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Thermodynamic Modelling and Comparison of the Properties of Refrigerant/Absorbent Pairs of a Vapour Absorption Refrigeration System (VARS)

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Abstract- An absorption refrigerator is a refrigerator that uses a heat source which provides the energy needed to drive the cooling process. Technically speaking, absorption refrigerators are a popular alternative to regular compressor refrigerators where electricity is unreliable, costly, or unavailable, where noise from the compressor is problematic, or where surplus heat is available. Like the compression system, the absorption refrigerator uses refrigerant with low boiling point. When this refrigerant evaporates (boils) it takes some heat away with it, providing the cooling effect. This refrigerator uses a heat source which provides the energy needed to drive the cooling process. This work upholds that though lithium bromide is more soluble in water than in methanol, the addition of zinc bromide improved the solubility of lithium bromide in methanol. It was also discovered that NH_3-H_20 system has its own advantage; in that the refrigerant ammonia makes the system very feasible in sub-zero regions. The most usual combination of absorber-refrigerant pair in such system is lithium bromide-water (LiBr-H_2O), where water vapour is the refrigerant, and lithium bromide, the absorbent. Other absorber-refrigerant pair that was considered is ammonia-water (Nh_3-H_2O). LiBr-H_2O pair is most promising in chiller application due to high safety, high volatility ratio, high affinity, high stability, and high latent heat.

Indexed Terms- Thermodynamic Modelling, Thermodynamic Properties, Refrigerant, Absorbent, Vapour Absorption Refrigeration System

I. INTRODUCTION

A major application area of thermodynamics is refrigeration, which is the transfer of heat from a low temperature region to a high temperature one. Refrigeration is a thermodynamic process in which external work is provided in order to move heat from one location of lower temperature to another location maintained at a higher temperature. (Mohanty and Padhiary, 2015). The primary purpose of refrigeration is lowering the temperature of an enclosed space or substance, and then maintaining that lower temperature. The term *cooling* refers generally to any natural or artificial process by which heat is dissipated. Cold is the absence of heat, hence, in order to decrease a temperature, one removes heat rather than adding cold. Devices that produce refrigeration are called refrigerators, and the cycles on which they operate are called refrigeration cycles. The most frequently used refrigeration cycle is the vapour-compression refrigeration cycle in which the refrigerant is vaporized and condensed alternately, and is compressed in the vapour phase. Vapour-compression refrigeration dates back to 1834 when the Englishman Jacob Perkins received a patent for a closed-cycle ice machine using *ether* or other volatile fluids as refrigerants. Initially, vapour-compression refrigeration systems were large, and were mainly used for ice making, brewing, and cold storage. They lacked automatic controls and were steam-engine driven. In the 1890s, electric motor-driven smaller machines equipped with automatic controls started to replace the older units. By 1930, the continued improvements made it possible to have vapour-compression refrigeration systems that were relatively efficient, reliable, small, and expensive. Another well known refrigeration cycle that has started gaining prominence in Nigeria, is the absorption refrigeration; where the refrigerant is dissolved in a liquid before it is *compressed*. As the name implies, absorption refrigeration systems involve the absorption of a refrigerant by a transport medium (Madu, 2018). Presently, most of the cooling produced in homes and industries is by vapour-compression or vapour absorption refrigeration system. The compressor of these vapour-compression systems use a huge amount of electrical energy generated by burning fossil fuel. However, the scarcity of energy, and the depletion of fossil fuel around the world, especially, in Nigeria, makes it expedient to develop a refrigeration system that may run on an alternative energy source/s (Madu, 2015). The power from the sun intercepted by the earth very closely approximates to 1.8 x 10^{11} MW. The present and future energy needs of the world, could be supplied on a continuous basis by this solar irradiation. (Bajpai, 2012). Nigeria is blessed with abundant solar radiated energy; with an estimated annual sunshine period of 3000 hours. This advantage, provided by nature, finds ready application in solar powered vapour absorption refrigerating system (VARS), where cooling is achieved using a more benign, cheaper, and eco-friendly contrivance.

Designing a refrigeration system that will not be dependent on the power supplied by the electricity generation company of Nigeria, is one of the major reasons for embarking on this research. This could be beneficial realizing the average estimated period of annual sunshine. Just as it is known and has been stated earlier, Nigeria is a country that is being confronted with issues of power supply. Great deal of refrigeration done in this country, relies heavily on electricity as a source of power. Regrettably, at no time has the need for power supply been met, giving rise to poor storage of goods. Sequel to this hotchpotch, it is very incumbent that a system with an alternative source of power be introduced, to reduce the over dependency on electric power supply. Absorption Refrigeration System readily satisfies this yawning need because it can get its power from different source such as solar, coal, e.t.c. This kind of refrigeration can be used adequately in Nigeria where energy from the SUN is not rationed, but in constant supply. In the past, refrigerators used chlorofluorocarbon as refrigerant, but this gas was found harmful to the atmosphere if a leakage occurs. Therefore, other chemicals such as tetrafluoroethane, lithium-water and ammonia-water, could be used in slightly different process, which is the Vapour Absorption Refrigeration System (VARS).

An attempt is made in this journal paper to undertake a comparison of the thermodynamic properties of the refrigerant/absorbent pairs of a vapour absorption refrigeration system (vars). Our aim is to perform a thermodynamic analysis of a refrigeration system that uses an alternative energy source rather than electricity. In this regard solar energy becomes the readily available energy that enhances its workability. Realizing this aim is achievable through the following objectives;

- The establishment of analytical methods for the performance features of the Water/Lithium Bromide (H_2O/LiBr) absorption system.
- The system is designed as a solar-driven water (refrigerant) and Lithium Bromide (absorbent) absorption refrigeration system. An ammonia-water pair will not work adequately in the tropical area, like Nigeria. Moreover, as Adegoka (1987) opines, "the H_2O/LiBr pair operates at a lower regeneration temperature than the ammonia-water pair."
- The achievement of a relatively high COP for the system brought about by the alternation of the leading system parameters. These changes would be in the area of the temperature of the fluid (liquid) entering the generator, the cooling load at the evaporator, the temperature of the cooling refrigerant fluid in the condenser.

A plenty of energy is required to sustain industrial growth and agricultural production. The existing sources of energy such as coal, fossil fuel, etc., may not be adequate to meet the ever increasing energy demands. These conventional sources of energy are also depleting, and may get exhausted at the end of the millennium. Moreover, the price of energy has been increasing exponentially all over the world. It is a fact that industrial and home refrigeration are part of the most energy consuming sectors. Unlike the conventional Compression Refrigeration Systems, the Gas Absorption Refrigeration Systems require lower energy. This energy source can be easily procured since nature has made it available to everyone. It, therefore, stands to reason, to aver that this research would solve the problem of refrigeration in temperate countries arising from epileptic power (electricity) supply. Absorption Refrigeration Systems (A. R. S.) have become more attractive, especially when some factors such as total energy utilization and electricity demand management are considered. Also, these systems (A. R. S.) can be operated by using cheap alternative energy sources such as geothermal, biomass, solar energy or a waste byproduct heat sources. The main way of improving efficiency is through thermodynamics analysis, which had been the primary concern of this thesis. By producing an absorption refrigeration system, energy costs are not only being cut down, but the environment is also preserved as this system does not use any of the CFCs or HCFC gases (Madu, 2015). Since this system runs on low-grade thermal energy, it is preferred when low-grade energy such as waste heat or solar energy is available and conventional electricity energy is unavailable or unreliable in supply. The CFC or HCFC gases cause high global warming potential (GWP) and ozone depletion potential (ODP). These abnormalities could be remedied by using environmental friendly systems like H_2O/LiBr or NH_3/H_2O vapour absorption refrigeration system. The gas absorption refrigeration systems can actually, make use of different energy source as already indicated. Considering the engineering factor of availability, this work limits itself to solar energy source, since the other sources of energy are capital intensive. Besides, only the prevailing geo-climatic conditions of the Eastern zone of Nigeria will be taken cognizance of.

II. THERMODYNAMIC MODELING OF H_20-LIBR AR-SYSTEM

The thermodynamic modeling of absorption refrigeration (AR) system is based on the energy and mass conservation equations. In order to analyze the AR system, mass, component and energy balance must be performed for each state in the system circle. The modeling is carried out based on the flow diagram of Figs 1 and 2 (Tesha, 2009).

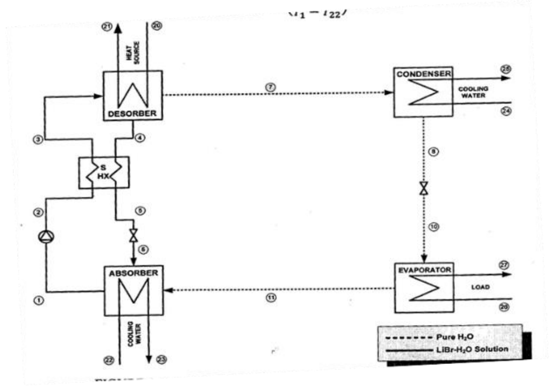


Fig. 1: Thermodynamic Cycle of Single Effect H2O-LiBr Absorption Refrigeration System (Tesha, 2009)

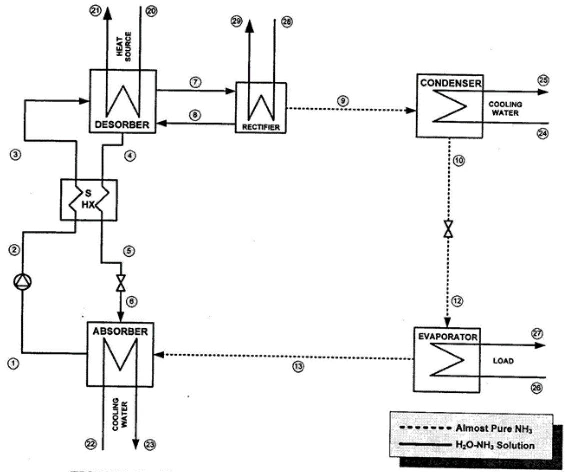


Fig. 2: Thermodynamic Cycle of Single Effect NH_3-H_2O Absorption refrigeration system (Tesha, 2009)

2.1 Absorber

The absorber is a chamber where the absorbent and the refrigerant vapour are mixed together. It is equipped with a heat rejector system, i.e. bundles of tubes as in the condenser, and operates under a low pressure level which corresponds to the evaporator temperature. A lower absorber temperature means more refrigerating capacity due to a higher refrigerant's flow rate from the evaporator. The energy balance during the mixing of the refrigerant vapour and the absorbent is equal to the heat rejection process that is expressed by equation (1);

$$m_6.h_6 + m_{11}.h_{11} - m_1.h_1 = m_{22}(h_{23} - h_{22}) \quad (1)$$

Mass flow equilibrium between the refrigerant and the absorbent that flows in and out of the absorber is a function of the concentration of lithium bromide (Fig. 1) or ammonia (Fig. 2) for each type of AR systems.

$$m_1 x_1 = m_6.x_6 + m_{11}.x_{11} \quad (2)$$

This is for H_20 – LiBr system and for NH_3-H_20 system we have as follows;

$$m_1x_1 = m_6x_6 + m_{13}x_{13} \quad (3)$$

For a pure refrigerant species e.g. there is no water or lithium bromide fraction in the refrigerant, the formula in (2) and (3) can be simplified as;

$$m_1x_1 = m_6x_6 \quad (4)$$

The log mean temperature difference for the absorber which is used in the calculation of absorber area can be obtained from equation (5).

$$LMTD_A = \frac{(T_6 - T_{23}) - (T_1 - T_{22})}{In\left(\frac{T_6 - T_{23}}{T_1 - T_{22}}\right)} \quad (5)$$

2.2 Generator/Desorber

The generator or desorber operates under high pressure which is controlled either by the temperature of the incoming heat to the desorber or the condensation temperature required by the cooling water entering the condenser. The desorption process generates vapor and extracts the refrigerant from the working fluid by the addition of the external heat from the heat source. It could be desorption of water (refrigerant) out of a water–lithium bromide solution or ammonia (refrigerant) out of an ammonia-water solution. The refrigerant vapour travels to the condenser while the liquid absorbent is gravitationally settled at the bottom of the desorber. The pressure difference between the generator and the absorber then causes it (the absorbent) to flow out to the absorber through the expansion value. Fluorides, Kalogirou, Tassou, and Wrobel (2003), reported that a water-lithium bromide system has lower temperature requirements for a refrigerant desorption process (75^0-120^0c) than the ammonia-water system (125^0-180^0c). A strong lithium bromide (less water) solution and a weak ammonia (more water) solution is produced during desorption process for both lithium bromide and ammonia system respectively. These strong lithium bromide and weak ammonia solutions act as the absorber and the mass flow equilibrium across the process is given as:

$$m_3.x_3 = m_4.x_4 + m_7x_7 \quad (6)$$

And energy balance expressed as:

$$m_4h_4 + m_{7.}h_7 - m_3h_3 = m_{20}(h_{20} - h_{20}) \quad (7)$$

As log mean temperature difference becomes:

$$LMTD_d = \frac{(T_{20} - T_4) - (T_{21} - T_3)}{In\left(\frac{T_{20} - 4}{T_{21} - T_3}\right)} \quad (8)$$

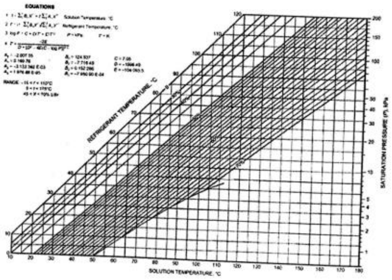


Fig. 3: Equilibrium Chart for Aqueous Lithium Bromide Solution (ASHRAE, 2005)

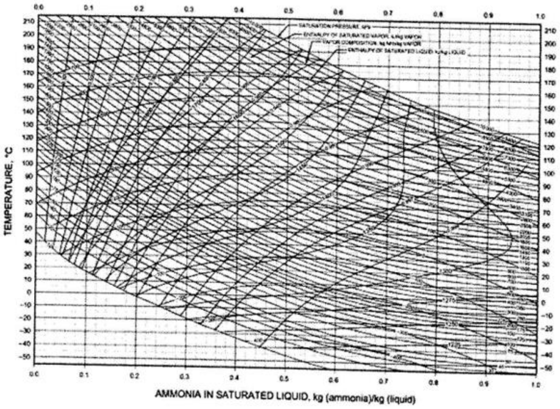
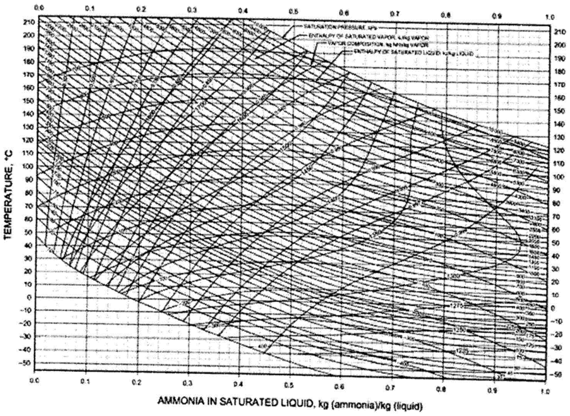


Fig. 4: Enthalpy Concentration Diagram for Water-Ammonia Solutions (ASHRAE, 2005)

2.3 Rectifier (Rectification/Reflux Cooling)



The rectifier is one interesting difference between the NH_3-H_20 and H_20-LiBr system, this is further appreciated through the study of Figs. 3 and 4 (ASHRAE 2005). Ammonia is highly soluble in water where the solubility increases as the water temperature decreases at constant pressure (Fig. 4). In normal conditions, the boiling point of ammonia is 33 - 35^0C, low enough compared to water, but since water has the un-negligible vapour pressure, the refrigerant ammonia vapour that is generated by the desorber still contains a certain amount of water fraction. This presence of water in an ammonia refrigerant has to be minimized due to chance of freezing when the system is employed for refrigeration process below ^{0}C, lowering the evaporator pressure and affecting the system's performance. However, to give the purity of ammonia, a rectifier is introduced. A rectifier has the same water cooling effect as a condenser but with a relatively small capacity of condensation. The idea is to condense the available water fraction in the strong ammonia solution and send it back to the generator as reflux. Ammonia-water vapour mixture is cooled slightly so that small portion of the vapour condenses and returns to the generator. Also ammonia-water vapour mixture is in contact with a cooled surface in the reflux cooler. Hence, a portion of vapour (mainly water vapour) is condensed and returned as reflux to the generator. These actions of removing water from the original vapour, the remaining ammonia water vapour is enriched with ammonia.

Energy balance for the rectification process is given as:

$$m_y.h_y - m_8.h_8 - m_9.h_g = m_{28}(h_{29} - h_{28}) \quad (9)$$

And the log mean temperature difference:

$$LMTD_{rec} = \frac{(T_7 - T_{29}) - (T_g - T_{28})}{In\left(\frac{T_7 - T_{29}}{T_g - T_{28}}\right)} \quad (10)$$

2.4 Condenser

The vapour phase of refrigerant from the generator/desorber is altered to a liquid by the condenser. This liquid state of the refrigerant is a must in order for the refrigeration process to run. By rejecting the refrigerant vapour's latent heat to the sink, the condensing process of a high pressure refrigerant vapour is carried out, this will follow an energy/heat balance formulation thus:

$$m_y(h_7 - h_8) = m_{24}(h_{25} - h_{24}) \quad (11)$$

$$LMTD_c = \frac{(T_7 - T_{25}) - (T_8 - T_{24})}{In\left(\frac{T_2 - T_{24}}{T_8 - T_{24}}\right)} \quad (12)$$

The Cooled refrigerant liquid is then passed through the expansion value from the condenser. The expansion value lowers the pressure level this may lead to some quantities of the refrigerant flashing into vapour.

2.5 Evaporator

In the evaporator the temperature of evaporation regulates the lower pressure level of the absorption system. Due to the addition of latent heat from the refrigeration environment, the two phase refrigerant continues to evaporate. A complete evaporation process will convert the two phase refrigerant into vapour.

Energy balance for the evaporator is given as:

$$m_{10}(h_{11} - h_{10}) = m_{26}(h_{26} - h_{25}) \quad (13)$$

This is for H_20 –LiBr system and for NH_3 – H_20 system we have:

$$m_{12}(h_{13} - h_{12}) = m_{26}(h_{26} - h_{27}) \quad (14)$$

The log mean temperature difference is given as:

$$LMTD_e = \frac{(T_{26} - T_{11}) - (T_{27} - T_{10})}{In\left(\frac{T_{26} - T_{11}}{T_{27} - T_{10}}\right)} \quad (15)$$

2.6 Expansion Value

The expansion valve is a component of the absorption refrigeration process that reduces the pressure and splits the two different pressure levels. In a simple model of a single effect AR system, the pressure change is assumed to occur only at the expansion valve and the solution pump. The presence of the Solution Heat Exchange (SHX) and Refrigerant Heat Exchange (RHX) will drive the expansion valve's input fluid close to a sub-cooled state, and at the end will affect the amount of the steam flash out of the expansion valve. Also, the possibility of a lower temperature at the end of the flashing process some amount of energy must be taken from the fluid phase in order to drive the phase change.

2.7 Solution Heat Exchange

This is a heat exchange unit with the purpose of pro-heating the solution before it enters the generator and removing unwanted heat from the absorbent. The heat exchange process within the solution heat exchanger reduces the amount of heat from the heat source in the generator and also reduces the quality of heat to be rejected by the heat sink (cooling water) in the absorber as well. The presence of heat exchanger increases the overall performance of an absorption refrigeration system i.e. increase in coefficient of performance (COP), as shown in Fig.5.

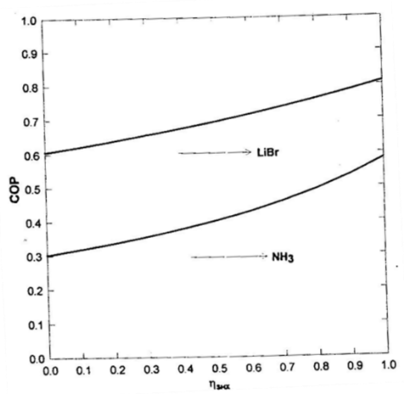


Fig. 5: A Typical Effect of a Solution Heat Exchanger's Effectiveness on COP of Refrigeration (Tesha, 2009)

The temperature of the absorbent that leaves the hot stream side has to be calculated through equation (16)

$$T_5 = T_2\ x\ \eta_{shx} + \left(1 - \eta_{shx}\right) x\ T_4 \qquad (16)$$

And to complete the variable needed for the energy balance calculation in (17)

$$m_2(h_3 - h_2) = m_4(h_4 - h_5) \qquad (17)$$

Hence for the solution heat exchanger model in Fig. 1, the log mean temperature difference is expressed as:

$$LMTD_{shx} = \frac{(T_4 - T_3) - (T_5 - T_2)}{In\left(\frac{T_4 - T_3}{T_5 - T_2}\right)} \qquad (18)$$

2.8 Solution Pump

A solution pump will mainly circulate and lift the solution from the lower pressure level side to the higher pressure level side of the system. To maintain this pressure difference, a centrifugal type pump is preferable. Assuming the solution is an incompressible liquid, i.e. the specific volume of the liquid (v) will not change during the pumping process, the power requirement to lift the solution with mass flow in from pressure level P_1 to P_2 and certain pump efficiency is expressed as:

$$W_{pump} = \frac{M_1 - V_1(P_2 - P_1)}{\eta_{pump}} \qquad (19)$$

According to Herold, Radermacher and Klein (1996), although the existence of the solution pump can be ignored thermodynamically, practical experience shows that the pump is a critical component that must be carefully engineered, especially during the consideration process of ; (a) pump seals (to avoid air leakage) (b) pump cast (c) sufficient suction head (to avoid cavitations) the energy balance across the solution pump is expressed as:

$$m_1\ .h_1 + W_{pump} = m_2\ .h_2 \qquad (20)$$

III. REFRIGERANT/ABSORBENT PAIR FOR VARS

The need for two or more substances that should work together as a single solution of working fluid produced several variants of refrigerant–absorbent pairs in the absorption refrigeration industry. The refrigerant should be more volatile than the absorbent so that the two can be separated easily. Water is usually used as the refrigerant for solid absorbents (Gunther, 1957). Many researchers have reported the use of solar energy for the absorption systems working in various refrigerant–absorbent combinations, namely:

- Ammonia – Water (Farber, 1965; Swartman and Swaminathan, 1971; Swartman, Ha and Newton, 1974; Staicovici, 2000).
- Water –Lithium Bromide (Gommed and Grossman, 1990; Kouremenos, Antono poulos and Rogdakis, 1990; Faithi, and Quaskit, 2001 etc).
- Lithium Bromide – Zinc Bromide Methanol
- Lithium Chloride – Water (Collier, 1979).
- Ammonia –Calcium Chloride (Iloeje, 1977; Worsoe-Schmidt, 1983) etc.

The cycles of operation were either intermittent or continuous – open or closed. A suitable refrigerant–absorbent fluid is probably the single most important item in an absorption refrigeration system. The selection of a suitable combination involves simultaneous consideration of various factors which include qualitative considerations of desirable properties as well as an analysis of its theoretical performance in a refrigeration system. Ammonia – Water and Water-Lithium Bromide as conventional fluids still have desirable properties compared to other working fluid variants, especially for the high number of latent heat, so can minimize the need of refrigerant flow rate. The water-lithium bromide (H_2O – LiBr) is limited to temperature above the freezing point of water (4^0C -5^0C) while Ammonia –Water (NH_3 – H_20) is favourable for subzero refrigerant temperatures (Tesha, 2009).

However, the desirable properties of refrigerant absorbent mixtures or combinations for VARS can be outlined as follows:

1) The refrigerant should exhibit high solubility with solution in the absorber. This is to say that it should exhibit negative deviation from Raoult's law at absorber.
2) There should be large difference in the boiling points of refrigerant and absorbent (greater than 200^0C) so that only the refrigerant is boiled off in the generator.
3) It should exhibit small heat of mixing so that a high COP can be achieved. However, this requirement contradicts the first requirement. Hence, in practice a trade-off is required between solubility and heat of mixing.
4) The refrigerant-absorbent mixture should have high thermal conductivity and low viscosity for high performance.
5) It should not undergo crystallization or solidification inside the system.
6) The mixture should be safe, chemically stable, non-corrosive, inexpensive and readily available.

IV. NH_3-H_2O SYSTEM VIS-À-VIS H_2O-LIBR SYSTEM

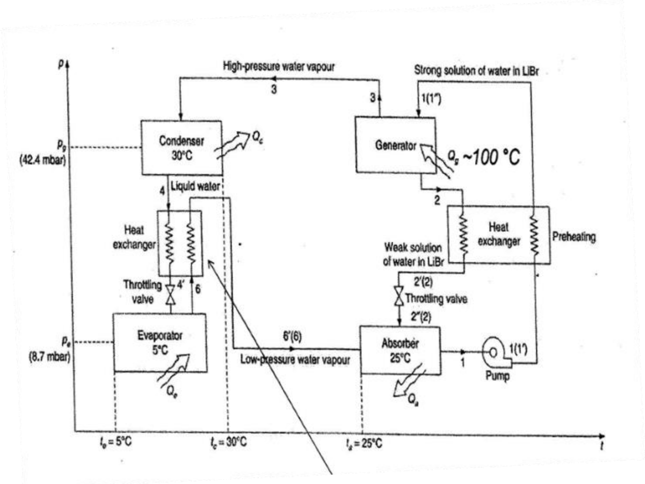
Among all the refrigerant-absorbent combination proposed or used in solar driver absorption refrigeration system, the NH_3-H_20 and the H_20-LiBr are the most popular. The performance coefficient of an absorption refrigeration/air condition system, is defined as the ratio of the heat transfer rate into the evaporator to the heat transfer rate into the generator, which can be calculated as a function of temperatures. Wilbur and Mitchell (1975), compared the coefficient of performance (COP) of absorption systems with different working fluid combinations. Adegoke (1987) also concluded that the H_20-LiBr system is more favoured for the following reasons;

i. It's simplicity in operation as the absorbent salt being nonvolatile hence no need for a rectifying column.
ii. It operates with higher COP and lower pump work.
iii. Regeneration temperatures of about 93^0C can operate a H_20-LiBr while NH_3-H_20 system will require at least 120^0C regeneration in temperature.
iv. Water, the refrigerant is cheap, non toxic and safe.
v. It is adaptable for using the low heat that can be supplied by flat-plate solar collectors.

However, the H20-LiBr system has its own limitations such as;

i. Low absorber temperature that cannot be maintained practically by air cooling.
ii. Lithium Bromide is corrosive to metals.
iii. Salt solubility in water is limited by temperature
iv. It cannot be used at sub-zero temperature regions.

The salt solubility is the most important limitation of the H_20-LiBr system. Improving the solubility of lithium bromide in water, a stronger solution will result which can minimize the solution circulation ratio-between the absorber and the generator (Fig. 6) and increase the temperature lift to reduce the heat load in the generator. Therefore, at relatively lower operating temperature in the generator, refrigeration can be obtained. Vamvakidis (1978) reported that though lithium bromide is more soluble in water than in methanol, the addition of zinc bromide improved the solubility of lithium bromide in methanol. However, NH_3-H_20 system has its own advantage in that as ammonia is the refrigerant, the system is very feasible in sub-zero regions (Fig. 7).



Subcooling/superheating heat exchanger

Fig. 6: Single Effect H_2O-LiBr Absorption Refrigeration System (Abo Akademi, 2014)

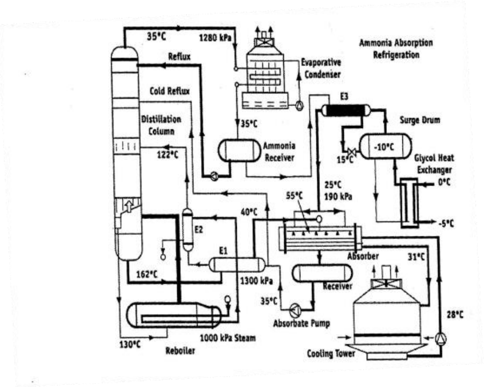


Fig. 7: A Practical NH_3-H_2O Absorption Refrigeration System (Abo Akademi, 2014)

CONCLUSION

The interest in gas absorption systems started to increase, firstly due to the oil crisis in the 1970s that led to a concern about energy shortage, and then later, in the 1990s, because of ecological problems related to the use of CFCs and HCFCs as refrigerants. Such refrigerants, when released to the atmosphere, deplete the ozone layer, and contribute to the greenhouse effect. Furthermore, with the increase of the energy consumption world-wide, especially in Nigeria, it is becoming even more urgent to find ways of using the energy resources as efficiently as possible. Thus, machines that can recover waste heat at low temperature levels, such as absorption refrigerators, can be an interesting alternative for a wiser energy management. In gas absorption systems, it is very important to select the appropriate working substance, the properties of which have a great effect on the performance of the cycles. The most usual combination of refrigerant- absorbent pair in VARS is lithium bromide-water ($LiBr/H_2O$), where water vapour is the refrigerant, and lithium bromide, the absorbent. Other absorber-refrigerant pair that was considered is ammonia-water (Nh_3/H_2O). $LiBr/H_2O$ pair is most promising in chiller application due to high safety, high volatility ratio, high affinity, high stability, and high latent heat.

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