

CHAPTER II

LITERATURE REVIEW

2.1 Natural Gas

Natural gas is often referred to gas consisting mainly of methane and can be found associated with other fossil fuels. It is well-known to be an important fuel source, a major feedstock for fertilizers, and notoriously a potent greenhouse gas. In retrospect, it had been dismissed as a useless byproduct of crude oil production until the second half of the 20th century, natural gas become an important energy source and now provides 23 percent of all energy consumed in the world. Cleanest-burning conventional fuel, natural gas is an economical, environmentally friendly and efficient energy source. It produces lower levels of greenhouse gas emissions than heavier hydrocarbon fuels, such as coal and oil do. Historically, natural gas also has been one of the most economical energy sources.

2.1.1 Natural Gas Storage

For using natural gas as a fuel, natural gas storage plays an important role to safely and efficiently store natural gas. Since, natural gas composes mainly of methane which is a small molecule; it is hard to store natural gas in a high density. Researchers have developed technologies to carry high amount of gas for transportation. The following are ways to store it.

2.1.1.1 Compressed Natural Gas (CNG)

Compressed natural gas or CNG is the well-known natural gas storage method for vehicle. This clean developed technology stores natural gas under high pressure condition up to 20-25MPa (200-250 bars). To operate under high pressure, high cost of cylinders used and high-pressure facilities required. Compressed natural gas storage tanks are available from many manufactures and have been certified by standard agencies worldwide. Steel aluminum and plastic are material mainly used in natural gas cylinder production today. Ultimately, the duty cycle of the vehicle will determine the most appropriate choice of cylinders. However, one perception that often arises is that the cylinders weigh too much or

take up too much space. As a result, there will be a need to fill up a CNG cylinder more frequently than a gasoline or diesel tank.

2.1.1.2 Liquefied Natural Gas (LNG)

LNG is another known gas storage method. Natural gas is liquefied under pressure of 10-20 bars at minus 161.5 °C. LNG requires the use of complex and expensive liquefaction equipment, thermos-like tanks and significant energy consumption (25-35% of the original energy gas content) for the liquefaction and degasification. LNG storage tanks can be in cylindrical or spherical shape. Even this technology are used in marine transportation, it is not yet mature enough for massive use in vehicles. On-board tank for a small vehicle costs almost as much as for a heavy vehicle and has much lower net volumetric storage efficiency. LNG vehicle refueling infrastructure costs even more than CNG

2.1.1.3 Adsorbed Natural Gas

ANG or adsorbed natural gas technology allows the storage of natural gas at substantially higher volumetric capacities than pressurized storage for an equivalent pressure, making use of adsorption of gas on a adsorption agent (adsorbent) like low-cost activated carbon material, molecular sieve in cylinder. In the other word, ANG is a technology providing a larger volume of natural gas that can be stored in the same container, at the same pressure or can be stored in the same volume of natural gas in the container at a much lower pressure.

2.2 Adsorption

Adsorption is a process by which a molecules or atoms in a gas or liquid phase, attaches to or sit on a solid surface. This process creates a film of the adsorbate (the molecules or atoms being accumulated) on the surface of the adsorbent. Distinguished from absorption process by which the fluid molecules or atoms are dissolved by a liquid or solid. The term sorption includes both processes, while desorption is the reverse of adsorption.

Adsorption is present in many systems and applications today. For transportation, adsorption agents or adsorbents; Activated carbon; Carbon nanotube; Molecular sieve and MOFs; are applied into vehicle cylinder tank to increase

capacity by providing high surface area for adsorbing gas molecules and also reducing repulsion between the molecules in gas phase in the same time. In this experiment, using unmodified Activated carbon and Carbon nanotube agents under high condition (20-25MPa) are studied to examples of adsorption agent that have been developed and studied. Even more and more researches have been done experiments and confirmed about this principle and also move forward to ANG (Adsorbed Natural Gas) technology which can make CNG system can operate at much lower pressure than non-adsorption system (new discovered adsorption agent can make storage can operate under pressure downed to 4MPa), there are no adsorption agent system used for vehicle storage in Thailand.

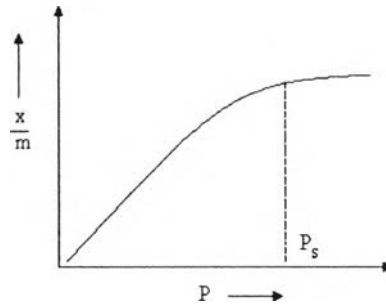
2.2.1 Isotherms

Adsorption is usually described through isotherms to determine the amount of adsorbate on the adsorbent as a function of its pressure (if gas) or concentration (if liquid) at constant temperature. The quantity adsorbed is nearly always normalized by the mass (or specific surface area) of the adsorbent to allow comparison of different materials. Many different types of isotherm can be observed by their unique characteristic which depend on types of adsorbate, types of adsorbent and intermolecular interactions between the gas and the surface

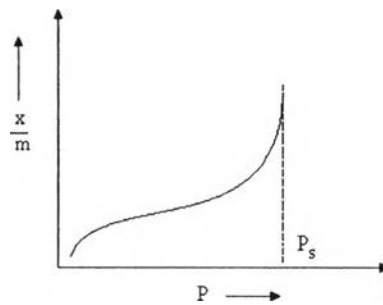
2.2.1.1 *Type of Adsorption Isotherm*

In 1940, the first systematic interpreting adsorption isotherm for gas-solid equilibria was introduced by Brunauer, Deming, Deming, and Teller (BDDT) [8]. They classified isotherm into five types. These BDDT isotherms and additional one introduced much later by Sin, which completes the IUPAC classification. Five types of isotherm are illustrated in following figures [9][10]. The BDDT and IUPAC classification have two deficiencies: they are incomplete and they give the incorrect impression that adsorption isotherms are always monotonic functions of pressure.

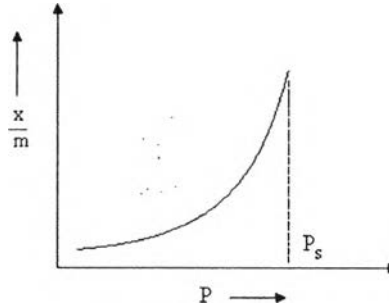
Type I Adsorption Isotherm: Typical of microporous solids and chemisorptions isotherms



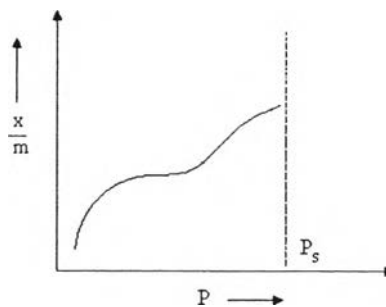
Type II Adsorption Isotherm: Finely divided non-porous solids.



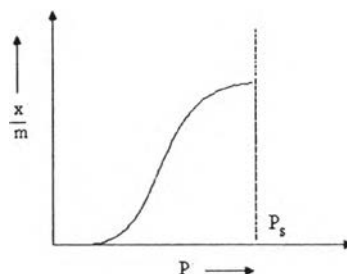
Type III Adsorption Isotherm: Typical of vapor adsorption



Type IV Adsorption Isotherm: The rare step-like isotherm type is shown by nitrogen adsorbed on special carbon.



Type V Adsorption Isotherm: The capillary condensation of the adsorbate in the mesopores of the solid (a hysteresis loop).



2.3 Activated Carbon

Activated carbon is used for adsorption of organic substances and non-polar adsorbates and it is also usually used for waste gas (and waste water) treatment. It is the most widely used adsorbent. Its usefulness derives mainly from its large micropore and mesopore volumes and the resulting high surface area. Highly porous, amorphous solid consisting of microcrystallites with a graphite lattice of activated carbon usually prepared in small pellets or a powder. It is non-polar and cheap. The raw material for activated carbon are carbonaceous matter such as coconut shell (Marcos *et al.*, 2007; Wan *et al.*, 2003; Wei *et al.*, 2008), corn cob (Abdel-Nasser *et al.*, 2000) and types of coal (Gong *et al.*, 2009; Li-Yeh *et al.*, 1999; Jian *et al.*, 1996); or complex one like polymer (Laura *et al.*, 2010). Anthracite and bituminous coals have been the major sources. Starting with initial pores present in the raw material, more pores, with desired size distributions, are created by the so-called activation process. There are two type of activation used in producing activated carbon.

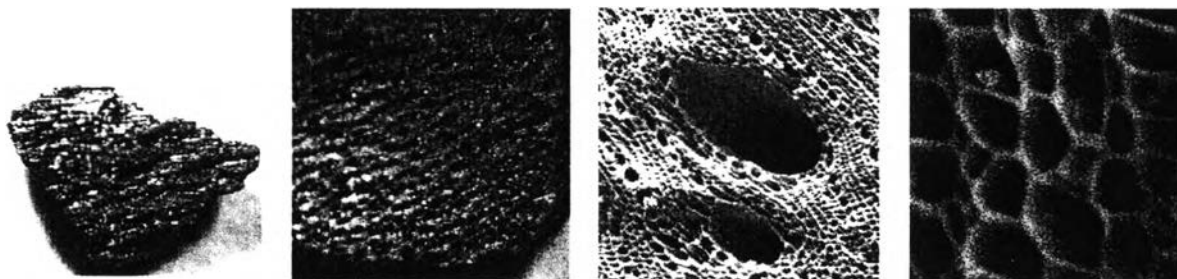


Figure 2.1 Surface and pores of activated carbon, as viewed by an electron microscope (magnification increase left to right).

2.3.1 Physical Activation

After initial treatment and pelletizing, one activation process involves carbonization at 400-500°C in oxygen-deficient condition to eliminate the bulk of volatile matter, and then partial treatment and partial gasification at 800-1,000°C to develop the porosity and surface area. A mild oxidizing gas such as CO₂, steam, or flue gas is used in the activation step because the intrinsic surface reaction rate is much slower than the pore diffusion rate, thereby assuring the uniform development of pores throughout the pellet. This activation step burns off the pore blocking structures created during the carbonization phase and so, they develop a porous, three-dimensional graphite lattice structure. The size of the pores developed during activation is a function of the time that they spend in this stage. Longer exposure times result in larger pore sizes.

2.3.2 Chemical Activation

The other commercial activation processes depend on the action of inorganic additives to degrade and dehydrate the cellulosic materials and, simultaneously, to prevent shrinkage during carbonization. Lignin can be used as a raw material by first blended with activators such as phosphoric acid, zinc chloride, potassium sulfide, or potassium thiocyanate, and then it is carbonized at temperatures up to 900°C. The product is usually in powder form and can be applied for both aqueous and gas phase adsorption.

2.4 Literature Review

In 2008, Macos *et al.* investigated the preparation of granular activated carbon from coconut shell by combining chemical activation with H₃PO₄ or ZnCl₂ followed by physical activation with CO₂. Granular activated carbon can be prepared from three different methods; chemical activation with H₃PO₄ or ZnCl₂, physical activation with CO₂, and combining chemical activation followed by physical activation. From their experiments, physical activation provides more homogeneous pore structure than chemical activation whereas chemical activation provides positive

2.4 Literature Review

In 2008, Macos *et al.* investigated the preparation of granular activated carbon from coconut shell by combining chemical activation with H_3PO_4 or ZnCl_2 followed by physical activation with CO_2 . Granular activated carbon can be prepared from three different methods; chemical activation with H_3PO_4 or ZnCl_2 , physical activation with CO_2 , and combining chemical activation followed by physical activation. From their experiments, physical activation provides more homogeneous pore structure than chemical activation whereas chemical activation provides positive effect on the material density. Moreover, they found an important point on using low proportion of chemicals (X_p and X_{Zn} values up to 0.15 and 0.32 respectively) permits the development of a narrow microporosity without inducing significant reduction of bulk density. According to these results, it was logical to check possibility to obtain carbons with improved volumetric adsorption capacity by combining both modes of activation.

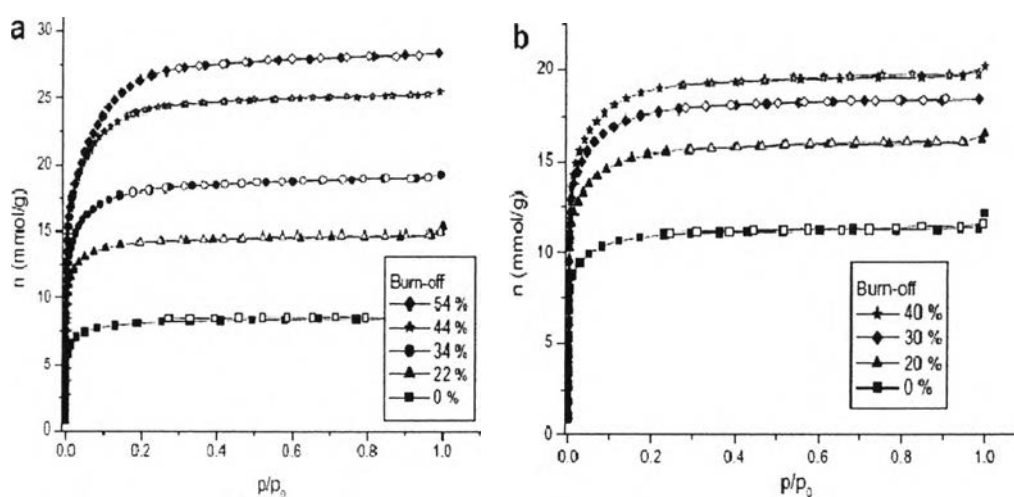


Figure 2.2 N_2 adsorption–desorption isotherms of granular carbons obtained by physical activation with CO_2 up to different burn-off values. The 0% of burn off corresponds to the samples generated by chemical activation of coconut shell (2.00–2.83 mm) with (a) H_3PO_4 ($X_P = 0.09$) or (b) ZnCl_2 ($X_{Zn} = 0.25$) followed only by carbonization up to 850°C . Full symbols: adsorption; open symbols: desorption.

Followed the above hypothesis, the combining procedure permitted well-developed and homogeneous porosity, as shown in Figure 2 the nitrogen adsorption-desorption isotherm, and in Table 1 the high bulk density. The volumetric adsorption capacity goes through a maximum around 85 V/V in whether H_3PO_4 or ZnCl_2 used in chemical activation when the adsorption capacity by mass unit and the bulk density increase in opposite direction.

Table 2.1 Bulk density and methane adsorption capacity for the carbons produced by physical activation with CO_2 up to different burn-off values

Chemical	Burn-off (%) ^a	Bulk density (g/cm^3)	$V_{\text{ads}} \text{CH}_4$ (V/V) ^b
H_3PO_4 ($X_{\text{P}}=0.09$)	0	0.68	64
	22	0.55	83
	34	0.49	85
	54	0.45	84
ZnCl_2 ($X_{\text{Zn}}=0.25$)	0	0.65	65
	20	0.56	84
	30	0.52	86
	40	0.49	83

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^a During physical activation with CO_2 .

^b Volume of methane adsorbed at 25°C and 3.5 MPa.

To increase the adsorption capacity, additional work on the effect of increasing the particle size of the precursor to 2.83-4.00 mm which gave rise to activated carbons with similar porosity but higher bulk density. This way leads to the maximum volumetric methane adsorption capacity at 90 V/V. Moreover, the mixture of large particle size (2.83-4.00mm) and small size particle (0.71-1.00mm) activated carbon with adequate proportion. The maximum adsorption capacity goes up to 95

V/V because of additional reduction of the inter-particle space. This value is the highest for granular activated carbons.

In 2007, Diana *et al.*, activated carbon adsorption characteristic prepared from coconut shells using chemical activation with zinc chloride followed by physical activation was studied. In experiment, they prepared two samples using (1) chemical activation with $ZnCl_2$ in 1:1 weight ratio and then part of this sample was followed by (2) physical activation. After that, nitrogen isotherm at 77K were measured in a surface area analyzer Quantachrome Autosorb-1 MP and shown in the following table.

Table 2.2 Textural parameters of the AC samples

Sample	BET area (m^2/g)	Total pore volume (cm^3/g)	Micropore volume (cm^3/g)	Average pore width (\AA)	Microporosity (%)
CAQ	1091	0.681	0.549	12.5	80.6
CAQF	2114	1.307	1.142	12.4	87.4

^a CAQ—chemical activation only.

^b CAQF—chemical activation with $ZnCl_2$ followed by physical activation.

The higher BET area, total pore volume, micropore volume and microporosity obviously show for CAQF. According to this observation, they decided to evaluate the methane adsorption properties and compare results to other data available in their literature. In Figure 3, the adsorption isotherm for excess adsorbed mass exhibits a type I isotherm, characteristic of monolayer microporous adsorbents. Moreover, decreasing amount of adsorption when temperature increased verifies physisorption behavior on the sample surface.

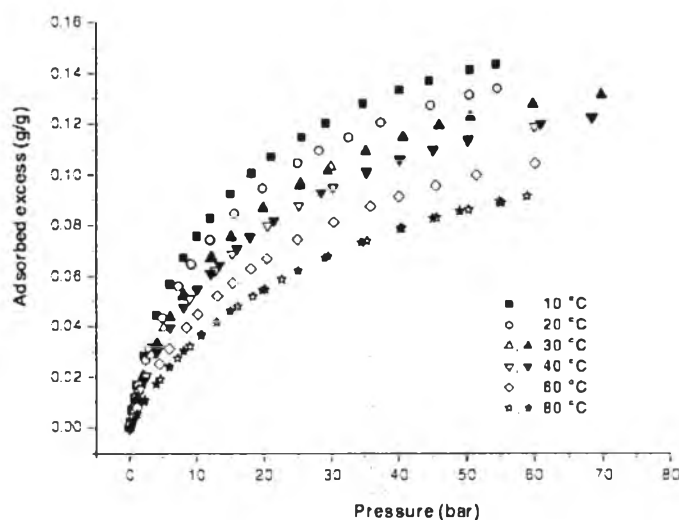


Figure 2.3 Excess adsorption isotherm of methane in CAQF-30.

Table 3 shows comparison between their result and previous experiment for methane adsorption capacity at 25 °C and 40 bar. Our sample CAQF has a comparable capacity 122.85 mg/g. However, the storage/delivery value are considerably lower than the previous report values, indicate the lower density in the sample that was prepare in this experiment.

Table 2.3 Adsorbed amount of methane at 25 °C and 40 bar

Sample	q_{ads} (mg/g)	Storage delivery (v/v)
CAQF	122.85	80/75
LAC54	136.00	155/135
AC Notri R1	111.58	NA
A20	133.00	155/140

In conclusion they suggested that activated carbons prepares from coconut shell (low-cost lignocelluloses waste) using chemical activation followed by physical activation may be further developed as potential adsorbents for natural storage applications.

In 2005, Shuji *et al.*, investigate on high pressure adsorption equilibria of methane and carbon dioxide on several activated carbons. The high-pressure excess adsorption equilibria of methane and carbon dioxide on five microporous activated carbons were measured. Adsorption isotherms were obtained at temperatures ranging from (273 to 333K) and at pressures ranging from (0.5 to 6000kPa) using a static volumetric apparatus.

Table 2.4 Physical specification of used AC sample

Activated carbon	Shape	Raw material	SBET (m ² /g) ^a	V (cm ³ /g) ^b	D ^c (g/cm ³)
Norit R 1 extra	cylinder	peat	1450	0.47	0.43
BPL	granular	coal	1150	0.43	0.51
Maxsorp	powder	chark	3250	1.79	0.29
A 10 fiber		petroleum pitch	1200	0.53	0.20
Activated carbon A	crushing	coconut shell	1207	0.54	0.60

SBET^a–BET surface area V^b–Pore volume D^c–Packed density

By using volumetric method, the adsorption isotherm on Norit R 1 extra activated carbon at four different temperatures was observed and compared with gravimetric method from previous work. At the same temperature, the volumetric method result from this experiment shows a good agreement as in following figures.

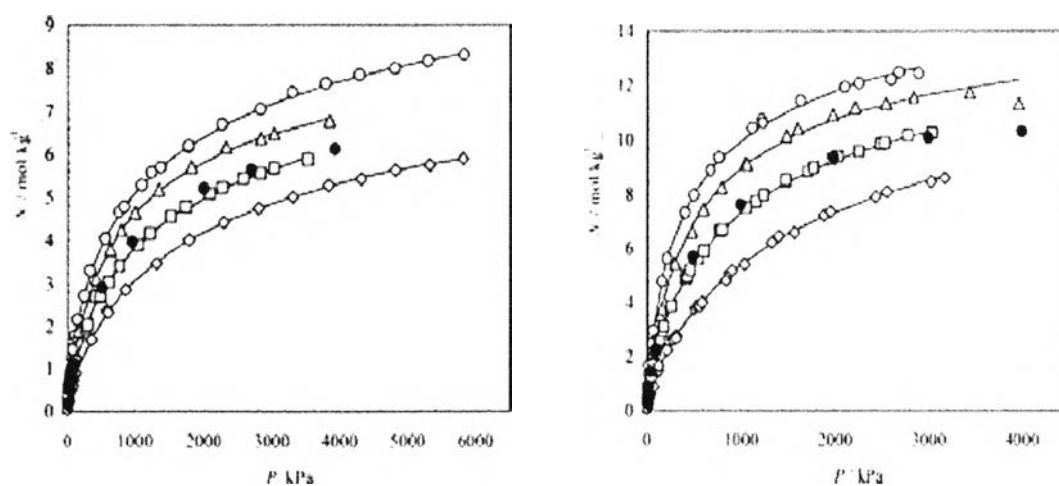


Figure 2.4 Adsorption isotherm of methane (left) and carbon dioxide (right) on Norit R 1 extra activated carbon; ○ -273K, △ -283K, □ -298K, ◇ -323K and ● -ref.

Then other adsorption isotherm on four commercial activated carbons were determined and also compared with result from their cited literature. As a result, the highest surface area adsorbent, Maxsorb, can adsorb gas molecule more than other four. Then they concluded that surface area of adsorbent has an effect on adsorption capacity. Furthermore, size of adsorbate or gas molecule and adsorbed temperature also have an effect on amount of adsorbed gas. Like in the following adsorption isotherms, all four activated carbons prefer carbon dioxide which has smaller diameter, more than methane to adsorb on their surface at the same temperature and amount of adsorbed gas on activated carbon surface decrease when temperature increased.

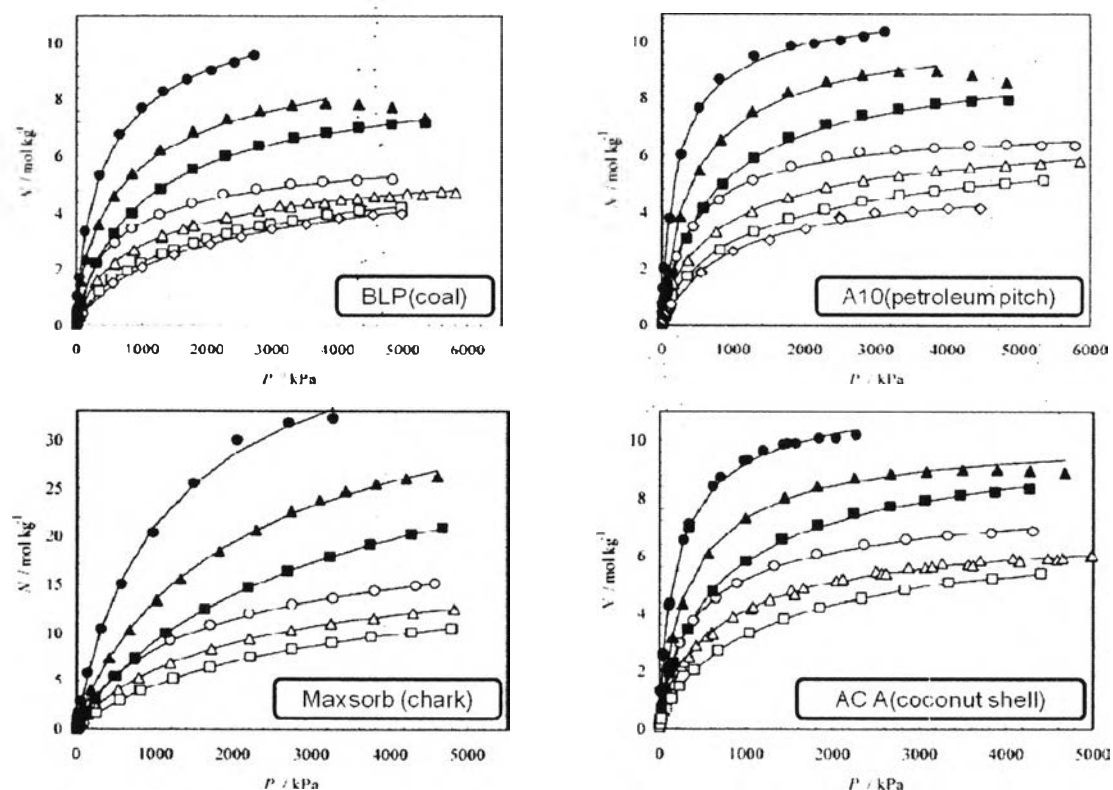


Figure 2.5 Adsorption isotherm of carbon dioxide and methane on four commercial activated carbons; \circ -methane at 273K, Δ -methane at 283K, \square -methane at 298K, \diamond -methane at 323K, \bullet -carbon dioxide at 273K, \blacktriangle -carbon dioxide at 298K and \blacksquare - carbon dioxide at 323K.

In 2004, Wan *et al.*, experiment was done to compare between activated carbon produced from palm shell and coconut shell in terms of pore size distribution of micro, meso and macropores. These researchers used coconut shell as a reference for shell type materials in assessing the other possible material for activated carbon production. Both types of activated carbon material are prepared using the same process. Carbonization and activation with steam or nitrogen were carried out at 850°C in fluidized bed reactor.

Higher fibrous structure content (halocellulose) material like coconut shell char can easily be activated to produce activated carbon as a result the activation rate of coconut shell char is almost five times higher than palm shell char. Another parameter effect on activation rate is char porosity. Materials with high porosity should contain high surface area and refer to high activation area. From BET analysis, palm shell has higher surface area than coconut shell (260 and 183 m²/g respectively), but palm shell have lower activation rate. So, they concluded that the activation rate could be attributed the high cellulose and halocellulose content in raw material.