# CHAPTER I

# INTRODUCTION

## 1.1 Introduction

The management of used tires[1] has become a growing problem in recent years. Used tires represent one of several special wastes that are difficult for municipalities to handle. Whole tires are difficult to landfill because they tend to float to the surface. Stockpiles of used tires are located in many communities, resulting in public health, environmental and aesthetic problems.

Over 242 million used tires are generated each year in the United states. In addition, about 2 billion used tires have accumulated in stockpiles or uncontrolled tire dumps across the country. Millions more are scattered in ravines, deserts, woods, and empty lots. Used tires provide breeding sites for mosquitoes which can spread diseases and large tire piles often constitute fire hazards. In Canada, a large mountain of tires caught on fires with widespread environmental consequences due to the oils and gases generated from the decomposing tires. The supply and demand data in Thailand are shown in **Table 1.1 and Figures 1.1-1.2.**

Used tires present unusual disposal problems. The important characteristics that make them desirable as tires are long life and durability which make the disposal almost impossible. The fact that tires are thermosetting polymers means that they cannot be remelted and separated into their chemical components. Tires are also virtually immune to biological degradation. Landfilling used tires is unacceptable for several reasons. Not the least of which is the fact that they tend to rise to, and break through, the surface liner.

**Table 1.1** Supply and demand data of tire, inner tire and support inner tire in Thailand since 1988-1995[2].

| Year | Supply (tons) | | | | Demand (tons) | | | |
|---|---|---|---|---|---|---|---|---|
| | Tire | Inner tire | Support inner tire | Total | Tire | Inner tire | Support inner tire | Total |
| 1988 | 47,517 | 2,303 | 966 | 50,786 | 43,353 | 2,250 | 855 | 46,458 |
| 1989 | 55,670 | 2,638 | 1,119 | 59,427 | 51,598 | 2,656 | 1,113 | 55,367 |
| 1990 | 62,381 | 3,132 | 1,378 | 66,891 | 60,347 | 3,364 | 1,381 | 65,092 |
| 1991 | 69,380 | 3,007 | 1,274 | 73,661 | 59,892 | 3,084 | 1,220 | 64,196 |
| 1992 | 83,509 | 3,701 | 1,368 | 88,578 | 71,192 | 3,429 | 1,509 | 76,130 |
| 1993 | 88,454 | 3,403 | 1,398 | 93,255 | 76,362 | 3,797 | 2,114 | 82,273 |
| 1994 | 101,836 | 4,512 | 1,512 | 107,860 | 83,909 | 4,731 | 1,577 | 90,217 |
| 1995 | 118,571 | 5,278 | 1,713 | 125,562 | 102,384 | 5,576 | 2,094 | 110,504 |

**source:** Bank of Thailand.

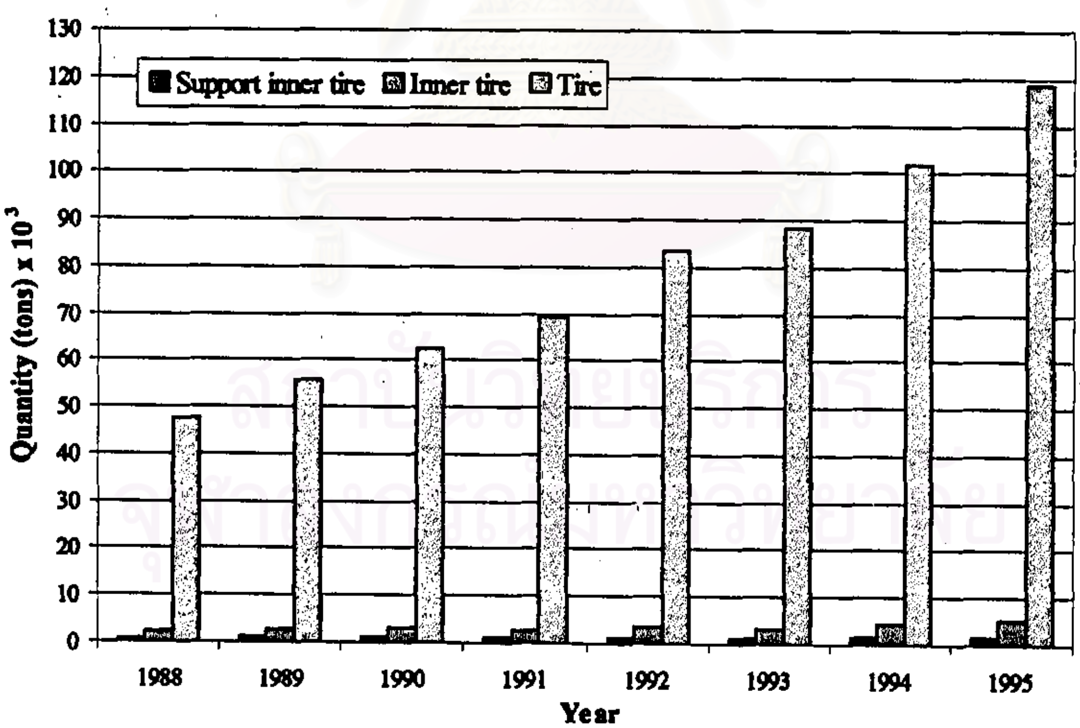



**Figure 1.1** Supply of tire, inner tire and support inner tire since 1988-1995[2].

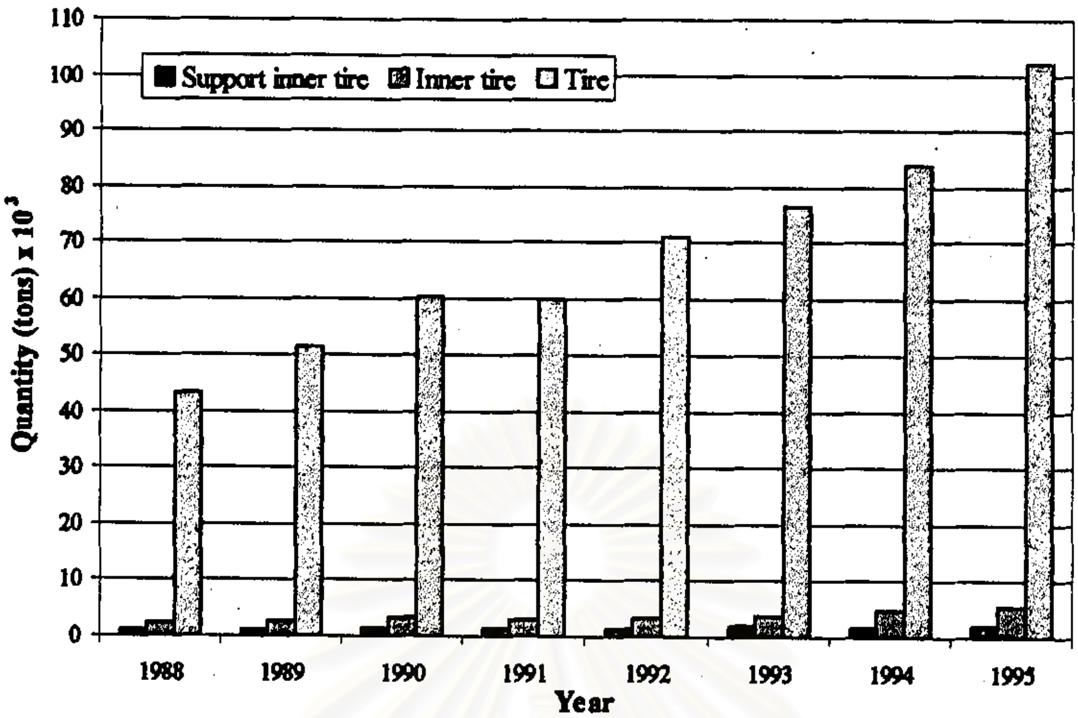



**Figure 1.2** Demand of tire, inner tire and support inner tire since 1988-1995[2].

Source reduction measures for tires include the following[1]: design of extended life tires, reuse of used tires and retreading. Some recycling alternatives use whole tires, thus requiring no extensive processing; other alternatives require that tires be split of punched to make products; and still other alternatives involve tires that are finely ground enabling the manufacture of crumb rubber products. Some applications for each alternative are listed below[1]:

Whole tire applications

- Artificial reefs and breakwaters
- Playground equipment
- Erosion control
- Highway crash barriers

Split or punched tire applications

- Floor mats, belts, gaskets, shoe soles, dock bumpers, seals, muffler hangers, shims, washers and insulators

Shredded tire applications

Lightweight road construction material

Playground gravel substitutes

Sludge composting

Ground rubber applications

Rubber and plastic products; for example, molded floor mats, mud guards, carpet padding and plastic adhesives

Rubber railroad crossings

Additives for asphalt pavements

Some of the attractive options for use of used tires include burning, either alone or with another fuel. Used tires have a fuel value of 12,000 to 16,000 Btu per pound, slightly higher than that of coal, in a variety of energy-intensive processes, such as cement kilns and utility boilers. However, tires burning has had repeated problems with products of incomplete combustion emitted into the atmosphere from uncontrolled burning of used tires. About 40 substances[3] have been assigned limits on emissions into the environment. Alkyl-substituted mono- and polyaromatic hydrocarbons were the predominant emission products. The best solution for an environmental and economic standpoint is to thermally reprocess the used tires into valuable products such as activated carbon.

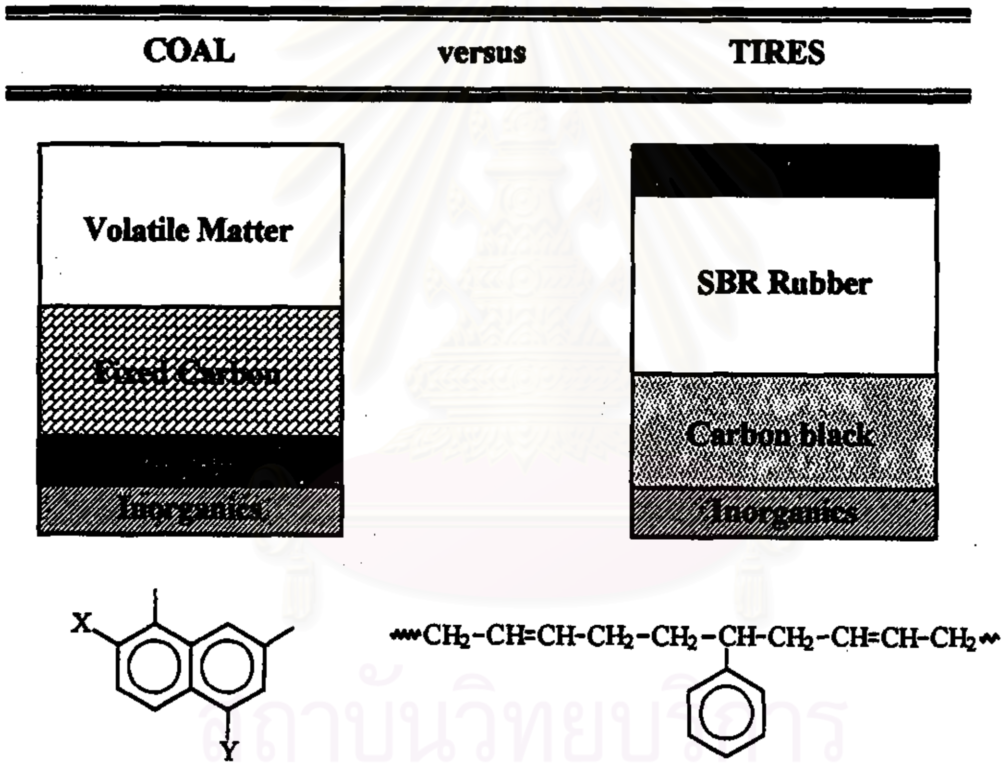
Tires[4] contain vulcanized rubber in addition to the rubberized fabric with reinforcing textile cords, steel of fabric belts and steel-wire reinforcing beads. The most commonly used tire rubber is styrene-butadiene copolymer (SBR) containing about 25 wt% styrene. Other rubbers used in tire manufacture include natural rubber (cis-polyisoprene), synthetic cis-polyisoprene and cis-polybutadiene. The carbon black is used to strengthen the rubber and aid abrasion resistance, and the extender oil is a mixture of aromatic hydrocarbons which serves to soften the rubber and improve workability. Sulfur is used to cross link the polymer chains within the rubber and also hardens and prevents excessive deformation at elevated temperatures. The accelerator is typically an organo-sulfur compound which acts as a catalyst for the vulcanization process. The zinc oxide and stearic acid also act to control the vulcanization process and in addition enhance the physical properties of the rubber.

**Table 1.2** Composition (wt%) of average tire[5].

| Compound basic composition | Examples of main compounding ingredients |
|---|---|
| Rubber | natural rubber, synthetic rubber |
| Vulcanizing agent | sulfur, organic vulcanizing |
| Vulcanizing accelerator | thiazole-type accelerator |
| Promotor | zinc oxide, stearic acid |
| Antioxidant | amine-type antioxidants, phenolic antioxidants, wax |
| Reinforcing cord | textile, steel |
| Filler | carbon black, silica |
| Softener | petroleum-type process oil, aromatic oil |

Used tires contain polymeric aromatic structures which are similar to those of coal in some respects. Thus, the well-developed techniques used in coal pyrolysis should also be applicable to the pyrolysis of used tires. Comparison of the structure and composition of coal and tires is shown in **Figure 1.3**.

Pyrolysis has been widely used for converting solid fossil fuels into liquid and gaseous hydrocarbons, a process which results in a solid char residue. Pyrolysis involves the thermal breakdown of used tires under oxygen exclusion[6]. Long polymer chains are degraded to fragments, which take the form of gas, oil, and solid carbon residue. Gases produced from tire pyrolysis are mainly hydrogen, carbon dioxide, carbon monoxide, methane, ethane and butadiene, with lower concentrations of propane, propene, butane, and other hydrocarbon gases. The yield of oil from tire pyrolysis is high, reflecting the potential of tire rubber to act as a substitute for fossil fuel and chemical feedstocks. The oils are mainly alkanes, alkenes, ketons or aldehydes as well as aromatic, polyaromatic and substituted aromatic groups, low sulfur content and are considered relatively good fuels. The oil product from tire pyrolysis is a potential source of energy and chemicals. The oils may be used directly as fuel of added to petroleum refinery feedstocks. The derived oil product may also be an important source of refined chemicals as it contains high concentrations of such chemical feedstocks as benzene, toluene and xylene. The carbon residue will become a marketable product if its properties are similar to those of commercial carbons. The carbon residue with a large adsorption capacity, however, can be produced only by activating the carbon residue under such conditions that the activation agent (steam, carbon dioxide, etc.) reacts with the carbon, it called " activated carbon".




**ELEMENTAL ANALYSIS**

| | | | |
|---|---|---|---|
| C | 82.4 | C | 88 |
| H | 5.5 | H | 8 |
| O | 8 | O | 2 |
| N | 1.7 | N | 0.5 |
| S | 2.4 | S | 1.7 |

**Figure 1.3** Comparison of the structure and elemental analysis of coal and tires[6].

Activated carbon is widely used as adsorbents in gas and liquid-phase separation processes, purification of products, and gas cleaning operations. One of the most important fields in terms of consumption is in water and wastewater treatment, where activated carbon with a relatively high surface area and a well developed porosity are needed. To obtain these activated carbons from cheap and readily available precursors becomes an interesting objective. Quantity and value of import and export of activated carbon in Thailand between 1988-1998 are shown in **Table 1.3** and **Figures 1.4-1.5.**

**Table 1.3** Quantity and value of import and export of activated carbon between 1988-1998 (Activated carbon code 3802.100-004)[7].

| Year | Import | | Export | |
|---|---|---|---|---|
| | Quantity (kg) | Value (bath) | Quantity (kg) | Value (bath) |
| 1988 | 1,932,203 | 52,327,284 | 260,802 | 8,118,737 |
| 1989 | 2,649,582 | 72,244,916 | 378,375 | 13,348,250 |
| 1990 | 2,321,914 | 75,358,548 | 663,917 | 25,001,383 |
| 1991 | 2,641,830 | 77,949,916 | 1,056,294 | 36,448,330 |
| 1992 | 2,706,967 | 101,418,463 | 1,027,131 | 34,008,219 |
| 1993 | 2,908,243 | 96,311,517 | 478,921 | 15,885,489 |
| 1994 | 2,816,400 | 103,186,178 | 522,068 | 18,246,436 |
| 1995 | 2,883,399 | 124,605,555 | 1,764,739 | 48,257,484 |
| 1996 | 3,047,195 | 100,836,897 | 2,937,245 | 75,682,676 |
| 1997 | 3,598,415 | 127,139,283 | 2,807,200 | 99,373,426 |
| 1998 (Jan-Apr.) | 1,090,437 | 40,559,567 | 1,160,900 | 54,840,113 |

**source**: Department of Business Economic, Finance Ministry.

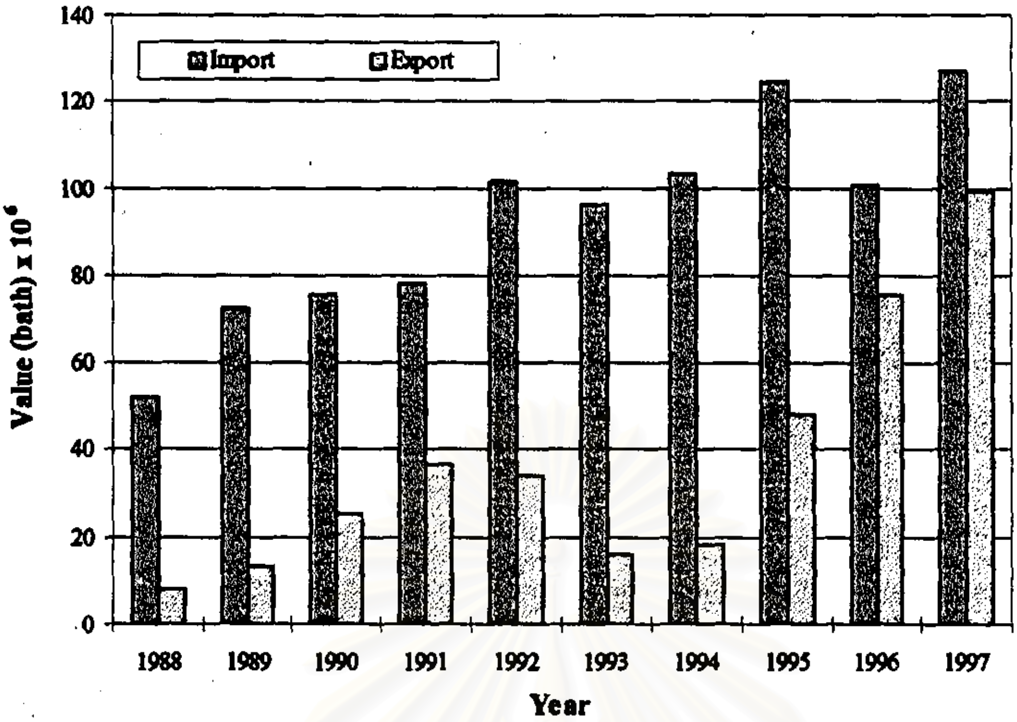



**Figure 1.4** Value of import and export of activated carbon in Thailand between 1988-1997[7].

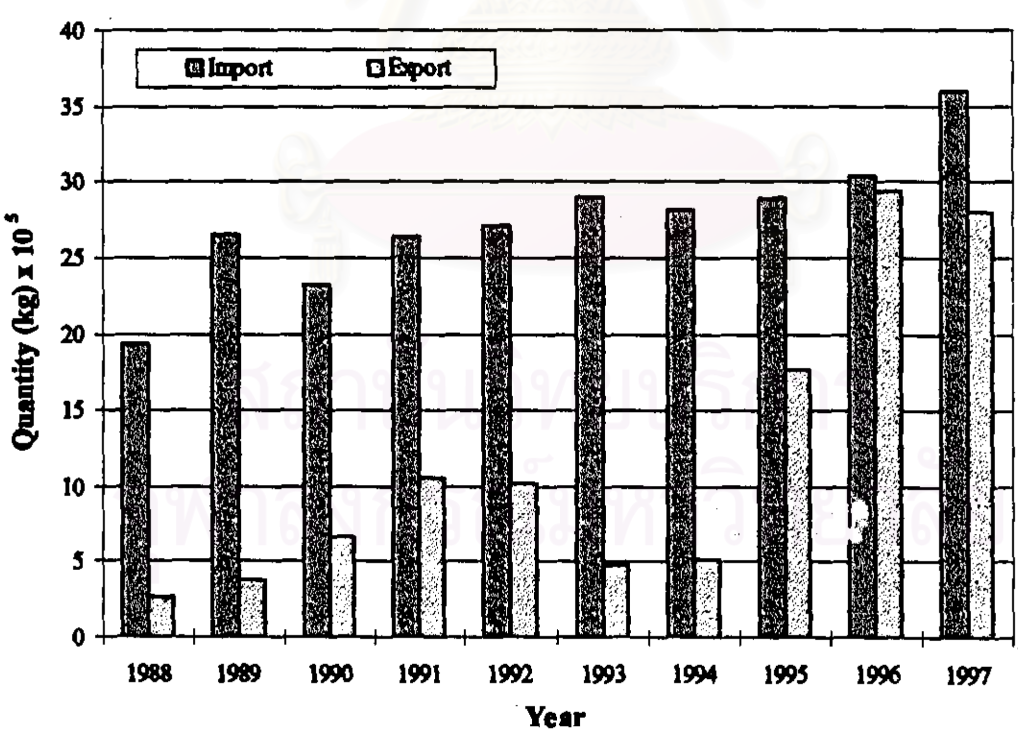



**Figure 1.5** Quantity of import and export of activated carbon in Thailand between 1988-1997[7].

Activated carbon is produced industrially from various raw material such as peat, coal, wood and coconut shells. Used tire is one of the interesting raw material because it is soft and easy for carbonization and main structures are carbon. Each year, used tires increase but they are just useless. Hence, the optimum condition in the production of activated carbon from used tires by carbonization followed by superheated steam and carbon dioxide activation in a fixed bed reactor has been studied in order to turn used tires into something which is valuable, and to decrease pollution too.

## 1.2 Objectives

1. To convert used tires to activated carbon by superheated steam and carbon dioxide activation in a fixed bed reactor.
2. To find optimum condition in the production of activated carbon from used tires.
3. To study physical and chemical properties of the resulted activated carbon.

## 1.3 Scope of the research

1. Determination of the optimum condition for carbonization from used tires by variation of the following parameters:
   (a) The optimum temperature
   (b) The optimum time
2. Proximate analysis of chars from carbonization step.
3. Determination of the optimum condition for activation by variation of the following parameters:
   (a) The optimum temperature and time
   (b) The optimum size of chars
   (c) The optimum flow rate of $CO_2$
4. Investigation of the properties of activated carbon such as % yield, % ash, bulk density, iodine number, methylene blue number and B.E.T. surface area.
5. Summarizing the results.