Adsorption Isotherms of Hydrogen on Granular Activated Carbon Derived From Coal and Derived From Coconut Shell

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ABSTRACT

The development of adsorption-based storage systems requires a basic understanding of the isotherms over a wide range of pressure and temperatures for various types of adsorbents. This research is to generate experimental isothermal adsorption data for the adsorption of hydrogen gas on activated carbon. The adsorption apparatus is based on a volumetric method, and the experiments were conducted at temperatures ranging from 273 to 308 K and pressures up to 4 MPa. Two types of activated carbon, (i) a granular coal from Indonesia and (ii) a coconut-shell activated carbon that is produced in the laboratory, were used in the experiments. The experimental data are analyzed using the Langmuir, Toth, and Langmuir–Freundlich isotherm models.

Introduction

In recent years, the exhaustion of fossil fuel, such as oil, coal, and natural gas, has been a worldwide concern. To alleviate the pressing situation, the efficient use of the various energy resources is desirable [1]. Hydrogen is one of the promising and potential new energy sources to substitute for fossil fuel. The advantage of using hydrogen is its high calorific value as a fuel and its possibility to be produced from renewable energy sources. However, storage of hydrogen is a major problem, which has to be solved before the hydrogen economy can have a breakthrough [2]. The current technology of hydrogen storage involves compression up to 700 bar of pressure or liquefying of hydrogen up to −252.8°C (20.3 K) for temperature [3].

Any feasible storage method must satisfy the demands of both energy density and cost competitiveness. Several means of hydrogen storage for hydrogen-powered vehicles including liquid hydrogen, compressed hydrogen, in-situ decomposed hydrogen, and the hydrogen released from hydrides, have not been proven to be practical technologies that can compete with gasoline-powered cars [4].

Physisorption on activated carbon has been proposed to lower the storage pressure of compressed gas fuels such as natural gas and hydrogen. For example, the storage density of adsorbed natural gas can be three-fourths that of compressed natural gas at one-sixth the gas pressure, in addition to the advantage of allowing the use of on-board conformable tanks, and at room temperature. The study of adsorption with hydrogen as adsorbate and porous carbon material as adsorbent at isotherm temperature 77 K is presented in Table 1 [3, 5–9]. Hydrogen storage in porous materials at 77 K isotherm temperature produced a good adsorption capacity, but to achieve a temperature of 77 K and maintain this constant temperature is expensive. Recently, research on hydrogen adsorption storage has focused on finding the ideal adsorbent that, used at room temperature, allows the storage of interesting amounts of H_2 [10].

Effective hydrogen adsorption storage technology by activated carbon is essential for the utilization of new energy. The development of adsorption-based storage systems requires a basic understanding of the isotherms over a wide range of pressure and temperatures [11] for various types of adsorbents. These data are essential for designing the storage system at a given gas feed, product specifications, and environmental conditions [12].

This article reports the ongoing effort toward generating experimental isothermal adsorption data for the adsorption of hydrogen gas on activated carbon. The adsorption apparatus is based on a volumetric method, and the experiments were conducted at temperatures ranging from 273 to 308 K and pressures up to 4 MPa. Two types of activated carbon, (i) a granular coal from Indonesia (GC) and (ii) a coconut-shell activated carbon

**Table 1.** Adsorption isotherm of hydrogen on activated carbon at 77 K.

A_{BET} (m²/g)	P (bar)	C_o (wt%)	Reference
2780 3190	29 20	5.2 7.08	[3, 5]
884	10	2.02	[6]
3400	1	2.89	[7]
2772	40	5.3	[8]
300	54	1.75	[9]

(CS) that is produced in the laboratory, were used in the experiments. These data were correlated with the Langmuir, Toth, and Langmuir–Freundlich models; therefore, these models can be used in designing the gas storage system.

Experiment

Materials

Hydrogen with purity 99.99% was used in the experiment as the adsorbate. Two types of activated carbon have been investigated, namely, granular coal-derived activated carbon and granular coconut-shell-derived activated carbon. The physical activation for granular coal-derived activated carbon and granular coconut-shell-derived activated carbon was completed in a vertical autoclave activation reactor placed inside a furnace. The production processes include the carbonization/oxidation. The fresh coal and coconut shell were first heat treated by flowing O_2 at 100 ml/min at 573 K for 6 h. A scanning electron micrograph (SEM) of the Granular Coal Derived activated carbon is shown in Figure 1 with 500× magnification. Table 2
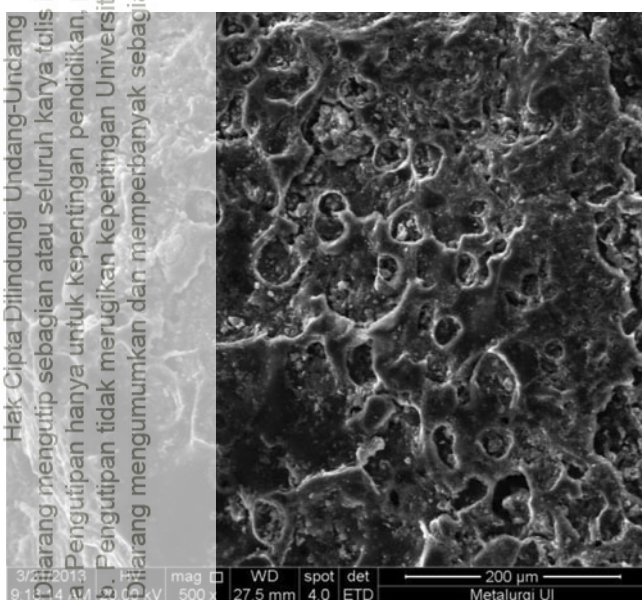
Figure 1. Scanning electron micrographs (SEM) photo of granular coal-derived activated carbon at 500× magnification.

**Table 2.** Surface area of sample activated carbon.

Sample of activated carbon	Surface area (m²/g)
Granular coal	729.944
Coconut shell	414.900

gives the physical properties for the granuclar coal-derived and granular coconut-shell-derived activated carbons.

These structural characteristics are determined using a Quantachrome gas sorption instrument (Autosorb-1). The surface area was calculated by the Brunauer–Emmett–Teller (BET) method from N_2 adsorption isotherm data, which has been performed at 77.3 K. The pore size distribution (PSD) was obtained by the nonlocal density functional theory (NLDFT) method.

Apparatus and procedures

A schematic diagram of the experiment apparatus is shown in Figure 2, where the apparatus consists of an adsorption cell and a charging cell with internal volumes of (85.5 and 1170 ml), respectively, from stainless steel (SS304). The adsorption cell and charging cell are connected through a small tube. The apparatus is immersed in a Hüber constant-temperature water bath, which is controlled to preselected temperatures with a precision of ±0.2 K. The pressure in both cells is measured using an absolute pressure transmitter (Druck, PTX 1400), with a pressure range of 0 to 40 MPa and ±0.15% full-scale
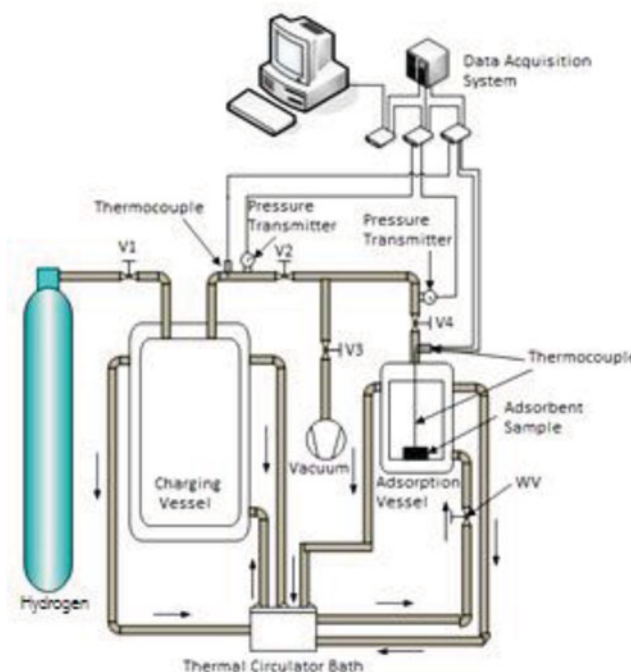
Figure 2. Schematic diagram of the experimental apparatus.

uncertainty. Class-A type K thermocouples were used for the temperature measurement. A thermocouple was installed in the measuring cell keeping in contact with adsorbent in the adsorption cell. This enables a direct temperature of the adsorbent to be obtained precisely. A data logger with sampling interval 10 s was used to record all pressure and temperature. Since hydrogen gas is highly flammable, during the experiment the exhaust fan is always turned on to anticipate of hydrogen leaks and then discharged into the environment. The detail experimental procedures were described previously by Martin et al. [12].

Data reduction

The amount of gas adsorbed is required to obtain the isotherm parameters of the single-component adsorbate and adsorbent system. It is calculated using the density, which is a function of temperature and pressure inside the charging vessel and adsorption vessel; details of data reduction were describe previously by Martin et al. [12].

Three different adsorption isotherm models, (i) Langmuir, (ii) Toth, and (iii) Langmuir–Freundlich, were used to correlate the experimental data. The Langmuir model is the simplest model and describes monolayer type adsorption in microporous solids. This model presumes a homogeneous surface for the adsorbents, where the adsorption energy is constant over all sites. This model also assumes that the adsorption on the surface is localized and each site can accommodate only one molecule or atom [13]. The Langmuir model is represented by

$$\frac{C}{C_0} = \frac{k_0 \exp\left(\frac{h_{st}}{RT}\right) P}{1 + k_0 \exp\left(\frac{h_{st}}{RT}\right) P} \quad (1)$$

where C_0 is the saturated amount adsorbed, k_0 is the equilibrium constant, P is the equilibrium pressure, R is the gas constant, and h_{st} is the isosteric heat of adsorption. This model has limitations for material heterogeneity and to fit with high-pressure data.

The Toth and the Langmuir–Freundlich (L-F) models are usually used for heterogeneous adsorbents such as activated carbon to predict the behavior at both low- and high-pressure conditions [13]. The Toth model is written as

$$\frac{C}{C_0} = \frac{k_0 \exp\left(\frac{h_{st}}{RT}\right) P}{\left\{1 + \left[k_0 \exp\left(\frac{h_{st}}{RT}\right) P\right]^t\right\}^{\frac{1}{t}}} \quad (2)$$

The Langmuir–Freundlich model is represented by

$$\frac{C}{C_0} = \frac{\left[k_0 \exp\left(\frac{h_{st}}{RT}\right) P\right]^{\frac{1}{t}}}{\left\{1 + \left[k_0 \exp\left(\frac{h_{st}}{RT}\right) P\right]^t\right\}^{\frac{1}{t}}} \quad (3)$$

where C is the amount adsorbed, C_0 is the saturated amount adsorbed, k_0 is the equilibrium constant, R is the gas constant, P is the equilibrium pressure, h_{st} is the isosteric heat of adsorption, and t is the heterogeneity of the adsorbent. The detailed data were previously presented by Loh et al. [14]

Results and discussion

The isotherms data for the GC (filled symbols, •, 273 K; ■, 298 K; ♦, 308 K) and CS (empty symbols, ○, 273 K; □, 298 K; ◊, 308 K) activated carbons with hydrogen are graphically presented on a pressure–concentration–temperature (P-Co-T) plane in Figure 3. Hydrogen adsorption data onto two materials of granular activated carbon, derived from granular coal and derived from coconut shell, were compared. The experiments cover the temperature ranging from 273 to 308 K and pressures up to 4 MPa. The specific uptake C_0 for each sample is significantly different at any given set of conditions and type of adsorbent. The value of C_0 highly depends on the surface area and pore volume of the adsorbent. Table 3 and Table 4 show that the granular activated carbon derived from coal (GC) has a higher adsorption capacity than granular activated carbon derived from coconut shell (CS) because the surface area of CS activated carbon is lower than that of GC activated carbon.

The regressed isotherms with the Langmuir, Toth, and Langmuir–Freundlich models are superimposed onto the isotherms data for GC + H$_2$ and CS + H$_2$ in Figures 3a, 3b, 3c, 3d, 3e, and 3f, respectively. The numerical values of the adsorption parameters (C_0, k_0, h_{st}, and t) are presented in Table 5. The error regression has also been calculated using the isotherm model results with the experimental data:

$$\text{error of regression} = \frac{\sqrt{\frac{1}{N}\sum_{i=1}^{N}\left(C_{exp} - C_{model}\right)^2}}{\frac{1}{N}\sum_{1=1}^{N} C_{exp}} \quad (4)$$

where N is the number of data points.

The adsorption parameters were fitted by the Langmuir, Toth, and Langmuir–Freundlich models for hydrogen and activated carbon SC and GC. For GC the regression values agree within ±9% with the Langmuir and Toth models, and ±7.4% with the Langmuir–Freundlich
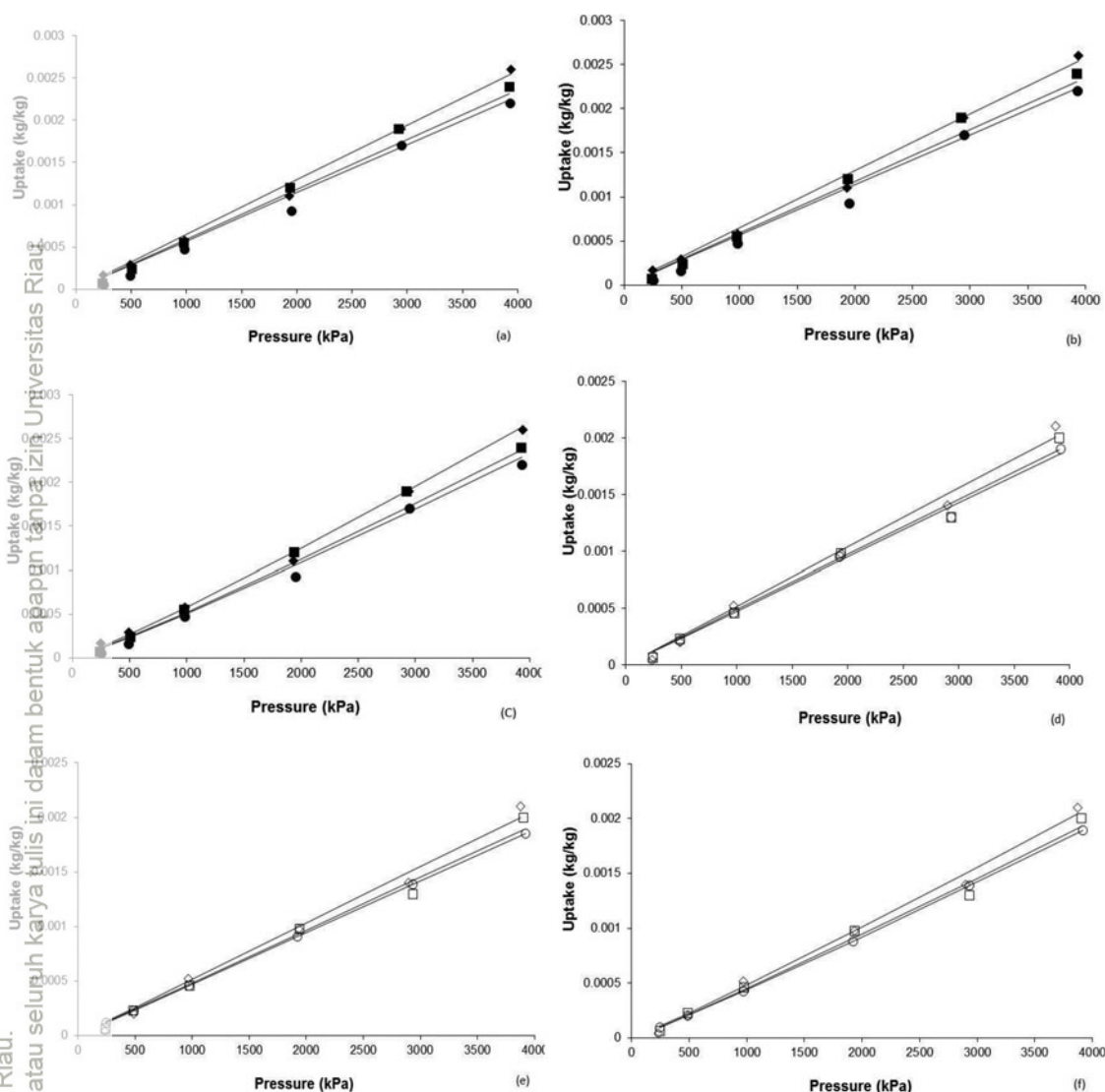
Figure 3. Adsorption isotherms of H_2 on granular coal (•, 273 K; ■, 298 K; ♦, 308 K) and coconut shell (○, 273 K; □, 298 K; ◇, 308 K) activated carbons. Solid lines represent the Langmuir model for H_2 on (a) granular coal and (c) coconut shell, Toth model for H_2 on (b) granular coal and (d) coconut shell, and Langmuir–Freundlich model for H_2 on (c) granular coal and (f) coconut shell activated carbons.

(L-F) model. Similarly, for SC the isotherms data with the average regression error are of 7.58%, 7.6%, and 5.86% respectively. It is observed that all of the isotherm models (Langmuir, Toth, and L-F models) are suitably accurate enough with experimental uncertainties of less than 10% to predict the uptake of hydrogen on two types of activated carbons. For GC from the Langmuir, Toth, and L-F isotherm models, the isosteric heat of adsorption,

Table 3. Hydrogen uptake on granular coal activated carbon.

P, kPa	C, kg kg⁻¹	P, kPa	C, kg kg⁻¹	P, kPa	C, kg kg⁻¹
T = 273 K		T = 298 K		T = 308 K	
249.99	1.7×10^{-4}	241.90	6.4×10^{-5}	251.68	5.2×10^{-5}
492.22	3.9×10^{-4}	509.17	2.4×10^{-4}	493.48	1.6×10^{-4}
986.62	6.8×10^{-4}	975.78	5.5×10^{-4}	983.64	4.7×10^{-4}
1934.3	1.1×10^{-3}	1939.5	1.2×10^{-3}	1954.6	9.2×10^{-4}
2943.8	1.9×10^{-3}	2922.1	1.9×10^{-3}	2950.4	1.7×10^{-3}
3939.2	2.6×10^{-3}	3923.0	2.4×10^{-3}	3935.2	2.2×10^{-3}

Table 4. Hydrogen uptake on coconut shell activated carbon.

P, kPa	C, kg kg⁻¹	P, kPa	C, kg kg⁻¹	P, kPa	C, kg kg⁻¹
T = 273 K		T = 298 K		T = 308 K	
237.29	4.5×10^{-5}	245.20	6.3×10^{-5}	245.75	7.7×10^{-5}
489.48	2.0×10^{-4}	485.81	2.3×10^{-4}	491.18	2.2×10^{-4}
970.32	5.2×10^{-4}	980.38	4.6×10^{-4}	973.85	4.6×10^{-4}
1937.0	9.8×10^{-4}	1938.8	9.8×10^{-4}	1924.3	9.5×10^{-4}
2899.4	1.4×10^{-3}	2931.6	1.3×10^{-3}	2931.4	1.3×10^{-3}
3873.5	2.1×10^{-3}	3903.0	2.0×10^{-3}	3919.3	1.9×10^{-3}

Table 5. Adsorption parameters for Langmuir, Toth, and Langmuir–Freundlich (L-F) models.

Parameters	Coal			Coconut shell		
	Langmuir	Toth	L-F	Langmuir	Toth	L-F
C_o, kg kg^{-1}	0.00213	0.001926	0.001908	0.002050	0.001485	0.001876
h_{st}/R, K	1236.66	1278.74	1278.54	881.71	880.77	838.13
k_o, kPa^{-1}	0.000102	0.000109	0.000206	0.000116	0.000161	0.000203
t	1	0.9033	0.901	1	0.9	0.934
Average regression error (%)	9.05	9.09	7.44	7.58	7.615	6.857

h_{st}, can be obtained in the range of 10.3 to 10.6 KJ/mol. Meanwhile the isosteric heat of adsorption values determined for SC for the same models are lower, 6.97 to 7.3 KJ/mol.

Conclusions

The adsorption of hydrogen gas (H$_2$) on activated carbon has been measured at working conditions, pressures up to 4 MPa, and temperature ranges from 273 to 308 K for granular activated carbon using a constant volume–variable pressure (CVVP) method. From the experiment, it is found that the granular activated carbon derived from coal has a higher adsorption capacity than granular activated carbon derived from coconut shell because the surface area of CS activated carbon is lower than for GC activated carbon. The adsorption isotherm data were regressed with the Langmuir, Tóth, and Langmuir–Freundlich models with reasonable accuracy, that is, an average regression error of around 9%. In this current study the Langmuir–Freundlich equation is found to provide a more accurate correlation than the Langmuir and Tóth models.

Nomenclature

A_{BET} Brunauer–Emmet–Teller surface area, (m^2/g)
C adsorbed phase concentration at equilibrium
C_o limiting adsorption capacity of the adsorbent, kg/kg adsorbent
h_{st} isosteric heat of adsorption, kJ/kg
k_o equilibrium constant, 1/kPa
P equilibrium pressure, Pa
R universal gas constant, kJ/ kg-mol-K
T equilibrium temperature, °C
t parameter that indicates the heterogeneity of the adsorbent

Notes on contributors

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