Energy Conversion and Management 50 (2009) 2665–2669

Contents lists available at ScienceDirect

Energy Conversion and Management

journal homepage: www.elsevier.com/locate/enconman

Enrichment of ammonia concentration from aqua-ammonia vapors by using 3A molecular sieve

J.S. Chiou *, T.M. Lin, K.Y. She, W.M. Chen

Department of Mechanical Engineering, National Cheng Kung University, Tainan 701, Taiwan

ARTICLE INFO

Article history:
Received 18 November 2008
Accepted 21 June 2009
Available online 16 July 2009

Keywords:
Aqua-ammonia refrigeration system
Absorption chiller
3A molecular sieve

ABSTRACT

In aqua-ammonia refrigeration systems, the ammonia is the refrigerant and the water is the absorbent, the vapor produced in the generator always contains a small fraction of water. The removed of this residual water is a crucial issue in order to guarantee a reliable and efficient operation of these systems.

Currently, the thermal distillation methods (via a rectifier and/or an analyzer) are used to further separate the water from aqua-ammonia mixtures. In this study, a molecular sieve module is used for ammonia purification.

A thermal system with a 3A molecular sieve module was set up, and the conditions of working fluid entering into the sieve module is similar to that entering into the rectifier tower of a typical aqua-ammonia absorption system. Results from ammonia enrichment tests indicate the concentration of ammonia can be raised from about 80% up to about 99% if siever installation was properly arranged.

1. Introduction

Unlike the popular vapor-compression refrigeration systems, which is operated by work (compression work is usually driven by electric power), the absorption refrigeration system is referred to be a heat-operated cycle because most of the operating cost is associated with providing the heat that drives off the vapor from the high-pressure liquid. Since the heat needs to operate the absorption system can be the low temperature heat either recovering from waste heat or collecting from solar energy, the use of absorption systems may help reduce global warming gases emitted from the fossil-fuel power plants.

Another difference between absorption system and conventional vapor-compression system is the working fluid used. Most of refrigerants used by vapor-compression systems have either ozone depletion potential (such as CFC and HCFC refrigerants) or global warming potential (CFC, HCFC, and HFC refrigerants), the refrigerants used in the commercialized absorption system is either H_2O (for H_2O–LiBr system) or NH_3 (for NH_3–H_2O system), both H_2O and NH_3 are nature substances.

Although the absorption systems possess the great advantage from the view point of environmental protection, however, some inherited drawbacks limit their wide application. For example, the coldest temperature of H_2O–LiBr system can not be lower than 0 °C and the system must be operated under vacuum condition because the refrigerant is H_2O. Under vacuum condition, the chambers and the associated piping are then very bulky and some other factors such as LiBr crystallization and corrosive problem restrain the system's popularity.

Beside the H_2O–LiBr system, the other well accepted absorption refrigeration system is the aqua-ammonia system, in which NH_3 is the refrigerant and H_2O is the absorbent. This system can be well suited for subzero application because the normal boiling point of NH_3 is −33 °C, and the system is operated under positive pressure(above 1 atm) condition, and thus free from the problem of air leak-in.

In aqua-ammonia systems, the generator (or called desorber) is used to separate the vapor of NH_3 and the vapor of H_2O. Since NH_3 (refrigerant) and H_2O (absorbent) are both volatility and have strong affinity to each other, the heating process executed at generator can not completely separate NH_3 and H_2O. However, the existence of water vapor leaving the generator and going to refrigerant circuit (including condenser and evaporator) will strongly offset the system performance [1,2]. In practical application an analyzer and a rectifying column are usually installed at the downstream of generator to strip away water further such that the NH_3 concentration can be above 99% before entering into condenser. Either analyzer or rectifier is a kind of heat exchanger, the degree of ammonia purification is thus exponentially proportional to the area of heat and mass transfers. The size of rectifier is inevitably very bulky if the degree of ammonia purity is very high. In fact, the size of a rectifying tower is sometimes larger than the total size of the rest of system components. The cost of system facility and footprint will then be too high to be practical.

---

* Corresponding author. Tel.: +886 6 2757575x62176; fax: +886 6 2352973.
E-mail address: jschiou@mail.ncku.edu.tw (J.S. Chiou).

0196-8904/$ - see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.enconman.2009.06.022

Considering the 3A molecular sieve has a very strong water absorption ability even under a extremely low moisture environment [3], in this study, we try to investigate the feasibility of using a molecular sieve module to replace the very bulky rectifier in the aqua-ammonia absorption systems.

2. Molecular sieves

Molecular sieves are crystalline metal alumino-silicates (basically ceramic materials). When combined with oxygen atoms the resulting tetrahedral produce a three-dimensional interconnecting cage-like structure, with a huge internal surface area into which various gases and liquids are adsorbed. By controlling the ratios of cation exchange and the cation used, it is possible to synthesize crystalline structures with varying pore size. This provides molecular sieves their unique advantage of being able "selectively adsorb" materials, pulling in materials smaller than the size of their pore openings while excluding materials that are larger. With this important capability, molecular sieves are extensively used in a wide variety of applications including catalysis, gas separation, and as drying agents [4,5].

The 3A molecular sieve, is made by substituting potassium cations for the inherent sodium ions of 4A structure, has a pore size of three angstrom (3 Å), the smallest size currently available in the market. Since the pore size of the 3A sieve is very close to the critical diameter of a water molecule (the dimension of water molecular is 2.65 Å), and because of the potassium cation incorporated into crystal, the 3A sieve has a very strong affinity for the polar water molecule. As pointed out by Holland et al. [6], the adsorption ability for a molecular sieve is also determined by the dipolar coupling moment between adsorbed molecules and cations inside the zeolite cavities. A molecule with high dipole moment (such as water) is preferably adsorbed by molecular sieve [7].

Both the critical diameters of H_2O (at 2.65 Å) and NH_3 (at 2.6 Å) [4] are smaller than the pole size of 3A molecular sieves. The dipole moment of a water molecule is 1.844 D, whereas that of ammonia is 1.46 D [7]. It is thus interesting to know how much difference between H_2O and NH_3 molecules in term of adsorption preference by 3A molecular sieve.

3. Experimental apparatus

A test loop including a molecular sieve module was set up like Fig. 1. Initially, the liquid of $NH_3 + H_2O$ mixture with 27 wt.% of NH_3 was filled into the heating vessel (via valve 1) and the absorption vessel (via valve 4) to a fixed level. Temperature of heating vessel heated by the embedded electrical heater can be controlled by a PID controller. At a fixed temperature the associated high-pressure vapors ($NH_3 + H_2O$) in the heating vessel will flow through the module of molecular sieve once the valve 2 is opened. Some of sample mixtures can be extracted out at valve 2 (before sieve module) and valve 3 (after sieve module). The vapor pressure will drop to nearly 1 atm after vapor flow passing the pressure relief valve (valve 4). The low pressure vapor will finally be dissolved in the aqua-ammonia solution inside the adsorption vessel. A delicate servo-controlled pump is used to pump a certain amount of liquid mixture from the absorption vessel to the heating vessel in order to compensate the amount which is vaporized in the heating vessel.

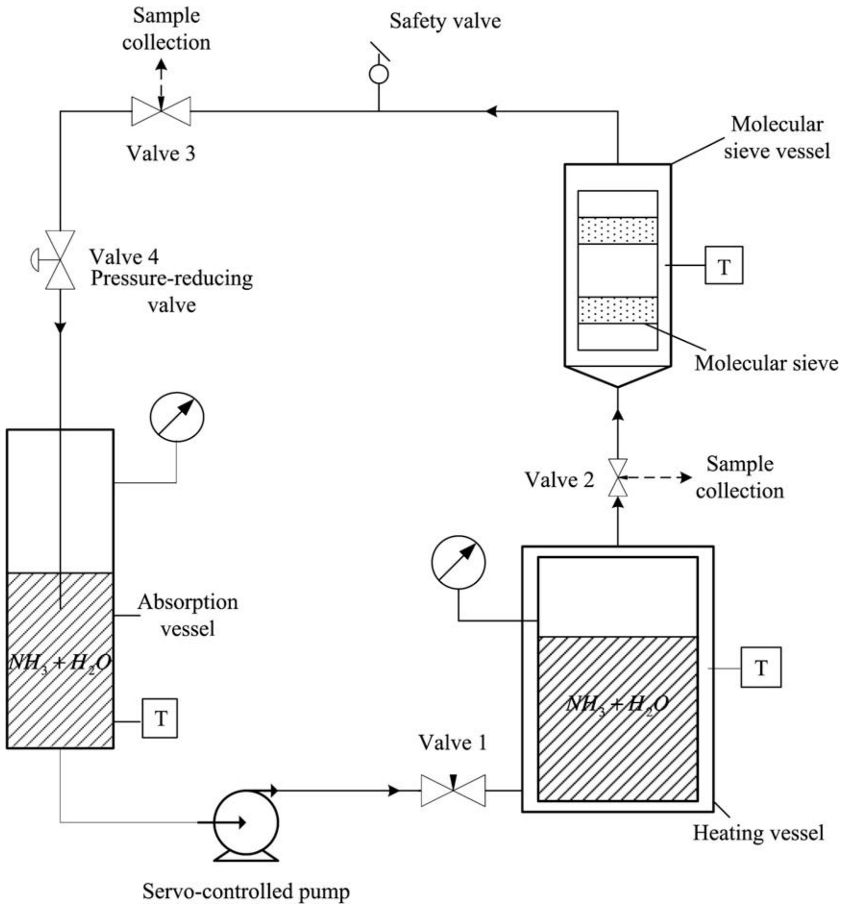

Fig. 1. Schematic drawing of enrichment test.