

Corvinus University of Budapest
Faculty of Food Science
Department of Food Engineering

DOCTORAL THESIS

Theoretical and Experimental Investigation of Membranes for Oily Streams Separation and Purification

András KORIS

PhD School/Program

Name: PhD School of Food Science

Field: Food Science

Head: Prof. Péter Fodor
Department of Applied Chemistry
Faculty of Food Science
Corvinus University of Budapest

Supervisor: Prof. Gyula Vatai
Department of Food Engineering
Faculty of Food Science
Corvinus University of Budapest

The applicant met the requirement of the PhD regulations of the Corvinus University of Budapest and the thesis is accepted for the defence process.

Budapest
2007

.....
Signature of Head of School Signature of Supervisor

1. Introduction

In the food-industry, as well in other industries, energy efficiency, environmentally friendly processes are important keys for a company to be successful on the market. Membrane techniques are possible alternative, “green” methods for conventional liquid separation processes. Generally membrane separation processes are possible solution for the following problems:

- high energy consumption during the processing of liquids, for example concentration by thermal evaporation,
- decrease of essential and healthy substances in the liquid product what is typical phenomena of high temperature processes,
- production of high amount non-reusable and non-dischargeable wastewater.

My Ph.D. thesis deals with the treatment of crude vegetable oil by membrane filtration and also oily wastewater separation by membrane filtration. Laboratory researches were carried out to prepare a membrane apparatus for the vegetable oil refining industry (degumming) and for the treatment of several oily wastewaters. After the experiments models were applied to understand the behavior of such liquids and also to support the design of an industrial application.

2. Aims

Degumming is an important process at the refining of vegetable oils, e.g. sunflower-seed oil and alternative energy source rape-seed oil. Degumming means

removal of phosphatides. My main target in these fields was to find the appropriate membrane to separate triglycerides and gums and to determine the optimal operating parameters. Generally the industrial need can be summarized as follows: 10 mg/L or lower total phosphorus content in the permeate, high productivity and resistance for mechanical and chemical effects.

Large amount of oily-, and fatty wastewater is produced in the food industry every year, e.g. in the above mentioned vegetable oil industry. Stable oil-in-water emulsions are a kind of oily waters; generally the treatment of such wastes is accomplished by using additives and thermal separation method. My main target in these researches were to find a membrane which is suitable for industrial application; which has high separation factor for oil to meet the environmental regulation (50 mg/L), has high productivity and has good resistance against mechanical and chemical effects.

In my last research I have combined membrane filtration with other unit operations; static mixing and gas injection. The aim of this work was to increase the production and to reduce energy consumption of membrane processes.

3. Materials and methods

Oil degumming experiments were conducted on a laboratory sized membrane apparatus. Model solution and crude sunflower-seed oil were used as test materials. The model solution was prepared from refined sunflower-seed oil and lecithin. Different pore-sized (6 to 100 kDa molecular weight cut off) membranes made from several materials (polymeric and ceramic) were involved in the membrane-screening. Flat-sheet and tube type membranes were used. The total phosphorus content was measured by the Hungarian standard method

“yellow color reaction of phosphor-vanado-molybdenum” (MSZ 19810-84). Organic solvents, *i*-propanol and ethanol were used for conditioning and cleaning the membranes after oil filtration.

The experiments for the separation of oily wastewater were carried out on laboratory-sized equipment as well. The emulsion what I used in these research was prepared from industrial emulsion oil (Unisol) and distilled water with 0,5 and 5% concentration. Membranes made from different materials and also with several nominal pore size were tested during the laboratory experiments. The concentration of the oil content was measured with spectrophotometer (MSZ 260-22: 1974).

To intensify the membrane filtration of oily liquids Kenics static mixer was installed in the membrane apparatus. Latest gas injection into the liquid flow was realized on the apparatus for economical reasons.

4. Summary of results

The main results in the topic of membrane degumming of crude vegetable oils are:

- the 20 nm pore sized ceramic membrane has better gum retention than polymeric membranes; TI-70-20-Z ceramic membrane had gum retention of 97 %, the polymeric PP2N membrane had only 91%,
- with the TI-70-20-Z ceramic membrane less than 10 mg/L total phosphorus content can be realized in the permeate,
- the initial pure water flux of the membrane could be re-established after oil filtration,

- Higher permeate flux can be gained if the membranes are treated with organic solvents; ethanol was better for polypropylene membranes and *i*-propanol for ceramic membranes.
- Polymeric membranes such as polysulphon, polyvinylidene-difluorite and polypropylene suffered irreversible fouling during oil filtration; the initial pure water flux cannot be established after several hours of use.

The main results in the topic of economical treatment of oily wastewaters are:

- the ceramic membrane TI-70-20-Z proved the best overall performance; great retention for oil (>99,95%), high durability and no irreversible fouling was observed,
- decreased specific energy consumption and better permeate flux was realized after static mixer was installed in the membrane apparatus.
- according to the resistance-in-series model the explanation found in the reduction of polarization resistance (R_p),
- the overall performance of a static mixer-membrane filtration apparatus is limited by the high pressure-drop along the membrane module,
- to reduce this pressure-drop gas (air) injection was successfully applied; in this combination the energy consumption could be further decreased according to my calculations.

5. Conclusions

As a result my work in the field of edible oil refining, a new economical, environmental and material friendly separation method was developed to remove gums from crude vegetable oils. The optimal operating parameters were calculated and effective cleaning method was also recommended.

As a result of my work in the field of oily emulsion separation, a new, complex, economical and environmental friendly separation method was developed, where membrane filtration, static mixing and gas injection were joined together. From the experimental data the optimal operating parameters were calculated and optimal cleaning method were also found.

6. Publications and Presentations of the Applicant in the Topic

Articles in English with Impact Factor:

1. **A. Koris**, Gy. Vatai: *Dry degumming of vegetable oils by membrane filtration*. Desalination, Volume 148, Issues 1-3, 10 September 2002, Pages 149-153, 2002
2. Hu X., Bekassy-Molnár E., **Koris A.**: *Study of modelling the transmembrane pressure and gel resistance in ultrafiltration of oily emulsion*. Desalination 163. p355–360, 2003
3. Darko M. Krstić, **András K. Koris** and Miodrag N. Tekić: *Do static turbulence promoters have potential in cross-flow membrane filtration applications?* Desalination, Volume 191, Issues 1-3, 10 May 2006, Pages 371-375, 2006

4. **A. Koris**, E. Marki: *Ceramic ultrafiltration membranes for non-solvent vegetable oil degumming (phospholipid removal)*. Desalination, Volume 200, Issues 1-3, 20 November 2006, Pages 537-539, 2006
5. Darko M. Krstić, Wilhelm Höflinger, **András K. Koris** and Gyula N. Vatai: *Energy-saving potential of cross-flow ultrafiltration with inserted static mixer: Application to an oil-in-water emulsion*. Separation and Purification Technology, Volume 57, Issue 1, 1 October 2007, Pages 134-139, 2007

Articles in Hungarian:

1. **Koris A.**, Vatai Gy.: *A nyersolaj membránszűrésének vizsgálata*. Olaj, Szappan, Kozmetika. LI. évf. 2. szám március-április 50-53 o. 2002
2. **Koris A.**: *Az ultraszűrés során keletkező gélréteg ellenállásának modellezése olajtartalmú emulzió szétválasztásánál*. Olaj, Szappan, Kozmetika. LI. évf. 6. szám november-december 217-221 o. 2002
3. **Koris A.**, Hu X., Borsos K.: *Ultraszűrés és nanoszűrés hatékonyságának vizsgálata olajos szennyvizek kezelésénél*. Membrántechnika VIII évf. 4. szám, 2004

English Conference Presentations with Full Text:

1. **A. Koris**, Gy. Vatai, G. Kapcsos: *Membrane filtration for deodorization distillate*. 29th Conference SSCHE, Proceedings on CD ROM, Tatranské Matliare (SK), 27 – 31 May, 2002.
2. **A. Koris**, Gy. Vatai: *Membrane filtration for vegetable oil degumming*. 15th International Congress of Chemical and Process Engineering CHISA, Prague 25-29 Aug. 2002 p. 265-266, 2002
3. X. G. Hu, J. Mora, **A. Koris**, E. Békássy-Molnár, Gy. Vatai.: *Effect of transmembrane pressure on ultrafiltration behaviour of emulsified oily wastewater*, 15th International Congress of Chemical and Process Engineering (CHISA), Praha-Czech Republic, augusztus 25-29, CD-ROM, 2002
4. **Koris A.**, Vatai G., Hu X.: *Membrane behaviour in case of edible oil filtration*. Lecture, Proceedings, PERMEA 2003, Slovakia, 7-11 September, 2003
5. **Koris A.**, Krstic D., Ubori Cs.: *Examination of Membrane Separation for Oil-in-Water Emulsions*. VI. Nemzetközi Élelmiszertudományi Konferencia 2004 május 20-21, Szeged, proceedings, 2004
6. **A. Koris**, H. Xianguo, Gy. Vatai : *Ultrafiltration and nanofiltration of oil-in-water emulsions: comparison of resistances*. Scientific reunion of the special program of the Alexander von Humboldt Foundation concerning the reconstruction of the South Eastern Europe: Sustainability for Humanity and Environment in the extended connection field Science – Economy – Policy, Timisoara, Romania, lecture, proceedings I. p. 141-144, 24-25 Febr. 2005
7. X. Hu, E. Bekassy-Molnar, Gy. Vatai, **A. Koris**: *Ultrafiltration of oily emulsions for metal cutting fluid: role of feed temperature*. PERMEA 2005, proceedings WWW-O04, 2005
8. **A. Koris**, D. Krstic, X. Hu, Gy. Vatai: *Ultrafiltration of oil-in-water emulsion: flux enhancement with static mixer*. PERMEA 2005, proceedings WWW-P08, 2005
9. D. M. Krstic, **A. Koris**, M. N. Tekic: *Do static turbulence promoters have potential in cross-flow membrane filtration applications?* Proceedings, ICOM 2005, Korea 2005
10. **A. Koris**, E. Marki, D. Vane, G. Vatai: *Integration of Dry Membrane Degumming into the Refinery Process*. VII. Nemzetközi Élelmiszertudományi Konferencia 2006 Szeged, lecture, proceedings, 2006
11. **A. Koris**, E. Marki: *Ceramic ultrafiltration membranes for non-solvent vegetable oil degumming (phospholipid removal)*. Euromembrane 2006, Food Application Session, 2006
12. G. Vatai, D.M. Krstic, W. Höflinger, **A. Koris**, M.N. Tekic: *Combining air sparging and the use of a static mixer in cross-flow ultrafiltration of oil/water emulsion*. Euromed 2006
13. **A. Koris**, D. M. Krstić, G. Vatai, I. Gaspar, X. Hu: *Effect of static mixing inside a tubular membrane on the ultrafiltration of an oil-in-water emulsion*. PERMEA 2007 proceedings, 2007

Hungarian Conference Presentations with Full Text:

1. **Koris A.**, Vatai Gy.: *Dezodorizációs párlat membránszeparációja*. Műszaki Kémiai Napok '02, Veszprém, előadás, 2002.
2. **Koris András**, Vatai Gyula, Márki Edit: *Napraforgó olaj nyálkamentesítése membránszeparációval, biodízel előállításához*. MTA-AMB XXXI. Tematikus Kutatás és Fejlesztési Tanácskozás, Gödöllő, Január 23. Konferencia kiadvány (Cd) 2007

English Conference Presentations with Summary:

1. **A. Koris**, Gy. Vatai, Z. Kemény: *Experimental Investigation and Modelling of Dry membrane Degumming*. 93th AOCS Annual Meeting and Expo, Montréal (CAN), poster, 2002
2. **A. Koris**, I. Gaspar, X. Hu, G. Vatai, E. Bekassy-Molnar: *Static mixing for economical cleaning of oily wastewater by membrane separation*. HUNN-TTD II. Book of abstract p.68, 2007

Hungarian Conference Presentations with Summary:

1. **Koris A.**, Felföldi J.: *Számítógépes nedvességtartalom-mérő berendezés tervezése vákuumszárító berendezéshez*. XXIV. OTDK Gyöngyös, 1999.
2. **Koris A.**, Vatai Gy., Békássyné M. E.: *Gilcerin tartalmú víz membránszűrése*. Műszaki Kémiai Napok '01, Veszprém, poszter, 2001.

3. **Koris A.**, Vatai Gy., Holló B.: *A membrán kondicionálásának hatása a növényolaj szűrésére*. XI. Membrántechnikai Konferencia, Tata, 2001, előadás.
4. **Koris A.**, Vatai Gy., Szécsi T.: *Különböző membránok viselkedése étolaj szűrésékor*. Műszaki Kémiai Napok '03, Veszprém, 2003. április 8-10., előadás
5. Ubori Cs., **Koris A.**, Krstic D.: *Olaj-víz emulzió besűrítéssel ultraszűréssel*. Műszaki Kémiai Napok '04, Veszprém, 2004. április 20-22., proceedings, előadás
6. Gáspár I., **Koris A.**, Vatai G.: *Olaj-víz emulzió statikus keveréssel kombinált membránszűrési besűrítésének optimális műveleti paraméterei*. *Műszaki Kémiai Napok '07, Veszprém, 2007. április 20-22., proceedings, poszter 2007*
7. Váné D., **Koris A.**, Vatai Gy.: *Nyers növényolaj membránszűrési foszfátmentesítésének számítógépes modellezése*. XVIII. LOV Tudományos Ülésszak, Budapest, összefoglaló 244. o., poszter, 2007
8. Gáspár I., **Koris A.**, Yuefei W., Vatai Gy.: *Áramlási viszonyok modellezése olaj-víz emulzió membránszűrésénél*. XVIII. LOV Tudományos Ülésszak, Budapest, összefoglaló 216. o., poszter, 2007