

Experimental and Simulation Study on Malaysian Activated Carbon as Adsorbent In A Dual Purpose Solar System

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Abstract: - Tests to compare and understand the adsorption capability of some locally produced activated charcoal (coconut shell) samples with methanol were taken under laboratory conditions. An experimental test rig was set up. Data obtained from the experiments were fitted to Dubinin-Radushkevitch ($D-R$) and Dubinin-Astakhov ($D-A$) equations. The results obtained and can be used to select the most favorable pair. Activated carbon AC-5060 shows the best adsorption capacity for methanol and the highest coefficient of performance (COP). This is chosen as the adsorbent in a dual purpose solar adsorption system. The adsorption system is subjected to parametric analyses. The parameters such as second adsorber bed temperature, condenser temperature, and mass of ice are varied and performance evaluated. Malaysian activated carbon is not significant for ice making in the dual purpose adsorption systems at condenser- adsorption temperature equal or higher than 35°C. The most efficient way to improve the dual purpose system under the hot climate is to search for enhanced adsorbent material in terms of adsorption capacity and thermal conductivity.

Key-Words: - Malaysian activated carbon, adsorption properties, $D-R$ and $D-A$ Equations, coefficient of performance (COP), dual purpose adsorption system.

1 Introduction

The potential theory of adsorption is based on the idea that at the surface of the solid adsorbent, the molecules of the gas are compressed by the forces of attraction acting from the surface to a certain distance into the surrounding space. It is purely a thermodynamic approach, suitable for adsorption in microporous materials.

The $D-R$ equation was developed by Dubinin and Radushkevich (1947) [1] and has been widely used to describe adsorption isotherms of sub-critical vapors in microporous solids such as activated carbon and zeolite. This equation describes fairly well many carbonaceous solids with low degree of burned-out. For carbonaceous solids resulting from a high degree of burn-out during activation, the degree of heterogeneity increases because of a wider pore size distribution, and for such cases the $D-R$ equation does not describe well the equilibrium data. To take into account of this surface heterogeneity, Dubinin and Astakhov (1970) [2]

proposed the ($D-A$) equation to fit the experimental data better.

The working form of the $D-R$ equation is:

$$W = W_0 \exp \left\{ -D \left(T \ln \frac{P_s}{P} \right)^2 \right\} \quad 1$$

where W is the volume filled by the adsorbate m^3/kg , W_0 is the maximum volume of the adsorption space m^3/kg , T is absolute temperature, P_s is saturated vapor pressure of adsorbate at temperature T , and P is equilibrium pressure. $D-A$ equation provides flexibility in the description of adsorption data of many microporous solids ranging from a narrow to wide microspores size distribution. The $D-A$ equation contains a third variable n as follows:

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

where n is usually between 1 and 3 and is equal to 2 in the $D - R$ equation. The introduction of the new parameter n improves the fit but does not necessarily have a direct physical significance as reported by Critoph (1988) [3]. Taking the logarithm, we obtain the linear form:

$$\ln W = \ln W_0 - D \left(T \ln \frac{P_s}{P} \right)^n \quad 3$$

The parameters D and W_0 can be determined experimentally by plotting $\ln W$ vs. $\left(T \ln \frac{P_s}{P} \right)^n$ from measurements of W , T and P .

2 Materials and Method

The schematic diagram of the test rig for testing adsorptive properties (isobars) between activated carbon and methanol is shown in Figure 1. It consists of two main components, container A and B. Container A is a stainless steel vessel with capacity of 200 gm activated carbon, and B is a graduated glass cylinder. Three Coconut shell Malaysian samples AC-4050, AC-5060, and AC-6070 of (2.36-0.6) mm mesh size were studied. The containers are connected by 0.25" (inch) copper pipe. The system pressure is measured by a pressure gauge. The valves V1 and V2 will be used to isolate the parts when necessary. Each container contains K-type thermocouple to measure the temperature. Oil-bath and water-bath will be used to control the temperature of each container.

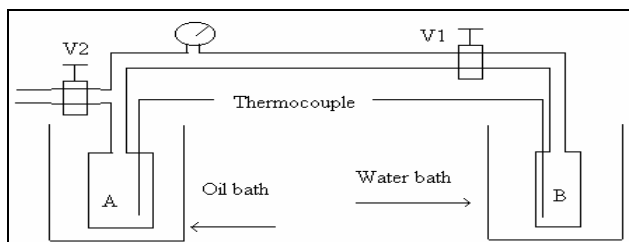
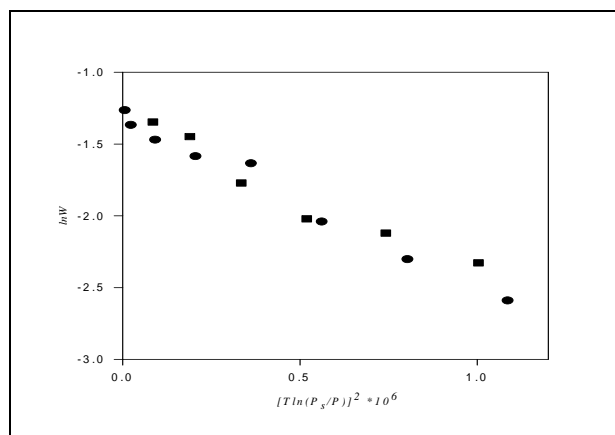


Fig. 1: The schematic diagram of the test rig for testing adsorptive properties (isobars) between activated carbon and methanol.

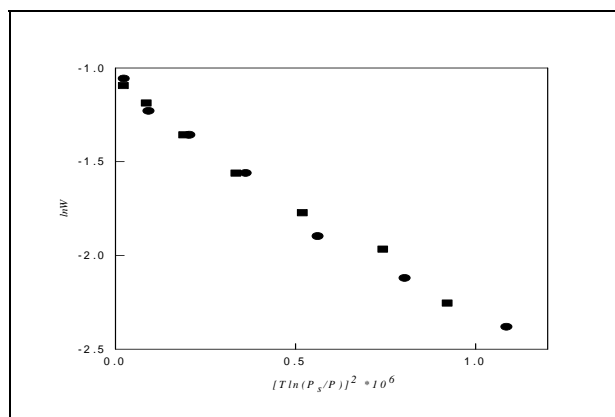
3 Analysis

Figures (2), (3), and (4) show the $D - R$ representation of the tested activated carbon on

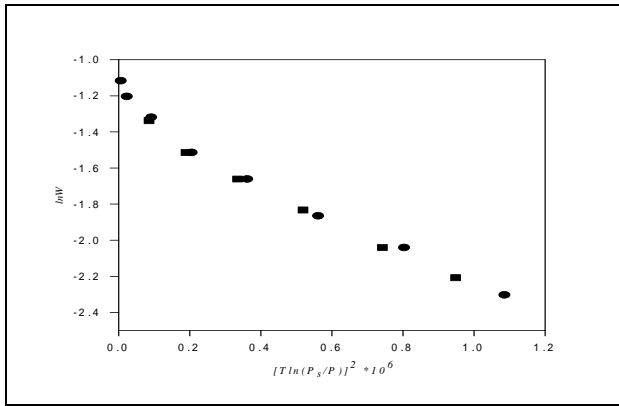
$\ln W$ vs. $\left(T \ln \left(\frac{P_s}{P} \right) \right)^n$ graph with $n = 2$ in a temperature range 30°C to 110°C and the experimental points determined at two isobars are merged to a single line. According to Rand (1976) [4] classification, the activated carbons produce a curve that is convex downwards i.e. a B-type deviation which is the typical shape of the highly activated charcoal, while non-activated charcoal has a curve that is convex upwards. However, there are deviations from linearity as seen in the $D - R$ plots. That implies the $D - R$ representation cannot fit the experimental data well, or can't express the adsorptive characteristics of activated carbon-methanol well. This agrees with the results reported by Hu Jing (1992) [5].



● P = 0.348 ■ P = 0.215
Fig. 2: $D - R$ representation of AC - 4050.



● P = 0.348 ■ P = 0.215
Fig. 3: $D - R$ representation of AC - 5060



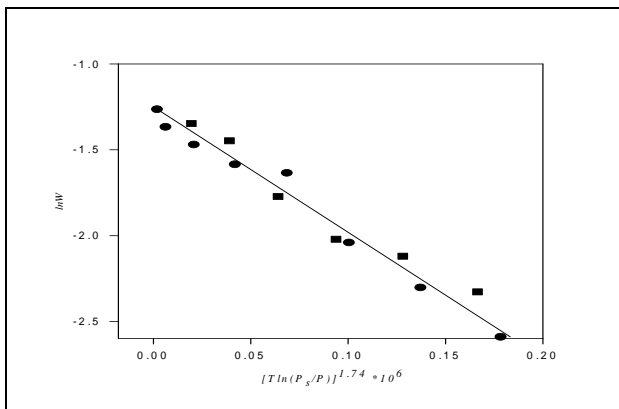
● P = 0.348 ■ P = 0.215
Fig. 4: *D - R* representation of AC - 6070.

By varying *n* from 2, the *D - R* representations of the charcoal are given where the values found producing the best linear relation for the activated

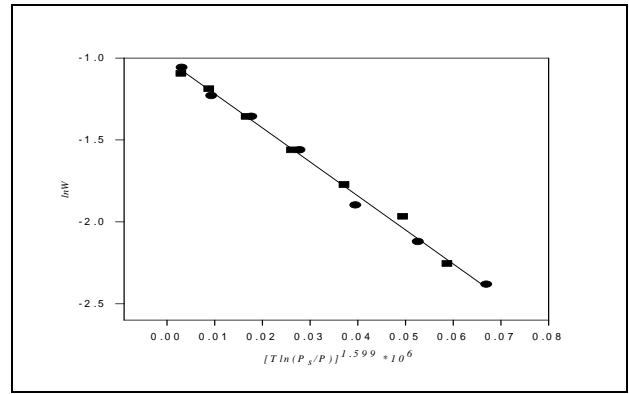
carbon between $\ln W$ and $\left(T \ln \frac{P_s}{P}\right)^n$.

Table (1) gives the numerical values of the parameters of the activated carbon samples studied in the project. Figures (5), (6), and (7) show the *D - A* representation of the three activated carbon samples. *D - A* representation of AC - 5060 and AC - 6070 render the experimental data with sufficient accuracy to be used in the engineering design.

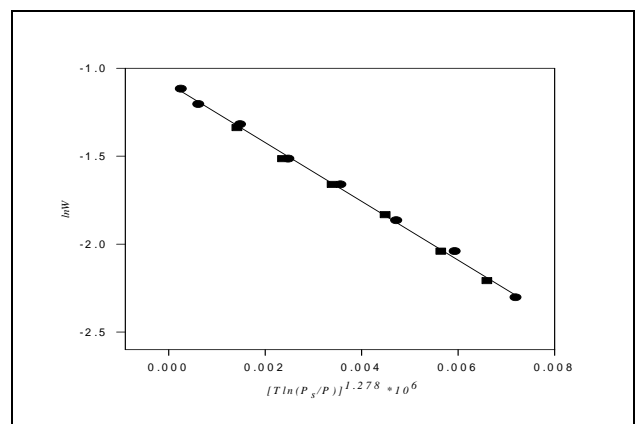
There are still some deviations from linearity for *D - A* representation of AC - 4050; this may be attributed to the simplified experimental set up and also due to presence of macropores in the charcoal.



● P = 0.348 ■ P = 0.215 — Linear Regression
Fig. 5: *D - A* representation of AC - 4050.



● P = 0.348 ■ P = 0.215 — Linear Regression
Fig 6: *D - A* representation of AC - 5060



● P = 0.348 ■ P = 0.215 — Linear Regression
Fig 7: *D - A* representation of AC - 6070

Table 1 Numerical parametric values of the activated carbon samples

Charcoal	W_0 (ml/g)	n	D	R^2
AC - 4050	0.28	1.74	$7.05 \cdot 10^{-6}$	0.97
AC - 5060	0.36	1.59	$20.7 \cdot 10^{-6}$	0.99
AC - 6070	0.34	1.27	$167 \cdot 10^{-6}$	1.00

From the *D - A* Equation we obtain:

$$\ln P = \ln P_s + \left[A \left(\frac{-1}{T} \right) \right] \tag{4}$$

$$A = \left[\frac{\ln \left(\frac{W_0}{W} \right)}{D} \right]^{\frac{1}{n}} \tag{5}$$

The saturation pressure P_s of the adsorbate can be expressed as a function of temperature, thus:

$$\ln P_s = A_0 + \frac{A_1}{T} + \frac{A_2}{T^2} + \frac{A_3}{T^3} \quad 6$$

where A_0, A_1, A_2, A_3 are constants. If quadratic and higher terms is omitted in this expansion and substitute for $\ln P_s$ in Eq (4), we obtain a linear relation between $\ln P$ and $(\frac{-1}{T})$. If W is constant, which means X is also a constant, then we obtain the relation $\ln P = m(\frac{-1}{T}) + C$, where m can be written as:

$$m = \left[\frac{\ln\left(\frac{W_0}{W}\right)}{D} \right]^{\frac{1}{n}} - A_1 \quad 7$$

which is a constant and equal to slope $\frac{d}{d(-T^{-1})}(\ln P)$ of the constant mass concentration

line on the $\ln P$ vs. $(\frac{-1}{T})$ diagram. Thus, we obtain

from $\frac{d}{d(-T^{-1})}(\ln P) = \frac{h_{ad}(X)}{R}$ the following result:

$$h_{ad} = m\left(\frac{R}{M}\right) \quad 8$$

This expression shows that the heat of adsorption h_{ad} is just the slope m of the constant X line on $\ln P$ vs. $(\frac{-1}{T})$ diagram multiplied by $(\frac{R}{M})$. M is the molecular weight of the methanol (kg/mole).

Once the data is obtained along the two isobars and the constants of Dubinin equation are known, the isoster can easily be obtained by plotting the experimental data on $\ln P$ vs. $(\frac{-1}{T})$ graph. The

isosters, according to $\frac{d}{dT}(\ln P) = \frac{h_{ad}(X)}{RT^2}$ are straight lines connecting two corresponding isosters

points on the coordinate $\ln P$ vs. $(\frac{-1}{T})$. For design

purposes, the ideal refrigeration cycle, which consists of two isobars and two isosters can easily

be traced in such a diagram $\ln P$ vs. $(\frac{-1}{T})$ or so

called $P-T-X$ or (Claperon diagram). The pressure- temperature- concentration $P-T-X$ charts for the charcoal tested are shown in Figures (8), (9) and (10).

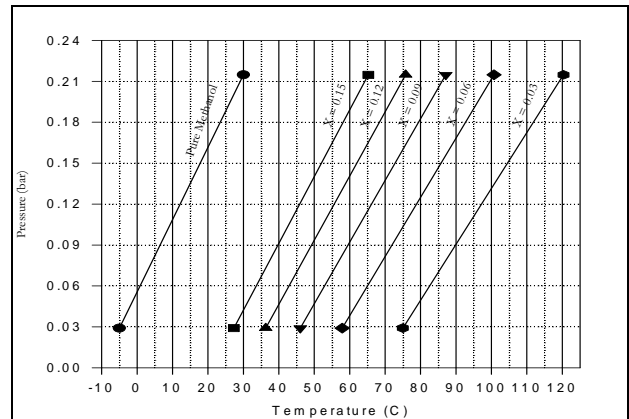


Fig. 8: $P-T-X$ chart for AC-4050-methanol pair

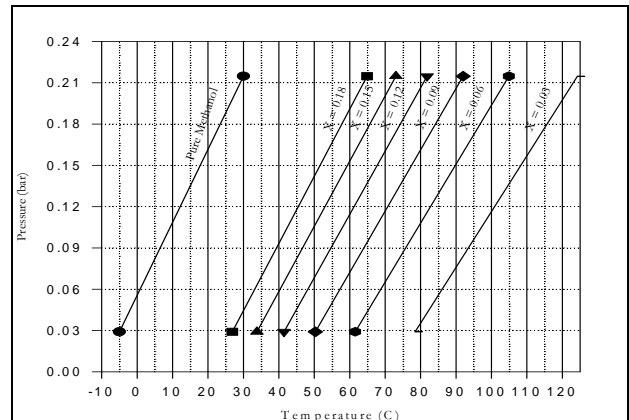


Fig. 9: $P-T-X$ chart for AC-5060-methanol pair

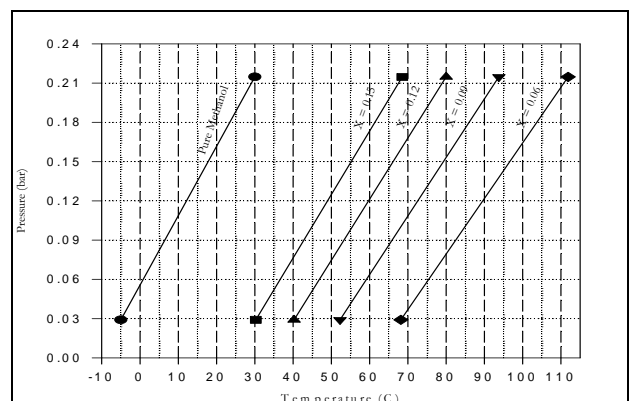


Fig. 10: $P - T - X$ chart for $AC - 6070$ -methanol pair

Since the constants of Dubinin equation W_0 , D and n are known and methanol properties is known, the relationship between $P - T - X$ can be calculated. The knowledge of any two parameters of $P - T - X$ the third can be calculated, and thus the coefficient of performance COP can be calculated to evaluate the effect of different types of activated carbons on solar adsorption refrigeration and for different applications.

The ideal refrigeration cycle, consists of two isosters ($a_2 \rightarrow g_1, g_2 \rightarrow a_1$) and two isobars ($g_1 \rightarrow g_2, a_1 \rightarrow a_2$). The sensible heating and sensible cooling occur along two isosters; desorption and adsorption processes follow the isobars.

The process starts at point a_2 , where maximum adsorption took place at temperature T_{a2} , the concentration is X_{conc} . Heating is commenced and the refrigerant that is adsorbed and the activated carbon itself get heated from T_{a2} until a pressure P_{con} (condenser pressure) is reached at (point g_1). Since no desorption has taken place yet and with concentration being the same (X_{conc}), T_{g1} can be estimated.

The threshold temperature T_{g1} can be calculated by the following integration from a_2 to g_1 , thus:

$$\ln \frac{P_{con}}{P_{evp}} = \int_{a_2}^{g_1} \frac{h_{ad}(X)}{RT^2} dT \tag{9}$$

$$\ln \frac{P_{con}}{P_{evp}} = \int_{evp}^{con} \frac{L}{RT^2} dT \tag{10}$$

Equating the two Eq's (9) and (10) give:

$$L \left(\frac{1}{T_{con}} - \frac{1}{T_{evp}} \right) = h_{ad} \left(\frac{1}{T_{g1}} - \frac{1}{T_{a2}} \right) \tag{11}$$

$$\frac{1}{T_{g1}} = \frac{L}{h_{ad}} \left(\frac{1}{T_{con}} - \frac{1}{T_{evp}} \right) + \frac{1}{T_{a2}} \tag{12}$$

Desorption starts at point g_1 , and with continued heating the maximum temperature attainable (T_{g2}) is reached, since the pressure and T_{g2} are known, the new concentration X_{dil} at point g_2 can be calculated.

Cooling takes place at constant concentration X_{dil} , from $g_2 \rightarrow a_1$ till the evaporator pressure P_{evp} is reached. Since P_{evp} , X_{dil} are known, the threshold temperature T_{a1} can be calculated as:

$$T_{a1} = \frac{A_1 - A}{\ln(P_{evp}) - A_0} \tag{13}$$

Adsorption begins at point a_1 and continues until the concentration reaches the maximum value (X_{conc}). Thus the cycle is completed. The coefficient of performance (COP) of the ideal cycle is defined as:

$$COP_{cycle} = \frac{Q_{evp}}{Q_{heating-process}} \tag{14}$$

COP doesn't take into account the efficiency of the heat exchangers and the heat losses from the system. $Q_{heating-process}$, Q_{evp} are the heat used to generate refrigerant during heating process and the heat transferred during refrigeration process respectively. $Q_{heating-process}$, Q_{evp} can be written as in Eq's (15) and (16) respectively.

$$Q_{heating-process} = (C_a + C_{ac})(T_{g2} - T_{a2}) + X_{conc} C_{l,meth}(T_{g1} - T_{a2}) + (X_{conc} - X_{dil})h + \left(\frac{X_{conc} + X_{dil}}{2} \right) C_{l,meth}(T_{g2} - T_{g1}) \tag{15}$$

$$Q_{evp} = (X_{conc} - X_{dil}) \{ L_{meth} + C_{meth}(T_{con} - T_{evp}) \} \tag{16}$$

4 Discussion and Results

From Fig (11) and Table (1), $AC - 5060$ has the best performance followed by $AC - 4050$, and finally $AC - 6070$. Also $AC - 5060$ has the highest value for W_0 , which means its adsorption capacity for methanol is the largest followed by $AC - 6070$, and $AC - 4050$ respectively. For the

following design parameters: $T_{evp} = -5^{\circ}\text{C}$, $T_{con} = T_{a2} = 30^{\circ}\text{C}$, $T_{g2} = 100^{\circ}\text{C}$, the thermodynamic coefficient of performance COP is in the range of 0.40-0.50 for samples of Malaysian activated carbon. Delgado et al. (1982) [5] reported that COP of his activated carbon-methanol adsorption refrigerator unit was 0.40; COP was in the range of 0.40-0.50 as reported by Grenier and Pons (1984) [6] also.

Also it is seen from Figure (11), the thermodynamic coefficient of performance COP for the three activated carbons with methanol is a function of activated carbon temperature in the range of 70-110°C, and did not change significantly from 110-140°C. This means above a certain generating temperature, the desorbed methanol is not a function of the temperature of activated carbon only but it is affected by the adsorptive properties of activated carbon.

Hu Jing (1992) [7] studied adsorption characteristics of many types of charcoals with methanol; these types were from (Thailand), (China), (U.K) and normal (raw) charcoal. Adsorption capacity of charcoal (W_0) was 0.98, 0.53, 0.40, 0.38, 0.36 and 0.15 respectively. Under the following design parameters: $T_{evp} = -0^{\circ}\text{C}$, $T_{con} = 35^{\circ}\text{C}$, $T_{a2} = 30^{\circ}\text{C}$, $T_{g2} = 100^{\circ}\text{C}$; it was reported that the thermodynamic coefficients of performance COP 's were in the range of 0.49 to 0.30, where the highest COP is (0.49) and the lowest COP is (0.3) for the raw charcoal.

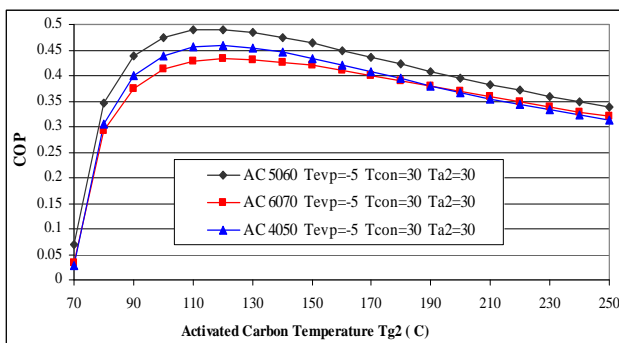


Fig. 11 Refrigeration cycle performance with different Malaysian activated carbon.

Dual-purpose solar adsorption system for domestic refrigeration and water heating is a consequence of the continuous research in the field of single-purpose solar adsorption refrigeration system with respect to the practical needs of

industries and customers; and reflects the novel idea of hybridizing ordinary solar water heating system and solar adsorption refrigeration. It is expected to perform even better in the solar industry market, **Alghoul et al (2007) [8]**.

The dual purpose solar adsorption system was subjected to thermodynamic analysis where its performance under an optimum choice of parameters was reported in **Alghoul et al (2009) [9]**. We will now discuss the effect that some parameters have on the key performance indices. These parameters include desorption temperature of the second adsorber bed, condenser temperature, and the mass of ice. For reference to the equations please refer to the above paper.

The design of the dual purpose continuous solar adsorption system is also described in detail in **Alghoul et al 2009 [9]**. The main components are shown in fig. 12.

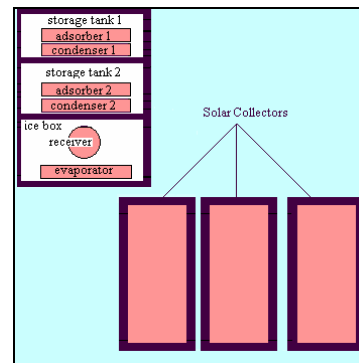


Fig. 12 Main components of the dual purpose continuous solar adsorption system of refrigerator and water heater

Basically the system consists of two adsorber beds and two condensers connected in such a way that the processes of desorption and adsorption occur individually in each of them during half cycle as depicted in fig. 13. Adsorber bed 1 is immersed in water together with condenser 1 in storage tank 1 while adsorber 2 is immersed in water together with condenser 2 in storage tank 2.

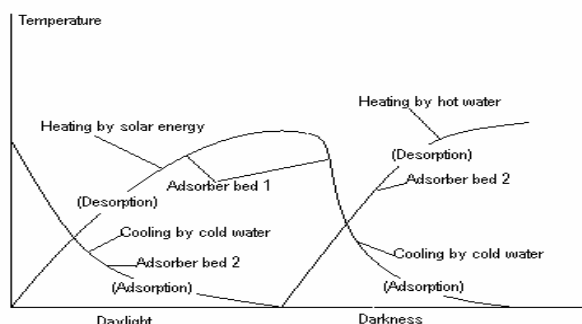


Fig.13 Adsorption and desorption cycles of adsorber bed 1 and adsorber bed 2. Cooling is affected by cold water and heating by solar energy and hot water.

The system uses AC 5060 Malaysian activated carbon with properties given in table 1 as adsorbent and methanol as adsorbate. During daylight solar collector is used to heat the water in storage tank 1, which in turn is used to heat adsorber bed 1 to produce desorption. At the same time adsorber bed 2 undergoes adsorption at a lower temperature of the water in storage tank 2. During darkness, the hot water produced earlier by the solar collector and also from the heat recovered from condenser 1 in storage tank 1 is used to increase the temperature of the water in storage tank 2 to enable adsorber bed 2 to desorb enough methanol. Meanwhile, after draining the hot water of storage tank 1 into storage tank 2, storage tank 1 is refilled with city water to allow adsorber bed 1 to cool and initiate the adsorption process.

1. Effect of desorption temperature on the system performance

The effect of the desorption temperature of the second adsorber bed on the performance of the system has been analyzed and is given in table 2 for the following setups:

- Mass of ice = 12kg
- Generating temperature of the first adsorber bed = 95°C
- Temperature of hot water = 98°C
- Temperature of condenser = 30°C
- Minimum desorption temperature of adsorber beds 1 and 2 = 30°C

The mass of adsorber bed, activated carbon and hot water are determined by the temperatures of the first and second adsorber beds. Producing the specified amount of ice at different generating

temperature is carried out by heating the activated carbon to high generating temperature so that the desorbed mass of the methanol increases. In this way the coefficient of performance of the refrigeration cycle also increases. The same mass of methanol can be desorbed by heating more mass of activated carbon at lower generating temperature. However, the coefficient of performance of the refrigeration cycle is then reduced. By employing efficient solar collectors it is possible to produce hot water up to 98°C and as such the temperature of the desorption process of the first adsorber bed during daylight is set to be 95°C.

Table 2 Performance of system for different second adsorber bed temperatures

Temperature of second adsorber bed (°C)	95	90	85	80	75
Maximum relative concentration of adsorbate in adsorbent(%)	0.166	0.166	0.166	0.166	0.166
Minimum relative concentration of adsorbate in adsorbent (%)	0.082	0.096	0.110	0.126	0.143
Mass of activated carbon (kg)	25	29	36	51	88
Mass of adsorber bed (kg)	37	43	55	77	134
Number of adsorber tubes	19	22	28	39	68
Mass of hot water (kg)	451	172	116	96	101
Solar collector area (m ²)	12.56	5.12	3.60	3.07	3.21
$Q_{domestic.hot.}$ (kJ)	143846	61471	44692	38725	40235

$COP_{cycle-ice}$	0.467	0.446	0.413	0.361	0.269
$COP_{dual.syst}$	0.025	0.059	0.085	0.100	0.096
$COP_{dual.syst}$	0.674	0.706	0.730	0.742	0.738
$COP_{dual-syst}$	0.699	0.765	0.815	0.842	0.834

To choose the optimum final desorption temperature for the second adsorber bed, three factors must be taken into considerations – the coefficient of performance of the refrigeration cycle, mass of activated carbon and the number of adsorber tubes. From the values shown in table 2, at low desorption temperature (75-80°C); the coefficient of performance of the refrigeration cycle is low. This means that the desorbed methanol is small, and a big mass of activated carbon is required to release enough methanol. At high desorption temperature (90-95°C), the coefficient of performance of the refrigeration cycle is high, but the mass of hot water is too much for domestic consumption and the use of large collector area is also not economical. Furthermore the energy of the domestic hot water produced from the heat recovered is high when the desorption temperature of the second adsorber bed is decreased. Thus, the decrease in the desorption temperature of the second adsorber bed necessitates the use of heavier adsorber bed since heavier adsorber bed will reject more sensible heat during the cooling process. Also the decrease in the desorption temperature of the second adsorber bed will require more mass of activated carbon to desorb enough methanol. At the same time, the increase mass of activated carbon will result in the use of more adsorber tubes and large water storage tank. The big adsorber bed will increase the size and cost of the system and decrease the coefficient of performance of the adsorption refrigeration cycle. With all these arguments a practical desorption temperature is seen to be 85°C.

2. Effect of condenser temperature on system performance

The amount of condensed methanol depends not only on the temperature of the adsorber bed but also on the condensing temperature. At high condenser temperature the amount of condensed methanol is

small so that more activated carbon is required to release enough methanol. The coefficient of performance of the refrigeration cycle is therefore small. At low condenser temperature the desorbed methanol is increased so less mass of activated carbon can be used to produce the same mass of methanol. The coefficient of performance is thus increased. In table 3 we show the effect of using condenser temperature of 35°C instead of the 30°C. The shortcomings in using this temperature for the condenser are low coefficient of performance of the refrigeration cycle, over load domestic hot water supply, big solar collector area, heavier second adsorber bed leading to bulky and costly system.

Table 3: System performance at condenser temperature of 35°C

	1 st adsorber bed	2 nd adsorber bed	Dual system
Mass of activated carbon (kg)	43	119	162
Mass of adsorber bed (kg)	65	181	246
Number of adsorber tubes	33	92	125
Mass of hot water (kg)			236
Size of solar collector (m ²)			6.96
$COP_{cycle-ice}$	0.365	0.204	0.284

3. Effect of the mass of ice on the system performance

Within 24 hours, a reasonable capacity of the dual system to produce domestic ice is 12 kg. This is shown in table 5. If more ice is to be produced (18 or 24 kg), the system will require larger solar collector and will be bulky and costly. The amount of hot water produced is also too much for domestic consumption. The only possible way to increase the mass of ice with reasonable price, size, area of solar collector and volume of domestic hot water is to use an activated carbon with high adsorption capacity and high conductivity.

Table 5: Performance of system with variation in the mass of ice produced

Temperature of evaporator = -5°C

Temperature of condenser =30°C Temperature of hot water = 98°C Temperature of first adsorber bed = 95°C Temperature of second adsorber bed =85°C			
Mas of ice (kg)	12	18	24
Mass of activated carbon (kg)	61	90	121
Mass of adsorber bed (kg)	91	135	182
Number of adsorber tubes	47	70	93
Mass of hot water (kg)	116	173	231
Area of solar collector (m ²)	3.60	5.39	7.18

In search of new adsorbent materials, Wang et al. (1997) [10] had reported that, for specially treated ACF, the measured adsorption capacity of methanol is two to three times greater than that of normal activated carbon, and the estimated adsorption time is only about 1/5 to 1/10 of that of normal activated carbon used by Meunier et al. (1986) [11]. Tamaniot-Telto and Critoph (2000) [12] investigated the thermo physical properties of two types of monolithic activated carbons with an intention to design and fabricate a high performance generator for sorption refrigeration systems and heat pumps using ammonia as refrigerant. It was found that, reduction in volume from granular bed to monolithic bed was up to 50%, which could lead to a substantial economic gain.

5. Conclusion

Malaysian activated carbon has similar adsorption properties as many types of activated carbons used in different countries. From the *COP* point of view, activated carbon - methanol adsorption machine can be powered successfully by heat source of maximum 110°C. Malaysian activated carbon as adsorbent material is not recommended in our dual purpose adsorption system at condenser- adsorption temperature equal or higher than 35°C. The most efficient way to improve the dual purpose system under the hot climate is to search for enhanced adsorbent material in terms of adsorption capacity and thermal conductivity.

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