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A new integrated membrane process for producing clarified apple juice and apple juice aroma concentrate

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Abstract

An integrated membrane process for producing apple juice and apple juice aroma concentrates is proposed. The process involves the following operations: an integrated membrane reactor to clarify the raw juice; reverse osmosis (RO) to preconcentrate the juice up to 25°Brix; pervaporation (PV) to recover and concentrate aroma compounds, and a final evaporation step to concentrate apple juice up to 72°Brix. These operations were tested in laboratory and pilot plant units. Promising results were obtained with the membrane operations involved. In order to have an economic process assessment, the pilot plant units were assembled into an integrated unit and operated with raw apple juice. The products were more clear and brilliant than apple juice produced by conventional methods. The integrated membrane process also seemed to be more advantageous on the basis of economics than the conventional one.

Keywords: Apple juice; Clarification; Concentration; Aroma; Membrane techniques

1. Introduction

Apples are amongst the most widely grown and consumed of temperate fruit crops. Annual world apple production was estimated to be more than 40 million tons in 1992 and 1993, of which more than 5 million tons were processed to obtain apple juice (Lea, 1990; Root, 1996).

Concentrated fruit juices were first sold in the US market in 1945 (Stacy, 1988). At that time, the greatest volume of apple juice was processed into a 70–75°Brix concentrate to reduce volume and weight, which resulted in lower costs for packaging, storage and transportation. Now apple juice concentrate may be stored and shipped throughout the world as a relatively stable product. Concentration has also solved the problem of the seasonal nature of crops and allowed the economic utilisation of perishable agricultural products (Rao, 1989).

The composition of the apple juice depends on the variety, origin, growing conditions of the apples, the quality of the fruit, processing procedures and storage. The major components of apple juice are carbohydrates, acids, nitrogen compounds, polyphenols, minerals and vitamins. Table 1 shows the approximate composition of the raw apple juice obtained after pressing apples (Lee & Mattick, 1989; Lea, 1990).

The aroma complex of apple juice is a highly volatile fraction of principally esters, aldehydes and alcohols, but also ethers, fatty acids, lactones, terpenes and ketones. The total concentration of aroma compounds is of the order of 200 ppm. Each group of aroma compounds gives a typical character to the apple juice flavour. Esters and aldehydes are present at considerably lower concentrations than alcohols, but as they have very low aroma threshold values, typically at ppb levels, they are responsible for the major part of the total aroma intensity of the juice. Alcohols have considerably

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Nomenclature

C	concentration (ppm)
J	flux (g/m^2 h)
R	rejection (%)
Re	Reynolds number
T	temperature (°C)
t	time (min)
TMP	transmembrane pressure (bar)
k	mass transfer coefficient (g/m^2 h)
β	enrichment factor (dimensionless)
μ	viscosity (cp)

Subscripts

bl	boundary layer
C	concentrate
F	feed
fm	feed near the membrane wall
i	component
int	intrinsic
m	membrane
ov	overall
P	permeate
w	pure water

Table 1
Approximate composition of apple juice

Compound	Concentration (g/l)
Water	860–900
Sugars	100–120
Fructose	46–70
Sucrose	27
Glucose	20
Malic acid	3–7
Pectin	1–5
Starch	0.5–5
Polyphenols	1
Proteins	0.6
Vitamins (mainly ascorbic acid)	0.05
Ashes	2

higher aroma threshold values, typically at ppm levels, but are quantitatively the largest group of aroma components in apple juice and they still make an important contribution to the fruity flavour of the juice (Simpson, 1979; Dimick & Hoskin, 1981; Morton, 1990).

The aim of this work was to develop an alternative technology for the production of aroma-enriched apple juice concentrate which integrates membrane processes: enzymatic membrane reactor (EMR), reverse osmosis (RO), and pervaporation (PV). The proposed technology was compared with the conventional one for apple juice production in terms of product quality and overall process economics.

2. Conventional methods for apple juice concentrate production

Fig. 1 shows a flow diagram of the conventional process for apple juice production. The process starts with the harvesting, transport and washing of the fresh fruit. Once the apples have been washed, they are milled to a pulp and then pressed. During the pressing step pectolytic enzymes are often added to the pulp, of the order of 80–120 ml per metric ton of apple mash, in order to break down the fruit cell structure, so that pulp pressability and process yield are improved (Lea, 1990; Root, 1996).

The raw apple juice obtained after pressing is very turbid, viscous, dark in colour and contains a significant amount of colloidal compounds which are stabilised in suspension by polysaccharides such as pectin, starch and gums. This product must be clarified prior to its commercial use. Clarification involves the removal of juice components, mainly pectin, which cause cloudiness. Apple juice clarification begins with depectinisation which is achieved by pectolytic enzymes. Enzymes hydrolyse pectin and cause the pectin–protein complexes to flocculate giving larger particles that settle, lowering also the viscosity of the system, so that the juice is much easier to filter. This process is usually carried out at 50°C for 2 h or at 20°C for 8–12 h. Amylases are also added during enzyme treatment to break down starch molecules which may cause cloudiness during storage (Kilara & Van Buren, 1989).

After enzyme treatment, fining agents are used to enhance settling of formed flocs. The most common fining agent is gelatine. Typical levels for gelatine addition are 50–500 g/m^3 of juice. Other suitable agents are bentonite, tannic acid or silica sol.

Settled solids and other suspended matter are removed by conventional filtration. Filter aids such as diatomaceous earth or kieselguhr are used to facilitate the filtration process.

Evaporation is the conventional method for concentrating clarified apple juice. It is performed in multiple effect evaporators at temperatures between 45°C and 90°C. Simultaneously with water evaporation low molecular weight volatile flavour compounds are entrained and therefore it is a common practice to remove the aroma compounds before concentration. Generally, the raw apple juice is heated in the second stage of the evaporator up to 80°C and a vapour containing the volatile aroma compounds is obtained. It is then concentrated to an aroma-enriched solution by distillation. This step also yields dearomatised raw apple juice. This juice is then clarified and afterwards is concentrated in the remaining evaporator stages (Rao, 1989; Root, 1996).

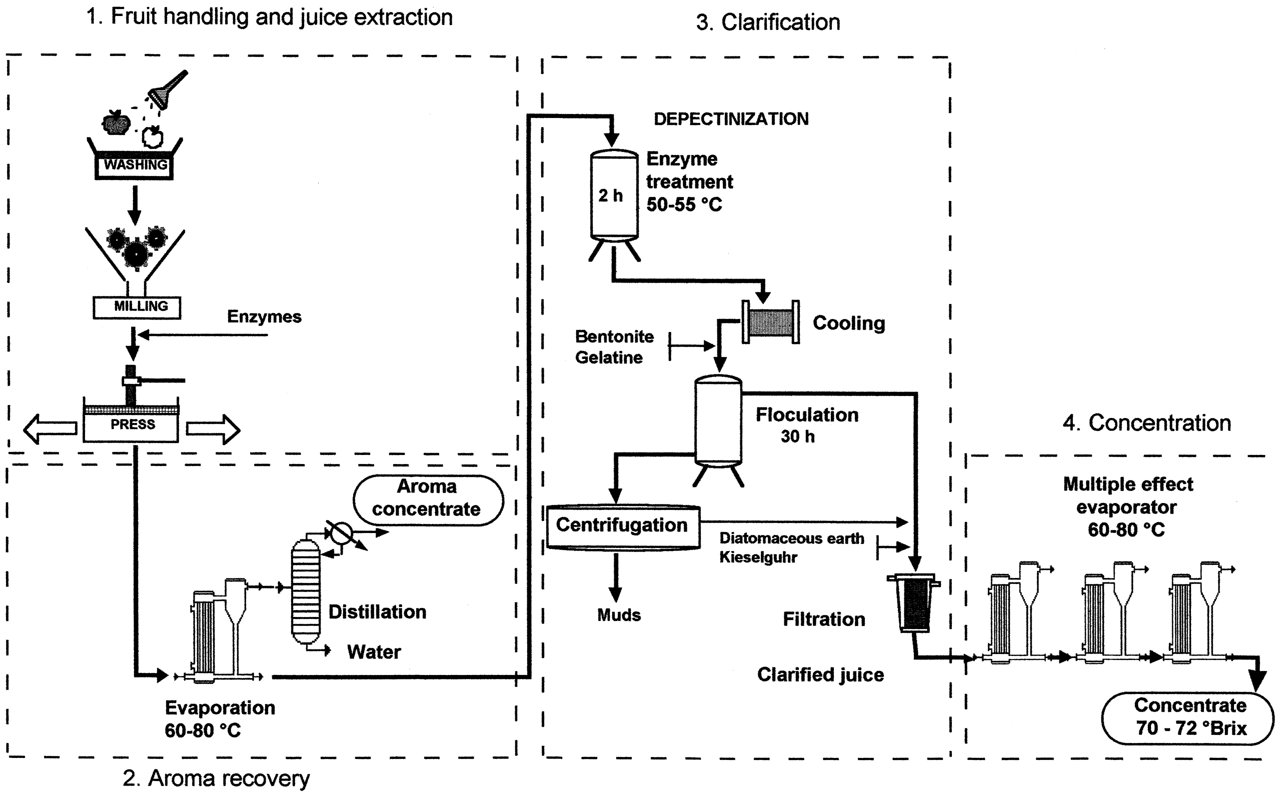


Fig. 1. Conventional process for the production of apple juice concentrate and apple juice aroma.

3. An integrated membrane process to produce apple juice and aroma concentrates

Conventional methods to clarify apple juice are labour-intensive, time-consuming and discontinuously-operated. The use of additives (fining agents and filter aids) may leave a slight after taste in the juice. Moreover, the solids obtained after filtration, which contain enzymes, filter aids, and fining agents, cannot be reused and cause pollution problems. The apple juice concentrate from evaporation also has certain drawbacks, e.g. heat degradation of aroma compounds, important losses of volatile aroma compounds and high energy consumption.

In order to avoid some of the problems of conventional apple juice processing methods, a novel technology is proposed in this work. The new process, depicted in Fig. 2, involves the following operations:

- Clarification of raw apple juice using an EMR.
- Apple juice preconcentration by RO.
- Aroma compounds recovery and concentration by RV.
- Final concentration up to 72°Brix using conventional evaporation.

Table 2 summarises the goals of the different stages of the process. These operations are described and explained in detail in the following sections.

3.1. Clarification of apple juice using an EMR

Enzymatic processing of foods is characterised by high reaction specificity at low temperature, making it environmentally friendly. One drawback of enzymatic reactions is that they often involve unfavourable equilibrium conditions for complete conversion to desired products. To overcome this restriction, reactions are typically performed in systems, where one or more products are continuously removed through an integrated separation step.

Membrane technology can offer specific advantages in combination with enzyme technology. The possibility of very efficient separation at low temperature (enzyme reaction) is one appealing aspect. Membranes also offer other alternatives that make enzyme technology more flexible. Use of enzymes in a membrane reactor, or in a circulating loop, extends the enzyme life considerably thus permitting a higher turnover per enzyme molecule. Such systems allow to use more expensive enzymes with special properties.

In the production of apple juice, membranes are used more frequently for clarification. Membrane filters techniques (microfiltration and ultrafiltration) are beginning to replace diatomaceous earth filtration, after enzymatic pulping. In this new approach, by choosing an effective membrane configuration, it is possible to

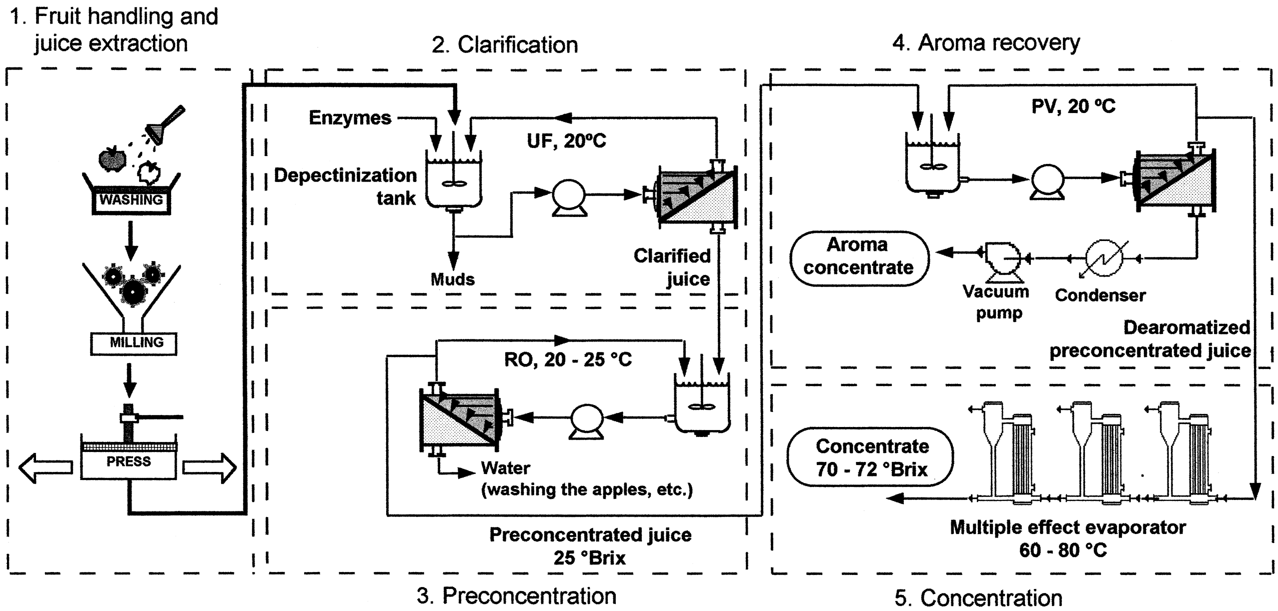


Fig. 2. Integrated membrane process for the production of apple juice concentrate and apple juice aroma.

Table 2
Goals of each stage of the process

Enzymatic membrane reactor	Reverse osmosis	Pervaporation	Evaporation
(1) To have direct pulping and clarification in one step (2) To improve yield (3) To prolong enzyme life (4) To reduce costs of the process (5) To reduce waste production (6) To avoid the use of additives (fining agents and filter aids) (7) To reduce operation time	(1) To preconcentrate apple juice up to 25°Brix so that: (a) Thermal damage is minimised (b) Aroma losses due to evaporation are decreased (c) Energy consumption and capital inversion are reduced	(1) To improve the sensorial quality of concentrated apple juice by: (a) Minimising aroma losses due to evaporation (b) Eliminating heat degradation of aroma products	(1) To reach the final concentration of 72°Brix

perform direct pulping and clarification in one step. A membrane reactor combines juice clarification with enzyme recirculation. In this way enzyme costs are reduced, waste production may be lowered and yield of the process is improved. Furthermore, completely decolourised juice can be obtained. After a number of lab-scale tests, this approach is currently being scaled-up to pilot levels to produce 250 l of juice per hour.

3.1.1. Development path

A schematic of the conventional apple juice process shown in Fig. 1. This process can be very efficient, provided apple quality and enzymes have optimal conditions. The first pressing step yields a high quality juice and can be regarded as an using product. With the enzymatic treatment the remaining pulp (celluloses, etc.) is liquefied to soluble sugars. The efficiency of this process can be 90–95%, hence only small amounts of solid waste are produced. However, the enzyme is removed in the filtration step and is used only once.

The quality of the apples is an intrinsic variable that can give difficulties. During the year, when apples from storage silos are used, the cellulosic composition of the apples varies. This sometimes has a significant effect on juice quality. By changing the enzyme cocktail, the efficiency of the process can be improved to an acceptable level, but this may require expensive enzymes.

Here an EMR is employed for the clarification and maceration of the juice. In this context, the enzyme is used in multiple cycles. The immobilisation of enzymes on the membrane is also feasible. Some major advantages of this approach are:

1. Less enzyme is used.
2. Better enzymes may be used without *economic runaway*.
3. Less waste may be produced.
4. Maceration and clarification are integrated in one single stage.

The enzyme complex used in this research was Rapidase (Genecor, Belgium). The main effect of enzyme on juice properties is viscosity reduction, as a result of the pectin hydrolysis reaction. In Fig. 3, the viscosity change of apple juice treated for 1 h with Rapidase is illustrated. The juice viscosity reduction in the enzyme membrane reactor allows an increase in the permeate flux. However, permeate flux is a function of membrane configuration and, of course, of operating conditions, which have to be chosen correctly to avoid severe fouling phenomena. Spiral-wound membranes for highly viscous juice might in principle not be advisable, if high permeate fluxes are desired. The performance of tubular membranes seems to be better in terms of permeate flux compared with spiral-wound membranes. New spiral-wound modules, however, with optimal spacers might compete with the tubular configuration.

In the development of the EMR, it is crucial to use membranes which have high retention and high flux characteristics. Therefore, experiments were first performed using a flat cell membrane (membrane area 20–30 cm^2). With this arrangement, influence of membrane type, pressure, cross-flow velocity and spacer type was investigated. Other experiments were performed using polyamide (PA) capillary (3.4×10^{-2} m^2) (Berghoff, Germany) and polysulphone (PS) spiral-wound (25×10^{-2} m^2) (Separem S.p.A., Italy) membranes, at laboratory and semi-pilot scales, respectively. In a second step, a pilot plant was built using spiral-wound modules (Fig. 4). It consisted of a feed tank equipped with a stainless steel spiral for cooling the juice, two spiral-wound membrane modules of 0.5 m^2 each, a prefilter with a mesh of 0.5 mm and a screw pump. A set of experiments was also carried out using a tubular

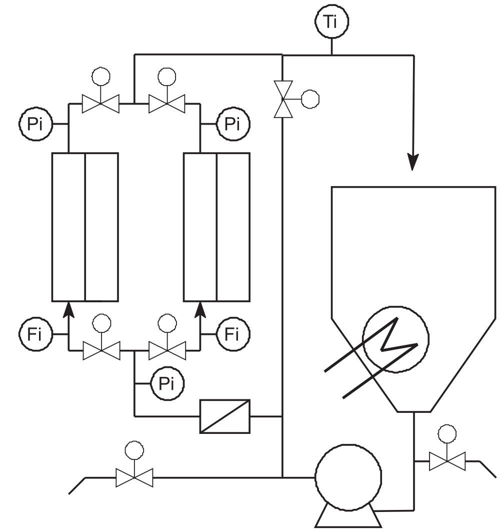


Fig. 4. Schematic of the pilot EMR.

polyvinilidene fluoride (PVDF) membrane of 18 kDa cut-off and 0.23 m^2 membrane area (Koch Membrane Systems, USA). Experiments were performed using pretreated juice (clarification) as well as raw juice (maceration and clarification).

A mathematical model in order to describe the effects of enzymatic reaction, temperature, axial feed velocity and transmembrane pressure on permeate flux of tubular membrane system was developed and validated through comparison of theoretical predictions with experimental results (Todisco, Tallarico & Drioli, 1998).

Figs. 5 and 6 show a comparison between theoretical predictions and experimental data as a function of transient ultrafiltration flux for the tubular PVDF membrane, at Reynolds numbers of 5400 and 11 700, respectively. The model predictions are very close to the experimental values. The only significant deviations were found at the highest Reynolds number. This is due to a change of viscosity with time.

The curves refer to three kinds of experiments in which ultrafiltration of raw apple juice is compared with ultrafiltration of raw juice to which 0.5% enzyme solution was added, and when the juice is pretreated for 1 h using the same enzyme solution before ultrafiltration. From these results it can be concluded that a better performance is obtained when enzymatic juice treatment is performed before ultrafiltration.

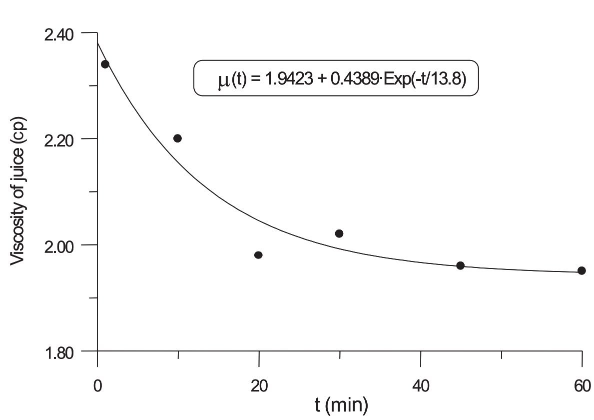


Fig. 3. Time course of viscosity of apple juice treated with 0.5% of Rapidase solution a $T = 25°C$.

3.1.2. Results

In order to keep the enzyme in the circulation loop, a spiral-wound module with a cut-off of at least 20 kDa should be used. A diamond shape type spacer with a thickness of 2.0 mm was employed. The modules were constructed by SEPAREM S.p.A. (Italy). For pretreated juice, the filtration data from the pilot experiments were comparable to those from the at laboratory scale

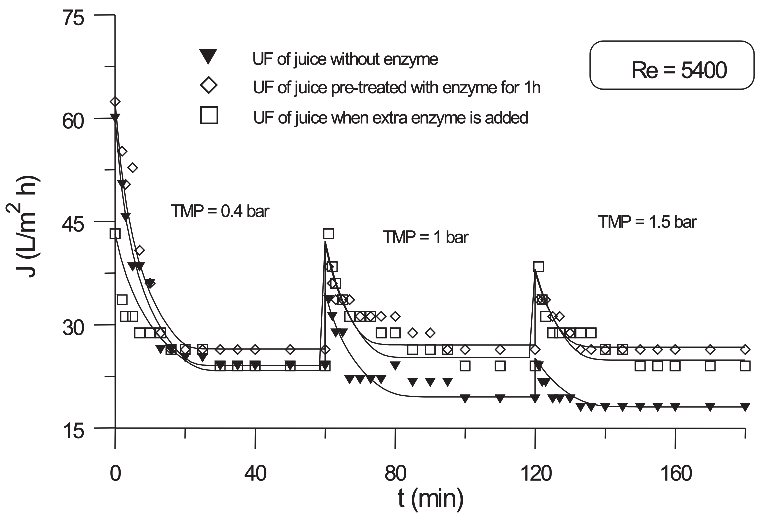


Fig. 5. Comparison between theoretical and experimental results in terms of ultrafiltration flux of apple juice at Reynolds number of 5400 and different values of transmembrane pressure.

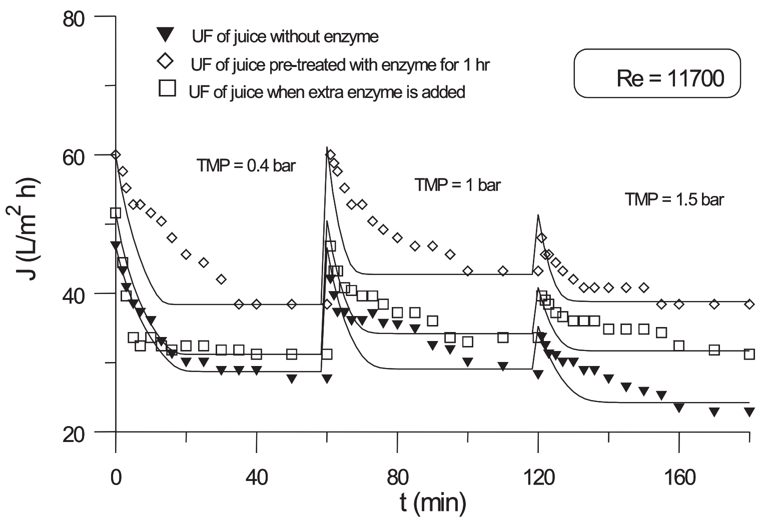


Fig. 6. Comparison between theoretical and experimental results in terms of ultrafiltration flux of apple juice at Reynolds number of 11 700 and different values of transmembrane pressure.

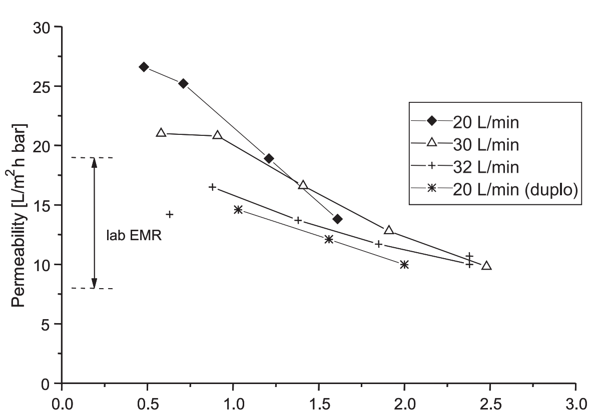


Fig. 7. Performance of the enzymatic membrane reactor using pre-treated juice (the four experiments indicated in the legend are in chronological order).

or slightly better (see Fig. 7). There is an optimal feed pressure with respect to the permeability reached. Pressures higher than 1.5 bar do not result in a higher permeability.

When enzyme is fed to the reactor, the average flux is lowered considerably (flux reductions between 6% and 30% were recorded depending on the feed flow). Apparently the enzyme itself, or products of the enzymatic reaction cause increasing membrane fouling. The influence of the enzyme on the permeate flux in a recycling experiment using capillary and spiral-wound membranes was investigated. The juice was treated with the same amount of enzyme (0.5% v/v) before ultrafiltration. In order to compare their performances, the ratio of steady-state permeate flux over pure water permeate flux (J/J_w) for both membranes was evaluated. The result was that the spiral-wound membranes offer the best performance, being the ratio (J/J_w) 3-fold higher than for capillary membranes. Fig. 8 shows the relation between enzyme and flux observed in a semi-pilot scale experiment; it indicates that increasing fouling can occur when an increasing amount of enzyme was added. For practical batch experiments where the juice is processed as far as possible, Fig. 9 indicates that increasing fouling can occur.

In filtration experiments with 500 l of pretreated juice, the membrane reactor yield decreased considerably. Although cleaning was performed repeatedly, fouling components were difficult to remove. Experiments with raw juice resulted in an extremely fouled membrane. The pressure drop through the module became excessive and fouling could not be removed. This was due to relatively large particles in the raw juice that coagulated throughout the membrane module. However, tubular membranes performed much better with raw apple juice and did not show excessive fouling. In principle, these membranes could be used for combined maceration and clarification of the juice. Also, the use of immobilised enzyme results in a better performance with respect to fouling and cleaning.

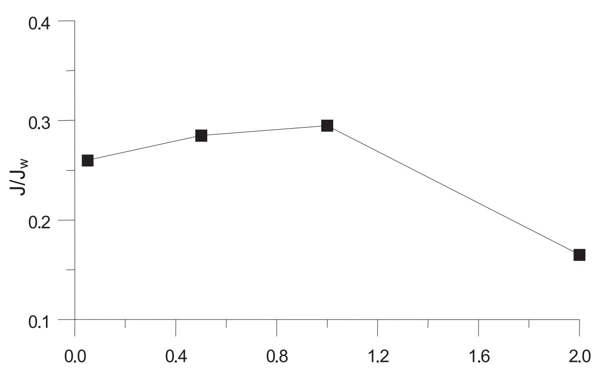


Fig. 8. The influence of enzyme concentration on the performance of the membrane.

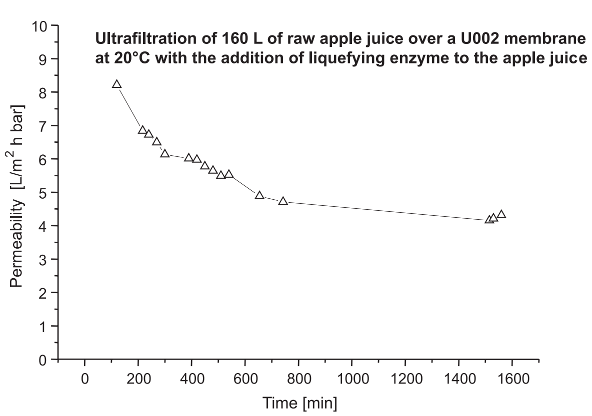


Fig. 9. Flux decrease during a long-term batch experiment (with added enzyme) showing the excessive fouling of the membrane.

3.2. Reverse osmosis to preconcentrate apple juice

Conventional methods, such as evaporation, to concentrate fruit juices require high temperatures and high energy consumption. RO is an alternate membrane process that can be used to preconcentrate fruit juices at ambient temperature. Thus, thermal damage is minimised and lower capital and operating costs may be expected (Sheu & Wiley, 1983; Rao, 1989; Álvarez, Álvarez, Riera & Álvarez, 1997).

However, it is not possible to concentrate apple juice by RO over 30–35°Brix due to the high osmotic pressure of concentrated apple juices. Therefore, a final evaporation step is needed to reach a concentration of 72°Brix. To demonstrate the advantages of the proposed concentration process, a RO pilot unit was designed and constructed by Separem S.p.A.

3.2.1. Materials and methods

3.2.1.1. Apparatus. The pilot RO unit for apple juice concentration is shown in Fig. 10. The pilot plant consists of a feed tank supplied with a heating device, prefilter, centrifugal pump, plate and frame heat exchanger, high-pressure volumetric pump, vessel for housing one RO spiral-wound membrane element and a control board.

3.2.1.2. RO membranes. Several sanitary grade spiral-wound RO membrane modules were developed by Separem S.p.A to preconcentrate the apple juice. The best results were obtained with the membrane unit MSCE 4040 R99. It was consisted of an aromatic PA membrane with total effective area of 6.0 m^2 and a typical NaCl rejection of 99.2% (at a transmembrane pressure of 15 bar, temperature of 25°C and NaCl concentration of 3500 ppm). Maximum operating pressure and temperature allowed by the membrane were 70 bar and 50°C, respectively. This membrane was used for pilot plant tests.

3.2.1.3. Feed solutions. Three different feed solutions were used in all the experiments:

- Conventionally clarified apple juice made of a cultivar of Spanish Granny Smith apples supplied by the apple processing company Valle, Ballina y Fernández, S.A. (VBF S.A.) (Villaviciosa, Spain).
- A solution obtained by diluting the apple juice concentrate produced by VBF S.A. The concentration of the feed solution was 10 ± 0.5°Brix for all of the experiments.
- Apple juice clarified by an EMR previously described.

3.2.1.4. Cleaning solutions. Several cleaning procedures were tested. Alkaline cleaning was carried out with 20 g/l of Sepaclean ALI DT13 ALP (Separem S.p.A) alkaline

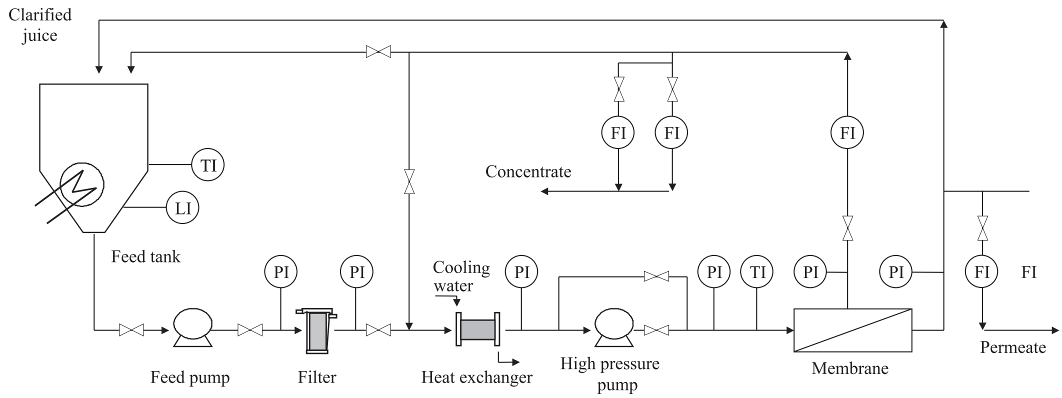


Fig. 10. The RO pilot unit.

detergent for 2 h at temperatures between 35°C and 40°C. Acid cleaning was performed with Ultrasil 75 (Henkel, USA) for 40 min at temperatures below 25°C. Enzymatic cleaning with SUCCOZYM commercial enzyme product (Essenco S.p.A., Italy) was also tried.

3.2.1.5. Analysis. Salt rejection was measured by conductivity. Apple juice concentration was measured with a hand-hold refractometer (Shibuya Optical, Japan) and expressed as °Brix. Rejection of apple juice aroma compounds was also determined in some of the experiments. Analysis of the main identified aroma compounds was carried out on permeate, retentate and feed solutions by gas chromatography, following the procedure described in Álvarez, Riera, Álvarez & Coca (1998).

3.2.1.6. Experimental procedure. Operating parameters were previously optimised at laboratory scale: pressure 70 bar, temperature 25°C, axial flow rate 4000 l/h, recovery 55%. The RO pilot unit was tested (both operative parameters and cleaning regime) with conventionally depectinised apple juice feed. The RO pilot unit was then integrated with the EMR and the evaporator units into a Demonstration Pilot Plant in order to simulate continuous operation on real "in plant" conditions. It was operated for three weeks at the production plant of the VBF S.A. with a feed of raw apple juice. The parameters selected to test the performance of the RO unit were: permeate flow, concentration of apple juice measured as °Brix, and retention of aroma compounds. Additionally, an organoleptical evaluation of the streams was performed.

The efficiency of the cleaning method was ascertained by checking the water flux and NaCl rejection of a 1 g/l NaCl solution at 15 bar and 25°C.

3.2.2. Testing of process parameters

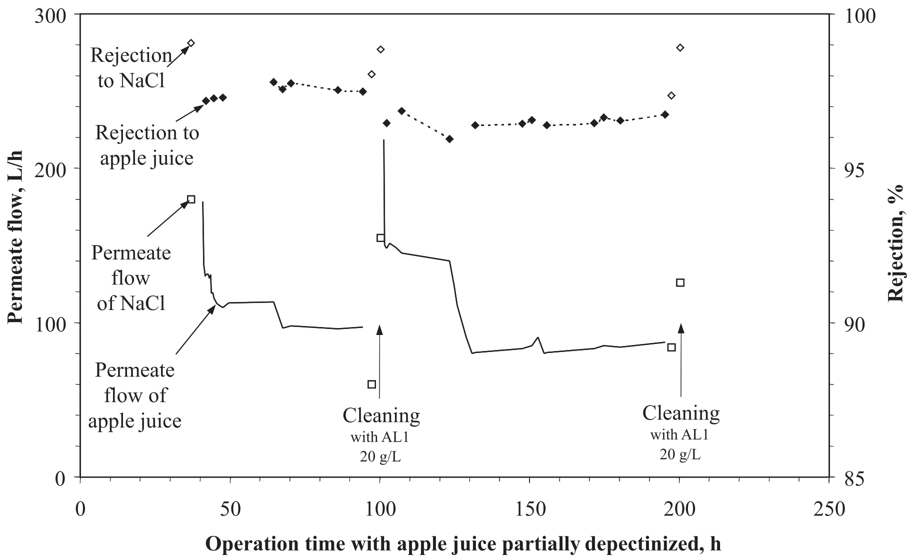
The previously optimised process parameters of the RO system were tested using the RO pilot plant in two experiments. The operational parameters were kept constant: pressure 70 bar, temperature 25°C, axial flow rate 4000 l/h, recovery 55%. After the tests with apple juice, the spiral-wound membrane module was rinsed, the standard characterisation with NaCl was carried out, and was cleaned with the selected cleaning procedure (alkaline cleaning). Fig. 11 shows permeate flows and rejections as a function of the operation time. Fig. 12 shows rejections (measured as rejection to conductivity) and permeate flow during the test.

The aim of the Project for the RO unit was to reach 25°Brix soluble solids concentration in the concentrate stream and 50 l/h of permeate flow. These conditions were reached with a permeate flow of 90 l/h.

Cleaning of the membrane with the SUCCOZYM commercial enzyme cocktail did not prove to be more efficient than cleaning with alkaline detergent SEPA-CLEAN AL1. The original permeate flux and rejection values of the new element could not be reached with alkaline cleaning, but the permeate flux and rejection of the membrane element could be kept constant when the selected cleaning procedure was used.

3.2.3. Demonstration run of pilot unit on real "in-plant" conditions

Initial tests of the RO pilot unit were carried out with the diluted solution of apple juice concentrate. The RO unit was operated for three weeks in a way such that after the concentration of about 350 l of juice (about 130 min), the feed solution was recycled above the membrane surface until the next concentration run (which was performed on the following day). In this way, the membrane element was operated continuously with apple juice feed for one week, and then it was cleaned and characterised with NaCl solution. Feed solutions were changed daily to avoid spoiling of the juice. Once the UF permeate of the EMR process reached a volume of 500 l, the feed to the RO unit was changed into the UF permeate, and the product of the EMR unit was con-



Effluent:	apple juice	NaCl 1000 ppm
Pressure:	70 bar	15 bar
Temperature:	25 °C	25 °C
Permeate recovery	55 %	10 %

Fig. 11. Permeate flow rate and rejection as function of the operation time.

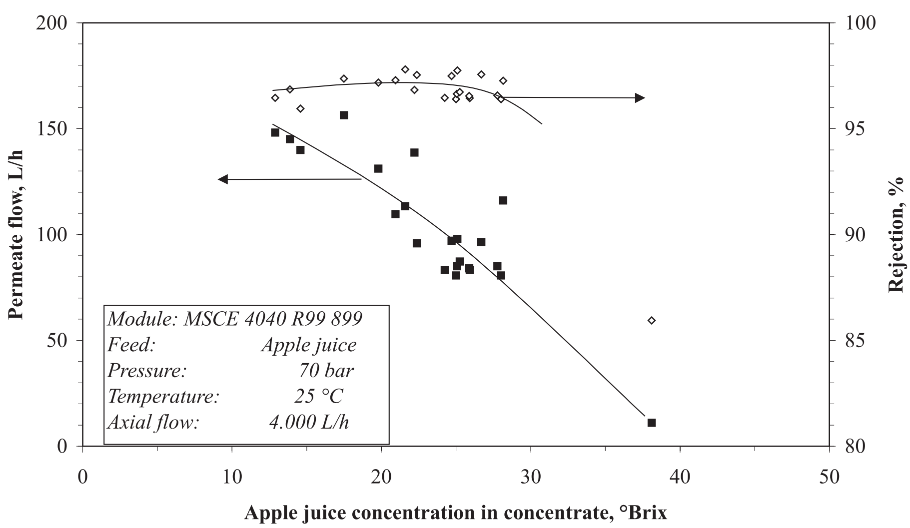


Fig. 12. Permeate flow rate and rejection as function of the soluble solids content of concentrate.

centrated by the RO unit. The organoleptic evaluation was carried out with streams from this run.

The membrane was cleaned with 20 g/l SEPACLEAN AL1 alkaline detergent for 1 h before starting the apple juice test, then it was rinsed and characterised with 1 g/l NaCl. The concentration was carried out at 70 bar, 25°C and 4000 l/h feed flow. Additional cleanings were also carried out with ULTRASIL 75 acid detergent. The permeate flow and rejection of NaCl and apple juice during the three-week run are shown in Fig. 13.

The concentration of apple juice in the concentrate was kept between 25.5 and 26.6°Brix, with a permeate flow between 75 and 110 l/h. The aim of this part of the project was totally fulfiled: treated apple juice at a flow of 50–100 l/h and concentration of apple juice in concentrate higher than 25°Brix.

Aroma compounds concentrations were determined in the feed, permeate and retentate streams when treating the EMR permeate. Rejection (R) was calculated using the following expression:

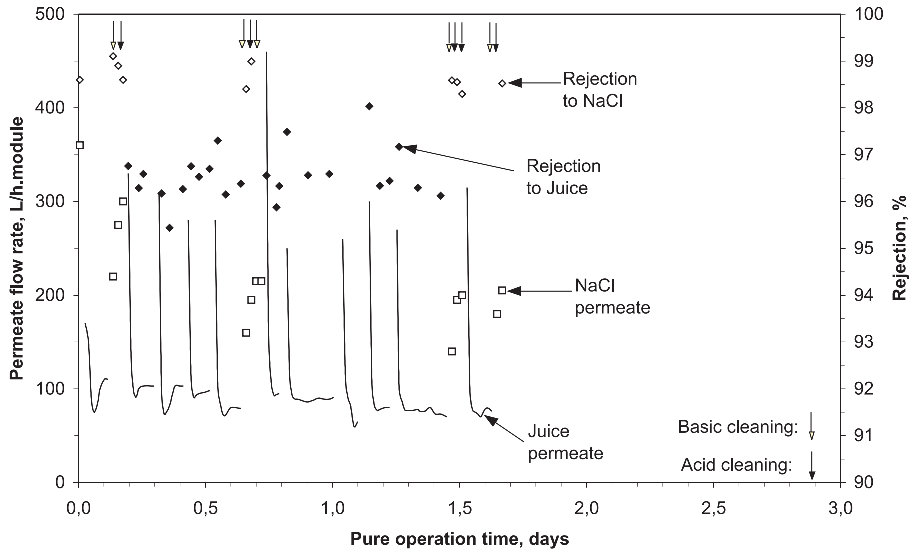


Fig. 13. Results of test of RO pilot unit on real in-plant conditions.

$$R = \left[1 - \frac{C_P}{(C_F + C_C)/2}\right] \times 100, \quad (1)$$

where C_F, C_P and C_C are the concentrations of the aroma compounds in the feed, permeate and concentrate streams, respectively. Three of the reference aroma compounds (isoamyl acetate, hexyl acetate and isoamyl alcohol) were not detected in any of the streams. Fig. 14 shows the results obtained.

It can be observed that rejection is high for all of the compounds except for ethyl acetate.

Permeate flow and NaCl rejection did not reach the initial values (360 l/h and 98.6%, respectively), even in the case of subsequent *alkaline-acid-alkaline* cleaning, which was considered to be the most efficient cleaning sequence after testing. However, the permeate flux and apple juice rejection did not decrease significantly after three weeks of continuous operation with apple juice.

3.3. Pervaporative aroma recovery

Aroma compounds are very sensitive to heat treatment. During conventional apple juice concentration, both physical and chemical losses of aroma compounds occur to a great extent, as a result of evaporation and chemical alteration. This leads to a decreased quality of the final product. By introducing PV to the integrated process, the aroma compounds could be removed from the apple juice prior to evaporation and fed back later to the concentrated juice, resulting in an improved organoleptic quality.

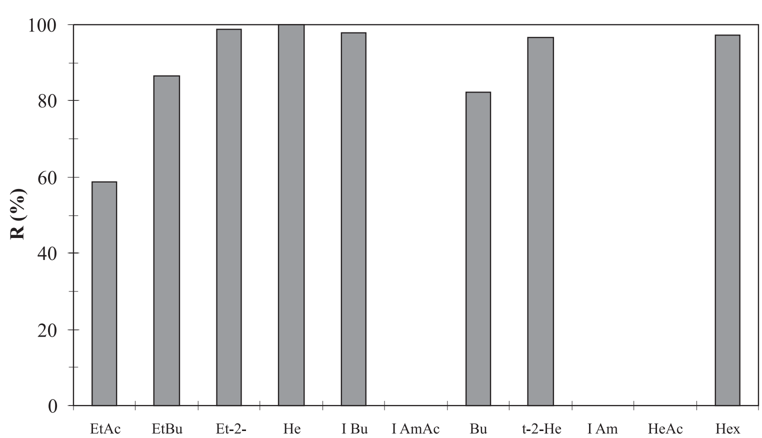


Fig. 14. Rejection of aroma compounds during the RO pilot plant experiments. Notation: EtAc – ethyl acetate; EtBu – ethyl butanoate; Et-2-MeBu – ethyl-2-methyl butanoate; He – hexanal; I Bu – isobutanol; I AmAc – isoamyl acetate; Bu – butanol; *t*-2-He – *trans*-2-hexenal; I Am – isoamyl alcohol; HeAc – hexyl acetate; Hex – hexanol (TMP: 70 bar; *T*: 25°C; feed flow: 4000 l/h).

One aim of the project was to characterise the juice by identification of aroma compounds and to develop a model solution of apple juice aromas on the basis of the identification. This model solution could then be used for the screening of commercially available membranes in terms of separation, mass transfer properties, etc. (Börjesson, Karlsson & Trägårdh, 1996). Another aim was to study the influence of process conditions, i.e. feed flow velocity (Olsson & Trägårdh, 1999a), feed temperature (Olsson & Trägårdh, 1999b) and permeate pressure (Olsson & Trägårdh, 1999c), on selectivities and mass transfer properties for subsequent optimisation purposes. Fouling and cleaning aspects were also to be considered. Furthermore, results should be verified with experiments performed with apple juice.

3.3.1. Pervaporation

Pervaporation is a membrane technique in which a liquid feed mixture is separated by means of partial vaporisation through a non-porous permselective membrane. The driving force for mass transfer in the process is accomplished by applying a difference in partial pressures of the solutes, the aroma compounds in this case, across the membrane. In vacuum PV, the driving force is achieved through reduction of the total pressure at the permeate side of the membrane. The permeate is then collected by condensation. The resistance to mass transfer from the bulk of the feed to the bulk of the permeate can be split into several consecutive steps: diffusion through the liquid feed boundary layer from the bulk of the feed to the feed side of the membrane, adsorption into the membrane, diffusion through the membrane, desorption into the vapour phase at the permeate side of the membrane and diffusion to the bulk of the permeate. Resistance to mass transfer in the last step is commonly assumed to be negligible because of the low total permeate pressure. The assumption that the fluxes through each of the steps are equal yields

$$\frac{1}{k_{\mathrm{ov},i}} = \frac{1}{k_{\mathrm{bl},i}} + \frac{1}{k_{\mathrm{m},i}}, \tag{2}$$

where $k_{\mathrm{ov},i}$ is the overall mass transfer coefficient, $k_{\mathrm{bl},i}$ the mass transfer coefficient of the feed boundary layer and $k_{\mathrm{m},i}$ is the mass transfer coefficient of the membrane, which includes adsorption to, diffusion through and desorption from the membrane. Another important property is selectivity. The intrinsic enrichment factor for component i, $\beta_{\mathrm{int},i}$, is defined as

$$\beta_{\mathrm{int},i} = \frac{c_{\mathrm{p},i}}{c_{\mathrm{fm},i}}, \tag{3}$$

where $c_{\mathrm{fm},i}$ is the concentration of component i in at the feed side of the membrane and $c_{\mathrm{p},i}$ the concentration of component i in the permeate. It represents a measure of the selectivity of the whole process. Due to concentration polarisation at the feed boundary layer, the concentrations of aroma compounds are lower near the feed side of the membrane than in the bulk of the feed solution, and the apparent selectivity could be considerably lower.

3.3.2. Experimental

3.3.2.1. Apparatus. The experimental setup is shown in Fig. 15. Two different plate-and-frame modules were used (Börjesson et al., 1996; Olsson & Trägårdh, 1999a). The module especially designed for high-*Re* numbers was used for membrane screening tests. In the first part, the velocity profile is developed. The second part contains the membrane. The retentate was recirculated to the temperature-controlled feed vessel. Vacuum was achieved with a vacuum pump, which also served to separate inert gases from the permeate.

3.3.2.2. Material. Pervaporation membranes. Six different membranes were used: two poly-octylmethylsiloxane membranes with different porous support layers, POMS-PEI and POMS-PVDF (GKSS Forschungzentrum), three polydimethylsiloxane membranes, PDMS-1060 and PDMS-1070 (Deutsche Carbone AG,

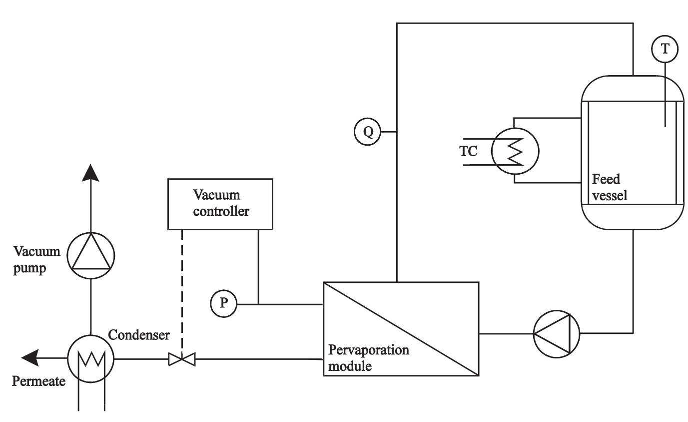


Fig. 15. The PV apparatus.

Membrantrennverfahren GFT) and PT1100 (Hoechst Celanese), and one polyether-block-polyamide membrane, PEBA (GKSS Forschungzentrum). The PDMS-1070 membrane contained well-defined regions of silicalite to increase the selectivity for alcohols.

Feed solutions. Three experimental feed solutions were used:

- A model solution of apple juice aroma compounds, containing 10 selected aroma compounds, each at a concentration of 10 ppm in Milli-Q water. The aroma compounds chosen were four alcohols (isobutanol, butanol, isoamyl alcohol and hexanol), one aldehyde (*trans*-2-hexenal), and five esters (ethyl acetate, ethyl butanoate, ethyl-2-methyl butanoate, isoamyl acetate and hexyl acetate).
- Clarified and depectinised apple juice made from a cultivar of Spanish Granny Smith apples.
- Clarified and depectinised apple juice made from a cultivar of Spanish Granny Smith apples with a standard addition of aroma compounds. This standard addition corresponded to an increase of 10 ppm of each of the aroma compounds present in the model solution.

Cleaning solutions. Alkaline cleaning solutions, a 2% solution of SEPACLEAN AL1 DT13 (Separem S.p.A.) dissolved in deionised water, and a 1% solution of Divos 100 (Diversey AB) were used.

3.3.2.3. Analysis. As PV of natural apple juice would involve significant analytical problems, a model solution of apple juice aroma compounds was developed based on identification of aroma compounds in the apple juice by gas chromatography (GC) and gas chromatography coupled to a mass spectrometer (GC–MS). The concentrations of aroma compounds in the bulk of the feed and in the permeate, respectively, could then be monitored by GC. The method is described in (Börjesson et al., 1996). For experiments were performed with natural apple juice, this analysis could only be carried out on the permeate. The total flux was determined gravimetrically.

3.3.2.4. Experimental procedure. After conditioning, and when the feed temperature was deemed to be stable and mass transfer equilibria established , permeate was collected. For experiments conducted with apple juice, cleaning was performed after each experiment. The equipment was rinsed with deionised water and then cleaned either with the Sepaclean solution for 2 h at 40°C or with the Divos solution for 1 h at 60°C. Deionised water was used for the final rinse.

3.3.3. Membrane performance

Four of the membranes studied, i.e. PDMS-1060, PDMS-PT1100, POMS-PEI and POMS-PVDF, proved to perform well for this application, resulting in 100-fold to 1000-fold enrichment of aroma compounds from the model solution with mass transfer coefficients up to 300 kg/m^2 h. By comparison of the performance of these membranes, it was concluded that the recovery of aroma compounds from apple juice using the PDMS-1060 membrane was the least effective. POMS membranes require a larger membrane area than PDMS-PT1100 to recover the same amount of aroma compounds from apple juice. However, the POMS-PVDF membrane and especially the PDMS-PT1100 membrane would require a more expensive downstream process due to the larger amount of water that has to be condensed. The other two membranes, i.e. the PDMS-1070 and the PEBA membranes, were not suitable for this application due to instability or poor mass transfer properties.

For the POMS membranes and the PDMS-PT1100 membrane, the validity of these results was studied in the subsequent experiments, performed with apple juice. The POMS membranes yielded comparable permeate concentrations, i.e. comparable selectivities, whereas the PDMS-PT1100 membrane yielded permeate concentrations about half as high as the POMS membranes. When comparing the aroma fluxes, the POMS-PVDF and the PDMS-PT1100 membranes yielded comparable results, while the POMS-PEI membrane produced about 30–50% lower aroma fluxes, indicating poorer mass transfer properties of the aroma compounds. It could also be concluded that for the PDMS-PT1100 membrane the water flux was higher than twice the value obtained for the POMS membranes. All results were in good agreement with previous results using the model solution. Thus, it seems possible to predict the process behaviour for apple juice PV, if results with the model solution are available.

Total fluxes before, during and after the experiments performed with apple juice, did not change significantly (Table 3). It was evident that the juice did not cause any major fouling problems for these membranes under these process conditions, i.e. at 20°C, *Re* 11 000 and 2 mbar. After 24 h of PV, using the PDMS-PT1100 membrane, the total flux still remained constant.

3.3.4. Operation parameters

Additional experiments with the model solution were performed to study the influence of operation parameters, such as feed temperature, feed flow velocity and permeate pressure. All of these parameters proved to considerably affect the performance of the PV process, altering both mass transfer rates and overall selectivities of the aroma compounds.

Based on these results, additional experiments were performed with apple juice as well as with apple juice to which aroma compounds had been added, using the PDMS-1060 membrane at real "in plant" conditions. At 30°C, *Re* 500 and 7 mbar, the total flux was 100 g/m^2 h.

To estimate the overall selectivities and the overall mass transfer rates of the components, the permeate

Table 3
The total flux obtained from experiments performed with apple juice, for three different membranes, at 20°C, *Re* 11 000 and 2 mbar

Membrane	Total flux before exp. (g/m^2 h)	Total flux during exp. (g/m^2h)	Total flux after exp. (g/m^2 h)
POMS-PEI	43	42	41
POMS-PVDF	68	67	68
PDMS-PT1100	150	140	140

concentrations, which measure the overall selectivities, and the aroma fluxes, which measure the overall mass transfer rates, were determined with juice to which a standard addition had been made at 20°C, *Re* 500 and 7 mbar (Fig. 16). Permeate concentrations and overall fluxes of the components obtained from experiments performed with apple juice with the standard addition of aroma compounds were in the same range as the corresponding values obtained from experiments performed with the model solution.

As shown in Table 4, total fluxes for the POMS–PEI and the PDMS-1060 membranes were not significantly affected when the feed solution was changed. It was also noted that cleaning did not significantly affect the performance of these membranes.

3.4. Analytical characterisation of the streams obtained from the pilot unit on real in plant conditions

3.4.1. Materials and methods

The parameters chosen to carry out the analytical characterisation of the streams were the following:

- *Density*: measured with a digital densimeter (Anton Paar, Austria).
- *Colour*: determined as the absorbance at 420 nm using a Philips UV/Vis spectrophotometer (England).
- *Turbidity*: determined by means of a ratio turbidimeter (Hach, USA) and expressed as Nephelometric Turbidity Units (NTU).
- *Viscosity*: measured with a Cannon–Fenske capillary viscosimeter at 25°C (Afora, Spain).
- *pH*: measured using a Crison pHmeter (Crison, Spain).
- *Total acidity*: determined by titration with 1 N NaOH up to pH 8.3. The result was expressed as malic acid %. An automatic titrator from Crison (Spain) was used.
- *Soluble solids content*: measured with a refractometer and expressed as Brix degrees.
- *Total phenolic compounds*: The Singleton method was used as described in Singleton and Rossi, 1965.
- *Pectin content*: The concentration of pectin in the samples was quantified by precipitation with ethanol and using the *m*-hydroxydiphenol method as described in Blumenkrantz and Asboe-Hansen, 1973.
- *Organoleptic evaluation*: It was carried out by a panel of experts from the company VBF S.A.

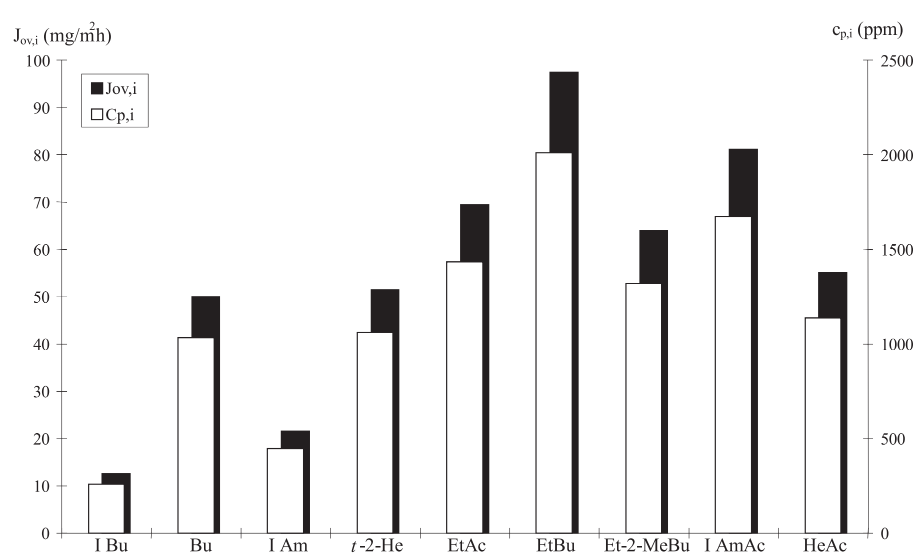


Fig. 16. The permeate concentrations, $C_{p,i}$, and the overall flux, $J_{ov,i}$, for different aroma compounds, *i*, obtained from an experiment performed with the clarified and depectinised apple juice (PDMS-1060 at 20°C, Re 500 and 7 mbar). Notation: I Bu – isobutanol; Bu – butanol; I Am – isoamyl alcohol; *t*-2-He – *trans*-2-hexenal; EtAc – ethyl acetate; EtBu – ethyl butanoate; Et-2-MeBu – ethyl-2-methyl butanoate; I AmAc – isoamyl acetate; HeAc – hexyl acetate.

Table 4
The total fluxes obtained from experiments performed with two different membranes at 20°C, *Re* 320 for the POMS-PEI membrane and *Re* 420 for the PDMS-1060 membrane and <1 mbar

Feed solution	Total flux (g/m^2 h)	
	POMS-PEI	PDMS-1060
Milli-Q water (before exp.)	–	69
Milli-Q water (before exp.)	–	69
Model solution	58	69
Model solution	59	72
Apple juice + standard addition of aroma compounds	57	65
Apple juice + standard addition of aroma compounds	57	67
Milli-Q water (after cleaning with Sepaclean)	54	71

3.4.2. Results

First of all, the performance of the EMR was checked in terms of the quality of the clarified apple juice obtained. The key parameter that quantifies the degree of clarification of the apple juice is turbidity. The aim was to produce an apple juice of less than 0.3 NTU. Table 5 shows the analytical characterisation of the raw apple juice and of clarified juice obtained from the EMR.

When comparing the EMR permeate with the raw apple juice, it can be observed that the density and pH of both juices were practically the same, while the viscosity was reduced due to the enzymatic treatment and the UF process. A high decrease in colour and turbidity was observed. Turbidity of the clarified juices ranged between 0.2 and 0.6 NTU, the turbidity of most of the samples being lower than 0.3 NTU. These results were considered to be excellent by the apple processing company. It could be also observed that soluble solids content decreased from 9.8°Brix for the raw apple juice to 9.2°Brix, for the clarified juice. This fact means that part of the soluble solids was retained by the membrane. Total acidity and total phenolic compounds content also decreased during the process.

Several samples of conventionally clarified apple juice were also analysed. It should be pointed out that the turbidity of the EMR permeate was much lower than that of the conventionally clarified juice (7.8 NTU).

The RO preconcentration process was evaluated in terms of aroma compounds rejection. As shown in Fig. 14, rejection was over 90% for most of the aroma compounds considered. Almost 100% rejection of sugars, acids and phenolic compounds was recorded.

Finally, an organoleptic evaluation of the EMR permeate, the 25°Brix RO preconcentrated juice and the RO preconcentrate diluted to 10°Brix was carried out. Results are shown in Table 6. All of the juices were of very good quality, regarding odour and flavour. However, experts noticed a rather light green colour in the three products, which could be due to the variety of apples used, as the green colour was not found in any of the experiments carried out before the integration of the pilot units. These products were much clearer and more brilliant than the apple juice produced by conventional methods. Furthermore, no differences were found between the EMR permeate and the RO preconcentrated juice diluted to 10°Brix. It can therefore be concluded that the quality of the apple juice produced by the novel integrated membrane process was very satisfactory.

Table 5
Analytical characterisation of raw juice and UF permeate

Parameter	Raw juice	UF permeate
Density	1.043 g/l	1.043 g/l
Colour (420 nm)	>3	0.390
Turbidity	1 242 NTU	0.2–0.6 NTU
Total acidity	0.489% malic acid	0.329% malic acid
pH	3.73	3.71
Soluble solids	9.82°Brix	9.2°Brix
Total phenolic compounds	773 ppm tannic acid	206 ppm tannic acid
Pectins	–	<5 ppm
Viscosity (25°C)	2.277 cp	1.1621 cp

Table 6
Organoleptic evaluation of the products

Parameter	EMR permeate (9.2°Brix)	RO preconcent. (26.8°Brix)	RO preconcent. diluted to 10°Brix
Colour	A bit modified slight green colour	Green colour persisted	Green colour persisted
Odour	Very good	Very good	Very good
Flavour	Very good	Very good	Very good

4. Comparison between conventional methods and the integrated membrane process: an economic evaluation

As previously mentioned, the process proposed in this work yields very high quality apple juice and aroma concentrates.

In this section, both the conventional and the new processes for producing apple juice and aroma concentrates are compared on the basis of economics. Process design basis was to produce 2500 kg of apple juice per hour. Taking into account the periods when apples are available, 3500 tons of apple juice concentrate would be produced annually in these plants. Table 7 summarises investment and operating costs for both processes. Information on equipment costs, raw material costs and selling price of the product were made available by the company VBF S.A. Membrane cost was supplied by Separem S.p.A. Total capital investment and total operating costs were estimated as suggested by Peters and Timmerhaus (1991) with the assessment of the VBF S.A.

As shown in Table 7, the total capital investment of the new integrated membrane process accounts for 14% less than the capital investment of the conventional process.

Regarding the manufacturing costs associated with both processes, it can be noticed that apple consumption decreases by 5% when using the integrated membrane technology. This fact is due to the corresponding increase in process yield. Membrane replacement only represents 2% of operating costs. Membrane life was estimated to be 2, 3 and 2 year for UF, RO and PV membranes, respectively. Total manufacturing costs decreased by 8% when concentrating the apple juice using the technology proposed in this work, mainly because less energy is required to concentrate the juice.

A profitability analysis, shown in Table 8, has also been carried out. It shows that the integrated membrane process has a higher profitability than the conventional one. Net profit and return on investment were estimated to be about 16% and 34% higher than conventional ones, respectively.

Taking into account the approximations made for the economical evaluation, it can be stated that both processes are more or less similar in terms of economics, being the membrane process proposed in this research even slightly more profitable.

5. Conclusions

A membrane reactor can be used for the production of clarified apple juice with lower enzyme costs. The

Table 7
Capital investment and manufacturing costs for the conventional and integrated membrane processes

Item	Cost (ECU)	
	Conventional process	Membrane process
Investment		
Apples storage	1.7×10^5	1.7×10^5
Washing and inspecting apples	0.1×10^5	0.1×10^5
Milling apples	0.4×10^5	0.4×10^5
Clarification	6.4×10^5	3.9×10^5
Preconcentration (RO)		1.3×10^5
Aroma compounds recovery and apple juice concentration	4.2×10^5	5.1×10^5
Total	13.73×10^5	12.48×10^5
Total capital investment	47.72×10^5	43.38×10^5
Operating costs		
Raw material (apples)	810.0 ECU/ton conc.	770.0 ECU/t conc.
Membranes		19.7 ECU/t conc.
Others	99.9 ECU/ton conc.	50.2 ECU/t conc
Total variable cost	909.9 ECU/ton conc.	839.9 ECU/ton conc.
Labour, maintenance and other fixed costs	151.9 ECU/ton conc.	145.0 ECU/ton conc.
Total manufacturing costs	1061.8 ECU/ton conc.	984.9 ECU/ton conc.

Table 8
Profitability analysis for the conventional and integrated membrane processes[a]

	Conventional process	Membrane process
(a) Revenue (ECU/year)	5.469×10^6	5.469×10^6
(b) Annual manufacture cost (ECU/year)	3.716×10^6	3.432×10^6
(c) Gross profit (a – b) (ECU/year)	1.753×10^6	2.037×10^6
(d) Taxes (33%) (ECU/year)	0.578×10^6	0.672×10^6
(e) Net profit (ECU/year)	1.175×10^6	1.365×10^6
(f) Gross margin (c/a)	0.32	0.37
(g) Return on investment $\left(\frac{\text{Net profit}}{\text{Total investment}} \times 100\right)$	24.6%	33.0%
(h) Payback time $\left(\frac{\text{Total investment}}{\text{Net profit}}\right)$	4.1 years	3.0 years

influence of rapidase concentration on EMRs efficiency has been investigated using free and immobilised systems. Results of experiments, carried out on lab and semi-pilot scales, showed that to obtain a better permeate flux, it is advisable to operate with immobilised enzyme and using an initial enzyme percentage of 0.5 (v/v). There is thus an optimal enzyme concentration that should be used in such a reactor. Fouling can be severe, especially in spiral-wound membrane modules, what is not prohibitive for the process.

A RO unit can be used to preconcentrate the previously clarified apple juice. The process goals for the RO unit were to reach 25°Brix soluble solids concentration at 50–100 l/h permeate flow. The objectives of economic operation were completely fulfiled during the testing of selected operation parameters, and also during the on-site tests of the Integrated Pilot Plant. Permeate flow between 75 and 110 l/h and concentrations of apple juice between 25.5 and 26.6°Brix were obtained. Permeate flow and NaCl rejection did not reach the values of the new membrane even in the case of subsequent *alkaline-acid-alkaline* cleaning (which was the most effective cleaning sequence), but the permeate flux and rejection did not decrease significantly after three weeks of continuous operation with apple juice. Rejection of aroma compounds exceeded 90% for most of the compounds considered.

PV was found to be well suited for aroma recovery from apple juice. High overall enrichment factors in the range 100–1000 and overall mass transfer coefficients in the range 5–500 kg/m^2 h were obtained. All process parameters studied, i.e. feed temperature, feed flow velocity and permeate pressure, considerably influenced the process performance. The results emphasise the importance of short residence times at elevated temperatures in the whole integrated process, in order to limit the loss of volatile aroma compounds. Fouling did not give rise to any detectable problems and cleaning did not significantly affect the performance of the membranes.

Organoleptic evaluation of the clarified and preconcentrated apple juices was excellent in terms of odour and flavour. The products were clearer and more brilliant than the apple juice produced by conventional methods.

The integrated membrane process shows also comparable or slightly higher profitability than the conventional process.

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References

Álvarez, S., Riera, F. A., Álvarez, R., & Coca, J. (1998). Permeation of apple aroma compounds in reverse osmosis. *Separation and Purification Technology*, *14*, 209–220.

Álvarez, V., Álvarez, S., Riera, F. A., & Álvarez, R. (1997). Permeate flux prediction in apple juice concentration by reverse osmosis. *Journal of Membrane Science*, *127*, 25–34.

Blumenkrantz, N., & Asboe-Hansen, G. (1973). A new method for quantitative determination of uronic acids. *Analytical Biology*, *54*, 484.

Börjesson, J., Karlsson, H. O. E., & Trägårdh, G. (1996). Pervaporation of a model apple juice aroma solution: comparison of membrane performance. *Journal of Membrane Science*, *119*, 229–239.

Dimick, P. S., & Hoskin, J. C. (1981). Review of apple flavour – state of the art. *CRC Critical Review in Food Science and Nutrition*, *18*, 387–409.

Kilara, A., & Van Buren, J. P. (1989). Clarification of apple juice. In D. L. Downing, *Processed apple products* (pp. 54–76). New York: Van Nostrand Reinhold.

Lea, A. G. J. (1990). Apple juice. In D. Hicks, *Production and packaging of noncarbonated fruit juices and fruit beverages* (pp. 182–225). New York: Blackie and Son.

Lee, C. Y., & Mattick, L. R. (1989). Composition and nutritive value of apple products. In D. L. Downing, *Processed apple products* (pp. 303–322). New York: Van Nostrand Reinhold.

Morton, I. D. (1990). The flavour of fruits. In I. D. Morton, & A. J. Macleod, *Food flavours*, *part C* (pp. 1–41). Amsterdam: Elsevier.

Olsson, J., & Trägårdh, G. (1999a). Influence of feed flow velocity on pervaporative aroma recovery from a model solution of apple juice aroma compounds. *Journal of Food Engineering*, *39* (1), 107–115.

Olsson, J., & Trägårdh, G. (1999b). Influence of temperature on membrane permeability during prevaporative aroma recovery. *Separation Science and Technology*, 34 (8), 1643–1659.

Olsson, J., & Trägårdh, G. (1999c). Predictions of the influence of permeate pressure on selectivity during pervaporation of volatile orgainc compounds from water. Submitted.

Peters, M. S., & Timmerhaus, K.D. (eds.) (1991). Plant design and economics for chemical engineers. McGraw Hill, Singapore, Malaysia.

Rao, M. A. (1989). Concentration of apple juice. In D. L. Downing, *Processed apple products* (pp. 137–168). New York: Van Nostrand Reinhold.

Root, W. H. (1996). Apples and apple processing. In L. P. Somogyi, D. M. Barret, & Y. H. Hui, *Processing fruits: science and technology, vol. II* (pp. 1–35). Lancaster: Technomic.

Sheu, M. J., & Wiley, R. C. (1983). Preconcentration of apple juice by reverse osmosis. *Journal of Food Science*, *48*, 422–429.

Simpson, R. F. (1979). Some important aroma components of white wine. *Food Technology*, *31*, 516–522.

Singleton, V. L., & Rossi, J. A. (1965). Colorimetry of total phenolics with phosphomolydic phosphotungstatic acid reagents. *American Journal of Enology and Viticulture*, *16*, 144.

Stacy, J. D. (1988). The new growth era for fruit juices. *Beverage World*, *7*, 33–37.

Todisco, S., Tallarico, P., & Drioli, E. (1998). Modelling and analysis of the effects of ultrafiltration on the quality of freshly squeezed orange juice. *Italian Food and Beverage Technology*, *12*, 3–8.