Filtration and Emulsification with Nano Engineered Membranes

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ABSTRACT

With nano and micro engineering techniques it is possible to manufacture very precise perforated membranes. The pores, which are well defined by photolithographic methods, allow accurate separation of particles by size. The membrane thickness is usually smaller than the pore size resulting in operational process fluxes that are one to two decades higher than obtained with convential filtration methods. We will present experimental results for microfiltration of lager beer (cold sterilization).

Many emulsions today are obtained by stirring or by use of high pressure homogenisers. A new technique to produce emulsions is cross flow membrane emulsification (XME), a process in which the to-be-dispersed phase (for instance oil) is pressed through a membrane. Subsequently formed droplets at the membrane surface are then carried away by the continuous phase (for instance water) flowing across the membrane. Under ideal conditions, XME is able to produce quasi-monodisperse emulsions.
We will present results for making very monodisperse emulsions (GSD<1.03) for biomedical applications.

1 NANO ENGINEERED MEMBRANES

Nano engineered membranes filters are characterised by thin membrane layers with uniformly sized pores and for most applications the membrane layer is sustained by a support. Inorganic membrane and in particular ceramic membranes [1] have a number of advantages above polymeric membranes like high temperature stability, relative inert to chemicals, applicable at high pressures, easy to sterilise and recyclable. However they have not been used extensively because of their high costs and relatively poor control in pore size distribution.

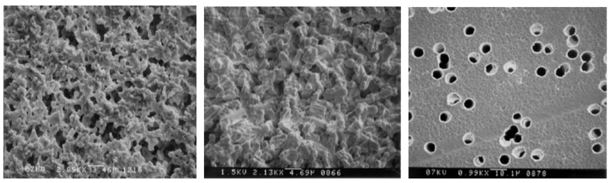

Figure 1: SEM micrographs of membrane filters. Left: Organic phase separated membrane filter, Middle: Ceramic sintered filter, Right: polymeric track etched membrane filter.

Also the effective membrane layer is very thick in comparison to the mean pore size (typically 50-1000 times), which results in a reduced flow rate. A composite filtration membrane having a relatively thin filtration or sieving layer with a high pore density and a narrow pore size distribution on a macroporous support will show good separation behaviour and a high flow rate (see Fig. 2). The support contributes to the mechanical strength of the total composite membrane.

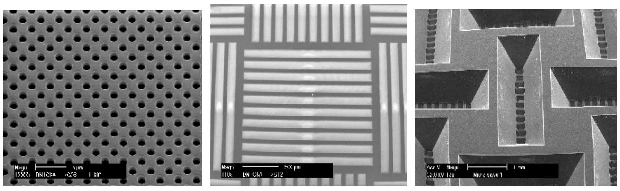

Figure 2: SEM micrographs. Left: detail of nano engineered membrane surface for microfiltration, Middle: overview of membrane surface, Right: support side of a nano engineered membrane structure for microfiltration.

2 FILTRATION WITH NANO ENGINEERED MEMBRANES

Compared to other microfiltration membranes, nano engineered membranes have an extremely small flow resistance [2]. An accumulation of retained particles in front of the membrane (cake layer formation) will -more than for other membranes- greatly increase the flow resistance. It is therefore important to keep the surface free of particles during filtration. This is usually done by applying a cross-flow in which larger particles will be removed from the membrane surface. Permeate flow reversal (back pulsing) is a more advanced method to remove smaller particles from the surface of the membrane filter. The required cross-flow velocity to remove larger particles is dependent on several variables such as the ratio between the particle and the pore size, the transmembrane pressure and cross-flow channel dimensions. An additional advantage of a clean membrane surface is that the retention characteristics of the filtration process is only determined by the membrane layer itself and not by the additional permeation characteristics of the cake layer.

2.1 Filtration of Lager Beer

Nowadays tubular ceramic or polymeric membrane systems are being developed as an alternative for diatomaceous earth filtration. Complications in using these type of filtration membranes are yeast cell clogging and protein adsorption leading to a fast flux decline and subsequent elaborate in-line cleaning procedures [3]. The use of nano engineered membranes for the filtration of lager beer have been carried out.

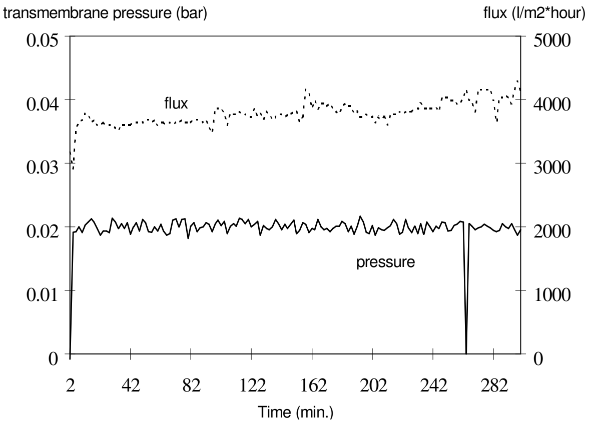

Figure 3: Behaviour of flux and pressure in yeast-cell filtration of lager beer with nano engineered membranes.

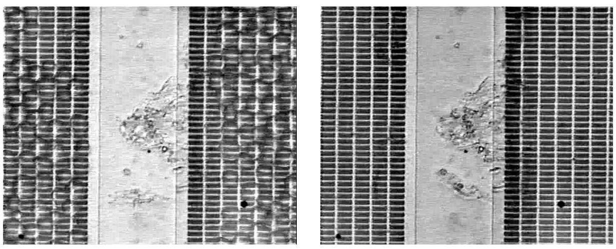

Figure 4: Loosely-attached flock on a nano-engineered membrane with 1.5 × 7.5 μm^2 slits during filtration of rough lager beer. The picture on the left shows the situation during filtration and the picture on the right immediately after a backpulse.

Besides the fouling process the influence of pore size on permeate flux and turbidity was investigated. Centrifuged beer appeared to give a significantly clearer permeate than rough beer. For centrifuged beer and a nano engineered membrane with a pore diameter of 0.55 μm a haze of 0.23 EBC was obtained during 10.5 hours of filtration at an average flux of $2.21 \cdot 10^3$ l/m^{2}hr. For a membrane with slit-shaped perforations of 0.70×3.0 μm^2 a haze of 0.46 EBC was obtained during 9 hours of filtration at an average flux of $1.43 \cdot 10^4$ l/m^{2}hr. This flux is about two orders of magnitude higher than is commonly obtained with membrane-filtration of lager beer. Concentration of the beer by a factor of 12 in a 3 hour run hardly influenced the magnitude of the flux.

3 EMULSIFICATION WITH NANO ENGINEERED MEMBRANES

An emulsion is a dispersion of droplets of one immiscible liquid within another liquid. An emulsifier may be added to stabilise the dispersion. Emulsions are indispensable in the modern food, pharmaceutical and cosmetic industry and are categorized as: oil-in-water (o/w) emulsions, such as liquid cream or milk, in which oil is the dispersed phase and water the continuous phase, and water-in-oil (w/o) emulsions, such as margarine, in which water is the dispersed phase and oil the continuous phase.

3.1 Cross Flow Emulsification

A new technique to produce emulsions is cross flow membrane emulsification [4]: a process in which the to-be-dispersed phase, for instance oil, is pressed through a membrane and droplets formed at the membrane surface are carried away with the continuous phase, for instance water, flowing across the membrane, resulting in an oil in water (o/w) emulsion. When the emulsion droplet grows a number of relevant forces are acting on the droplet that tries to hold or to remove the droplet from the pore. The main force F_γ, holding the droplet is the surface tension γ multiplied by the circumference of the neck D_n.

$$F_\gamma = \pi \cdot D_n \cdot \gamma$$

During the growing of the droplet the diameter of the neck of the droplet will decrease. Just before droplet detachment, the drag force F_d of the continuous phase should equal approximately the surface tension force F_γ. If one substitutes the approximation $D_n = D_p$, and the definition of the Laplace pressure at the pore $P_p = 4\gamma/D_p$, one obtains the simple expression:

$$\frac{P_p}{\tau_w} = 10.2\left(\frac{D_d}{D_p}\right)^2$$

3.2 Emulsification Experiments

Cross flow emulsification experiments have been performed with use of a rectangular cross flow channel with a height of 350 micron and a width of 2.5 cm at room temperature conditions. Sunflower oil has been used for the disperse phase and a 0.5 % Tween 20 aqueous solution for the continuous phase. The micro engineered silicon nitride orifice has a diameter of 4.0 ± 0.2 micron. Before each experiment the orifice was subjected to a RF oxygen plasma to obtain maximum hydrophilicity of the membrane surface. The Laplace pressure of the orifice was experimentally determined at 5000 ± 100 Pascal.

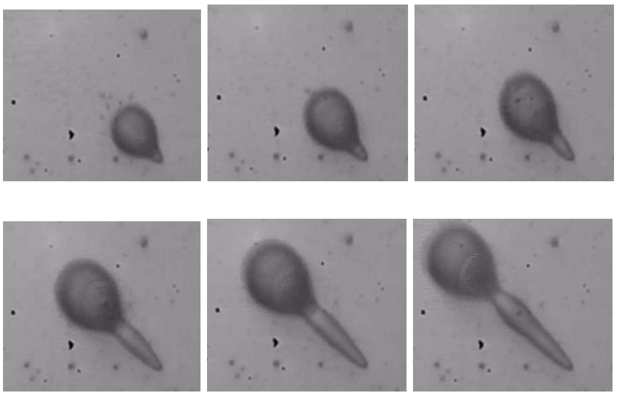

Figure 5: Subsequent growing stages of a droplet sunflower oil in a Tween 20 (0.5%) aqueous solution. Time frame is 40 msec/shot, at all shots clearly a neck is visible with a maximum diameter of about 10 micron.

Shear rate τ_w Pascal	Trans-Membrane Pressure Pascal	Droplet size Micron
0.4	6100	120
0.9	6000	95
2	5900	71
4	5900	58
8	5900	46
12	5900	40
16	5900	28

Table 1: Droplet size as a function of the shear rate for a micro-orifice membrane and can be well predicted with above equation.

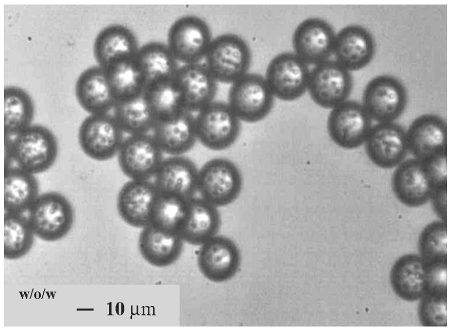

Figure 6: Photograph of a typical w/o/w mulitphase emulsion that has been obtained with the nano engineered membrane. The primary emulsion is a (polydisperse) water in sunflower oil emulsion with a mean droplet radius of 4.6 micron obtained with sonification. The secondary emulsion has a mean droplet radius of 34 micron with a size distribution GSD < 1.15.

ACKNOWLEDGMENTS

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