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OFF-GAS PURIFICATION BY MEANS OF MEMBRANE VAPOR SEPARATION SYSTEMS

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ABSTRACT

The separation and recovery of volatile hydrocarbon vapors from gasoline tank farm off-gases can in Europe be considered to be a state-of-the-art technology (1). A new application in the treatment of gasoline vapors is the installation of a membrane module in vapor return lines from petrol dispensers to storage tanks at gasoline stations to enhance the vapor recovery efficiency of this system. For solvent vapor recovery, some membrane systems have been installed in the chemical and pharmaceutical industry (2). This paper deals with design features and operating experience.

INTRODUCTION

Organic vapor emissions in Germany are governed by the clean air acts, the so-called TA-Luft (3). This act set guidelines for the approval of new installations dealing with volatile organic compounds (VOCs) and laid down a schedule for retrofitting existing installations to meet the new emission control standards. In August 1991 the federal government of Germany passed two statutory orders to reduce hydrocarbon emissions generated by storage, handling, and transportation of gasoline from the refinery to the gasoline station (stage I) and the car refueling (stage II) (4).

Stage I includes the off-gas treatment of tank farms. In the meantime, 20 vapor recovery units (VRUs) have been installed or are being ordered for these applications (status October 1993). A new field is the enhancement of recovery efficiency of vapor return systems at gasoline stations by integration of a membrane module. Part of the stage II regulation is the limitation of the vapor volume.

The recycled gasoline vapor/air stream must be equal to the pumped liquid gasoline volume. Consequently, vacuum-supported vapor return systems are limited in their efficiency. The integration of a membrane module allows the sucking of a volume surplus at the filling point which results in higher vapor return rates. The sucked vapor/air stream is separated by means of membranes in a hydrocarbon vapor enriched permeate stream to the order of ≤ 100 % of the liquid volume and in a depleted stream vented to the atmosphere.

MEMBRANES

The membranes that are used for gasoline and solvent vapor separation have to be selective for hydrocarbon vapors versus air compounds such as nitrogen and oxygen. They also have to be chemically and mechanically stable. The membranes that are used for these applications are thin-film composite membranes in a flat-sheet configuration with a dense elastomeric film as a top layer (FIGURE 1).

The choice of polymer for the microporous substrate was taken in accordance with the expected chemical attack. The module/membrane arrangement is composed of round, flat-sheet membranes which are thermally welded at the cutting edges forming a membrane envelope. These envelopes are placed on a central permeate tube. The membrane stack is divided into asymmetrical compartments by means of baffle plates. The number of parallel-arranged envelopes is dependent on the reduction of feed volume flow caused by permeation through the membrane (FIGURE 2). The material of the nonwoven substrate must be selected in accordance with the melting point of the glassy polymer of the microporous substrate because of the adjustment of the welding properties.

Design criteria of a membrane process. This composite membrane is selective in its separation of organic vapors from airstreams. The order of permeation rate success is depicted in FIGURE 3.

FIGURE 4 shows the flow scheme of a standard "end of pipe" vapor recovery unit. The membrane stage is used to separate the organic vapors from the off-gas stream and to improve the recovery conditions.

Downstream of the membrane unit, the concentration of the organic compounds is enhanced and the portion of inert gases is decreased. The location of the recovery stage depends on the intake concentration and the vapor pressure of

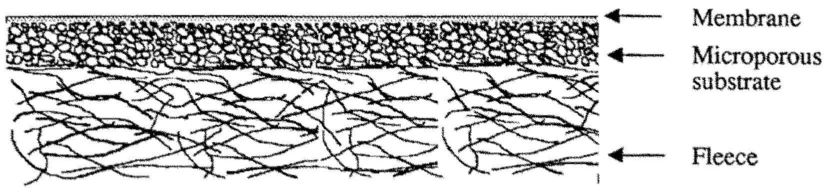


FIGURE 1. Schematic of a thin-film composite membrane.

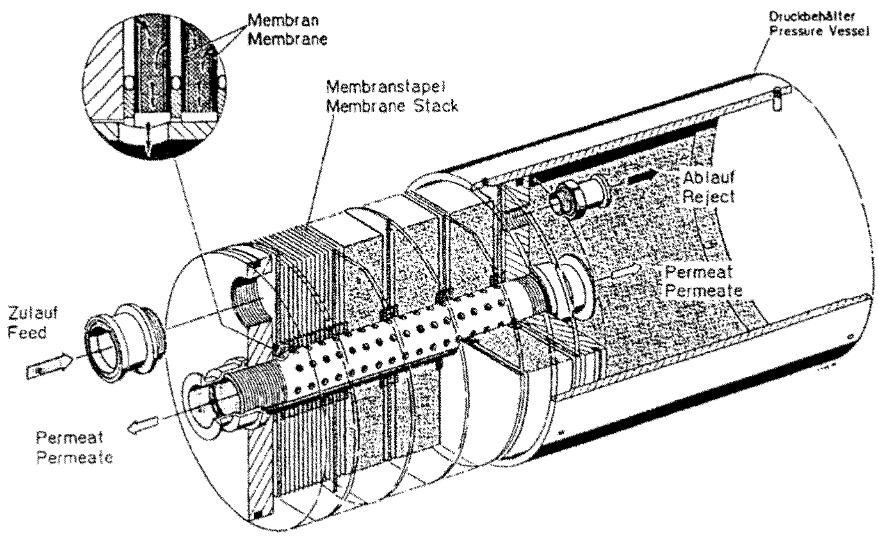


FIGURE 2. Membrane module type GS.

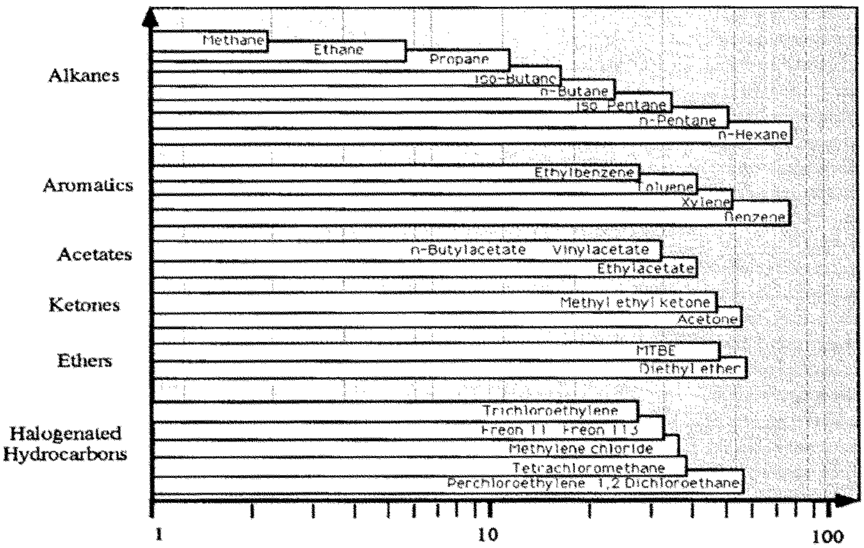


FIGURE 3. Membrane selectivity of various hydrocarbon vapors vs nitrogen.

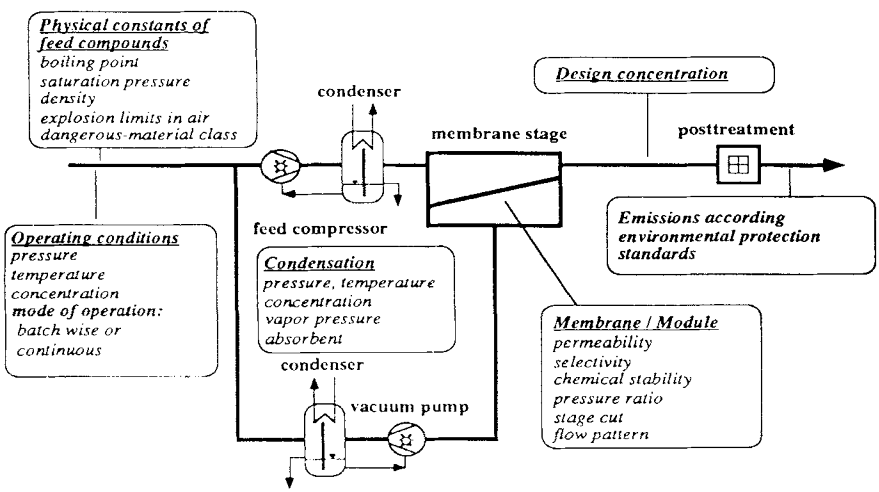


FIGURE 4. Flow scheme of membrane separation process.

the organic vapors (5). The use of a feed compressor depends on the available feed pressure and the required pressure ratio of the membrane process.

Dichloroethane separation. The goal for 1,2 dichloroethane separation from the off-gas of a production facility was the reduction of the feed concentration from approx. 80 g/m^3 to < 330 mg/m^3. This 1,2 dichloroethane depleted stream was introduced into a main vent stream which was fed into a central incineration system. The separation of organic vapors only by condensation is limited by the vapor pressure of the organic compounds. The saturation concentration of various organic vapors with respect to temperature is plotted in FIGURE 5.

This shows that the saturation concentration of 1,2 dichloroethane at -10 °C is approx. 65 g/m^3. Another disadvantage of cooling below 0 °C is the formation of ice at the condenser surface in the presence of water vapor in the gas stream. The basic construction criteria are given in FIGURE 6.

These are the conditions for the maximum intake flow. During daily operation, the intake flow fluctuates depending on the utilization rate of the production plant. Because of the fixed membrane area and vacuum pump capacity, the dichloroethane depletion increases with the reduction of intake flow. The vapor recovery unit operates at nearly atmospheric feed pressure. This unit has only one pump for maintenance of the separation process. The liquid ring vacuum pump at the downstream side of the membrane is used to provide the driving force for membrane separation. It is also used to boost the noncondensed recycled permeate stream, which is mixed with the vent gas of the production facility forming the feed for the membrane stage. The unit has been in trouble-free operation since spring 1993.

VAPOR RECOVERY AT GASOLINE STATIONS

Two systems are on the market. The balance system, which consists of a nozzle covered with a flexible bellow for sealing the space between the car filling point and the atmosphere. While the vehicle is refueled, positive pressure is generated in the tank. Empty space in the underground storage tank occurs negative pressure, when the fuel is pumped out. Because of the close connection, the positive pressure of the car tank and the negative pressure of the storage tank try to balance without external force.

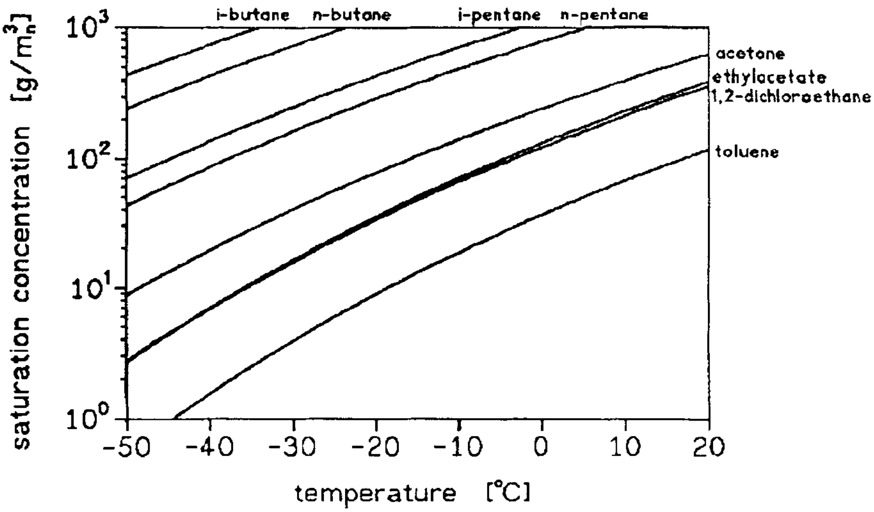


FIGURE 5. Saturation concentration of various organic vapors vs temperature.

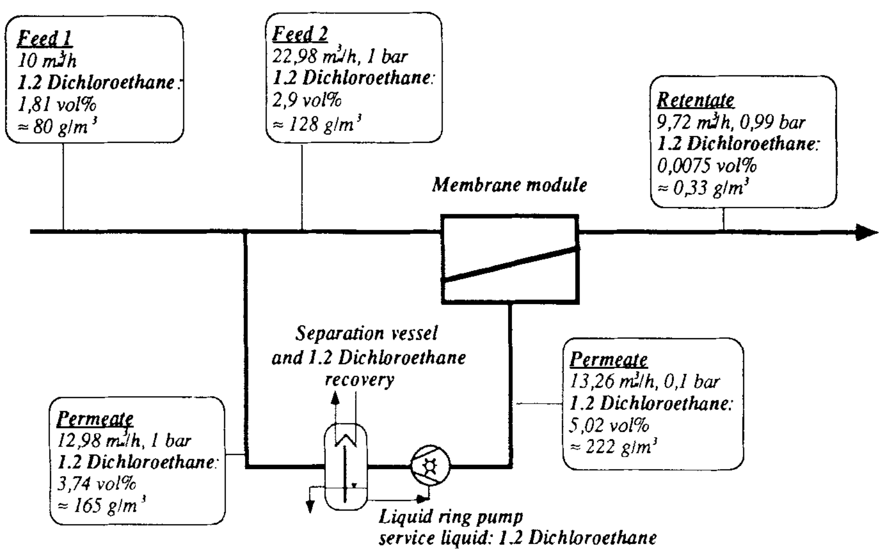


FIGURE 6. Flow scheme of a 1,2 dichloroethane recovery unit.

Vacuum-assisted systems use vacuum pumps at each side of each dispenser or use a central vacuum system, which serves the complete gasoline station. The limitation of recovery rate to approx. 75 % in "state-of-the-art" systems is a result of the stipulated ratio of 1:1 for sucked gasoline to returned vapor flow. These restrictions have been overcome by the integration of a membrane module (8) into the vapor return line (FIGURE 7).

The membrane module separates the air/vapor stream. A hydrocarbon enriched vapor flow (10), which is equal in volume to the pumped liquid gasoline, is fed back to the underground storage tank (13). The nozzle (1) is equipped with a vapor spout to suck out the gasoline vapors. The vapors are fed out by an internal vapor channel of the nozzle and a coaxial vapor line of the delivery hose (2). The vacuum required to suck the gasoline vapors is created by the vacuum pump (11) which is placed behind the membrane module. The vacuum pump (12) on the downstream side of the membrane module generates the vacuum, which is necessary for creating the driving force for the membrane separation process. Both vacuum pumps have been adjusted with regard to their performance characteristics. The working points from full load to partial load are on the horizontal level of the characteristic curve (FIGURE 8).

The dependence of feed and permeate pressure vs feed flow is depicted in FIGURE 9. The dotted line shows the pressure difference at the operating points. This allows the running of the separation process with nearly the same pressure ratio to obtain a defined recovery rate. In case of a deficiency in volume, if the recycled flow falls below the ratio of 100% pumped gasoline, the balance can be equalized using a breather pipe.

Layout of a demonstration plant. The demonstration plant was designed to serve a gasoline station with an annual turnover of 5 million liters of gasoline. Such a station was equipped with five gasoline pumps, which can be operated on both sides. The maximum filling velocity of a gasoline pump is 40 L/min; the average pumping speed is approx. 35 L/min. The sucked gas volume at full load operation was thus determined to be 20 m^3/h.

This calculation is based on the following assumptions:

- Feed concentration: 20 vol % HC

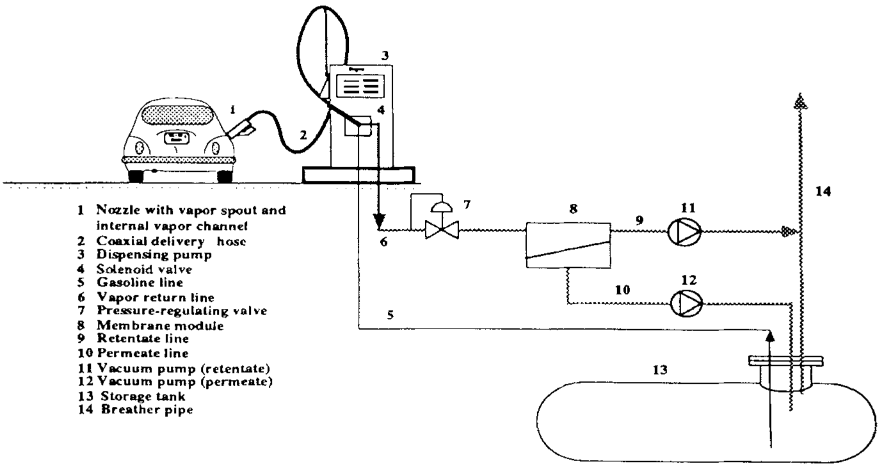


FIGURE 7. Vapor return system at gasoline stations.

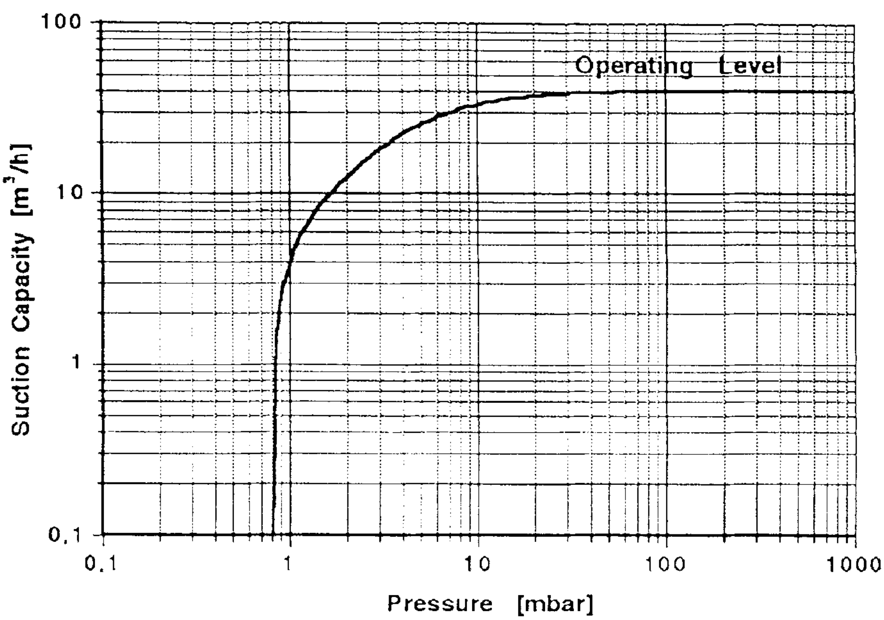


FIGURE 8. Characteristic curve of a rotary vane vacuum pump.

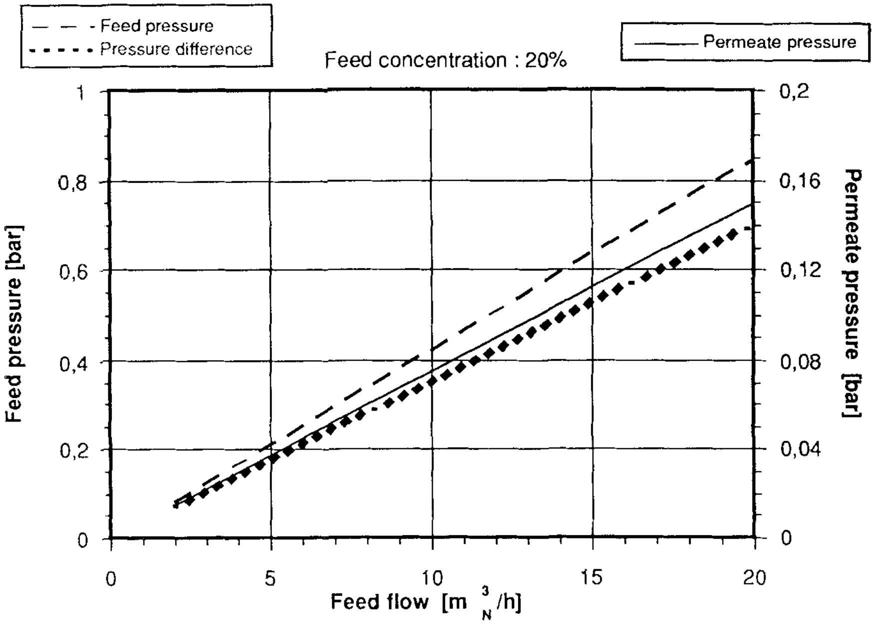
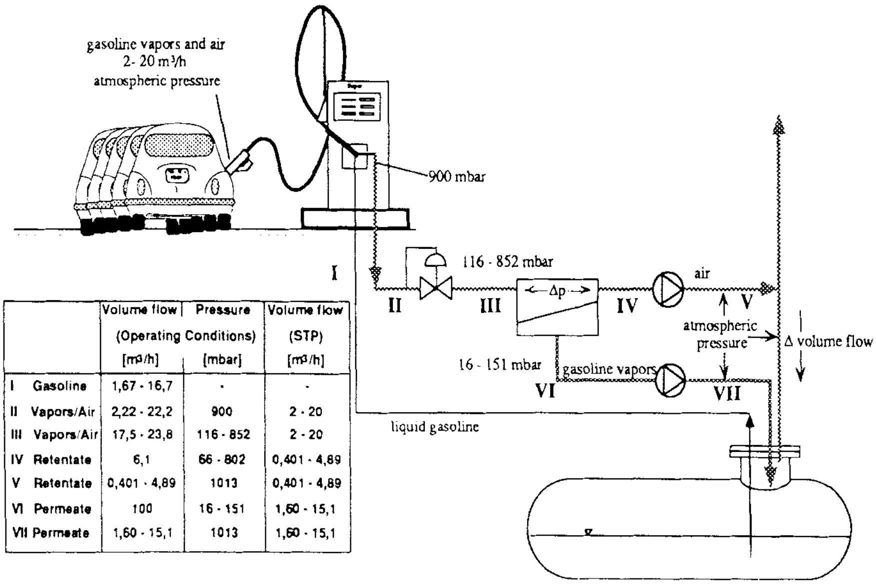


FIGURE 9. Dependence of feed and permeate pressure vs feed flow.

- Rate of utilization: 80%
- Surplus volume of sucked gas volume: 20%
- Fuel rate: 35 L/min.

The operating levels of 10% to full load conditions are shown in FIGURE 10. The volume flows are indicated in operating and STP conditions.

Influence of design and operating parameters. The layout of the gasoline station vapor recovery plant is governed by the feed pressure of the membrane stage at full load, membrane selectivity and permeability, residual retentate concentration permitted permeate volume flow, and the capacity of the permeate vacuum pump. The following calculations are based on a suction capacity of 100 m^3/h of the permeate pump and 5.8 m^3/h of the retentate pump. The dependence of recovery rate [%] and retentate concentration [% HC] versus installed membrane area are plotted in FIGURE 11.



	Volume flow (Operating Conditions) [m³/h]	Pressure [mbar]	Volume flow (STP) [m³/h]
I Gasoline	1,67 - 16,7	-	-
II Vapors/Air	2,22 - 22,2	900	2 - 20
III Vapors/Air	17,5 - 23,8	116 - 852	2 - 20
IV Retentate	6,1	66 - 802	0,401 - 4,89
V Retentate	0,401 - 4,89	1013	0,401 - 4,89
VI Permeate	100	16 - 151	1,60 - 15,1
VII Permeate	1,60 - 15,1	1013	1,60 - 15,1

FIGURE 10. Operating conditions of the demonstration plant.

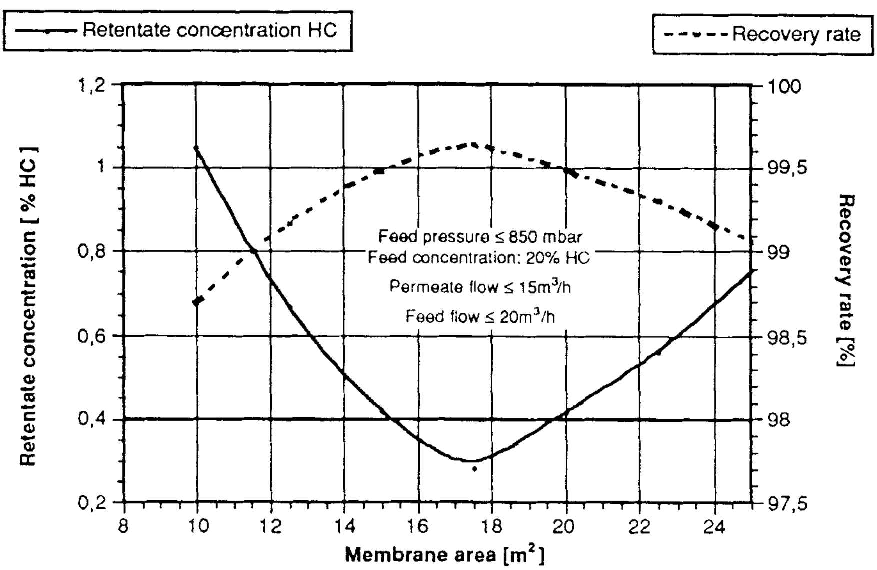


FIGURE 11. Retentate concentration and recovery rate vs membrane area.

It is shown that based on conditions indicated, the highest recovery rate that is associated with the lowest retentate concentration can be achieved at 17 m^2 of membrane area. FIGURE 12 explains this behavior. At 17 m^2 of membrane area, the optimal operating point is at 850 mbar feed pressure and a permeate flow of 15 m^3/h. With a decrease in membrane area, the permeate flow decreases and the hydrocarbon concentration of the retentate increases. At more than 20 m^2 membrane area, the feed pressure must decrease to prevent an increase of the retentate flow over the limit of 15 m^3/h. The ratio of feed pressure vs permeate pressure is the key parameter for the retentate purity. The decrease of feed pressure results in a reduction of the pressure ratio and an increase of HC concentration of the retentate. Pressure losses of the membrane module have an influence on the separation performance. At a defined feed pressure, the suction pressure of the retentate has to be increased to compensate the pressure drop along the flow path.

The pressure drop across the feed flow path in the module under technical conditions is approx. 20 to 40 mbar. Because of the asymmetrically arranged membrane compartments in the module with a decrease of membrane area in accordance to the reduction of flow volume caused by permeation through the membranes, a linear pressure drop was assumed. The calculations are based on an operating vacuum pump capacity of the permeate pump of 100 m^3/h and of the retentate pump of 5.8 m^3/h. The achieved pressure ratio and stage cut are dependent on one another.

In FIGURE 13, the pressure ratio and stage cut are plotted vs feed flow at 0, 20, and 40 mbar pressure loss. In the theoretical case of 0-mbar pressure drop, pressure ratio and stage cut are constant over the feed flow range. In the case of a pressure drop, the feed pressure will increase. This causes higher permeation rates, which are associated with a slight increase of permeate pressure. Based on the pump characteristics, pressure ratio and stage cut extend with an increase of pressure losses. This effect declines with the rise of feed flow.

The range of hydrocarbon retentate concentration and recovery rate vs feed flow at an average pressure loss of 20 mbar and 20 vol % hydrocarbon intake concentration is depicted in FIGURE 14. It shows that the retentate concentration varies from 0.2 vol % HC, which is a 99.77% recovery rate, to 0.25 vol % HC and 99.67% recovery rate.

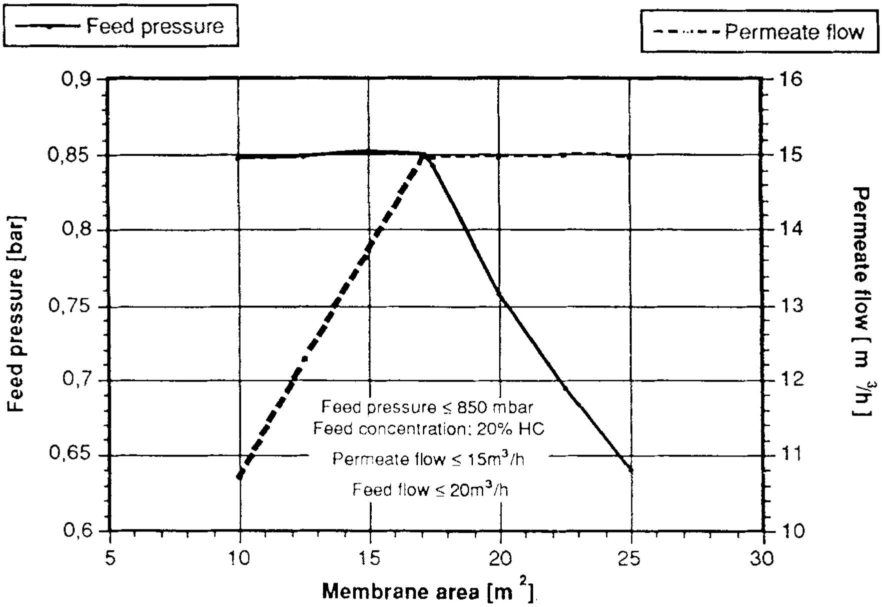


FIGURE 12. Feed pressure and permeate flow vs membrane area.

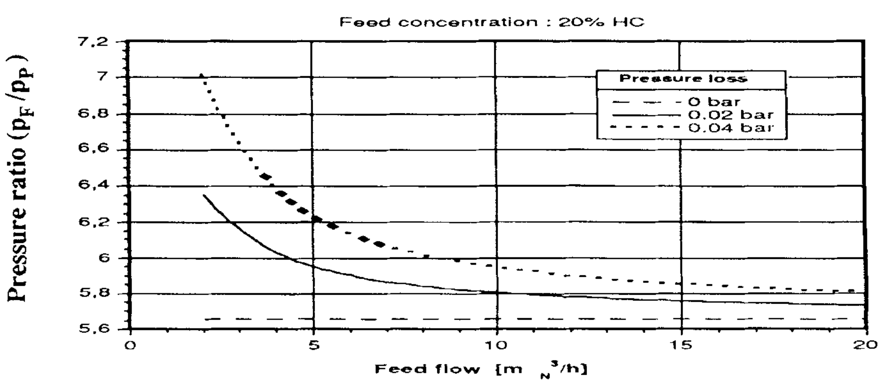


FIGURE 13. Feed flow vs pressure ratio in dependence of pressure loss.

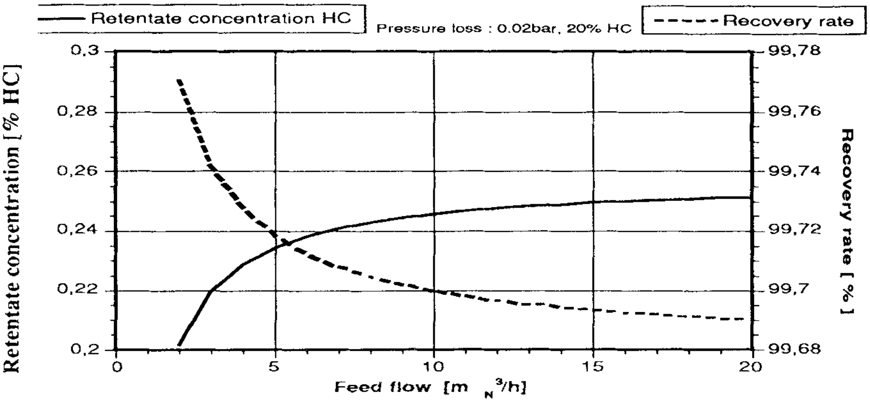


FIGURE 14. Feed flow vs retentate concentration and recovery rate.

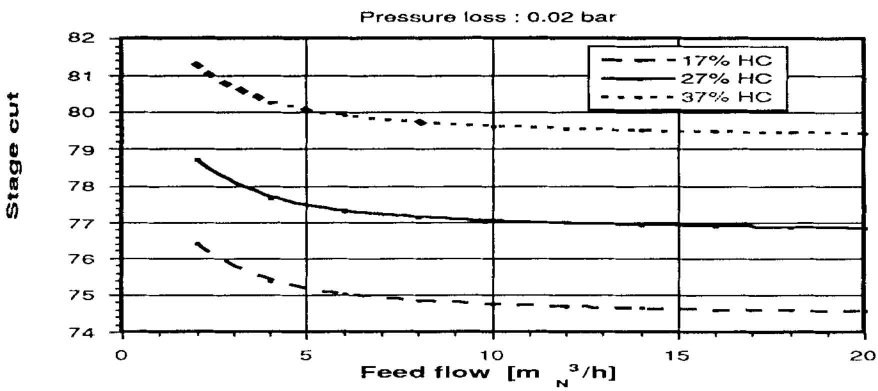


FIGURE 15. Feed flow vs stage cut in dependence of intake concentration.

The influence of intake HC concentration is plotted in FIGURE 15. Higher HC intake concentrations cause higher permeation through the membrane, which, in turn, results in a higher stage cut, pressure ratio, and recovery efficiency.

CONCLUSION

The design of vapor separation and recovery plants by means of membranes is very complex. The layout of a unit is governed by feed concentration and flux densities of the various compounds, membrane selectivity, required retentate purity, flow limitations, pump capacities, and the location of the recovery stage. End of pipe installations are either equipped with a feed compressor and a permeate vacuum pump or only with a vacuum pump at atmospheric feed pressure or a feed pressure provided by a vent gas system. In the case of a stipulated constant ratio of feed flow to permeate flow at fluctuating feed flows, the vacuum pump must be installed in the retentate and permeate line. It is essential that the characteristic curves are well-suited with regard to one another.

REFERENCES

1. M. Schell, J. Brockmöller and G. Höhne, Membran- und Adsorptionstechnik als kombiniertes Verfahren zur Kohlenwasserstoffrückgewinnung. VDI-Kolloquium "Fortschritte bei der thermischen, katalytischen, sorptiven und biologischen Abgasreinigung", 1. bis 3. März 1993 in Mannheim.

2. M. Herbst, Industrielle Gastrenntechnik mittels selektiver Membranen. Vakuum in der Praxis, Vol. 5, (2) 103 (1993).

3. Erste Allgemeine Verwaltungsvorschrift zum Bundes-Immissionsschutzgesetz/Technische Anleitung zur Reinhaltung der Luft. Bundesrat, Drucksache 60/86, 30.01.86.

4. Der Bundesminister für Umwelt, Naturschutz und Reaktorsicherheit, Pressemitteilung 58/91, Bonn, 14.08.91.

5. K. Ohlrogge, J. Wind and R.-D. Behling, Industrial Applications of Membrane Systems to Separate Hydrocarbon Vapors from Gas Stream. 3rd International Conference on Effective Membrane Process - New Perspectives. Bath, UK, on 12-14 May 1993. BHR Group Conference Series, Publication No. 3, 331-339.