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Adsorption characteristics of Hydrofluoroolefin on molecular sieves of CMS 5A and Linde 13X as a refrigerant-adsorbent pairs for heat pump applications

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Abstract
The characteristics of both adsorbent-adsorbate pairs play an important role in several kinds of adsorption refrigeration/heat pump applications. Therefore, the present work aims to investigate the ability of two different molecular sieves, carbon molecular sieve (CMS) 5A and Lined 13X, to absorb Hydrofluoroolefin refrigerant R1234yf on its surface. An experimental testing facility is designed and constructed to measure the adsorption characteristics. Numerous runs were performed with the proposed test facility. Experimental results indicate that the Linde 13X is more suitable than CMS 5A for adsorption of refrigerant R1234yf. In addition, a thermal model based on Dubinin-Astakhov was adopted to predict the adsorption load. The results of the model are very essential in determining the adsorption load at various operating conditions in which the performance of the intermittent heat pump system using the proposed pair could be evaluated. The results agree with the experimental data with a maximum average error of ± 7 %.

Keywords: Hydrofluoroolefin; Adsorption; Molecular sieves; Solid adsorption.

1. Introduction

Conventional vapor refrigeration and heat pump systems using HFC are always questioned not only because they consume more high-quality energy and involve moving parts but also they contribute to the green-house effect. It is worth to mention that their use is phased down in order to reduce and ultimately eliminate direct emissions of high-GWP refrigerants. As a consequence of the phasing out of HFCs and candidates to replace vapor compression systems, sorption systems appear to be potential option.

In the field of sorption system technology there are many choices among several systems, such as chemical reaction heat pump, liquid absorption, and solid adsorption heat pump. Many investigations have been done on testing some refrigerants in the solid-adsorption heat pump cycle. The previous attempts in this area showed that the most usable refrigerant-adsorbent pairs are ammonia-carbon, methanol-carbon, ammonia-salt and water-zealot. The studies concluded that each of the previous refrigerants has some disadvantage such as: the flammability, bad odor, and low working pressures.

Faraday, 1848, noted the cooling effect obtained by adsorbing ammonia into silver chloride. Some studies that have been done in this field leads to using sulfur dioxide and silica gel for the air-conditioning of railway carriages in the USA in the 1920's. Then, the adsorption heat pump technology had been abandoned till the 1970's. At the beginning of last decade of the Twentieth Century, solid sorption heat pump has received much attention. Various kinds of adsorption heat pumps were developed, mostly of activated carbon-methanol as introduced by [1, 2], salts ammonia, carbon methanol, and zeolite-water as discussed by [3, 4]. In addition, the merits of using different refrigerants with carbon in thermal systems been has investigated by [5]. The improvements of system performance could be reached by utilizing the forced convection principles in the adsorption-desorption processes in the adsorption heat pump systems showed by [6]. Wange et al. 1998 [7], developed and designed a spiral plate heat exchanger for the adsorber. The author concluded that the spiral plate heat exchanger was suitable for adsorption heat refrigeration system. In addition their results showed that the good heat transfer properties ensured short cycle time for adsorption systems.

Alternative cooling/heating options based on solid and liquid sorption systems are being explored all over the world as illustrated by [8, 9]. Adsorption systems for refrigeration and heat pump have been studied for many years as discussed by [10-12]. A number of heat pump systems has been built and tested as presented by [11-17].

New thermodynamic cycles, such as thermal wave cycle as presented by [18], and thermal swing adsorption heat pump system as investigated by [19], were proposed for possible future potentials. Ben Amar et al., [20], Miles and Shelton, [21], and Pons and Feng, [22], discussed the physics of adsorption phenomena and the ability to simulate the adsorption process by thermodynamic models and evaluate the different operating parameters numerically. The authors proved that the validation of such models by comparing its results with experimental results for a wide range of operating parameters. Rangarajan et al., [23], presented a new model called the Simplified Local Density (SLD) model, for describing the physical adsorption of gases on flat walls using cubic equation of state. Ramkumar and lira, [24], presented an engineering model to describe physical adsorption of pure gases and binary mixtures from sub to super critical conditions on flat walls, slits and pores using a signal temperature independent for fluid-solid interaction. The authors claimed that the model bridges the gap between the simple and sophisticated models. The model predicted the adsorption characteristics of ethylene and ethylene-methane mixture on activated carbon at different bed temperature.

During the last two decades, Adsorption heat pump systems have gained more and more interest and developed very fast as a type of environmentally friendly system and a kind of effective means of using low-grad heat sources and do not require any synthetic lubricants [25, 26]. Applications show that adsorption and desorption processes are potential application of heat pump technology, if it is well developed.

As presented by Muhsin and Ersan [27], the adsorption characteristics of the refrigerants R134a and R404a onto activated carbon is investigated experimentally. An experimental setup working with a constant-volume variable pressure method was used in the experimental measurements. Mohamed et. Al. [28] studied a new adsorbent/refrigerant pair to be used in adsorption cooling applications, adsorption isotherms and kinetics of Difluoroethane (HFC-152a) onto highly porous activated carbon Maxsorb III at temperatures ranging from 25 to 75°C have been investigated.

Since all refrigerants, that have been investigated, have some undesirable characteristics. One of these is the greenhouse effect. These bad effects have been covered by using alternative refrigerants in conventional vapor-compression systems. Hydrofluoroolefins (HFOs) are nothing new for chemistry. Much like traditional hydrofluorocarbons (HFCs), they composed from hydrogen, fluorine and carbon. R1234yf has become a refrigerant of a choice and many cars manufacturers have adopted new refrigerant in nearly 50 vehicle models [1]. In addition, HFOs found in a number of applications. In refrigeration and heat pump technology HFO-1234yf has been chosen to replace R134a in MAC systems; HFO-1234ze(E) and HFO-1233zd(E) are used in chillers [29, 30] and HFO-1336mzz has suggested for high temperature heat pumps [31].

Unlike R134a, new refrigerant has very low effect on global warming. This feature is common for other HFOs, for a number of which their integrated over 100 yr. contribution to global warming is not greater than that of CO_2 [2]. This is mainly due to their short lifetime that is within a couple of weeks for many HFOs

The renewed interest in the study of adsorption heat pump is based on the various advantages of the system, such as, non HFC's problems, simplicity in construction, cost-effective, and mean while they can be driven directly by low grad energy. In addition to, the design of adsorption refrigeration/heat pump systems, the characteristics of both adsorbent-adsorbate (refrigerant) pairs play an important role in various kinds of applications. Therefore, one of the alternative refrigerants, Refrigerant R1234yf is selected as an adsorbate in heat pump systems. While, two different types of adsorbent materials such as Linde 13X and CMS 5A were selected to be tested with such refrigerant. An experimental facility was designed, constructed and commissioned to determine the behavior of adsorption of R1234yf on the specified pairs. An experimental producer was adapted to control the bed temperature and refrigerant pressures. The measurements of adsorption load at pressure ranged from 50 psig (340 kPa) to145 psig (986 kPa) and temperature ranged from 25 °C to 120 °C were recorded for R1234yf -CMS 5A and R1234yf -Linde 13X pairs. Numerous runs were conducted. A thermal model of Dubinin-Astakhov equation was adapted to determine the adsorption load at different operating conditions. New values of Dubinin-Astakhov constants were obtained under the different operating conditions. The importance of this research work is to provide information about the amount of the Hydrofluoroolefin refrigerant needed to be adsorbed in the molecular sieves. this will give the designer of the heat pump applications a complete vision concerning the continuous heat regenerative adsorption refrigeration cycles.

2. Experimental facility

The schematic diagram for the test rig, as shown in Figure 1, consist of three main units. The first unit is an electric oven that has a maximum power of 10 kW. The oven controls the molecular sieve temperature during each experiment. The oven door has small open, through which the refrigerant pipe is passed. The refrigerant flowing inside the pipe is feed to the molecular sieve inside the bed vessel. The second unit is the constant oil temperature bath used to control the refrigerant temperature which in turn controls the refrigerant pressure. In this unit an electric heater of 18 kW is used to increase the oil bath temperature above the atmospheric temperature. A conventional compression refrigeration cycle, which operates with R22 as working fluid, is used to cool down the oil temperature. In addition, the refrigerant tank is mounted inside the oil and connected to the bed of the molecular sieve through an insulated copper tube. The molecular sieve grains are contained in the third unit called the bed vessel. The vessel is located inside the oven and connected to the refrigerant pipeline coming from the refrigerant tank. The bed temperature is measured by thermocouple immersed in thermocouple well. Also, the pressure and temperature of the refrigerant are measured at the inlet of the oven. The adsorption load is determined by weighing the bed vessel before and after the adsorption process.

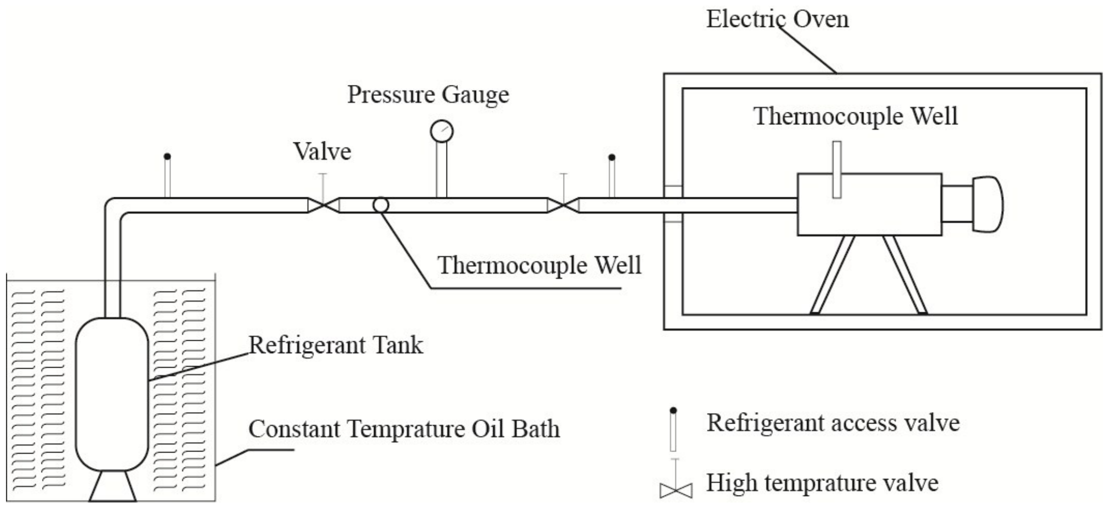


Figure 1. Schematic diagram of the Experimental Facility.

3. Experimental procedure

The vessel is washed up with acetone to assure the absence of welding flux to avoid the contamination of the bed. The vessel is then tested under about 50 psig (340 kPa) pressure, which is about two times of operating pressure against leakage. This pressure value remains constant for about 24 hours while no leakage was observed. The vessel was then weight before and after filing it with molecular sieve in order to determine the mass of the bed. The fresh sieves may adsorb a water vapor in its internal voids. Since the water vapor would affect the ability of refrigerant adsorption, the molecular sieve was heated to 200 °C and is subjected to a hard vacuum for about two hours to achieve a maximum dehydration. The vessel was then re-weighed to determine the actual weight of dry molecular sieve and the amount of rejected water vapor.

The bed vessel was placed in the oven and connected to the refrigerant tube coming from the refrigerant tank placed in the contestant oil temperature bath. Electric oven thermostat was adjusted for the desired bed temperature, which was measured by digital thermometer. The refrigerant tank temperature was adjusted by oil bath thermostat in order to keep the refrigerant pressure constant through the experiment. The refrigerant R1234yf is then allowed to flow to the vessel. The vessel was disconnected and weighted for each twenty minutes. Hence, the adsorbed mass during each time intervals was determined. This process had been continued until equilibrium was achieved. The collected data represent the variation of adsorbed mass with time at certain bed temperature and refrigerant pressure. The same procedure was repeated for another set of bed temperatures and refrigerant pressures. The final equilibrium adsorption masses were recorded at the desired set of pressures and temperatures. These data were plotted to construct the isobar and isothermal curves for the refrigerant with each type of molecular sieve.

4. Results and discussion

The experiments were conducted using R1234yf as adsorbate on two different molecular sieves, which are CMS and Linde 13X. The experimental data were taken according to the experimental procedures discussed before. In order to discuss the results, it is essentially to distinguish between two concept that are refrigerant charged mass and refrigerant adsorbed mass. The term charged mass means that the refrigerant is just filling the external voids molecular sieve and did not absorbed to its surface. While the other term indicates that the refrigerant molecules was adsorbed to the external and internal void surfaces of the molecular sieves grains. This classification is based on the kinetic parameter of the refrigerant and the pore size of the molecular sieve, when the refrigerant was adsorbed; the heat of adsorption was released. This in turn increases the temperature of the bed. Furthermore, the bed temperature was measured to distinguish between these two concepts. If the bed temperature is increased during the feeding of the refrigerant to the bed then adsorption process will be taken place. Otherwise if else the mass of refrigerant consumed in the bed is considered as charged mass through the external voids of the packed bed. The results were divided into two groups which are discussed as follows.

4.1 Results of R1234yf on CMS 5A

During a series of experiments, the refrigerant charged mass into the carbon molecular sieve 5A is measured at various bed temperatures ranged from 20 °C to 95 °C and at the refrigerant pressures ranged from 50 psig (340 kPa) to 145 psig (986 kPa) at time intervals of 20 minutes each expect the first interval. The results are summarized and presented in figures (2A) to (5B). Each figure shows the transit behavior of the refrigerant charged mass of at a certain bed temperature and refrigerant pressure. The results show generally that during the first 20 minutes the mass of refrigerant entered the test section was rapidly increased at all bed temperatures and all refrigerant pressures, and then it was kept constant at its maximum value. It was also realized that the bed temperature is not varied during each experiment. This indicates that the mass entered the test section is due to the difference between the pressure of packed bed in the testing section and the pressure of the refrigerant charged into the test section.

Figure (2A) shows that, at the refrigerant pressure of 50 psig (340 kPa) the maximum charged mass is varied from 8 to 16 grams when the bed temperature charged from 95 °C to 20 °C, respectively. For the same experiment it is realized also that the bed temperature is kept constant, as shown in figure (2B). This indicates that the CMS 5A does not adsorb the charged mass. The behavior of the bed at pressure of 60 psig (408 kPa) and 80 psig (544 kPa) is the same of that for pressure 50 psig (340 kPa), as shown in Figures (2C) to (3B). Therefore, the charged mass did not adsorbed to the molecular sieves yet.

At refrigerant pressure of p0 psig (612 kPa) it is noted that the charged increased rapidly with time at bed temperature 25 °C, as shown in Figure (3C). The charged mass reached 494g, which is about 106% of the carbon molecular sieve mass. Since the maximum porosity of the CMS 5A is 40%, the value of charged mass is more than the vacancy of the solid bed. This indicates no adsorption has occurred in the bed. It is also realized that from Figure (3D) that the bed temperature increased suddenly in the first interval to 28 °C and then decreased to its initial value. The reason behind this observation is due to the higher temperature of the refrigerant entered the test section, which heats up the bed for a while, and then condenses on the outer surface of the bed particles, therefore the temperature is reduced to its initial value. At bed temperature 33 °C and 35 °C, the charged mass increases in the first interval because the refrigerant pressure compresses the refrigerant into the vessel and then decreases until the equilibrium occurs. This decreasing is resulting from the evaporation of the charges mass due to the increasing in the bed temperature as time elapsed as shown in Figure (3D).

Additional runs were conducted to assure the last explanation at pressure 100 psig (680 kPa), 120 psig (816 kPa) 145psig and (986 kPa). The results confirm the same behavior of the bed at pressure 90 psig (612 kPa) as shown in Figures (4A) to (5B). The charged mass increases to its highest value, about (486-496 g), while the bed temperature is less than the saturation temperature of the refrigerant. Also, when the bed temperature is higher than the refrigerant saturation temperature the mass is increased in the first interval and then decreased to the equilibrium. All of these results and their explanations indicate that CMS 5A molecular sieves is not suitable as an absorbent materials with refrigerant R1234yf as adsorbate in the specified range of refrigerant pressure and bed temperatures.

4.2 Results of R1234yf on Linde 13X

The Linde 13X was selected as another adsorbent material because it has a large pore size, 10 Å, as compared to CMS 5A, which has a pore size only of about 5 Å. the refrigerant quaintly is measured at various bed temperature ranged from 27.5 °C to 120 °C and at the refrigerant pressure ranged from 50 psig (340 kPa) to 100 psig (680 kPa) at time intervals of 20 minutes. The results of the isobar test of this pair are shown in Figures ranged from (5C) to (7C). The results show that the mass of refrigerant entering the bed increased rapidly in the first 20 minutes and then it increased slowly to its equilibrium value. The bed temperature history indicates that the bed temperature generally increased in the first interval. This indicated that the mass entering the bed vessel is absorbed to the molecular sieves. The bed temperature then decreases with time while the absorbed mass reaches to its final equilibrium value. Therefore, all of the charged refrigerant masses are considered to be adsorbed mass.

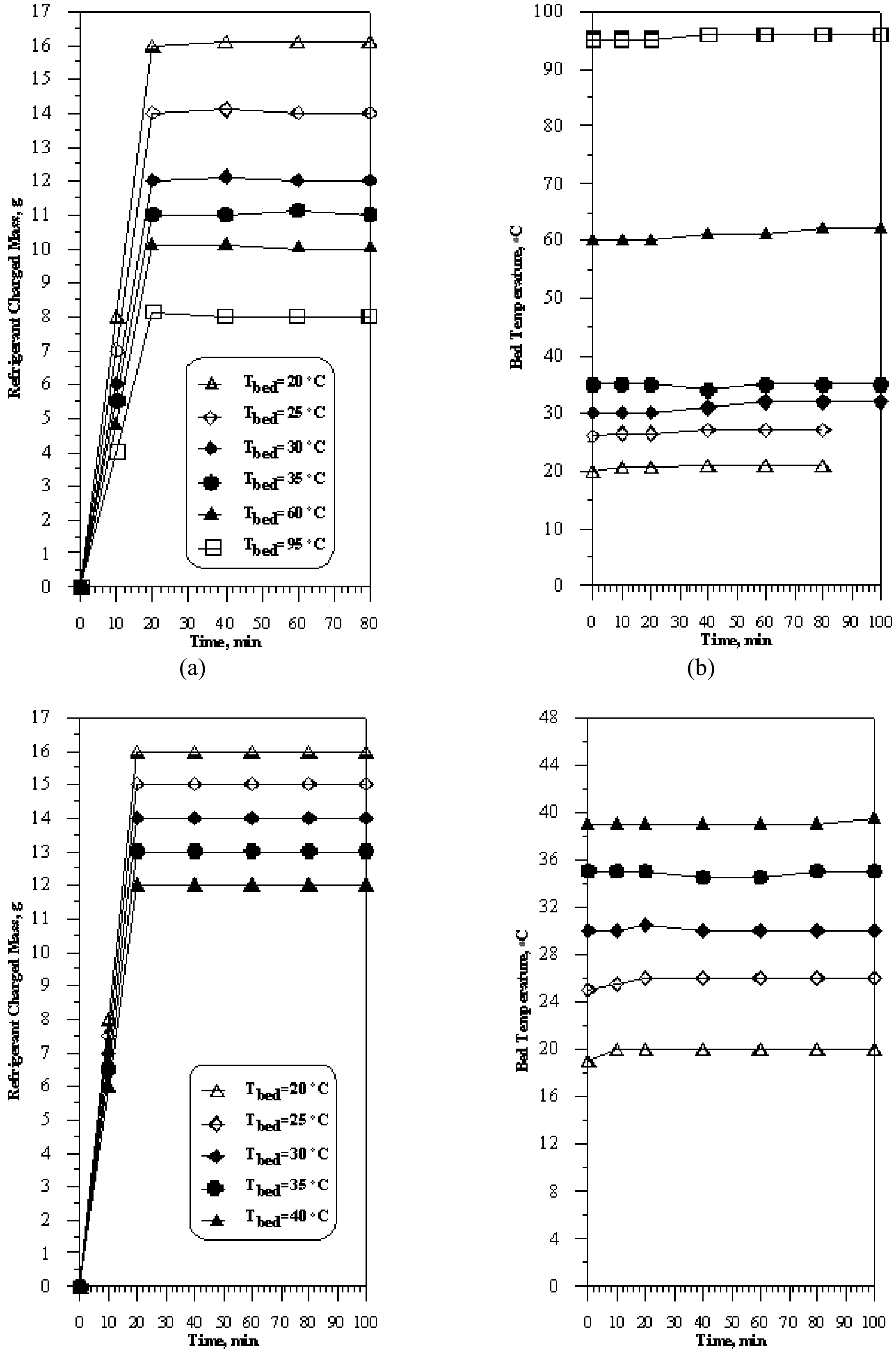
Figure (5C), as an example, shows that the adsorbed mass increased rapidly in the first interval and then it is increased slowly to the final equilibrium adsorbed mass. The rapid increasing of the absorbed mass is resulted from the pressure difference between the incoming refrigerant and the initial pressure inside the evacuated vessel. This pressure difference compresses the refrigerant into the vessel causing high adsorbed mass. The molecular sieves then begin to adsorb the refrigerant naturally after the first interval until it reaches to the equilibrium condition. This behavior of adsorption occurs at any pressure or at any bed temperatures as indicated in the other figures.

The final or maximum adsorbed mass changed with the bed temperature, when the bed temperature is increased as the adsorbed mass is decreased. For example, at bed temperature is of 27.5 °C the final adsorbed mass is 108g while at 120 °C the mass is decreased to 63g which equal to 58.3 % of the previous value. In other word, when the bed temperature increased from 27.5 °C to 120 °C about 41.7 % of the absorbed mass at 27.5 °C could be regenerated at a constant pressure of 50 psig (430 kPa).

When the pressure increased to 65 psig (440 kPa), as shown in Figure (6A), the maximum adsorbed load at any bed temperature increased by a value more than that of pressure 50 psig (340 kPa). The adsorbed mass at 27.5 °C and 65 psig (440 kPa) is recorded as 122g while it equals to 72g at the bed temperature of 120 C. At this pressure, the maximum adsorbed equal to 28 % of the bed mass. The temperature rise from 27.5 °C to 120 °C could give a regenerated refrigerant mass of 41 % of its adsorbed mass at 27.5 C. It was noticed that the same behavior is achieved at refrigerant pressure of 80 psig (544 k Pa), 90 psig (612 kPa) and 100 psig (680 kPa) at different bed temperature, as depicted in Figures (6C), (7A) and (7C), respectively.

The effect of refrigerant pressure on the adsorbed mass at the same bed temperature is shown in Figures (8A) to (9). It is clear that the adsorbed mass increases as the refrigerant pressure increases at each temperature. At bed temperature of 27.5 °C, the final adsorbed mass increases from 108g to 143g when the pressure is increased from 50 psig (340 kPa) to 100 psig (680 kPa). In other word, the pressure swing from 100 psig (680 kPa) to 50 psig (340 kPa) at 27.5 °C could regenerate about 24.5% of its adsorbed mass at 100 psig (680 kPa).

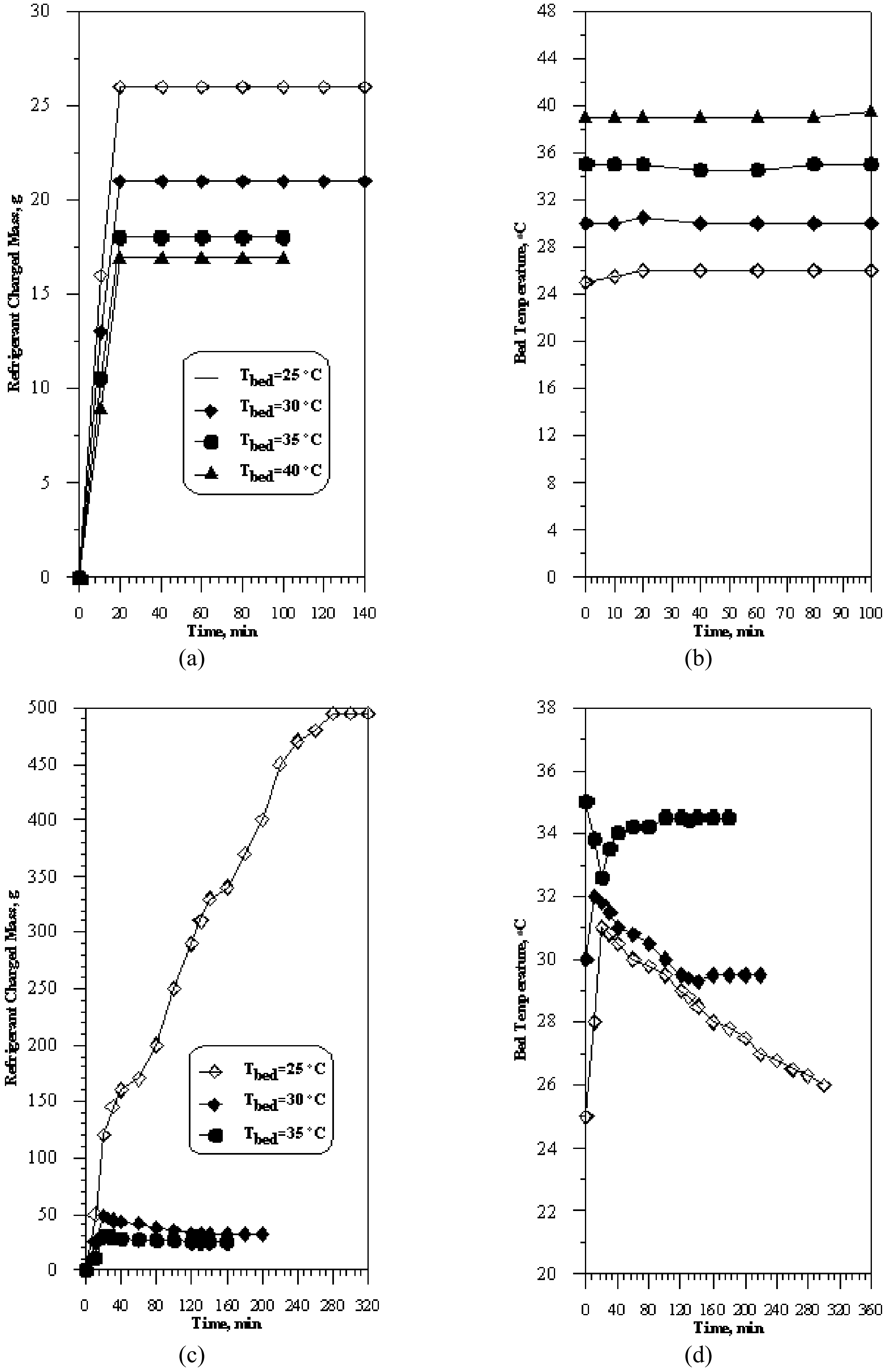
At bed temperature of 120 °C, the adsorbed mass increased with about 23.8% for a pressure swing from 50 psig (340 kPa) to100 psig (680 kPa). Therefore, the effect of the pressure swing of adsorbed mass increases as the bed temperature decreases, while the effect of temperature swing, from 27.5 °C to 120 °C, on adsorbed masses are increased by factors, 71.4% at 50 psig (340 kPa) and 83.3 % at 100 psig (680 kPa) respectively.



(a) (b)

(c) (d)

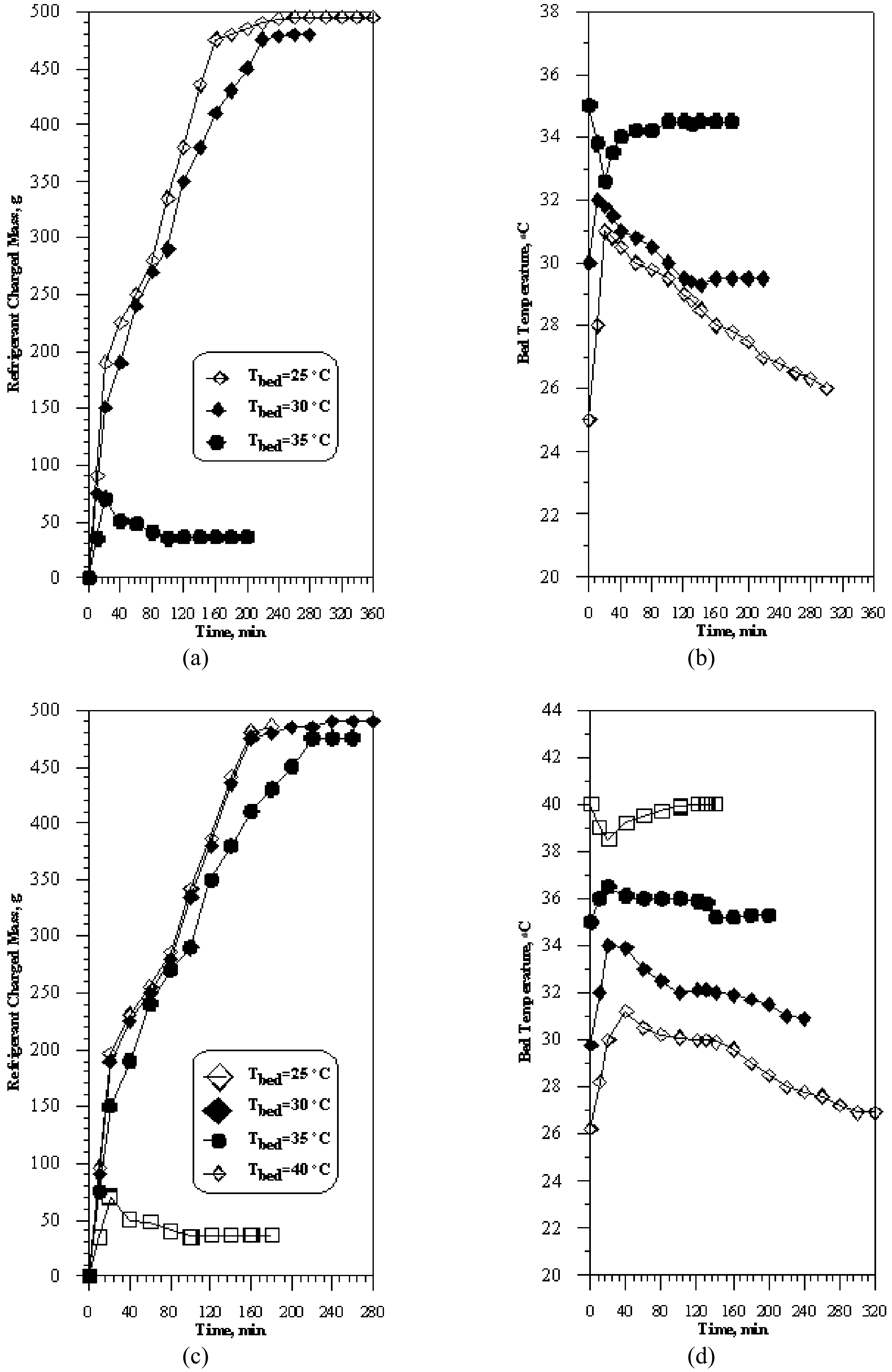
Figure 2. (a) Transient behavior of R1234yf Charged Mass on CMS 5A at different Bed Temperatures at P_{sat}= 50 Psig, T_{sat} 12.13 °C, (b) The Fluctuation of Bed Temperatures During System Operation for CMA 5A at Psat= 50 Psig, Tsat 12.13 °C, (c) Transient behavior of R1234yf Charged Mass on CMS 5A at different Bed Temperatures at P_{sat}= 60 Psig, T_{sat} 16.76 °C, (d) The Fluctuation of Bed Temperatures During System Operation for CMA 5A at P_{sat}= 60 Psig, T_{sat} 16.76 °C.



(a) (b)

(c) (d)

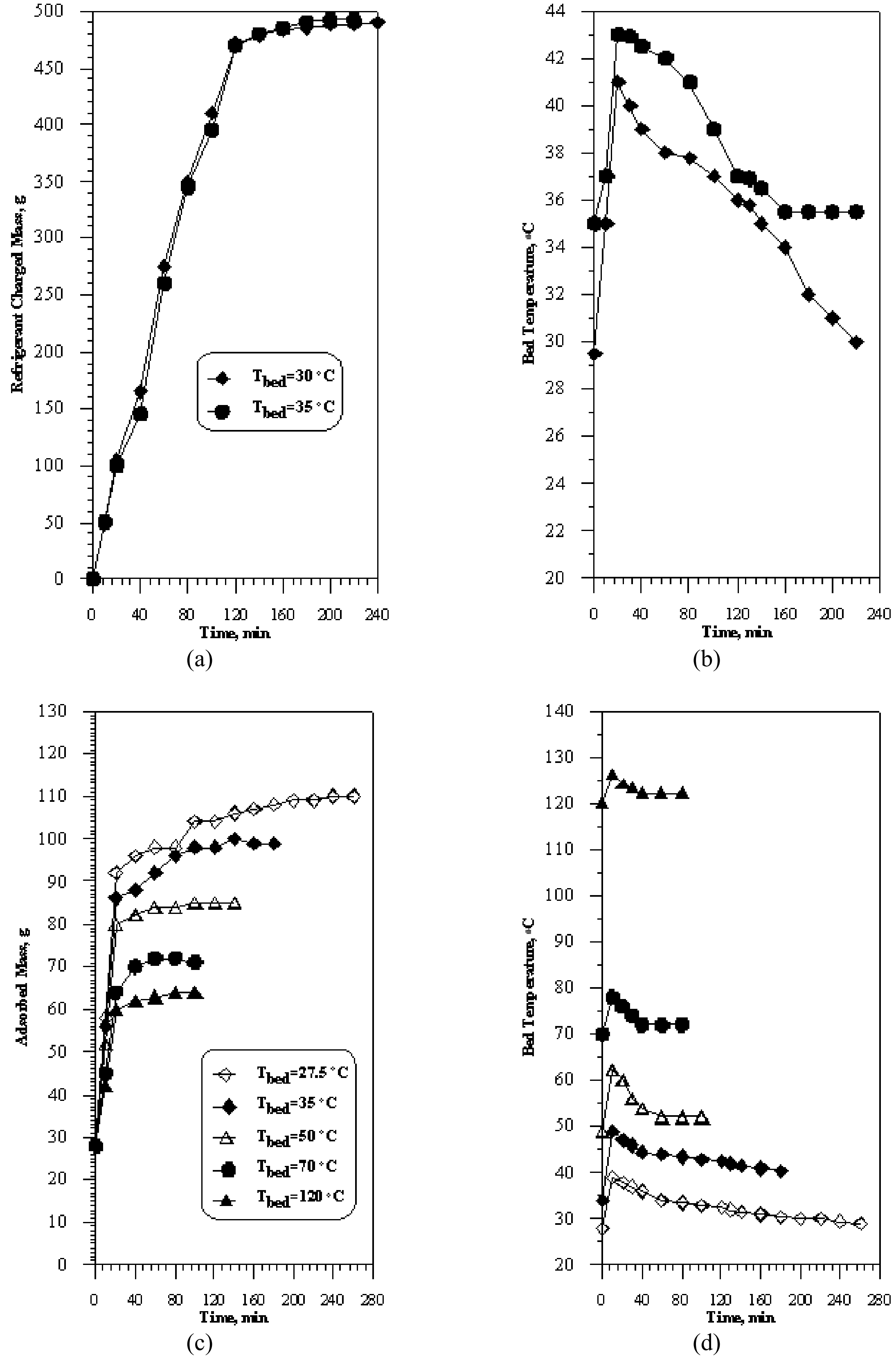
Figure 3. (a) Transient behavior of R1234yf Charged Mass on CMS 5A at different Bed Temperatures at P_{sat}= 80 Psig, T_{sat} 24.32 °C, (b) The Fluctuation of Bed Temperatures During System Operation for CMA 5A at P_{sat}= 80 Psig, T_{sat} 24.32 °C, (c) Transient behavior of R1234yf Charged Mass on CMS 5A at different Bed Temperatures at P_{sat}= 90 Psig, T_{sat} 27.22 °C, (d) The Fluctuation of Bed Temperatures During System Operation for CMA 5A at P_{sat}= 90 Psig, T_{sat} 27.22 °C.



(a) (b)

(c) (d)

Figure 4. (a) Transient behavior of R1234yf Charged Mass on CMS 5A at different Bed Temperatures at P_{sat}= 100 Psig, T_{sat} 30.89 °C, (b) The Fluctuation of Bed Temperatures During System Operation for CMA 5A at P_{sat}= 100 Psig, T_{sat} 30.89 °C, (c) Transient behavior of R1234yf Charged Mass on CMS 5A at different Bed Temperatures at P_{sat}= 120 Psig, T_{sat} 36.67 °C, (d) The Fluctuation of Bed Temperatures During System Operation for CMA 5A at P_{sat}= 120 Psig, T_{sat} 36.67 °C.



(a) (b)

(c) (d)

Figure 5. (a) Transient behavior of R1234yf Charged Mass on CMS 5A at different Bed Temperatures at P_{sat}= 145 Psig, T_{sat} 43.01 °C, (b) The Fluctuation of Bed Temperatures During System Operation for CMA 5A at P_{sat}= 145 Psig, T_{sat} 43.01 °C, (c) Transient behavior of R1234yf Adsorbed on Linde 13X at different Bed Temperatures at P_{sat}= 50 Psig, T_{sat} 12.13 °C, (d) The Fluctuation of Bed Temperatures During System Operation for Linde 13X at P_{sat}= 50 Psig, T_{sat} 12.13 °C.

The final equilibrium condition on the adsorbed mass at different operating conditions f bed temperatures and refrigerant pressure can be summarized using either isobar or the isothermal curves. Each one of these curves is used in the design of the absorption systems. The isothermal curve is used for design of system that operates on the temperature swing cycle while the isobar curves are suitable for system using the pressure swing cycle. The isobar curve of refrigerant 134a with Linde 13X molecular sieve is shown in Figure 10 while isothermal curve is shown in Figure 11. The effect of bed temperature and refrigerant pressure on the adsorbed load is summarized in Table 1. This table represents the adsorption load for two zones of adsorption which are considered to be rapid adsorption and normal adsorption zones. The rapid adsorption in the first was caused by the pressure difference between the pressure in the evacuated bed and the pressure of the refrigerant in tank. While the normal adsorption was caused by normal attractive forces excreted between the adsorbate and adsorbate molecules.

4.3 The thermal model

Based on [32], the Polanyi potential theory suppose that the potential ε is offered located around the surface of the adsorbed and adsorbent gas exists in a compressed state by the attractive forces acting from the surface. The forces effects states from adsorbent grain surfaces, where $\varepsilon = \varepsilon_{max}$ to a define distance where $\varepsilon = 0$, into the surrounding space. In this region the adsorbate density is not constant because it is in a compressed state, begin a maximum at the solid surface and minimum at $\varepsilon=0$. Polanyi proposed that the adsorption potential ε may be represented by the following equation:

$$\varepsilon = \mathrm{RT}\ln\frac{\mathrm{P}}{\mathrm{P_{sat}}} \tag{1}$$

where: P is the compressed adsorbate pressure of on equipotential surface, P_{max} is the equilibrium pressure of the vapor-adsorbate, T is the temperature of the adsorbent bed, and R gas constant

Based on the theory of Dubinin-Astakhov, V is the volume occupied by the adsorbate which is linked to the total pore volume V_0 and ε by the next equation:

$$V = Vo\ exp\left[-\left(\frac{B}{B2}\right)\varepsilon 2\right] \tag{2}$$

Where the ratio of the adsorbate molar volume at a temperature T to that of a reference gas (normally benzene) at the same temperature is the affinity coefficient B. This coefficient depends on the adsorbate only. It was found that the value of B decreases as the micro-porosity of the adsorbent increases.

Substituting equation (1) into equation (2) yields:

$$V = Vo\ exp\left[-\left(\frac{B}{B2}\right)\left(\mathrm{RT}\ln\frac{\mathrm{P}}{\mathrm{P_{sat}}}\right)2\right] \tag{3}$$

From the previous equation, it can be seen that V equals Vo when P equals P_{sat}. Another modification that was suggested is the presence of the pressure effect. Thus Vo varies with gas pressure P_{sat} may be assumed. Then the next relation can be gotten as follow:

$$\mathrm{V(T, Psat) = Vo(Psat)exp}\left[-\left(\frac{\mathrm{B}}{\mathrm{B2}}\right)\left(\mathrm{RTln}\frac{\mathrm{P}}{\mathrm{Pmax}}\right)2\right] \tag{4}$$

Also, Clausius-Claperyon equation represent the relation between temperature and pressure for saturated adsorbate.

$$\mathrm{Lnp} = \mathrm{A} - \frac{\mathrm{C}}{\mathrm{T}} \tag{5}$$

Substituting equation (5) into equation (4) produce the following equation:

$$\mathrm{V(T, Tsat) = Vo(Tsat)exp}\left[-\left(\frac{\mathrm{B}}{\mathrm{B2}}\right)\left(\mathrm{RC}\frac{\mathrm{T}}{\mathrm{Tmax}} - \mathrm{RC}\right)2\right] \tag{6}$$

Then, Substitute the density ρ(T) into the previous equation, the mass adsorbed M (T, Tsat) becomes:

$$\mathrm{M(T, Tsat) = Mo(Tsat)exp}\left[-\left(\frac{\mathrm{B}}{\mathrm{B2}}\right)\left(\mathrm{RC}\frac{\mathrm{T}}{\mathrm{Tmax}}-\mathrm{RC}\right)2\right] \tag{7}$$

Where Mo (T_{sat}) equals Vo (T_{sat}) ρ(T_{sat}) since ρ(T) is constant as ρ(T_{sat}) around the surface of the adsorbent when T equals Tsat.

An extension of the equation is introduced as equation (8), which employs a variable index x instead of 2, to allow a better fit to some adsorbent characteristics,

$$\mathrm{M(T, Tsat) = Mo(Tsat)exp}\left[-\left(\frac{\mathrm{B}}{\mathrm{B2}}\right)\left(\mathrm{RC}\frac{\mathrm{T}}{\mathrm{Tmax}}-\mathrm{RC}\right)\mathrm{n}\right] \tag{8}$$

By substituting the mass ratio X of adsorbed mass of adsorbent in this relation, and rewriting it in another way that replaces T with T_{bed} equation (8) becomes:

$$\mathrm{X(Tbed, Tsat) = Xo(Tsat)exp}\left[-\mathrm{K}\left(\frac{\mathrm{Tbed}}{\mathrm{Tmax}}-1\right)\mathrm{n}\right] \tag{9}$$

Where k is the value $\left(\frac{\mathrm{B}}{\mathrm{B2}}\right)(\mathrm{RC})\mathrm{n}$, which is effected by the characteristics of both adsorbent and adsorbate and which is independent of temperature. This final theoretical model equation was used to correlate the experimental data in order to predict the adsorption loading at any operating conditions.

By assuming the values of X_o, K and n to be constant for the operating pairs. Datafit is used to get the values of these constants. The results of this program and the statistical parameters of the results are shown in table (2). The resulted correlations could be used to predict the adsorption load of refrigerant R134a on the Linde 13X molecular sieve at any condition within the experimental range. The maximum error in the estimated values of the adsorption load by the correlation is about± 7 %. Finally, the comparison between the experimental data and the correlation is also presented in Figure 12.

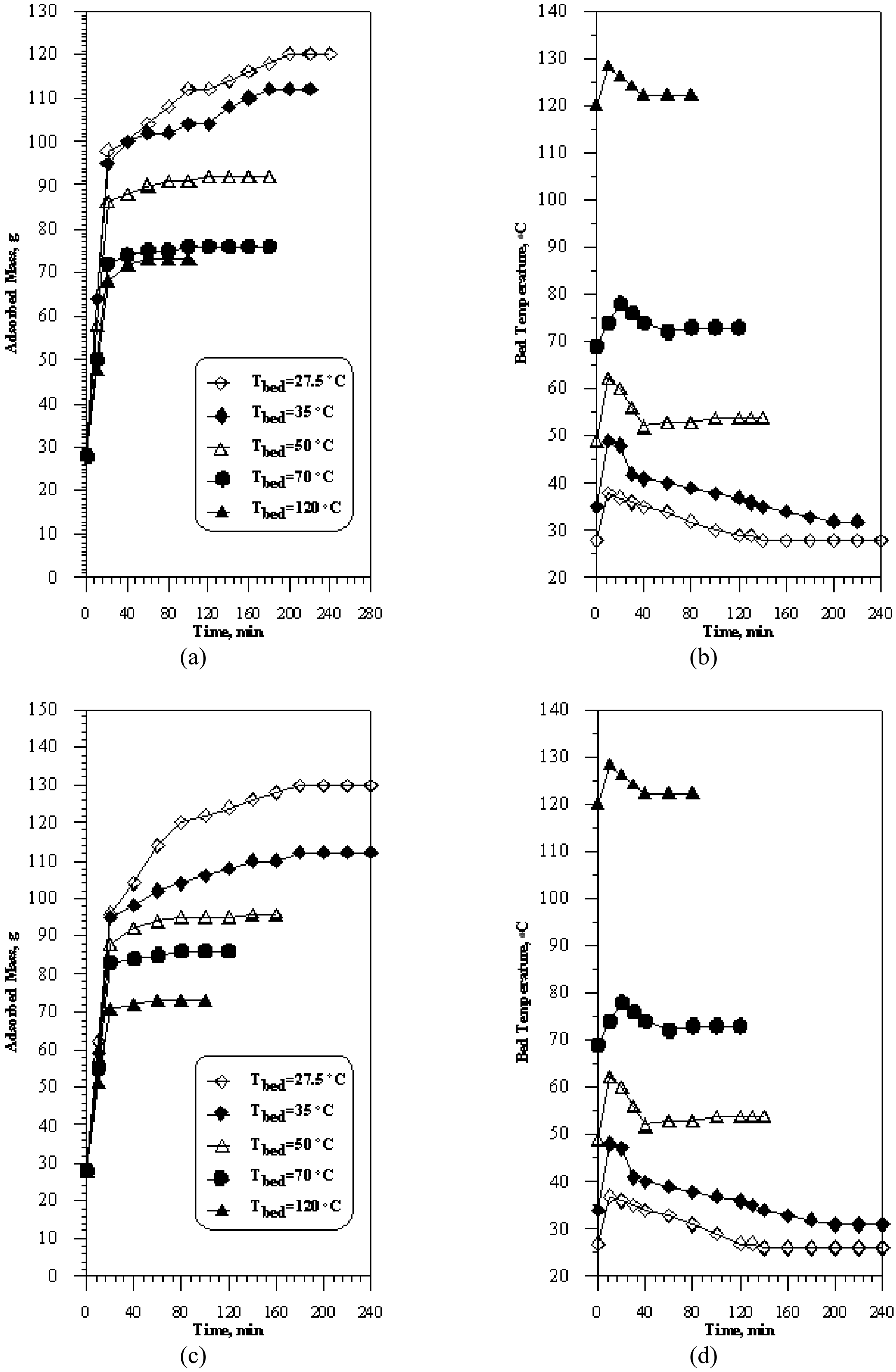
Table 1. Experimental Results of Adsorption Load of R1234yf on Linde 13X.

Refrigerant Pressure Psig (kPa)	Adsorption Load, %									
	Rapid Adsorption at different bed temperature, °C					Normal Adsorption at different bed temperature, °C				
	27.5	35	50	70	120	27.5	35	50	70	120
50 (340)	20.9	19.8	18.6	14.7	13.8	24.8	23.4	20	16.6	14.5
65 (440)	22.3	21.4	19.8	16.8	15.9	28	25.7	21.6	17.9	16.6
80 (544)	22.1	21.6	20.2	19.1	16.6	29.9	26.7	22.5	20	17
90 (612)	25.1	23	21.4	19.3	16.8	31.3	28	23.7	17.9	17.7
100 (680)	28	23.5	21.6	20.2	17.7	32.8	29.2	24.4	21.2	17.9

Table 2. Statistical data of the thermal model.

Nonlinear iteration limit = 1000
Diverging nonlinear limit = 50
Number of Nonlinear iterations performed = 55
Residual tolerance = 1E-16
Sum of residual = 3.16329805176319E-04
Average residual = 1.37534697902747E-05
Residual sum of square (Absolute) = 3.13612353716896E-03
Residual sum of square (Relative) = 3.13612353716896E-03
Standard Error of the Estimate = 1.22204425474557E-02
Coefficient of Multiple Determination (R^2) = 0.929545763
Proportion of Variance Explained = 92.9545763
Adjusted coefficient of Multiple determination (Ra^2) = 0.9261907993
Regression Variable Results

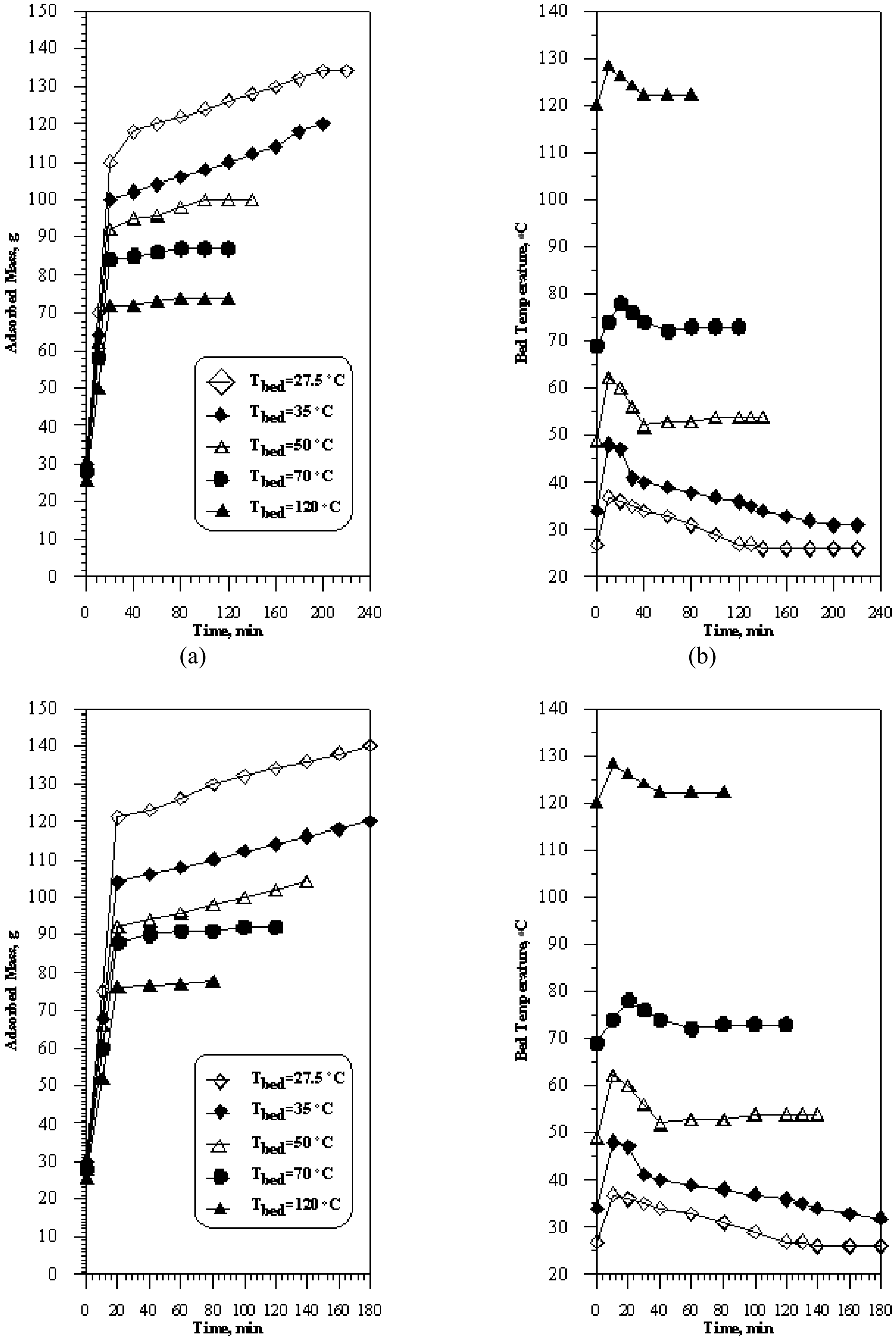
Xo	K	n
0.3767574603	0.469987058	035



(a) (b)

(c) (d)

Figure 6. (a) Transient behavior of R1234yf Adsorbed on Linde 13X at different Bed Temperatures at P_{sat}= 65 Psig, T_{sat} 18.66 °C, (b) The Fluctuation of Bed Temperatures During System Operation for Linde 13X at P_{sat}= 65 Psig, T_{sat} 18.66 °C, (c) Transient behavior of R1234yf Adsorbed on Linde 13X at different Bed Temperatures at P_{sat}= 80 Psig, T_{sat} 24.32 °C, (d) The Fluctuation of Bed Temperatures During System Operation for Linde 13X at P_{sat}= 80 Psig, T_{sat} 24.32 °C.



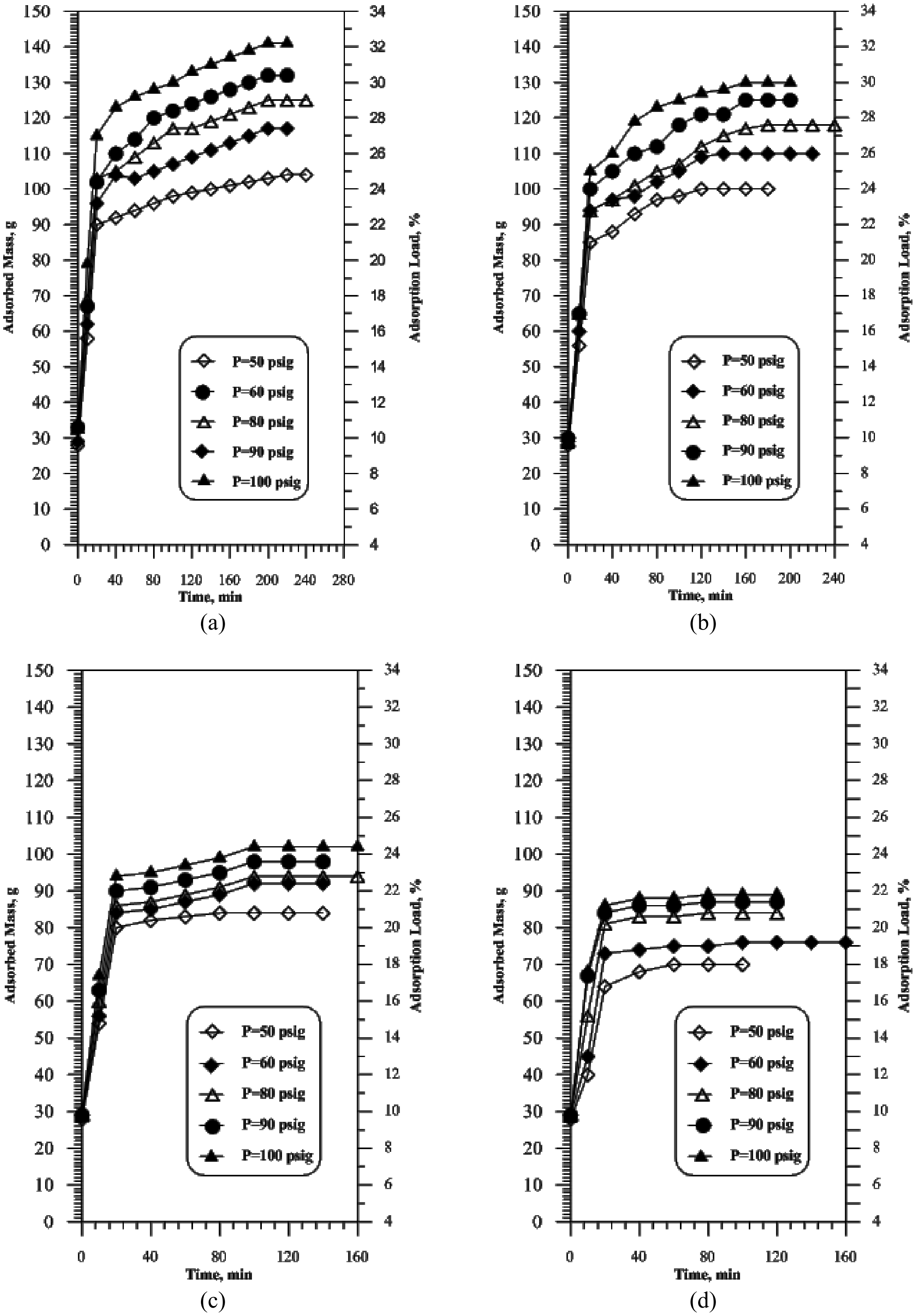
(a)

(b)

(c)

(d)

Figure 7. (a) Transient behavior of R1234yf Adsorbed on Linde 13X at different Bed Temperatures at P_{sat}= 90 Psig, T_{sat} 27.72 °C, (b) The Fluctuation of Bed Temperatures During System Operation for Linde 13X at P_{sat}= 90 Psig, T_{sat} 27.72 °C, (c) Transient behavior of R1234yf Adsorbed on Linde 13X at different Bed Temperatures at P_{sat}= 100 Psig, T_{sat} 30.89 °C, (d) The Fluctuation of Bed Temperatures During System Operation for Linde 13X at P_{sat}= 100 Psig, T_{sat} 30.89 °C.



(a) (b)

(c) (d)

Figure 8. (a) Transient behavior of R1234yf Adsorbed on Linde 13X at different Bed Refrigerant Pressures at T_{bed} = 27.5 °C, (b) Transient behavior of R1234yf Adsorbed on Linde 13X at different Bed Refrigerant Pressures at T_{bed} = 35 °C, (c) Transient behavior of R1234yf Adsorbed on Linde 13X at different Bed Refrigerant Pressures at T_{bed} = 50 °C, (d) Transient behavior of R1234yf Adsorbed on Linde 13X at different Bed Refrigerant Pressures at T_{bed} = 70 °C.

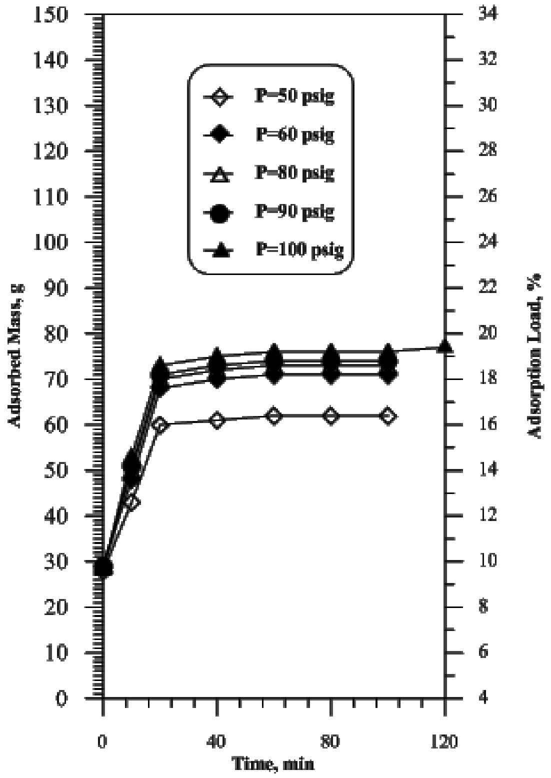


Figure 9. Transient behavior of R1234yf Adsorbed on Linde 13X at different Bed Refrigerant Pressures at $T_{bed} = 120$ °C.

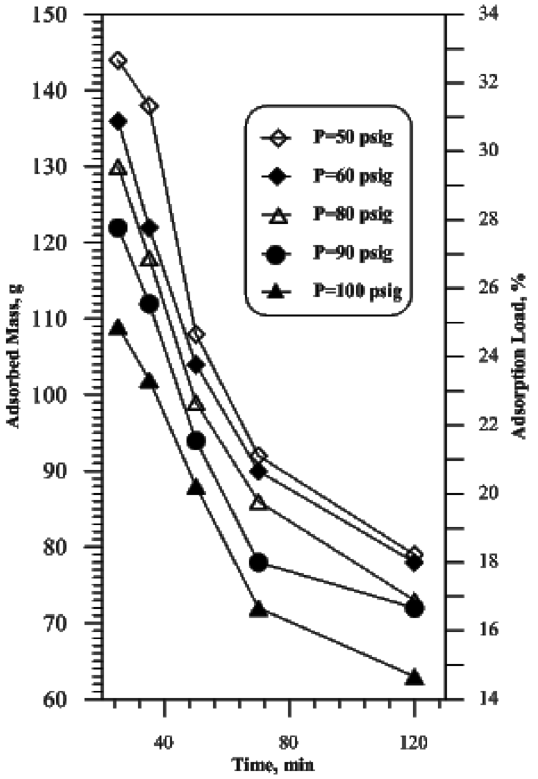


Figure 10. Effect of Bed Temperatures on Adsorption Loading at different Refrigerant Pressures for Linde 13X.

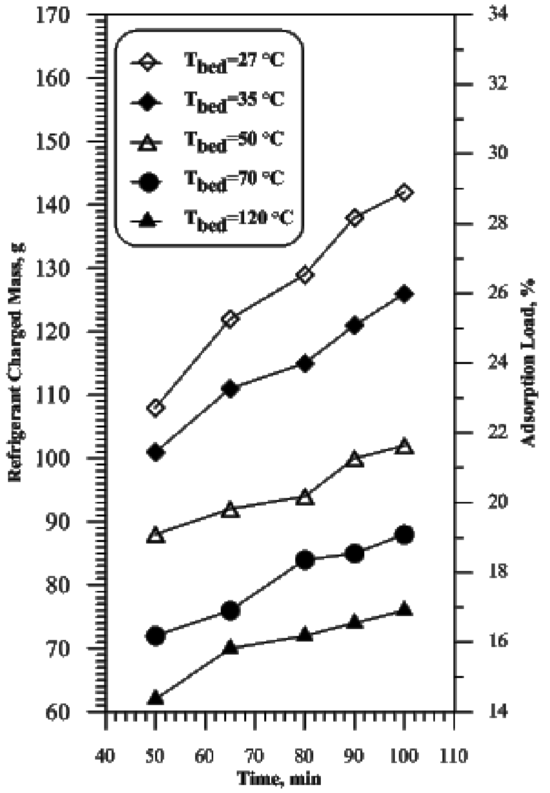


Figure 11. Effect of Refrigerant Pressures on Adsorption Loading at different Temperatures for Linde 13X.

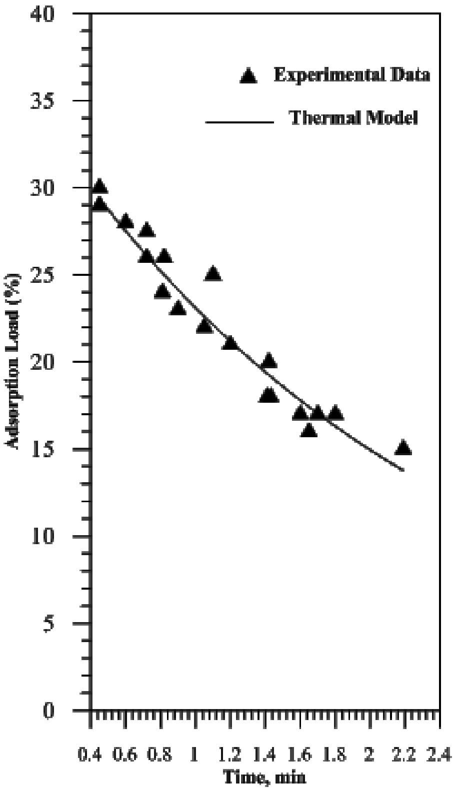


Figure 12. Theoretical Model Based on Dubinin Astakhove Theory.

5. Conclusion

The results show that the Linde 13X molecular sieve has the capability of adsorbing refrigerant R1234yf on its surface. Adsorption load of about 33% is achieved at a refrigerant pressure of 100 psig (680 kPa) and bed temperature of 27.5 °C. In addition, Linde 13X molecular sieves have been proved to be durable during the experimental runs. Therefore, it is recommended to be used in the thermal compression adsorption heat pump systems.

Experimental results indicate that the Linde 13X is more suitable than CMS 5A for adsorption of refrigerant R1234yf. In addition, a thermal model based on Dubinin-Astakhov was adopted to predict the adsorption load for R134a on Linde 13X. In the model, several main factors affecting the characteristics of the adsorption process were considered, such as the characteristics of the working pairs and the working condition. The results of the model are very essential in determining the adsorption load at different operating conditions in which the performance of the intermittent heat pump system using the proposed pair could be evaluated. The results agree with the experimental data with a maximum average error of ± 7 %..

On the other hand, the results indicate that the CMS 5A molecular sieves does not have the capability to adsorb refrigerant R1234yf on its surface in the specified experimental range of the temperatures, ranged from (20 °C to 95 °C), and refrigerant pressure, ranged from 50 psig (340 kPa) to 145 psig (986 kPa). Therefore, it is not recommended to be used as adsorbent with R1234yf in heat pump applications.

Nomenclature

Symbols

A, C	Constant
B	Parameter depends on the adsorbate and adsorbent physical properties
K	Constant depends on the adsorbate on the adsorbent physical properties
M	Mass, kg
N	The index variable which depend on the adsorbent characteristics
P	Pressure, kPa
R	Gas constant, kJ/kg.K
T	Temperature, K
V	Volume, m^3
X	Mass ratio of adsorbed mass to that of adsorbent, kg/kg
X_o	The maximum adsorption load, kg/kg

Greek Symbols

ε	Adsorption potential
β	Affinity coefficient
ρ	Density, kg/m^3

Subscript

bed	Bed
ref	Refrigerant
sat	Saturation
o	Maximum

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