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Membrane Process for Organic Vapor Recovery from Air

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ABSTRACT: New organic vapor separation membrane has been developed. Air containing a relatively high organic vapor concentration is fed to the membrane and the organic vapor is selectively extracted. The organic vapor separation membrane is a composite membrane. It consists of a thin skin layer and a porous support layer and nonwoven polyester backing. The skin layer is the selective barrier layer composed of three dimensionally crosslinked elastomeric polymer. Polyimide which has a high resistance to solvents is used for the porous support layer. The composite membrane has an organic vapor permeation rate of 5-20 Nm3/m2hratm,depending on the types of the organic vapors. The permeation rate shows good correlation with the boiling point of the organic vapors. Spiral module type is used for actual application. Vapor concentration after treatment of the module is changed significantly depend on the vapor pressure ratio and flow rate difference between feed side and permeate side of the module.

KEY WORDS Organic Vapor / Gas / Composite Membrane / Polyimide / Spiral Module /

Industries producing solvent-containing exhaust streams are under increasing pressure from two sources--enviromental regulation and process economics. There is clearly growing concern over toxic air pollutants. Due to the rising fines for accidental releases of toxic chemicals and the negative publicity which accompanies these events, companies are placing a much higher priority on enviromental control systems. There is particular interest in downstream control technologies which do not create a solid or liquid disposal problem. In addition to reducing pollution, controlling organic vapore emissions makes good economic sense, that is , recovery of solvent contained in exhaust streams and the energy lost when high temrerature organic vapors are vented to the enviroment. Most treatment processes only prevent air pollution,and,despite the increased value of the solvent, its recovery is still not economically feasible except for very large exhaust streames and under particularly favorable conditions. The recently developed membrane process would become a effective method in these organic vapor recovery field from both economical point and enviromental regulation.

1.Structure of organic vapor separation membrane

The developed organic vapor separation membrane is a composite membrane. It is consists of a thin skin layer and porous support layer and nonwoven polyester backing. The skin layer is the selective barrier layer composed of three dimensionally crosslinked elastomeric polymer. Polyimide which has a high resistance to solvents is used for the porous support layer. A schematic of such a composit membrane is shown in Fig.1. Skin layer should be pore-free for high selectivity and be thin for high flux of gaseous molecules. Attempts to reduce the thickness of the skin layer with keeping high selectivity are being made.

The supporting membrane layer serves to stabilize the skin layer during the formation process and it is generally made with moderately porous so as not to present any resistance to the gas permeation. Therefore,for the manufacturing of industrial membranes, selection of the material for skin layer and support layer and formation techniques become very important.

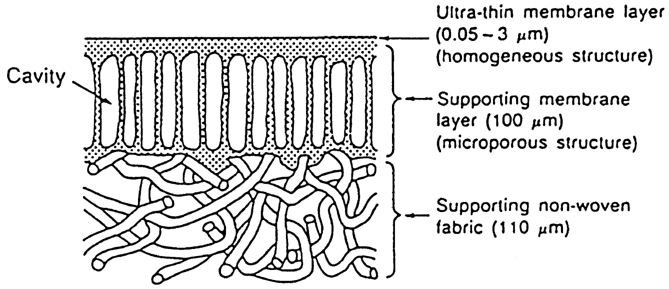


Fig. 1 Conceptual illustration of the cross section of a composite membrane

2.Performance of organic vapor separation membrane

(1)Permeability of organic vapor and permeate flux ratio

(A)Permeability measurements and apparatus

The membrane test apparatus shown schematically in Fig.2 was used to measure nitrogen and organic vapor permeabilities. The permeability apparatus consists of vapor containing feed side with gas circulation system and vaccum permeate side. Membrane is set in permeability cell and organic vapor is brought to feed side to an appropriate level, then vapor pressure increase in permeate vacuum side is measured. At the same time, gas or vapor components of both sides are measured by gas chromatography. Permeability(Nm3/m2.h.atm) is calculated by using these data.

(B)Organic vapor permeability

Organic vapor permeability of poliimide based membrane is shown in Fig.3, which shows vapor permeability vs. feed side vapor pressure. Some organic vapor show a increase in permeability with increased vapor pressure. On the other hand, nitrogen permeability does not depend on feed pressure. The relationship between permeability and boiling point is shown in Fig.4. Permeability increases with increasing boiling point of the vapor. Base on these data, it is shown that the transport of organic vapor through this membrane is determined more by its solubility than by its diffusion coefficient.

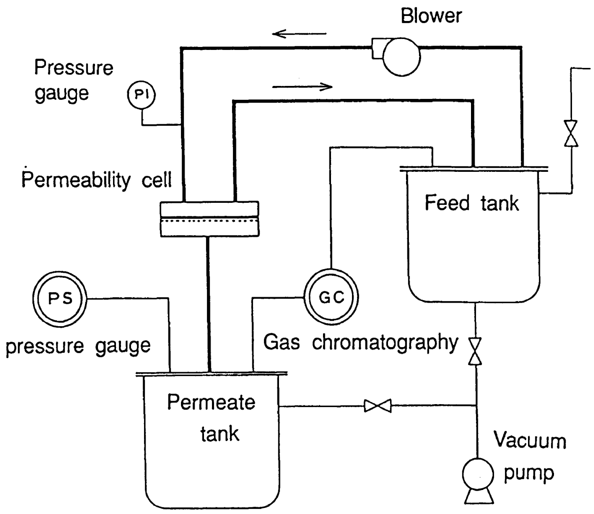


Fig. 2 Vapor permeability apparatus

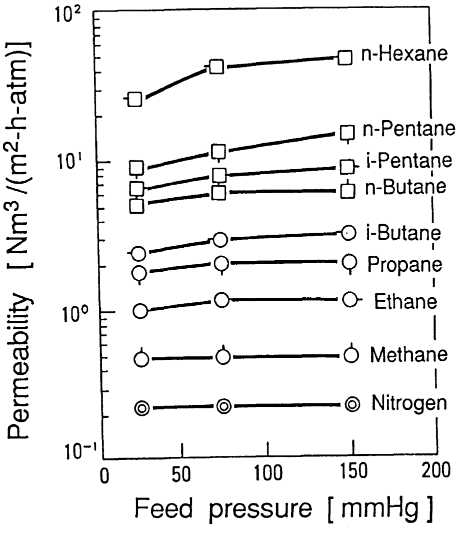


Fig. 3 (a) Organic vapor permeability (25 ℃)

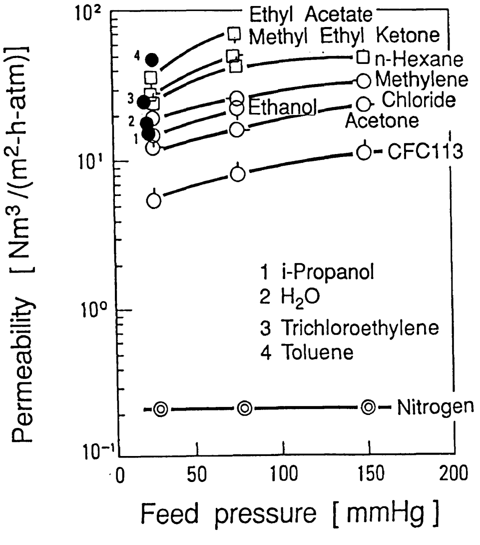


Fig. 3 (b) Organic vapor permeability (25 ℃)

(2)Selectivity and the thickness of skin layer

Fig.5 illustrates the effect of the skin layer thickness on selectivity in a pentane/nitrogen gas mixture system. Organic vapor flux through membrane decreases and selectivity increases with increasing the thickness of skin layer. Where the thickness of skin layer of the membrane is 3μm, the selectivity (C5/N2) is around 40.

(3)Selectivity and vapor permeate flux ratio

The performance of organic vapor separation membrane is expressed by selectivity and gas permeate flux. Selectivity can be described with the ratio of gas permeability in the standard conditions. Selectivity of the membrane for various vapors against nitrogen is shown in Table 1. More selective membrane can separate organic vapor more effectively. For actual application, more than 20 of selectivity for organic vapor against nitrogen would be required.

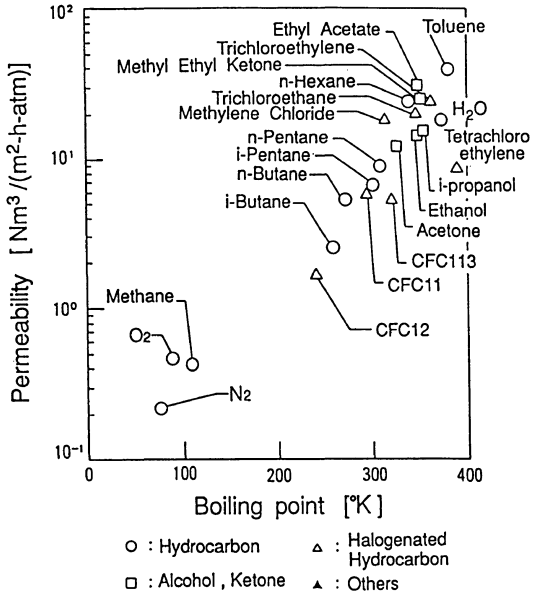


Fig. 4 The relationship between Selectivity and Boiling point (Feed Pressure 25mmHg)

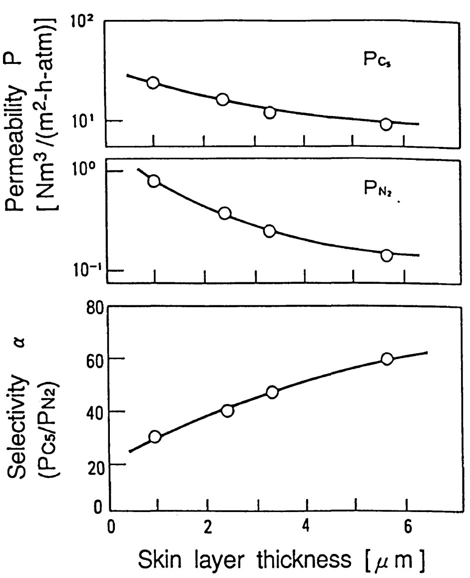


Fig. 5 The relationship between Selectivity and Skin layer thickness (n-Pentane / Nitrogen mixture : n-Pentane 10vol%)

Table 1 Selectivity of organic vapor separation membrane (25℃)

selectivity α = organic vapor permeability / nitrogen gas permeability

organic vapor	$\alpha_{25^\circ C}$	organic vapor	$\alpha_{25^\circ C}$
Methane	2.2	CFC113	25
Ethane	4.6	Acetone	55
Propane	8.4	H_2O	83
i-Butane	11	Trichloroethane	95
n-Butane	24	Methyl Ethyl Ketone	111
i-Pentane	30	Trichloroethylene	116
n-Pentane	40	Ethyl Acetate	139
n-Hexane	110	Toluene	183

(4)Spiral module performance

(A)Module form

The membrane is formed into spiral wound module. The spiral wound module design is illustrated in Fig.6. In this module design, a membrane envelope is wound around a porous central collection pipe. Mesh spacer material is used to form channels for the feed air and the permeate vapors.

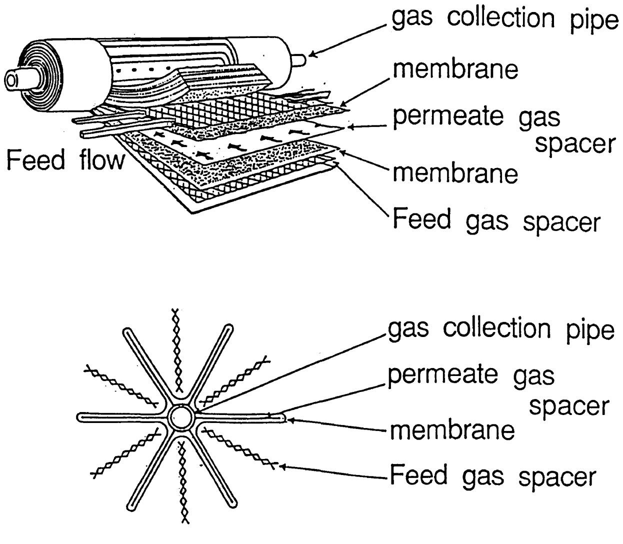


Fig. 6 Spiral - wound membrane module

(B)Module test apparatus

The module test apparatus is shown schematically in Fig.7. Organic vapor is made by the delivery of solvent to an evaporator. Nitrogen gas is added to organic vapor to maintain aimed concentration and a nitrogen-vapor mixtur is continually circurated around buffer tanks. This mixture is passed through the spiral module. The permeate side of the module is kept at a low pressure by a vacuum pump. Permeate vapor is traped by gas sampling holder and measured concentration. Gas flow through the module is measured after vacuum pump.

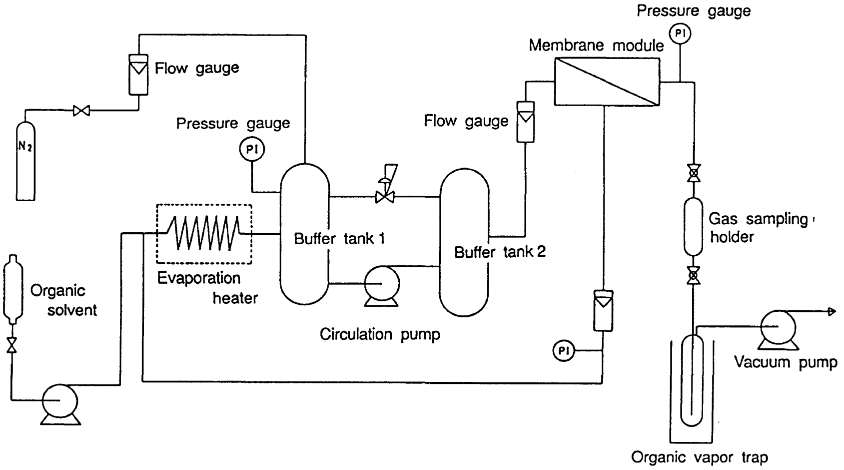
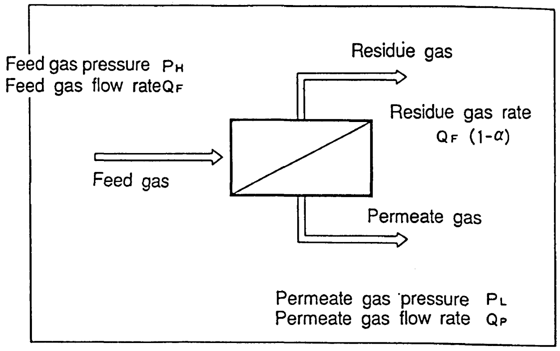


Fig. 7 Module evaluation apparatus



[Dimensionless parameter]

Operating pressure ratio $\gamma = P_L/P_H$

Stage cut $\alpha = Q_P/Q_F$

Fig. 8 Operating condition and Dimensionless parameter

(C)Module performance

When the organic vapor separating membrane module is used, the enriched organic vapor concentration changes remarkably depending on the operating pressure ratio (namely ratio of feed gas pressure to permeate gas pressure) and the stage cut (namely ratio of quantity of permeate gas to quantity of supplied gas). So, it is necessary to set optimum dimensionless variables such as operating pressure ratio and stage cut and to set the operating conditions ensuring the best use of performance of gas separating membrane. The dimensionless variables for operation of the organic vapor separating membrane module are shown in Fig.8.

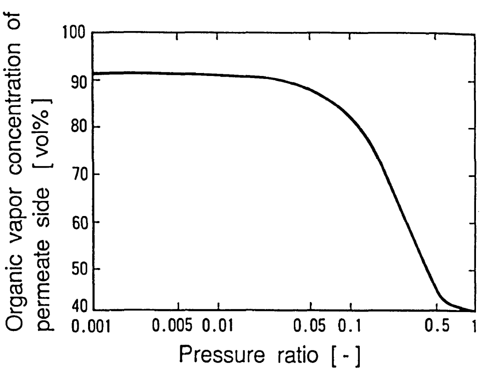


Fig. 9 The relationship between Pressure ratio and Organic vapor concentration of permeate side ($\alpha = 44$, Feed concentration=40%)

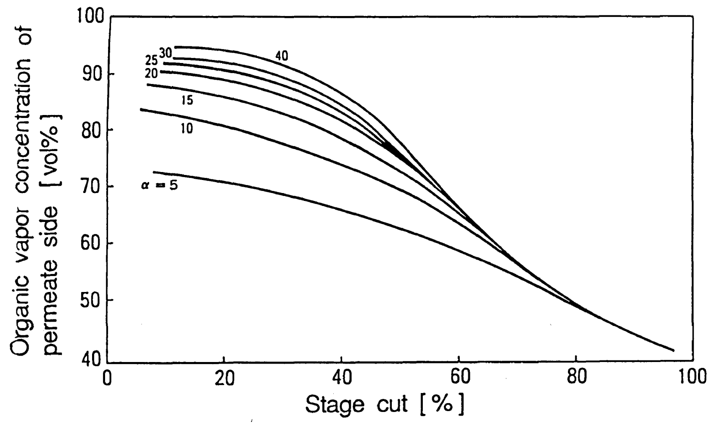


Fig. 10 Organic vapor concentration of permeate side vs. Stage cut
(Feed concentration=40%,Pressure ratio=0.1)

The best use of performance of gas separating membrane can be estimated by using cross flow model calculation. Organic vapor concentration of membrane permeate side is calculated by changing operation pressure ratio.(Fig.9) Organic vapor concentration increases with a decrease in pressure ratio, but concentration does not change a lot when pressure ratio decreases less than 0.01 due to gas permeability ratio becomes rate determining step at this stage. Fig.10. shows the change of organic vapor concentration of permeate side vs. stage cut. Organic vapor concentration increases with an increase in selectivity, but the difference of concentration is small when the stage cut is more than 60.

Pressure drop of permeate gas in the module and turbulence of feed gas flow also effect the module performance. Module performance should be measured at the actual application stage. Module performance especially selectivity is measured by using butane(40%)-nitrogen(60%) gas.(Fig.11) Selectivity increases with a decrese in stage cut. We can use the module more effectively when the module is used at lower stage cut. The most effective usage of module including economical evaluation should be considered at the actual application.

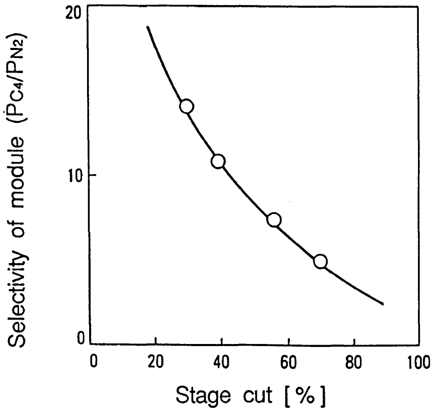


Fig. 11 Stage cut vs. Selectivity of module
(Feed flow; n-Butane / Nitrogen=40 / 60(vol%))

3.Practical application

Practical applications of this membrane for gasoline vapor separation and recovery membrane process are being conducted by NKK (Nippon Kokan Corp.) Fig.12. shows the flow diagram of the membrane separation process. At oil tank depots, when gasoline and other fuels are transferred, air mixture containing a high concentration of 15-50% gasoline vapor is generated. This mixture is treated to reduce the concentration of the gasoline vapor below 5%, and is then released into the atmosphere. In some districts in Japan, local governments advise the installation of recovery equipment. So far, conventionally absorption methods using a special oil as absorbent are employed for such purposes. The membrane separation process discussed here is far superior in its low facility cost, low running cost, and space saving installation.

This membrane separation process can be usefully applied to various petrochemical, synthetic fiber, polymer plastic, paint and painting, and semiconductor industries. By utilizing this process, air mixtures containig hexane, acetone, methyl ethyl ketone, isopropyl alcohol, toluene, and trichloroethylene vapors, which are generally used as solvents, and the vapor of naphtha can be effectively separated and recovered.

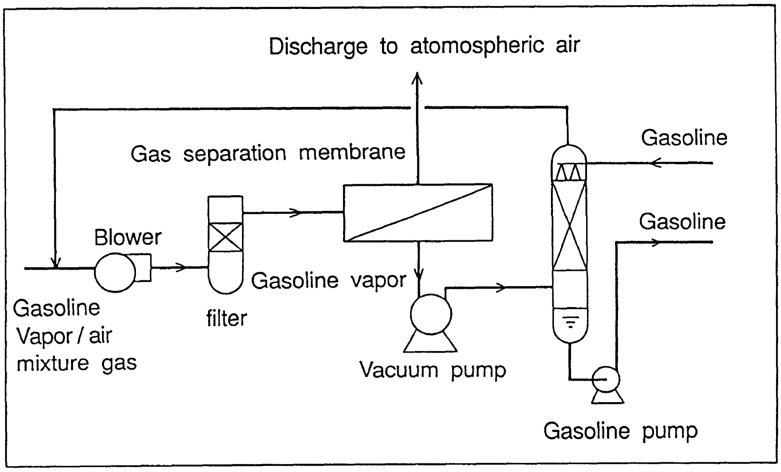


Fig. 12 Flow chart of the membrane separating process for gasoline vapor recovery

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