

CHAPTER II

LITERATURE REVIEW

2.1 Preparation of Activated Carbon from Waste Tires

N. Torikai, T. Meguro, and Y. Nakamura (1979) prepared activated carbon from residual carbon in tires by pyrolysis at 550°C for 30 minutes and activation in a stream of CO₂ at 900°C. They used rubber tires that contain three species of carbon blacks, which had different structures and diameters. They found that characteristic pore size distributions depended on the type of rubber species, natural or synthetic rubber, and particle size of carbon blacks present in the tires [2].

S. Ogasawara, M. Kuroda, and N. Wakao (1987) used automotive tires to produce activated carbon in a flow reactor. The results showed that H₂ 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 [3].

P.T. Williams, S. Besler, and D.T. Taylor (1990) pyrolysed shredded automotive tires in N₂ atmosphere at the pyrolysis temperature up to 720°C and at heating rates between 5 and 80°C/min. The %yield of char decreased as the pyrolysis temperature increased, while gas and oil products increased until 600°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. The surface area of the derived char showed a significant increase with increasing temperature and heating rate [4].

A.A. Merchant and M.A. Petrich (1993) produced activated carbon by pyrolyzing tires in a batch reactor and activating the resulting chars with superheated steam. A maximum micropore volume was observed as a function of conversion, but the total surface area increased monotonically with respect to conversion. They suggested that the porosity development during steam activation process consisted of micropore formation, followed by pore enlargement [5].

H. Teng, M.A. Serio, M.A. Wojtowicz, R. Bassilakis, and P.R. Solomon (1995) prepared activated carbon from used tires by pyrolysis in He or a mildly oxidizing atmosphere at up to 900°C and activation with CO₂ 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 [6].

R. Isarasaene and T. Vitidsant (1995) investigated the production of activated carbon from used tires in two consecutive processes: carbonization and superheated steam activation in a fixed bed reactor [7].

T.A. Brady, M. Rostam-Abadi, and M.J. Rood (1996) applied activated carbons from waste tires to use for natural gas storage and air pollution control. Their activated carbons had methane adsorption capacities (g/g) within 10% of the capacity observed for a commercial carbon. The methane storage capacity (V_m/V_s) of prepared activated carbon was almost 60% lower than the commercial carbon due to the much lower apparent density of tire char [8].

J. Sun, T.A. Brady, M.J. Rood, and C.M. Lehmann (1997) produced activated carbon for natural gas storage from scrap tires and Illinois coals by physical activation with steam or CO_2 and by chemical activation with KOH , H_3PO_4 , or ZnCl_2 . V_m/V_s values of tire-derived carbons were lower than those of coal-derived carbon because of their lower bulk densities. Compared with coal carbons, tire carbons had a higher percentage of mesopores and macropores [9].

A.M. Cunliffe and P.T. Wailliams (1998) used a nitrogen purged static-bed batch reactor to pyrolyse shredded scrap tyres at 450-600°C. Subsequently, tyre char was activated in a steam/nitrogen or carbon dioxide/nitrogen mixture at 835-935°C and then the prepared activated carbons were acid demineralized. All the obtained activated carbon had a greater mesopore volume than micropore volume, which was due to the predominantly mesoporous structure of the initial

tyre char. Tyre 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 tyre derived activated carbon over the investigated range [10].

T. Lortong and T. Vitidsant (1998) studied the production of activated carbon from used tires by the process of carbonization followed by activation with superheated steam and carbon dioxide in a fixed bed reactor to find the optimum conditions [11].

A.M. Cunliffe and P.T. Wailliams (1999) pyrolyzed used tires in a static bed batch reactor and activated the char in an equimolar mixture of either steam and nitrogen or carbon dioxide and nitrogen. Activation was a two-stage process, with an initial more rapid gasification of carbonized rubber deposits followed by less rapid gasification of carbon black. The burnoff achieved by carbon dioxide under otherwise identical conditions was on average 72% of that produced by steam. Acid demineralization of tire char prior to steam activation resulted in reactivity 22% less than that of the raw char. The results suggested that the demineralization process removed calcium ions which thereby reduced the catalytic effect of calcium on the gasification reaction [12].

J.L. Allen, J.L. Gatz, and P.C. Eklund (1999) prepared activated carbon by pyrolysis shredded used tires at 600-800°C in N₂ and then activation at 877°C in a steam-saturated nitrogen atmosphere. Prepared activated carbons were tested the butane working capacity (BWC) and to obtain optimal BWC, higher burn-off was found necessary. The results suggested that higher pyrolysis temperatures allowed mesoporosity to develop more readily and this porosity led to higher BWC [13].



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2.2 Preparation of Mesoporous Activated Carbon

A. Oya, S. Yoshida, J. Alcaniz-Monge, and A. Linares-Solano (1995) prepared activated carbon fiber by catalytic activation using cobalt. They mixed phenolic resin with cobalt-acetylacetonate, spun, cured, carbonized at 900°C, and finally activated at 750-900°C in steam. They suggested that the cobalt deposited a characteristic turbostratic carbon by catalytic graphitization during carbonization and simultaneously accelerated activation of fiber in steam catalytically to form mesopores preferentially [14].

H. Tamai, T. Kakii, Y. Hirota, T. Kumamoto, and H. Yasuda (1996) synthesized extremely large mesoporous activated carbons (mesopore ratio > 70%) by steam invigoration of pitches homogenized with 1-3 wt% of organo rare-earth complexes at 930°C. The resulting activated carbon was examined the adsorption of giant molecules, for example, vitamin B₁₂, blue acid 90 dyes, dextran, nystatin, and humic acid. They also found that the condensed polynuclear aromatics (COPNA) resin containing phenanthrene, perylene, and pyrene generated large mesopore volume [15].

D. Cazorla-Amoros, D. Ribes-Perez, M.C. Roman-Martinez, and A. Linares-Solano (1996) studied the effect of calcium on porosity development during activation of char from almond shell in steam and CO₂. The use of calcium in activation process could be a good procedure to create wider pores than can be achieved during the uncatalyzed carbon gasification. They also found that the effect of calcium on pore size distribution depended on the initial

porosity of carbon, the amount of calcium loaded, the calcium oxide sintering rate, and the rate of gasification [16].

N. Yoshizawa, Y. Yamada, T. Furuta, M. Shiraishi, S. Kojima, H. Tamai, and H. Yasuda (1997) attempted to prepare mesoporous activated carbon by steam activation of a mixture of coal and metal acetylacetonate at 900°C. The results showed that the porosity of activated carbon was influenced more by the type of acetylacetonate than by the rank of the coal. The activated carbon obtained from $\text{TiO}(\text{acac})_2$ had high mesoporosity even at an early stage of activation as evaluated by the BET and BJH analysis. They believed that the formation of mesoporosity in the activated carbon was closely related to the migration of TiO_2 from the carbon matrix [17].

R. Lebeda, J. Skubiszewska-Zieba, and W. Grzegorzczak (1998) investigated the effect of mode of calcium catalyst deposition on activated carbon produced from plum stones on the formation of micro- and mesoporous structures during gasification with steam. They presented that gasification of sample in presence of calcium catalyst caused the decrease of sorption capacity of micropores and the significant increase of mesopore surface. Moreover, the calcium catalyst deposited by the ion-exchange method was more effective in the creation of mesoporous structure than that deposited by the impregnation method [18].

H. Tamon, K. Nakagawa, T. Suzuki, and S. Nagano (1999) proposed a novel pre-treatment method of steam activation to develop mesoporosity of

activated carbons prepared from PET wastes. They mixed a calcium compound such as $\text{Ca}(\text{OH})_2$ and $\text{Ca}(\text{NO}_3)_2$ with raw material, carbonized this mixture, carried out HNO_3 acid treatment, and activated with steam, respectively. The results showed that activated carbons prepared with this novel pre-treatment had a larger mesoporosity than those without the pre-treatment [19].

Z. Liu, L. Ling, W. Qiao, C. Lu, D. Wu, and L. Liu (1999) studied the effects of various metals and their loading methods on the mesopore formation in pitch-based spherical activated carbon. They found that all loaded metals could increase the mesopore to micropore ratio and mesopore volume. Although different metals with the same loading method had similar effects on the formation of mesopore in the products, different loading methods of the same metal produced different size distribution of mesopores [20].

Z. Liu, L. Ling, W. Qiao, and L. Liu (1999) prepared pitch-based spherical activated carbon (PSAC) by steam activation under various carrier gases. The results showed that the ratio of mesopore volume in the product increased remarkably, but the micropore volume and micropore surface area decreased when the proportion of hydrogen increased. They concluded that PSAC with a higher ratio of mesopore could be prepared by the aid of hydrogen as well as iron [21].

S. Nagano, H. Tamon, T. Adzumi, K. Nakagawa, and T. Suzuki (2000) carbonized refuse derived fuel (RDF) produced from municipal solid wastes by partial combustion, and activated the carbonized RDF (cRDF) with steam. Since

the molecular sizes of dioxins determined by abinitio MO (molecular orbital) calculations were relatively large, the mesopores of activated carbons were necessary for adsorption of dioxins. They found that the activated carbon that was treated by HNO_3 prior to the steam activation had more mesopore volumes than the commercial activated carbon and should be effective for adsorption of dioxins. They also suggested that during the acid treatment the ash dissolution from cRDF resulted in the formation of active sites for developing mesopores [22].

Z. Hu and M.P. Srinivasan (2001) used coconut shells and palm seeds as raw materials to obtain activated carbons with high surface area by simultaneous treatment with zinc chloride and carbon dioxide as the physical and chemical agents, respectively. They also investigated the adsorption capacity and nature of the porosity by adsorption experiments using phenol, methylene blue, and erythrosine red. It was concluded that the capacities of the mesoporous activated carbon were much higher than those of microporous carbons for larger adsorbates [23].

Z. Hu, M.P. Srinivasan, and Y. Ni (2001) proposed an improved ZnCl_2 -chemical activation method to produce either microporous and mesoporous carbons from lignocellulosic materials such as coconut shells and palm seeds. The pore size of obtained activated carbon could be tailored in the range from supermicropore (1.5-2.0 nm) to small mesopore (2.0-3.49 nm). It was also reported that the adsorption of phenol, methylene blue, and erythrosine red on

prepared activated carbon from aqueous or ethanol solutions fit well the Freundlich equation [24].

K. Nakagawa, H. Tamon, T. Suzuki, and S. Nagano (2002) studied the preparation of activated carbon from Refuse Derived Fuel (RDF) at different carbonization condition and acid treatment. The lower heating rate in carbonization lead to higher carbonization yield and higher porosity of prepared carbon. The porosity of activated carbons prepared via acid treatment prior to steam activation was higher than that of carbons prepared without acid treatment, especially mesoporosity. According to water vapor adsorption isotherm, the surface of obtained activated carbons was hydrophobic [25].

K. Nakagawa, S.R. Mukai, T. Suzuki, and H. Tamon (2003) prepared activated carbons from carbonized PET by steam activation via pre-treatment by mixing PET with a metal salt [$\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Ca}(\text{OH})_2$, ZnO , and $\text{AlNH}_4(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$], and with acid treatment after carbonization. Activated carbons prepared with the pre-treatment for activation had larger mesoporosity than carbons prepared with no pre-treatment, and showed large adsorption capacity for $n\text{C}_4\text{H}_{10}$ and $i\text{C}_4\text{H}_{10}$. The metal salt has no influence on the microporous structure, but it does influence the mesoporous structure of prepared carbons. Application of the potential theory to adsorption data suggested that the pre-treatment contributes to the formation of pores larger than 0.5 nm at high burn-off [26].

2.3 Dye Adsorption on Activated Carbon

H. Tamon, T. Saito, M. Kishimura, M. Okazaki, and R. Toei (1990) applied ethanol regeneration to spent activated carbon that adsorbed an organic compound in aqueous solutions. High regeneration efficiency was achieved except for aromatic compounds substituted by electron-donating groups such as $-\text{NH}_2$, $-\text{OH}$, and $-\text{OCH}_3$. They also studied the solvent regeneration of carbon which adsorbed phenol using fixed-bed and found that the adsorption capacity of phenol on the regenerated carbon fell to 80% of that on the virgin carbon after five regeneration cycles [27].

S. H. Lin (1993) investigated the effectiveness of powered activated carbon (PAC) on the removal of chemical oxygen demand (COD) and a disperse dye, Red 60. The result revealed that the COD removal efficiency increased with decreasing particle mesh size. It was found that the multilayer BET isotherm fit the adsorption data better than the monolayer Freundlich and Langmuir isotherms [28].

M. Streat, J.W. Patrick, and M.J. Camporro Perez (1995) studied the sorption of phenol and *p*-chlorophenol from water on activated carbons derived from straw and used rubber tyres and compared with those from coal, coconut shell, and wood. Pseudo-equilibrium sorption of phenol and *p*-chlorophenol obeyed a Freundlich adsorption isotherm [29].

H. Tamon, M. Atsushi, and M. Okazaki (1996) studied the irreversible adsorption of electron-donating compounds such as phenol, aniline, L-

phenylalanine, and L-tyrosine on activated carbon and graphite. It was found that the irreversible amount adsorbed increased with the contact time. They proposed a two-state adsorption model to explain the irreversible adsorption. First, the compound was adsorbed in the precursor state and then moved to the irreversible state over a potential energy barrier after a long contact time [30].

H. Tamon and M. Okazaki (1996) measured adsorption and desorption equilibria of various kinds of aromatic compounds on an activated carbon and synthetic adsorbents. It was observed that in the desorption of aromatic compounds with electron-donating groups from activated carbon, the hysteresis occurred but on the other hand, the aromatic compounds with electron-attracting groups showed no hysteresis. In the adsorption on synthetic adsorbents, desorption isotherms coincided with adsorption ones. From the calculation of electronic state of adsorbents and adsorbates by semiempirical molecular orbital method, the irreversible adsorption appeared when the energy difference between HOMO value of adsorbate and LUMO value of adsorbent was small [31].

M. Sankar, G. Sekaran, S. Sadulla, and T. Ramasami (1999) 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 [32].

H. Tamai, T. Yoshida, M. Sasaki, and H. Yasuda (1999) 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 [33].

C. Hsieh and H. Teng (2000) 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-Radushkevich 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 [34].

C.C. Lin and H.S. Liu (2000) explored the adsorption of basic yellow dye on activated carbon from aqueous solutions under a centrifugal field and

interpreted the results by both a pseudo-first-order mechanism and intraparticle diffusion mechanism. The results revealed that the centrifugal force could enhance the rate constant, the rate parameter, and the diffusion coefficient [35].

C. Pelekani and V.L. Snoeyink (2001) used phenolic resin-based microporous activated carbon fibers with different micropore size distributions to investigate the role of pore size distribution in the mechanism of competitive adsorption between the organic micropollutant, atrazine, Congo red dye (CR) via kinetic and equilibrium experiments, including single-solute and simultaneous adsorption isotherms, and various modes of adsorbate preloading experiments [36].



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