488.76	560.16							560.16	5,928.59	560.16			1,929.64
O_2	kg/h								92.24		158.65	13.70							13.70	144.95				
H_2	kg/h																				27.10			
Tar	kg/h								359.98															
total		**850.00**	**3281.75**	**323.62**	**147.99**	**147.99**	**106.13**	**41.86**	**3889.08**	**5292.96**	**9182.04**	**791.07**	**850.29**	**850.29**	**1106.60**	**1106.60**	**256.31**	**311.20**	**1102.27**	**8390.96**	**1279.50**	**80.95**	**2713.10**	**2713.10**

Table 5.4.3.2 Summary of energy balance

Unit		Heat exchange	kcal	T or ΔT (^{o}C)	Heat source or sink or utility requirment
R-1 Carbonizer	Input	Heat of combustion	- 1,214,286	750	Waste tire (utility)
	Output	Heat of carbonization	+ 718,112	725	
		Sensible heat in products	+ 752,950	725	
		Enthalpy of water vapor	+ 82,472	100	
		Heat required for carbonizer	+ *339,248*		*Fuel gas (LPG) (utility)*
R-2 Activator	Input	Heat content in material fed to activator	- 106,354	750	Char (source)
		Heat content in steam	- 276,595	135	Steam (source)
		Heat content in carrier gas	- 173,571	800	Medium gas (source)
		Heat of reaction	- 46,059	900	
	Output	Heat required for activation	+ 445,945	900	
		Sensible heat in products	+ 501,086	875	
		Enthalpy of water vapor	+ 110,248	100	
		Heat required for activator	+ *454,700*		*Fuel gas (LPG) (utility)*
B-1 Afterburner	Input	Enthalpy of matterial in put	- 1,076,444	750	Exhause gas from carbonizer
		Heat of reaction	- 3,654,364	900	
	Output	Enthalpy of flue gas	+ 2,064,894	900	
		Enthalpy of water vapor	+ 402,723	100	
		Heat removed	- *2,263,191*		*Steam generator (sink)*
E-1 Heat exchanger		Heat transfer (exchuse gas from afterburner)	268,098	100	Hot water form E-2 (sink)
E-2 Water heater		Cool down the product	56,473	600	Water (sink)

5.4.4 Equipment sizing

All equipments of the activated carbon from waste tires plant are sized and summarized in the table 5.4.4.1

Table 5.4.4.1 Equipment schedule

Equipment	**Code**	**Equipment function**	**Equipment specification**		**Capacity**
			Diam. (m)	**Length(m)**	
Screw feeder		Feed waste tires to the carbonizer	0.23	5.0	850 kg/h
Rotary carbonizer	R-1	Carbonization	1.33	3.11	850 kg/h
Rotary activator	R-2	Activation	1.56	7.07	323 kg/h
After burner	B-1	Eliminate smoke and foul smell	1.43	4.50	2,255,464 kcal/h
Separator	S-1	Vapor/liquid separator	0.41	1.03	
	S-2	Hot water for	0.80	2.40	
Heat exchanger	E-1	Generate steam for activation step	tube (1/2 in) length area	61 tubes 0.6 m 2.46 m^2	56,473 kcal/h
	E-2	Preheat water	tube (3/4 in) length area	67 tubes 1.5 m 57.53 m^2	39,969 kcal/h
Pump	P-1	Feed water to the heat exchanger(E-1)	0.062 kW		850 kg/h
	P-2	Feed hot water to the heat exchanger(E-2)	0.042 kW		1118 kg/h
Air blower	A-1	Force air to the rotary carbonizer	49.81 kW		2007 kg/h
	A-2	Force air to the after burner	132.93 kW		5292 kg/h
	A-3	Force exhause gas form afterburner to the rotary activator	32.90 kW		311.20 kg/h

5.5 Economic feasibility study of the continuous process

5.5.1 Total capital invest ment

The sum of the fixed capital investment and the working capital is known as the total capital investment. Table 5.5.1.1 shows the total capital investment of the activated carbon production which is the new expanded unit.

Table 5.5.1.1 the total capital investment of the continuous activated carbon production

Component	**Percentage (%)**	**Cost (US$)**
A. Fixed cost		
Direct cost		
Delivered equipment cost	71	1,204,222
Purchased-equipment installation	2	33,922
Instrumentation and controls	2.5	42,402
Piping	2	33,922
Electrical systems	0.5	8,480
Buildings	1	16,961
Service facilities	0.5	8,480
total direct cost	*79.5*	*1,348,389*
Indirect cost		
Engineering and supervision	5	84,804
Legal expenses	0.5	8,480
total direct cost	*5.5*	*93,285*
Total Fixed cost	85	1,441,674
B. Working capital	15	254,413
Total capital investment	**100**	**1,696,087**

5.5.2 Total production cost

The determination of the necessary capital investment is only one part of a complete cost and evaluation estimate. Another equally important part is the estimation of the production cost of the plant. The total production cost is generally divided into the categories of manufacturing costs and general expenses. All expenses directly connected with the manufacturing operation or the physical equipment of a process plant itself. The manufacturing costs are divided into two main groups: (1)

direct manufacturing cost and (2) fixed charge. The general expenses are involved in any company's operations. The total production costs are calculated on an annual basis in this project which is summarized in the table 5.5.2.1.

Table 5.5.2.1 Summary of the total production cost

Component	**Value used in estimate**	**Cost (US$)**
A. Manufacturing cost		
Direct production costs		
Raw materials	C_{RM}	191,250
Operating labor	C_{OL}	40,838
Utility	C_{UT}	440,452
Direct supervisory and clerical assistance	15 % C_{OL}	6,126
Maintenance and repairs	2 % of FCI	28,833
Laboratory charges	10 % C_{OL}	4,084
Fixed charges		
Depreciation	6 % of FCI	77,850
Insurance	0.5 % of FCI	7,208
Finacing		138,707
Plant overhead costs	20 % of (C_{OL} + direct supervisory+maintenance)	15,159
Total manufacturing cost		*950,508*
B. General expenses		
Administrative costs (sharing)	10 % of (C_{OL} +direct supervisory+maintenance)	6,967
Distribution and marketing costs (sharing)	2.00 % COM	19,540
Research and development cost	0.25 % COM	2,400
Total general expenses		28,907
Total production cost		979,413

Direct manufacturing cost

These costs represent operating expenses that vary with production rate. Table 5.5.2.2 shows the summary of raw material and utility cost which were used for the activated carbon production.

Table 5.5.2.2 Summary of raw material and utility (base case)

	Usage	Unit	Unit price(US$)	Annual cost (US$)
Raw material	6,120	ton/year	31.25	191,250
Water	6,120	m^3/year	0.33	1,989
LPG	1,787	ton/year	204.00	364,600
Electricity	1,633,007	kWh/year	0.05	81,650

The plant will be operated for 300 days of the year. Raw material usage, waste tire rubber, was 6,120 tons per year. The price 31.25 US$/ton of waste tire (1250 baht/ton) was the price for whole tires, which pieces of metal/wire and cords were already removed. Water will be used to cooling down the hot activated carbon produced before passed though the heat exchanger to produced steam. Other utility required is electricity and fuel gas (LPG).The electricity is mainly used to drive all the motors in the plant and the consumption. It is estimated that the electric power requirement of the whole process is 227 kWh/day. Fuel gas (LPG), which is the clean fuel, was used to heating up the furnace for carbonization and activation.

The technique used to estimate operating labor requirements in this project is the correlation of Alkayat and Gerrard[20]. According to this method, the operating labor requirement for the plant is given below:

$$N_{OL} = (6.29 + 31.7P^2 + 0.23N_{np})^{0.5}$$

Where N_{OL} is the number of operator per shift, P is the number of processing steps involving the handling of particulate solid. N_{np} is the number of nonparticulate processing steps handing step and includes compression, heating and cooling, mixing, and reaction. In this project the value of P is 2(particle transportation and particle size control). In the table 5.3.4.1, it can count that the N_{np} is 5, so the number of operators per shift calculated is 11 persons/shift. A single operator works on the average 300 days a year, 8-hour shifts a day. Based on the Ministry of Labor of Thailand, the minimum daily wage rate in Bangkok and city environs is 165 baht per day per person or 20.63 bath/hr (8 hours per day per shift). The operating labor cost for this plant is 40,838 US$/year.

Fixed charge

These costs are independent of change in production rate. Fixed charges include insurance, and depreciation, which are charged at constant rates even when the plant is not in operation.

General expenses

These costs represent an overhead burden that is necessary to carry out business functions. General expenses include management, sales, financing, and research functions.

5.5.3 Profitability analysis

There are essentially three bases used for the evaluation of profitability. They are:

(1) Time

(2) Cash

(3) Interest rate

For each of these bases, it can consider discounted or nondiscounted techniques. The nondiscounted techniques do not take into account the time value of money. In this work, both types of methods for all the three bases were presented. The new production process is going to be built and will require the following basis and capital investments:

Life time of plant	15	years

Plant start-up at end of year 2

Plan of production capacity : base case 720 ton/year

Year	Production rate	Quantity(tons)
3	80%	576
4	90%	648
>5	100%	720

Working day	300	days/year
Investment		
Fixed capital during year 1	60%	of FCI

Fixed capital during year 2	40%	of FCI
Fixed capital investment (base case)	1,441,674	US$
Working capital	18%	of FCI
Working capital (at the end of year 2)	254,413	US$
Loan and payment		
Loan: Long term period	70%	of FCI
Payment time	15	year
Interest rate (base case)	8%	
Tax	30%	of net profit
Depreciation: Straight line depreciation method		
Salvage value	10%	of FCI
Activated carbon selling price (base case)	2	US$/kg
Discounted rate (base case)	5%	

The cumulative after-tax cash flow for the activated carbon production is illustrated in table 5.5.3.1. Using this data, the cumulative cash flow diagram is drawn, figure 5.5.3.1.

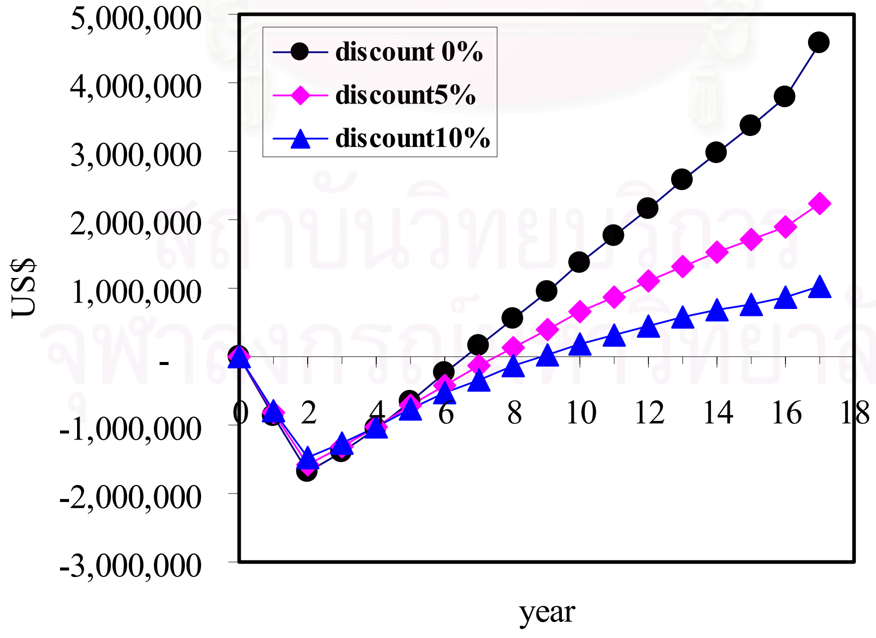


Figure 5.5.3.1 Cumulative cash flow diagram for discount and non discount criteria

Table 5.5.3.1 Nondiscounted and discounted after-tax cash flows (All numbers in US$)

End of year(k)	Investment	d_k^{SL}	$FCI_L-\sum d_k$	R	COMd	Tax	Net profit	Non-Discountes cash flow	Cumulative Non-Discountes	Discounted cash flow(5%)	Cumulative Discountes Cash flow
0	0										
1	(865,004)		865,004				(865,004)	(865004)	(865,004)	(823,814)	(823,814)
2	(831,083)		1,441,674				(831,083)	(831083)	(1,696,087)	(753,816)	(1,577,630)
3		86,500	1,355,174	1,152,000	769,442	88,817	293,740	293,740	(1,402,347)	253,744	(1,323,886)
4		86,500	1,268,673	1,296,000	835,503	112,199	348,298	348,298	(1,054,049)	286,545	(1,037,341)
5		86,500	1,182,173	1,440,000	901,564	135,581	402,855	402,855	(651,194)	315,648	(721,693)
6		86,500	1,095,672	1,440,000	901,564	135,581	402,855	402,855	(248,339)	300,617	(421,076)
7		86,500	1,009,172	1,440,000	901,564	135,581	402,855	402,855	154,517	286,302	(134,775)
8		86,500	922,671	1,440,000	901,564	135,581	402,855	402,855	557,372	272,668	137,893
9		86,500	836,171	1,440,000	901,564	135,581	402,855	402,855	960,227	259,684	397,577
10		86,500	749,670	1,440,000	901,564	135,581	402,855	402,855	1,363,082	247,318	644,895
11		86,500	663,170	1,440,000	901,564	135,581	402,855	402,855	1,765,937	235,541	880,437
12		86,500	576,670	1,440,000	901,564	135,581	402,855	402,855	2,168,792	224,325	1,104,761
13		86,500	490,169	1,440,000	901,564	135,581	402,855	402,855	2,571,647	213,643	1,318,404
14		86,500	403,669	1,440,000	901,564	135,581	402,855	402,855	2,974,503	203,469	1,521,873
15		86,500	317,168	1,440,000	901,564	135,581	402,855	402,855	3,377,358	193,780	1,715,653
16		86,500	230,668	1,440,000	901,564	135,581	402,855	402,855	3,780,213	184,553	1,900,206
17	398,580	86,500	144,167	1,440,000	901,564	135,581	801,436	801,436	4,581,648	349,664	2,249,870

Number in () are negative cash flows

Nondiscounted profitability criteria			**Discounted profitability criteria (at 5% discount rate)**		
Pay back period (PBP)	6.62	years	DPBP	7.49	years
Cumulative cash position (CCP)	4,581,648	US$	Net present value (NPV)	2249869.75	US$
Cumulative cash ratio (CCR)	3.70		Present value ratio (PVR)	1.99	
Rate of return on investment (ROI)	29.03	%	Discount cash flow rate of return (DCFROR)	19.22	%

Time criterion

The term used for this criterion is the payback period (PBP). The definition of the payback period is time required to recover the fixed capital investment for the project. The payback period is shown as a length of time on figure 5.5.3.1. It was found that the period of payback is 6.62 years for nondiscount rate and 7.49 years at discount rate at 5% from the start of the project.

Cash criterion

The criterion used here is the cumulative cash position (CCP), which is simply the worth of the project at the end of its life. Sometime, it is more useful to use the cumulative cash ratio (CCR) defined as:

$$\text{CCR} = \frac{\text{Sum of all positive cash flows}}{\text{Sum of all negative cash flows}}$$

The CCP and CCR are the cash criterion for nondiscounted technique. For discounted technique, it uses net present value (NPV) and present value ratio (PVR) which its definitions resemble those of nondiscounted technique.

Interest rate criterion

For nondiscount technique, the criterion used here is called the rate of return on investment (ROI) and represents the nondiscounted rate at which we make money from our fixed capital investment. The definition is given as:

$$\text{ROI} = \frac{\text{Average annual net profit}}{\text{Fixed capital investment (FCI)}}$$

For discounted technique, the term used for this criterion is the discounted cash flow rate of return (DCFROR) which is defined to be the interest rate at which all the cash flows must be discounted in order for the net present value of the project to be equal to zero. Therefore, the DCFROR represents the highest, after-tax interest or discount rate at which the project can just break even.

The PBP and NPV for several different discount rates were calculated and the results are shown in table 5.5.3.2

Table 5.5.3.2 PBP and NPV for this project as a function of discount rate

%Discount rate	NPV (US$)	PVR	PBP
0	4,581,648*	3.70*	6.6
5	2,249,870	2.43	7.5
10	1,018,755	1.69	8.8
15	334,709	1.24	10.4
20	- 61,455	0.95	-
25	- 298,111	0.76	-

* For nondiscounted technique, NPV and PVR are represented by CPV and CCR, respectively

The value of the DCFROR is found by interpolation from table 5.5.3.2. Therefore the DCFROR is 20.58%

5.5.4 Sensitivity analysis

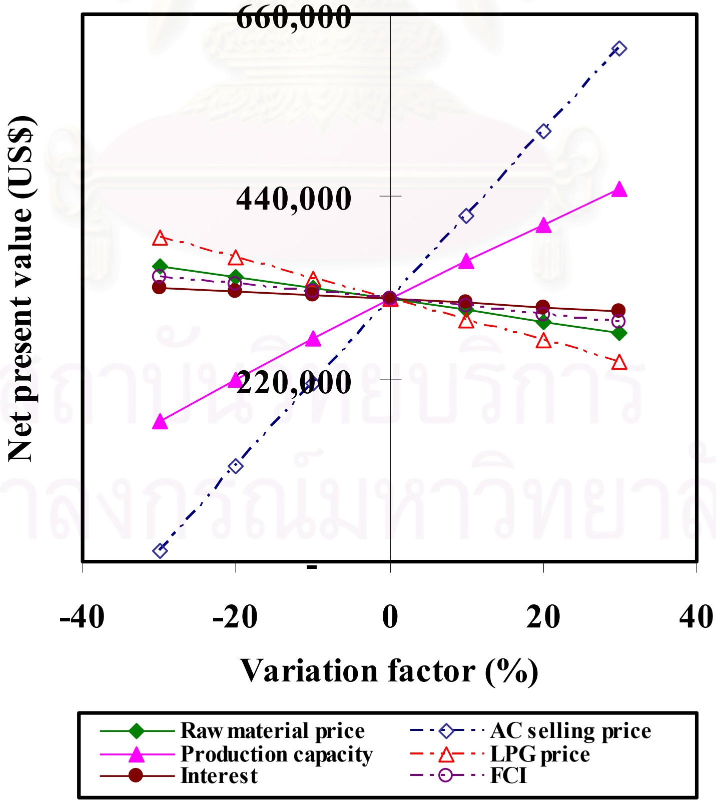


Figure 5.3.4.1 Sensitivity analysis in the variation factor of ± 30%

Similar to other chemical plant projects, factors and assumption used in estimation may fluctuate by different extents and lead to a variation in the economic performance of the entire project. Analysis on the major factors affecting the performance is therefore necessary in order to find out the implication of these factors on the profitability of the proposed plant. Figure 5.5.4.1 show the results of the sensitivity analysis by varying six major factors. These factors include: (1) Raw material price; (2) AC selling price; (3) Production capacity; (4) LPG price; (4) Interest rate; and (6) Fixed capital investment.

Raw material

It assumed that raw material price included the tipping fee for each tire delivered to the plant. Raw material cost is 31.25 US$/tons of whole tires. The variation of raw material cost in the range of 21.88-40.63 US$/tons of whole tires may result in a difference of ±12.7% (max) to the net present value at the discount rate of 0%.

AC selling price

The selling price for activated carbon is 2 US$ per kilogram with an annual production of 720 tons per year. When the selling price of activated carbon varies between US$ 1.4-2.6, the NPV (0% discount) of the project also differs by over 95.59% (max) due to the significant impact on the revenue. It is possible to have a higher selling price of activated carbon in the future, depending on the marketing demand.

Production capacity

The production capacity is one of the significant factors affecting the NPV of the project. The proposed plant is designed to produce activated carbon at a production rate of 2.4 tons/day and generates revenue of 1.44 million US$ every year. All of the revenue comes from activated carbon sales. Any alteration to the production capacity directly affects the cash flow every year.

LPG price

Fuel gas (LPG) was consumed to heating up the furnace for carbonization and activation. The price of LPG gas will be affected by the fluctuation of the oil price in the international market like other fuels. The LPG price has been varied in the range of 0.14-0.67 US$/kg, changing the NPV at the 0% discount rate of ± 23.69 % (max).

Interest

The plant is assumed that 70% of FCI is loaned from the bank and the interest rate is set at 8%. We have to pay the bank for 15 years. The interest rate directly affects the annual payment of the production cost. When the interest rate varies between 05.6 -10.4 the NPV (0% discount) also differs by ± 4.35%.

Fixed capital investment

Fixed capital for the entire project is estimated to be 1,441,674 US$. If the lower fixed capital investment (lower cost of equipment) is possible, the NPV could be improved.

Conclusion for section 5.4 and 5.5

The new expanded unit of activated carbon production from waste tires was designed in this work. The production capacity is 720 ton/year. The plant will be operated for 300 days of the year. Life time of plant is set at 15 years. Raw material usage, waste tire rubber, was 6,120 tons per year. The results form the economic analysis is summarized below;

o Fixed capital investment (FCI)	1,441,674	US$
o Working capital	254,413	US$
o Total capital investment	1,696,087	US$
o Loan : long term period	70%	of FCI
o Tax	30%	
o Manufacturing cost exclude depreciation (COMd)	901,564	US$/year
o Net present value (0% discount rate)	4,581,648	US$
o Cumulative cash ratio (CCR)	3.7	
o Pay back period (PBP) at 0% discount rate	6.42	years
o The rate of return on investment (ROI)	29.03%	
o Discounted cash flow rate of return (DCFROR)	20.58%	

From the above results, within a reasonable payback period (4.42 years after the commencement of production), the proposed process is generated a ROI up to

29.03% which is higher than the minimum acceptable rate of return (25%) [21]. Moreover, the cumulative cash ratio of this project is greater than unity implied that this project is potentially profitable. The rate of return in this project is 20.58% which is higher than the standard value (12%) for mature technology [20]. Results from economic sensitivity analysis have revealed that the variations of ± 30% in factors such as activated carbon selling price and production capacity are all positive to the further improvement on the NPV.

CHAPTER VI

CONCLUSION AND FUTURE WORKS

6.1 Conclusion

Activated carbons were prepared from waste tires by the conventional and practical method and the resulting physical and porous properties were characterized. Next, liquid-phase adsorption characteristics of the prepared activated carbons were obtained and compared with the commercial activated carbon. Based on the experiment, the design of continuous production process and economic feasibility was carried out. The conclusions for all experiment section are summarized as follows:

- Both conventional and practicaltical method can prepare highly mesoporous and fairly microporous activated carbon.
- The adsorption capacities for phenol on the prepared activated carbons are comparable to those of the commercial activated carbon.
- The obtained activated carbons had higher capacity red31 adsorption than the commercial one extended to 70% for practical one and 160% for the conventional one. It is suggested that the chemical nature influences the liquid-phase adsorption characteristics
- Highly mesoporous activated carbons prepared by practical and conventional method have large adsorption capacities for red31. It is confirmed that these activated carbon are good adsorbents for bulky molecules in aqueous solutions.
- Because of good liquid-phase adsorption-desorption characteristics, the activated carbons prepared in this work are expected to be suitable for wastewater treatment.

For continuous production process design of activated carbon from waste tires and economic feasibility, the production capacity is set at 720 ton/year capacity. The plant will be operated for 300 days of the year. Life time of plant is set at 15 years. Raw material usage, waste tire rubber, was 6,120 tons per year. The results form the economic analysis is summarized below;

Fixed capital investment (FCI)	1,441,674	US$
Working capital	254,413	US$
Total capital investment	1,696,087	US$
Loan : long term period	70%	of FCI
Tax	30%	
Manufacturing cost exclude depreciation (COMd)	901,564	US$/year
Net present value (0% discount rate)	4,581,648	US$
Cumulative cash ratio (CCR)	3.7	
Pay back period (PBP) at 0% discount rate	6.42	years
The rate of return on investment (ROI)	29.03%	
Discounted cash flow rate of return (DCFROR)	20.58%	

Within a reasonable payback period (4.42 years after the commencement of production), the proposed process is generated a ROI up to 29.03% which is higher than the minimum acceptable rate of return (25%). Moreover, the cumulative cash ratio of this project is greater than unity implied that this project is potentially profitable. The rate of return in this project is 20.58% which is higher than the standard value (12%) for mature technology. Results from economic sensitivity analysis have revealed that the variations of ± 30% in factors such as activated carbon selling price and production capacity are all positive to the further improvement on the NPV.

6.2 Future Works

- To evaluate the carbon structure and surface more precisely
- To study the affect of gas mixture ratio on the activated carbon properties.
- To scale-up the furnace for preparing the activated carbon in practical scale.

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APPENDICES

APPENDIX A

Data Used to Design the Continuous Production Process of Activated Carbon from Waste Tires

Table A1 Properties of waste tire [5]

Proximate analysis		**Ultimate analysis**	
Component	**% mass**	**Component**	**% mass**
Volatiles matter	66.50	Carbon	88.01
Fixed carbon	30.30	Hydrogen	8.20
Ash	2.40	Nitrogen	0.41
Moisture	0.80	Sulphur	1.02
		Oxygen	2.36
Total	100.00		100.00
Density			550 kg/m^3
GCV			40 MJ / kg

Table A2 Properties of char

Proximate analysis	
Component	**% wt**
Moisture	1.39
Ash	10.89
VM	7.54
FC	80.18
Total	100.00
Density (kg/m^3)	400
GCV (kcal/kg)	7,061.46

Table A3 Properties of activated carbon

Proximate analysis	
Component	**%wt**
Moisture	1.07
VM	7.71
FC	71.06
Ash	20.16
total	100.00
GCV (kcal/kg)	**6,340.99**

Table A4 Production yield in wt% of ash free form the carbonization of waste tires [4]

Composition	**% Wt**
H_2O	3.12
CO_2	0.54
CO	1.29
CH_4	0.32
C_2H_4	0.07
SO_2	0.27
NH_3	0.34
tar	51.05
char	43.00
total	100.00

Table A5 Component analysis of tar [2]

Component	**% wt**
Carbon	87.35
Hydrogen	10.01
Nitrogen	0.65
Sulfur	1.99
total	**100**
GCV (kcal/kg)	10,000.00

APPENDIX B

Equipments sizing of the activated carbon from waste tires plant

B1. Rotary Carbonizer (Using heuristics and guidelines in reference [22])

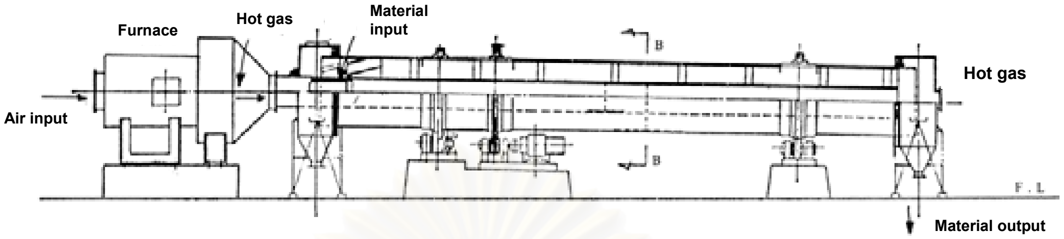


Figure B1 Schematic of the rotary kiln

Resident time 0.5 hr

Estimation of volume of the carbonizer(rotary kiln)

Raw material in the reactor not more than (assume) 18 % of total V

ρ_b of raw material 550 kg/m^3

Raw material feeding rate 850 kg/hr (mass balance)

Volumetric flow rate = (850/550) = 1.55 m^3/hr

Volume of carbonizer = (1.55 x 0.5)/0.18 = 4.29 m^3

Diameter (D_T) 1.31 m (from part b)

Length 3.19 m

Cross sectional area 1.35 m^2 (from part b)

a) Rotating speed, N

N x D_T = 12 m/min *referent value: 7-12 m/min*

N x D_T = 720 m/hr

So, N = 9.17 rounds/min

b) Mass flow rate of hot air, G

G = 2,500 kg/hr m^2 *(referent value for large particle)*

Flow rate of hot air = 3,362.70 kg/hr (from material balance around carbonizer)

Cross section area = (3,362.70/2,500) = 1.35 m^2

Diameter of dryer = 1.31 m

c) Lifters, n

n/D_T = 10 *referent value: 8-10*

n = (10)(1.31) = 13

d) Ratio of material in dryer, X

X = 18 % *referent value: 6-20%*

e) Angle, S_d

X = (0.4 F/60 N Sd DT) (100)

F = feed rate of raw material, m3/hr m2

= $W_o/\{p_b$(pi DT2/4)}

Where,

W_o = feeding rate = 850 kg/hr

p_b = density of raw material = 550 kg/m^3

So,

F = 1.15 $m^3/hr\ m^2$

And,

S_d = 0.0035 *Check point --> referent value: 0~0.06*

f) Pressure drop

Referent value = 1 mm water/m

Pressure drop = (1)(3.19) = 3.19 mm water

g) Power, P

P = D_T x L

Where,

L = the length of the dryer = 3.19 m

Therefore,

P = 4.18 HP

h) Volumetric heat transfer coefficient, h_a

$h_a D_T$ = $0.56 (n-1) G 0.46$ *Check point --> n must be 6~16*

Where,

$n = n$ when n less than or equal 16 and $n=16$ when $n>16$

So, ha = 189.11 kcal/hr m^3 °C *Check point --> referent value: 100~200*

B2. Rotary Activator(Using heuristics and guidelines in reference [22])

Resident time 3 hr

Estimation of volume of the activator (rotary kiln)

Raw material in the reactor not more than			18	% of total V (assume)
ρ_b of raw material(char)			400	kg/m^3
Raw material feeding rate			324	kg/hr (mass balance)
Volumetric flow rate	=	(324/400)	=	0.81 m^3/hr
Volume of the activator	=	(0.81 x 3)/0.18	=	13.48 m^3
Diameter (D_T)				1.56 m (from part b)
Length				7.07 m
Cross sectional area				1.91 m^2 (from part b)

a) Rotating speed, N

N x D_T = 12 m/min *referent value: 7-12 m/min*

N x D_T = 720 m/hr

N = 7.70 rounds/min

b) Mass flow rate of hot air, G

G = 2000 kg/hr m^2 *(referent value for small particle)*

Flow rate of hot air = 3,816.97 kg/hr

Cross section area = 1.91 m^2

Diameter of dryer = 1.56 m

c) Lifters, n

n/D_T = 10 *referent value: 8-10*

n = 16

d) Ratio of material in dryer, X

X = 18 % *referent value: 6-20%*

e) Angle, S_d

X = $(0.4\ F/60\ N\ S_d\ D_T)\ (100)$

F = feed rate of raw material, $m^3/hr\ m^2$

= $W_o/\{p_b(pi\ DT2/4)\}$

Where,

W_o = feed rate = 324 kg/hr (mass balance)

p_b = density of raw mat = 400 kg/m^3

So, F = 0.42 $m^3/hr\ m^2$

And, S_d = 0.0013 *Check point --> relevant value: 0~0.06*

f) Pressure drop

Referent value = 1 mm water/m

Pressure drop = (1)(7.07) = 7.07 mm water

g) Power, P

P = $D_T L$

Where,

L = the length of the activator = 7.07 m

Therefore,

P = 11.01 HP

h) Volumetric heat transfer coefficient, ha

$h_a DT$ = 0.56 (n-1) G 0.46 *Check point --> n must be 6~16*

Where,

n = n when n less than or equal 16 and n=16 when n>16

So, h_a = 172.93 kcal/hr m^3 ^oC *Check point --> relevant value: 100~200*

B3. Afterburner

Table B3 summary of the designed parameter of afterburner

Parameter of design	**After burner**	**Unit**
Flue gas mass flow rate , W	3,889	kg/hr
Air	5,293	kg/hr
Density of flue gas	0.355	kg/m^3
T of air in	25	^{o}C
T of flue gas	750	^{o}C
T of burner	900	^{o}C
Volumetric flow rate of flue gas and air	= (9182/0.355)/3600 = 7.19	m^3/s
Velocity of flue gas and air mixture (assume)	4.5	m/s
Residence time	1	s
Energy balance		
Heat of combustion	3,654,364.10	kcal/hr
Heat transfer rate(Q)	2,263,190.64	kcal/hr
Combustion density	326.49	kW/m^3
Size of afterburner	= (7.19)(1) = 7.19	m^3
Cross sectional area	= 7.19/4.5 = 1.60	m^2
diameter	1.43	m
long	= 7.19/1.60 = 4.5	m

B4. Heat exchanger (Water heater; E-1)

Table B4.1 Summary of properties of the streams used

Fluid properties	Unit	hot stream	inside tube
Material		Activated carbon	water
Average Temp.	^oC	600	67.50
Physical properties of the fluid at average temperature			
Density (ρ)	kg/m^3	400	968.29
Specific heat (Cp)	kcal/kg C	0.64	1.02
Thermal conductivity(k)	kcal/hr m C	0.45	0.59
Viscosity (μ)	kg/m hr		1.12
Surface tension	N/m		0.05
Flow rate of stream (V)	kg/hr	148	
Pr = ($Cp\mu/k$)			1.93
Pressure	kPa		400
Critical pressure	kPa		22090

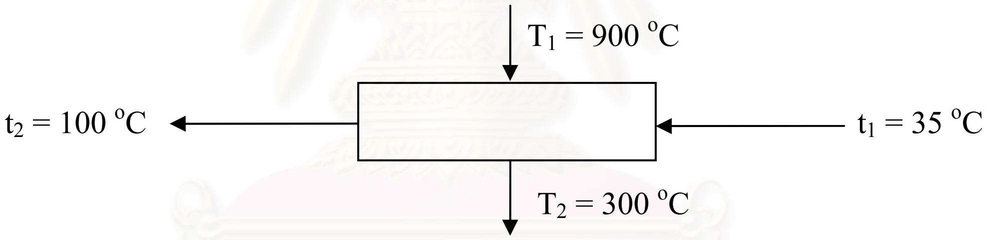


Figure B4.1 flow diagram of hot and cool stream

(a) Heat transfer rate, Q

$Q = m_s C_p \Delta T$ (heat transfer form the hot stream)

Where, m_s = mass flow rate of particle = 148 kg/hr

Cp = heat capacity of particle = 0.64 kcal/kg C

$\Delta T = 600^oC$

So, Q = 56,473 kcal/hr

(b) Water flow rate, W (Cool stream)

Q = 56,473 kcal/hr (heat source = heat sink)

Latent heat of water = 516 kcal/kg (from Perry’s Chemical engineers’ handbook)

Cp of water = 1.02 kcal/kg ^oC

ΔT = 65 ^oC

Water flow rate , W = 850 kg/hr

(c) Estimate heat transfer area, A

- *Long mean temperature differenc, LTMD*

$$LTMD = \frac{(T_2 - t_1) - (T_1 - t_2)}{\ln\left(\frac{T_2 - t_1}{T_1 - t_2}\right)} \qquad \text{…..(B4.1)}$$

LTMD = 484^oC (use data from figure B4.2)

LTMD correction factor;

R = $(T_1-T_2)/ (t_2-t_1)$ = 9.23

S = $(t_2-t_1)/ (T_1-t_1)$ = 0.08

From figure h (Perry's chemical engineering handbook; 11-6), it can find out that LTMD correction factor for cross flow system is 0.98

So, the corrected LTMD = 474.53^oC

- *Heat transfer area, A*

$$q = U_o A \text{ (LTMD)} \qquad \text{….(B4.2)}$$

Assume U_o = 58 kcal/h m^2 ^oC

By solving equation B4.1, heat transfer area, A is 2.05 m^2

For safety system, the safety factor which is set at 20 % was multiplied.

So, the safety heat transfer area = 2.46 m^2

By trial and error method, the pipe ½ in. (0.0213 m) in diameter and 0.06 m of length was choused. Dimensions of the tube used are show in table B4.2

Table B4.2 Tube dimension

Tube dimension		**SI unit**	**dimension**
Norminal pipe size		in	1/2
Outside diameter		m	0.0213
Schedule No			40ST,40S
Wall thickness		m	0.0028
Inside diameter		m	0.0158
Cross-sectional area	Metal	m^2	0.00016
	Flow	m^2	0.000196
Circumference	Outside	m or surface m^2/m of length	0.0671
	Inside		0.0497
thermal conductivity		kcal/hr m C	18.4539

So, amount of tubes used, N = A/ (Circumference x length) = 61 tubes

The arrangement of the tube: triangular

Row = 10 rows

Tube = 5 tubes/row

Length = 0.60 m

Pitch (a) = 1.25 in. = 0.032 m

Pitch (b) = 1.08 in. = 0.027 m

Spacing area between tubes = 0.03 m^2

LTMD = 474.53 C

Area = 2.46 m^2

Assume: Uo = 58.00 kcal/h $m^{2o}C$

Amount of tube used, N = 61 tubes

(d) Overall heat transfer coefficient

<u>Inside tube</u>

Cross sectional area (for the fluid) = (0.000196 m2/tube) (61 tubes)

= 0.012 m^2

- *Reynolds number , Re*

$$Re = Gd_i/\mu \qquad \text{….(B4.3)}$$

Where, G = mass flux of fluid inside tube = W/A

= (850 kg/hr)/ (0.012 m^2) = 70,878.66 kg/hr m^2

v = G/density = 0.02 m/s

From table B4.1 and B4.2

Di = 0.0158 m

μ = 1.1160 kg/m hr

By solving eq. B4.3, Re = 1,225 → larminar flow (Re>2100)

- *Heat transfer coefficient inside tube, h_i*

For laminar flow (Re<2100)

$$\boxed{\frac{h}{CpG} = 1.86\left(\frac{Cp\mu}{k}\right)^{-\frac{2}{3}}\left(\frac{DiG}{\mu}\right)^{-2/3}\left(\frac{\mu_b}{\mu_w}\right)^{0.14}\left(\frac{L}{Di}\right)^{-1/3}} \qquad \text{….(B4.4)}$$

From the above results, all parameters in equation B4.4 can be solved.

By applying the known parameters to equation B4.4, h_i = 258 kcal/hr C m^2

<u>Outside tube</u>

- *Effectiveness thermal conductivity of pack bed, K_e [24]*

Assume; flow rate of solid is very slow

$$\boxed{\frac{k_e^o}{k_F} = e\left(1 + \frac{h_{rv}\cdot D_p}{k_F}\right) + \frac{1-e}{\dfrac{1}{\dfrac{1}{\phi} + \dfrac{h_{rs}D_p}{k_F}} + \dfrac{2}{3}\left(\dfrac{k_F}{k_s}\right)}} \qquad \text{….(B4.5)}$$

$$\boxed{h_{rs} = 0.1952\left\{\frac{\varepsilon}{2-\varepsilon}\right\}\left\{\frac{t+273}{100}\right\}^3} \qquad \text{….(B4.6)}$$

$$\boxed{h_{rv} = \left[0.1952 / \left\{1 + \frac{e}{2(1-e)}\right\}\right]\left(\frac{t+273}{100}\right)^3} \quad \text{....(B4.7)}$$

$$\boxed{\frac{k_e^o}{k_F} = e + \frac{1-e}{\phi + \frac{2}{3}\left(\frac{k_F}{k_S}\right)}} \quad \text{....(B4.8)}$$

Where

D_p = Diameter of particle = 0.003 m

e = Void bed = $1-\rho_b/\rho_t$ = 0.2 : ρ_b is bulk density, and ρ_t is true density

t = temperature (C) = 600 C

ε = Black emissivity = 0.8 (Perry's chemical engineering handbook) k_F = Thermal conductivity of fluid = 0.09541 kcal/h m^{o}C

k_S = Thermal conductivity of solid = 0.45 kcal/h m C

k_F/k_S = 0.21

From fig.1 [23], ø = 0.6

By substitute the known parameters into equation B4.5-B4.8

h_{rs}, radiative heat transfer coefficient. = 519.50 kcal/m^2 h^{o}C

h_{rv}, radiative heat transfer coefficient. = 115.44 kcal/m^2 h^{o}C

k^o_e/k_F = 4.99

k_e = 0.48 kcal/h m C

- *Heat transfer coefficient to wall of tube*

$$\boxed{\frac{1}{h_w D_p / k_F} = \frac{1}{2}\left\{\frac{1}{k_{er}/k_F} - \frac{1}{k_{ew}/k_F}\right\}} \quad \text{....(B4.9)}$$

$$\boxed{\frac{k_{ew}}{k_F} = \frac{k_{ew}^o}{k_F} + \frac{1}{\frac{1}{\alpha_v\left(C_p\mu/k_F\right)\left(D_pG/\mu\right)} + \frac{2}{h_w^* D_p / k_F}}} \quad \text{....(B4.10)}$$

$$\boxed{\frac{k_{ew}^{o}}{k_F}=e_w\left(1+\frac{1}{2}\frac{h_{rv}D_p}{k_F}\right)+\frac{1-e_w}{\dfrac{1}{\left(\dfrac{1}{\phi_w}+\dfrac{1}{2}\dfrac{h_{rs}D_p}{k_F}\right)}+\dfrac{1}{3}\left(\dfrac{k_F}{k_S}\right)}} \qquad \text{....(B4.11)}$$

Where,

e_w = Average void bed at wall = 0.7

h_{rv} = Radiative heat transfer coefficient = 115.44 kcal/m^2 h^oC

h_{rs} = Radiative heat transfer coeff = 519.50 kcal/m^2 h^oC

C_p = Specific heat capacity = 7.58 kcal/kmole ^oC

μ = Viscosity of fluid = 0.10 kg/m h

k_F = Thermal conductivity of fluid = 0.095 kcal/h m^oC

k_s = Thermal conductivity of solid = 0.45 kcal/h m ^oC

k_F/k_S = 0.212

So, from figure 1[23] $\o_w$ = 1.8

By substitute the known value into equation B4.11,

k^o_{ew}/k_F = 3.589

$$\boxed{\frac{h_w^{*}D_p}{k_F}=C\left(\frac{C_p\mu}{k_F}\right)^{1/3}\left(\frac{D_pG}{\mu}\right)^{1/2}} \qquad \text{....(B4.12)}$$

where, C is constant value :C = 2.6 for liquid and, C = 4 for gas

Assume: flue gas mix with product = 0.2

So, gas flow with AC = (0.2)(148 kg of product/hr) = 29.6 kg/hr

Free space area = (0.2)(spacing area) = (0.2)(0.03) = 0.006 m^2

G = W/A = (29.6)/(0.006) = 4,6444.12 kg/hr m^2

$C_p\mu/k_F$ = 7.978

D_pG/μ = 138.67

By substitute the known value into equation B4.12,

$k^*_wD_p/k_F$ = 94.12

$$\boxed{\frac{k_{er}}{k_F}=\frac{k_e^{o}}{k_F}+(\alpha\beta)\left(\frac{C_p\mu}{k_F}\right)\left(\frac{D_pG}{\mu}\right)} \qquad \text{....(B4.13)}$$

k^{o}_{e}/k_F = 4.99

$\alpha\beta$ is found from figure 2 [23]

$\alpha\beta$ = 0.06

From equation B4.13, k_{er}/k_F = 71.37

- *Heat transfer coefficient outside tube, h_o*

$$\boxed{\frac{h_o D_p}{k_F} = \left(\frac{D_p}{D}\right)\left(\frac{k_e}{k_F}\right)\left\{a_1^2 + \phi(b)/\xi\right\}} \qquad \text{....(B4.14)}$$

where, a^2_1 and ø(b) are found from figure 3 [23]

ø(b) = 0.035

a^2_1 = 2.2

By substitute the all known value from above results in equation B4.14,

$h_o D_p/k_F$ = 3.17

h_o = 100.93 kcal/h m^2 °C

<u>*Overall heat transfer coefficient*</u>

$$\boxed{\frac{1}{U_o} = \frac{1}{h_o} + R_{fo} + R_{fi} + \frac{\Delta x}{k}\left(\frac{A_o}{A_m}\right) + \left(R_{fi} + \frac{1}{h_i}\right)\frac{A_o}{A_i}}$$

h_o = 100.93 kcal/h m2 C

h_i = 258.16 kcal/h m2 C

R_{fo} = 0.0010 h m^2 C/kcal

R_{fi} = 0.0004 h m^2 C/kcal

Δx = 0.0028 m

A_o/A_m = 1.15

Ao/Ai = 1.35

k = 18.45 kcal/h m°C

U_o = 57.81 kcal/h m^{2o}C{This value is nearly assumed value→ok.}

(e) Pressure drop inside tube[Perry's Chemical engineers' handbook]

For no phase change

$$\boxed{\Delta P_f = \frac{4fG^2LN_l}{\rho D_i\phi_t}}$$

Where

f , Fanning's friction factor

Re = 12.99

So , f = 16/(DiG/μ) for DiG/μ less than 2100

G, Massvelosity = 19.69 kg/s m^2

L, Length of tube = 0.60 m

N, Number of pass of fluid inside tube = 1.00

ρ = 968.29 kg/m^3

Φ (μb/μw) = 1.00

So, pressure drop inside tube is 74.9 Pa.

From the above results, it was summarized in the table B4.3

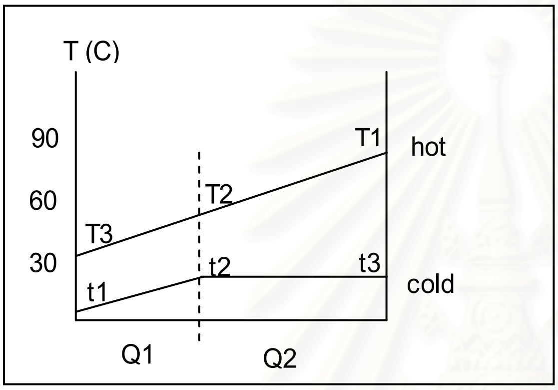
Table B4.3 Summary of the heat exchanger (Water heater; E-1)

Parameter of design		**Unit**
Q	56,473	kcal/hr
LTMD (corrected)	474.53	C
Uo (assume)	58.00	kcal/h m^2 C
A (multiplied safety factor 20%)	2.46	m^2
Length of tube	0.60	m
Number of tube	***61***	tubes
inside tube		
Pressure	4	bar
Water flow rate , W	850	kg/hr
Vapor fraction	0	
Vapor produced	0	kg/hr
G (inside tube)	70,879	kg/hr m^2
Velocity of fluid inside tube	0.020	m/s
Re (inside tube)	1,003	
Friction factor		
Pressure drop inside tube	74.90	Pa
Outside tube		
W (particle)	148	kg/hr
Cp (particle)	0.636	kcal/kg C
Spacing area	0.032	m^2
k (particle)	0.45	kcal/h m C
G (outside tube)	4644.12	kg/hr m^2
Velocity of solid outsidetube : v_s	0.003	m/s
Overall heat transfer coefficient		
Heat transfer coefficient inside tube, h_i	***258.16***	kcal/hr C m2
Heat transfer coefficient outside tube h_o	***100.93***	kcal/h m^2 C
R_{fo}	0.00103	h m^2 C/kcal
R_{fi}	0.0004	h m^2 C/kcal
Δx	0.003	m
A_o/A_m	1.15	
A_o/A_i	1.35	
k	18.45	kcal/h m C
U_o	***57.8***	kcal/h m^2 C
Size of Heat exchanger (for cooling down A.C.):		
wide	0.16	m
long	0.60	m
high	0.33	m

B5. Heat exchanger (E-2)

Assumption:

- vapor fraction, x = 0.4
- It is divided into two parts of calculation (1) changing temperature (none phase change) and (2) phase change and water-steam mixture (at constant temperature)



Hot stream

T_1 = 900°C

T_2 = 815 °C

T_3 = 800 °C

Cold stream

t_1 = 100 °C

t_2 = 135 °C

t_3 = 135 °C

Dimention of tubes

Norminal pipe size = 3/4 in

Outside diameter = 0.027 m

Wall thickness = 0.003 m

Inside diameter = 0.021 m

Arrangement of the tubes: Triangular

Number of rows = 6 rows

Tube = 11 tubes/row

Length = 1.5 m

Pitch = 0.095 m

Based on conceptual design of heat exchanger in 'Heat transfer design methods edited by John J. Mckette,1992' the important parameters and size of heat exchanger (E-2) was summarize in table B5

Table B5 summary of the designed heat exchanger (E-2)

Parameter of design	**Part 1**	**Part 2(phase change)**	**Total**	**Unit**
Q	*39,575*	*228,523*	*268,098*	kcal/hr
LTMD (corrected)	*690*	722		C
Uo (assume)	**45.5**	**55.5**		kcal/h m^2 C
A (multiplied safety factor 0.2)	1.51	55.50	57.01	m^2
Length of tube	0.27	1.23	1.50	m
Number of tube			***66***	tubes
inside tube				
Pressure			3	bar
Water flow rate , W			1107	kg/hr
Vapor fraction			0.4	
Vapor produced			443	kg/hr
G (inside tube)			48,280.7	kg/hr m^2
Velocity	0.01	0.03		m/s
Re (inside tube)	905	2,238.95		
Friction factor	0.018	0.008		
Pressure drop inside tube	0.00095	104.78	104.79	Pa
Outside tube				
W (flue gas)			9,182.04	kg/hr
Cp (flue gas)			0.636	kCal/kg C
Spacing area			0.91	m^2
G (flue gas)			10,062.85	kg/hr m^2
Velocity of flue gas			8.96	m/s
Re (outside tube)			1,961.21	
Friction factor			0.077	
Pressure drop outside tube			23.14	Pa
Overall heat transfer coefficient				
Heat transfer coefficient inside tube, h_i	***292***	***2,908.35***		kcal/hr^{o}Cm^2
Heat transfer coefficient outside tube h_o	***62***	***62***		kcal/h m^2 C
Rfo	0.0004	0.0004		h m^2 C/kcal
Rfi	0.0004	0.0004		h m^2 C/kcal
Δx	0.0029	0.0029		m
Ao/Am	1.1206	1.1206		
Ao/Ai	1.2743	1.2743		
k	18.40	18.40		kcal/h m C
Uo	***45.3***	***55.2***		kcal/h m^2 C
Size of Heat exchanger(horizontal)				
wide			1.15	m
long			1.5	m
high			0.67	m

B6. Separator (S-1) Vessel – phase separator *(From R. Turton, R. C. Bailie, W. B. Whiting, J. A. Shaeiwits,"Analysis, Synthesis and Design of chemical processee", 2^{nd} Edition, Prentice Hall,p. 333)*

Type : Vertical vessel (liquid / gas separator)

Optimum length / diameter (L / D) = 3 (2.5 -5 is common)

Holdup time = 5 min for gas / liquid separator

Gas velocity u is given by

$$u = k\sqrt{\frac{\rho_l}{\rho_v} - 1} \quad \text{m/s}$$

where ρ_l = 928.51 kg/m^3

ρ_v = 1.81 kg/m^3

k = 0.0305 for vessels without mesh entertainers

(All of the constant values given from "Perry's Handbook of Chemical Engineering")

Good performance obtained at 30-100% of u ; for the typical value is 75%

Vapor flow = 447 kg/h P = 3 bar T = 135 °C ρ_v = 1.81 kg/m^3

Liquid flow = 671 kg/h P = 3 bar T = 135 °C ρ_l = 92851 kg/m^3

(Flow rate are given from the design calculation)

$$u = 0.0305\sqrt{\frac{92851}{1.81} - 1} = 0.69 \quad \text{m/s}$$

$$u_{act} = (0.75)(0.69) = 0.5175 \quad \text{m/s}$$

$$\text{Mass flow rate of vapor} = \frac{u\rho_v \Pi D^2}{4} = 447/3600 = 0.124 \quad \text{kg/s}$$

$$D^2 = 0.1687 \quad \text{m}^2$$

$$D = 0.41 \quad \text{m}$$

$$\therefore \quad \text{V of liquid} = \frac{0.5L\Pi D^2}{4} = 0.066 \quad \text{Lm}^3$$

$$\text{5 minutes of liquid flow} = (5)(60)(671)/928.51/3600 = 0.0602 \quad \text{m}^3$$

$$\therefore \quad \text{L} = \frac{0.0602}{0.066} = 0.912 \quad \text{m}$$

$L/D = 0.912/0.41 = 2.22$

$\therefore L = 1.025$ m

$V = 0.54$ m^3

B7. Liquid drum (S-2)

Type: Horizontal

Liquid velocity = 1118 kg/h

Holdup time = 7 (for a product feeding another equipment 5-10 min is common)

Performance = 73.5 % (good performance can be expected at velocity 30-100% of velocity)

Liquid flow = 1521 kg/h P = 3 bar T = 135 °C ρ_l = 958.365 kg/m^3

7 minutes of liquid flow rate = (7)(60)(1521)/958.365/3600 = 0.185 m^3

$$\therefore \quad \text{V of liquid} = \frac{0.5(3D)\Pi D^2}{4} = 0.375D^3 \ \text{m}^3$$

$\therefore$ D^3 = 0.5066 m^3

D = 0.8 m

$\therefore$ L = 2.4 m

V = 4.8 m^3

B8. Pump(P-1) *(From R. Turton, R. C. Bailie, W. B. Whiting, J. A. Shaeiwits,"Analysis, Synthesis and Design of chemical processee", 2nd Edition, Prentice Hall,p. 334)*

Power of pumping liquids: kW = (1.67) [Flow(m^3 / min)][ΔP(bar)] / ε

Where ε = Fractional Efficiency

Water flow rate = 850 kg/h *(From the designed data)*

Density = 994.032 kg/m^3 , T = 35 °C = 308 K (*From "Perry's Handbook of Chemical Engineering")*

ΔP = 2 bar

Head of pump $= \dfrac{2x10^5\,Pa}{994x9.8} = 20.53$ m

Volumetric flow rate = (850) /60/994.032 = 0.014 m^3/min (0.84 m^3/h)

Fluid pumping power = (1.67)(0.014)(2) = 0.04676 kW

Type : Rotary pump

The typical efficiency (ε) = 0.75

$\therefore$ Power of pump (P) = 0.04676/0.75 = 0.062 kW

B9. Pump (P-2)

Water flow rate = 1,118 kg/h *(From the design data)*

ρ = 958.4 kg/m^3

ΔP = 1 bar

Head of pump = $\dfrac{1x10^5\,Pa}{958.4x9.8}$ = 10.64 m

Volumetric flow arte = $\dfrac{1{,}118}{(60)(958.4)}$ = 0.019 m^3/min

Power = (67)(0.019)(1) = 0.0317 kW

Type : Rotary pump

The typical efficiency (ε) = 0.75

Power of pump (P) = 0.042 kW

B10. Air blower (A-1) *(From R. Turton, R. C. Bailie, W. B. Whiting, J. A. Shaeiwits,"Analysis, Synthesis and Design of chemical processee", 2nd Edition, Prentice Hall,p. 334, 344)*

Theorical reversible adiabatic power($W_{\text{rev adiab}}$) = $mz_1RT_1[(\{P_2/P_1\}^a-1)]/a$

Where T_1 is inlet temperature, R = gas constant, z_1 = compressibility, m = molar flow rate, a = (k-1)/k and k = C_p/C_v

Flow = 2007.07 kg/h T = 35 °C

P_1 = 1 bar

K = 1.41

a = 0.2908

$$m = \frac{2007.07}{(3600)(29)} = 0.019 \text{ kmol/s}$$

$W = (0.019)\,(1)\,(8.314)\,(308\,[(2)^{0.2908}-1]/0.2908$

= 37.36 kW

The typical efficiency of this equipment is 75%

W_{actual} = 49.81 kW

B11. Air blower (A-2)

The calculation of this equipment is the same as A-1 and from the design data we gave;

Flow = 5892.96 kg/h T = 35 °C

P_1 = 1 bar

K = 1.41 a = 0.2908

$$m = \frac{5292.46}{(3600)(29)} = 0.051 \text{ kmol/s } [46125 \text{ m}^3\text{/h} = 128 \text{ m}^3\text{/s}]$$

W = 99.698 kW

The typical efficiency of this equipment is 75%

W_{actual} = 132.93 kW

B12. Air blower (A-3)

The calculation of this equipment is the same as A-1 and from the design data we gave;

Flow = 17.29 kmol/h (311.20 kg/h) T = 800 ^{o}C

$$V = \frac{1073}{273}(17.29)(22.4) = 1522.238\ m^3/h$$

P_1 = 1 bar

P_2 = 2 bar

W = 32.9 kW

The typical efficiency of this equipment is 75%

W_{actual} = 43.87 kW

B13. Screw feeder (horizontal) (*From M. S. Peters, K. D. Timmerhaus, and R. E. West. "Plant design and Economics for Chemical engineer." 5th ed. P.550-566)*

$P = 0.07\ m^{0.85}L$

m = the mass flow rate of the solid(waste tires) = 850 kg/h = 0.236 kg/s

Density $\approx$ 550 kg/m^3 *(From designed data)*

$$\therefore \quad \text{Bulk capacity} = \frac{0.236}{550} = 0.000525 \quad m^3/s$$

$$= 1.89 \quad m^3/h$$

L = 5 m (assume)

$$P = 0.07\,(0.236)^{0.85}(5) = 0.1025 \quad kW$$

From capacity of the conveyer, the diameter can be shooed from figure 12-60 from the book referred above. So the diameter of screw feeder is 0.23 m.

APPENDIX C

Purchase cost of equipment

C1. Summary of purchase cost of equipment

Equipment	Code	Equipment function	Equipment specification		Capacity	Cost (US$)*
			Diam. (m)	**Length(m)**		
Screw feeder		Feed waste tires to the carbonizer	0.23	5.0	850 kg/h	2,286
Rotary carbonizer	R-1	Carbonization	1.33	3.11	850 kg/h	404,685
Rotary activator	R-2	Activation	1.56	7.07	323 kg/h	452,683
After burner	B-1	Eliminate smoke and foul smell	1.43	4.50	2,255,464 kcal/h	308,950
Separator	S-1	Vapor/liquid separator	0.41	1.03		13,223
	S-2	Hot water for	0.80	2.40		783
Heat exchanger	E-1	Generate steam for activation step	tube (1/2 in) length area	61 tubes 0.6 m 2.46 m^2	56,473 kcal/h	686
	E-2	Preheat water	tube (3/4 in) length area	67 tubes 1.5 m 57.53 m^2	39,969 kcal/h	784
Pump	P-1	Feed water to the heat exchanger(E-1)	0.062 kW		850 kg/h	1,763
	P-2	Feed hot water to the heat exchanger(E-2)	0.042 kW		1118 kg/h	3,657
Air blower	A-1	Force air to the rotary carbonizer	49.81 kW		2007 kg/h	1,567
	A-2	Force air to the after burner	132.93 kW		5292 kg/h	1,968
	A-3	Force exhause gas form afterburner to the rotary activator	32.90 kW		311.20 kg/h	4,858
Screening					106 kg/h	6,330
total						1,204,222

* The costs of delivered equipment are multiplied by the location factor (0.6) and local tax (7%)

Method used to calculate the equipment cost is in the references [20,21,25]

VITA

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