ACTIVATED CARBON/REFRIGERANT COMBINATIONS FOR SOLAR REFRIGERATION APPLICATION

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ABSTRACT
Experimental study of three adsorbent/adsorbate combinations for use in adsorption refrigerators is presented. Activated carbon is the adsorbent while ammonia, ethanol and methanol are the adsorbate. The pressure-temperature-concentration (P-T-X) diagrams of the different combinations are also presented. From the results, the coefficient of performance (COP) of the ideal refrigeration cycle within the ranges applicable to solar adsorption refrigeration machines are estimated. It was found that it is possible to use all the combinations in adsorption refrigerator. However, while activated carbon/methanol is preferred at low grade heat, activated carbon/ammonia requires the use of advanced flat-plate collectors such as those with multiple glazing and/or selectively coated collector plates to be powered by solar energy.

INTRODUCTION
Adsorption is simply a process in which fluid molecules are trapped on the surface and within the pores of a solid. It is essentially a surface phenomenon. The pore structure of adsorptive solids can be divided into three approximate groups [1]: micropore (radii < 15 Å), transitional (radii between 15-200 Å) and macropores (radii > 200 Å). The solid pore structure of interest for solar refrigeration is the micropore. There are two types of adsorption processes: physical adsorption and chemical adsorption or chemisorptions. In physical adsorption, Van der Waal forces are responsible for the adsorption process and species so adsorbed are characterized by low heats of adsorption, relative ease of desorption and a significant temperature dependence upon the equilibrium capacities. On the other hand, chemical adsorption results from purely chemical interaction of adsorbent and adsorbate. It is characterized by very high heat of adsorption.

The use of adsorption process in cold production is not a new phenomenon. However, the first generation adsorption machines were gradually displaced by the vapour compression machines until the end of 19th century when they completely lost their relevance. Soon after World War I, in the 1920s, due to increasing cost of energy, absorption/adsorption refrigeration machines experienced a renaissance. More recently, increasing attention has been focused on solar adsorption refrigeration units as a viable means of extending vaccine cold chain to remote rural areas. The principle of operation have been described in the literature [2-4]. One interesting feature of the unit is its low operating temperature range which makes it possible to be powered by low grade heat. Besides, the common refrigerants used as the working fluid in the units do not pose any problem to the environment. The challenge to researchers is the continued search for
adsorbent/refrigerant combinations that could overcome the limitations of existing systems and thus improve refrigeration cycle performance.

Critoph [2] evaluated several refrigerants with zeolite and activated carbon and concluded that activated carbon gives better COP. Studies by a group of researchers in France [3] have compared the thermodynamic performance of zeolite-water and activated carbon-methanol combinations for use in solar ice maker. The results indicate that activated carbon-methanol pair has COP in the range 0.4-0.5 compared with less than 0.3 for zeolite-water pair. Activated carbon can be easily manufactured in the country of use and it is known to possess a large adsorptive power due to its highly developed porous structure. It is therefore necessary to try it with other adsorbates in order to establish which pair that will present the best performance as an adsorbent-refrigerant pair for solar powered adsorption refrigerator.

This work is therefore aimed at comparing methanol, ethanol and ammonia as adsorbate on activated carbon adsorbent to ascertain the pair that will give the best adsorbent-adsorbate pair for solar refrigeration. Methanol, ethanol and ammonia were chosen for this work because methanol is known to present good performance with activated carbon hence it is used here more for comparison. Ethanol is similar to methanol but it is more easily available thus could reduce cost if it presents good results. Ammonia is known to have high vapour pressure thus its operation is above atmospheric pressure. With it the problem of ingress of air, which greatly affects the performance of systems that operate at pressures below atmospheric, like activated carbon-methanol, will be solved. Also ammonia is known to withstand high temperature without disintegrating.

EQUILIBRIUM STATE OF ADSORBENT/REFRIGERANT COMBINATION

It is possible to determine the characteristics of the ideal refrigerating cycles from the pressure-temperature-concentration (P-T-X) diagram (See Fig. 1). Such data are also useful to establish the properties of any adsorbent-adsorbate combination specific to adsorption refrigeration. In particular, the solid-vapour equilibrium is obtained from the Clausius-Clapeyron equation

\[ \frac{dP}{dT} = \frac{\Delta H}{T(V_v - V_L)} \]  

where \( P \) is the vapour pressure, \( T \) is the absolute temperature, \( \Delta H \) is the isosteric heat of adsorption per unit mass of adsorbent for the transition, \( V_v \) and \( V_L \) are the specific volumes of the vapour and liquid phases of the refrigerant respectively. In practice, \( V_v > V_L \), and also it may be assumed that the perfect gas law is obeyed approximately by the vapour. Thus,

\[ \frac{dP}{dT} = \frac{\Delta H}{RT^2} \]  

Hence by integrating,

\[ \log P = \frac{\Delta H}{RT} + \text{constant} \]  

This linear relationship between \( \log P \) and \( 1/T \) is determined in practice to a first approximation. From the plot, we can estimate the isosteric heat of adsorption from the gradient of the equilibrium line.

EXPERIMENT FOR P-T-X DATA

The schematic diagram of the test rig used for vapour pressure measurements is shown in Fig. 2. It consists of a constant temperature bath, pressure vessel, vacuum pump and instruments for measuring pressure and temperature. These were used to obtain the pressure, temperature and concentration data for a pair during the experiments.

The pressure vessel containing a known quantity of activated carbon was immersed in oil contained in a bath. The adsorbent sample was heated by heating the oil bath through an electrical heater. The pressure vessel was first evacuated at high temperature using a vacuum pump. It was later allowed to cool. A known volume of adsorbate was administered by opening the inlet valves. The temperature of the vessel was then raised in stages to the desired maximum temperature and the pressure measured. With the volume, pressure and temperature known, the P-T-X diagram for each adsorbent refrigerant pair is prepared. The isosteric heat of adsorption is
estimated as detailed in the preceding section and the coefficient of performance (COP) is evaluated from eqns 4-6 below taken from ref [5].

\[ \text{COP} = \frac{Q_c}{Q_{in}} \]  

(4)

Where the useful cooling, \( Q_c \), in KJ/kg of adsorbent is given by:

\[ Q_c = L(\Delta X) - C_{PR}(T_{con} - T_{ev}) \]  

(5)

The heating input per kilogram of adsorbent, \( Q_{in} \) is given by:

\[ Q_{in} = Q_{sen} + \Delta H \]  

(6)

\( Q_{sen} \) is the sensible heat needed to heat the adsorbent and its containing vessel to the maximum temperature.

RESULTS AND DISCUSSION

The results are presented in Figs. 3-8. Figs. 3-5 show the P-T-X plots for methanol, ethanol and ammonia respectively, while Figs. 6-8 show the COP as a function of maximum generating temperature at various condensing temperatures. Methanol recorded the highest concentration of 23% as seen from Fig. 3 while ethanol and ammonia achieved maximum concentrations of 19% each. If a cooling cycle is imposed on Figs. 3-5, assuming a condensing temperature of 35°C and an evaporating temperature of 0°C, it can be seen that the maximum concentration change of 18% is achieved by methanol followed by ammonia with 14% change while ethanol gave 11% which was the least.

Figs. 6-8 show that for the three condensing temperatures of 25°C, 30°C and 35°C, methanol gave better COP than ethanol even though the same trend was recorded for both. For a condensing temperature of 25°C however, the maximum COP achieved with methanol was the same with that achieved using ethanol. The maximum COP using ammonia at condensing temperatures of 25°C and 30°C were higher than that of methanol, but the same at condensing temperatures of 25°C and 30°C were higher than that of methanol, but the same at condensing temperature of 35°C. Although maximum higher COPs were obtained using ammonia, which can be attributed to its higher latent heat of vaporisation, \( L = 1365 \text{KJ/Kg} \) and lower isosteric heat of sorption, \( \Delta H = 942.12 \text{KJ/Kg} \) (for methanol, \( L = 1102 \text{KJ/Kg} \) and \( \Delta H = 1480.75 \text{KJ/Kg} \); for ethanol, \( L = 842 \text{KJ/Kg} \) and \( \Delta H = 943.84 \text{KJ/Kg} \), the temperature range over which generation could be achieved is higher than the temperature that could be obtained using the conventional flat plate solar collector without a selective surface. Generally, Figs. 6-8 show that methanol gives higher COP over a wider range at maximum operating temperature as can be seen from the gradual rise and drop in COP before the best maximum operating temperature is attained and after it is exceeded. Ammonia and ethanol have much more defined peak COP that begins to drop sharply once that best maximum operating temperature is exceeded.

CONCLUSION

Three refrigerants: methanol, ethanol and ammonia, for use in solar adsorption refrigeration with activated carbon as the adsorbent have been compared. The P-T-X diagram and the COPs estimated from them show that for a flat plate solar collector without a selective surface, activated carbon-methanol is preferred. Activated carbon-ammonia requires high operating temperatures that can only be attained using selective surfaces or concentrating solar collectors. The performances recorded with activated carbon-ethanol pair show that in regions where methanol may not be easily available, ethanol can be used as the adsorbate on activated carbon. However, much lower operating pressure will be required for this purpose. Overall, the results show that methanol, ethanol and ammonia are all good adsorbates on activated carbon for use in solar cooling.

NOMENCLATURE

- \( \text{C}_{PR} \) : Specific heat capacity of refrigerant, KJ/Kg °C
- \( L \) : Latent heat of vaporization, KJ/Kg
- \( P \) : Vapour pressure, bar
- \( Q_c \) : Useful cooling in KJ/Kg of adsorbent
\( Q_{in} \) - Heat input per kilogramme of adsorbent, KJ/Kg
\( Q_{sin} \) - Sensible heat of adsorbent and container per kg of adsorbent, KJ/Kg
\( R \) - Universal gas constant,
\( T \) - Temperature, °C
\( V \) - Specific volume, m\(^3\)/kg
\( \Delta H \) - Isosteric heat of adsorption, KJ/Kg
\( \Delta X \) - Refrigerant concentration change

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REFERENCES


Fig. 1 P-T-X Diagram of an ideal intermittent adsorption cycle.

Fig. 2: Schematic diagram of test rig.
Fig. 3: P-T-X Diagram for activated carbon-methanol pair

Fig. 4: P-T-X Diagram for activated carbon-ethanol pair
Fig. 5: P-T-X Diagram for activated carbon-ammonia pair

Fig. 6: COP vs Maximum Generating Temperature at $T_e = 25^\circ C$ and $T_e = 0^\circ C$. 
Fig. 7: COP vs Maximum Generating Temperature at $T_e = 30^\circ$C and $T_c = 0^\circ$C.

Fig. 8: COP vs Maximum Generating Temperature at $T_e = 35^\circ$C and $T_c = 0^\circ$C.