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K. Ohlrogge[a]; K. -V. Peinemann[a]; J. Wind[a]; R. -D. Behling[a]
[a] GKSS-Forschungszentrum Geesthacht GmbH, Geesthacht

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THE SEPARATION OF HYDROCARBON VAPORS WITH MEMBRANES

K. Ohlrogge, K.-V. Peinemann, J. Wind and R.-D. Behling
GKSS-Forschungszentrum
Geesthacht GmbH
P.O. Box 11 60
D-2054 Geesthacht

1. INTRODUCTION

Many industrial processes which handle volatile hydrocarbons produce organic vapors. These vapors which are generated during storage, trans- portation and the handling of hydrocarbons cause environmental problems. The contaminants dispersed in the air are contributing factors to the development of photochemical smog. In addition they represent valuable resources which should be recovered. GKSS has developed a membrane and a membrane process for the recovery of off gases from gasoline storage and handling [1, 2]. A 300 m^3/h vapor recovery unit for the treatment of off gases from a gasoline tank farm started operation in October 1989. Experiments for MTBE (methyl-tert-butyl-ether) recovery were performed under real conditions at a railroad truck loading station.

2. MEMBRANES FOR HYDROCARBON VAPOR SEPARATION

The membrane which has been developed for the separation hydrocarbon vapors is a thin film composite membrane (Fig. 1). This membrane consists of three layers of different materials. The first layer is a commercially available nonwoven polyester with a very porous structure. The second layer is a microporous membrane which is applied to the nonwoven polyester fleece by the Loeb-Sourirajan technique. This microporous membrane consists of polyetherimide (Trade name Ultem, General Electric). This material was chosen because of its chemical stability against aromatic fuel components e.g. benzene, and its high permeability at a defined pore size. The third layer is the selective barrier layer. This barrier layer is porefree and consists of an elastomeric material. Its thickness ranges between 0.5 and 2 μm. Permeation experiments have been carried out to obtain basic data for the calculation of technical membrane applications to separate hydrocarbon vapors from off streams.

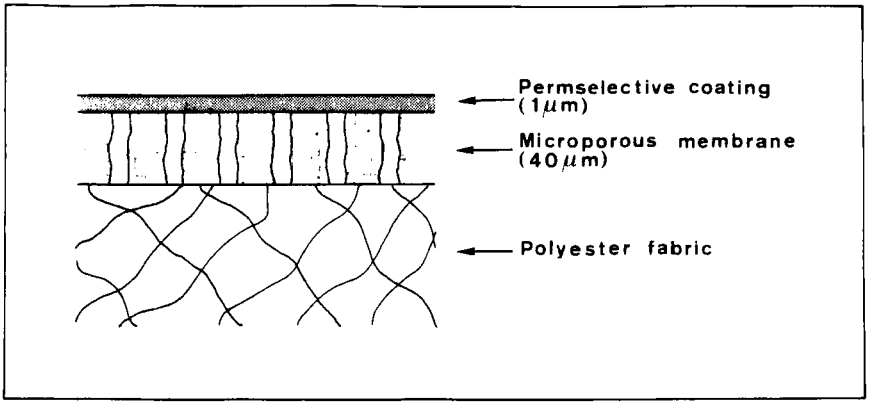

Fig. 1. Schematic of composite membrane

3. TEST FACILITIES AND MEMBRANE DATA

The first measurements were performed with pure gases. To obtain information on the permeation behavior from saturation pressure to pressures below atmospheric pressure, a new experimental setup was designed (Fig. 2).

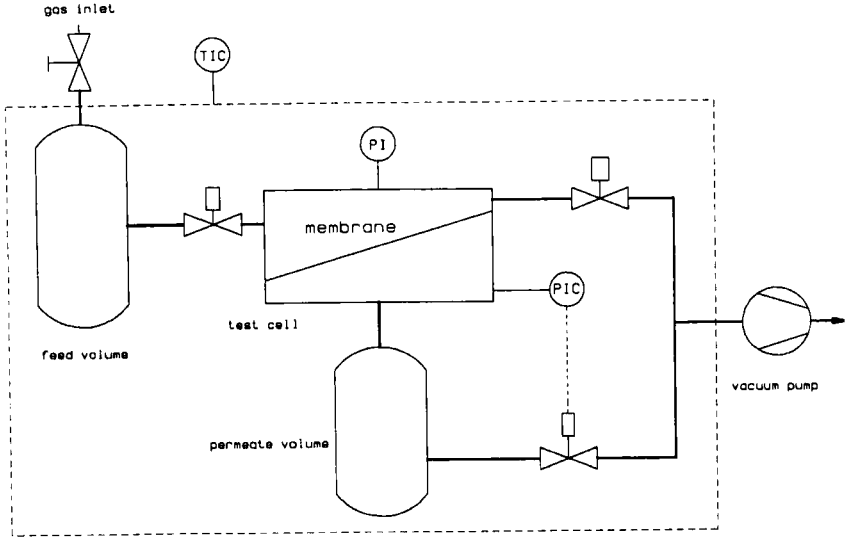

Fig. 2. Test set up

This facility consists of a vessel for the feed volume, a membrane test cell, a vessel for the permeate volume, a vacuum pump, some solenoid valves, pressure and temperature gauges and a computer for data recording and controlling the experiment [3]. To start an experiment, the whole system is first evacuated to a pressure of approximately 10^{-3} mbar. The test component has to be injected into the feed vessel up to a defined pressure. To carry out the permeation experiment, the valve between the feed vessel and membrane test cell has to be opened. Because of the permeation of the feed gas, the feed pressure decreases and the permeate pressure increases. The valve between the permeate vessel and the vacuum pump is closed while the permeation experiment starts. The solenoid valves have selected set points to open and to close. The valve is opened when the permeate pressure reaches the upper set point as a result of the increase in pressure in the permeate vessel, and closed again when the vacuum pump evacuates the vessel to the pressure of the lower set point.

This procedure is repeated until the feed pressure reaches a given permeate pressure (Fig. 3). The computer system stores all converted signals of the temperature and pressure gauges. Using the pressure increase in the known permeate volume, the data obtained have been processed to calculate the flux through a given membrane area. Fluxes of various hydrocarbon vapors, oxygen and nitrogen are depicted in figures 4, 5 and 6. The flux rates are given in m^3 (STP)/m^2 h bar units.

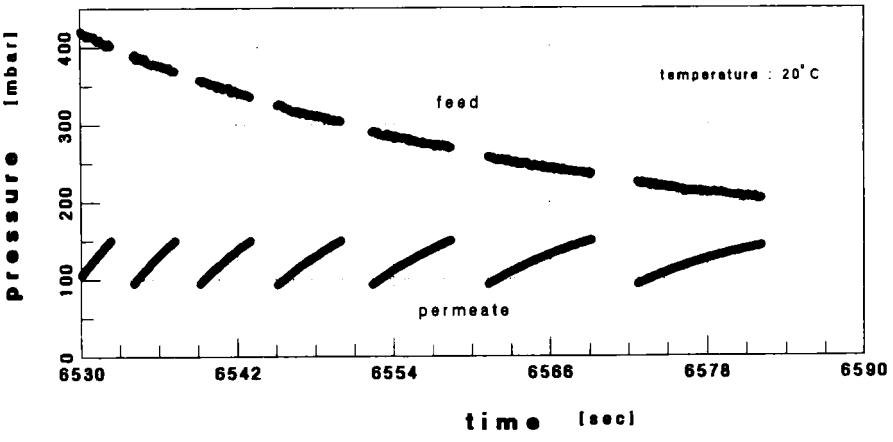

Fig. 3. Pressure progression of a measurement using butane

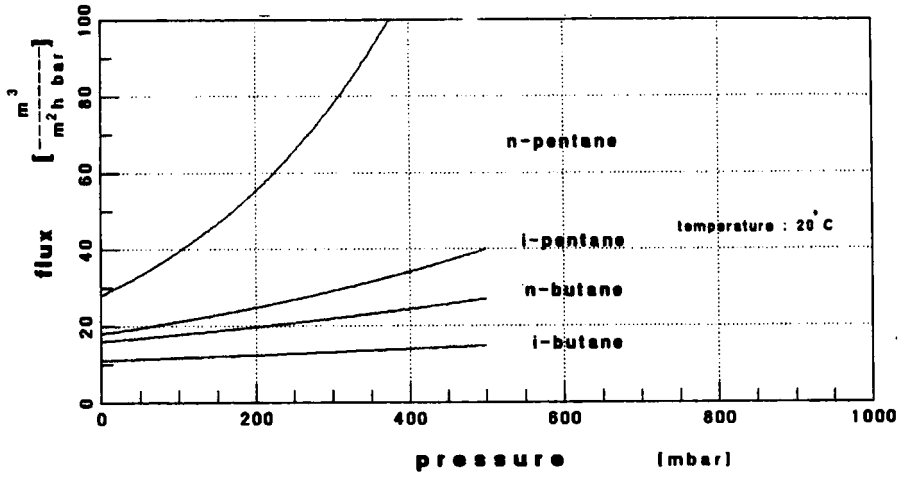

Fig. 4. Flux vs. feed pressure

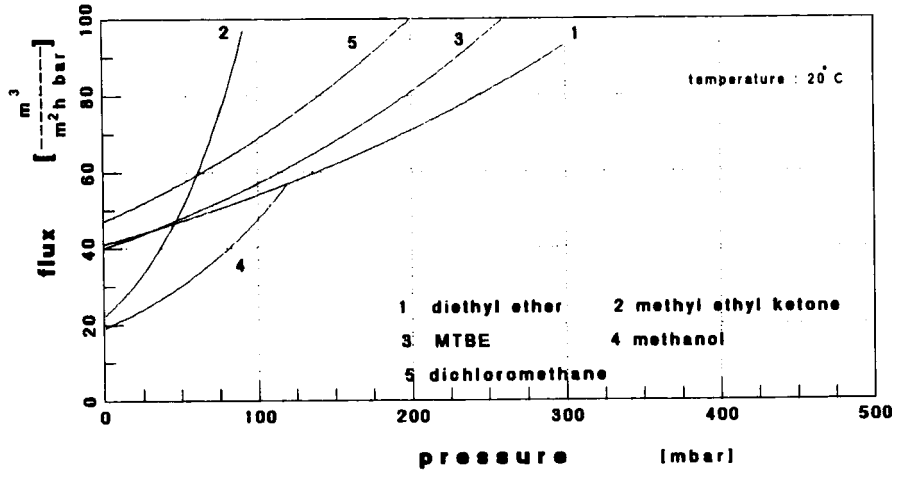

Fig. 5. Flux of various hydrocarbons vs. feed pressure

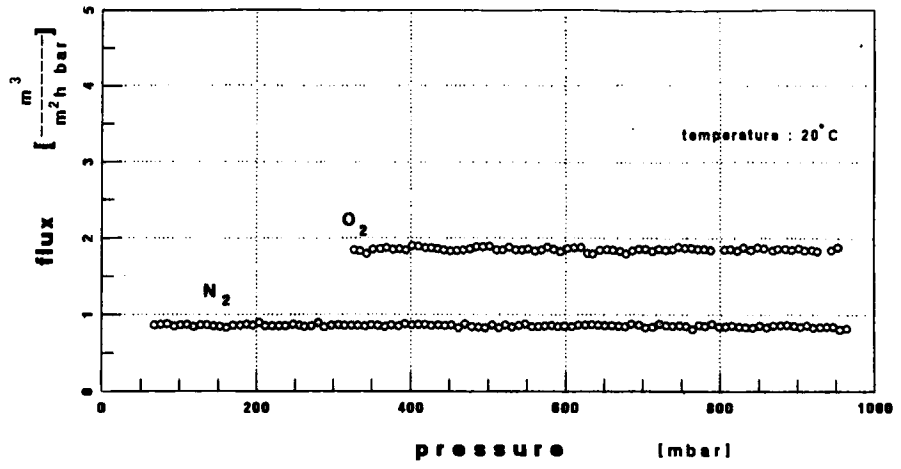

Fig. 6. Flux of oxygen and nitrogen vs. feed pressure

A loop system has been developed to perform experiments with gas mixtures to evaluate the effects of the components of the mixture (Fig. 7). This system consists of a mixing vessel, feed compressor, membrane test cell, vacuum pump, flow meters, pressure and temperature gauges and sampling devices for on-line gas chromatography analysis.

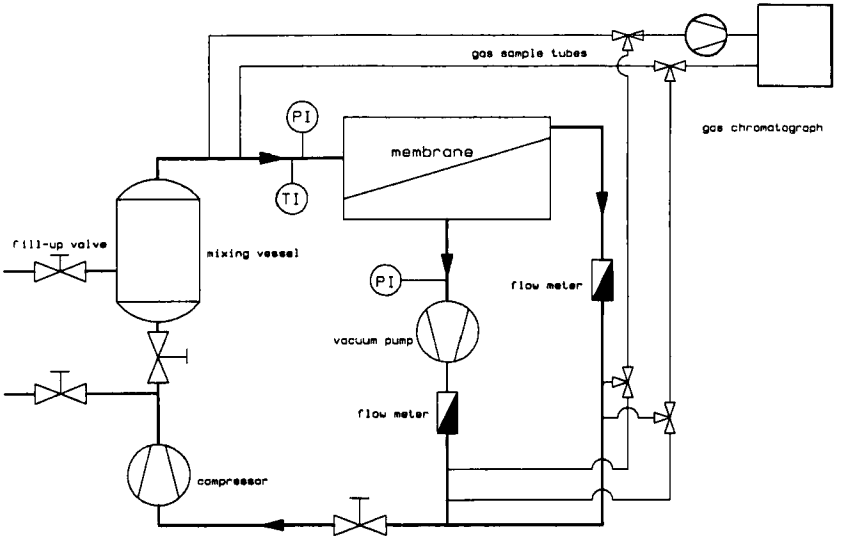

Fig. 7. Test loop

Before starting the experiment, the system is evacuated. Then, the loop is filled with a permanent gas e.g. nitrogen, which is mixed with an organic component. The feed, retentate and permeate streams are connected on-line to the gas chromatograph in a loop like sampling system. It is shown in figure 8 that the nitrogen flux increases with butane partial pressure in nearly the same manner as the butane flux itself. The separation factor is almost the same and independent of the partial pressure of the organic vapor.

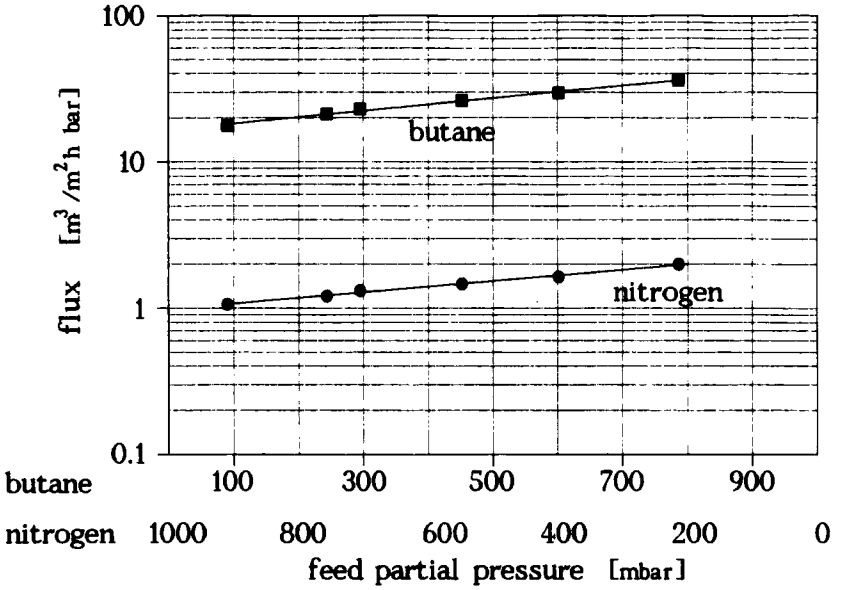

Fig. 8. Butane and nitrogen flux vs. feed partial pressure

This behavior was verified by experiments with gas mixtures containing various alkanes diluted with nitrogen (Fig. 9).

The swelling of the membrane, caused by the high solubility of the hydrocarbons in the membrane material, is the reason for the pressure dependence of the gas flux through the membrane. The results of these experiments show the importance of performing tests with gas mixtures under conditions which are relevant to practical applications.
The calculation of the separation factor using only the pure gas data would lead to an incorrect vapor partial pressure dependence of the separation factor. In tests with pure gases, the nitrogen

flux is pressure independent and has a constant value, whereas the fluxes of organic vapors increase with increasing partial pressures.

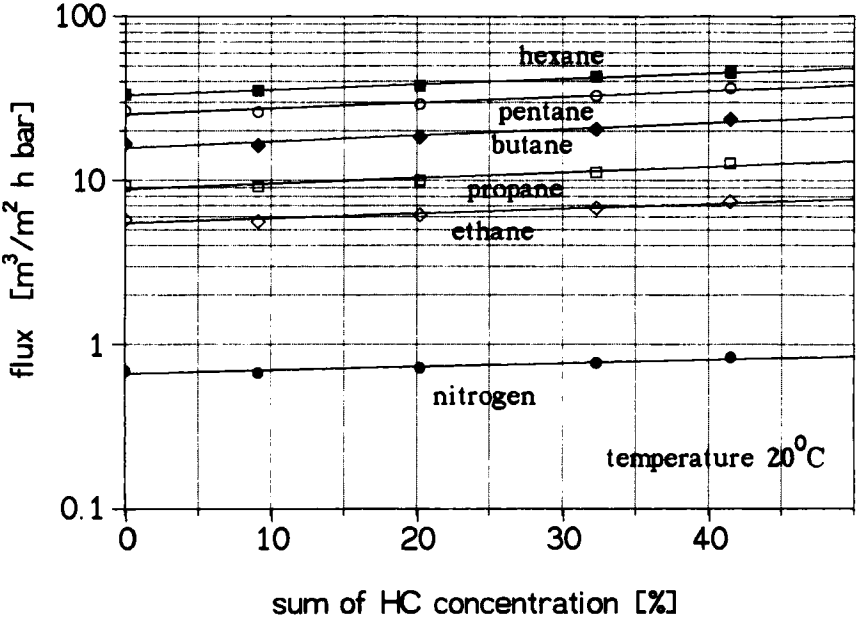

Fig. 9. Sum of HC concentration vs. flux

4. GASOLINE VAPOR RECOVERY

The data obtained are the basis for the layout of technical plants for the treatment of off-gases. The first application to be realized was built in a gasoline tank farm in Munich. The design of the plant (Fig. 10) was tailored to the requirements of a remote site without the infrastructure of a refinery. Electricity was the only form of energy which could be provided. The amount of off-gas varies, and depends on the number of trucks to be loaded. To avoid the influence of loading peaks a gasometer is installed to supply a constant flow to the recovery plant.
The off gases (3) emitted at the loading terminal are transferred to a gasometer (4). The gasometer acts like a buffer and has a volume of 300 m³. At a given filling point the recovery unit starts operation. A feed compressor (3) pumps the off gas to the first membrane stage. The feed pressure is 2 bar. A vacuum pump

(7) is used to maintain a pressure of 200 mbar on the downstream side of the membrane. The permeate is compressed (8) to liquify (9) the hydrocarbons. This compressed permeate stream has a residual concentration of hydrocarbons which depends on the final pressure and temperature.

To make use of this pressure a second membrane stage is installed. With regard to the relatively high pressure and the possibility to achieve a high compression ratio of feed side to permeate side, a small membrane area of this stage is necessary to adjust low hydrocarbon concentrations in the retentate stream. The permeate of this stage is mixed with the permeate from stage 1 and fed back to the pressure condensation unit. The retentate streams of both membrane stages are combined before they are introduced into a catalytic incinerator (11) for a post treatment to meet the required emission standard.

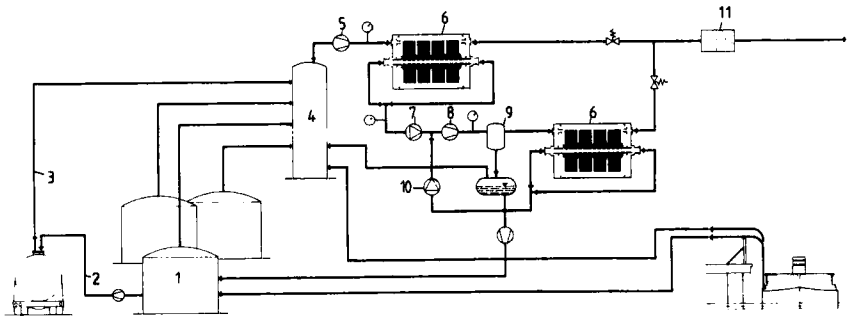

Fig. 10. Flow scheme of a vapor recovery unit

A typical composition of the off-gas from gasoline loading is shown in table 1. These data are taken in different runs from off-gas at 10 to 14 °C atmospheric temperature.

The total retentate concentration varies depending on feed concentration, pressure ratio across the membrane, and the total volume flow.

Some of the results obtained during operation of the system are depicted in tables 2 and 3.

Table 1. Feedgas concentrations

Component	Concentration (vol.%)		
C_1	0.022	0.031	0.009
C_2	0.032	0.039	0.041
C_3	0.325	0.454	0.676
C_4	9.593	14.188	12.943
C_5	5.916	7.102	9.159
C_6	1.192	1.592	1.492
Benzene	0.188	0.227	0.197
C_7	0.114	0.136	0.070
Toluene	0.104	0.107	0.062
C_8	0.007	0.006	0.003
Xylene	0.019	0.013	0.012
$\sum$	17.51	23.90	24.66

Table 2. Retentate concentrations

Component	Retentate concentration (vol.%)		
C_1	0.0377	0.0243	0.0139
C_2	0.0079	0.0081	0.0167
C_3	0.0153	0.0285	0.0411
C_4	0.1753	0.2584	0.2217
C_5	0.0366	0.0290	0.0596
C_6	0.0055	0.0059	0.0067
Benzene	0.0004	0.0018	0.0007
$>C_6$	<0.01	<0.01	<0.01
$\sum$	0.28	0.36	0.36

Table 3. Depletion rates

	Component						
	C_1	C_2	C_3	C_4	C_5	C_6	Benzene
Depletion rate (%)	~20	>80	>98	>99	>99.5	>99.5	>99.5

5. MTBE RECOVERY

A second application is the separation of MTBE from off-gases. MTBE is used as an octane enhancer. Because of environmental problems, lead in gasoline has to be substituted by a product which is ecologically acceptable and shows antiknock properties.

Table 4. Physical constants of MTBE (Methyl-tert-butyl-ether)

Formulae	Mol wt g/mol	Density	Boiling point °C	Saturation pressure (mbar) 20 °C	30 °C	50 °C
$C_5H_{12}O$	88.15	0.7407	55.3	268	406	850

Saturation concentration (g/m³) 20 °C	30 °C	50 °C
969	1420	2790

A container unit (Fig. 11) with a hydrocarbon separation system was built to perform tests under technical conditions in a bypass to existing vent systems. The main components are a liquid ring compressor, membrane modules, a liquid ring vacuum pump, a cooling unit, flow meters and pressure and temperature gauges. The intake and vent lines are protected by flame arresters.

For the experiments of MTBE separation from off gases of a railroad truck loading station, MTBE was used as the liquid for the compressor and the vacuum pump. This MTBE was cooled to 5- 10 °C by an external cooling unit. The compressor has a maximum capacity of 30 Nm³/h at 2 bar pressure. The capacity of the vacuum pump is 20 m³/h. The off gas is introduced into the compressor at atmospheric pressure. In the pump there is an intensive contact between the pressurized gas and the cold ring liquid. Part of the MTBE is condensed in the liquid of the pump and the separation vessel.

The feed gas with a residual MTBE concentration which depends on feed pressure and temperature is fed into the membrane module. The membrane splits the gas stream into an MTBE enriched permeate stream und a depleted retentate stream. The MTBE enriched permeate stream is introduced into the vacuum pump. MTBE condenses in the pump and the separation vessel. The treated permeate is fed to the suction line of the compressor and mixed with the feed gas from the loading terminal. The condensed MTBE flows via an overflow of the separation vessel of the liquid ring pump to an external vessel.

The experiments performed using different process parameters e.g. pressure, pressure ratio, membrane area, feed volume are the basis for the design of a recovery plant.

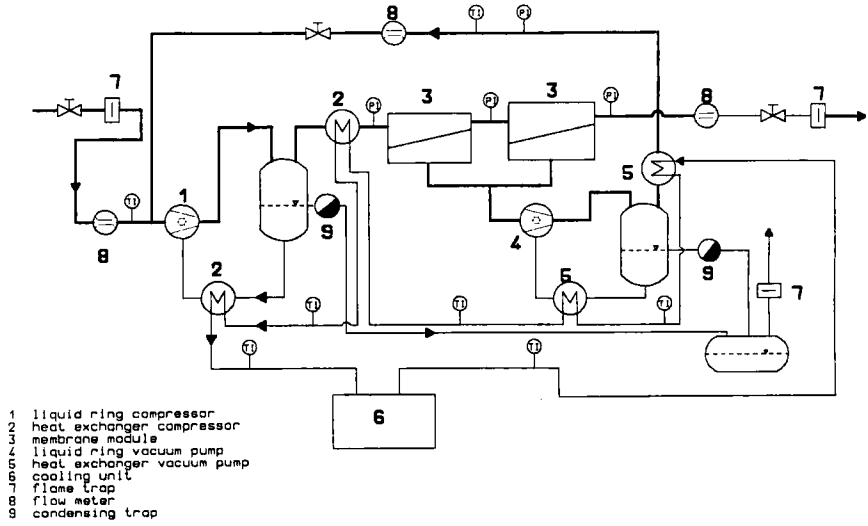

Fig. 11. Flow scheme of a test container

Table 5 shows the process data obtained.

Table 5. MTBE Recovery Tests

Membrane Area	Feed Vol.	Pressure			MTBE Concentration		Recovery Rate
		Feed	Retentate	Permeate	Feed	Retentate	
m^2	m^3/h		bar		%	%	%
17.44	16.6	1.3	1.25	0.350	20	0.7	97.2
17.44	16.5	1.45	1.35	0.320	23.62	1.42	95.3
17.44	15.7	1.4	1.2	0.320	21.6	0.7	97.4
8.72	9.2	1.95	1.9	0.264	16.93	0.06	99.75
8.72	11.1	1.86	1.78	0.243	21.39	0.08	99.74
8.72	14.7	1.7	1.55	0.227	19.29	0.16	99.3

6. CONCLUSIONS

The two applications show that the separation of volatile vapors generated from gasoline or gasoline by-products is feasible. The condensation process of the organic compound in the gas stream has to be designed according to the physical constants of the compound and the requirements of the installation site. The application of a liquid ring pump as compressor or vacuum pump has some advantages

- easy operation
- easier handling of explosive gas mixtures
- low noise operation
- condensation in the ring liquid of the pump.

It is shown that in the case of gasoline vapors a separation rate of 95-99 % is technically feasible. To meet the German TA-Luft standard of 150 mg HC/m³ a post treatment of the retentate e.g. incineration is necessary.

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