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El-Sharkawy, Ibrahim Ibrahim

Interdisciplinary Graduate School of Engineering Science, Kyushu University

Saha, Bidyut Baran

Interdisciplinary Graduate School of Engineering Science, Kyushu University

Chakraborty, Anutosh

Interdisciplinary Graduate School of Engineering Science, Kyushu University

Koyama, Shigeru

Interdisciplinary Graduate School of Engineering Science, Kyushu University

他

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Linear Driving Force Approximation for Gasoline Vapors Recovery using Activated Carbons

Ibrahim Ibrahim El-SHARKAWY^{*1}, Bidyut Baran SAHA^{*1,†}, Anutosh CHAKRABORTY^{*1}, Shigeru KOYAMA^{*1}, Jingming HE^{*2} and Kim Choon NG^{*2}
[†]E-mail of corresponding author: *bidyutb@cm.kyushu-u.ac.jp*

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This study deals with the experimental investigation of adsorption equilibrium and kinetics of gasoline vapors onto one specimen of activated carbon powder namely Maxsorb III and another specimen of activated carbon fiber felt which is known as ACF-1500. The experiments have been conducted at assorted adsorbent temperatures between 20 to 60°C by using a thermogravimetric analyzer (TGA) unit under a controlled environment of pressure and temperature. Vapor uptake, adsorption temperatures and pressures are logged continuously. The Dubinin- Radushkevich (D-R) equation is found to be suitable to correlate the adsorption isotherms whilst the linear driving force (LDF) model is used to represent the adsorption kinetics. Experimental results show that although the Maxsorb III/gasoline pair has more than twice the uptake of ACF-1500/gasoline pair at equilibrium condition, but the latter has about 10-fold improvement in the overall heat transfer coefficient (k_{sa}).

Key words: *Activated carbon, Adsorption equilibrium, Linear driving force approximation*

1. Introduction

In recent years, server environmental pollution caused by the continuous increase in the number of automobiles added the emphasis on the emission control from the vehicle in many countries.^{1,2)} Automobiles produce two types of emissions: the exhaust emission from the by-products of combustions such as CO, CO₂, NO_x, sulfur and carbon particles, and the evaporative emission from the evaporation of the fuel itself. Consequently, research efforts are needed to recover the gasoline vapors for the sake of environmental protection. Recovering of gasoline vapors by adsorption technique is one of the most promising and cost effective methods. However, the design of such adsorption systems needs accurate data about adsorption equilibrium and the adsorption kinetics. Liu et al.³⁾ studied the recovery of butane, benzene and/or heptane vapors from nitrogen using BAX activated carbon to simulate the recovery of gasoline vapors during tank filling operations. Whilst, the adsorption

isotherms of gasoline vapors on activated carbon are measured by Ryu et al.⁴⁾ using the static volume method. In this study, the authors consider gasoline as a pseudo-pure component and the experimental results show that activated carbon can adsorb about 2 mol of gasoline per kg of activated carbon at an adsorption temperature of 20°C. Adsorption isotherms of gasoline vapors onto zeolite have been studied by Ryu et al.⁵⁾ and they have used the Töth equation for determining the adsorption isotherms.

From the literature review; there is a dearth of accurate data on the adsorption kinetics of gasoline vapors onto carbon-based adsorbents. The motivation of this paper is to conduct detail experimental investigation of the adsorption equilibrium and adsorption kinetics of gasoline vapors onto two types of carbon-based adsorbents namely, the Maxsorb III and the ACF-1500 using a thermogravimetric analyzer (TGA) unit where experiments are conducted under a controlled environment of pressure and temperature. Mass of adsorbed gasoline vapors, adsorbent temperature are logged out with a time interval between 0.5 to 1.0 s and thus making it possible to estimate the adsorption kinetics accurately.

^{*1} Interdisciplinary Graduate School of Engineering Sciences, Kyushu University, Japan

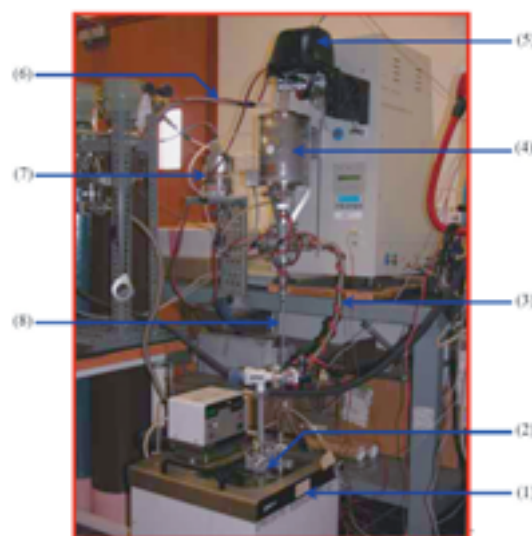
^{*2} Department of Mechanical Engineering, National University of Singapore, Singapore

2. Experimental Procedure

In the present study, a TGA unit of type Chan-2121 with an accuracy of 0.1 μg is used to measure the kinetics of gasoline vapors onto Maxsorb III and ACF-1500, respectively. Figure 1 shows a pictorial photograph of the experimental apparatus which comprises the TGA unit, a controlled temperature evaporator, vacuum pump, MKS pressure controller, MKS-Baratron pressure sensor and a thermocouple of type K to track the pressure and temperature changes with time during the experiments. More details about the experimental apparatus have been reported in earlier publications of the present authors^(6,7,8). In the present study, however a built-in microprocessor and a compact vortex chiller system is incorporated into the TGA unit enabling the adsorption isotherms to be studied at temperatures below the room temperature. The system pressure is recorded by using a MKS-Baratron pressure sensor (type 631A). A diaphragm type vacuum pump is used to evacuate the system continuously in response to the MKS (type 651C) pressure controller so as to maintain a pre-set reaction chamber pressure. At the inlet and outlet of the reaction chamber, two porous type stainless steel filters are installed to minimize the pressure fluctuations in the sample cell under the continuous operation of the vacuum pump.

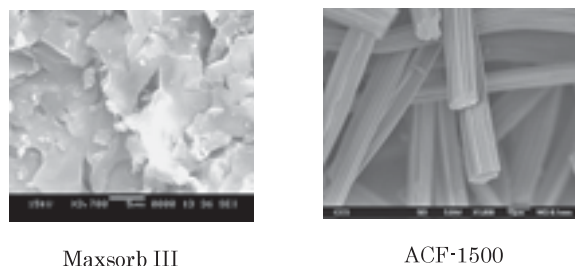
To protect the microbalance from the damage which might occur due to the chemical reaction of gasoline vapors, a small amount of low density helium gas with a constant flow rate of 20 ml/min is injected from the top of the TGA unit into the microbalance dome during the whole experiment. Helium gas is extracted from the top section of the TGA unit to minimize the mixing of gasoline vapor and helium gas. To avoid any condensation, an electric tape heater is mounted at the external surface of the tube connecting the evaporator and the TGA reacting chamber, maintaining the tube surface temperature at least at 10°C higher than the gasoline vapor temperature.

The adsorbent samples, typically about 87 mg of Maxsorb III and 32.5 mg of ACF-1500, are firstly weighted in the moisture analyzer before the insertion of any assorted adsorbent into the TGA unit. Then it was heated "in situ" at a temperature of 140°C for several hours in order to ensure that the assorted adsorbent is fully degasified prior to the set of kinetic experiments. It is then cooled down to the room temperature under a dry atmospheric condition. After that, the assorted adsorbent is



(1): Water circulator, (2): Evaporator, (3): To the reacting chamber, (4): Reacting chamber, (5): Microbalance dome, (6): To the vacuum pump, (7): Pressure sensor, and (8): Thermocouple.

Fig. 1. Photograph of the experimental facility.



Maxsorb III

ACF-1500

Fig. 2. SEM of Maxsorb III and ACF-1500

placed into the sample bowl of the TGA unit. Prior to each adsorption test, the sample is first regenerated under vacuum condition at a temperature of 120°C and is maintained for several hours to ensure a thorough desorption process. The sample is then cooled down to the required adsorption temperature until system is stabilized.

A series of adsorption experiments are carried out at different sample temperatures namely 20°C, 30°C, 40°C, 50°C and 60°C. The system pressure is kept constant at about 24 mbar where a minimum fluctuation of the system pressure is achieved. Through the experiments, the evaporator containing the gasoline liquid is kept constant at a temperature of 15°C by using the constant temperature water bath and a water circulator. As the commercial gasoline has many components, it is considered to behave as a pseudo-pure component at the designated evaporator temperature.

The assorted adsorbents are the activated carbon of type Maxsorb III, developed by the Kansai Coke & Chemicals Co., Ltd., Japan, and

ACF-1500 supplied by the Tonghui Industrial & Trading Co., Ltd. China. The porous properties of the adsorbents were analyzed by using N₂ adsorption where the BET (Brunauer-Emmet-Teller) surface area and BJH (Barrett-Joyner-Halenda) pore size distribution were experimentally investigated. The porous properties of the both adsorbents are furnished in Table 1 and their photographic structures are shown in Fig. 2.

Table 2 Porous Characteristics of Maxsorb III and ACF-1500.

Adsorbent	Specific Surface Area [m ² ·g ⁻¹]	Pore Volume [ml·g ⁻¹]	Average Particle Diameter [μm]
Maxsorb III	3010	1.70	70
ACF-1500	1300-1500	0.8-1.2	17-20

3. Adsorption Equilibrium and Kinetics

A widely accepted correlation of adsorption equilibrium of gases and vapors onto the microporous adsorbents has been developed by Dubinin and co-workers from the idea that originally introduced by Polanyi and Berenyi.⁹⁾ The theory is tested experimentally and it is reported that it is one of the most suitable correlations for adsorption equilibrium data for activated carbon based adsorbents.¹⁰⁾ Consequently, the Dubinin-Astakhov (D-A) equation (Eq. 1) is used to fit the present experimental data of gasoline vapors adsorption onto both of the Maxsorb III and the ACF-1500, i.e.:

$$W = W_0 \exp \left\{ -D \left[T \ln \left(\frac{P_s}{P} \right) \right]^n \right\}, \quad (1)$$

where W is the mass of gasoline adsorbed per kg of adsorbent, W_0 is in kg·kg⁻¹ that defines the maximum adsorption capacity, T is in K which denotes the adsorption temperature, P is in kPa that stands for equilibrium pressure and P_s also is in kPa that denotes the saturated pressure of adsorbate corresponding to the adsorption temperature. The saturated pressure of gasoline is measured experimentally and the data are correlated by using the curve fitting. It is noted that D is adsorption constant that depends on the assorted adsorbent-adsorbate pair and it could be evaluated experimentally by the fitting of Eq. (1). The constant n is an exponent parameter

that gives the best fitting of $\ln(W)$ versus $(T \ln(P_s/P))^n$ in Eq. (1). The parameter n may have any positive numerical value, however when n equals 2, the Eq. (1) is reduced to the Dubinin-Radushkevich (D-R) equation as shown in Eq. (2) below:

$$W = W_0 \exp \left\{ -D \left[T \ln \left(\frac{P_s}{P} \right) \right]^2 \right\}, \quad (2)$$

To estimate the adsorption kinetics of gasoline vapors onto both types of adsorbents. The well known linear driving force equation (Eq. 3)¹¹⁾ is used:

$$\frac{\partial w}{\partial t} = k_s a_v (W - w), \quad (3)$$

where $k_s a_v$ [s⁻¹] is the overall mass transfer coefficient, and w [kg·kg⁻¹] is the instantaneous uptake. Integrating Eq. (3) by using the initial conditions ($w=w_{in}$ at $t=t_{in}$) Eq. (4) below can be derived⁷⁾:

$$\frac{W - w}{W - w_{in}} = \exp[-k_s a_v (t - t_{in})], \quad (4)$$

where t_{in} is the required time to stabilize the system pressure and w_{in} is the corresponding uptake. Equation 4 can be rearranged to give a simple expression of the instantaneous uptake, w , as shown in Eq. (5) below:

$$\frac{w - w_{in}}{W - w_{in}} = 1 - \exp[-k_s a_v (t - t_{in})] \quad (5)$$

The numerical value of $k_s a_v$ at each isotherm could be estimated by linearizing Eq. (4). However, the overall mass transfer coefficient can be expressed as a function of the surface diffusion as given by Eq. (6).¹¹⁾

$$k_s a_v = \frac{F_0 D_s}{R_p^2}, \quad (6)$$

where F_0 is a constant, D_s is the surface diffusion, R_p is the particle radius. The relation between the surface diffusion and the adsorption temperature can be given by the Arrhenius equation (Eq. 7) as shown below:

$$D_s = D_{so} \exp \left(\frac{-E_a}{RT} \right), \quad (7)$$

where D_{so} is a pre-exponential constant, E_a is the activation energy of the adsorbate. By

multiplying both sides of Eq. (7) by $F_0/(R_p)^2$ one can get,

$$k_s a_v = D_{so}^* \exp\left(\frac{-\bar{E}_a}{RT}\right), \quad (8)$$

where D_{so}^* is a pre-exponential constant. As gasoline has many components, \bar{E}_a (in Eq. 8) represents the molar weighted activation energy of gasoline vapors. Therefore, by plotting $\ln(k_s a_v)$ versus $(1/T)$ one can get the numerical values of D_{so}^* and \bar{E}_a for the assorted adsorbent/adsorbate pair.

4. Results and Discussion

Figures 3(a) and 3(b) show the variation of mass uptake versus time for the gasoline

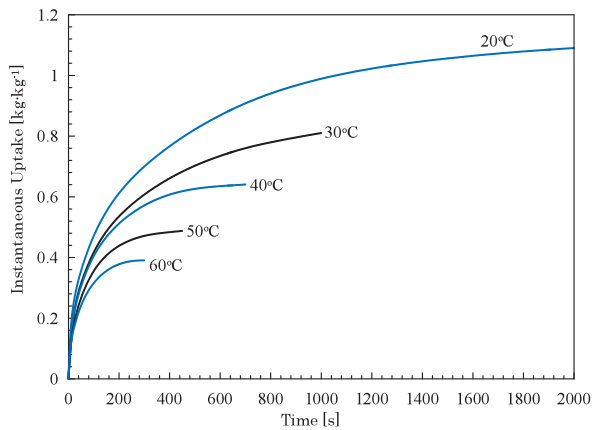


Fig. 3(a) Kinetics uptake of gasoline vapors onto Maxsorb III at assorted adsorption temperatures.

vapors adsorption onto the Maxsorb III and the ACF-1500, respectively. Experiments have been carried out at five assorted adsorption temperatures in the range between 20 and 60°C at a temperature step of 10°C. It can be seen from Figures 3(a) and 3(b) that within adsorption time interval of about 2000s, the Maxsorb III can adsorb gasoline vapors as high as 1.1 kg·kg⁻¹ at adsorption temperature of 20°C. However, only about 300 s is needed to reach the equilibrium uptake (0.39 kg·kg⁻¹) at adsorption temperature of 60°C. As for ACF-1500/gasoline pair, it takes relatively shorter time of about 400 s, to reach the equilibrium uptake of 0.4 kg·kg⁻¹ at adsorption temperature of 20°C. This equilibrium uptake decreases up to 0.21 kg·kg⁻¹ at adsorption temperature of 60°C which means that Maxsorb III/gasoline pair has more than twice the uptake of ACF-1500/gasoline pair at the same equilibrium conditions. As the uptake is measured directly by using the TGA unit which

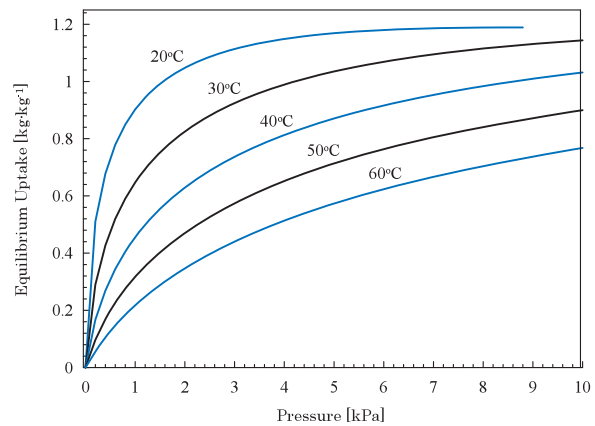


Fig. 4(a) Adsorption isotherms of gasoline vapors onto Maxsorb III as predicted by using D-R equation.

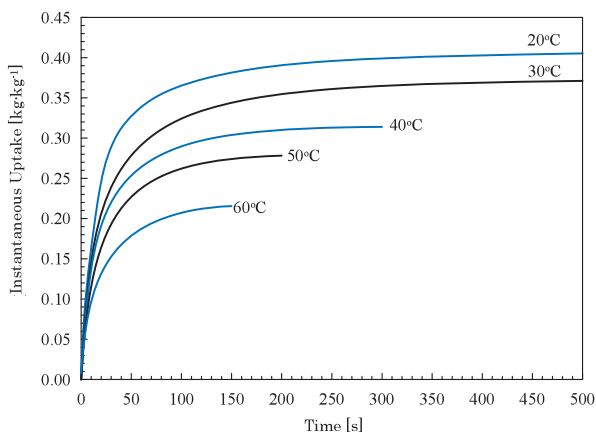


Fig. 3(b) Kinetics uptake of gasoline vapors onto ACF-1500 at assorted adsorption temperatures.

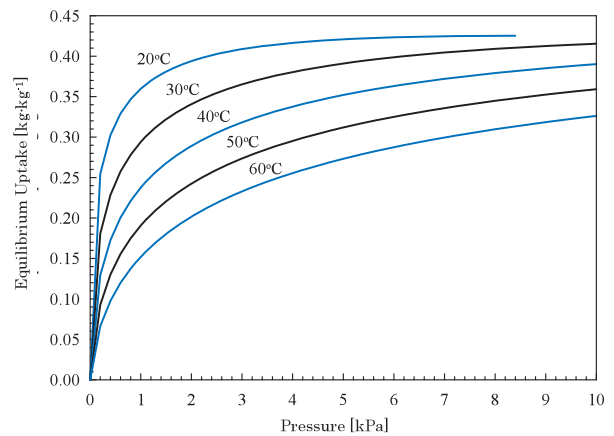


Fig. 4(b) Adsorption isotherms of gasoline vapors onto ACF-1500 as predicted by using D-R equation.

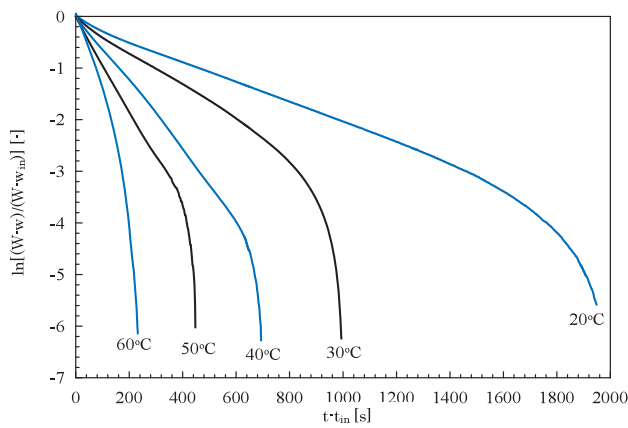


Fig. 5(a) Variation of $\ln[(W-w)/(W-w_{in})]$ versus $(t-t_{in})$ for gasoline vapors and Maxsorb III at assorted adsorption temperature.

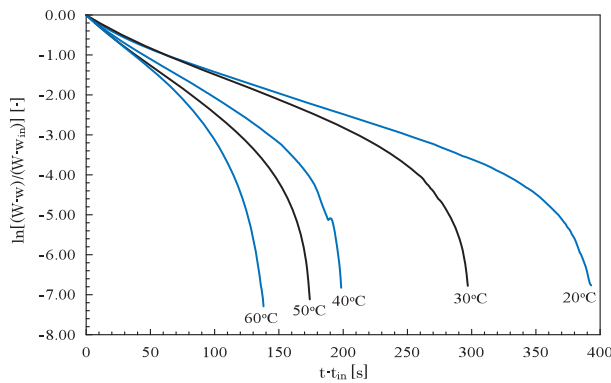


Fig. 5(b) Variation of $\ln[(W-w)/(W-w_{in})]$ versus $(t-t_{in})$ for gasoline vapors and ACF-1500 at assorted adsorption temperature.

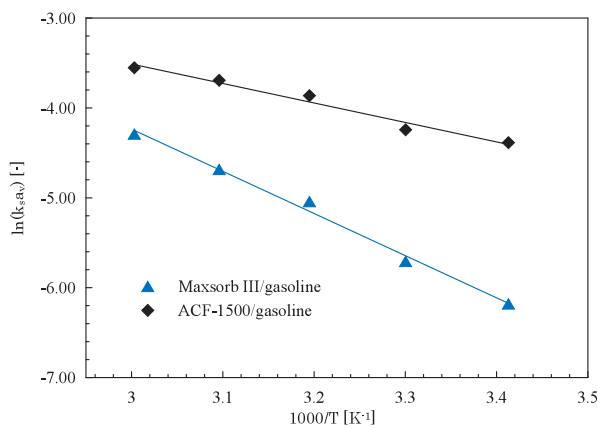


Fig. 6 Variation of $k_s a_v$ versus $(1/T)$.

has an accuracy of $\pm 0.1 \mu\text{g}$, the error bars could not be seen on Figs. 3(a) and 3(b). The Dubinin-Astakhov (D-A) equation (Eq. 1) is used to describe the experimental adsorption isotherms of both of Maxsorb III/gasoline and ACF-1500/gasoline pairs. It is found that the best fitting of the experimental data when n

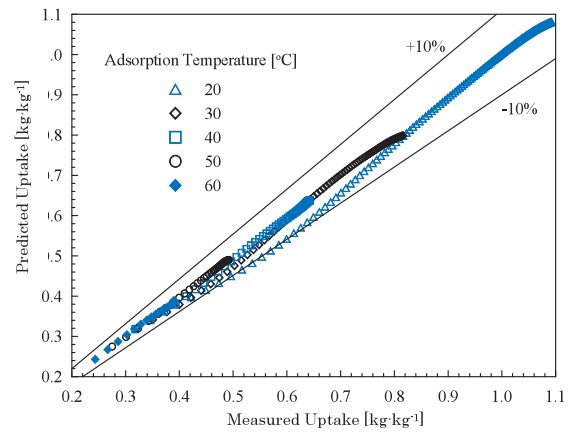


Fig. 7(a) Compression between measured and predicted uptake of gasoline vapors onto Maxsorb III.

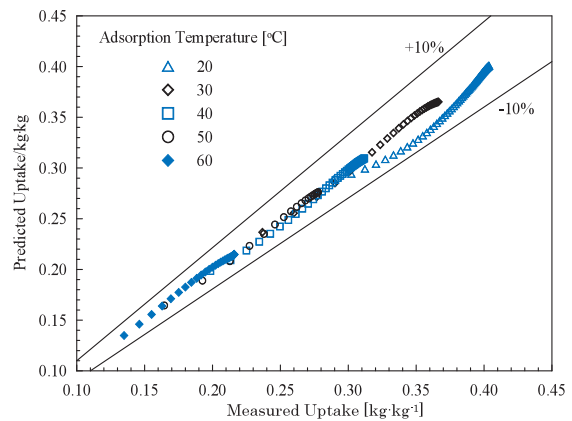


Fig. 7(b) Compression between measured and predicted uptake of gasoline vapors onto ACF-1500.

equals 2 implying that the D-R equation (Eq. 2) is the most suitable correlation for the adsorption of gasoline vapors onto the Maxsorb III and ACF-1500. The numerical values of W_0 and D in the D-R equation are given in Table 2 whilst Figures 4(a) and 4(b) show the prediction of adsorption isotherms of Maxsorb III/gasoline and ACF/gasoline pairs using D-R equation (Eq. 2).

Using the linear driving model together with the experimental data, the overall mass transfer coefficient, $k_s a_v$, can be estimated at each isotherm by plotting of $\ln[(W-w)/(W-w_{in})]$ versus $(t-t_{in})$ as shown in Figures 5(a) and 5(b). Each isotherm yields a straight line through the origin and the linearity can be noticed until approaching the equilibrium condition. In Figs. 5(a) and 5(b), the initial time is selected to be the time required to stabilize the system pressure which is about 50 s. Buoyancy effect of the crucible holding the adsorbent samples may give in the TGA chamber. This procedure provides a simple method to avoid any error

Table 2 Experimental Constants of D-R equation.

Adsorbent	W ₀ [kg·kg ⁻¹]	D[K ⁻²]
Maxsorb III	1.189	6.99×10 ⁻⁷
ACF-1500	0.425	4.244×10 ⁻⁷

that might occurs in the micro-balance readings during the early times of adsorption process.

Figure 6 shows the variation of $\ln(k_s a_v)$ versus the $(1/T)$ for Maxsorb III/gasoline and ACF-1500/gasoline pairs. As can be seen that the fitting trend follows that of the classical Arrhenius equation and it yields a straight line with a slope of (\bar{E}_a/R) from which the average activation energy of the gasoline vapors can be estimated. It is found that the numerical values of the average activation energy are 39 and 18 [kJ·mol⁻¹] for Maxsorb III/gasoline and ACF-1500/gasoline pairs, respectively. The numerical values of D_{so}^* is found to be 18916.7 for the Maxsorb III/gasoline pair and 19.911 for the ACF-1500/gasoline pair. The significant difference in the numerical values of D_{so}^* for both of the assorted pairs is due to the fact that, the diameter of the Maxsorb III particle is about 6 folds that of ACF-1500. It is also worthy to note that, the overall mass transfer coefficient of ACF-1500 pair is about 10 times that of Maxsorb III/gasoline pair because the diffusion path through the ACFs is much shorter than that of granular activated carbon which clearly assure fast intraparticle diffusion and adsorption kinetics.¹²⁾

A comparison between the experimental uptake and that predicted by using Eq. (5) is shown in Figs 7(a) and 7(b) for both of adsorbent-adsorbate pairs at the assorted adsorption temperatures. A good agreement for the bulk of data can be observed and the

maximum error is found to be about ±10%.

5. Conclusions

Adsorption equilibrium and kinetics of gasoline onto activated carbon of type Maxsorb III and activated carbon fiber felt of type ACF-1500 have been successfully measured by using a thermogravimetric analyzer (TGA) unit. Experiments have been conducted within adsorption temperature range between 20 and 60°C. Dubinin-Astakhov (D-A) equation is used to correlated the adsorption equilibrium. It is found that the adsorption capacity at the equilibrium condition of Maxsorb III/gasoline pair has more than twice the uptake that of ACF-1500/gasoline pair. Linear driving force (LDF) model is used to estimate the adsorption kinetics of both of pairs. Experimental results show that the overall mass transfer coefficient of ACF-1500/gasoline pair is about 10 times larger than that of the Maxsorb III/gasoline pair. Thus, AC is recommended for gasoline vapors recovery for long time scale applications, however, the ACF-1500 is preferred for short time scale applications.

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