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Concentration of osmotic dehydration solutions using membrane separation processes

Memoria presentada por
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SYMBOLS AND ABBREVIATIONS

SYMBOLS

ρ_P – permeate density [g/l];

A_m – membrane area [m^2];

a_w – water activity;

C_b – stripping solution concentration in the bulk [mol/dm^3];

CD – concentration degree;

C_{FR} – final sugar concentration in the retentate [ºBrix];

c_i – solute concentration in the pore [mol/m^3];

C_{IR} – initial sugar concentration in the retentate [ºBrix];

C_m – stripping solution concentration in the membrane [mol/dm^3];

C_p – concentration of permeate [ºBrix];

C_R – concentration of retentate (feed) [ºBrix];

d_h – hydraulic diameter [m];

$D_{i,p}$ – hindered diffusivity [m^2/s];

d_p – pore diameter [m];

D_S^M – diffusion coefficient of solute by the membrane [m^2/s];

D_w – diffusion coefficient in water [m^2/s];

h_F, h_{SS} and h_M – are the heat transfer coefficients of the boundary layers (feed and stripping solution, respectively) and the membrane [W/m^2K];

J – permeate flux [l/m^2h or kg/m^2h];

j_i – solute flux [kg/m^2h];

J_M – molar vapour flux [mol/m^2s];

J_v- volume flux [m^3/m^2s],

k – mass transfer coefficient [m/s];

k_B – Boltzman constant [1.3807×10^{-23} J/K];

K_F, K_M, K_{SS} – mass transfer resistance at feed layer, membrane and stripping solution, respectively [kg/m^2sPa];

$K_{i,c}$ – hindrance factor for convection;

m_{fin} - final sample weight [g];

m_{ini} - initial sample weight [g];

m_P – permeate mass [g];

m_{sfin} - mass solids after osmosis [g];

m_{sin} - mass solids before osmosis [g];

N – cross-flow velocity [m/s];

P_{Alm} – is the logarithmic mean pressure of the air within the pores [Pa],

p_{food} – water vapour in any kind of food [Pa];

p_{water} – water vapour pressure of pure water [Pa];

P_{wF} – water vapour pressure at the feed side [Pa],

P_{wSS} – water vapour pressure at the sit stripping solution side [Pa]

R – sugar retention [%];

SG - solid gain [%];

T_F and T_{SS} – are the bulk temperatures of the feed and stripping solution, respectively [K];

T_{FM} and T_{SSM} – are the temperatures of the feed and the stripping solution near the membrane [K];

V- the solute velocity [m/s];

WL -water loss [%];

WR - weight reduction [%];

α, β, γ – constants of Sh number;

δ –membrane thickness [m];

ε – membrane porosity [%];

λ – latent heat of vaporisation [W/m^2K];

μ – viscosity of the liquid [Pa×s];

ρ – density [kg/m^3];

σ – mean collision diameter [m];

χ – tortuosity factor;

ζ – zeta potential [V];

ΔEs – induced streaming potential [V]l;

Δp – applied pressure [Pa];

ε_0 – permittivity in vacuum [C/Vm];

ε_1 – dielectric constant;

κ – conductivity [S/m];

Q – heat flux [W/m^2];

ABBREVIATIONS

AFM-Atomic force microscopy;

ATP-Attenuated total reflection;

DO-direct osmosis;

FTIR-Fourier transform infrared;

HHP- high hydrostatic pressure;

HTT-heat treatment techniques;

IF-Irreversible fouling;

IR-ionizing radiation;

MF-microfiltration;

NF-nanofiltration;

OD-osmotic dehydration;

off-site DO-off-site direct osmosis;

OMD-osmotic membrane distillation;

on-site DO-on-site direct osmosis;

OS-osmotic solution;

PEF-pulsed electric fields;

PP-Polypropylene;

PTFE-polytetrafluoroethylene

PVDF-Polyvinylidene fluoride;

RO-reverse osmosis;

SEM-Scanning electron microscopy;

SS-stripping solution;

UF-ultrafiltration;

UR-ultraviolet radiation;

RESUMEN

El procesado de alimentos conlleva, en mayoría de los casos, la generación de subproductos o residuos que pueden ser reutilizados o revalorizados mediante la utilización de técnicas de separación por membrana. Estas técnicas ofrecen la posibilidad de tratar las soluciones en condiciones de operación muy suaves, y no comportan en mayoría de las ocasiones, una alteración de los componentes a recuperar. Actualmente, las técnicas de separación por membrana, debido a su alta calidad y relativamente bajos costes, se encuentran completamente integradas en la mayoría de procesos productivos que requieren de una etapa de separación. Sin embargo, la investigación en el área de las técnicas de separación por membrana sigue abriendo nuevos campos de aplicación, que surgen con la mejora de las condiciones tecnológicas de los equipos y la posibilidad de obtener nuevas membranas adaptables a necesidades específicas.

En concreto, en este proyecto se utilizaron técnicas de separación por membranas para concentrar soluciones de azúcar procedentes de deshidratación osmótica (en adelante OD). El principal objetivo fue estudiar el potencial de varias técnicas de separación, haciendo hincapié en los flujos obtenidos durante la reconcentración y en la calidad de la solución reconcentrada.

La deshidratación osmótica es un tratamiento que permite una eliminación parcial del agua en un alimento y/o la incorporación de solutos de una manera controlada, respetando la calidad inicial del producto. El proceso consiste en introducir los alimentos en una solución hipertónica, controlando las condiciones de operación para favorecer, en mayor o menor grado la incorporación de solutos y la deshidratación del alimento. La aplicación de OD puede resultar en la mejora de las propiedades nutricionales y funcionales de los alimentos y en la reducción de la energía requerida para la deshidratación. El principal problema de la aplicación industrial de la OD radica en la gestión de la solución procedente del proceso. La reutilización de esta solución plantea una doble ventaja: primero desde el punto de vista ambiental, ya que se elimina un efluente del proceso que a menudo no puede ser vertido directamente, y segundo el ahorro económico que representa la recuperación de las materias primas que muchas veces contienen solutos de importante valor económico.

Los métodos de separación por membrana utilizados para recuperar las soluciones de OD fueron los siguientes: nanofiltración, osmosis directa y destilación osmótica por

membranas. La nanofiltración (NF) presenta altos niveles de retención y un menor gasto de energía que la osmosis inversa, y en la industria azucarera se aplica como uno de los pasos en la clarificación y concentración de jarabes. En los procesos de contactores de membranas: osmosis directa (DO) y destilación osmótica por membranas (OMD), a diferencia de los procesos basados en el tamizaje, el flujo depende solamente de la diferencia de potencial osmótico. Las únicas presiones hidráulicas requeridas son las necesarias para bombear la solución de azúcar y la solución osmótica hasta la superficie de la membrana. Estas características hacen que estos procesos presenten como muy prometedores para la reconcentración de soluciones de azúcar de concentraciones elevadas.

Los experimentos de filtración se llevaron a cabo utilizando plantas piloto diseñadas y construidas expresamente para el presente proyecto. Durante todos los procesos de separación por membranas, se empleó como solución modelo una solución de sacarosa a diferentes concentraciones (5-60 ºBrix), debido a que las soluciones aplicadas en la deshidratación osmótica de frutas son habitualmente soluciones de azucares (sacarosa, glucosa o jarabes).

Durante los experimentos de NF se evaluó el funcionamiento de las membranas planas: Desal5-DK (GE- Osmonics), MPF-34 (Koch Membrane), NFT-50 (DSS) y tubulares: MPT-34 (Koch Membrane) y AFC 80 (PCIMembranes). Además de la solución de azúcar de diferentes concentraciones (5-20 ºBrix), se concentraron zumos de pera y manzana.

La reconcentración mediante osmosis directa se realizó utilizando dos modos de operación: off-site e on-site. En el modo off-site, la reconcentración por ósmosis directa se llevó a cabo en una planta de filtración provista de un módulo plano o tubular, dependiendo de la membrana. En el módulo se llevó a cabo la concentración. En el modo on-site, la deshidratación se realizaba conjuntamente con la reconcentración de la solución osmótica. La solución de reconcentración de la osmosis directa en off-site (off-site DO) fue NaCl, mientras la solución de reconcentración de la osmosis directa on-site (on-site DO) fue una solución de sacarosa más concentrada que la solución osmótica (60 para una solución osmótica de 40 y 68 para una solución de 50 ºBrix). Para garantizar el flujo de agua entre las dos soluciones y altas retenciones de azúcar durante la off-site DO, se utilizaron membranas de NF planas (Desal5-DK y MPF-34) y tubulares (MPT-34 y AFC80). La reconcentración por osmosis directa on-site se levó a cabo empleando una membrana de microfiltración (Durapore, Millipore), ya que la

solución de reconcentración (SS) es la misma que la solución osmótica y la alta viscosidad de la SS restringe mucho el flujo de agua si se utiliza una membrana más densa.

En la deshidratación por membranas (OMD) se utilizaron membranas hidrófobas (11806, Sartorius) que presentan una retención teórica del 100 %. Se comparó el rendimiento de dos soluciones de reconcentración: NaCl y $CaCl_2$.

Con el fin de obtener información referente a la influencia de las propiedades de las membranas sobre el desarrollo del proceso de concentración de las soluciones procedentes de la deshidratación osmótica, se realizó un estudio detallado de las propiedades de las membranas aplicadas mediante AFM, SEM, FTIR, ángulo de contacto y medidas de potencial zeta.

Con la finalidad de generar soluciones osmóticas para someterlas a reconcentración, y también para disponer de productos procedentes de deshidratación osmótica con soluciones frescas que pudieran compararse con aquellas procedentes de OD con solución reconcentrada, se deshidrataron diferentes lotes de manzana (*Granny Smith*) con soluciones de sacarosa de 40, 50 y 60 ºBrix. Estas pruebas permitieron determinar también el tímelo de operación para una máxima pérdida de agua con relativamente poca impregnación de las manzanas. Después de cada experimento se analizaron los siguientes parámetros: concentración de azúcar, pH, absorbancia a 420 nm de las soluciones y humedad de las manzanas.

La nanofiltración, aplicada en la primera fase del presente estudio, resultó ser viable solamente para la reconcentración de soluciones de concentraciones hasta 24 ºBrix. El aumento de la temperatura de 25 hasta 35 ºC para las dos membranas tubulares ocasionó un incremento del flujo de permeado, y el mismo efecto tuvo el aumento de presión transmembranaria de 8 a 12 bar.

Se comprobó que el factor más importante para la eficacia del proceso es disponer de una membrana que combine altos flujos y retenciones durante el proceso. La deposición de las partículas de sacarosa y/o los zumos se caracterizó mediante SEM y la topología de la capa filtrante de la membrana se identificó usando AFM. La topología de la capa filtrante de las membranas era diferente para cada una de ellas, a pesar de que todas estaban preparadas con el mismo material (poliamida). En las imágenes de los cortes transversales de las membranas realizados con SEM, se observaron los cambios en la estructura de las membranas producidos por la aplicación de presión durante los

experimentos y las altas temperaturas empleadas durante su acondicionamiento. Gracias a las imágenes de SEM se pudo verificar también la eficacia del proceso de acondicionamiento de membranas.

A diferencia de NF, tanto la ósmosis directa como la destilación osmótica por membrana permiten la reconcentración de soluciones concentradas de sacarosa (hasta 60 ºBrix). La eficacia de estas dos últimas técnicas se evaluó en unción de los flujos de agua obtenidos.

El sistema de ósmosis directa on-site propuesto para la reconcentración de las soluciones de OD permitió reutilizar las soluciones osmóticas como mínimo cuatro veces. Para la solución osmótica de 40 ºBrix la humedad de las manzanas fue similar utilizando solución fresca o reconcentrada. En cambio, una solución osmótica de 50 ºBrix, la pérdida de agua de las manzanas fue mayor cuando la deshidratación osmótica se llevó a cabo con reconcentración on-site de la solución osmótica. Los análisis de concentración de azúcar de las soluciones osmóticas y de la solución de reconcentración indican que la membrana elegida para los experimentos facilita el transporte óptimo de solutos y agua entre las dos soluciones. Además, el sistema de reconcentración por membrana propuesto es muy sencillo y de bajo coste porque no requiere presurización.

La osmosis directa en off-site proporcionó flujos mucho mayores que los obtenidos con el sistema on-site (1.3 kg/m^2h para la solución osmótica de 50 ºBrix respecto a 0.0023 kg/m^2h durante on-site DO para la misma solución). Sin embargo, el transporte de solutos de la solución de reconcentración hacía la solución osmótica puede ser considerado un obstáculo para su aplicación a escala industrial.

Los flujos de agua más elevados fueron obtenidos utilizando la OMD (2.01 kg/m^2h para la solución osmótica de 50 ºBrix y con $CaCl_2$ con la solución de reconcentración). Otra gran ventaja de este proceso es la retención de solutos que proporciona, hecho confirmado por los análisis realizados.

El estudio sobre el transporte durante los procesos de contactores de membranas indicó que la viscosidad es la propiedad limitante para la solución osmótica y la actividad de agua/alta presión osmótica como la propiedad más importante a la hora de elegir una solución de reconcentración. Para todos los procesos de separación aplicados, el aumento de la concentración de azúcar de la solución osmótica comporta una disminución notable del flujo de agua.

El desarrollo de un posible proceso de deshidratación osmótica con una etapa de reconcentración de la solución osmótica mediante procesos con contactores de membrana ha permitido calcular el área requerida para realizar la reconcentración: 3.6, 9.7, 1608 m^2 para OMD, off-site DO e on-site DO, respectivamente.

Las conclusiones del trabajo confirman la posibilidad de utilizar procesos por membrana para realizar la reconcentración de soluciones osmóticas. No obstante se ha constatado que técnicas más tradicionales basadas en diferencias de presión (NF) no son adecuadas cuando las soluciones presentan elevadas viscosidades. Por lo tanto, procesos en los que la presión aplicada es solamente aquella necesaria para circular los fluidos y que se basan en diferencias de actividad de agua o presión de vapor para establecer los flujos de agua, son los más adecuados.

ABSTRACT

The main objective of the present study is to evaluate membrane separation processes that reconcentrate osmotic dehydration spent solutions. The reconcentration is performed using nanofiltration, direct osmosis and osmotic membrane distillation. The nanofiltration (NF) process is carried out using a cross-flow filtration plant with flat sheet and tubular membranes. Direct osmosis is studied in two modes: off-site and on-site. During off-site direct osmosis (off-site DO), osmotic and stripping solutions are brought into contact in a membrane module. During on-site direct osmosis (on-site DO), however, the osmotic solution is reconcentrated at the same time as the osmotic dehydration process.

Off-site DO was performed using NF membranes and NaCl as the stripping solution (SS), while on-site DO was performed with a microfiltration membrane and hypertonic sucrose solutions. During osmotic membrane distillation (OMD), NaCl and CaCl2 were tested as SS.

In order to get detailed information about the influence of the membrane properties on the process performance, the NF membranes were characterised. The membrane properties evaluated were: topology, morphology, zeta potential, contact angle and chemical composition of the filtration layer.

Because the most common osmotic agents used in fruit osmotic dehydration, are sugar solutions (sucrose, glucose or syrups), a sucrose solution of different concentrations (5-60 ºBrix) was used as the model for the membrane separation study. Apples were osmotically dehydrated to obtain actual osmotic solutions (OS) and to study how reconcentrated osmotic solutions affect the properties of osmodehydrated apples. The first aim of the OD experiments was to determine the operation time when maximum dehydration and no solid gain occur, depending on the OS concentration. This time was found to be 3.5 h for 40 and 50 ºBrix, and 3 h for 60 ºBrix sucrose solution.

The maximum sucrose concentration obtained during the nanofiltration process (24 ºBrix) restricts NF application to diluted solutions (e.g. in the fruit juice pre-concentration step). Of the membrane properties analysed, the separation layer characteristics were found to be decisive for achieving high fluxes and retention. The highest fluxes and retentions were obtained with the flat-sheet Desal5-DK membrane,

with vertically arranged particles in the separation layer, while the other membranes (tubular: AFC80 and MPT-34 and flat-sheet: MPF-34) have separation layer particles that are arranged more horizontally. The arrangement of the separation layer particles affected their density and the Desal5-DK membrane is the least porous. The studies on membrane recovery showed that the membrane recovery methods applied were effective.

Membrane contactor techniques (direct osmosis and osmotic membrane distillation) made it possible to concentrate highly viscous sucrose and osmotic dehydration solutions. During OMD, water fluxes were higher when $CaCl_2$ was used as the stripping solution. The fluxes were higher despite the higher viscosity of $CaCl_2$ and suggest that water activity is the decisive SS property if high water fluxes are to be achieved in OMD. Viscosity was found to be the critical feed solution property and fluxes were significantly reduced when the sucrose concentration was increased. At lower sucrose concentrations (40-50 ºBrix), the feed composition also influenced the fluxes obtained, but at high concentrations (60 ºBrix) it was negligible. Analytical tests revealed that the 11806 PTFE membrane provided 100 % solute retention for sugar and both stripping solutions.

Off-site and on-site direct osmosis gave lower fluxes than OMD and, since hydrophilic membranes were used, some solutes were transferred between the feed and stripping solutions. As in the NF process, Desal5-DK performed best, first because of its properties (described above) and, second, because it is not very thick, which reduces the mass transfer resistance between the solutions and provides better contact.

The fluxes between the membrane contactor techniques were lowest when on-site direct osmosis was used, mainly because of the low driving force and problems related to stirring and the design of the membrane support.

The apples osmodehydrated during the on-site DO were used in the sensory analysis. The panellists indicated that the apples that were osmodehydrated using the reconcentrated solution were the best.

As the final step, a feasible osmotic dehydration process with a coupled membrane contactor reconcentration step was proposed and osmotic membrane distillation was seen to be the most suitable process for carrying out OS reconcentration.

1 THEORETICAL BACKGROUND

1.1 OSMOTIC DEHYDRATION AS AN ALTERNATIVE FOOD PRESERVATION METHOD

One of the primary criteria in evaluating food preservation methods is how effective they are at inactivating pathogens (WHO, 2002). However, from the consumers' point of view, food appearance (size, shape, form, colour, condition and absence of defects) is decisive in their choice of purchase (Kays, 1999). Consumers expect food to look fresh, taste natural, be microbially safe, have no additives such as preservatives and humectants, and have an extended shelf-life (Hugas et al., 2002). In response to consumer demand, research in the food industry aims to develop mild food preserving methods.

The commonly used heat treatment techniques (HTT) of thermal pasteurisation and sterilisation are efficient at microbial elimination, but deteriorate the sensory and nutritional characteristics of the final product. Excessive heat applied during HTT may cause undesirable protein denaturation, non-enzymatic browning, and loss of vitamins and volatile flavour compounds. A possible solution to this problem is to optimise the thermal processing for maximum efficiency against microbial contaminants and minimum deterioration of food quality. High-temperature short-time pasteurisation and ultra high temperature sterilisation minimise vitamin losses, but the final product's taste and texture are still spoiled by the heat. Therefore, the best option would be to substitute HTT by some alternative technique, or combine it with some pre-treatment preserving method, which will decrease the heat exposure time.

A promising pre-treatment method is osmotic dehydration (OD), which is the subject of this study. Osmotic dehydration (OD) provides a high quality product with a high content of naturally occurring vitamins and microelements. This chapter discusses DO properties and possible applications, and makes a comparative study between DO and other new food preservation methods.

1.1.1 FOOD PRESERVATION METHODS: STATE OF THE ART

Despite the positive effects that heat processes have on microbial inactivation, it is difficult to obtain high quality food. Therefore, finding an effective method that does not harm the product is a real challenge. Any new food preservation method must not

only inactivate microbes efficiently, it must also preserve the food's natural taste, colour and appearance. The alternatives to HTT processes that have emerged recently are non-thermal preserving methods (Lado and Yousef, 2002), such as:

- High hydrostatic pressure processing (HHP), where food is exposed to a high hydrostatic pressure - up to 1000 MPa (described below);
- Pulsed electric fields (PEF), where food is treated with pulses at high electric field intensity (5-55 kV/cm) a for few milliseconds (described below);
- Ionizing radiation (gamma and electron beams), which generates doses of 0.1 to 30 kGy to inactivate microorganisms (described below);
- Ultraviolet radiation energy, which is a non-ionising radiation with germicidal properties at wavelengths in the range 200-280 nm (described below);
- Osmotic dehydration (OD), which involves partial dehydration of water-rich foodstuffs which are immersed in hypertonic aqueous solutions of various edible solutes (see section 2.2).

Non-thermal methods can be divided into two groups, depending on the mechanism of food preservation. During HHP, PEF, ionizing radiation and UV microorganisms are inactivated by breaking their cell walls or affecting their nucleic acids. The mechanical extermination of microbes has a positive health effect, but can also cause unwanted biochemical changes in the products treated. The food's physical properties are preserved during OD, whose preserving characteristics are attributed to the reduction of water activity.

Water activity (a_w) is the most important factor that affects the stability of dehydrated and dry products during storage. It can be expressed as the ratio of the water vapour in any kind of food (p_{food}) to the water vapour pressure of pure water (p_{water}), Eq. 1.

$$a_w = p_{food} / p_{water} \qquad \text{Eq. 1}$$

Water activity is determinant for microbial growth and can be associated with most degradation reactions of a chemical, enzymatic and physical nature (Maltini et al., 2003). Knowledge about the a_w levels at which microbial growth stops is essential for food preservation purposes. The lowest limit for growth in foods or any other item is

0.6, but most bacteria can be inhibited at a_w of 0.8. To stop yeast and moulds growing a_w must be as low as 0.75 to 0.7 (Table 1).

Table 1. Factors affecting the growth of some foodborne pathogens (FDA, 1999).

Microorganism	Growth temperature [ºC]	Growth pH	Water activity
Staphylococus aureus	7 - 45	4.2 - 9.3	>0.86
Clostridium botulinum (A+B)	10 - 49	4.7 - 9	>0.93
Clostridium perfingens	10 - 52	5.5 - 8	>0.93
Bacillus cereus	10 - 49	4.9 - 9.3	>0.95
Escherichia coli	2.5 - 45	4.6 - 9.5	>0.935
Salmonella spp.	6.5 - 47	4.5 - ?	>0.95
Vibrio cholerae O1	8 - 42	6 - 9.6	>0.95

Control of the a_w helps to maintain proper product structure, texture, stability, density and rehydration properties. Water activity influences non-enzymatic browning, lipid oxidation, vitamins degradation, enzymatic reactions and protein denaturation (Figure 1).

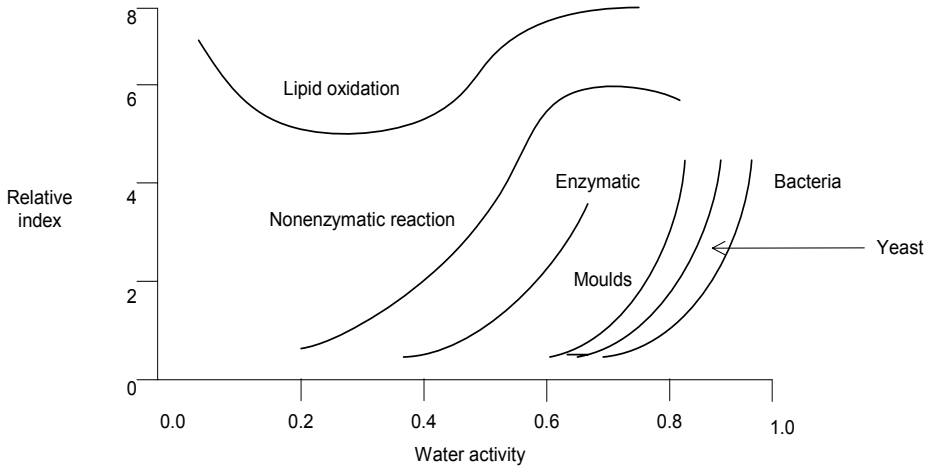

Figure 1. Enzymatic and chemical changes related to a_w values (Barbosa-Cánovas and Vega-Mercado, 1996).

As well as the alternative food preservation methods mentioned above, the following processes can be used: radiofrequency (Hugas et al., 2002), ozonation (Guzel-Seydim et al., 2004), ultrasonification (Knorr et al., 2004), magnetic field pulses (Rubow, 1997) and, last but not least membrane separation techniques to treat liquid foods (Warczok and Güell, 2005 A).

HIGH HYDROSTATIC PRESSURE PROCESSING

T This method, designed for processing packed food is highly suitable for solid food: i.e. meat (Hugas et al., 2002) and seafood (Murchie et al., 2005). High hydrostatic pressure (HPP) efficiently inactivates microorganisms and denatures several enzymes, while preserving the main organoleptic properties (Polydera et al., 2003). Its effectiveness depends on: pressure, pH, temperature, type of enzyme, type of pathogen and pathogen shape and size. Yeast, moulds and vegetative cells are pressure sensitive and can be inactivated by mild treatments ~ 300-600 MPa. Bacteria inactivation is much more complicated and HPP optimization is necessary. Some bacteria strains (e.g. *Staphylococus aureus* 485, *Escherichia coli* O157:H7 933 and *Salmonella* Enteritidis FDA) are resistant to pressure, which makes it necessary to apply heat together with HHP (Alpas et al., 1999). Also, most bacteria spores are resistant to high pressure. If inadequate HPP process parameters (pressure, exposure time, temperature) are applied, bacteria will only be injured. This may lead to cell repair and development of gene-regulated resistance to HPP (Benito et al., 1999). This problem is associated mainly with liquid (juices) and semi-liquid (purees) food.

Another important issue in fruit and vegetable processing is enzyme inactivation to impede enzymatic browning. Whitaker (1996) stated that it is not possible to completely inactivate enzymes by hydrostatic pressure and at the same time maintain integrity of the food tissues. Gomes and Ledward (1996) reported browning of mushrooms, apple and potato after HHP treatment. When Préstamo and Arroyo treated spinach leaves with HPP (1998) cell membranes were damaged and there were signs of nutrient loss and enzymatic browning. HPP may also have a negative effect on the flavour of treated food. Krebbers et al. (2003) found that tomato puree treated by HPP at ambient temperature possessed a rancid flavour, absent in conventionally treated food. Another important drawback of HPP is its high investment cost (Devlieghere et al, 2004). Despite its disadvantages for fruit products, HPP is one of the most commonly used

non-thermal preserving methods and to ensure that food-borne pathogens do not develop it is combined with heat. The relation between final product stability, food type and treatment conditions is presented in Table 2.

Table 2. Examples of HHP treatment conditions depending on food type.

Food type	Treatment conditions	Final product stability	Reference
Salmon (*Salmo salar*)	150 MPa; 5 ºC; 10 min	Chilled storage, 8 days stability	Amanatidou et al., 2000
Tomato puree	700 MPa; 20 ºC; 2 min	Chilled storage	Krebbers et al., 2003
	700 MPa; 90ºC; 2×30 s	Ambient stability	
Orange juice	450 MPa; 50 ºC; 30 min	Ambient short time stability	Bayindirli et al., 2006
Lychee fruit (*Litchi chinesis* Sonn.)	600 MPa; 60 ºC; 20 min	Ambient short time stability	Phunchaisri and Apichartsrangkoon, 2005
Pretreated meat	600 MPa; 31ºC; 6 min	Chilled storage	Garriga et al., 2004

PULSED ELECTRIC FIELDS

Electric pulses were first used in food preservation at the beginning of the 20th century when electric resistance (ohmic heating) was coupled with pasteurisation and used to inactivate micro-organisms in milk (Bendicho et al., 2002). In 1928, Fetterman designed the ¨ElectroPure Process¨ in which milk was heated to 70 ºC and then passed through carbon electrodes in an electric heating chamber to inactivate *Mycobacterium tuberculosis* and *Escherichia coli*. From that moment, application of electric heating became a very common milk preservation method, and between 1928 and 1938 about 200 millions of litter of milk were treated. In the late 30s this food treatment by electric pulses was put to one side until the 60s, when there was a revival of interest in non-thermal preservation methods.

Nowadays, the use of electricity as a food preservation method has evolved and there are now several patents for pulsed electric fields (PEF) in liquid food treatment (Vega-Mercado et al., 1997). PEF cannot be used to preserve solid food (fish and meat) because it is not suitable because it has a negative influence on muscles texture and microstructure (Gudmundsson et al., 2001).

Liquid foods contain many ions, so they can be considered to be electrical conductors. High current flux for short periods is required to generate electric fields within food, because re-charging time is long. The basic PEF processing set-up consists of a voltage power supply, a capacitor, a charging resistance, a discharge switch and a treatment chamber (Rastogi, 2003). The energy discharged to generate the electric field in the food is stored in the capacitor. This discharge is controlled by high-voltage switches that can operate at high power and repetition rate. In the treatment chamber, the temperature is maintained by using a cooling system in the electrodes. The discharged pulses can have different forms: exponential decay, square, oscillating and when the process is affected or not by the polarity of the discharge, are obtained bipolar or unipolar pulses, respectively. The most effective in food sanitation are exponential decay and square pulses. The PEF circuits that produce exponential decay and square pulses are presented in Figure 2.

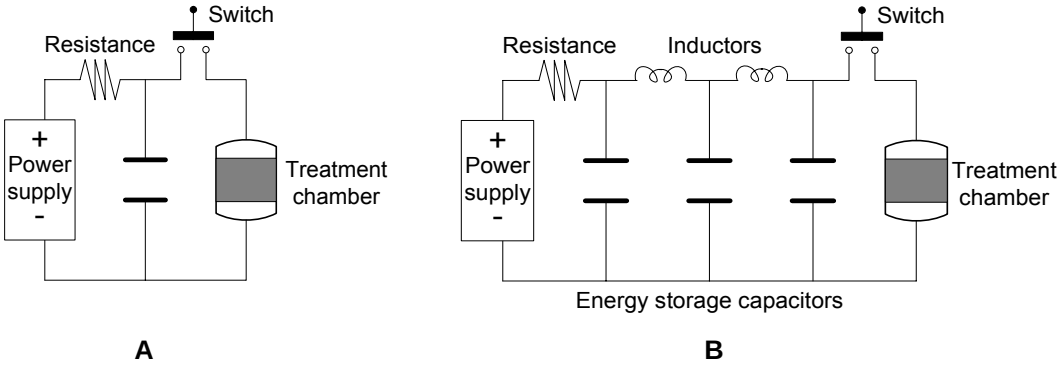

Figure 2. Two basic PEF circuits producing and exponential decay pulse (A) and a square pulse (B).

The square pulse configuration (Figure 2, A) is preferred to the exponential pulse (Figure 2, B), because it provides longer discharges, which minimise the energy absorption of the food, increase PEF effectiveness and reduce food degradation (Rastogi, 2003).

Microbial inactivation by PEF can be affected by the strength of the electric field, pulse length, pulse shape, number of pulses and initial temperature (Wouters et al., 2001). One possible explanation for the PEF cell inactivation mechanism is the dielectric rupture theory proposed by Zimmermann et al. (1974). According to this

theory, if the external electric field induces a transmembrane potential over ~ 1 V (natural cell membrane potential), the membrane will break. Depending on the voltage of the field, this rupture of the cell membrane can be either reversible or irreversible. PEF results in considerable inactivation of bacteria, yeasts and moulds, while spores are tolerant to the treatment. This can be attributed to the high dehydration of spores, which reduces conductivity and inhibits the development of a voltage sufficient to breach the surrounding membrane (Gould, 2000).

PEF can be applied to treat fruit juices, milk, dry herbs, liquid egg and liquid whole egg. Some of the studies made on possible PEF applications are presented in Table 3.

Table 3. PEF as a preservation method for liquid foods.

Food type	Treatment conditions*	Final product stability	Reference
Spanish vegetable soup- gazpacho	35 kV/cm, 800 Hz, 50 ºC, 4 µs, 750 µs	Chilled storage	Sánchez-Moreno, 2005
Apple juice	35 kV/cm, 952 Hz, 26-27 ºC, 1.92 µs, 94 µs, 85 l/h	Chilled storage	Evrendilek et al., 2000
Milk	30-50 kV/cm, 250 Hz, below 40 ºC, 3-7 µs, 460 µs, 60 ml/min	Chilled storage	Evrendilek et al., 2004
Tiger nut milk	20-35 kV/cm, 35 ºC, 100-475 µs, 60 ml/min	Chilled storage	Cortés et al., 2005

* Peak electric strength, pulse repetition rate, temperature, pulse duration time, mean total treatment time, flow rate

IONIZING RADIATION

Ionizing radiation (IR) is one of the most controversial food preservation methods. Even though in 1992 WHO considered IR to be safe and nutritionally adequate under the established Good Manufacturing Practice, many consumers still remain sceptical (Delincée, 1998). The maximum dose applied does not usually exceed 10 kGy, but there is no maximum limit recommended by WHO. However, in case of application of doses higher than 10 kGy a detailed toxicological study is required.

During IR, gamma radiation from isotopes e.g. ^{60}Co, ^{137}Cs or electron beams are used. The ^{60}Co, ^{137}Cs irradiation facilitates the food penetration, but operation costs and environmental risks are high. Electron beams are easy to control and do not have such

important environmental impact as ^{60}Co, ^{137}Cs irradiation, but their food penetration is limited and manipulation costs are high (Pradell, 2003).

The target of IR is DNA destruction. IR is very efficient at reducing microorganisms in food, and it is considered as a viable fumigation treatment, which in some cases can improve shelf-life and product quality. Jakabi et al. (2003) obtained a 6 log reduction of *Salmonella* Enteritidis, *Salmonella* Infantis and *Vibrio Parahamolyticus* in oysters. The highest irradiation (3 kGy) neither killed the oysters nor affected their sensory properties. Nevertheless, IR may cause undesirable biochemical changes in food. Beaulieu et al. (2002) demonstrated that under a high rate of irradiation of 32 kGy/h, the cellular membrane integrity of mushrooms is lost, which leads to disorders in membrane permeability and enhances enzymatic browning. An increase in browning was also observed at lower irradiation rates. A 1.74 kGy/h irradiation of Witloof chicory increased its membrane permeability, and facilitated browning through enzyme-substrate contact (Hanotel et al., 1995). Undesirable texture changes (textural toughening and disruption of skeletal muscle) were observed during a 2.2-2.9 kGy (0.92 kGy/h) irradiation of chicken breasts (Yoon, 2003). These textural and biochemical changes can be avoided by combining IR with other food preservation techniques. Examples of successful IR applications for different food types are presented in Table 4.

Table 4. Application of IR in food processing.

Food type	Treatment conditions*	Final product stability	Reference
Lettuce	^{60}Co, 0.7 kGy, pre-treatment: immersion in chlorine 200 ppm	Chilled storage	Goularte et al., 2004
Rice	^{60}Co, 1 kGy/h, 1 kGy, 25 ºC	Ambient stability	Sung, 2005
NASA foodbars	^{60}Co, 15-25 kGy, pre-treatment: dipping in 15 % potassium sorbate	Chilled storage	Tou et al., 2003
Egg	^{60}Co, 1 kGy/h, 0.5-5 kGy, 23 ºC	Chilled storage	Pinto et al., 2004

* Source, dose-rate, dose, temperature

The weakest point of IR is its control (dose and labelling). Recently many studies have been made about possible analytical methods for detecting irradiated food. De Jesus et al. (2000) used electron spin resonance measurements to identify products irradiated with doses as low as 100 Gy. Soika and Delincée (2000) evaluated the

sensitivity of thermoluminescence, which turned out to be a reliable method for discriminating irradiated and non-irradiated food. Next to HPP, IR is one of the most frequently used non-thermal preserving methods for solid food treatment.

ULTRAVIOLET RADIATION

The low energy content of ultraviolet radiation (UR) restricts its influence only to the food surface. Considering solid particles shielding, UR applications are restrained mainly to liquid food (Hugo, 1995).

Ultraviolet (UV) light occupies wavelengths in the non-ionising spectrum range between 200 nm (X-ray) and 400 nm (visible light). The UV spectrum is divided into three sub-groups: UV-A (320-400 nm), UV-B (280-320 nm) and UV-C (200-280 nm). The most effective at exterminating microbes is UV-C, which is widely used for water sanitization (Bintsis et al., 2000). Microbial inactivation by UV-C is either a result of UV content for some application or intense local heating for the others. Its germicide effect is also enhanced by the formation of peroxides, free radicals and bacteriophage activation during photoradiation (Ibarz et al., 2005). As in IR, nucleic acids are the most radiation-sensitive compounds.

The influence that UV-C light has on the shelf-life of iceberg lettuce and white cabbage shelf-life was investigated by Gómez-López et al. (2005). After the UR, vegetables presented bad visual quality, off-odours and leaf edge browning, but as far as microbial safety was concerned one extra storage day at 7 ºC was gained. Therefore, the authors suggested using antibrowning pre-treatment to avoid biochemical deterioration. Results were much better during juice and liquid egg photoradiation carried out by Ngadi et al. (2003). By radiating apple juice and liquid egg at 254 nm, E. coli O157:H7 5 log was reduced without affecting product quality. For four weeks storage at room temperature, both UR radiation products showed no change in colour. The major drawback of UR is the possible mutation of partly inactivated bacteria, resulting in the development of new virulent strains (Yousef and Lado, 2002).

1.1.2 OSMOTIC DEHYDRATION

Osmotic dehydration (OD) is one of the first food preservation methods, and it is becoming an attractive complementary processing step in the chain of integrated food processing (Rastogi et al, 2002). The first modern studies about OD were made by Pointing and co-workers in 1966, and since then there has been increased interest in OD processes. The potential of OD was also recognized by the European Commission, which founded a project entitled ¨Improvement of food quality by application of osmotic treatments in conventional and new processes¨ (FAIR-CT96-1118).

The main advantages of OD are the following (Moreno et al., 2000; Moreira et al., 2003):

- It improves and/or preserves nutritional properties. OD treated food has a high content of naturally occurring vitamins and microelements and can also be impregnated with additional substances;
- It improves functional properties. Water activity diminishes, which increases microbial stability and slows down deteriorating reactions. This has a positive influence on shelf-life;
- It reduces the energy and time needed for dehydration;
- It is simple, and equipment and operation costs are low.

OD involves soaking foods (fruit, vegetables, fish and meat) in a hypertonic (osmotic) solution i.e. concentrated sugar, salt, alcohols or soluble starch solutions, which partially dehydrates the food (Mújica-Paz et al., 2003, Erle and Schubert, 2001). During the process, two major simultaneous counter-current flows occur: the solute is transferred from the solution into the food and water flows out of the food into the solution, which is stronger than the previous one. OD usually takes place while the liquid solution is being agitated, thus reducing the external resistance and increasing the overall mass transfer rate. The efficiency of the OD process may be affected by (Uddin et al., 2004; Ozen et al, 2002):

- the composition and concentration of the osmotic solution;
- the physical-chemical and structural properties of food:cell porosity and packaging, membrane permeability;
- the operation parameters: time, temperature (optimum is 20-50 ºC), work pressure (atmospheric, vacuum) and agitation rate;

- the relation between the volume of osmotic solution and dehydrated material;
- the food pre-treatment: mechanical and chemical;
- the application of ultrasounds, PEF and HPP during the OD.

Osmodehydration results in extended shelf-life, fewer aroma losses in dried and semidried foodstuffs, reduction of the freezing load and/or the possibility to freeze the food without causing unwanted textural changes and dripping during thawing (Petrotos and Lazarides, 2001).

So far, OD has been applied in the dehydration of a wide range of foodstuffs and most of the applications are with fruits (Table 5). Fruits contain about 75 % water and the fact that OD can remove 50 % of this water is the main reason for its popularity.

Table 5. Application of OD in food processing.

Food type	Treatment conditions*	Observations	Reference
Apple, Pinneapple	50, 60, 70 ºBrix sucrose; 30, 40, 50 ºC; 1-5 h; 4:1	Peeled fruit	Sujata and Das, 2005
Banana (var. Cavendish)	40, 50, 60, 70 ºBrix sucrose; 25-45 ºC; 1 h; 20:1	Peeled, d=25 mm, height 45 mm	Rastogi et al., 1997
Bovine meat	150 mM $CaCl_2$; cold room; 3 h ; 2:1	Lean meat	Gerelt et al., 2005
Cherry Tomato (*L. Esculentum* var. Cerasiforme)	10, 25 % (w/w) NaCl, NaCl-sucrose (3:2); room temperature; 0.5–3 h; 10:1	Skin perforated with needles (promotes mass transfer)	Azoubel and Murr, 2000
Cantaloupe (*C. melo*, var. Edisto)	45-55 ºBrix sucrose; 40-50 ºC; 1-2 h; 20:1	Peeled, cork-bored	Corzo and Gomez, 2004
Chestnut (*Castanea sativa* Mill.)	40 50 56.6 ºBrix glucose; 25, 35, 45 ºC; 8 h ; 10:1	Peeled to parenchyma	Chenlo et al., 2005
Cod fillet	NaCl stagnant brine; room temperature; 23, 47 h	Filet with skin	Walde, 2002
Mushrooms (*Agaricus bisporus*)	10, 15 % (w/w) NaCl; 20; 45 ºC; 10, 30, 50, 70, 110 min; 5:1	Mushroom halfs	Torringa, 2001
Pear (*Pyrus communis* L. var. d'Anjou	55 ºBrix sucrose; 40 ºC; 2h	1cm^3 cubes	Park et al., 2002

*Osmotic solution concentration and type; temperature; immersion time; osmotic solution to food ratio

Despite the advantages of OD and its simplicity, the industrial application is bottlenecked by the problem of how to manage the spent solution.

OSMOTIC DEHYDRATION MECHANISM

The driving force behind the OD process is the activity gradient provided by the osmotic solution (OS) with the osmotic pressure overcoming the cell osmotic pressure. Most of a mass transfer takes place through the semi-permeable cell membrane. During OD, water flows from the inside of the food to the OS, and OS solutes also flow to the food. Because of the differential permeability of cellular membranes usually much more water than solute is transferred (Rodriges and Mauro, 2004). Simultaneously, food solutes (sugars, organic acids, minerals, vitamins, etc.) flow to the OS, since the cell membranes are not completely selective (Mayor et al., 2005). This nutrient loss depends strongly on food type and can be considered quantitatively negligible. However, it can affect the sensory characteristics of the food. The highest dehydration rates are observed at the beginning of the OD process, and after reaching the compositional and chemical equilibrium, mass and volume increase again and impregnation takes place (Figure 3).

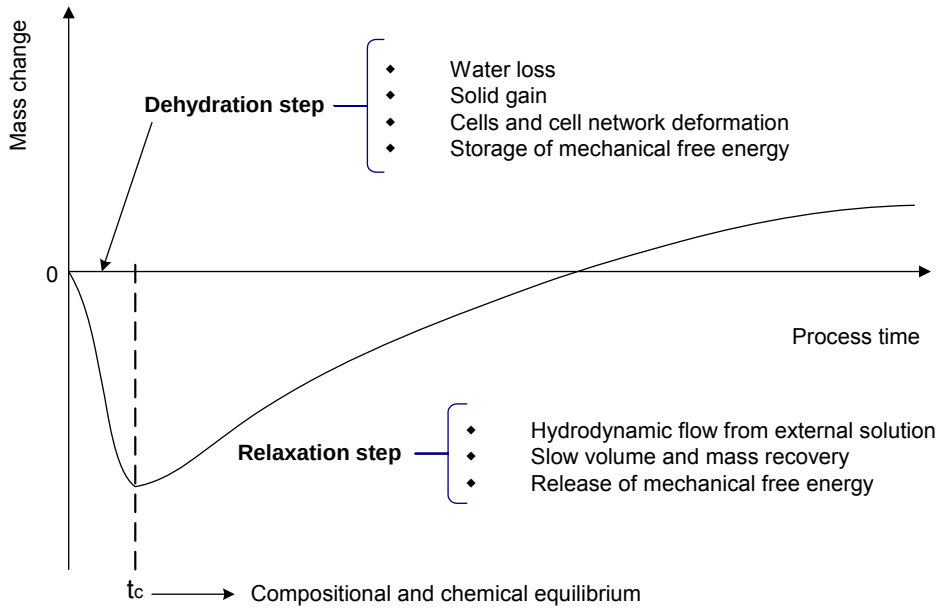

Figure 3. Pathway in long term osmotic dehydration process (adapted from Fito and Chiralt, 2003).

The information from Figure 3 is very useful in OD process design, because it helps in time adjustment for different processes e.i. candying, salting or dehydration.

On cell scale, the water output or solute uptake during OD takes place via capillary channels, which constitute most of the extracellular space. This space can be filled with water or solutes, which make up the main pathway for mass transfer. This type of transport is called apoplast. In another mass transfer path, called symplast, the water and solutes flow through intercellular channels thanks to differences in cell pressure. Water is also directly transported from the tissue surface to the solution, but is minor compared to apoplast or symplast (Shi and Le Manguer, 2003). During OD, the inside of the tissue remains intact and the transport follows one of the described modes. Meanwhile, the outside forms a penetration zone, where some of the cells are damaged or shrink because of the osmotic stress, and most of the osmotic solutes can be found only in the penetration zone even after log-term immersion (Shi and Le Maguer, 2002). The scheme of mass transfer in OD-treated tissue is presented in Figure 4.

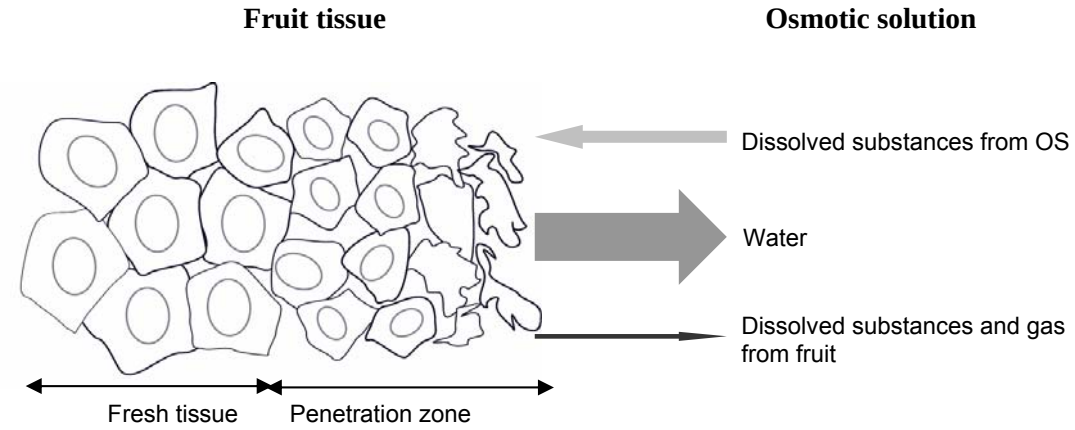

Figure 4. Mass transfer in fruit tissue during osmotic dehydration

Detailed studies about mass transfer throughout the osmodehydration revealed it to be a complex process, during which a variety of phenomena take place: convection and diffusion in the OS and in the intercellular spaces filled with liquid, liquid movement through the pores due to capillary forces and symplastic transport between cells.

Mavroudis et al. (2004) attempted to clarify solute uptake in the OD process by evaluating the accessibility of intercellular space (pore) in the inner and outer cortex of

the apple. Results showed that porosity decreased by about 50-60 % and that bulk density increased by about 10 % between the skin and the apple. The authors noticed also that pore penetration of the apple cannot explain the extent or the speed of the uptake of solids. Mass exchange may sometimes have an effect on the organoleptic and nutritional quality of dehydrated food (Sablani et al., 2002; Prothon et al., 2004).

The resistance on enzymatic browning is significant in OD-treated food. Quiles et al. (2005) investigated polyphenol oxidase (PPO) activity in apples after OD. Because of water flow out of the food and OS penetration in the food, air was displaced by sugar. This decreased the availability and of O_2 in the microstructural surrounding of PPO decreasing its activity, and the same the enzymatic browning.

OPTIMIZATION AND COUPLING OF OSMOTIC DEHYDRATIO N

There is an increasing amount of information available on mass transfer modelling which helps to control the quality of the OD product and means that less experimental work need to be done. However, it must be emphasized that the modelling of osmotic processes is limited by the complexity and diversity of food tissues, and by several structural reactions on the osmotic stress (Chiralt and Fito, 2003). In general, the models developed so far are based on one of the following approaches:

- Fickian diffusion.
  Based on Fick´s II law, this is most frequently used to develop a mathematical model for OD. Boundary conditions include: constant concentration of OS, negligible surface resistance compared with internal diffusion resistance, neglected shrinkage during OD, isothermality and transport restricted to water and sugar only - other solutes are neglected (Matusek and Merész, 2002).
- Irreversible thermodynamics.
  This approach considers the transfer of both water and solutes during the OD process and takes into account possible changes occurring in plant tissue during the process (e.g. shrinkage).
- Multicomponent diffusion.
  This evaluates the influence of individual components–transfer mechanisms, mass transfer rates and equilibrium moisture content– on overall transfer function (kinetics and final equilibrium of the system).

OD mass exchange can be improved by the food pre-treatment as well as the application of mechanical methods during the process. Waxy and hard skin of some fruits and vegetables can be a tough barrier for the diffusion phenomenon during OD. Cherries dehydrated in sucrose solution after 24 h soaking showed 57 % water loss, while blackcurrants treated in the same conditions showed only 9 %. Therefore, peeling or peel softening is necessary in some cases. Small, hard-to-peel fruits should either undergo a peel softening –chemical treatment– or be cut into smaller pieces, thus exposing the fruit core. Sunjka and Raghavan (2004) tested mechanical and chemical pre-treatments in order to increase water removal during cranberry (*Vaccinium macrocarpon*) osmodehydration. Chemical pre-treatment involved immersing cranberries in an alkaline solution of oleate ester (0.5 % NaOH in 2 % ethyl oleate) for different times and at different temperatures. Mechanical pre-treatment consisted of cutting fruit into two or four pieces. Water loss was greater for fruit cut into four pieces and chemical peel softening had no influence.

Lenart and Piotrowski (2001) evaluated coating with semipermeable edible films, assuming that the coated plant tissue usually has a greater water loss/solid gain ratio than the uncoated one. In their study, commercial carbohydrates such as pectin, Capsul-E, Hi-Flo, maltodextrin, potato starch and Purity Gum were used to coat apples before the OD treatment. Of all the substances used, only pectin gave satisfying results (increase in water loss and decrease in solid gain), while the others resulted in an unacceptably higher water content and solid gain.

Increase of the porosity is another way to yield mass transfer rates. Porosity plays an important role, especially at the beginning of the osmodehydration when, gas entrapped in fruit tissue slows down mass transfer. Thus, mechanical fruit pre-treatment will facilitate food degassing with an augmentation of the cells permeabilization (Taiwo et al., 2003). Pulsed electric fields (PEF) used by the Ade-Omowaye et al. (2001, 2003) seam to be a good option to enhance water loss during OD and to limit solute uptake, resulting in minimal alteration of the product taste. In the work by Ade-Omowaye (2003), red bell peppers membrane permeabilisation was induced by PEF of 1, 1.5 and 2 kV field strength with a constant pulse number of 20 at pulse duration of 400 ± 50 μs. The OD treatment was carried out with a sucrose/sodium chloride, 21.9 and 2 ºBrix, respectively, and 50 ºBrix sucrose at 30 ºC. The water loss increased 11-25 %, while solid gain only 2-5 % compared with untreated samples. The authors observed also, that

the pore formation and pore growth within the cell membrane after PEF was time dependent and not an instantaneous process.

Other methods used to accelerate mass transfer during OD are vacuum pressure, HPP and ultrasounds. The most commonly used is vacuum pulse (Cháfer et al, 2003, Barat et al., 2001 and Moreno et al., 2004). Taiwo et al. (2003) compared the influence of HPP, PEF, vacuum and ultrasounds on the OD of strawberries. Pretreatment with HPP and PEF improved mass transfer and conserved the product properties (colour and compactness). The application of a vacuum during OD decreased the processing time and facilitated solid gain, reducing floating of berries during further processing. Sonication at the applied process parameters did not significantly affect mass transfer during OD.

Osmodehydrated foods have medium moisture content and are usually dried or frozen so that they remain stable over a long period. Convective drying is the most common drying method. Lewicki and Lukaszczuk (2000) used it as the final step for OD-treated apples and then compared the quality of dried products quality that had or had not been pretreated with OD. After OD with convective drying, apples showed less stiffness and shrinkage. This is because mass transfer during OD affects the outer parts of the food leaving the core with preserved properties (section 2. 2. 1). Various drying methods and dryers of osmodehydrated cranberries were studied by Grabowski et al. (2002). They evaluated energy consumption and product quality, and found that vibrated fluid bed and pulsed fluid bed were the best dryers. When comparing the drying of cranberries (*Vaccinium macrocarpon*) that had or had not been treated with OD it was found that the treated ones were better in both product quality and total process energy consumption.

Important savings are also noted in freezing if food is previously osmodehydrated (Li and Sun, 2002). A total of 93 % of dehydrofrozen apples were accepted by a sensory analysis panel in a study run by Bunger et al. (2004). Despite all records about the positive influence of OD on frozen products, the latest study by Talens et al. (2003) reveals that, at least on the volatile profile of kiwi, OD pre-treatment did not cause a notable change in comparison with fresh-frozen kiwi. The authors did not evaluate the preservation of textural properties, which is usually reported as an advantage of osmodehydrofreezing. Chiralt et al. (2001) analysed the mechanical response of kiwi, mango and strawberry that had or had not been pretreated by OD. The cryoprotectant effect of the OD pre-treatment was only achieved for strawberries that were firmer and

tougher after freezing-thawing. The fact that the OD pretreatment had no significant effects on the other two fruits suggested that specific optimisation would be necessary for each fruit, bearing in mind its final consumption application. Dermesonlouoglou et al. (2005) indicated that the OD process was an appropriate pre-treatment for watermelon freezing. The cryoprotectant effect of OD was noted in the increase in lycopene content, colour, texture and hardness in comparison with un-treated samples. During sensory analysis, samples frozen for 180 days and previously dehydrated with oligofructose and high DE maltodextrin received better overall acceptance than samples after 180 days freezing without pre-treatment. These results suggest that OD is a fine pre-treatment method for freezing fruits with a fragile texture such as watermelon.

OSMOTIC DEHYDRATION SOLUTIONS

Choosing the correct solution is the key factor in a successful OD process. This choice depends on the expected water loss, solid gain, texture and organoleptic properties of the food. One of the basic factors in the choice of OS is the water loss /solid gain ratio, because of its importance in the promotion/reduction of impregnation (Sacchetti et al., 2001). At low OS concentrations, the solutes reach deeper layers of the tissue (Rodrigues and Mauro, 2004), while high concentrations lead to faster water loss (Waliszewski et al., 2002 A). The osmotic solution must have low a_w, acceptable taste and be harmless for health. Sweet solutions (sucrose, glucose, fructose or corn syrup, sorbitol) are often used for fruit processing and salty ones (NaCl, $CaCl_2$) for vegetable, meat and fish processing. To make OD more viable economically, spent solutions from other processes may be used e.g. cheese whey was used to osmodehydrated bell peppers (Torreggiani et al., 1995). In fruit treatment, solutions of compounds with low molecular weights (fructose) usually give better results in terms of the weight reduction/solid gain than the high molecular weight sucrose. From the consumers' point of view, fruit juices and must are the best and most acceptable osmotic solutions to be used during fruit OD (Escriche et al., 2002).

Depending on the effect desired, OS can be enriched with various substances. Chitin at concentrations as low as 0.01 % was found to inhibit a decrease in lightness (L) during OD (Waliszewski et al., 2002 B). Its effect was independent of the process parameters and did not change the decrease in PPO activity in different dehydration conditions. The same authors (Waliszewki et al., 2002 C) also checked the influence

that EDTA solutions (100 ppm) had on colour and PPO activity, and their results were very similar to those obtained when chitin was used as the colour protector. In the same study, banana slices were soaked in 50, 60 and 70 ºBrix sucrose solution at 50, 60 and 70 ºC. To enhance water loss and preserve organoleptic properties, salt can be added to the solution at low concentrations (Lerici et al., 1985). Sereno et al. (2001) evaluated the influence of NaCl added to sucrose solution on the water loss/solid gain ratio during apple OD. Higher salt concentrations led to faster moisture reduction in osmodehydrated apples, but the water loss/solid gain ratio was lower than when only sucrose is used, probably because of the structural changes produced by NaCl.

Managing OS is the bottleneck of the OD process and it restrains industrial implementation. Thus, from the process and economic point of view it is necessary to find an effective recycling method. If the OS concentration remains high, the effectiveness of dehydration and the hygienic state of food (low water activity) are guaranteed (Gianotti et al., 2001). Preserving substances added to the OS and waste reduction are also important. Binary (water-sugar) solutions can be reconcentrated by heat or by adding dry sugar, but those methods are not viable in mixed solutions (Raoult-Wack, 1994), first because of the thermal spoilage of heat-sensitive compounds and second, because it is impossible to estimate the exact quantity of the reactants to be added. So far, all the studies about OS management have focused on the development of plants that require minimal OS quantities or the application of heat treatments combined with coarse filtration or acid precipitation (Dalla Rosa and Giroux, 2001).

So far, membrane filtration applied in the present study to reconcentrate OS, has not been experimentally evaluated and suggestions are only made. Romero Barranco et al. (2001) suggested ultrafiltration as a method for regenerating the spent brines of table olives. The authors pointed out the savings in energy consumption compared with evaporation and lack of groundwater contamination by elimination of evaporation ponds as main advantages of ultrafiltration. Gekas et al., 1998 in a state of the art about the application of membrane technology in the food industry, indicated nanofiltration as a method to separate solutions from scalding and DO process, due to the possibility of separation of ions and micromolecules.

The only experimental attempt of membrane separation application in OS recycling was carried out by Proimaki and Gekas (2000). These authors proposed a novel system to concentrate OS using a direct osmosis process. In that system the sucrose solution was reconcentrated by a sucrose solution of higher concentration. The drawback of the

mentioned study was the design of the experimental set-up that impeded to obtain accurate results. The system proposed by Proimaki and Gekas was the origin of the on-site OS reconcentration by direct osmosis investigated in the present study.

THE MARKET FOR OSMOTIC DEHYDRATION PRODUCTS

The purpose for which OD products are used will depend on their degree of stability. OD products that lose about 70 % of their water content are ready to eat and can be consumed as snack items or shakes (after grinding and mixing with milk or other liquid foods). Osmodehydrated food can therefore be used in the dairy, bakery and candy industries. If a fresher appearance is required, dehydration must be about 30 %, which makes it possible for medium stability products to be dried, frozen or treated with additives. These OD pre-treated products can be used in the dairy, bakery and candy industries and also to produce fruit and vegetable concentrates. In Europe, France and Italy are the countries that have developed the most advanced technologies for osmodehydration, and in Asia, the OD candying of tropical fruits is a very popular fruit preservation method.

Robles-Manzanares et al. (2004) studied the best dehydration and drying conditions to obtain quince (*Cydonia oblonga* Mill.) to be used as an ingredient in breakfast cereals or cocktail snacks. Quince pieces were dehydrated in fructose solutions of 45, 55 and 60 ºBrix at 30, 40 and 50 ºC. The best effect on colour, water activity, ascorbic acid preservation and texture was dehydration at 45 and 55 ºBrix at 30 ºC. Afterwards, OD samples were air dried by convection at 70 ºC for 3 h. In comparison with the untreated quince, dried OD-treated quince had a fresher appearance.

Osmodehydrated fruit was also used in jam production. García-Martínez (2002) manufactured kiwi and orange jam directly from OD-treated fruits and obtained products of higher quality than commercially available ones.

OD can also be applied as a pre-treatment in deep fat frying of potato strips (Krokida et al., 2001). French fries fried after OD presented better colour (less browning) and less oil uptake than those that were not treated and those pretreated with air drying.

1.2 MEMBRANE FILTRATION

In the food industry membrane separation has become a key process for concentration, fractionation and purification of liquid foods and for wastewater treatment. Its advantages, such as: low operation temperature, no special chemicals required, uncomplicated operation and possibility of automation, makes membrane separation a very good alternative to traditional methods for liquid foods treatment. Economical aspects are also an important issue, potential energy savings for the total food and drink industry can be estimated as 50 % (Eichhammer, 1995). Savings that can be obtained during juice production are a good example. In the case of involving a plant producing 250,000 l of juice/day, if traditional juice stabilization adding bentonite or gelatine and filtration with diatomaceous earth is replaced with ultrafiltration, annual costs dropped from US$348,800 to US$72,400 (Mondor and Brodeur, 2002). Moreover, the depectinization time and enzyme quantity are reduced, and the final product quality and quantity are increased.

So far, pressure driven processes: microfiltration, ultrafiltration, nanofiltration and reverse osmosis are the most frequently used membrane separation processes. The most common applications of those processes are listed below (Warczok and Güell, 2005).

- Microfiltration (MF) is appreciated especially in brewing, sugar and lactic industries where separation of big particles is required.
- Ultrafiltration (UF) is commonly applied to clarify, concentrate, decolorize and fractionate juices, sugar solutions, proteins and dairy and grain milling products.
- Nanofiltration (NF) can be used for wastewater treatment, milk concentration and demineralization, and finally for must concentration.
- Reverse osmosis (RO) can be applied in wastewater treatment, sugar, aroma and milk concentration, volatile acidity reduction and alcohol adjustment.

In fruit and vegetables sector: pervaporation, gas separation and electrodialysis are also applied. Pervaporation, developed as a possible process for aroma recovery in late 80´s (Bengsston et al., 1989), is already applied industrially due to its effectiveness. Gas separation is used mainly during vegetables and fruits packaging in modified atmosphere. Electrodialysis was pointed out by Vera et al. (2003) as a promising method for juice deacidification that promotes pH increase, preserves organoleptic properties and produces a valuable by-product (citric acid).

Introduction of membrane processes in other steps of food processing can be impeded by their operational limitations as fouling and concentration polarisation. New membranes and optimization of filtration process helps to reduce those limitations, but in case of pressure driven processes as MF, UF, NF and RO fouling and concentration polarisation are still an important drawback. Currently studied membrane contactor methods seem to be an alternative for pressure driven processes. Membrane contactors advantages as: low fouling, possibility of treatment of highly viscous solutions and high retention of species, make them useful for liquid foods treatment.

1.2.1 NANOFILTRATION

Nanofiltration, guarantees fine separation up to a molecular weight of 180 and a relatively low energy consumption (21% less than reverse osmosis, Comb, 1991). NF, like RO, is affected by the charge of the particles being rejected, thus its performance depends on steric (sieving) and charge (Donnan) effects. NF is capable of concentrating particles that have a molecular weight greater than 1 kDa and has found applications in: agricultural drainage water reclamation (Cohen et al., 2001), beverage production (Comb, 1991), desalination and concentration in dye production (Yu et al., 2001) and also in reuse of vapour condensate from milk processing (Chmiel et al., 2000). Because of its unique properties NF is a promising technique for the food industry and for sugar, in particular. So far, in the sugar industry NF has been used as one of the steps in the clarification and concentration of raw juice (Koekoek et al., 1998) and also in the processing of nonsugar compounds (Gyura, 2002). The diafiltration mode of NF was successfully applied as a method for purification of fructo-oligosaccharides (Li et al., 2004).

NF TRANSPORT AND THE INFLUENCE OF OPERATION PARAMETERS ON PROCESS PERFORMANCE

To describe the transport during NF for uncharged solutes as a sugar solution, Nernst-Planck equation is used. This equation correlated the solute flux (j_i) with diffusivity ($D_{i,p}$), and the solute velocity (V), solute concentration in the pore (c_i) and convection factor ($K_{i,c}$) (Eq.2).

$$j_i = -D_{i,p}\frac{dc_i}{dx} + K_{i.c}c_i V \text{ ,} \qquad \text{Eq. 2}$$

NF membranes can be assumed as homogenous or porous (Bowen et al., 1997). If a NF membrane is considered porous, the pores are considered to be only a few times the size of the water molecules. For porous membranes all the variables from Eq. 2 (c_i, V and j_i), are defined in terms of radially averaged quantities. While for homogenous membranes c_i and V are constant at any plane in the x direction.

Even though NF reduces sugar losses, decreases energy consumption and makes it possible to minimize the size of the evaporators during raw juice clarification and concentration, limiting flux phenomena can restrict its applications. The limiting flux phenomena are caused by membrane properties, solute characteristics and process parameters. The effects of these three factors on the membrane separation process have been discussed in detail (Van der Bruggen et al., 1999; Aydogan et al., 1998; Mänttari et al., 2000).

The influence of process parameters has been studied by Koekoek et al. (1998), who carried out long-term nanofiltration of thin juice using spiral and tubular membranes. They observed a decrease in water permeation and sugar retention, as well as an increase in permeate purity after several days of treatment, and a combination of different operational conditions. In addition, Aydogan et al. (1998) reported a separation of glucose and sucrose by nanofiltration. They showed that the increase in the feed rate increased the permeate flux and retention, and minimized the concentration polarisation effect. The increase of working pressure from 32 to 45 bar during grape juice NF doubled the permeability of NF Desal-DS membranes (Ferrarini et al., 2001). As for the temperature, an increase of about 3 % was observed per degree of temperature rise.

Mänttäri et al. (2000) studied the influence of polysaccharides and humic acid on membrane fouling during nanofiltration. In laboratory conditions, they analyzed the parameters that can influence membrane fouling during the nanofiltration of residual water from the pulp and paper industry. Specifically, they considered charge of filtered materials, pH and process velocity as the factors affecting fouling. They concluded that electrostatic attraction depends only on the flow of the substances with an electrical charge, and that the electrostatic repulsion is overcome by hydrophobic interactions, which cause more fouling on the more hydrophobic membrane. The problem of fouling and pre-cleaning as a way of increasing a critical flux was studied by Mänttäri and

Nyström (2000). They determined the influence of operation conditions on filtration efficiency (flux, retention and fouling) during NF of polysaccharides. The authors evaluated a critical flux of Nitto Denko NTR-7450 and Desal5-DK membranes using karaya gum (polymer of galactose, rhamnose and partially acetylated glucoronic acid) and locust bean gum (mannose polymer with galactose branches). The critical flux increased with increase of the velocity and decrease of the concentration. The NTR-7450 membrane showed a significant irreversible fouling compared with the Desal5-DK. This fact is associated to its higher hydrophobicity that promoted the adsorption of the model substance by hydrophobic interaction. The alkaline pre-cleaning improved water fluxes up to 30 %, but its influence on critical flux was insignificant. Moreover, the pre-cleaning improved the water fluxes after filtration compared to pure water fluxes of the un-treated membranes before filtration.

So far, nearly all the NF applications to sugar separation have been carried out using diluted sugar solutions and the aim of the present study was to reconcentrate highly concentrated osmotic solutions. Therefore, the first objective to optimise NF parameters to concentrated osmotic solutions and/or to use NF as a pre-treatment step of osmotic membrane contactors techniques. In order to obtain detailed information about the process, particular attention has been paid to membrane properties and the characterization of operation parameters. First, the influence of the operational conditions (pressure and temperature) on the efficiency of the concentration process was determined; afterwards, membranes were characterized using atomic force microscopy and scanning electron microscopy. As for the feed, only changes in concentration during the experiments were measured, since any additional information about sucrose solutions is widely available. Information about membrane and process parameters presented in this work can be used as a basis for optimizing sugar concentration by NF at low pressures.

1.2.2 MEMBRANE CONTACTORS

Membrane contactors term refers to the configuration with membrane acting as a barrier between two phases permitting mass transfer of the components able to pass through. Membrane may be wetted by one of the phases or be filled with gas or with a liquid which is not miscible with both adjacent phases. Basic configurations of membrane contactors are the following: liquid supported membranes (Figure 5, A),

membrane absorption or desorption (Figure 5, B), membrane distillation (Figure 5, C), osmotic membrane distillation (Figure 5, D) and direct osmosis (Figure 5, E).

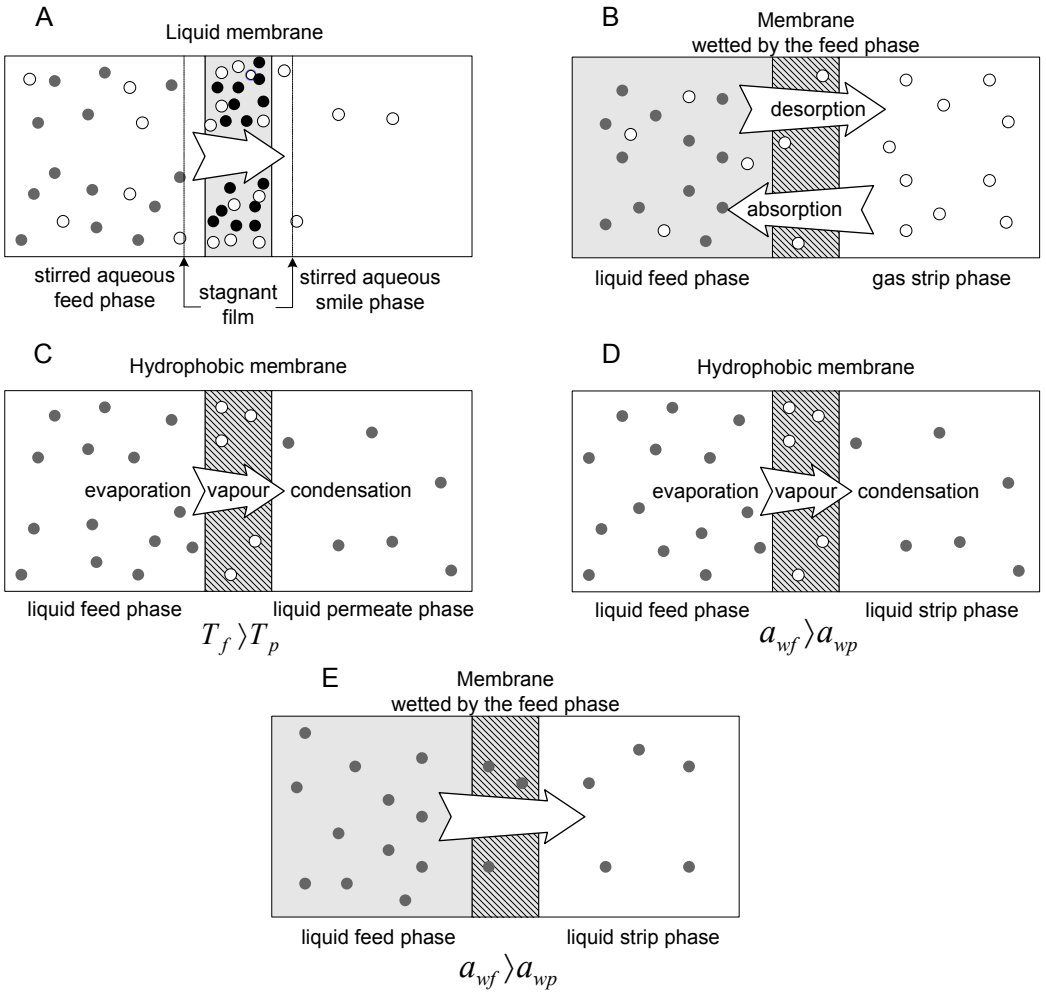

Figure 5. Configurations of membrane contactors: supported liquid membrane (A), membrane absorption and desorption (B), membrane distillation (C), osmotic membrane distillation (D), direct osmosis (E) (adapted from Kunz et al, 1996).

Membrane distillation, osmotic membrane distillation and direct osmosis are the membrane contactors methods that can be used in liquid foods treatment. The driving force for mass transfer in those processes is induced by vapour pressure difference across the membrane (Cath et al., 2004; Kunz et al., 1996). Those three mentioned

processes are reported as possible methods for concentration of sugar solutions and juices. Nene et al. (2002) used membrane distillation to concentrate raw cane-sugar syrup and membrane clarified sugarcane juice, maintaining sugar at 75 ºC and water at 25 ºC. The need of application of high temperatures to run the process is the major restriction of application of membrane distillation in the food industry. Therefore, membrane distillation finds its application mostly in purification and demineralisation of sea water (Tomaszewska, 1999). Osmotic membrane distillation was used to concentrate orange and passionfruit juice resulting in high flavour quality of the concentrated product (Shaw et al., 2001). Direct osmosis was found as a fine technique to improve aroma attributes of red radish concentrate extracts (Rodriguez-Saona, 2001).

In the present study, to reconcentrate solutions from osmotic dehydration, osmotic membrane distillation and direct osmosis were chosen. Membrane distillation was rejected due to possible temperature influence on the solution, temperature polarisation across the membrane and conductive heat loss through the membrane during the process (Cath et al., 2004). Moreover, a comparative study between membrane distillation and osmotic membrane distillation used to concentrate orange juice, revealed the superiority of the last process in both water fluxes and aroma retention (Alves and Coelhoso, 2005). In the referenced work, thermal polarisation during membrane distillation decreased water flux for more than 50 %. No significant temperature change resulted also in an increase of the aroma compounds retention (ethyl butyrate and citral) during osmotic membrane distillation.

Osmotic membrane distillation (OMD) and direct osmosis (DO) performance depends strongly on stripping solution properties. The properties that the stripping solution to be used in OMD/DO should exhibit are: high solubility in water (low water activity), low volatility and viscosity, high superficial tension and non-toxicity.

1.2.3 DIRECT OSMOSIS

First direct osmosis industrial approach was developed by Osmotek Inc. as a pre-treatment step in RO wastewater purification and possible method for liquid food concentration. Nevertheless, the first DO studies concerned grape juice concentration carried out by Popper et al. in 1966. Since early 90´s DO is one of the tested alternatives to thermal food processing, however membrane distillation and osmotic membrane distillation are known better and only scarce information about DO is available.

As is shown in Figure 5 mass transport in DO is promoted by the water activity difference between the feed and the stripping solution of lower water activity. This kind of transport generates high driving force (vapour pressure difference), which is significantly greater than hydraulic forces in pressure driven process. Greater driving force allows higher concentrations for viscous solutions e.g.: sugar solution and juices, what reduces the investment costs.

The membranes used in DO are semi-permeable membranes and usually the same membranes as in RO and NF are used. Those membranes are highly selective, but the diffusion of small amount of stripping solution is unavoidable (Dalla Rosa and Giroux, 2001). Retentions during DO can be increased using an innovative Osmotek, Inc. system with double DO (semi-permeable)/OMD (hydrophobic, microporous) membrane. During the process, water diffuses from the feed side through the semi-permeable membrane, evaporates through the hydrophobic membrane (that provides 100 % theoretical retention) and finally condenses in the stripping solution. This novel system was proposed by Cath et al. (2005) as a pre-treatment step together with OD for wastewater reclamation in space. The final filtration step in that system was RO. DO flux depended strongly on the type of the membrane used, and it ranged from 10 to 25 l/m^2h for cellulose triacetate membrane specifically designed for this process and from 0.5 to 2 l/m^2h for commercially available RO cellulose diacetate/triacetate and polyamide membranes. Water flux increase for the dual DO/OMD process was highly dependent on temperature increase. Taking into account the energy consumption, the proposed three steps method requires 54-108 kJ/l, while the other studied methods i.e. filtration beds with post-treatment oxidation or bioreactor with RO require 198-1332 kJ/l.

Since the membrane during DO is not exposed to the additional pressure, the fouling is very low and only concentration polarisation occurs. Low potential of limiting flux phenomena, low energy consumption, simplicity and reliability are the main DO advantages.

INFLUENCE OF OPERATIONAL PARAMETERS ON DO PROCESS PERFORMANCE

The effect of operational parameters and module configuration was widely studied by Petrotos et al. (1998, 1999), in the investigation about application of DO for tomato juice concentration. The parameters that are important for DO efficiency are:

Stripping and feed solutions characteristics: type, viscosity, concentration, temperature. Petrotos et al. (1998) used NaCl, $CaCl_2$, $Ca(NO_3)_2$, glucose, sucrose and polyethylene glycol (PEG400) as stripping solutions. In their study the initial concentration of tomato juice was 4.3-11.7 ºBrix and the osmotic pressure for the first concentration was 8.7 bar. The characteristics of evaluated stripping solutions (SS), juice flows and the fluxes obtained are presented on Table 6.

Table 6. Experimental conditions during DO of tomato juice (Petrotos et al., 1998).

	NaCl	**$CaCl_2$**	**$Ca(NO_3)_2$**	**glucose**	**sucrose**	**PEG400**
SS flow rate [l/h]	565	554	572	552	570	555
Tomato juice flow rate [l/h]	502	510	498	500	501	504
SS concentration [%(w/w)]	22	29	29	63	58	50
SS viscosity at 25 ºC [cP]	1.9	2.3	2.9	14	40	103
Overall osmotic pressure [bar]	280	548	176	303	134	337
Flux [kg/m^2h]	3.1	2.3	1.8	0.7	0.5	0.4

As can be seen on Table 6, the salts, and especially NaCl, were better stripping solutions than carbohydrates and PEG400. These results might be attributed to the lower viscosity of salts. Lower viscosity of the stripping solution results first in a reduction of external polarisation on the SS side and also implies higher diffusivity what diminishes resistivity of the solute in the membrane backing material lowering internal polarisation.

Naturally, for water treatment by DO other types of SS have to be used. McCutcheon et al. (2005) applied ammonium bicarbonate to extract water from the saline feed.

The increment of SS concentration also affects positively the flux. The higher the SS concentration, the higher the driving force in the system. The opposite effect is noted for the feed solution, since the increase in feed concentration results in lower water flux due to viscosity and osmotic pressure increase. An important issue about feed characteristics in case of fruit and vegetables juices is their pre-treatment. Petrotos et al. (1998) evidenced the 39 % increase if UF treated tomato juice was subjected to DO instead of raw juice.

Regarding temperature change, Petrotos et al. (1998) showed that the increase from 26 to 60 ºC enhanced the permeate flux by 64%. The first effect of temperature increase

is that viscosity is lowered, and the second is the increase in the diffusion coefficients of SS and the feed.

The feed flow rate increase did not show any important effect in permeate flux during DO. The same tendency was observed by Voit el al. (2005) during RO concentration of tomato juice.

Membrane thickness affects strongly the DO process performance. Reducing of membrane supportive layer can increase significantly the permeate flux. This observation is relevant also for other membrane contactor processes as OMD and membrane distillation. In their DO study Petrotos et al. (1998) determine the increase in permeate flux to be exponentially dependant on membrane backing material reduction. In contrast, Beaudry and Lampi (1990) stated the permeate flux is linearly correlated with membrane thickness.

TRANSPORT PHENOMENA IN DIRECT OSMOSIS

During DO water activity gradient induces the diffusion, but as was mentioned before, a very low convective flow promoted by the coupling effects in the solvent flow also occurs. These phenomena are characteristic for RO membranes, normally used during DO. Ghiu et al. (2002) evaluated the salt permeability trough RO membranes when the convective transport is negligible. To explain the mechanisms of solute and solvent transport and separation, the authors applied the preferential sorption capillary flow model. In this model the solute is transported by the diffusion through the pores due to chemical potential difference and the flux (J) is proportional to the concentration difference across the membrane:

$$J_S = (D_{SM} K_S / \delta)(C_{SM} - C_{SF}) \qquad \text{Eq. 3}$$

where: $D_{SM}K_S/\delta$ – is the salt permeability parameter,

D_{SM} – solute diffusion coefficient in the membrane,

K_S – solute partition coefficient between adjacent solution and membrane,

δ – membrane thickness,

C_{SM} – solute concentration in the membrane,

C_{SF} – solute concentration in the feed

The authors concluded that the permeation of the electrolytes with the same cation (NaCl, $CaCl_2$) is controlled by the anion diffusivity and the salts like $MgCl_2$ or $CaCl_2$ interact with the membrane surface charge. A good correlation between electrolytes permeation and their diffusion coefficient in an infinite dilute solution, suggested the unimportance of solute absorption in the membrane in the process of solute-solvent separation.

DO APPLICATIONS AND PROCESS CONFIGURATIONS

The main possible applications of DO are concentration of liquid foods (Petrotos and Lazarides, 2001) and treatment of landfill leachate (Daniels, 1999). To secure high fluxes, the SS should be maintained at constant concentration. If a natural source of SS (sea water) is available, the reconcentration of diluted solution might be unnecessary, (Karode, 2001). Commonly, the SS does not contain any valuable components and the recovery can be carried out be evaporation. The best way of SS recovery would be membrane processes, due to lower energy consumption. Since the stripping solution is usually a salt, Karode et al. (2000) proposed RO as a method for SS recovery. The authors found the feasibility of RO application conditioned by the development of membranes resistant to concentration polarisation.

In the present study the reconcentration of osmotic solution using DO in two modes is evaluated: on-site direct osmosis and off-site direct osmosis. The first mode was developed according to the method proposed by Proimaki and Gekas (2000). In this configuration, reconcentration of the osmotic solution takes place simultaneously to the osmotic dehydration process and the stripping solution is the same as the OS, but more concentrated. In the so called off-site direct osmosis, the concentration takes place by using an external membrane module with the OS and the SS circulating in a counter-current mode.

1.2.4 OSMOTIC MEMBRANE DISTILLATION

Osmotic membrane distillation is known also as osmotic evaporation, membrane evaporation, transmembrane distillation, thermo-pervaporation, isothermal membrane distillation, gas membrane extraction or osmotic concentration by membrane. During osmotic membrane distillation (OMD) microporous, hydrophobic (e.g. PTFE, PP)

membrane is used. Both sides of the porous membrane are in contact with two solutions (usually aqueous) of different water activity, e.g. OD sugar solution and concentrated salt solution. The water activity difference between the two liquid phases translates into a vapour pressure difference across the membrane. This difference induces the three steps mass transfer mechanisms: evaporation at the diluted feed, vapour transport through the membrane pores and finally the vapour condensation at the stripping solution side. Since water transport involves evaporation and condensation, a temperature gradient through the membrane is generated, even if bulk temperatures of both liquids are equal. Therefore, OMD should be considered as mass and heat transfer process, not only a mass transfer as DO. This thermal effect tends to reduce the driving force for water transport (Celere and Gostoli, 2002). Mass transfer and the temperature profile of OMD are presented on Figure 6:

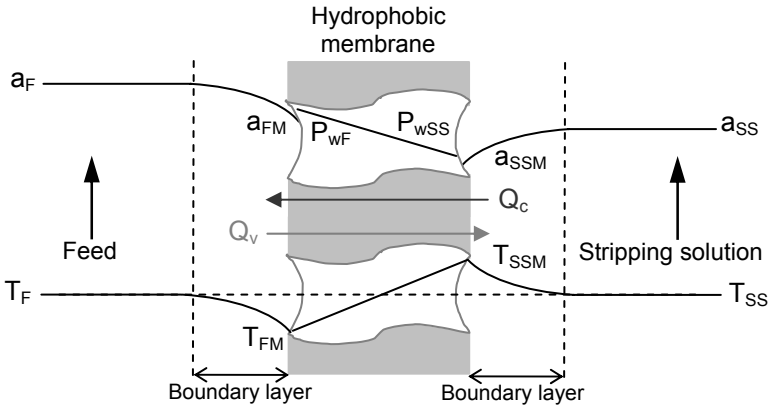

Figure 6. Mass transport and temperature profiles during OMD process in stirred cell.

MASS TRANSFER ASPECTS

Mass flux in OMD can be estimated by diverse models, that is, the Knudsen, Poiseuille, ordinary diffusion or combination of the models (Bui et al., 2005). Practical use of the mentioned models requires detailed knowledge about the process parameters and membrane properties. Limitation of the models makes their application restricted to particular process. In any case, a linear relationship between the transmembrane mass flux (J) and the driving force – the vapour pressure difference, is the common base for all the models (Celere and Gostoli, 2004):

$$J = K_M \frac{P_{wF} - P_{wSS}}{P_{Alm}} \quad \text{Eq. 4}$$

where: K_M – is the membrane mass transfer coefficient,

P_{Alm} – is the logarithmic mean pressure of the air within the pores,

P_{wF} – water vapour pressure at the feed side,

P_{wSS} – water vapour pressure at the sit stripping solution side

P_{Alm} is an important factor at high temperatures or at reduced pressures (Gostoli, 1999) and is neglected by most of the authors.

The overall mass transfer coefficient depends on the membrane morphology, solution concentration, module design, hydrodynamic conditions and temperature; and it can be expressed by Eq. 5 that considers the three resistances for water transport:

$$K = \left(\frac{1}{K_F} + \frac{1}{K_M} + \frac{1}{K_{SS}} \right)^{-1} \quad \text{Eq. 5}$$

where: K_F, K_M, K_{SS} – mass transfer resistance at feed layer, membrane and stripping solution, respectively

If the concentration polarisation is negligible, mass transfer depends only on membrane resistance, so:

$$K = K_M \quad \text{Eq. 6}$$

The water vapour pressures of the feed and stripping solutions are calculated at the fluid membrane interfaces:

$$P_{wX} = P^*_{wX} \times a_{wX} \quad \text{Eq. 7}$$

where: P^*_{wX} – pure water vapour pressure of the feed or stripping solution at the interface,

a_{wX} – water activity of the feed or stripping solution at the interface

If the temperature is considered equal at the both sides of the membranes ($P^*_{wF} = P^*_{wSS} = P^*_w$), thus the in reference to the bulk solution Eq. 4 can be written as:

$$J = KP^*_w \left(a_{wF} - a_{wSS} \right) \quad \text{Eq. 8}$$

The performance of OMD depends strongly on the selection of the low water activity stripping solution (Celere and Gostoli, 2004). Usually, inorganic salts (NaCl, $CaCl_2$, $MgCl_2$, $MgSO_4$) or organic solvents (glycerol, polyglycerol) can be used as stripping solutions.

Like other membrane processes, OMD is affected by concentration polarisation. Concentration in the bulk phase differs strongly form the composition near the membrane interface, due to the water transport across the membrane. In consequence, driving force for mass transfer diminishes and water flux is reduced. Concentration polarisation can be decreased by optimisation of process parameters as stirring or stripping solution properties. Dependence of the individual mass transfer coefficients can be correlated with Sherwood (Sh), Reynolds (Re) and Schmidt (Sc) numbers (Eq. 9 and 10):

$$Sh = \alpha \, \mathrm{Re}^{\beta} \, Sc^{\gamma} \qquad \text{Eq. 9}$$

$$\text{where: } Sh = \frac{k d_h}{D_w}, \qquad \mathrm{Re} = \frac{\rho N d_h^{\,2}}{\mu}, \qquad Sc = \frac{\mu}{\rho D_w} \qquad \text{Eq. 10}$$

where: α, β, γ – are constants;
k – mass transfer coefficient,
d_h – hydraulic diameter,
D_w – diffusion coefficient in water,
ρ – density,
N – cross-flow velocity,
μ – viscosity of the liquid

Alves and Coelhoso (2002) determined the constants: α = 1.63, β = 0.56 and γ = 0.33, using calcium chloride and glycerol as stripping solutions during OMD in stirred cell of similar geometry as the one used in the present study.

The mass transfer coefficient (k) depends on the solution physical properties, and on the hydrodynamic properties of the system. It describes thus, the solute transfer in the liquid phase. The liquid concentration difference near the membrane and in the bulk phase induces a diffusive flow according to Fick´s law, which compensates the convective flow in the opposite direction. A mass balance in the liquid phase can be expressed as (Eq. 11):

$$J_v = k \ln\left(\frac{C_b}{C_m}\right) \text{ and } k = \frac{D_s^M}{\delta} \quad \text{Eq. 11}$$

where: J_v- volume flux,

D_S^M – diffusion coefficient of solute by the membrane,

C_b – stripping solution concentration in the bulk,

C_m – stripping solution concentration in the membrane

THERMAL EFFECT

Heat transfer through the membrane is given by the convective transport ($J\lambda$), and the conductive transport related to the temperature gradient ($h\Delta T$). Therefore, heat flux (Q [W/m^2]) can be written as:

$$Q = h_F\left(T_F - T_{FM}\right) = J_M \lambda - h_M\left(T_{SSM} - T_{FM}\right) = h_{SS}\left(T_{SSM} - T_{SS}\right) \quad \text{Eq. 12}$$

where: J_M – molar vapour flux,

λ – latent heat of vaporisation,

h_F, h_{SS} and h_M – are the heat transfer coefficients of the boundary layers (feed and stripping solution, respectively) and the membrane,

T_F and T_{SS} – are the bulk temperatures of the feed and stripping solution, respectively,

T_{FM} and T_{SSM} – are the temperatures of the feed and the stripping solution near the membrane

If overall heat transfer coefficient (U) is considered:

$$Q = U\left[\frac{J\lambda}{h_M} - \left(T_{SS} - T_F\right)\right] \quad \text{Eq. 13}$$

where $$U = \left(\frac{1}{h_F} + \frac{1}{h_M} + \frac{1}{h_{SS}}\right)^{-1} \quad \text{Eq. 14}$$

Most of the researchers find OMD as a process controlled by mass transport only and neglect the importance of temperature gradient influence on the flux. Nagaraj et al.,

(2005) considered temperature gradient unimportant if plate and frame module is used, due to short contact time between solutions and the membrane. The assumptions made for stirring cell (pure water/NaCl) by Gostoli (1999) indicate that the membrane permeability can decrease theoretically 15 % compared with the experimental values. On the other hand, Courel et al. (2000 B) found out that the high vapour flux of 12 kg/m^2h generated a temperature gradient of 2 ºC inducing 30 % reduction of driving force. Temperature polarisation did not play any important role compared with membrane heat transfer resistance.

MEMBRANE PROPERTIES

The membrane characteristics: porosity, pore size, tortuosity etc. are crucial for OMD efficiency. The possibility of wetting of the hydrophobic microporous membrane and consequent loss of flux and separation performance is the major drawback of OMD. Key criteria to be considered in membrane choice are (Kunz et al., 1996; Romero et al., 2003):

- Porosity – flux is proportional to the membrane porosity, thus, highly porous membrane is recommended.
- Pore size – flux is proportional to radius (r^2 – in Poiseuille model, r – Knudsen model), so pores should be as large as possible.
- Thickness – flux is proportional to the inverse of pore length, therefore, membrane as thin as possible is required.
- Stability – membrane's thickness should assure effective heat transfer with minimum temperature polarisation and adequate stability of the membranes.
- Conductivity – membrane should be as conductive as possible in order to minimise the heat gradient across the membrane.

Mathematically, the effect of membrane properties on diffusive transport of water vapour is described frequently either by Knudsen diffusion or molecular diffusion (Gostoli, 1999). Knudsen diffusion reflects the relation between considerable mean free path and pore size. In this case diffusing molecules collide frequently with pore walls (Eq. 15).

$$K_{MK} = \frac{1}{3}\frac{d_p \varepsilon}{\chi \delta}\left(\frac{8M}{\pi RT}\right)^{0.5} \qquad \text{Eq. 15}$$

where: d_p – pore diameter,
ε – membrane porosity,
χ – tortuosity factor,
δ –membrane thickness

Molecular diffusion is the controlling mechanism for pore size superior respect to the mean molecular free path (Eq.16).

$$K_{MD} = \frac{\varepsilon M}{\chi \delta} \frac{PD}{RT} \qquad \text{Eq. 16}$$

To determine which of the mechanisms is the dominating one, Knudsen number that compares mean molecular free path (l) can be calculated following the equations 17 and 18.

$$K_{Nr} = \frac{l}{2r} \qquad \text{Eq. 17,}$$

$$\text{where} \qquad l = \frac{k_B T}{p\sqrt{2}\pi\sigma^2} \qquad \text{Eq. 18}$$

where: k_B – Boltzman constant,
σ – mean collision diameter [m]

For small pore size, $K_{Nr} \geq 10$ collisions with pore walls are more frequent, therefore Knudsen diffusion is the dominating mechanism. If pore size is relatively big $K_{Nr} \leq 0.01$, more collisions between the molecules occur, thus molecular diffusion is the regulation mechanism. Between the mentioned limit values, both mechanisms take place (Courel et al., 2000 B).

The membrane pore size is also important for the optimal retention of volatile substances. Barbe et al. (1998) evaluated the retention of flavour/fragrance components, finding membranes with relatively large pore size to retain better the organic volatiles than membranes with smaller pore size.

OMD APPLICATION

The OMD allows treating very viscous solutions, e.g. concentrated sugar solutions, and also guarantees gentle operation conditions (low temperature, atmospheric pressure) which are important for food processing. OMD was recommended for fruit juice concentration because of high quality of final product and low capital investment and low energy consumption during the process (Jiao et al., 2004).

Comparing juice concentration carried out with the up to now used pressure driven processes, OMD seems to give better results. Rodrigues et al. (2004) contrasted the efficiency of reverse osmosis and OMD in camu-camu juice concentration. The advantage of RO is the high flux during the concentration (50 kg/m^{2}h), but after all, low concentration was obtained (255 g/kg of TSS containing only 4 % of ascorbic acid). Two step OMD, despite the low flux (10 kg/m^{2}h), allowed to concentrate the juice up to 634 g/kg of TSS, with 10 % of ascorbic acid.

The best way to enhance the fluxes during OMD is by integrating it with other membrane processes. Ultrafiltration applied as grape juice pre-treatment by Bailey et al (2000) resulted in an appreciable OMD flux increment. An additional advantage of the UF pre-treatment is the juice surface tension reduction, with a consequent reduction in the tendency for membrane to wet-out. Cisse et al. (2005) coupled two step OMD and microfiltration to produce orange juice. The final product quality was high and similar to the freshly squeezed one. In order to maintain the aromatic bouquet of the juice, the authors recommended the membrane pre-conditioning with the juice and cold regeneration of the stripping solution.

To avoid two step OMD and thus to reduce the concentration time, Cassano et al. (2003) proposed the OMD as the final filtration step proceeded by ultrafiltration and reverse osmosis. Like in the previously mentioned investigations, the quality of the final product was much better than the quality of the product obtained with traditional thermal processes. Both aroma and colour were similar to those of the fresh juice, and also the total antioxidant activity was maintained. Very high juice concentration (from 250-200 up to 600-660 g/kg of TSS) achieved during the OMD was another advantage of this process. The lack of membrane pre-treatment can diminish significantly final juice concentration in case of fruit with high insoluble solids content. Possible application of pre-treatment can reduce OMD operation time and improved product quality.

Minimal flavour and fragrance losses during OMD make it useful to produce low-alcohol beverages. OMD permits a selective removal of single volatile solute from aqueous solution (e.g.: ethanol from wine and other ferments) using water as extracting solvent (Hogan et al., 1998).

OMD is also a promising method in concentration of oily substances i.e. essential oils. However, the concentration of oily feeds is possible only after increasing the membrane hydrophobicity. So far, with the purpose of fulfilling this objective membrane coating with hydrogels has been performed. Poly(vinyl alcohol) coating (Mansouri and Fane, 1999) stabilized the membrane and did not affect the flux during the 24 h concentration of 0.2, 0.5 and 1 % (w/w) limonene. Xu et al. (2005) covered the membranes with alginic acid-silica hydrogel gaining in membrane stability and detecting a 10 % decrease in water flux for treated and un-treated membranes. The authors did not notice any wetting after processing 1.2 % (w/w) orange oil for 72 h. In both cases, the un-treated membrane was immediately damaged during concentration of 0.2 % (w/w) limonene and orange oil, respectively.

Flux in OMD can be enhanced by application of acoustic fields. Narayan et al. (2002) applied ultrasounds in order to increase water flux during sugarcane juice OMD with 5 M NaCl and 5.3 M $CaCl_2$ as stripping solutions. After coupling the acoustic transducer to the membrane cell, the flux increased from 0.51 to 0.73 and from 0.81 to 0.94 l/m^2h for NaCl and $CaCl_2$, respectively.

2 OBJECTIVES

The main objective of the present study was to evaluate the use of membrane separation techniques to reconcentrate spent solutions from the osmotic dehydration of fruits. In order to fulfil the main objective, several milestones had to be reached:

- An osmotic dehydration process had to be selected that would generate actual osmotic solutions and fruit control samples, since it is crucial to investigate the effect of reconcentrated osmotic solutions on the chemical, physical and sensory properties of fruits.
- Suitable membrane techniques had to be selected to treat highly viscous sucrose solutions.
- Appropriate experimental set-ups had to be designed and built up to process and reconcentrate osmotic solutions.
- The following aspects of the performance of each selected membrane process had to be evaluated: the final degree of reconcentration, water fluxes, solute transport, membrane fouling and effect of concentration polarisation.

3 MATERIALS AND METHODS

3.1 OSMOTIC DEHYDRATION

3.1.1 APPLE SAMPLES AND OSMOTIC DEHYDRATION SOLUTION

As raw material for the osmotic dehydration (OD), apples (*Malus domestica Borkh*) of the *Granny Smith* variety were selected because they are resistant to oxidation and have a high nutritional value and because of their aroma and all-year-round availability. The composition of *Granny Smith* apples is detailed in Table 7.

Table 7. Chemical composition of *Granny Smith* apples. Basic composition (Thomai et al., 1998); mineral levels (Cunningham et al., 2001).

Basic composition				**Mineral levels [mg/100 g]**					
Soluble Solids [%]	Titrable acidity [%]	Starch Index	Internal Ethylene [ppm]	Potassium	Sodium	Calcium	Magnesium	Iron	Zinc
12.35	0.84	4.18	0.37	120	2	5	5	0.1	0.1

A comparison of the polyphenol oxidase content (enzyme responsible for browning) of several varieties of apples is shown in Table 8.

Table 8. Relative polyphenol oxidase (PPO) in different varieties of apples (Janovitz-Klapp et al., 1989).

Apple variety	**Relative PPO activity**	
	Peel	**Cortex**
Red Delicious	100	100
Golden Delicious	33	30
McIntosh	46	80
Fuji	57	71
Gala	30	48
Granny Smith	**43**	**73**
Jonagold	43	43
Elstar	10	20

Apples of uniform quality were purchased at the local market and stored at 8ºC. Depending on the season, the apples were from France and Italy (January-September) or Chile (October-December).

Since the quality of the osmodehydrated fruit can be altered by enzymatic browning, this was controlled by adding 1 % ascorbic acid to the osmotic solution. Because of its reducing properties and pH-lowering ability, ascorbic acid is the most common anti-browning agent used (Pointing et al., 1972). It has a direct effect on polyphenol oxidase and inverts the browning reaction, reducing the o-benzoquinones back to o-diphenols (Whitaker, 1994). Harmlessness and compatibility with sample taste were also important in the selection of ascorbic acid but the decisive factor was its positive influence on human health (Giménez et al., 2002).

As sample browning can also be strongly affected by cutting conditions (Bolin et al., 1977), the apples were cut with special knifes that were sharpened every day. To prepare the samples for OD treatment, the apples were peeled, cored and cut into 1 cm^3 pieces. The ratio between the weight of the apples and the volume of the osmotic solution was 1: 25. This high ratio was chosen to ensure that the volume of the osmotic solution was high enough for reconcentration experiments.

The osmotic solution was a sucrose hypertonic solution. As with all chemicals used in food technology, the decisive factor for this choice was the efficiency of sucrose and the fact that it has no effect on human health. The initial concentrations of the osmotic solutions were 40, 50 and 60 ºBrix. A sucrose concentration of under 40 ºBrix provides a low driving force for fruit osmotic dehydration, while a sucrose concentration of over 60 ºBrix can be unstable and crystallize.

3.1.2 EXPERIMENTAL SET-UP

The OD experimental set-up was designed according to the specifications for OD equipment design described by Marouzé et al., 2001 and consisted of two parts: a basket to allocate the apples (Figure 7 A) and a vessel to be filled with osmotic solution (Figure 7 B). During the experiments, the OD set-up was placed on a magnetic stirrer. This set-up was designed in our laboratory and made from methacrylate and stainless steel.

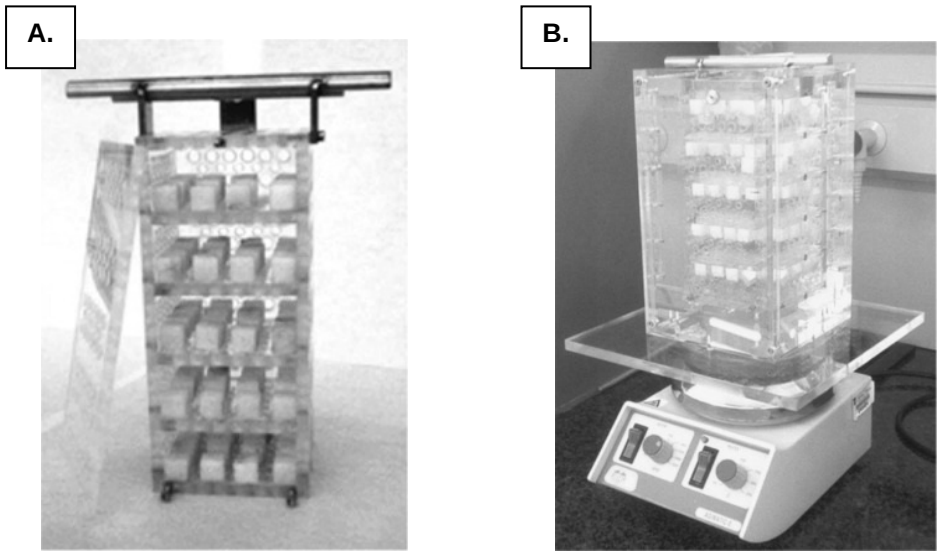

Figure 7. OD basket (A) and vessel with the osmotic solution (B) used during experiments.

The basket consisted of 5 shelves on which 16 apple squares were placed without being in contact with each other. Contact with the osmotic solution was guaranteed by the height of the shelves and the cavities in all the walls of the basket and the shelves. The size of the basket was (21 x 7 x 7) cm. The size of the vessel was (23.5 x 14 x 14) cm and this contained 2.7 l of osmotic solution. The stability of the set-up during stirring was assured by the vessel's base size, which was (25 x 25) cm.

3.1.3 IMPREGNATION-DEHYDRATION TREATMENT

Apple cubes were weighed and placed in the OD basket (Figure 7, A). The total weight of the apples was 115.5 ± 0.5 g. The prepared basket was then submerged in the osmotic hypertonic solution (Figure 7, B). During the experiment, the temperature and stirring rate were constantly controlled and the vessel was covered to minimize deterioration of the apples due to light.

The aim of the first experiments was to determine the optimum time and solution concentration to apply in the OD experiments to generate a osmotic solution for reconcentration. To select the minimum operation time required for maximum

dehydration without solute gain, OD experiments were carried out for 1, 1.5, 2, 2.5, 3, 3.5 and 4 hours.

After OD treatment, the apple cubes were flushed with deionised water to eliminate the sugar that had accumulated on their surface, blotted with absorbing paper and weighed. Part of the apples (~ 20 %) was then separated to check water activity. With the rest of the apples, water loss, weight reduction and solute gain were determined following official AOAC method 920.151. According to this method, the apples were first dried in the electric oven (UE 300, Memmert) for 12 h at 55 ºC and then in a vacuum dryer (Vaciotem, J. P. Selecta) at 70 ºC for 12 h. Dry apples were weighed for the final time, analyzed with a hygrometer and left in sealed bags for sensory analysis. After and before the experiment apples and osmotic solution were characterised, the details are described in the next section.

Consecutive steps of OD treatment are presented in Figure 8. All experiments were run in duplicate and sample analysis was done in triplicate.

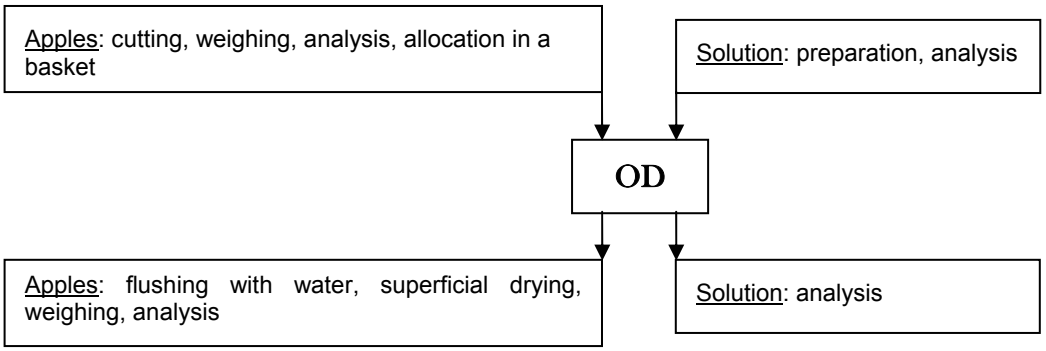

Figure 8. Scheme of OD process with subsequent steps.

3.1.4 ANALYTICAL METHODS

SOLUTION CHARACTERIZATION BEFORE AND AFTER OD

- Total sugar content—expressed in Brix degrees (total soluble solids in 100 g of water)—was measured with a refractometer ABBE Digital Zuzi Model 315. Before each measurement, the precision of the results was verified with standard 60±0.2 and 79.7±0.2 ºBrix solutions. All measurements were taken at a constant temperature of 20 ºC.

- pH was measured with pH-meter Basic 20 Crison in order to evaluate malic acid transfer from the apples to the osmotic solution and possible impregnation of the apples with ascorbic acid.
- Colour was measured using a CECIL 2021 series 2000 spectrophotometer by reading absorbance at 420 nm. This allowed to check the extent of the dilution of osmotic solution.

APPLE CHARACTERIZATION BEFORE AND AFTER OD TREATMENT

- Water activity (described in paragraph 3.1.1) was obtained using a hygrometer Novasina.
- Water loss, weight reduction and solid gain were calculated from the following equations (19 – 22) (Moreira and Sereno, 2003):

$$\Delta M = \frac{m_{fin} - m_{ini}}{m_{fin}} \times 100 \qquad \text{Eq. 19}$$

$$WR = \frac{m_{ini} - m_{fin}}{m_{ini}} \times 100 \qquad \text{Eq. 20}$$

$$SG = \frac{m_{sfin} - m_{\sin}}{m_{ini}} \times 100 \qquad \text{Eq. 21}$$

$$WL = WR + SG \qquad \text{Eq. 22}$$

where: Δ M- mass change [%],
WR - weight reduction [%],
SG - solid gain [%],
WL -water loss [%],
m_{ini} - initial sample weight [g],
m_{fin} - final sample weight,
m_{sfin} - solids after osmosis [g],
m_{sin} - solids before osmosis [g]

Moisture content in the apple samples was determined gravimetrically. The moisture content of a product in dry base can be defined as the percentage weight of water in

relation to the dry weight of the product. To analyze moisture content, apple samples of weight similar to the total weight of OD-treated apples were dried according to the AOAC method 920.151 (the same as for OD-treated apples). The steps taken to measure moisture content are shown in Figure 9. Moisture content was measured in duplicate.

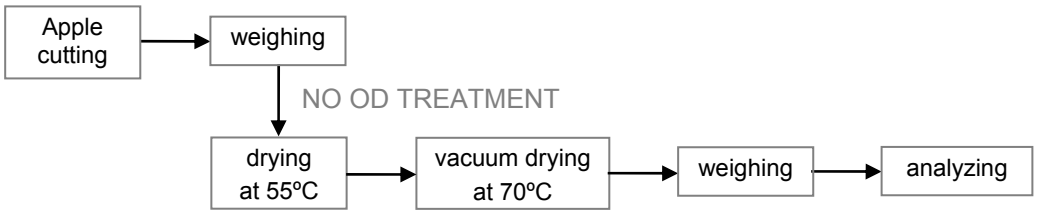

Figure 9. Scheme of moisture content measurements.

3.2 NANOFILTRATION

3.2.1 MEMBRANES AND EXPERIMENTAL SET-UP

Two tubular membranes (AFC80 from PCI Membranes and MPT-34 from Koch Membranes) and three flat sheet membranes (Desal5-DK from GE Osmonics, MPT-43 from Koch Membranes and NFT-50 from Danish Desalination Systems) were used. The main properties and characteristics of the membranes are listed in Table 9. Tubular membranes were used to analyze how temperature and pressure affected sucrose reconcentration for different initial sugar concentrations. The flat sheet membranes, on the other hand, made it possible to determine surface changes produced by the sugar deposition after the experiments.

Table 9. Main properties of the nanofiltration membranes.

Membrane	Working pH*	Maximum T [°C]*	Maximum P [bar]*	Retention [%] or maximum molecular mass [MM] retained*
AFC80	1.5- 10.5	70	60	80% NaCl
MPT/F-34	0- 14	80	50	MM 200
Desal5-DK	1- 11.5	50	50	<50% NaCl, 98% $MgSO_4$
NFT-50	1- 11.5	50	55	≥99% $MgSO_4$

*Data provided by the manufacturer

The active filtration area was 21.85 and 6.1×10^{-3} m^2 for the tubular and flat sheet membranes, respectively. The filtration layer of AFC80, MPT-34, MPF-34 and Desal5-DK membranes was made from polyamide which indicates a negative surface charge, other layers of Desal5-DK were made from polyester (Mänttäri and Nyström, 2000).

All the filtration runs were carried out in the cross-flow filtration plant shown in Figure 10.

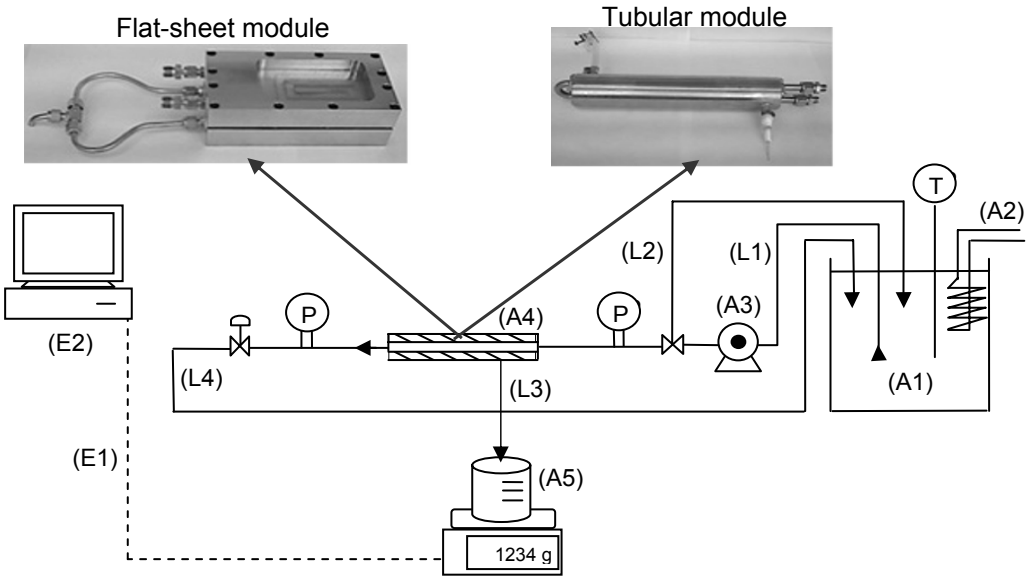

Figure 10. Nanofiltration pilot plant.

A1- feed reservoir; A2- cooling system; A3- membrane pump; A4- nanofiltration module; A5- permeate reservoir; A6- balance; E1- electrical connection; E2- personal computer; L1- feed; L2- by pass; L3- permeate; L- retentate; P- manometer; T- thermometer

The plant was designed to operate either with a flat module (designed in our laboratory) or a tubular B1 module by PCI Membranes.

3.2.2 NANOFILTRATION EXPERIMENTS

All membranes used in this study were treated before use with 0.2 % (v/v) solution of HNO_3 and 0.2 % (w/w) solution of NaOH. All solutions (pre-treatment, rinsing and experimental) were prepared with Milli-Q water (18.2 μScm). Sucrose solutions (5, 10,

15 and 20 ºBrix) were concentrated using nanofiltration at 8, 10 and 12 bar and 25, 30 and 35 ºC. The properties of the sucrose solutions are listed in Table 10.

Table 10. Properties of sucrose solutions (Weast, 1989).

Concentration [^{o}Brix]	Concentration [g/l]	Density [g/cm^3]	Viscosity [10^{-3} Pa×s]
5	50.9	1.018	1.144
10	103.8	1.038	1.333
15	158.9	1.059	1.589
20	216.2	1.081	1.941

Cross-flow nanofiltration experiments lasted for 3 h. Before and after the experiments, the clean water flux was determined for each membrane, so reversible fouling could also be determined. All experiments were run in duplicate, and samples of permeate and retentate were taken every half hour. Pressure and temperature were controlled and kept constant during the experiment. To reduce concentration polarisation, the maximum flow was applied. The scheme of the experimental procedure is shown in Figure 11.

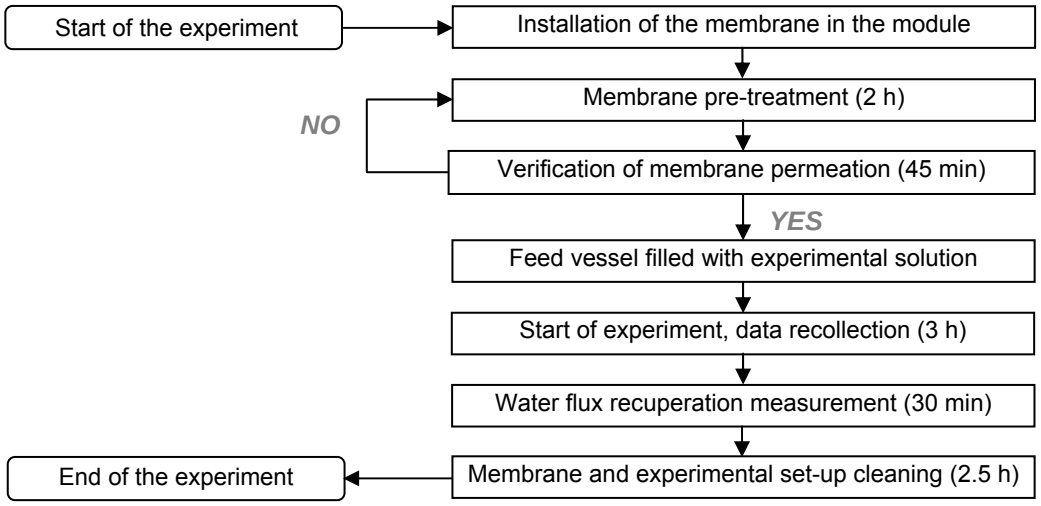

Figure 11. Flow chart of nanofiltration experiments.

Each membrane was re-used between 3 and 10 times depending on the initial flux recovery after the cleaning procedure.

3.2.3 PEAR AND APPLE JUICE

Apart from sucrose solutions, fruit juices were nanofiltrated following the same procedure as for sucrose solutions. Apple and pear concentrates were used to prepare fruit juice solutions. The properties of the concentrates are listed in Table 11. The initial concentration of the fruit juice solutions was fixed at 10 °Brix, because this value is similar to that of industrial juices before concentration.

Table 11. Properties of pear and apple concentrates.

Property	**Pear Juice***	**Apple Juice***
Concentration [°Brix]	65 – 71	65 – 71
pH	3.2 – 4.3	1.6 – 3.8
Color (440 nm)	55 (±15) %	min. 45 %
Acids content (w/w)	1.6 – 2.5 %	1.0 – 2.5 %
Yeast and molds	Less than 100 cfu/g	Less than 100 cfu/g
Aerobic Microorganisms	Less than 2000 cfu/g	Less than 1000 cfu/g
Mycotoxins	Irreducible minimum	Irreducible minimum

*Data provided by the manufacturer- Indu Lérida S.A.

3.2.4 SAMPLE ANALYSIS

Sugar concentration was measured with a refractometer (ABBE Digital Zuzi Model 315). To characterize the membranes AFM and SEM were used.

3.2.5 PARAMETERS USED TO EVALUATE NANOFILTRATION PERFORMANCE

To evaluate the efficiency of the nanofiltration process, concentration degree, retention of sucrose, and permeate fluxes were determined. The concentration degree (CD) was calculated from Eq. 23, where (C_{FR}) is the final sugar concentration in the retentate and (C_{IR}) is the initial sugar concentration in the retentate.

$$CD = \frac{C_{FR}}{C_{IR}} \qquad \text{Eq. 23}$$

Sugar retention (R) is calculated from Eq. 24, where C_p is the concentration of permeate and C_R is the concentration of retentate (feed).

$$R = \left(1 - \frac{C_P}{C_R}\right) \times 100\ \% \qquad \text{Eq. 24}$$

Permeate fluxes (J) depended on A_m (membrane area), m_P (permeate mass) and ρ_P (permeate density) as follows (Eq. 25).

$$J = \frac{m_P / \rho_P}{A_m \times t} = \left[\, l / m^2 h = LMH \, \right] \qquad \text{Eq. 25}$$

To estimate the sucrose deposition into/onto the membrane, the yield of irreversible fouling (IF) was calculated. IF (Eq. 26), defined by Mänttäri and Nyström (2000), is given by the relation between the values for pure water flux observed before and after the experiment.

$$\text{IF} = \frac{PWF_b - PWF_a}{PWF_b} \times 100\,\% \qquad \text{Eq. 26}$$

where PWF_b is the pure water flux before the experiment and PWF_a is the pure water flux after the experiment.

3.3 OSMOTIC MEMBRANE DISTILLATION

3.3.1 MEMBRANES AND EXPERIMENTAL SET-UP

The OMD experimental set-up was a methacrylate cell with two symmetrical compartments. The volume of both compartments was 140 ml. The stripping solution and the sucrose solution in OMD cell were separated by a hydrophobic, symmetric, polytetrafluoroethylene membrane (Type 11806, Sartorius) with a nominal pore size of 0.45 μm and thickness of approximately 80 μm. This membrane is resistant to high temperatures (up to 200 ºC), presents very good chemical compatibility (with acids, bases and solvents) and is permanently hydrophobic. The membrane active area was 1.25×10^{-3} m^2. Sealed OMD cell was connected to a feed tank on one side and to a calibrated glass pipette on the other (Figure 12).

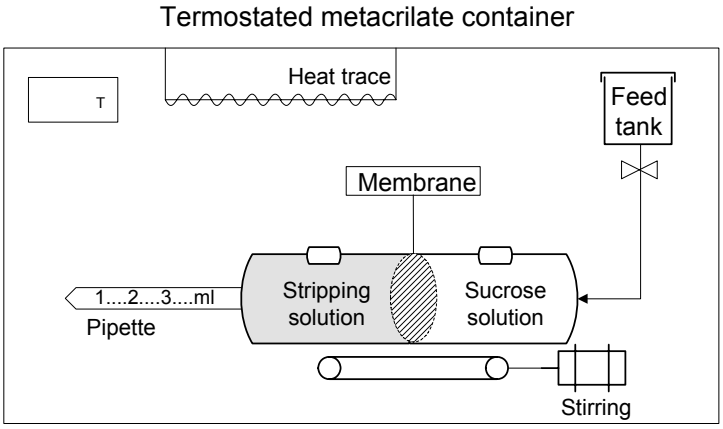

Figure 12. Experimental set-up used during osmotic membrane distillation experiments.

Both compartments were hermetically sealed, so the volume of solution passing through the pipette was equal to the volume of water transferred through the membrane from the sucrose solution to the stripping solution.

Both solutions were constantly agitated at 400 rpm. The OMD set-up was placed inside a methacrylate container and maintained at a temperature of 35 ^{o}C. The experimental set-up was designed and built at Mikołaj Kopernik University, Toruń, Poland.

3.3.2 EXPERIMENTAL PROCEDURE

The experiments lasted 3 h and water flux was measured throughout the entire run. During the first two hours of the experiments, water fluxes were measured continuously and during the last hour they were measured every 20 minutes.

$CaCl_2$ (POCH, Poland) and NaCl (Standard, Poland) were chosen as stripping solutions. The initial concentration of the stripping solutions was 50 and 24.6 % (w/w) for $CaCl_2$ and NaCl, respectively. The chosen concentrations guaranteed a high driving force. At 50 % (w/w) concentration, the $CaCl_2$ solution presented very low water activity. At higher concentrations the decrease in water activity was negligible and the viscosity increased significantly (Figure 13). The NaCl concentration was close to the saturation point (26.4 % w/w), its viscosity is very low, but water activity is much higher than the water activity of $CaCl_2$ (Figure 14).

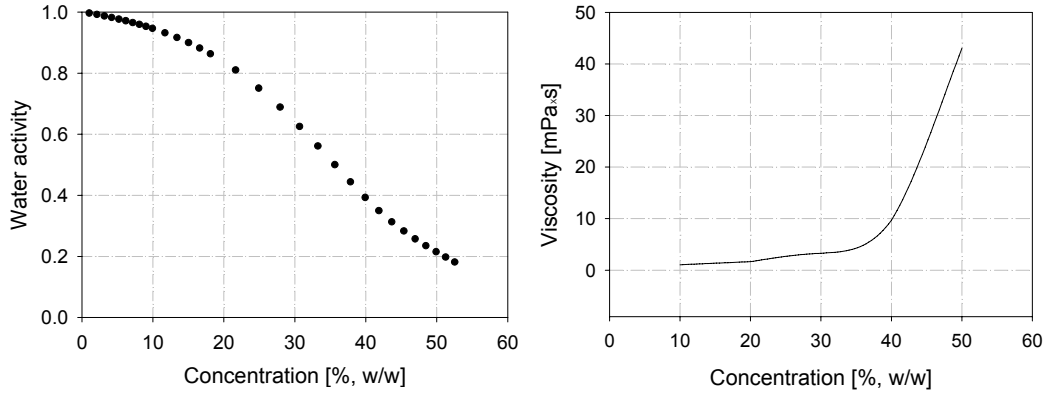

Figure 13. The relation between Calcium chloride concentration [%, w/w], water activity (25 ºC) and viscosity (35 ºC) (Robinson and Stokes, 1959).

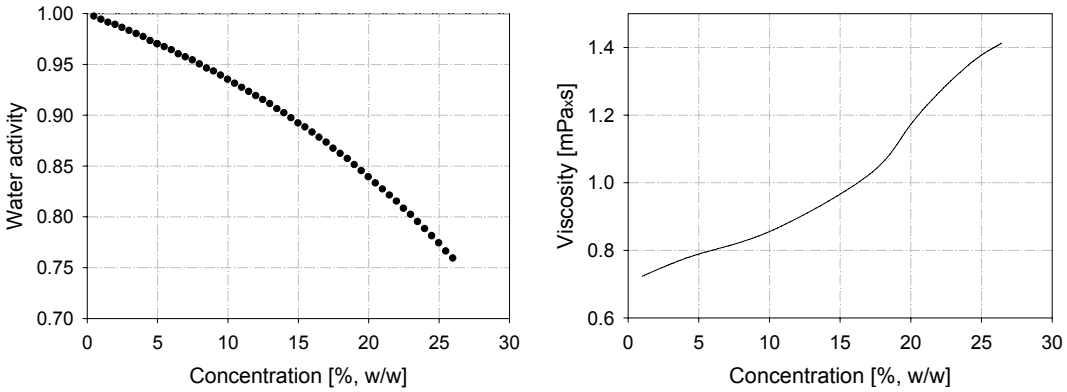

Figure 14. The relation between Sodium chloride concentration [%, w/w], water activity (15-50 ºC) and viscosity (35 ºC) (Keim et al., 1999).

After analysing the water fluxes obtained with both stripping solutions, $CaCl_2$ was used to reconcentrate sucrose solutions obtained from the apple OD treatments. The OD process was carried out as described before and the operation time was 3.5 h for 40 and 50 ºBrix sucrose solutions and 3 h for the 60 ºBrix solution. The OD was performed at

small-scale set-up (Figure 15), which kept all the characteristics of the experimental set-up described in section 3.1.2.

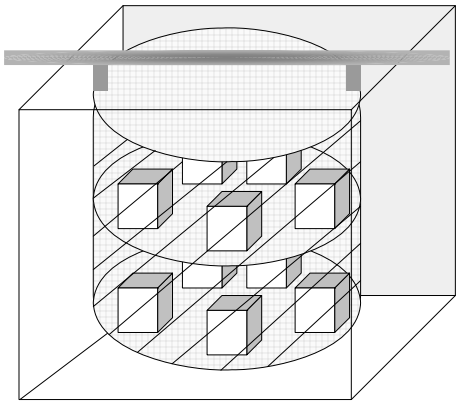

Figure 15. Small-scale osmotic dehydration set-up used to obtain the OS for OMD.

The properties of the stripping solutions and sucrose solutions are listed below in Table 12.

Table 12. Properties of sucrose (Keim et al., 1999, AvH Association, 1997), $CaCl_2$ and NaCl (Robinson and Stokes, 1959).

	Sucrose				**$CaCl_2$**	**NaCl**
Concentration [ºBrix]	30	40	50	60	-----	-----
Concentration [% (w/w)]	30	40	50	60	50	24.60
Dynamic viscosity [mPa×s] 35ºC	2.1	3.8	8.4	26.3	43.02	1.3
Osmotic pressure [bar] º25C	32	51	82	131	2121	356
Water activity [25ºC]	0.971	0.955	0.936	0.898	0.214	0.772

The presence of sucrose and reducing sugars in the stripping solution was analyzed using analytical assay (GAB Sistemática Analítica S. L., Spain). The presence of $CaCl_2$ and NaCl was checked in sucrose and stripping solutions using complexometric titration with EDTA solution and a potentiometric method, respectively (Manual de Análisis y Control de Vinos y Alcoholes). Sugar concentration was measured with a refractometer

(RL1, PZO Poland). All experiments were run in duplicate and the sample analysis was done in triplicate. For each experiment a new membrane was used.

3.4 OFF-SITE DIRECT OSMOSIS

3.4.1 PRELIMINARY STUDIES FOR SELECTION OF STRIPPING SOLUTION AND MEMBRANE CONFIGURATION

As a first step to carry out off-site direct osmosis, small-scale studies about membrane retention, coordination and the effect of SS concentration were performed. In these studies small methacrylate modules were used. The modules consisted of two compartments of similar size, with membranes placed between them (Figure 16). The volumes of SS and feed were 120 ml and the active membrane area was 13.5×10^{-3} m^2. During the experiments different concentrations of NaCl as SS were applied and the membrane used was Desal5-DK.

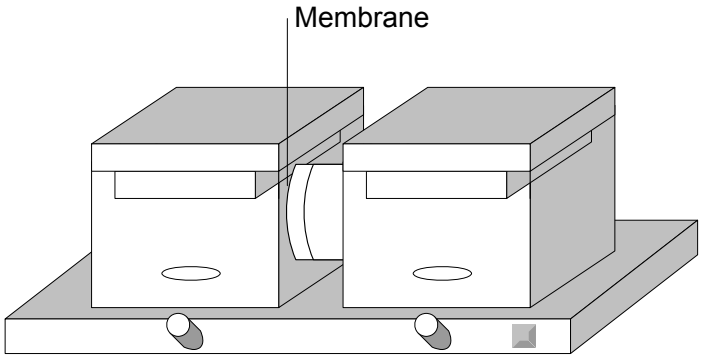

Figure 16. Experimental set-up to study the membrane coordination and to adjust the SS concentration.

3.4.2 MEMBRANES AND EXPERIMENTAL SET-UP

To check the relation between water transport and membrane type, membranes of various densities, thicknesses and configurations were used. The experiments were carried out using two flat sheet membranes (Desal5-DK, GE Osmonics and MPF-34, Koch Membrane) and two tubular membranes (AFC99, PCI Membrane and MPT-34,

Koch Membrane). The MPT-34, MPF-34 and Desal5-DK membranes are NF membranes, the most selective of which is Desal5-DK. The AFC99 membrane is an RO membrane with 99 % rejection of NaCl. The properties of the other NF membranes are listed in Table 9. The experimental set-up used is presented on Figure 17.

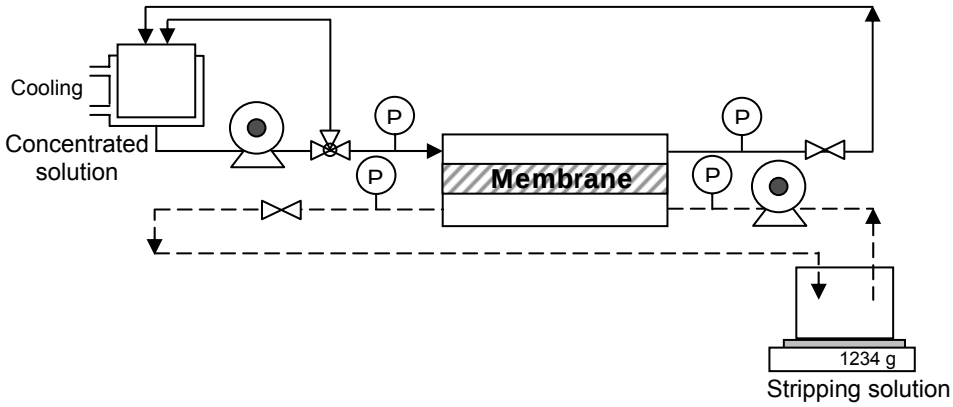

Figure 17. Off-site direct osmosis set-up (solid line- concentrated solution, scattered line- stripping solution).

3.4.3 EXPERIMENTAL PROCEDURE

The solutions were prepared from commercially available sucrose and the concentrations tested were 5, 20, 40, 50, 55 and 60 ºBrix (with osmotic pressures of 4.46, 20.73, 49.78, 82.15, 102.17 and 125.95 bar, respectively). As stripping solution, 25.0 % (w/w) NaCl (JTBaker) was chosen because of its high osmotic pressure (356.89 bar) and low dynamic viscosity (1.33 mPa×s) (Petrotos et al., 1998). The fact that it has no effect on human health was also important. A high NaCl concentration, close to the saturation point (26.4 % w/w), guarantees a high osmotic pressure gradient. Experiments lasted for 3 h at a constant temperature of 35 ºC for the sugar solution and 29 ºC for the stripping solution. The volume ratio between the sugar and stripping solution was 1:2.4 to prevent the stripping solution from diluting. Both solutions were covered to restrain possible evaporation.

After the experiments with sucrose solutions, osmotic solutions of 40 and 50 ºBrix were reconcentrated following the same procedure as for sucrose solutions.

At the end of the experiments, the concentrations of salt and reducing sugars were measured in the sugar solution, and the stripping solution was analysed to verify the presence of reducing sugars and sucrose. Sucrose and reducing sugars were analyzed by an analytic assay (GAB Sistemática Analítica S. L., Spain) and the concentration of chlorine ions was checked using a potentiometric method (Manual de Análisis y Control de Vinos y Alcoholes). All experiments were run in duplicate and the sample analysis was done in triplicate. Tubular membranes were re-used for several experiments applying cleaning cycles and flat-sheet membranes were used only once.

3.5 ON-SITE DIRECT OSMOSIS

3.5.1 MEMBRANES AND EXPERIMENTAL SET-UP

Experimental set-up for on-site direct osmosis consisted of a basket (the same as for OD) (Figure 7 A), a membrane support vessel and a methacrylate bath (Figure 18).

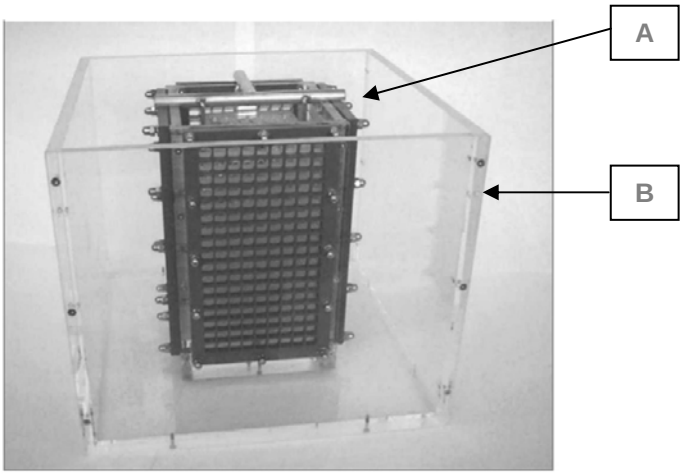

Figure 18. On-site direct osmosis equipment. A- membrane support vessel with the OD basket inside, B- methacrylate bath.

In each experiment two sucrose solutions prepared from commercially available sucrose were used: osmotic solution (40 or 50 ºBrix) for vessel A; and a reconcentration solution (more concentrated solution (60 or 68 ºBrix)) for vessel B. Both solutions were

separated by a hydrophilic (Durapore, Millipore) membrane with nominal cut-off 0.22 μm or Desal5-DK membrane described in section 3.2.1. The microfiltration, Durapore membrane made from polyvinylidene fluoride (PVDF) provides a high flow rate and throughput, low extractables and particle shedding, low protein adsorption, and broad chemical compatibility. The total active membrane area was 0.067 m^2. To prevent enzymatic browning, ascorbic acid was added to both solutions.

A schematic representation of the experimental set-up used for on-site direct osmosis, showing water and solute transport, is shown in detail in Figure 19.

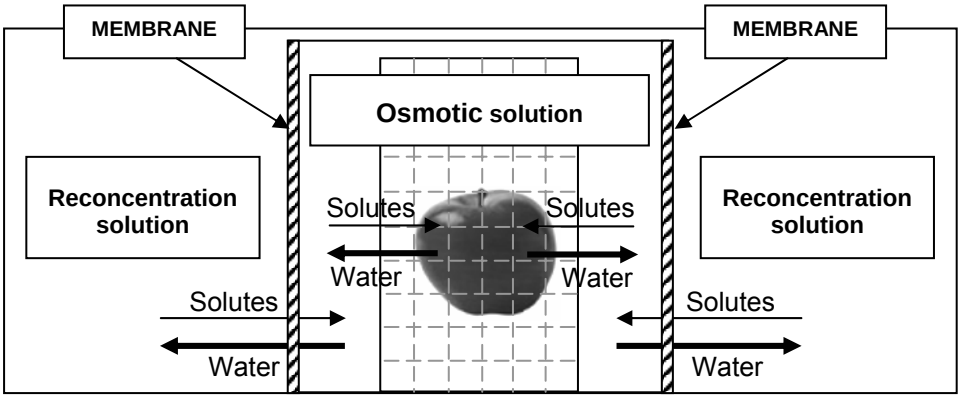

Figure 19. Scheme of the reconcentration system of osmotic solution by on-site direct osmosis.

Both the osmotic and the reconcentration solutions were stirred continuously. The osmotic solution was stirred with magnetic stirrer at the same rate as during osmotic dehydration experiments, and the reconcentration solution was stirred with a homogenizer immersed in the solution.

3.5.2 EXPERIMENTAL PROCEDURE

Once the solutions were prepared and placed in the vessel; the apple samples were conditioned for OD treatment, as explained previously (section 3.1.3); and placed in the OD basket, which was introduced into the vessel that contained the osmotic solution and new membranes. After the first OD experiments, the OD time was fixed at 3.5 h (section 4.1), since the apples presented the maximum water loss without solid gain for solutions of 40 and 50 ºBrix. Experiments were run under ambient temperature, which was 25±2 ºC.

To simulate the continuous industrial process, the osmotic dehydration of apples was run in cycles in which the osmotic solution was reused. Each cycle consisted of four consecutive OD processes in which a fresh apple batch was used, and the osmotic solution was maintained throughout the cycle (Figure 20).

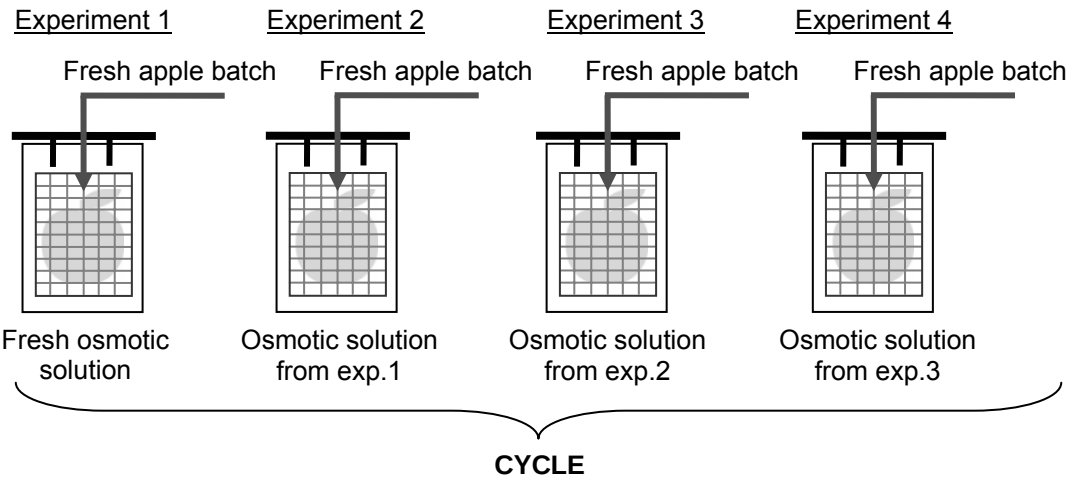

Figure 20. Graphic representation of osmotic dehydration during the on-site osmosis experiments.

Before the experiments the membranes were dampened: the Durapore membrane with Milli-Q water only and Desal5-DK by ultrasonication during 15 s (ultrasonication over 30 s tends to damage the membrane). Before each cycle the vessel was left with Milli-Q water for 30 min in order to check its hermeticity. To reduce evaporation of the solutions, the experimental set-up was kept covered. Bulk temperature was monitored throughout the experiment. The ratio between apples and osmotic solution was 1:26, which was close to the ratio of the OD experiments without reconcentration. The difference resulted from the module design. The initial volume of the reconcentration solution was 5510 ml. The samples (apples and both solutions) were analysed following the methods described in section 3.1.4. The samples of the solutions for colour analysis were filtered using cellulose filters to eliminate the apple pieces. All experiments were run in duplicate and sample analysis was done in triplicate.

3.6 MEMBRANE CHARACTERISATION

The topology of the membranes before and after nanofiltration was verified using AFM (Atomic Force Microscopy) (Nanoscope III, tapping mode). The morphology of the membranes was determined by SEM (Scanning Electron Microscopy) (JSM-6400), which also made it possible to measure the thickness of the membrane layers in some cases. The samples for SEM analysis were dried by displacing water with alcohol. The AFM and SEM samples were cut from the central part of the membranes. Both microscopic techniques were also applied to evaluate whether the membrane cleaning procedures were efficient. The AFM measurements were performed with the assistance of the Group of Thermodynamics from the University of Valladolid.

Other membrane properties: contact angle, zeta potential and the chemical character of the separation layer, were tested at the Technical University of Lappeenranta (Finland). The membranes tested were flat-sheet (Desal5-DK, MPF-34) and tubular (MPT-34 y AFC80). For the flat-sheet membranes, all the measurements mentioned were carried out, while for the tubular membranes only zeta potential was measured, because the other two measurements require a flat, smooth surface.

Contact angle measurements were performed using Sessile Drop and Dynamic Wilhelmy plate methods. The former is a static, optical contact angle method. The latter calculates an average advancing and receding contact angle. Each measurement was repeated 20 times. The contact angle apparatus was designed at the Technical University of Lappeenranta.

Membrane zeta potential was measured on the surface and inside the pores of the membranes. The equipment used to measure the streaming potential was described by Pihlajamäki (1998). The measurements were made at a constant temperature of 25 ºC with KCl 1 mM as electrolyte solution. The zeta potentials were calculated using the Helmholtz-Smoluchowski equation (Eq. 27):

$$\zeta = \frac{\Delta E_s}{\Delta p} \frac{\kappa \mu}{\varepsilon_0 \varepsilon_1} \qquad \text{Eq. 27}$$

where: ζ – zeta potential,

ΔEs – induced streaming potential,

Δp – is applied pressure,

ε_0 – permittivity in vacuum,

ε_1 – dielectric constant,

κ – conductivity

FTIR (Fourier Transform Infrared) analysis gave information about the chemical composition of the separation layer. The FTIR results were corrected using ATR (Attenuated Total Reflection) and the analyses were performed on a Perkin-Elmer 2000 apparatus with a resolution of 2.0 cm^{-1} and a KBr crystal as the internal reflection element.

3.7 SENSORY ANALYSIS

The main objective of sensory analysis was to evaluate the extent to which the use of a reconcentrated solution in osmotic dehydration affected the taste of apples. To ensure the best sensory analysis conditions, the panellists were carefully selected and trained before the tests. The scheme of the sensory evaluation process is presented in Figure 21. First, a triangle test for sucrose concentration discrimination was carried out with a group of 45 panellists. After the results of this test had been evaluated a final group of 14 panellists was chosen. Finally, sensory analysis of osmodehydrated apples using a fresh and reconcentrated OS was performed.

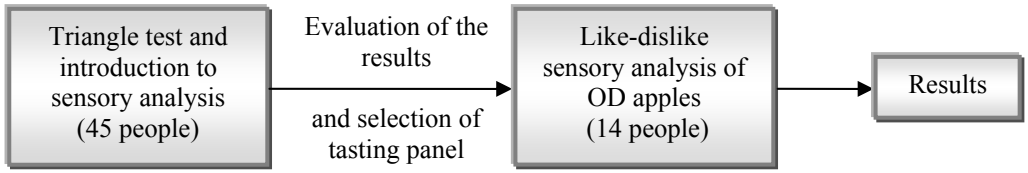

Figure 21. Flow-chart of sensory analysis procedure.

3.7.1 TRIANGLE TEST

Since sugar concentration is of utmost importance in the quality of OD-treated apples, the differences in this parameter in apples osmodehydrated with fresh and reconcentrated OS were considered. Therefore, the main factor for selecting panellists was their ability to discriminate between small differences in sugar concentration. The

tool used to select the panellists was a triangle test. The samples tested were sucrose-water solutions at concentrations of 0.4 and 0.5 % (w/w). During the test, each panellist had to indicate the odd sample among three given samples. Each test was repeated 3 times. As a result of the triangle test, 14 panellists of different ages, geographical origin, diet habits and sex (7 women and 7 men) were selected.

3.7.2 SENSORY EVALUATION OF OD-TREATED APPLES

The final step in sensory analysis was the like-dislike evaluation of OD treated apples. The panellists were asked to evaluate 6 dried samples of untreated and OD-treated apples with fresh and reconcentrated 40 and 50 ºBrix sucrose solutions:

Sample 1. Untreated apples

Sample 2. Apples osmodehydrated in a fresh 40 ºBrix solution

Sample 3. Apples osmodehydrated in a 40 ºBrix solution reconcentrated four times

Sample 4. Untreated apples

Sample 5. Apples osmodehydrated in a fresh 50 ºBrix solution

Sample 6. Apples osmodehydrated in a 50 ºBrix solution reconcentrated four times

The main parameters to evaluate were sweetness and overall taste. The degree of sweetness is one of the main factors in the efficiency of the reconcentrated solution in the DO process, and overall taste is considered as the most important factor by apple consumers (Romero, 2002). The other parameters were aroma, acidity, bitterness, mould, colour and overall appearance. The samples were evaluated on a 5-point scale: from null to extreme sweetness, aroma, acidity, bitterness, mould; and very bad-very good for colour, overall appearance and taste in general. The panellists were also given the chance to make some additional comments about the sample.

The sensory analysis tests were prepared following the instructions from Meilgaard et al. (1999) and Carpenter et al. (2000). The triangle test and sensory analysis took place in the morning and the panellists did not eat before the tests. To ensure the best results, each assessor was asked to cleanse the palate with fresh water between the samples.

The scoresheets from both the triangle test and the sensory evaluation of OD apples are presented in Appendix 1 and 2, respectively.

4 RESULTS AND DISCUSSION

The results section is divided into two main parts:

- Osmotic dehydration
- Membrane separation processes

The first part presents the results of the osmotic dehydration of *Granny Smith* apples using 40, 50 and 60 ºBrix sucrose solutions. A typical osmotic dehydration pathway is obtained. From this pathway it is possible to determine the optimum operation time required to generate an osmotic solution. The osmodehydrated apples obtained in this part served as control samples to evaluate the effect of using reconcentrated solutions on the physical and sensory properties of fruits (see section 4.1).

The second part applies membrane separation processes (nanofiltration, osmotic membrane distillation and direct osmosis) to reconcentrate sucrose solutions.

Nanofiltration (NF) was evaluated as a pre-concentration step in the concentration of diluted sucrose solutions and fruit juices (see section 4.2).

Osmotic membrane distillation (OMD) was applied to reconcentrate pure sucrose and osmotic spent solutions (see section 4.3).

Direct osmosis, as mentioned in section 1.2.3, was studied in two modes: off-site and on-site. During off-site direct osmosis (off-site DO), osmotic and stripping solutions were brought into contact in a membrane module (see section 4.4). During on-site direct osmosis (on-site DO), however, the osmotic solution was reconcentrated at the same time as the osmotic dehydration process (see section 4.5). The osmodehydrated apples obtained during the on-site DO were then evaluated by sensory analysis (see section 4.6).

Finally, the feasible industrial OD process with integrated OS recovery was designed to compare the efficiency of the membrane processes studied (see section 4.7).

4.1 OSMOTIC DEHYDRATION

Apples (var. *Granny Smith*) were osmotically dehydrated using sucrose solutions of 40, 50 and 60 ºBrix at times between 1-4 h. During the OD process, the physical properties of the OS underwent changes because it was diluted. Figure 22 presents the changes in the total soluble solid content (sucrose concentration) of the three osmotic solutions during the osmotic dehydration process.

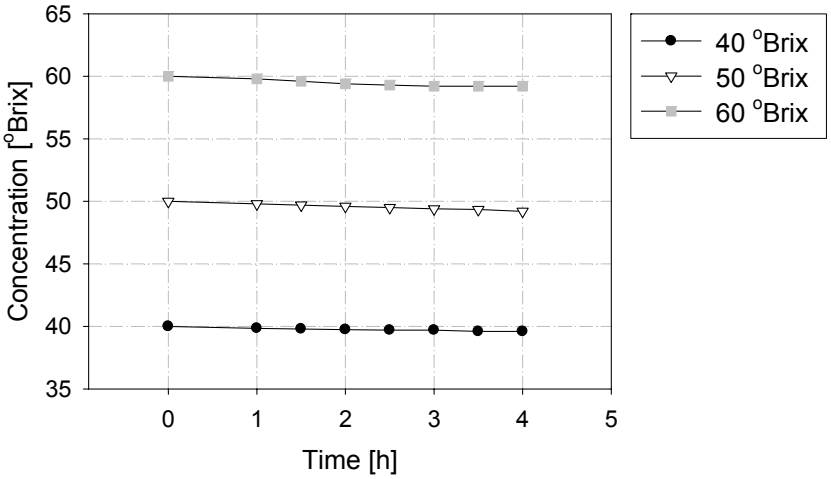

Figure 22. Soluble solids content in the osmotic solutions during the osmotic dehydration process.

Figure 22 shows that during an osmotic dehydration batch, the change in the sucrose concentration of the osmotic solution is small, independently of the initial concentration of the OS. However, it is also noted that, the higher the initial sucrose concentration of the osmotic solution is, the greater the final decrease. It is important to note that the small changes in the OS concentration during a 4 h osmotic dehydration process can be attributed to the ratio between the volume of apples and OS (1:25), and also to the specific pathway of the osmotic dehydration process (presented in Figure 23).

Other properties analysed for the osmotic solution were: a_w, pH and colour. The changes in pH and colour were difficult to measure because of the high density of the

solutions and the apple pieces present in the solution after the osmotic dehydration process. Nevertheless, pH and colour before and after the OD were comparable for all the operation times and the average values calculated for those properties are presented in Table 13.

Table 13. pH and colour before and after osmotic dehydration for the three osmotic solutions.

	Osmotic solution concentration [ºBrix]		
	40	**50**	**60**
$pH_{\text{before OD}}$	3.03	3.03	3.02
$pH_{\text{after OD}}$	2.97	3.01	3.01
$A_{420\ \text{before OD}}$	0.009	0.012	0.014
$A_{420\ \text{after OD}}$	0.009	0.012	0.014

The analysis of the osmotic solutions demonstrated that the OD process had no important effect on their pH or colour. Colour did not change at all and pH decreased only slightly. The pH decrease was higher for the 40 ºBrix solution probably because of a measurement error or the lower density of the solution. The change in water activity for the three osmotic solutions is presented in Figure 23.

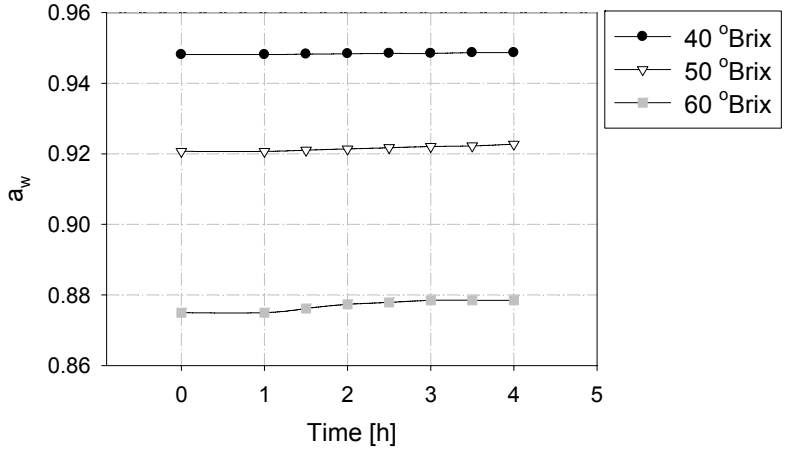

Figure 23. Change in water activity change for three osmotic solutions during osmotic dehydration.

As can be seen in Figure 23, water activity is almost constant during the osmotic dehydration process for the 40 and 50 ºBrix sucrose solutions. On the other hand, the

water activity for the 60 ºBrix sucrose solution increases with the process time. This can be explained by a higher water activity gradient, which results in the apples losing more water and the OS being more diluted.

One of the objectives of osmotic dehydration experiments was to determine the typical pathway of the OD process and consequently to get information about the dehydration time for each of the sucrose concentrations. Figure 24, shows the OD pathway for sucrose solutions of 40, 50 and 60 ºBrix. Mass change was calculated using Eq. 19 and the operating conditions for the osmotic dehydration process were an apple/OS ratio of 1:25 and ambient temperature.

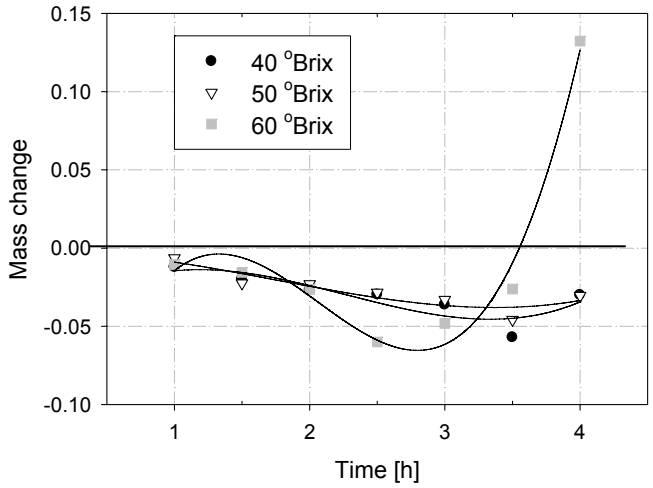

Figure 24. Correlation between mass change and time during the osmotic dehydration of apples using three different osmotic solutions.

The maximum dehydration time for each of the curves plotted in Figure 24 can be found at the inflection point (section 1.1.2). For the 40 and 50 ºBrix osmotic solution this point is reached after 3.5 h, and for the 60 ºBrix osmotic solution dehydration time is slightly shorter (3 h) because of the higher driving force. The maximum dehydration time is used in the section below, which studies the filtration of actual osmotic solutions. Therefore, in the OD processes carried out to obtain the actual OS, the OD process lasted 3.5 h for 40 and 50 ºBrix solutions, and 3 h for a 60 ºBrix solution.

4.2 NANOFILTRATION

4.2.1 INFLUENCE OF TEMPERATURE AND PRESSURE ON CONCENTRATION DEGREE AND RETENTION

To study the effect of temperature and pressure on sucrose concentration by NF, an AFC80 tubular membrane and solutions of 5, 10, 15 and 20 °Brix were used. First, sucrose solutions were filtrated under pressures of 8, 10 and 12 bar at 25 ºC. Afterwards, filtration at constant pressure of 12 bar and varying temperature (25, 30 and 35 ºC) was carried out. The results are presented in Figure 25.

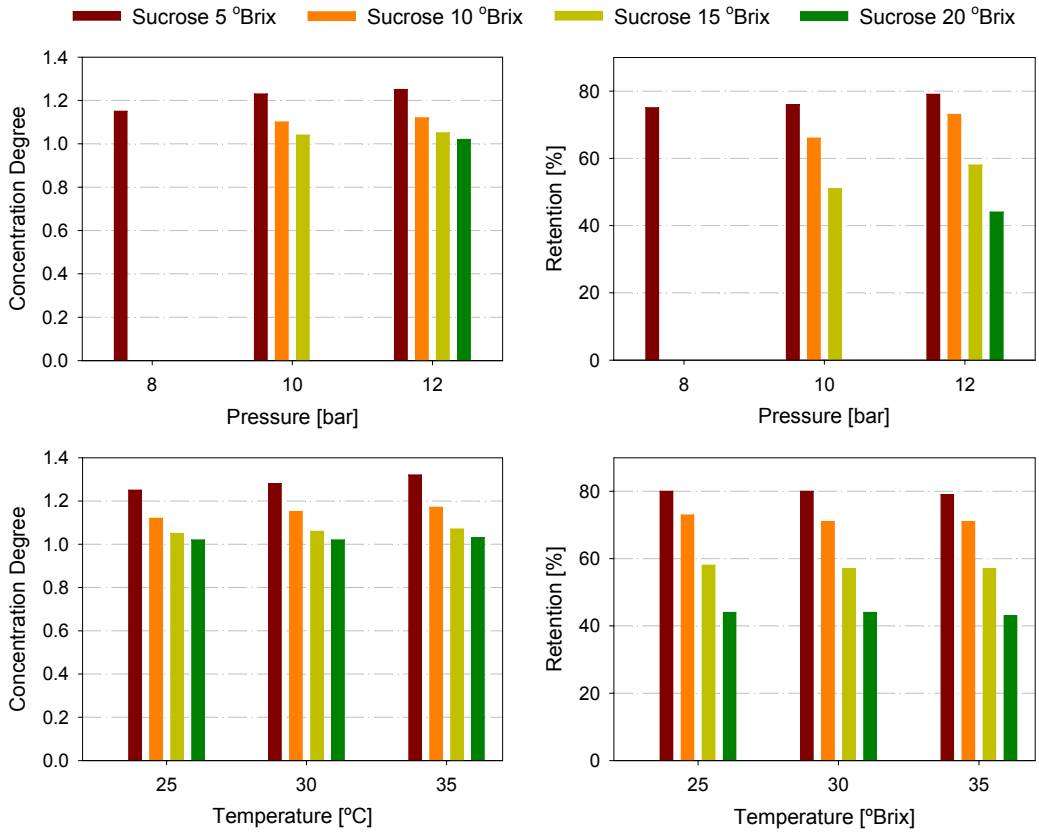

Figure 25. Influence of pressure on concentration degree and retention (T= 25 ºC) and temperature on concentration degree and retention (P= 12 bar).

The results indicate that the temperature only has a slight influence on the concentration degree. Figure 25 also shows that retention does not vary with temperature.

Both CD and R increased when pressure increased (Figure 25). However, this effect is less significant in the case of retention. For example, the increase in retention was highest for the 15 °Brix solution, which gave a 10 % increase from 10 to 12 bar. The highest increase in CD, however, was 34 % for a solution of 5 °Brix, for the same pressure increase.

The increase in temperature and pressure resulted in an increase of permeate flux, and this explains the changes in CD and R. It is also worth mentioning that the increase in CD with temperature is linear for the range of temperature and concentrations studied in the present work.

4.2.2 INFLUENCE OF MEMBRANE TYPE ON CONCENTRATION DEGREE AND RETENTION

TUBULAR MEMBRANES

One of the aims of our work was to find the most suitable commercial NF membrane for concentrating sugar solutions. In accordance with previous experiments, a temperature of 30 ºC and ΔP=12 bar were selected for this part of the work. The two tubular and the three flat sheet membranes described in the Materials and Methods section were tested under the conditions mentioned above. After the nanofiltration of a 10 ºBrix sucrose solution using tubular membranes, CD was higher for the AFC80 than for the MPT-34 (Table 14).

Table 14. Filtration parameters for the two tubular membranes AFC80 and MPT-34 (P= 12 bar, T= 30 ºC).

Membrane	PWFb [LMH]	J [LMH]	R [%]	CD
AFC80	27	8	71	1.15
MPT-34	27	5	97	1.10

The results indicate that there is no direct correlation between the retention of the membrane and the concentration degree obtained, in the same experimental conditions. Since high values of permeate flux are just as important as high retention values, the AFC80 membrane seems to be more appropriate for concentrating sucrose solutions (taking into account the operational parameters in this study). Although the AFC80 membrane gave lower retention values (Table 14), its higher permeate flux (8 and 5 LMH for AFC80 and MPT-34, respectively) resulted in a higher concentration degree.

The separation skin of the two membranes is made of the same material and their pure water flux also had the same value of 27 LMH. Therefore, the variations in permeate fluxes and retentions obtained during sucrose nanofiltration can be attributed to differences in preparation and the molecular structure of the membranes. Membrane morphology and separation skin structure are analyzed in the sections below.

FLAT-SHEET MEMBRANES

Experiments with flat-sheet membranes made it possible to examine the morphological changes in the membranes due to sucrose deposition and to compare the performance of membranes with different configurations.

Three membranes were used: NFT-50, MPF-34 and Desal5-DK. In these experiments concentrations were best with the Desal5-DK membrane. This membrane presents not only very high retention, but also the highest permeate fluxes, which results in a very high concentration degree (Table 15).

Table 15. Filtration parameters for the flat-sheet membranes NFT-50, MPF-34 and Desal5-DK (ΔP=12 bar, T=30 ºC).

Membrane	PWFb [LMH]	J [LMH]	R [%]	CD
NFT-50	3	0.7	92	1.02
MPF-34	18	5	93	1.08
Desal5-DK	66	14	99	1.15

The Desal5-DK also gave the highest concentration degree, as the R and J data had led us to expect from. Although MPF-34 gave a lower J and a slightly lower R than the Desal5-DK membrane, MPF-34 gave a CD of 1.08. The concentration degrees obtained for NFT-50 were the lowest because of the very low permeate flux values. This

membrane may give better results in different operational conditions (e.g. higher pressure).

After the NF process, the fouling performance of all the membranes was verified by determining the irreversible fouling (IF). The yield of solute deposition onto/into the membrane surface expressed in terms of IF is valuable information for verifying the NF process.

The IF values for tubular and flat-sheet membranes were very low (4 %) and all the membranes recovered 96 % of the pure water flux. This low IF value indicates that the membrane fouling was only superficial and the sucrose particles were not absorbed into the membrane.

4.2.3 AFM CHARACTERIZATION

AFM images of the membrane surface provided information that helped to interpret the experimental data. Figure 26 shows the clean and fouled images of AFC80, MPT-34 and Desal5-DK membranes. The images of the clean membranes (Figure 26, A) clearly show the particles of separation layer material (PSLM), and the images of the fouled membranes (Figure 26, B) show the sucrose deposition.

The difference in the PSLM arrangements in the three membranes analyzed can be easily seen on the clean membrane images (Figure 26, A). These kidney-shaped particles are arranged vertically for the AFC80 membrane, while they are slightly horizontal for the MPT-34 (both membranes have polyamide separation layer). The spherical protuberances of the Desal5-DK membrane suggest different separation layer material and/or rather horizontal arrangement of the PSLM. The different PSLM arrangements resulted in variations in roughness and porosity. The most open structure seems to correspond to the MPT-34 membrane: its PSLM have a rather accidental distribution and are separated by some free areas. The AFC80 is more compact and some round cavities can be observed. The most compact surface that has no cavities is the surface of Desal5-DK, suggesting that this is the membrane with the smallest mean pore size. It is important to mention AFM imaging does not make it possible to determine the exact pore size (if there are any), since AFM analysis is restricted to the surface. Therefore, the term ¨mean pore size¨ refers to the spaces between the polyamide particles on the membrane surface.

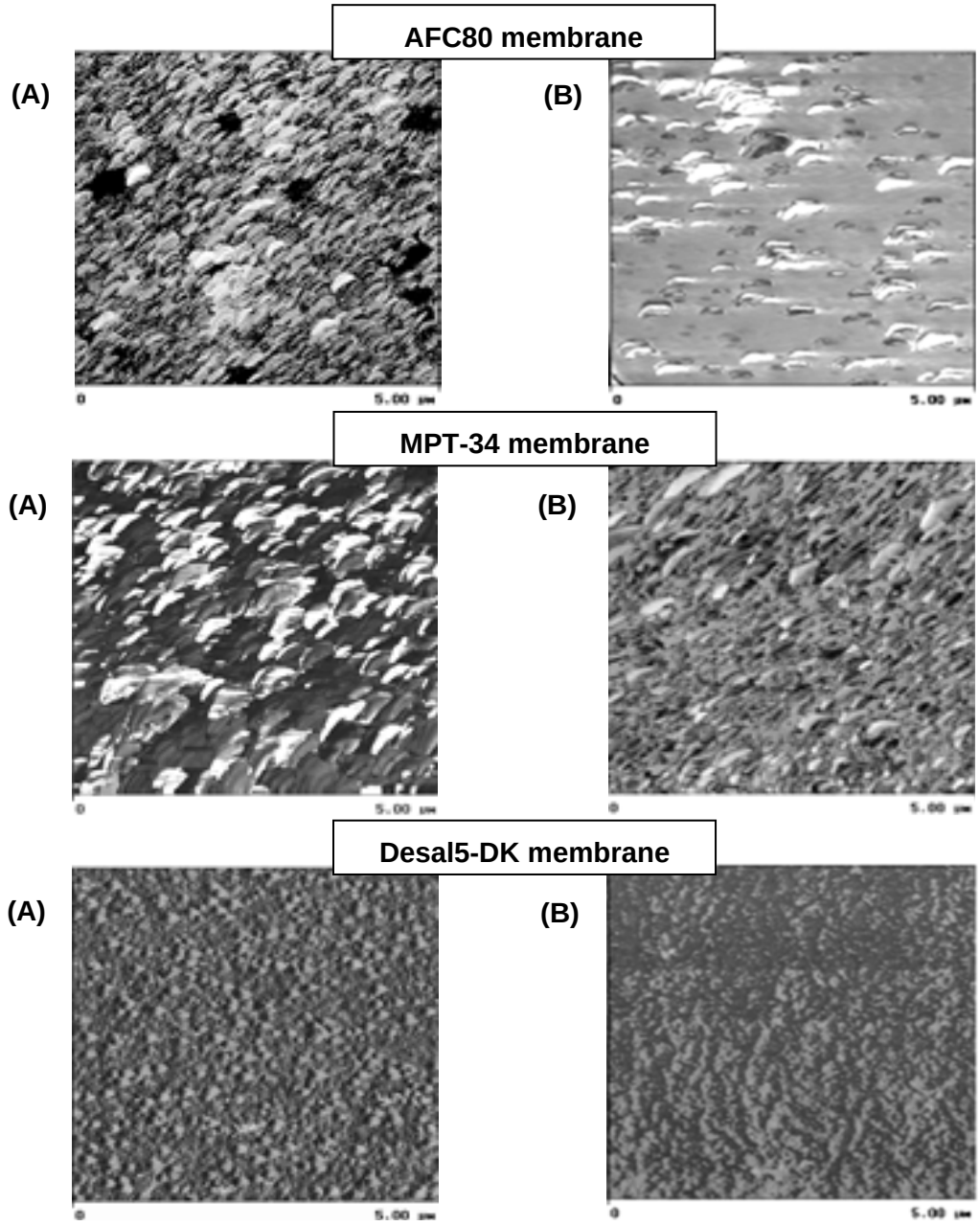

Figure 26. Separation skin of the AFC80, MPT-34 and Desal5-DK membranes. (A)– clean membrane, (B)– membrane after sucrose nanofiltration. Bright areas– peaks, dark areas– valleys.

The surface roughness of the membranes can be evaluated more easily by looking at the images of membranes after sucrose NF (Figure 26, B images). After NF, nearly the entire surface of the membrane is covered with sucrose and the deposition film can be observed. To analyse the roughness, the differences between the PSLM protuberances of each membrane are studied. Of the three membranes, the AFC80 has the fewest protuberances, and the MPT-34 has the biggest and most numerous. There is only a slight difference between the protuberances of the MPT-34 and Desal5-DK, which suggests that their roughness is quite similar.

The AFM images are useful for explaining nanofiltration results. The more open structure of the AFC80 membrane enables the solution to pass through more easily, giving lower retention and higher permeate flux. In contrast, the rough structure of the MPT-34 membrane retains more solutes and decreases the permeate flux. The high retention and high permeate flux of Desal5-DK can be correlated with vertical and compressed PP.

Thanks to the AFM membrane characterisation, it was also possible to study the cleaning procedure applied to the membranes. Images of the original membranes and the ones recovered after the cleaning cycle showed no differences, and no deposited particles were noticed. Thus, it can be concluded that the cleaning procedure is effective, and will enhance the lifetime of the membrane.

The membrane characterisation performed by AFM also made it possible to determine the mean pore size of the original and fouled flat-sheet membranes. The results are shown in Table 16.

Table 16. Mean pore size for the original and treated flat-sheet membranes.

Membrane	Mean Pore size of clean membranes [nm]	Mean Pore size after experiments with sucrose [nm]
AFC80	3.51±0.04	0.18±0.03
MPT-34	4.36±0.04	0.2±0.04
Desal5-DK	0.48±0.05	0.38±0.05

The mean pore size distribution of membranes after sucrose NF decreased significantly for MPT-34 and AFC80. The results showed a 95% decrease in mean pore size for AFC80 and MPT-34 and a 42% decrease for Desal5-DK in comparison with the

clean membranes. Therefore, it can be concluded that the structure of Desal5-DK is more resistant to fouling. All the values in Table 3 are in agreement with the conclusions drawn from observing the AFM images. On the AFM images, Desal5-DK seemed to be smoother than AFC80 and MPT-34 and to have smaller pores. This, together with the experimental data from section 3.1.2, shows that roughness of the membrane surface is one of the decisive properties for getting low irreversible fouling.

Similar results were obtained by Vrijenhoek et al. (2001), who analysed the influence of membrane surface properties on the colloidal fouling of NF and RO membranes. Using AFM, they found that more particles were deposited on rough than on smooth membranes. Thus, it can be concluded that smoother membranes will have less irreversible fouling, which seems to be independent of the filtered solution (sucrose or colloids).

It is worth mentioning that even though the mean pore size of the MPT-34 membrane was larger than those of the AFC80 and Desal5-DK, the density of pores was greater for the these latter membranes. Despite having significantly smaller pores than the other two membranes, the Desal5-DK membrane has much higher permeate fluxes, which may be caused by the limitations of the AFM analysis. Since AFM can only analyse the surface, it is not possible to predict the inner structure of the separation skin. Therefore, the Desal5-DK may only have a very dense surface and bigger pores underneath, while the large pores of the MPT-34 membrane may divide into smaller ones or narrow in the lower layers of the separation skin.

AFM analysis also gave information about the average roughness of the MPT-34, Desal5-DK and AFC80 membranes (Table 17). However, during the determination of the average roughness of the AFC80 membrane, some areas with irregularly high values (up to 355.2 nm) were found.

Table 17. Average roughness of AFC80, MPT-34 and Desal5-DK flat-sheet membranes before and after sucrose NF.

Membrane	Clean membrane [nm]	After sucrose NF [nm]
MPT-34	16.8±0.5	8.7±0.5
Desal5-DK	13.0±0.5	7.7±0.5
AFC80	6.1±0.5	5.7±0.5

The results of the average roughness calculations are in agreement with previous observations. The lowest fouling (roughness reduction) indicated which membrane had the smoothest surface (AFC80 – 7 % roughness reduction) while Desal5-DK and MPT-34 had a roughness reduction of 40 and 48 %, respectively. The information obtained from AFM analysis is highly valuable, because a fouling resistant membrane can make the pre-treatment step superfluous (Mänttäri et al., 2000).

4.2.4 SEM CHARACTERIZATION

The SEM technique made it possible to visualise the cross section of the membranes. Even though it does not permit the high magnifications required for NF membranes, some basic observations can be made about the effect of the experimental parameters and sucrose deposition. Figure 27 shows the images of the original, nanofiltered and recovered AFC80 membranes.

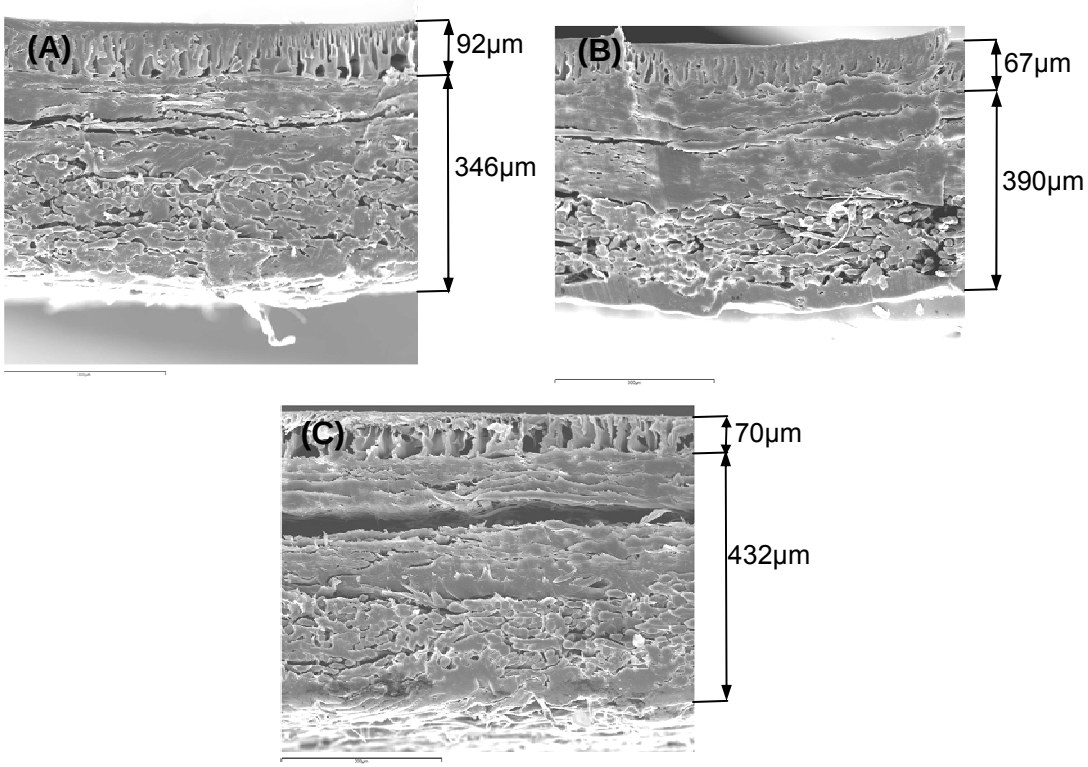

Figure 27. Cross section of the AFC80 membrane (A) original, (B) after 10 ºBrix sucrose nanofiltration and (C) recovered after the experiment.

Two layers can be observed in the images. The first is the separation skin (the very thin layer at the top of the figure) and the second is the support (the porous area below). The cross section of the original AFC80 membrane differentiates between the two layers mentioned above (separation skin and support). The separation skin has vertical pores in conical form, and is linked to a very compact area with thin horizontal layers, which is the first part of the support. The deeper part of the support is rather granulated with randomly-settled pores. A comparison of the structure of the original and the fouled membranes (Fig. 27 A and B), shows that the conical pores are filled with sucrose. The fouled membranes in the first part of the support layer also seem to be more full of sucrose (Fig, 27 B).

Original and recovered membranes look very similar (Fig. 27, A and C). The only difference is the compact structure of the porous layer of the original membrane, which may be caused by the sample preparation (e.g. the way it was cut). The recovered membrane has a void layer in the support. This void layer can be attributed to the effect of high pressure throughout the experiment and high temperature during the cleaning procedure. Despite these little differences, it can be concluded that the cleaning procedure was carried out correctly.

Figure 28 and 29, respectively, show images of the characterisation by SEM of the original MPT-34 and the Desal5-DK membrane after sucrose nanofiltration.

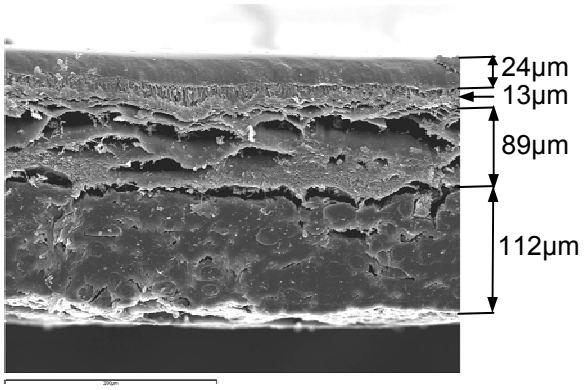

Figure 28. Image of the cross-section of the original MPT-34 membrane.

The cross section image of the MPT-34 membrane (Figure 28) is very similar to the image of the AFC80 membrane. A very thin separation skin and three support layers

can be observed. Images of the SEM characterisation of the Desal5-DK membrane can be seen in Figure 29.

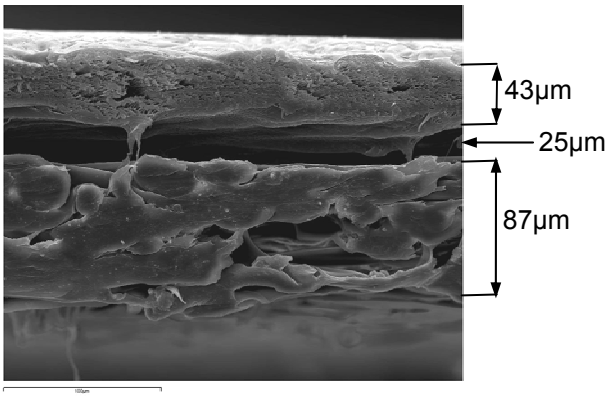

Figure 29. Image of the cross-section of the Desal5-DK membrane, treated with sucrose.

As can be seen, the Desal5-DK membrane has a very peculiar structure (Fig. 29). It is much less porous and the difference between the separation layer and support is considerable. It can be noted that the pores in the upper layer are full of sucrose.

4.2.5 JUICE NANOFILTRATION

CONCENTRATION WITH TUBULAR MEMBRANES

Apple and pear juice were nanofiltrated with tubular membranes to evaluate the feasibility of the process. Figure 30 shows the typical evolution of permeate flux versus time for two nanofiltration runs with each membrane.

As can be seen in Figure 30, the reproducibility of the results was very good. Regarding the differences between AFC80 and MPT-34 membranes performance, it can be noted that permeate flux decrease was slower for the AFC80 membrane, while for MPT-34 flux stabilised after the first hour of the experiment. From this point on only average steady-state permeate flux will be presented.

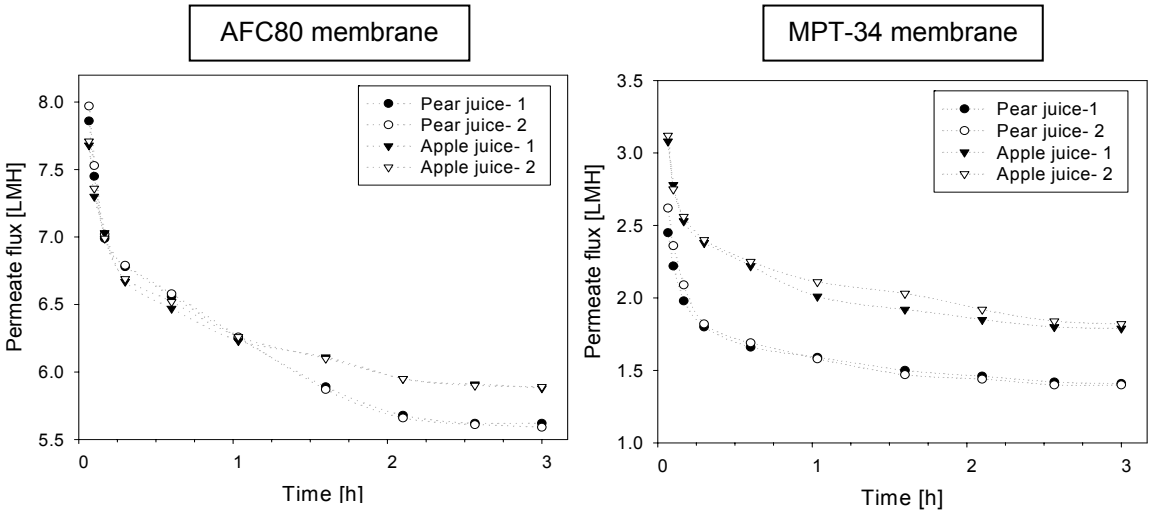

Figure 30. Comparison of permeate fluxes of AFC80 and MPT-34 membranes for two runs of pear and apple juices nanofiltration (P=12 bar, T=30ºC).

Both tubular membranes (AFC80 and MPT-34) had the same pure water flux (27 l/m^{2}h at 12 bar, 30 ºC) and their separation skin was made from the same material (polyamide). Nevertheless, the results for juice concentration were different for each of the membranes (Table 18), which suggests that the separation skin of each membrane was consisted of a different type of polyamide (section 4.4.3). There are also differences between the results of apple and pear juice processing for a given membrane, but these can be attributed to slight differences in the pH and composition of the initial fruit juices (Table 11).

Table 18. Comparison of filtration parameters for the two tubular membranes (AFC80 and MPT-34) and the two fruit juices.

		PEAR			**APPLE**		
Membrane	PWFb [LMH]	J [LMH]	R [%]	CD	J [LMH]	R [%]	CD
AFC 80	27	5.6	54	1.05	5.9	59	1.07
MPT-34	27	1.4	74	1.03	1.8	92	1.06

As can be seen from the results in Table III, the CDs obtained for the two tubular membranes are quite similar. However, there are some notable differences between the permeate fluxes and retention values obtained for each membrane and fruit juice. For the AFC80 membrane, the permeate flux during pear juice concentration was slightly lower than the one for apple juice. The retention values for this membrane also depended on the fruit juice treated. Higher retention and higher permeate flux resulted in apple juice having a higher concentration degree than pear juice. For the MPT- 34 membrane, retention values increased for both fruit juices, and reached 92 % for apple juice. These higher retention values for the MPT-34 membrane are the reason why the concentration degree was similar to the one obtained with the AFC80 membrane, even though in this case the permeate fluxes are about three times lower.

CONCENTRATION WITH FLAT-SHEET MEMBRANES

Concentration experiments with flat-sheet membranes made it possible to compare the influence of different membrane configurations on performance and to characterize morphological changes of the membrane due to solute deposition. Two flat-sheet membranes were used: MPF-34 and Desal5-DK. The results (Table 19) show that the Desal5-DK membrane achieves a very high permeate flux, sufficiently high retention and a higher concentration degree than the MPF-34 membrane.

Table 19. Results of pear juice nanofiltration using flat-sheet membranes.

	Retention [%]	**Pure water flux [LMH]**	**Permeate flux [LMH]**	**Concentration degree**
MPF-34	75	19	0.4	1.01
Desal5-DK	66	63	7	1.06

It is worth mentioning that CD values for Desal5-DK are similar to the ones for tubular membranes. When the MPF-34 membrane was used in the tubular and flat-sheet configurations, the CD was slightly higher for the tubular configuration.

AFM CHARACTERIZATION

As for sucrose NF, AFM and SEM were used for membrane characterization. Figure 31 compares the clean membrane with the AFC80 membrane after pear juice nanofiltration.

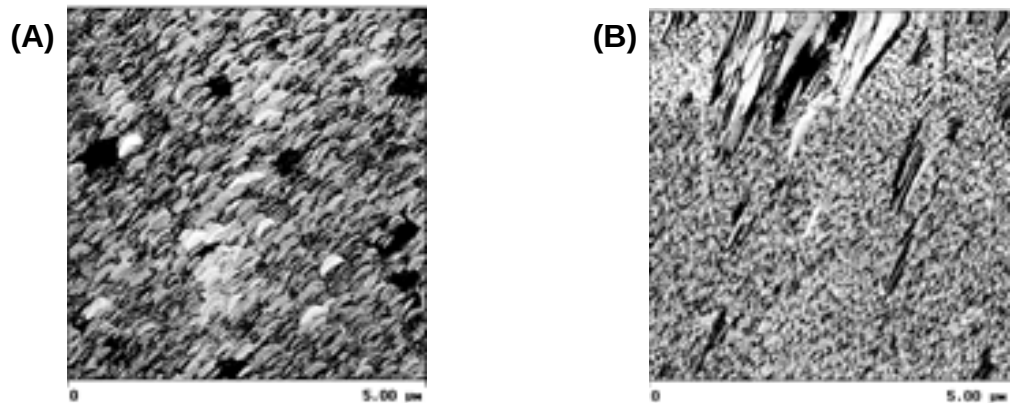

Figure 31. Separation skin of AFC80 membrane (A) original and (B) after pear juice NF.

The surface of the membrane after pear juice NF is completely covered by a solute layer and the polyamide particles in the separation skin can no longer be distinguished. The structure of this fouling layer is very interesting, because the influence of the operation flow on the membrane surface can be seen. The images suggest that particles of the solute stick to the membrane surface during the process and the passing flow drags them along.

Figure 32 shows the images of Desal5-DK membranes: original and after pear juice NF. The solute layer can clearly be seen in the images of the Desal5-Dk after NF, just as it can in the images of the AFC80 and MPT-34 membranes. The mean pore size estimated for the Desal5-DK membrane also gives information about the juice solutes deposited onto the membrane. The mean pore size after the juice NF was determined to be 0.28±0.06 nm, while for clean membrane it was 0.48±0.05. A comparison of the first value with the mean pore size determined for the Desal5-DK membrane after sucrose NF (Table 16) shows that the complexity of the juice has an important influence on fouling degree.

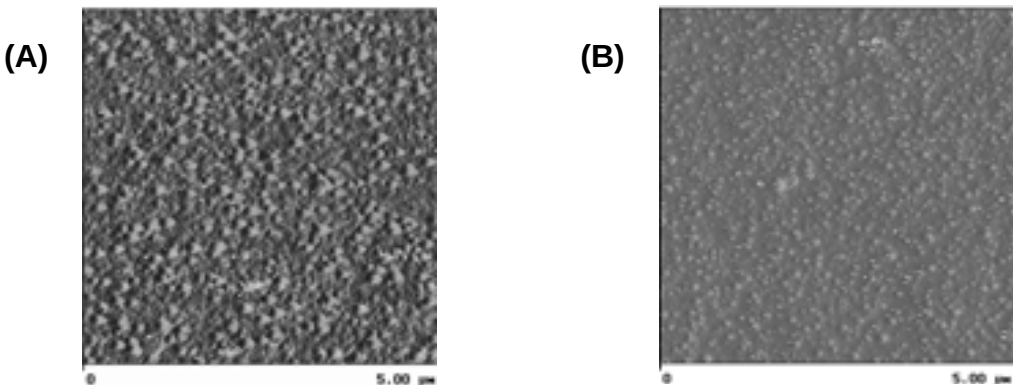

Figure 32. Surface of Desal5-DK membrane. (A) original membrane, (B) membrane treated with pear juice.

SEM CHARACTERISATION

SEM helped us to understand how the experimental parameters affected NF membranes and also to determine how juice particles are deposited onto/into the membrane separation skin. Cross-sections of AFC80 and Desal5-DK membranes after pear juice nanofiltration can be seen in Figure 33.

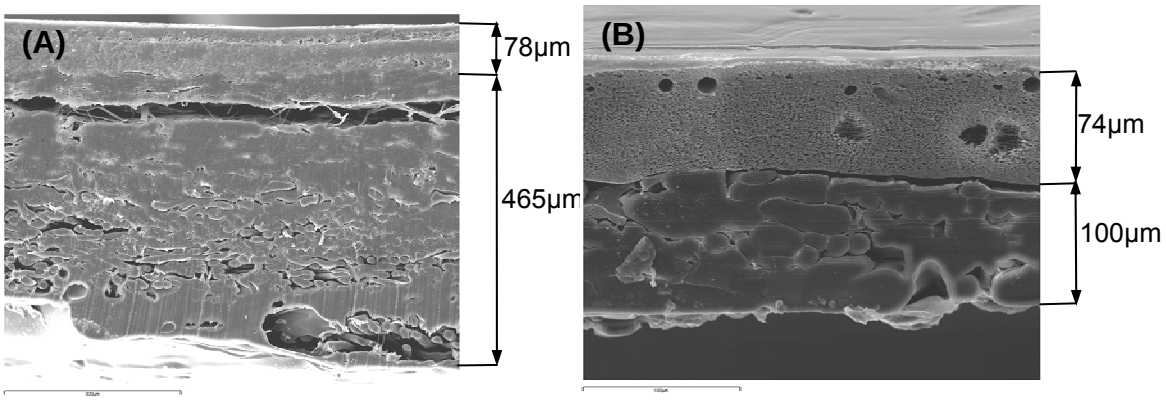

Figure 33. Cross-sections of AFC80 (A) and Desal5-DK (B) membranes, after pear juice NF.

In the AFC80 image in Figure 33 (A), it can be observed that the whole structure (and especially the porous upper part) is filled and covered with solute particles. As in the recovered membrane (Figure 27, B), the support layer is also delaminated.

The structure of the Desal5-DK membrane (Figure 33, B) is highly peculiar. It is much less porous and the difference between the separation skin and the support is considerable. Its filtration layer looks like a sponge filled with juice particles.

CONCENTRATION OF FRUCTOSE

The extent to which the sugar concentration affected fruit juices and a single sugar solution was determined by a fructose model solution of 10 °Brix treated by NF. The fructose solution was concentrated in experimental conditions that were identical to those of fruit juices 12 bar, 30 °C and the MPT-34 flat-sheet membrane. The results show that even though the concentration degree was the same as that of the pear juice under the same experimental conditions, retention was lower and permeate flux higher for the fructose solution (Table 20).

Table 20. Results obtained for the MPT-34 flat- sheet membrane.

	Concentration degree [%]	**Retention [%]**	**Permeate flux [LMH]**
Fructose	1.01	64	2
Pear Juice	1.01	75	0.4

The results can be correlated with the fact that the fructose molecules had smaller radii (0.26 nm) than MPT-34 pores (4.36±0.04 nm). It seems likely that most juice particles enter the pores and form a thin fouling layer, while some of the fructose molecules enter the small pores and pass through the larger ones. Both fructose and pear juice solution lead to the formation of a fouling layer, which can be easily flushed with water. The higher retention and lower permeate flux of pear juice indicate the existence of a significant fouling layer. Again, the concentration degree depends on retention as well as permeate flux. The low permeate flux observed for pear juice in combination with the high retention gives the same concentration degree as for fructose, which combines a high permeate flux with low retention. The main conclusion drawn from

this part is that the problems arising in juice concentration processes may be due to low values of retention and permeate flux.

CALCULATION OF IRREVERSIBLE FOULING

The yield of solute deposition onto/into a membrane surface, expressed in terms of irreversible fouling (IF) is valuable information for verifying the NF process. Figure 34 shows all the values of IF for tubular and flat-sheet membranes.

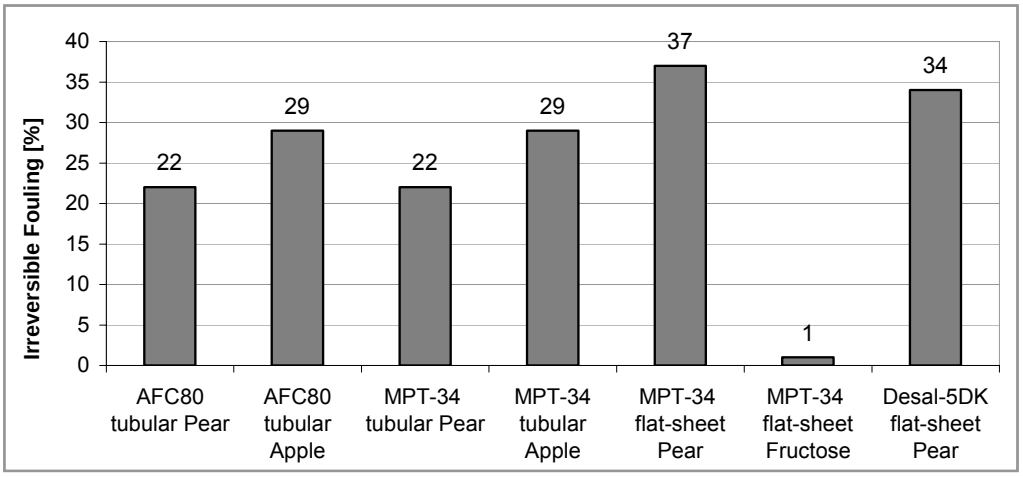

Figure 34. Irreversible fouling for tubular and flat-sheet membranes.

As mentioned above both tubular membranes (AFC80 and MPT-34) have the same initial pure water flux of 27 l/m^2h and IF was also identical after fruit juice nanofiltration (22 % and 29 % for pear and apple juice, respectively). IF results can be helpful for analysing the retention yields of fruit juices during NF experiments. The higher retention for apple juice can be correlated to a higher deposition of solutes into/onto the membrane surface and the formation of an additional separation layer.

The results of the tubular and flat-sheet membranes show that the module configuration has a significant influence on fouling. For the MPT-34 flat-sheet membrane pear juice IF was 68 % higher than for the tubular membrane (37 and 22 %, respectively). These data indicate that for long term applications, tubular membranes are more appropriate because of their longer lifetime and easier membrane recovery.

The results of MPT-34 and Desal5-DK flat-sheet membranes show that the IF is slightly lower for the Desal5-DK membrane than for the MPT-34 (34 and 37 %, respectively). This is due to the different configuration of the separation skin, which in the case of the Desal5-DK membrane is more open but not as rough.

Finally, the IF calculation showed that the presence of fructose in fruit juices had almost no influence on IF. Even though the initial concentrations of fruit juice and fructose solution were the same (10 °Brix), after nanofiltration the IF of fructose was significantly lower than that of pear juice (1 % and 37 %, respectively). This indicates that the fouling of fruit juices depends on all the components in juice and that the interactions between some of those components and the membrane are very strong.

4.3 OSMOTIC MEMBRANE DISTILLATION

4.3.1 INFLUENCE OF STRIPPING SOLUTION TYPE AND FEED CONCENTRATION ON WATER FLUX

For food applications, the most commonly used stripping solutions in the OMD process are NaCl and $CaCl_2$. Both solutions are harmless for humans if the concentrations absorbed are low (safe levels are lower for the $CaCl_2$) and both have low water activity. The usual concentrations applied are over 20 % (w/w) for NaCl and over 30 % for $CaCl_2$. For example, Versari et al. (2004) used NaCl at 22 % (w/w) to concentrate must and Alves et al. (2004) used $CaCl_2$ at 45 and 30 % (w/w) approx. to concentrate sucrose solutions of 12 ºBrix. The present study makes, a comparative study of the effectiveness of $CaCl_2$ (50 % w/w) and NaCl (25 % w/w) as stripping solutions.

The OMD experiments were carried out in a stirring cell in co-current mode using a PTFE membrane with a pore size of 0.45 μm. The experimental equipment was placed in a methacrylate closed vessel to maintain the temperature at 35 ºC throughout the OMD process (Figure 12). The initial concentration of sucrose solutions was 30, 40, 50 and 60 ºBrix. Regeneration procedures of OMD membranes are inefficient, and membrane life-time can be extended by adjusting operation parameters to avoid limiting flux phenomena (Gryta, 2005).

Figure 35 presents water fluxes for sucrose solutions of 30, 40, 50 and 60 ºBrix using both stripping solutions. The fluxes measured independently for feed and SS side were different by less than 1 % and were always lower for the feed solution. The same tendency was observed by Mansouri and Fane (1999), although their discrepancies between feed and SS fluxes were much more significant (about 7 %). The authors associated this difference with insufficient stirring in the OMD cell, which resulted in non-uniform temperature and concentration. The present investigation considers that the differences between feed and SS fluxes are more likely to be the effect of flux measurement problems than the result of insufficient stirring.

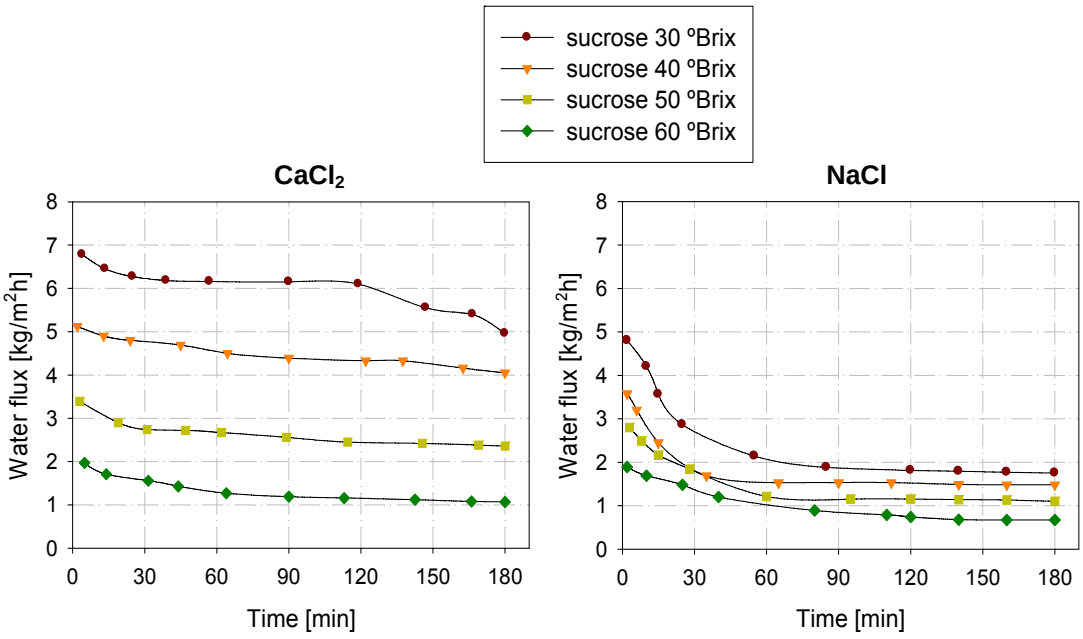

Figure 35. Relation between water flux and sucrose concentration using $CaCl_2$ and NaCl as stripping solutions.

The fluxes obtained for $CaCl_2$ point to water activity as being the decisive SS property if water fluxes are to be high in OMD. When highly viscous $CaCl_2$ was used as stripping solution, water fluxes were twice as high as when the not very viscous NaCl was used (Table 12). Despite the high viscosity of $CaCl_2$, the high water fluxes obtained indicated that the polarisation effect on the membrane surface from the stripping solution side could be neglected.

Since the water vapour partial pressure is the driving force in OMD, the decrease in water fluxes during the experiments was the result of the stripping solution being diluted. This problem can be solved by adjusting the ratio between the stripping solution and sucrose solution volumes. The water fluxes can also be increased by improving the agitation system and increasing the stirring rate.

Figure 35 also shows the influence of the sucrose solution concentration on water flux. For the feed (sucrose) solution, unlike SS, the viscosity is limiting for water flux. The decrease in water activity for the sucrose solution between 30 and 60 ºBrix (from 0.971 to 0.898 at 25 ºC, respectively) is relatively lower than the a_w changes for different concentrations of $CaCl_2$ (Figure 13) or NaCl. On the other hand, the significant

increase in dynamic viscosities observed for sucrose solutions (from 2.1 to 27.4 at 35 ºC, for 30 and 60 ºBrix, respectively) indicates that the feed solution viscosity is the most important property affecting the water transport of the feed solution. The exponential increase in the sucrose solution viscosity is associated with a considerable decrease in the diffusion coefficient, which reduces the water flux. Figure 36 plots the dependence of water flux and viscosity on sucrose concentration. The results were obtained using 50 % (w/w) $CaCl_2$ as SS.

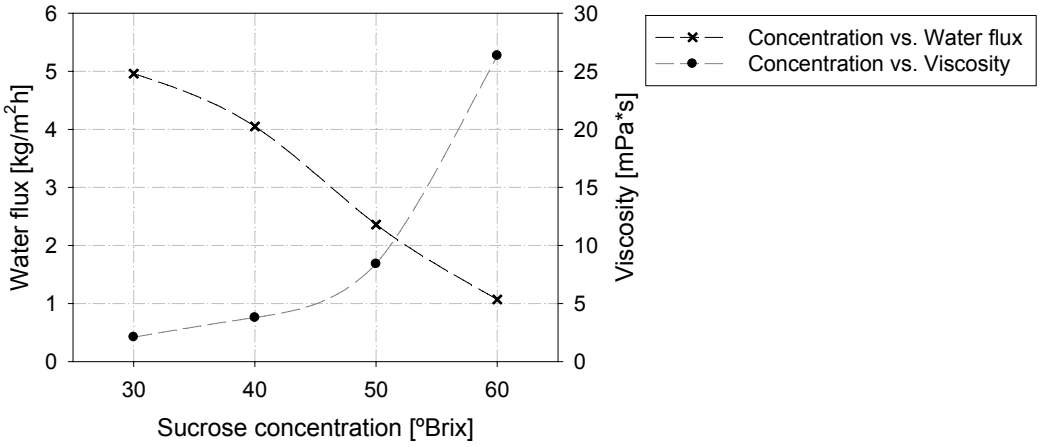

Figure 36. Influence of sucrose concentration on viscosity and water flux during OMD with $CaCl_2$ as SS.

The effect of SS and feed solution properties on water flux during OMD (see above) is in good agreement with the results obtained by Courel et al. (2000 A). In this study sucrose solutions of different concentrations (0-65 ºBrix) were dehydrated using $CaCl_2$ solutions of concentrations between 32.2 and 45.5 % (w/w). The water fluxes obtained were higher than the water fluxes obtained in the present study, 8 and 2.5 kg/m^{2}h for 40 and 60 ºBrix respectively, mainly due to high driving forces generated by adjusting the sucrose solution/SS ratio (to 2÷5 l) and better agitation. Although Courel et al. obtained higher fluxes, the influence of water activity and the viscosity of the solutions were the same.

Analytical tests for the presence of salts in the sucrose solution and sucrose or reductive sugars in the SS showed that the membrane remained hydrophobic throughout the experiments. Since no transfer of solutes was detected, the total flux through the

membrane was only a water flux, and the solute retention of the PTFE (Sartorius) membrane was 100 % under the conditions studied. PVDF and PP (Memcor, Australia) were tested by Bui and Nguyen (2005) and also showed no $CaCl_2$ leakage to the treated feed when apple juice was processed. High retention during the OMD process is one of its main advantages, while the major problem is to maintain the driving force throughout the process.

During the present study, the SS and the feed solution had the same volume and the high water fluxes diluted the SS. Nevertheless, the increase in the feed solution concentration was significant. The decrease in the concentration of the SS and the respective feed concentration increase are presented in Figure 37. The concentration changes for various sucrose solutions (30, 40, 50 and 60 ºBrix) were studied for longer periods of time (6 h) in order to get more information about the process.

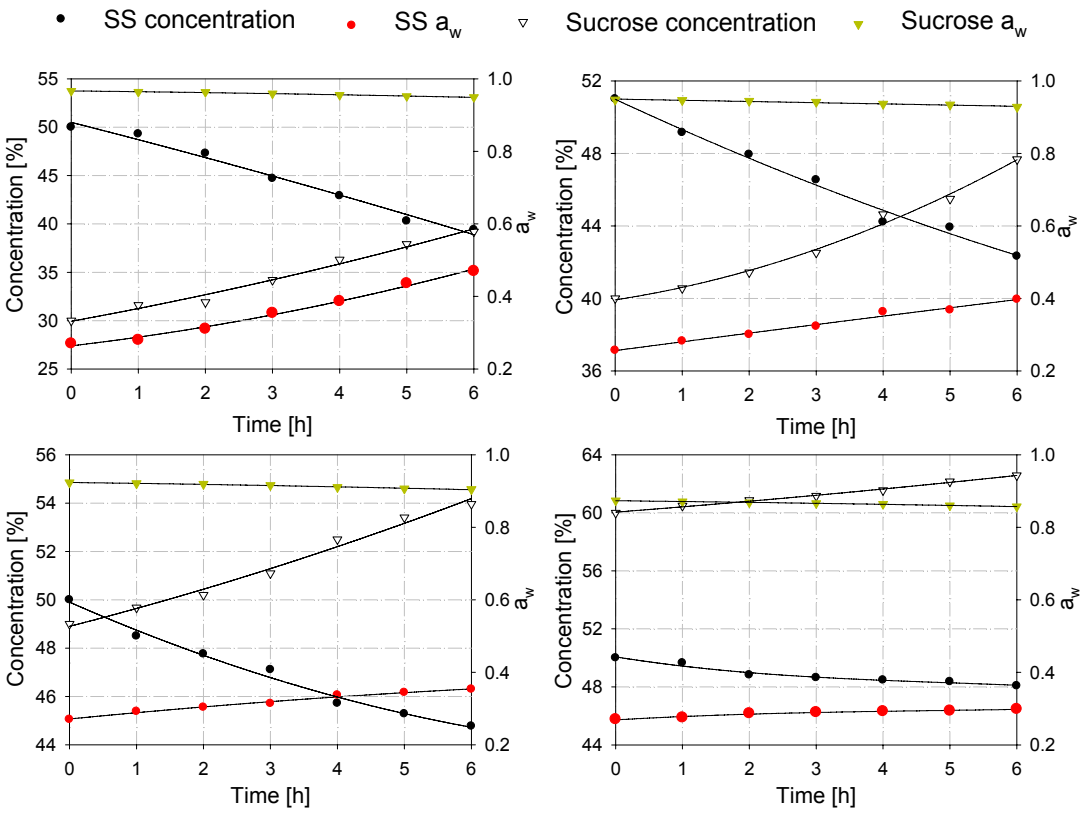

Figure 37. Change in SS and feed concentration and water activity over 6 h for 30, 40, 50 and 60 ºBrix sucrose.

As can be observed on Figure 37 the increase in sucrose concentration for 30 and 40 ºBrix sucrose solutions during a 6 h concentration process was considerable. The increase in the concentration of 50 and 60 ºBrix sucrose solutions was lower, mainly due to their higher viscosities. In any case, the dilution of $CaCl_2$ during the concentration of all sucrose solutions indicated that there should be included a concentration step for the SS (e.g. evaporator) if the SS concentration is to be maintained. These observations are in a good agreement with the results by Cassano et al. (2004), who used OMD to concentrate kiwifruit juice. The initial concentration of kiwifruit juice was 10 ºBrix and the final concentration was about 61 ºBrix. The SS solution they used was 60 % (w/w) $CaCl_2$ dihydrate. The experiments were run until the concentration of SS decreased to 11 % (w/w). Then the SS concentration was restored and, as a result, the flux increased. The initial flux obtained for the SS of 60 % and kiwifruit juice of 10 ºBrix was 1 kg/m^2h. After the concentration had been restored the flux reached 0.66 l/m^2h. This difference between the initial and recovered flux was attributed to the increase in feed solution viscosity.

After this set of experiments, $CaCl_2$ was chosen as the stripping solution to reconcentrate OD spent solutions.

4.3.2 RECONCENTRATION OF OSMOTIC SOLUTION BY OSMOTIC MEMBRANE DISTILLATION

The effectiveness of osmotic dehydration depends on the initial concentration of the osmotic solution; therefore, the OD experiments were performed for sucrose concentrations of 40, 50 and 60 ºBrix. *Granny Smith* apples were used for OD and the procedures to carry out the osmodehydration are explained in detail in section 3.1. After 3.5 h of osmotic dehydration, the resulting sucrose solutions were diluted by about 3±0.2 %, and some solutes and small pieces of apple were also transferred to the solution. The resulting sucrose solutions were reconcentrated using 50% (w/w) $CaCl_2$ and the same procedure as for pure sucrose solutions. Figure 38 compares the water fluxes measured during the OMD treatment of osmotic spent solutions and pure sucrose solutions.

The complexity of the osmotic spent solution had a negative effect on the water fluxes. However, this effect decreased as the initial concentration of the osmotic spent

solution increased. The water fluxes of osmotic spent solutions were 30 and 15% lower than those of 40 and 50 ºBrix sucrose solutions, respectively. However, for a 60 ºBrix osmotic solution the water fluxes were the same as the ones obtained for 60 ºBrix sucrose solution. This suggests that apple solutes released to the osmotic solution have less influence on water fluxes when the viscosity of the solution increases. Therefore, viscosity is thought to be one of the key parameters that influence water flux during OMD.

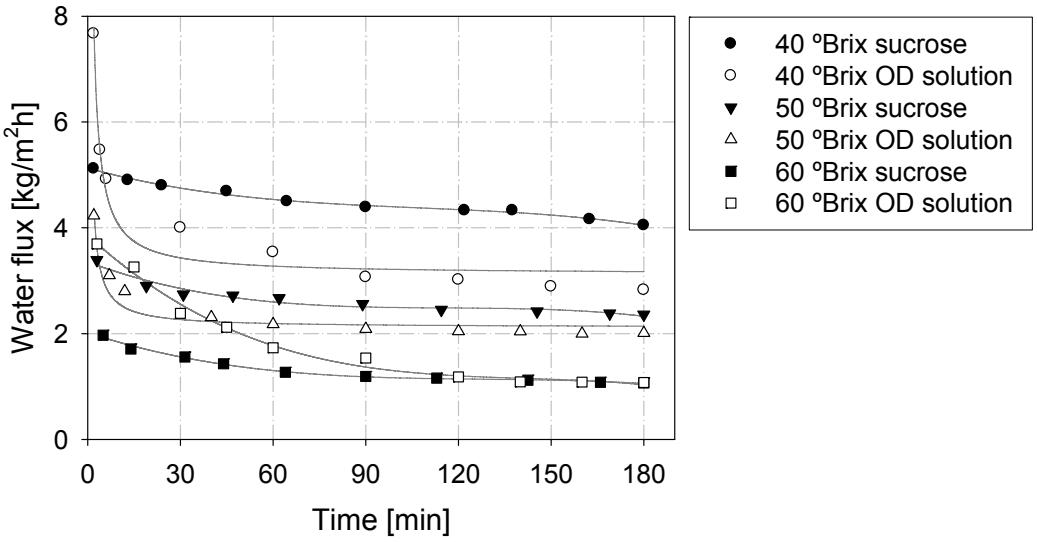

Figure 38. OMD water fluxes for pure sucrose and osmotic spent solutions using $CaCl_2$ 50 % (w/w) as SS.

Fruit pieces (which are critical to the decrease in water flux) L-malic acid, PPO, reductive sugars, ascorbic acid and aromas were among the substances that can be found in the osmotic spent solution.

The concentration polarisation effect can be evaluated by plotting the flux versus the driving force (P^*a_{wFeed}–P^*a_{wSS}). For the NaCl/water system, Versari et al. (2004) interpreted the linear relation between driving force and flux as an indication of the negligible concentration polarisation effect on the SS side during OMD. The authors considered that the low NaCl viscosity and high flow rates during experiments (100 l/h) were factors that enhanced the mass transfer coefficient. On the other hand, the low driving force limited the flux. Therefore, according to the film theory model (Eq. 28),

the NaCl concentration on the membrane side (C_{MSS}) was practically equal to the bulk concentration value (C_{BSS}), which means that the concentration polarisation was negligible.

$$\ln \frac{C_{BSS}}{C_{MSS}} = \frac{N}{\rho_{SS} K_{SS}} \qquad \text{Eq. 28}$$

Figure 39 presents the plot of the water flux versus the driving force for the present study. The driving force was calculated using a water vapour pressure of 5.62 kPa at 35 ºC (Weast, 1989).

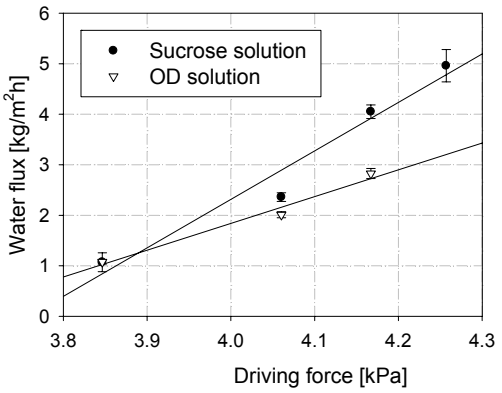

Figure 39. Effect of driving force effect on water flux while processing pure sucrose solution and osmotic solution using $CaCl_2$ 50 % (w/w) as SS.

As can be seen in Figure 39, for both sucrose and osmotic solutions, water flux was a linear function of the driving force calculated for the bulk phases. However, in the present study the high viscosity of the sucrose, osmotic and $CaCl_2$ solutions, could have promoted the formation of a concentration polarisation layer on the feed side for NaCl/Sucrose, and on both the feed and SS sides for $CaCl_2$/Sucrose and $CaCl_2$/OS. The results presented in Figure 39, do not show the concentration polarisation layer. Nonetheless, as stated above, the driving force was calculated for the bulk phases, and only for a short range. Therefore, it cannot be concluded that the concentration polarisation is negligible.

The overall mass transfer coefficients are presented in Figure 40. They were obtained using Eq. 8.

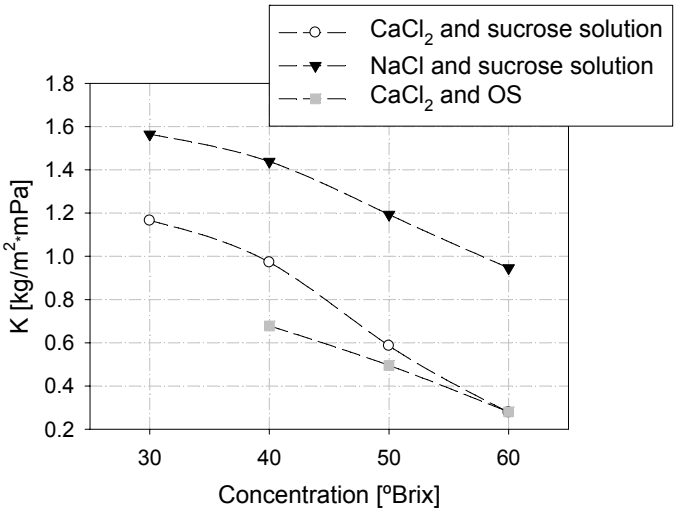

Figure 40. Overall mass transfer coefficient (K) during OMD.

For the $CaCl_2$/sucrose and $CaCl_2$/OS arrangements, the resistance for water vapour transport is the same for the membrane (K_M) and the stripping solution (K_{SS}). Therefore, the differences in K are thought to be due to the feed solution (K_F). In this case, the complexity of the OS affects water transport when the sugar concentration is lower than 60 ºBrix.

For the $CaCl_2$/sucrose and NaCl/sucrose arrangements, the resistance for water vapour transport is the same for the membrane and the feed solution. Therefore, in this case the values of K for the two arrangements depend on the resistance of the SS. NaCl has a much lower viscosity than $CaCl_2$, and the overall mass transfer coefficient is highest for all the sucrose solutions.

4.4 OFF-SITE DIRECT OSMOSIS

4.4.1 PRELIMINARY STUDIES

Preliminary studies were performed to determine the arrangement of the membrane in the membrane module, and also the most appropriate concentration of NaCl as stripping solution. Off-site direct osmosis was carried out using the experimental set-up presented in Figure 16.

During the experiments, the Desal5-DK membrane was tested first with the separation layer on the side of the feed and then on the side of SS. The NaCl concentration was variable and the sucrose concentration was constant. After the amount of Cl^- transported to the feed solution had been evaluated, retention was best when the separation layer was in contact with the SS.

Since a hydrophilic membrane is used in off-site direct osmosis, both water and solutes can be transferred between the stripping and the feed solutions. Therefore, the two factors that most affect the choice of stripping solution for off-site DO are that it must be harmless and that its osmotic pressure must be high enough to induce water transport. For this reason, a NaCl solution with a concentration near saturation point was chosen. The $CaCl_2$ solution was rejected because of its possible noxious effect on the OS.

The concentration of NaCl was set at 24.6 %, because higher salt concentration resulted in crystallisation on the cover of the membrane module if experiments (24 h) were long term.

As a result of the preliminary studies, the membranes with the separation layer facing the SS and 24.6 % of NaCl were selected.

4.4.2 INFLUENCE OF MEMBRANE TYPE AND PROCESS PARAMETERS ON WATER FLUX DURING OFF-SITE DIRECT OSMOSIS

Sucrose solutions of 5, 20, 40, 50, 55 and 60 ºBrix concentration were subjected to off-site DO using tubular (AFC 99 and MPT-34) and flat-sheet (Desal5-DK and MPF-34) membranes. The direct osmosis fluxes obtained during the experiments are

presented in Figure 41. The fluxes were calculated from the weight increase in stripping solution during the filtration.

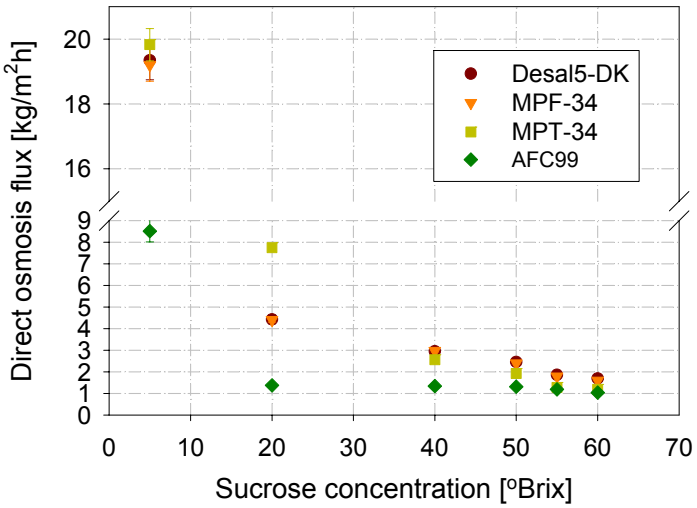

Figure 41. Direct osmosis flux obtained for sucrose solutions (5 to 60 ºBrix).

Although their active filtration area is three times bigger than that of flat-sheet membranes, tubular membranes gave about 50 % lower fluxes for sucrose solutions in the range of 40-50 ºBrix. This decrease in fluxes (Figure 41) is largely due to the membrane thickness. SEM analysis (section 4.2.4) shows that the mean thickness of AFC80 (similar to that of AFC99), Desal5-DK and MPF-34 membranes is 445±15, 175±10 and 235±10 µm, respectively. Therefore, the highest fluxes during sucrose processing with flat-sheet membranes (Desal5-DK and MPF-34) can be attributed to loss of resistance between the feed and the stripping solution.

Regarding flat-sheet membranes, fluxes were slightly higher for Desal5-DK, mainly due to the difference in thickness and the properties of the separation layer between the two membranes (section 4.2.3). The contact angle measurements revealed that the hydrophilic character of the flat-sheet membranes was similar. The contact angle evaluated using the dynamic Wilhelmy plate mode for Desal5-DK and MPF-34 was 37.5±0.0 and 37.2±0.0º, respectively. Contact angles measured using the sessile drop mode gave similar results, but the error was about 15 %. FTIR measurements showed

that the separation layer of MPF-24 and Desal5-DK membranes was quite similar (Figure 42).

The FTIR results are very difficult to interpret, first because of the reduced FTIR spectrum library, and second because the FTIR measurements also analyse the internal parts of the membrane, so some noise peaks can be added to the spectra. Therefore, the best way to interpret some cases (i.e. polymers) is to identify the main peaks and then to compare the spectra with a spectra of polymeric materials with the same chemical groups.

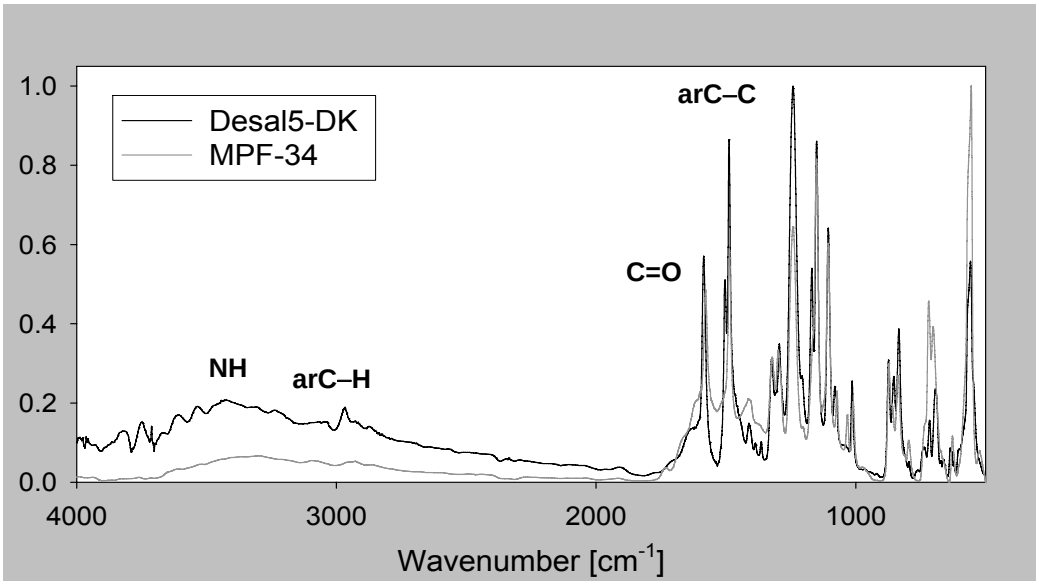

Figure 42. FTIR spectra of clean Desal5-DK and MPF-34 membranes (ar-aromatic).

In Figure 42, the typical groups for polyamides are indicated on the peaks. The following step in the FTIR spectra identification was to search for the polymer with spectra that were similar to the ones obtained for Desal5-DK and MPF-34. The polyaramide KEVLAR®, whose formula is $[C_{14}H_{10}N_2O_2]_n$ shows the best resemblance (Figure 43).

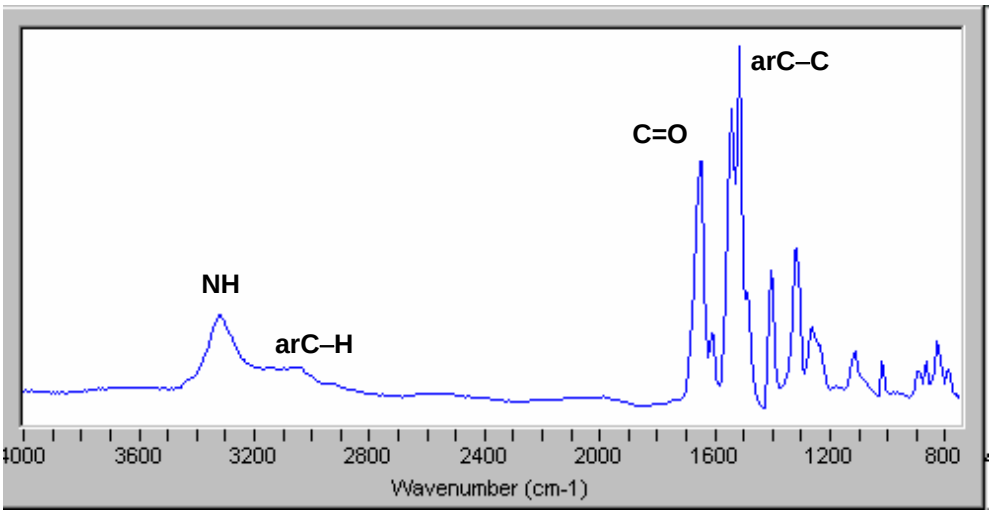

Figure 43. FTIR spectra of KEVLAR® (ar-aromatic).

The peaks in the range between 1400 and 500 cm-1 are considered to be repetitions of the marked peaks. In the case of the FTIR of Desal5-DK and MPT-34 membranes, some of the peaks found in the FTIR spectrum can be considered to be the ¨noise peaks¨ from the internal layer of the membranes or some depositions.

Figure 41 shows that the worst performance throughout the range of sucrose solutions tested was that of the AFC99 membrane. It has been reported that the AFC99 direct osmosis fluxes can be improved by decreasing the membrane thickness. During the concentration of 4.3 ºBrix tomato juice, Petrotos et al. (1998) reduced the overall AFC99 membrane thickness (but did not change the separation layer thickness) from 460 to 260 μm and this led to a fivefold increase in the water flux.

The trend in the feed solution characteristics was the same as in the OMD process, and the solution viscosity had an important influence on direct osmosis fluxes. Considering the SS, NaCl (Figure 14) osmotic pressure influence on the flux during off-site DO very evident.

Unlike OMD, in off-site DO water in the liquid phase is transported through the hydrophilic membrane. Therefore, the fouling might be promoted during the process and the concentration polarisation might be more significant than the concentration polarisation during OMD (Figure 44).

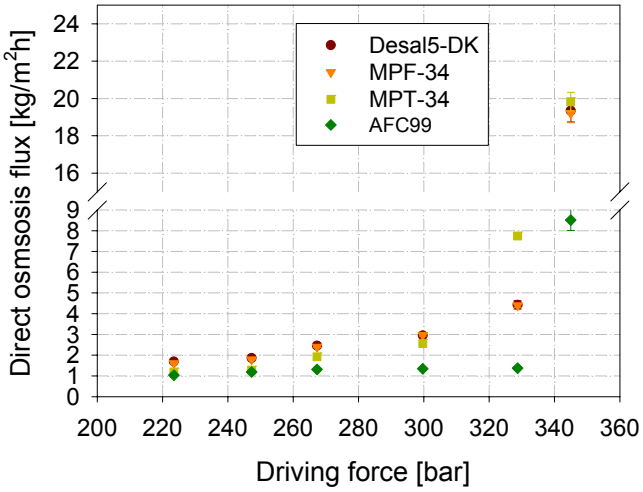

Figure 44. Influence of driving force on direct osmosis flux.

The off-site DO water flux can also be expressed as water permeability coefficient multiplied by the difference in the osmotic pressures of the feed and SS. Therefore, as for OMD, the slope of the driving force (Π_{SS}-Π_F-overpressure applied to ensure the contact between both solutions) versus the flux should give information about the concentration polarisation. The exponential curve in Figure 44 indicated the existence of concentration polarisation during the off-site DO.

4.4.3 CONCENTRATION OF THE SOLUTIONS FROM OSMOTIC DEHYDRATION

Among the membranes tested during off-site DO, the flat-sheet membrane Desal5-DK was the one that provided the highest fluxes. For this reason, the Desal5-DK membrane was chosen to concentrate osmotic solutions. The fluxes obtained while filtrating the sucrose and osmotic solutions are presented in Figure 45.

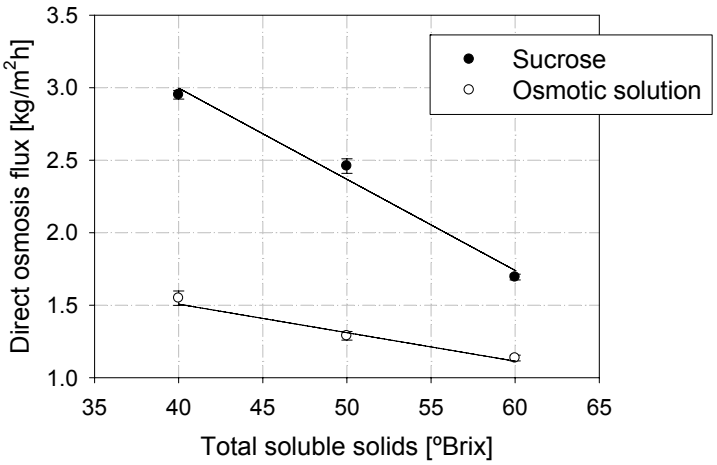

Figure 45. Direct osmosis fluxes for sucrose and osmotic solutions achieved during off-site DO using the Desal5-DK membrane.

The filtration of OS led to lower fluxes than the filtration of sucrose solution. This decrease was influenced by the complex composition of the OS and also by interactions between the membrane and the OS solutes.

4.4.4 MASS TRANSPORT DURING OFF-SITE DO

Transport of the electrolyte to the sugar solution, and the reducing sugar and/or sucrose to the SS solution was studied as well as the water flux. Table 21 presents the Cl^- concentration in the sugar solution, and the sucrose concentration in the osmotic solution for three different membranes and all the sucrose solutions tested (5-60 ºBrix).

Independently of the membrane, Cl^- concentration in the sucrose solution increases with the sugar concentration, and the opposite was found for the sugar concentration in the SS at the end of the 3-hour experiment (Table 21). This phenomenon seems to indicate that sucrose transport through the membrane could be related to water transport, while salt transport could be higher when water transport decreases.

Table 21. Concentration of Cl^- [g/l] in sucrose solution and sucrose [g/l] in NaCl solution after 3 h of off-site DO.

Membrane	**Sucrose concentration [ºBrix]**					
	5	20	40	50	55	60
	Cl^- concentration in the sucrose solution [g/l]					
Desal5-DK	0.009	0.07	0.41	0.60	0.70	0.82
MPT/F-34	0.20	1.60	1.14	1.10	1.60	5.10
AFC99	0.006	0.14	0.23	0.22	0.25	0.60
	Sucrose concentration in the SS [g/l]					
Desal5-DK	2.8	2.7	1.8	0.9	0.3	0.0
MPT/F-34	3.0	2.9	1.7	1.0	0.5	0.0
AFC99	3.3	3.0	1.9	1.2	1.0	0.5

Of all the membrane properties, the selectivity of the separation layer is the main factor that affects solute transfer between solutions. The most selective membrane is the AFC99, considered to be a RO membrane, the second most selective is the Desal5-DK, and the least selective is MPT/F-34. The low sucrose retention of the AFC99 membrane (Table 21) is quite unusual, since it is the densest of all the membranes tested.

The electric charge of the membrane is known to affect membrane selectivity, so the streaming potential of each membrane was measured. Figure 46 presents the results of the zeta potential measurements for flat-sheet (Desal5-DK and MPF-34) and tubular (AFC80 and MPT-34) membranes. The measurement set-up made it possible to evaluate the zeta potential on the surface of flat-sheet membranes and through the pores of the tubular ones.

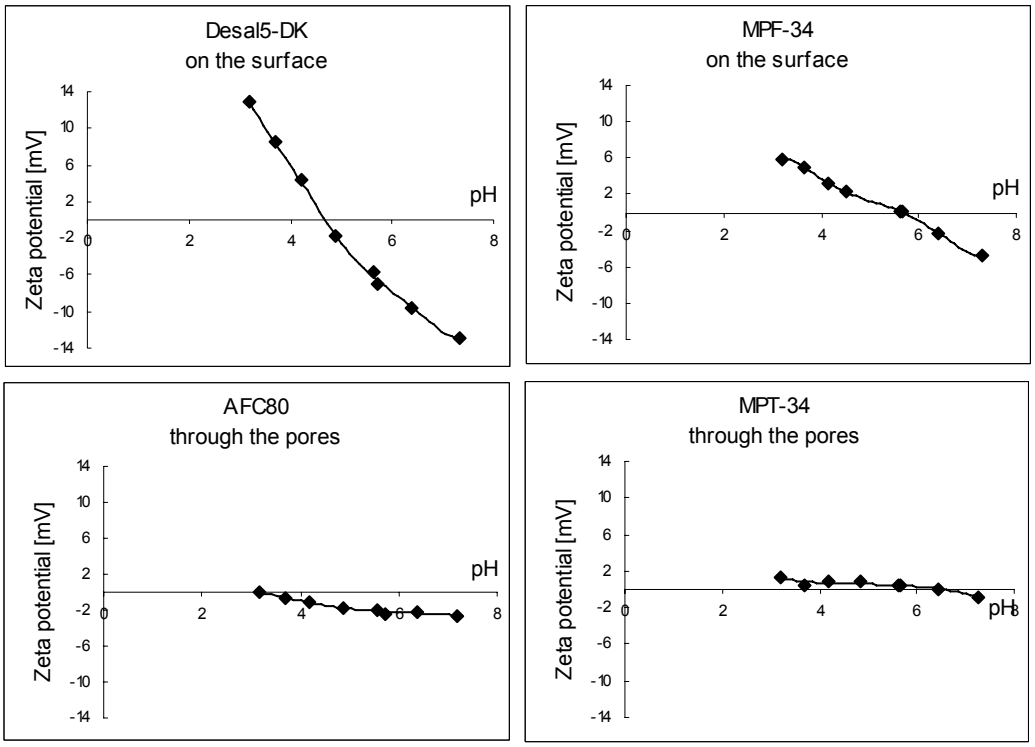

Figure 46. Zeta potential of Desal5-DK, MPF-34, AFC80 and MPT-34 membranes.

As can be observed in Figure 46, the Desal5-DK has the lowest charge, and the AFC80 membrane the lowest isoelectric point (3.2). The isoelectric points of the other membranes are 4.7, 5.5 and 6.5 for Desal5-DK, MPF-34 and MPT-34, respectively. Desal5-DK and AFC80 have a negative charge under the present working conditions (pH~6), while MPT/F-34 membranes have a slightly positive charge. The MPT/F-34 membrane charge could be one of the reasons for the significant transfer of Cl^- during off-site DO. It can be assumed that the positive charge of the MPT/F-34 membranes promoted ion transport to the feed solution. The ions were attracted to the membrane surface first (during the experiments the separation layer of the membrane is directed to the SS), and then the convective transport occurring in NF/RO membrane ions transported them to the feed solution. The large number of ions concentrated on the membrane surface and probably inside the pores were dragged along during the diffusive transport. The opposite effect may explain the low quantities of Cl^- in the feed solution during the off-site DO process with Desal5-DK and AFC99 membranes. The

negative charge of these membranes did not allow the ions to agglomerate, so fewer ions were transported to the feed.

To find out the membrane charge and how the solids released from fruits interacted, we measured the streaming potential of membranes after apple and pear juice filtration. The fruit solutes had no effect on the surface or the pore charge of the membranes.

4.5 ON-SITE DIRECT OSMOSIS

4.5.1 CHANGES IN SOLUTION PROPERTIES DURING ON-SITE DO

The system applied in on-site direct osmosis was based on the idea of Proimaki and Gekas (2000). The main advantage of this system is that the reconcentration unit is directly coupled to the OD process system. Thus, the osmotic solution is reconcentrated while it is being diluted. During on-site DO, microfiltration membranes were used and two OS/SS configurations were studied (40/60 and 50/68 ºBrix sucrose solutions). The experiments lasted 3.5 h and four consecutive osmotic dehydration experiments were performed, which provided the information about the dilution and/or concentration of the osmotic and stripping solutions. It should be noted that the osmotic solution was the same throughout the four experiments, and a fresh apple batch was loaded in each experiment. The experimental set-up and the methodology are described in section 3.5.

To verify the influence of the reconcentration, experiments with and without the reconcentration unit were carried out. Table 22 shows the concentration, pH and colour changes of the 40 ºBrix OS with and without reconcentration. The same data regarding the use of a stripping solution of 60 ºBrix are also provided in Table 22.

Table 22. Concentration, pH and colour change for 40 ºBrix with and without the reconcentration, and SS of 60 ºBrix.

	Experiment without reconcentration			**Experiment with reconcentration (on-site DO)**					
	OS of 40 ºBrix			**OS of 40 ºBrix**			**SS of 60 ºBrix**		
Exp. nr. *	Conc. [ºBrix]	pH	A_{420}	Conc. [ºBrix]	pH	A_{420}	Conc. [ºBrix]	pH	A_{420}
0	40.0	2.70±0.11	0.015	40.0	2.80±0.08	0.027	60.0	2.97±0.04	0.043
1	39.6	2.72±0.07	0.019	41.1	2.94±0.09	0.030	58.9	3.01±0.00	0.030
2	39.2	2.90±0.06	0.025	41.9	2.96±0.07	0.036	58.1	3.01±0.00	0.028
3	38.8	2.96±0.04	0.031	42.6	3.00±0.01	0.038	57.5	3.01±0.01	0.027
4	38.1	3.00±0.01	0.037	43.2	3.01±0.00	0.039	56.8	3.01±0.00	0.025

*Exp. nr –experiment number

Table 22 shows that the concentration of the OS increases when on-site DO is applied. However, during the traditional osmotic dehydration process (without reconcentration) the OS concentration decreased from 40.0 to 38.1 ºBrix in the last experiment. The pH increased slightly for all the solutions, but this can be attributed to an experimental error in the reading during the analysis. The colour intensity of the osmotic solutions increases because of the apple pieces (even though the solutions were filtrated before the analysis) and the browning reactions.

The concentration and colour of SS decrease because of the water transported from the OS, while pH increases only after the first experiment and then remains constant. The decrease in sugar concentration in the SS is proportional to its increase in the OS.

The results during the experiments with the osmotic solution of 50 ºBrix and SS of 68 ºBrix were similar to those for 40/60 ºBrix (Table 23).

Table 23. Concentration, pH and colour change for 50 ºBrix with and without the reconcentration, and SS of 68 ºBrix.

	Experiment without reconcentration			**Experiment with reconcentration (on-site DO)**					
	OS of 50 ºBrix			**OS of 50 ºBrix**			**SS of 60 ºBrix**		
Exp. nr. *	Conc. [ºBrix]	pH	A_{420}	Conc. [ºBrix]	pH	A_{420}	Conc. [ºBrix]	pH	A_{420}
0	50.0	3.10±0.10	0.024	50.0	3.10±0.12	0.045	68.0	3.30±0.09	0.069
1	49.4	3.21±0.08	0.031	50.2	3.23±0.10	0.047	67.9	3.46±0.00	0.062
2	48.8	3.31±0.01	0.033	50.4	3.34±0.03	0.048	67.6	3.47±0.00	0.060
3	48.3	3.35±0.02	0.048	50.6	3.40±0.01	0.051	67.4	3.47±0.00	0.057
4	47.6	3.37±0.01	0.057	50.8	3.45±0.00	0.054	67.2	3.47±0.01	0.054

*Exp. nr –experiment number

During this set of experiments, the OS without reconcentration reduced its concentration by about 5 %, which is comparable with the results obtained for the 40 ºBrix solution discussed above. As for the OS with reconcentration, Table 22 shows that the concentration increases less than when the OS had an initial concentration of 40 ºBrix. These results are due to the fact that the driving force is lower because the difference in water activity between the OS and SS is also lower. Another reason is that

the osmodehydration force of the 50 ºBrix solution is greater than the 40 ºBrix, which increases the water transport from the apples to the OS, resulting in higher OS dilution.

The 68 ºBrix SS properties underwent the same changes as 60 ºBrix SS. The dilution is proportional to the increase in concentration of the OS, the colour decreases because of the dilution, and finally the pH changes only affect the first experiment and then remain stable.

Apart from the concentration, pH and colour, the efficiency of the on-site DO reconcentration can be evaluated by determining the water activity of the osmodehydrated apples. From the analysis of the a_w it can be observed that when OS was reconcentrated in situ, the final a_w of the apples remained constant. However, when no OS reconcentration was performed, the final a_w of the apples decreased in each experiment as a result of the decrease in the initial OS concentration (decrease in the osmodehydration force) (Table 24).

Table 24. Water activity of apples osmodehydrated using 40 and 50 ºBrix OS with and without on-site DO.

	40 ºBrix without reconcentration				**40 ºBrix reconcentrated with 60 ºBrix SS**			
Experiment Nº	1	2	3	4	1	2	3	4
a_w (t=0)	0.972	0.970	0.971	0.974	0.977	0.971	0.976	0.979
a_w after the OD (t=3.5 h)	0.950	0.965	0.962	0.969	0.958	0.950	0.951	0.952
	50 ºBrix without reconcentration				**50 ºBrix reconcentrated with 68 ºBrix SS**			
Experiment Nº	1	2	3	4	1	2	3	4
a_w (t=0)	0.970	0.973	0.973	0.973	0.970	0.976	0.977	0.979
a_w after the OD (t=3.5 h)	0.950	0.951	0.959	0.964	0.950	0.948	0.946	0.949

*t=0: beginning of the experiment, t=3.5 h: sample after 3.5 h OD process

The significant increase in concentration of the 40 ºBrix osmotic solution during the on-site DO (Table 22) positively influenced the water activity gradient during the osmotic dehydration of the apples, and resulted in a greater decrease in the apples a_w at the end of each experiment (Table 24). On the other hand, the use of on-site direct osmosis coupled to osmotic dehydration with a 50 ºBrix osmotic solution did not

decrease the apples' water activity at the end of each experiment. In this case, a_w remained stable (Table 24), since the OS was not reconcentrated as much as the 40 ºBrix solution.

The change in the strength of OS osmodehydration can be determined by considering the weight reduction of OD treated apples. Figure 47 shows the weight reduction of apples treated with the reconcentrated DO and diluted OS.

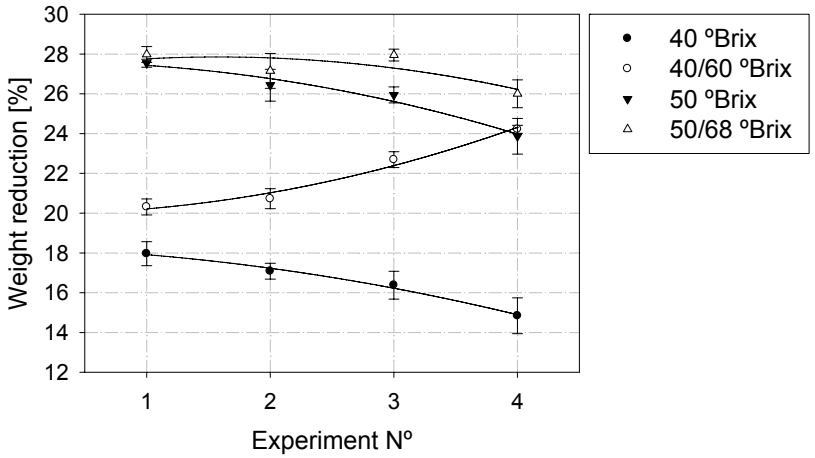

Figure 47. Weight reduction of the osmodehydrated apples using 40 and 50 ºBrix sucrose solution with and without on-site DO reconcentration.

The data presented in Figure 47 confirm the remarks made above. The dilution of both OS has a negative influence on the efficiency of the OD. As far as the reconcentrated solutions are concerned, the 40 ºBrix OS improved performance while the 50 ºBrix OS decreased efficiency slightly. The weight reduction during the 50/68 ºBrix reconcentration can be enhanced by using a better stirring mechanism and improving the experimental design. During on-site DO, the osmotic solution was stirred in the same way as during osmotic dehydration without reconcentration (using a magnetic stirrer at 350 rpm). The stripping solution during the on-site DO was stirred using 4 homogenizers at a low stirring rate of 100 rpm approx. Since the homogenizers were placed in the steady position, the stirring was unequal for all parts of the membrane and, at the edges, the solution mixing was minimum. Experimental design could also have a negative effect on the fluxes, because the cavities of the membrane support are deep and may obstruct proper solution mixing.

4.5.2 TRANSPORT DURING ON-SITE DO

The mass transported from and into the apples to the OS, and later from and into the OS to the SS could not be estimated exactly because of limitations in the experimental set-up. Water fluxes from the osmotic solution to the stripping solution were calculated using the decrease in water concentration of the 40 and 50 ºBrix sucrose solution at the end of each experiment. The fluxes were calculated assuming that only water was transported through the membrane from the OS to the SS. The water fluxes calculated using this approach are presented in Figure 48.

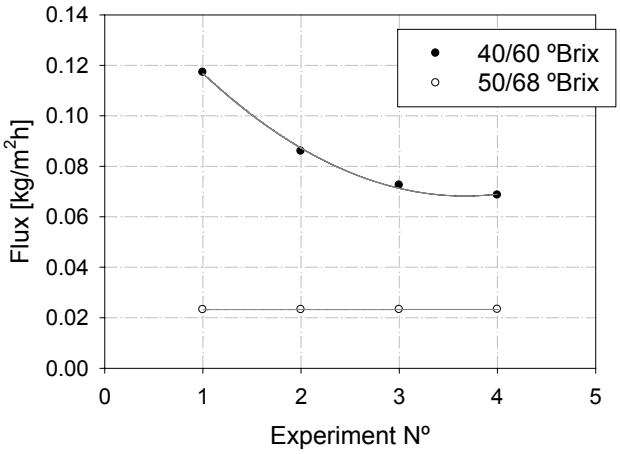

Figure 48. Water fluxes obtained during on-site DO using a microfiltration membrane.

The fluxes for the 40/60 ºBrix configuration (Figure 48) were higher than those of the 50/68 ºBrix configuration because of the higher driving force, the lower concentration polarisation and fouling. They decreased with the number of cycles, due to the increase in the OS viscosity. This decrease is more significant for the first two experiments and seems to stabilise for the last ones, perhaps because a stable concentration polarisation layer significantly affects the flux. 50/60 ºBrix configuration presented a very stable flux from the beginning of the experiments.

The water fluxes obtained in the present study were an order of magnitude higher than the theoretical flux estimated by Proimaki and Gekas (2000): 0.0063 kg/m^{2}h. This

may indicate that the concentration of the osmotic solution was promoted by counter-current sugar and water transport and not only by the dewatering of the OS.

To compare the effect of reconcentrating the osmotic solutions, the dehydration fluxes of the apples were calculated taking into account water and soluble solid loss. The solute flow to the apples is neglected, because the experiments were carried out using osmotic dehydration times in which the food was not impregnated (section 4.1).

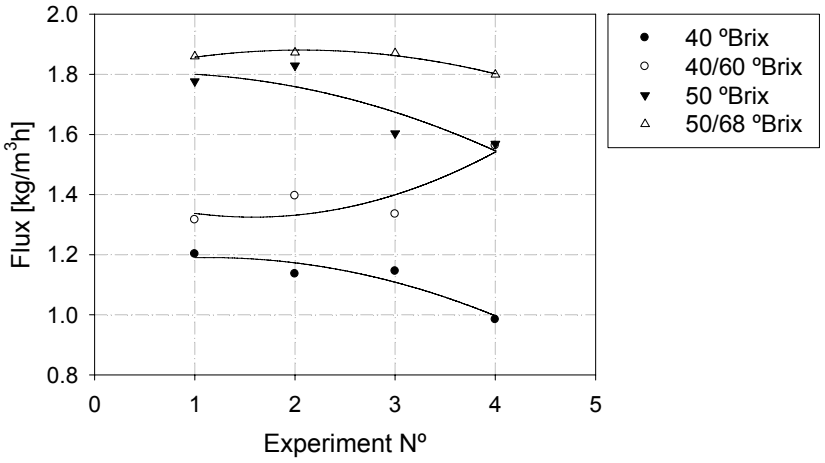

Figure 49. Water flux of the apples during osmotic dehydration with and without reconcentration of the osmotic solution.

Figure 49 shows the decreasing dehydration fluxes of the un-reconcentrated solutions. The reconcentrated solutions increase (40/60 ºBrix) or maintain their dehydration fluxes (50/60 ºBrix). The calculation of fluxes further confirms the efficiency of the on-site direct osmosis.

4.6 SENSORY ANALYSIS

Samples of dehydrated apples using reconcentrated OS were obtained during the experiments with on-site direct osmosis. Thus, the sensory analysis results are related to the data from section 4.5. The samples were evaluated on a scale from 0 to 5, with 5 being the best grade. The results of the main sensory analysis parameters—sweetness and overall taste—were best for apples osmodehydrated with 50 ºBrix solution reused four times (Table 25).

Table 25. Sensory analysis results considering sweetness and overall taste.

	Dried – without OD	**Dried – after 40 ºBrix OD**	**Dried – after 50 ºBrix-R4 OD**	**Dried – after 50 ºBrix OD**	**Dried – after 50 ºBrix-R4 OD**
Sweetness	2.64±0.8	3.36±0.9	3.14±0.8	3.71±0.7	3.71±0.8
Overall taste	2.92±1.0	3.64±1.2	3.43±0.9	3.54±1.0	3.86±0.9

*ºBrix-R4 osmotic solution reconcentrated 4 times

The degree of acceptance for the apples treated with 50 ºBrix solution-reused four times (50 ºBrix-R4) was nearly 4, which means: good for the overall taste and significant presence for the sweet taste. These good results can be explained by the increase in concentration of apple nutrients transported to the OS during the three previous OD processes. The effect of a greater nutrient concentration after OS reconcentration is twofold: (1) it reduces the flow of nutrients out of the last 50 ºBrix-R4 treated apples and (2) it promotes the impregnation of 50 ºBrix-R4 treated apples with nutrients from OS.

The positive influence of OS reuse was also observed by Szymczak et al. (1998) in their work on the reconcentration of 70 ºBrix sucrose solution in the osmodehydration of sour cherries. Sensory analysis revealed that the cherries dehydrated in the last (5^{th}) batch when the osmotic solution had not been changed were the ones that were most accepted by the panellists. However, to maintain the solution strength, the authors heated the solutions to 40 ºC, which resulted in colour degradation. In the long term, this may even deteriorate the solution and lead to the loss of the additives. Thermal reconcentration can also have a negative influence on the osmodehydrated product because it promotes browning. In the case of the sour cherries used in the study, the browning effect resulted in a tendency for the colour intensity to decrease when the

same solution was used. For fruits with lower concentrations of ascorbic acid, this trend would be more marked. García-Martínez et al. (2002 B) studied using the same osmotic solution ten times during the osmodehydration of kiwi. They did not notice any significant colour change in kiwi slices after a 55 ºBrix solution had been used ten times, which may be attributed to the short OD time and kiwi resistance to browning.

Colour and general aspect were also analysed in the present study. The values presented in Table 26 show once again that the panellists responded well to the 50 ºBrix-R4 treated apples.

Table 26. Sensory analysis results considering additional parameters.

	Dried – without OD	**Dried – after 40 ºBrix OD**	**Dried – after 50 ºBrix-R4 OD**	**Dried – after 50 ºBrix OD**	**Dried – after 50 ºBrix-R4 OD**
Acidity	1.79±1.2	1.79±1.3	1.36±1.50	1.29±1.4	1.50±1.2
Bitterness	0.71±0.9	0.36±0.1	0.57±0.1	0.57±0.3	0.50±0.8
Aroma	2.36±0.9	3.00±0.7	2.43±0.9	2.57±1.4	2.64±0.2
General aspect	3.00±0.8	3.00±0.4	2.50±0.9	3.36±0.5	3.64±0.8
Colour	3.21±1.1	3.00±1.1	2.21±1.0	3.31±0.8	3.50±0.8

The extremely good results for the colour and general aspects of the 50 ºBrix-R4 sample suggest that the membrane process used to reconcentrate the osmotic solution is a very promising method for OS reconcentration. The results obtained for the 50 ºBrix-fresh solution also made it possible to compare other parameters. The 50 ºBrix-R4 solution improved aroma, increased the level of acidity and decreased the bitterness. However, the ratings for aroma retention are best for the 40 ºBrix-fresh solution. This is because of the lower dehydration force of 40 ºBrix, which (1) reduced sugar impregnation in the sample (high sugar concentration may mask natural fruit aroma) and (2) decreased solute loss from the fruit. The aroma loss observed for the treatment with 50 ºBrix solution can be controlled by reducing the OD treatment time.

Finally, panellists preferred OD pretreated apples to fresh-dried apples, which indicates that OD is a promising food pre-treatment process.

In the present study the solutions were reused four times, but the evidence shows that in the on-site mode the reconcentration lasts as long as the osmotic solution and the reconcentration solution do not reach equilibrium.

4.7 INTEGRATION OF MEMBRANE CONTACTORS IN AN INDUSTRIAL-SCALE OSMOTIC DEHYDRATION PROCESS

The final step in the present study was to design a feasible industrial-scale osmotic dehydration process with an integrated reconcentration step that uses membrane contactors (Figure 50). For the DO process, a 50 ºBrix osmotic solution was used and the ratio between the OS and the fruits was kept at 25:1. The operation time was set at 3.5 h and it was assumed that fruits lost 80 kg of water throughout the osmotic dehydration process.

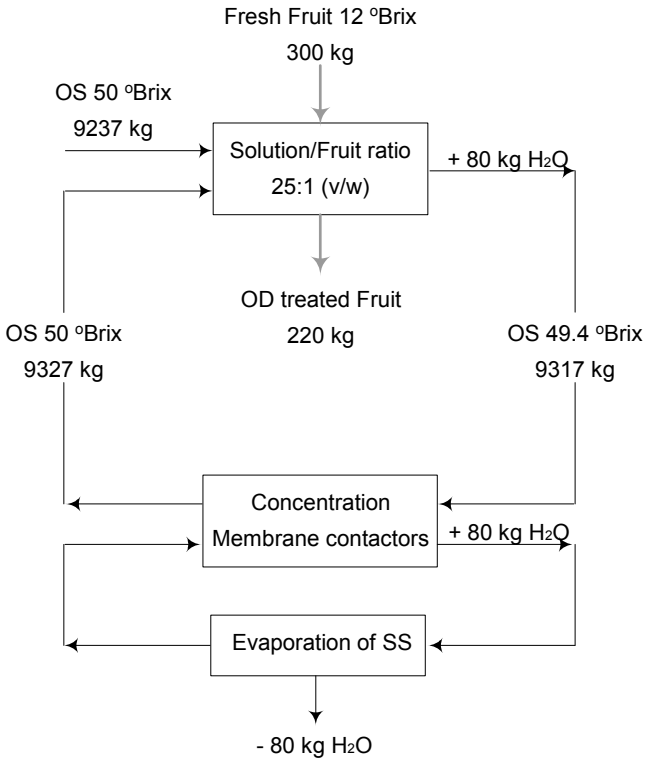

Figure 50. Scheme of the hypothetical osmotic dehydration process.

Osmotic membrane distillation or direct osmosis were considered as the concentration step in this OD process. Nanofiltration can be applied only as a pre-concentration step for diluted solutions. To compare these processes, the membrane area

required to eliminate 80 kg of water was calculated (Table 27). The concentration step is assumed to have maximum reconcentration efficiency and no osmotic solution losses.

Table 27. Membrane area required to eliminate kg of water using the membrane contactor techniques.

	OMD	**off-site DO**	**on-site DO (50/68 ºBrix)**
Membrane type	11806	Desal5-DK	Durapore
Membrane area [m^2]	3.6	9.7	1608

The membrane area that re-establishes the initial concentration of the osmotic solution is lowest when the OMD process is applied. The off-site DO requires a membrane area that is twice as big and the predicted membrane area for the on-site DO is extremely large. Therefore, only OMD and off-site DO can be regarded as feasible concentration methods.

Another issue to consider is the final quality of the reconcentrated osmotic solution. To obtain high quality solutions, the retention of the OS and SS solutes should be as high as possible. This is the case when a hydrophobic membrane is used, so OMD has another advantage over the other two processes.

5 CONCLUSIONS

The results of the present study confirm the viability of applying membrane separation processes to reconcentrate spent osmotic dehydration solutions. Of the membrane separation processes investigated—NF, DO (on-site and off-site modes) and OMD—the last one has the best overall performance as far as water fluxes and solute retention are concerned.

According to the results, NF is restricted to the treatment of diluted solutions, since the maximum sucrose concentration obtained was about 24 ºBrix. Therefore, NF can be applied as a pre-concentration step in fruit juice production, but if the concentration level of solutes is to be higher, it must be coupled with some other methods. The experiments using NF processes show that both temperature and pressure influenced the process performance. Nevertheless, the most important factor in process performance was the membrane, which should combine high fluxes and high retentions if results are to be optimal. Characterisation of the flat-sheet and tubular membranes by AFM showed differences in the membrane separation layers, even though they were all reported to be made from the same materials (polyamide). AFM analysis turned out to be a good tool for characterising the topology of nanofiltration membranes, and the only disadvantage is the loss of image resolution caused by the magnification required for NF membrane visualisation. The membrane morphology before and after the nanofiltration process was analysed using SEM. Cross-section images of the membranes showed that their structure underwent two kinds of changes during NF of sucrose solutions. Blocked pores and a fouling layer were observed in the separation layer. The support also underwent significant modifications, such as delamination or compaction caused by pressure or other process conditions.

Membrane contactors (osmotic membrane distillation and direct osmosis) were chosen because they both enable viscous solutions to be treated. As far as OMD stripping solutions are concerned, $CaCl_2$ was more efficient and provided higher water fluxes than NaCl. The analytical tests demonstrate that only water was transported through the membrane during the OMD process. The 100 % solute retention and relatively high water fluxes are the main advantages of the OMD process. Water transport during OMD was affected most by water activity for the SS, but by viscosity for the feed solution. The overall mass transfer coefficients showed higher values for NaCl, but the significantly higher water activity limited the driving force, and gave lower water fluxes than $CaCl_2$. The higher viscosity of $CaCl_2$ did not prevent water fluxes from being high, so water activity can be considered as the key property for the

SS. No concentration polarisation layer was found mainly due to the high stirring rate and temperature control. As for the feed solution, the more complex composition of an actual osmotic solution meant that water fluxes were lower than for pure sucrose solutions with the same initial concentration. However, as the initial concentration increased to 60 ºBrix, the difference between water fluxes for actual OS and sucrose solutions was negligible. Therefore, the decisive feed solution property was found to be its viscosity.

The main drawbacks of the industrial application of OMD are the unfeasibility of membrane reuse, and SS dilution. The first problem can be overcome by selecting the appropriate membrane (very resistant and long-life) and carefully controlling the process parameters (temperature and stirring rate). The best way to avoid excessive SS dilution is to adjust the SS/feed volume ratio, and reconcentrate the SS by adding an evaporation unit to the OMD separation plant.

Direct osmosis applied in two configurations (on-site and off-site) was also very efficient at reconcentrating the osmotic solutions. The main advantage of on-site DO is its simplicity, which means that the process can be more economic. However, the low water fluxes obtained during the reconcentration of a 50 ºBrix OS limit its industrial application. The water fluxes could be enhanced by improving the stirring mechanism and the design of the membrane support, which in the present work were found to be the bottleneck of the process.

Water fluxes were higher when off-site direct osmosis was used. However, the disadvantage of direct osmosis is the convective transport of the stripping solution on the osmotic solution side. This transport was found to be promoted by the electric charges of the NF membranes. Due to the attraction forces the positively charged membranes showed greater Cl^- ion transport than the negatively charged membranes. Among other membrane properties, membrane thickness is a very important factor. For sucrose solutions in the range 40-50 ºBrix, flat-sheet membranes showed 50 % higher fluxes than tubular membranes, even though their area was three times smaller. Moreover, the flat-sheet membranes were thinner than the tubular ones. Therefore, the key factor to obtain high water fluxes is to select a non-toxic stripping solution with high osmotic pressure, and a membrane dense enough to constitute a barrier between the solutions and thin enough to promote water transport.

During the sensorial analysis of apples that had been osmotically dehydrated with on-site OS reconcentration, the panellists indicated that the apples osmodehydrated using the reconcentrated solution were best. The tests were carried out for dried apples dehydrated before using fresh and four-times reconcentrated OS, and also for the blank sample (apples dried without previous osmodehydration). In nearly all the categories the ratings were lowest for the apples dried without the OD pre-treatment.

The design of a feasible osmotic dehydration process with an integrated osmotic solution reconcentration step indicated that osmotic membrane distillation is more economically viable than direct osmosis. For OMD, a membrane of only 3.6 m^2 was required to reconcentrate the 50 ºBrix solution, diluted after the OD of 300 kg of fresh fruit. When the best membrane is used in off-site DO and on-site DO, on the other hand, 9.7 and 1608 m^2 were required, respectively. Another advantage of OMD is of the fact that it totally rejects the solutes, which is especially important from both the operational and the consumers' point of view. The total retention for feed and SS decreases the reconcentration time. The high retention of flavours and fragrances improve the osmodehydrated food taste. Simplicity, possibility of automation and low investment and operation costs are the benefits of the OMD and DO processes. The major disadvantage of the OMD process is the possibility of thermal polarisation and care must be taken to maintain a stable temperature profile across the membrane. Even under initially isothermal conditions, the SS may be warmed by the heat of evaporation transported with the vapour. This reversed temperature profile can stop transport and lead to reversed transport. Another issue to be solved for the industrial application of OMD is the reconcentration of the stripping solution. The SS can be reconcentrated by evaporation, since it is not considered thermally labile and the only objective is the restitution of the initial SS concentration. For OMD, the thickness, strength, durability and low wet-out properties must all be taken into account when selecting a membrane.

Finally, it can be concluded that reconcentrating osmotic spent solutions with membrane separation processes leads to (1) lower DO operation costs (less OS is required and the additives are preserved), (2) fewer residues, and (3) better tasting osmodehydrated products.

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APPENDIX

Análisis sensorial de soluciones de azúcar

Nombre.....

Frecuencia del consumo de dulces.....

Fecha.....

Hay 3 series de muestras (A, B y C).

Dentro de cada serie de muestras, hay una muestra que tiene diferente concentración de azúcar.

Por favor, marque con un X la que le parece diferente.

(Apunte si según usted es más o menos dulce que las otras dos- opcional)

Serie	**Número de muestra**			**Diferencia de concentración [+ o -]**
A	1	2	3	
B	1	2	3	
C	1	2	3	

Análisis sensorial de manzanas procedentes de deshidratación osmótica

Táchese lo que proceda

	Intensidad de percepción*					
	0	1	2	3	4	5
Dulce						
Aromático						
Otro(s) atributo(s) tolerable(s)						
¿Cuál(es)?						
Ácido						
Agrio/ Avinado						
Moho/ Humedad						
Otro(s) atributo(s) intolerable(s)						
¿Cuál(es)?						

* 0- Ausencia total, 1- Casi imperceptible, 2- Ligera, 3- Media, 4- Grande, 5-Extrema

Grado de satisfacción						
	Intensidad de percepción*					
	0	1	2	3	4	5
Aspecto						
Color						
Sabor en general						
Observaciones						
Nombre de catador.....						
Frecuencia de consumo de manzanas.....						
Clave de muestra.....						
Fecha.....						

* 0- Muy malo, 1- Malo, 2- Regular, 3- Bastante bueno, 4- Bueno, 5- Muy bueno