CHAPTER II
LITERATURE REVIEW

2.1 Natural Gas

Natural gas is a type of fossil fuel, formed when layers of buried plants, and animals are exposed to intense heat and pressure over thousands of years. These underground organic matters is an energy source often used for heating, cooking, and electricity generation. It is also used as fuel for vehicles. Natural gas is a hydrocarbon gas mixture consisting primarily of methane, and also ethane (C_2H_6), propane (C_3H_8), butane (C_4H_{10}), pentane (C_5H_{12}). It often contains nitrogen and carbon dioxide impurities as shown in Table 2.1.

Table 2.1 Typical composition of natural gas (www.naturalgas.org)

Component	Chemical Formula	Composition (% wt)
Methane	CH_4	70-90%
Ethane	C_2H_6	0-20%
Propane	C_3H_8	
Butane	C_4H_{10}	
Carbon Dioxide	CO_2	0-8%
Oxygen	O_2	0-0.2%
Nitrogen	N_2	0-5%
Hydrogen sulphide	H_2S	0-5%
Rare gases	Ar, He, Ne, Xe	trace

Methane is colorless, odorless, and tasteless at room temperature thus it is one of the safest, cleanest, and most useful of all energy sources. Unlike other fossil fuels, natural gas is an environmentally friendly due to its clean burning and emits lower levels of harmful byproducts (60-90% less smog-producing pollutants and 30-40% less greenhouse gas emissions).

Currently, natural gas is cheaper than conventional fuels (gasoline and diesel). Consumption of the natural gas as a fuel for vehicle is rapidly increased. The consumption of natural gas is rapidly increasing in transportation sector in Thailand as a fuel for vehicle. However, natural gas has lower energy density than conventional and other alternative fuels at ambient conditions, which causes the driving range of natural gas based-fuels vehicle to be less than conventional vehicle.

The combustion of methane is shown as chemical equation 2.1. One molecule of methane is reacted with two molecules of oxygen, which in gaseous form to form one molecule of carbon dioxide in gaseous form which is low level emit, two molecules of water in liquid form, because of it is an exothermic reaction, the water released is usually in steam form with 891 kJ released from the reaction.

$$CH_{4[g]} + 2O_{2[g]} \rightarrow CO_{2[g]} + 2H_2O_{[l]} + 891\,kJ \tag{2.1}$$

2.2 Natural Gas Storage

When natural gas is used as a fuel, the storage method needs to be safe and effective. Scientists have tried to develop technologies to store large amounts of natural gas for transportation. Several ways to store natural gas are proposed and being implemented such as Compressed Natural Gas (CNG), Liquefied Natural Gas (LNG), and Adsorbed Natural Gas (ANG).

2.2.1 Compressed Natural Gas (CNG)

Compressed Natural Gas is a widely used method to increase the energy density of natural gas by compressing and storing it at high pressure (over 3,600 psi). Therefore, high pressure facilities and costly of cylinders are required. Furthermore, the CNG cylinder needs to be filled up more often than the gasoline or diesel tank (Solar *et al.*, 2010). Currently, the natural gas cylinder is produced mainly from steel, aluminum, and composite materials. To find the right type of cylinder for different vehicles, it depends on the duty cycle of the vehicle. Nevertheless, the cylinders are too heavy weight and use up a large amount of space.

2.2.2 Liquefied Natural Gas (LNG)

Natural gas can be stored as liquefied natural gas or LNG by cooling it to -161 °C at atmospheric pressure. However, this storage method shows many inconveniences including the use of complex and high liquefaction equipment. When pressure increases, it may result in a dangerous situation. Furthermore, the filling of the tank must be performed by a professional trained in cryogenic liquids handling. The shape of LNG storage tanks typically are cylinder or spherical. This storage method is applied to support the massive use in vehicles. For example, the cost of the on-board tank of a small vehicle is almost the same to the cost of heavy vehicle tank and it comes with even less net volumetric storage efficiency. Therefore, the cost of LNG vehicle refueling infrastructure is higher than CNG infrastructure (Solar *et al.*, 2010 and pttlng.com).

2.2.3 Adsorbed Natural Gas (ANG)

Adsorbed natural gas or ANG is another method of natural gas storage that can store natural gas at a low pressure. Pressures are relatively low, in the range of 290 to 580 psi at room temperature, which represents an interesting in both transportation and large scale applications. ANG works by using an adsorption agent or adsorbent which could be an inexpensive activated carbon material and molecular sieve in cylinder. Thus, ANG technology can support a greater storage volume of natural gas in the same container and at the same pressure than other technology or even in the same storage volume in the same container at a much lower pressure (Solar *et al.*, 2010).

2.3 Adsorption

Adsorption is a process that any substance accumulates on the surface of solid without penetrate into the bulk, in a concentration which is higher than in the bulk of substance. Adsorption can take place at any solid – fluid interface for gas – solid interface and liquid – solid interface. Adsorption process creates a film of the adsorbate (the molecules or atoms being adsorbed) on the surface of the adsorbent. It is different from absorption process by which the fluid molecules or atoms are diffuses into a liquid or solid to form a solution. The term "sorption" includes both adsorption and absoption process, while "desorption" is the reverse of adsorption.

Currently, adsorption is used and applied in many applications and systems. For example, the transportation system uses the adsorption agents such as, active carbon, carbon nanotube, molecular sieve or MOFs (Metal Organic Frameworks) in vehicle cylinder tank to maximize the capacity by enlarging the surface area of adsorbing gas molecules and also minimize the repulsion of molecules in gas phase. The experiment was carried out by using unmodified activated carbon and carbon nanotube agents under high condition to prove the agents abilities. Later, there are more studies and experiments to confirm this principle which brought in the improvement of CNG by using ANG, thus CNG can function at much lower pressure than non-adsorption system. The new discovered adsorption agent can fulfill this vision and allow CNG to function under pressure of 580 psi. However, there is none of the adsorption agent system used for vehicle storage in Thailand.

The adsorption is generally classified as physisorption and chemisorption. Physisorption or physical adsorption is based on the Van der Waals, dipole-dipole or London forces interactions between the adsorbed molecules and between the adsorbate and the substrate. The enthalpy is approximately 20 kJ/mol. Physisorption is a reversible process. Physisorption occurs mostly at low temperatures and occur as a preliminary state to chemisorption. The other type of adsorption is Chemisorption, and it occurs when there is the formation of a chemical (often covalent) linkage between adsorbate and substrate. The enthalpy is approximately 200 kJ/mol. Chemisorption is almost always exothermic and usually an irreversible process.

Physisorption is a process in which adsorbate molecules are transferred from the fluid phase on to the solid surface, while some are released again to the fluid state (Monocha, 2003) When the rates of adsorption and desorption process are equal, adsorption equilibrium will be obtained.

2.3.1 Adsorption Isotherms

When a gas comes into contact with a solid surface, atoms or molecules of the gas will be adsorbed on the surface in the bulk. Adsorption isotherm is the measurement of gas adsorbed as a function of partial pressures at a constant temperature. The amount adsorbed is nearly always normalized by the mass (or specific surface area) of the adsorbent in order to compare adsorption carpacity among different materials. Many different types of isotherm can be observed by their characteristics which depend on types of adsorbate, types of adsorbent and intermolecular interactions between the gas and the surface.

2.3.1.1 Type of Adsorption Isotherm

The adsorption isotherms are classified according to the molecular interactions between adsorbent surface and gas. Brunauer *et al.*, 1940; refers to Brunauer, Deming, Deming, and Teller or well known as BDDT, and IUPAC (1985) classified the types of the adsorption isotherms into five types. These BDDT isotherms and an additional one introduced much later by Sing, 1982, which completes the IUPAC classification. Six types of isotherm are illustrated in Figure 2.1.

Type I isotherm characterize microporous adsorbents. Microporous solids for this isotherm having relatively small external surfaces such as activated carbons. These isotherms reach a maximum value of adsorption without inflections. This isotherm is limited to the completion of a single monolayer of adsorbate at the adsorbent surface. At the first part of this isotherm having a relative pressure (p/p_0) from 0 to about 0.05 is an indication for the dimensions of the micropores. The steeper the gradient the narrower the micropores.

Type II isotherm (sigmoid or S–shaped) describes adsorption on non-porous or macroporous adsorbents. This isotherm indicates the beginning of an unlimited multilayer after completion of the monolayer (the region of relative pressure (p/p_0) > 0.1and $p/p_0 > 0.9$) and is found in adsorbents with a wide pore sizes distribution. At point B, a monolayer is completed and the adsorption occurs in successive layers at higher relative pressure.

Type III isotherm that is convex and describes adsorption with weak adsorbate-adsorbent interactions but strong interactions between adsorbate. This isotherm also describes the formation of multilayer and there is no flat region because the monolayer formation is disappeared.

Type IV isotherm is hysteresis loop, which is associated with capillary condensation occurring in mesopores. This isotherm is quite similar to type II at low relative pressure. The point of inflection indicates the completion of monolayer and the beginning of multilayer adsorption.

Type V isotherm represents mesoporous and microporous adsorbents and quite similar to type III but there is a capillary condensation in pores as the same pore size as type IV isotherm.

Finally, type VI isotherm describes stepwise multilayer adsorption on a uniform non-porous surface. Each step depends on the system and the temperature. These adsorption isotherms are for surfaces with an extremely homogeneous structure such as pyrolytic graphite that uses methane and argon as adsorbate but not N_2.

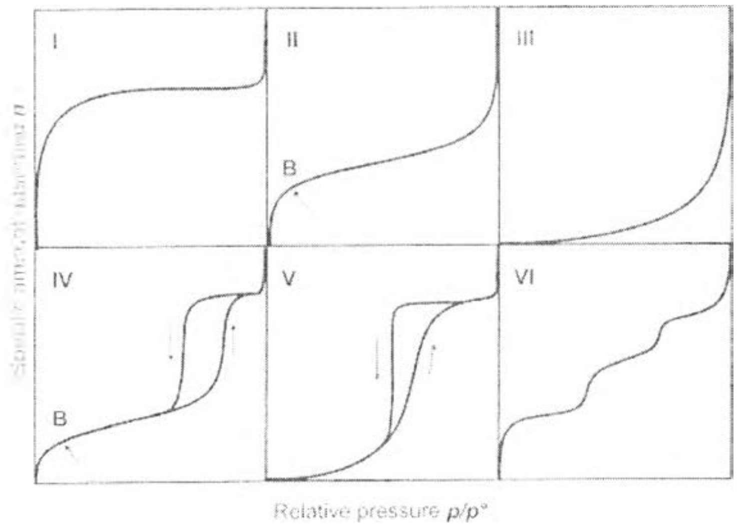

Figure 2.1 The IUPAC classification for adsorption isotherms (Rouquerol *et al.*, 1999).

2.4 Activated Carbon

Activated carbon is a high porous material and widely used as an adsorbent because of its large amount of micropores and well-developed pore structures and the resulting in high surface area (Li *et al.*, 2008). The raw material of activated carbon are carbonaceous matter with high carbon content and low level of inorganic compounds, such as coconut shell (Azevedo *et al.*, 2007), corn cob, wood (both soft and hard) and coal (anthracite, lignite, and bituminous coals) or complex one like polymer (Méndez-Liñán *et al.*, 2010).

Most carbonaceous materials have an internal surface area approximately 10-15 m^2/g. The internal surface area is controlled by oxidation of carbon atoms during the activation process. The activated carbon after activation step will have an internal surface area approximately between 700 and 1,200 m^2/g, depending on the operating conditions. As a generalization, pore diameters are usually categorized as follows: micropores < 20 Angstroms, mesopores 20-500 Angstroms, and macropores ≥500 Angstroms (Duad, 2004).

Activated carbon has not only used for sorption and catalytic applications but also used in the specific industrial applications such as oil and natural gas, food, pharmaceuticals, water treatment, hydro metallurgy, gold recovery and carbon-in-pulp process. Because the activated carbon is produced from naturally occurring raw materials; its properties could be varied. In order to minimize variability it is necessary to be very selective in raw material source, quality and also practice a high level of manufacturing quality control.

2.5 Nature of Activated Carbon Surface

Depending on the nature of partial oxidation reactions which occur during the activation of a carbon, 2 types of activated carbon can be produced. (Mattson and Mark, 1971; Hassler, 1974; Corapcioglu and Huang, 1987; Bansal et al., 1990): H-type and L-type.

"H type" activated carbon are produced under normal activation conditions in which high temperatures (above 750 °C) are used and exposure to steam or CO_2 is employed. H-type activated carbons exhibit positive charge in water by absorbing H^+ ions thus making water alkaline, and hydrophobic.

"L-type" activated carbon result from activation the carbons at low temperatures in air. L type behavior is expected to intensify after long exposure to the atmosphere even at ambient temperatures. These carbons are hydrophilic and take on a negative charge (OH^- ion) when immerse with water thus making water acid. These carbon also can neutralize strong base.

The differences between H-type and L-type carbons can be explained in term of oxidation processes which take place during activation, can resultant types of surface functional groups (carbon/ oxygen groups) which are created. With H-type carbons basic surface oxides predominate, whereas with L-type carbon acidic oxides predominate. There are various types of oxide groups for H and L- type carbon.

For H-type carbon,the predominant surface oxides are lactones, quinones, phenplic hydroxyls, and carboxylates (Ishizaki and Marti,1981). For L-type the predominant surface oxides are carboxyl, carbonyl, carboxylic acid, anhydride, lactone, cyclic peroxide groups (Corapcioglu and Huang, 1987).

2.6 Surface Modification and Ozone Treatment

Surface modification is the act of modifying the surface of a material by bringing physical, chemical or biological characteristics different from the ones originally found on the surface of a material. The modification can be done by different methods with a view to altering a wide range of characteristics of the surface, such as: roughness, hydrophilicity, surface charge, surface area, surface energy, biocompatibility, and reactivity.

Ozone, also known as trioxygen, is an inorganic molecule with the chemical formula O_3. It is a pale blue gas with a distinctively pungent smell. Ozone is formed from dioxygen by the action of ultraviolet light and also atmospheric electrical discharges, and is present in low concentrations throughout the Earth's atmosphere. Ozone's odor is sharp, reminiscent of chlorine, and detectable by many people at concentrations of as little as 10 ppb in air. In standard conditions, ozone is a pale blue gas that condenses at progressively cryogenic temperatures to a dark blue liquid and finally a violet-black solid.

Ozone is a powerful oxidant (far more than dioxygen) and has many industrial and consumer applications related to this oxidation reaction. Ozone oxidation has been occasionally used in the surface modification of activated carbon (Valde´s *et al.*, 2002) and also as a chemical method for its regeneration. Because ozone is a very strong oxidant (standard reduction potential, E0 = +0.076 V), it has been successfully used in the surface modification of carbon, which is a very stable chemically carbonaceous material (Jaramillo *et al.*, 2010).

The gas-phase oxidation of carbon by ozone is interpreted by a mechanism involving two chemical reactions at independent areas of the surface, C_{s1} and C_{s2}. The reactions at these sites are presented to be

$$C_{s1} + O_3 \rightarrow C_{s1}O_3 \quad (2.5.1)$$

$$C_{s2} + O_3 \rightarrow C_{s2}O + O_2 \quad (2.5.2)$$

where C_{s1}, and C_{s2} are the carbon atoms at edge sites S_1, and S_2, respectively (You *et al.*, 2002).

2.7 Literature Review

2.7.1 Natural Surface of Carbon and Surface Modification

Corapcioglu and Huang (1984) study the acidity of surface and characterization of some commercial activated carbons. They suggested that surface acidity of carbon, surface ash content and element composition can characterized surface properties of carbon. They used Alkalimetric titration and calculated by Gouy-Chapman theory of electrical double layer to determine surface acidity. Electrophoretic mobility measurement provided little information on the nature of the acidity of the activated carbons. From their results, they also suggest that, two types of activated carbon can be produced depending on the extent of oxidation reaction, H-type and L-type.

Chiang *et al.*, (2002) studied the surface characteristics of activated carbon as affected by ozone and alkaline treatment. They suggested that reaction between activated carbon and alkaline was another chemical means for the modification of surface property. Under alkaline environment, it was expected that OH^- ion will react with the surface functional groups of the activated carbon. Their main purpose was to evaluate the property changes on activated carbon surface by ozone and alkaline treatment. The surface chemical characteristics of treated activated carbon were determined in terms of surface functional groups and surface acidity. They used IR spectroscopic method and Boehm's titration technique to analyze surface functional groups and used electrophoretic mobility measurements to determine surface acidity. They found that ozone and NaOH treatment of activated carbon resulted in an increase of surface oxygen functional groups, especially in the phenolic and carboxylic categories. Because the increase in the formation energy of lactone was greater than that of other functional groups, the increase of lactone group intensity on activated carbon was not significant by either ozone or NaOH treatment. Based on their results obtained from this study and reported literature information, a preliminary pathway for O_3 reaction with activated carbon can be proposed. The reaction between carbon–hydrogen bond and ozone were introduced in two pathways, one was the formation of hydroxide compounds and the other was the generation of hydrotrioxide intermediates. Furthermore, carbon-carbon double bond may be produced from that hydroxide site. The hydrotrioxide intermediates will undergo three reaction pathways: First, the hydrotrioxide losses a hydrogen peroxide (H_2O_2) to form carbon–oxygen double bond. Second, the hydrotrioxide loss an O_2H to form radical •O. Finally, peroxide radical •OO were formed by deprotonated of hydrotrioxide. The peroxide and oxygen radical compounds might be further transformed to carboxylic compounds and subsequently lactone compounds.

Chingombe *et al.,* (2002) studied surface modification and characterization of a coal-based activated carbon. They used thermal and chemical methods such as nitric acid performed on coal-based activated carbon. The objective of their study was to investigate the effect of surface modification on the adsorption of trace metal ions and organic micropollutants from water. This study was highlights the first part of their research, i.e. the preparation and characterization of surface modified active carbon samples for environmental remediation. They found that nitric acid oxidation on activated carbon produced samples with weakly acidic functional groups and the presence of such groups. FTIR spectroscopy, pH titration, zeta potential measurements were used for their characterization to consist their functional group. Base on their result, there was a significantly decrease in microporosity of the oxidised samples. The humic substances that were formed as a by-product which caused loss in microporosity during the oxidation process. Main functional grourp were detected by X-ray photoelectron spectroscopy (XPS) analysis. Thermal treatment produced a carbon with some basic character while amination of the thermally treated carbon gave a sample containing some amino (–NH_2) groups.

2.7.2 Effect of Ozone on Serveral Type of Compound

You *et al*., (1994) compared the adsorption characteristics for VOCs on activated carbon and oxidized activated carbon. They investigated selected activated carbon, treated in NaOH solution and gas fluid with ozone from an ozone generator. The chemical and physical characteristics between the activated carbon and oxidized activated carbon were identified by FTIR, BET specific surface area and element analysis instruments. The system of adsorption apparatus consisted of a fixed adsorption column, quartz pan, electronic balance, and data acquisition system to measure the adsorption capacities and adsorption rates for VOCs under various operating conditions. VOCs, n-hexane, methyl-ethyl-ketone, and benzene were selected to evaluate the effect of adsorption characteristics on the activated carbon and oxidized activated carbon. The FTIR results of chemical analysis indicated the absorption bands and peaks measured at 1632 cm^{-1} on the oxidized activated carbons (in both activated carbon treated with NaOH ($AOHO_3$) and non-treated with NaOH activated carbon in ozone (AO_3)) are much stronger than on the activated carbon. Their result showed that carbonyl group was predominantly found to increase on the oxidized activated carbons ($AOHO_3$ and AO_3). Significant changed were observed for BET-specific areas for $AOHO_3$ and AO_3 but the carbon contented decreased slightly. They also concluded that the oxidized activated carbons showed greater affinity for polar adsorbate than former activated carbon, and for VOC adsorption, the overall effectived mass transfer coefficients, k_D, of AO_3, were larger than those of selected activated carbon and $AOHO_3$.

Chiang et al., (2002) studied surface characteristics of activated carbon as affected by ozone and alkaline treatment. Their purpose was to investigate the surface chemical characteristics of activated carbon treated by ozone and alkaline which were determined in terms of surface functional groups and surface acidity. IR spectroscopic method and Boehm's titration technique were used to analyze the functional groups on surface. Electrophoretic mobility measurements was use for determine the surface acidity of activated carbon. The oxygen concentration of activated carbon increased upon ozone and NaOH treatment. Surface functional groups increased mostly in the hydroxyl and carboxyl categories rather than the carbonyl category up on ozone and NaOH treatment.

Valde's *et al.*, (2002) studied effect of ozone treatment on surface properties of activated carbon. Their study was undertaken of modifications in the surface properties of a commercial activated carbon produced by its ozonation during different time periods. Surface chemistry of the activated carbon samples was characterized by selective neutralization, temperature-programmed desorption, X-ray photoelectron spectroscopy, and pH of the point of zero charge. Surface area and volume of micropores and mesopores were obtained from nitrogen adsorption isotherms at 77 K. Adsorption properties were determined by methylene blue adsorption index. Results showed that the higher the ozone dose, the higher is the oxidation of the carbon and the greater is the number of acid groups present on the carbon surface, especially carboxylic groups, whereas the pH of the point of zero charge decreased. The surface area, micropore volume, and methylene blue adsorption all reduce with higher doses. They also mention that the ozone attacked on the carbon and the fixation of oxygen groups on its surface.

Kingsley and Davidson (2005) studied the adsorption of toluene onto activated carbons exposed to 100 ppb ozone. They investigated the effect of 100 ppb ozone exposure on the adsorption of 1 ppm toluene on activated carbon are presented for dry (relative humidity less than 5%) and humid air (55% relative humidity). In dry air, the 10% toluene breakthrough times of granular carbon beds exposed to ozone for 208 days are 17% less than those of unexposed carbon beds. At 55% relative humidity, the corresponding reduction in toluene breakthrough time is 78%. For a humid environment with 100 ppb ozone, filter life would be reduced by more than half compared to the expected life based on tests in the absence of ozone. This degradation is attributed to changes in carbon surface chemistry, surface area, and pore volume that occur with relatively brief exposure to the ozone.

Park and Jin (2005) studied the effect of ozone treatment on ammonia removal of activated carbons (AC). They modified activated carbon via ozone treatment method to enhance the efficiency of removal of ammonia gas over the AC.

Surface properties of the AC were confirmed by X-ray photoelectron spectroscopy (XPS) analysis and N_2 adsorption isotherms at 77 K were investigated by BET and D–A methods to characterize the specific surface area, total pore volume, and micropore volume. The ammonia removal efficiency was confirmed by the gas-detecting tube technique. The results showed that the specific surface area and micropore volume of ACs were slightly destroyed as the ozone treatment time increased. However, the ozone treatment led to an increase in ammonia removal efficiency of ACs, mainly due to an increase of acid functional groups, such as carbonyl and ether groups, on carbon surfaces. It was revealed that the improvement of ammonia removal efficiency of ACs was greatly affected by the interfacial acid–base interactions between modified ACs and basic ammonia adsorbate.

Sanchez-Polo *et al.*, (2005) studied efficiency of activated carbon to transform ozone into •OH radicals. They found that the surface chemical and textural characteristics of the activated carbon determines its activity for the transformation of ozone into •OH radicals. The most efficient carbons in this process were those with high basicity and large surface. According to their results, the interaction between ozone and pyrrol groups presented on the surface of activated carbon increase the concentration of O^{-}_{2}• radicals. It's also enhancing ozone transformation into •OH radicals. On the other hand, as ozone exposures extended, the activity of activated carbon decreased. This may indicated that activated carbon does not really act as a catalyst but rather as a conventional initiator or promoter for the ozone transformation into •OH radicals. From their studies they suggest that the ozonation lead to an increase in decomposition constant (k_D), respectively, by favoring the removal of ozone-resistant contaminants.

Batterman and Metts (2006) studied the effect of volatile organic compounds loading on the ozone removal efficiency of activated carbon fliters. Activated carbon (AC) was used in air cleaning application to remove volatile organic compounds (VOCs) and ozone (O_3). The O_3 removal efficiency of AC filters after previous exposure to VOCs were investigated. Filter performance was tested using coconut shell AC and two common indoor VOCs, toluene and d-limonene, representing low and high reactivities with O_3. AC dosed with low, medium and high loadings (28–100% of capacity) of VOCs were exposed to humidified and ozonated air. O_3 breakthrough curves were measured, from which O_3 removal capacity and parameters of the Elovich chemisorption equation were determined. VOC-loaded filters were less efficient at removing O_3 and had different breakthrough behavior than unloaded filters. After 80 h of exposure, VOC-loaded AC samples exhibited 75–95% of the O_3 removal capacity of unloaded samples. O_3 breakthrough and removal capacity were not strongly influenced by the VOC-loading rate. Toluene-loaded filters showed rapid O_3 breakthrough due to poisoning of the AC, while pseudo-poisoning (initially higher O_3 adsorption rates that rapidly decrease) is suggested for limonene-loaded filters. Overall, VOC loadings provide an overall reduction in chemisorption rates, a modest reduction in O_3 removal capacity, and sometimes dramatic changes in breakthrough behavior, important considerations in filter applications in environments where both O_3 and VOCs are present.

Wu and You (2007) studied destruction of methyl ethyl ketone vapor by ozone on activated carbon. They attempted to combine the technologies of adsorption of volatile organic compounds (VOCs) on activated carbon and the oxidation of the VOCs by ozone (O_3). Their results showed that the destructive efficiencies of MEK by 1000 ppmv O_3 on activated carbon increased from 12.4% to 48.5%. From the power law kinetic model, the apparent kinetic constant, k, is obtained with a value of 0.0438 h^{-1}. The bed heights of activated carbon generally increased while the destruction of MEK exposure and caused the increasing in ozone concentration. When the ozone concentration is increased to 7800 ppmv and the amount of activated carbon is increased to 5 g the destructive efficiency of MEK is still greater than 95% even after a prolonged operational time. From their results, they indicated that an adsorption process in combination with ozone oxidation showed good potential for the control of VOCs and odor.

Álvarez *et al.*, (2011) studied granular activated carbon promoted ozonation of a food-processing secondary effluent. They reported in term of the application of a simultaneous combination of ozone and a granular activated carbon (O_3/GAC) as a tertiary treatment of a wastewater generated from the activity of various food processing industries. Prior to the O_3/GAC treatment, the wastewater was subjected to conventional primary and secondary treatments in a full-scale wastewater treatment plant (WWTP). The effluent from the WWTP presented high organic load (COD > 500 mg/l and TOC > 150 mg/l), which could be much reduced by the O_3/GAC treatment. Results from the O_3/GAC experiments were compared with those obtained in single ozonation, single adsorption on to GAC and sequential O_3–GAC adsorption experiments. While single processes and the sequential one showed limited capacity to remove organic matter for the food-processing effluent (COD removal <40%), the simultaneous O_3/GAC process led to decreases of COD up to 82% at the conditions here applied. The combined process also improved the ozone consumption, which decreased from about 19 g O_3/g TOC (single ozonation process) to 8.2–10.7 g O_3/g TOC (O_3/GAC process). The reusability of the GAC throughout a series of consecutive O_3/GAC experiments was studied with no apparent loss of activity for a neutral GAC (PZC = 6.7) but for a basic GAC (PZC = 9.1).

2.7.3 Methane Adsorption by Several Types of Adsorbents

Dreisbach *et al.*, (1999) studied the methane, nitrogen, carbon dioxide and their binary and under the pressure up to 870 psi with the steady temperature 25°C ternary mixtures adsorption on activated carbon under high pressure. The adsorption was measured by gravimetric method. Co-adsorption of the three mixtures CH_4/CO_2, CH_4/N_2, and CO_2/ N_2 were measured by the volume-gravimetric method in the same range of pressure and at the constant temperature. Five ternary mixtures $CH_4/CO_2/N_2$ isotherms were measured under the same pressure and temperature by using the volume-chromatographic method for constant concentrations of the adsorptive. In order to correct the measured data in volumetric or gravimetric experiments, the activated carbon so-called helium volume was used for adsorbed the surface excess amounts. The result of pure gas adsorption data are correlated with Langmuir isotherm which accounted in the adsorbent heterogeneity and fractal character of the internal microporous structure. Binary and ternary mixtures adsorption can be predicted by this model with the only pure gas adsorption parameters. There was a big success in this study as the predicted and experimental data were almost the same which suggested that prediction of the total amounts adsorbed came with deviation below 5%, the concentrations of the adsorbate of the binary mixtures with deviation below 9%, and the concentrations of the strongly adsorbed components of the ternary mixture in the adsorbate could be predicted from pure gas data with deviation below 15%.

Lozano-Castelló *et al.*, (2002) studied the methane storage applications by using different raw materials, activating agents, and preparation variables to compare the behavior of carbon materials with different morphologies. Activated carbons were prepared from chemical and physical process. Surface area and micropore size distribution (MPSD) were prepared on both types of materials. The results indicated that there was a direct relationship between the methane adsorption capacity of the adsorbent and micropore volume. Furthermore, the raw material and activation process method used for its preparation had no effect on adsorption capacity. Also, it showed that methane adsorption capacity depended on the MPSD.

Balathanigaimani *et al.*, (2006) studied the preparation and methane adsorption properties of powdered rice husk activated carbon. To achieve the storage natural gas by using adsorbed natural gas (ANG) was mainly based on the characteristics of the adsorbent. Thus the researchers focus on the different synthesized adsorbents including activated carbon from rice husk (AC-RH) compared with phenol based activated carbon (AC-PH_2O and AC-PKOH). The adsorption experiments were conducted by volumetric method under different constant temperatures (20, 30, 40, and 50 °C) and pressure up to 507 psi. The adsorbed amounts of methane on adsorbents were calculated by using a mass balance equation. The results showed that maximum methane adsorption was observed in AC-RH as its higher surface area than the other two adsorbents. The experimental data were correlated well with Langmuir-Fruendlich isotherms because of its flexibility and low percentage error. From Langmuir-Fruendlich isotherms indicate that AC-RH has heteroheneous surface while AC-PH_2O and AC-PKOH have homogeneous surfaces. Moreover, isosteric heat of adsorption was calculated by using Clausius-Clapeyron equation. The results from the Clausius-Clapeyron equation also confirmed the Langmuir-Fruendlich isotherm results.

Salehi *et al.*, (2007) studied the theoretical and experimental study to find out the accurate amount of methane adsorption and desorption by using four granular activated carbon or GAC samples under different physical conditions. The volumetric method was used to measure equilibrium of methane adsorption at temperature of 25°C and the pressure used up to 500 psia. Moreover, the different equilibrium pressures, a constant temperature, and various adsorption isotherm models were also studied. The results indicated that the physical characteristics of activated carbon which consisted of BET surface area, micropore volume, packing density, and pore size distribution were important factors in the amount of adsorption and desorption of methane.

Najibi *et al.*, (2008) studied the Methane/natural gas storage by measuring the capacity of three different activated carbons for both dry and wet conditions. The different of wet and dry conditions were only at before loading the activated carbon which was mixed with specific amounts of distilled water into the cell. This experiment used the water ratio (the ratio of the weight of water to the weight of dry activated carbon) at $R_w = 1$. This work was maintained at constant temperature (-196 °C) and pressure was up to 1450 psi. In all three types of activated carbons tested, the capacity of natural gas storage in dry condition was greater than in wet conditions, but the gas delivery was almost the same value. Hydrate might occurred in one of the activated carbon (NC120) at pressure greater than 580 psi while the amount of gas stored was less than in dry conditions overall the pressure. The study showed that the gas released from the activated carbons in each pressure in the dry conditions would change in composition. Moreover, it also indicated that the amount of heavy components were unable to come out of the bed even applied at very low pressures. Repeatability of the sorption/desorption processes–studying for industrial using, it found that the efficiency of repeatability was decreased for the natural gas after only a few cycles, probably due to accumulation of heavier components in the natural gas.

Alcañiz-Monge *et al.*, (2009) researched fundamentals on methane adsorption on microporous carbons. Also, methane (CH_4) adsorption on a series of microporous activated carbons (AC), activated carbon fibers (ACF) and superactivated carbons (SAC), under supercritical conditions (25 °C and 580 psi) were studied. The results showed that CH_4 adsorbed in narrow micropores which less than 0.7 nm and CH_4 adsorption data perfectly fitted in the characteristic curve with uniform micropore size distribution (MPSD). Conversely, carbons with heterogeneous MPSD, CH_4 adsorption data unable to fitted the characteristic curve. Pore size would effect on the adsorbed CH_4 density at supercritical conditions. Even though CH_4 could be adsorbed in the microporosity and filled it as a compressed gas, the methane adsorption was related to the specific BET surface area. A linear relationship was observed between the estimated BET surface areas obtained from both CH_4 and N_2.

Delavar *et al.*, (2010) studied the experimental evaluation for methane storage by granular activated carbon (GAC) through the equilibrium adsorption. The volumetric apparatus (pressure decay) was used for methane adsorption on GAC. The methane adsorption isotherms were determined by the measurement of equilibrium uptake of methane under pressures within range of 0-725 psi and at temperatures of 12-55 °C. Freundlich and Langmuir equations were proper to determine the model isotherm. The isosteric heat of methane adsorption was calculated from Sips isotherm model by the Clausius-Clapeyron equation. From their result they indicated that the isosteric heat of methane adsorption decrease with decreasing temperature or increasing amount of methane.