Mass transfer evaluation of substrate, intermediate products and inhibitors in membrane bioreactor on biogas production

M Hidayat 1*, I G Kurniawan 2, M A Prakosa 2, S Dökümüctü 3, R Millati 2, M N Cahyanto 2

1 Department of Chemical Engineering, Faculty of Engineering, UGM, 2 Department of Food and Agricultural Product Technology, Faculty of Agricultural Technology, UGM, 3 Chalmers University of Technology, Gothenburg, Sweden
*Corresponding author: mhidayat@ugm.ac.id

Abstract. Problem of fruit wastes can be minimized by fermenting them to produce biogas. Biogas production using membrane bioreactor (MBR) is an effort to prevent microbial washout especially with the presence of some inhibitors such as D-limonene and xanthone that are naturally originated from the fruits. In the membrane system, nutritional compounds such as glucose (substrate) and acetic acid (intermediate product) in fruit waste are expected to pass through, but the inhibitors are retained as membrane is hydrophilic and the inhibitors are hydrophobic.

Two membranes poly vinylidine difluoride (PVDF) and poly ether sulfone (PES) were used. In this study, permeability of inhibitors and nutritional compounds across the membranes were evaluated. In the separated experiments, D-limonene or xanthone solution as inhibitors and glucose or acetic acid as nutritional compounds at various concentrations were pumped through the membrane placed in a module. Flux of compounds through membrane was determined by collecting each milliliter of permeate at a certain time. The concentration of compounds in the feed and permeate were analyzed using gas chromatography or high performance liquid chromatography. Permeability of compounds were calculated the obtained concentration and flux.

The results showed that both membranes are able to retain the inhibitors while the substrate (glucose) and intermediate product (acetic acid) are let go across the membranes. The result showed that PES had better performance than PVDF in term of flux, while the selectivity is fairly the same for both membranes. Thus, it can be concluded that PES is more suitable for fermentation using membrane bioreactors.

Keywords: membrane bioreactor; D-limonene; xanthone, acetic acid, glucose, PVDF and PES

1. Introduction

The increase in population has an impact on increasing consumption of foods, fruits, clothes, housing etc. On the other hand, it also increases many wastes such as foods, vegetables, fruits etc. Converting waste into valuable product is an excellent idea, however it is often not easy to implement them. Fruit waste is suitable as a substrate for making biogas because it has a high content of organic compounds. However, it was found that biogas production from several types of fruit waste showed a lower yield of methane gas compared to the theory [1, 2]. This is due to the presence of antimicrobial components in fruit. In previous studies also found that there are flavor compounds in fruit that can be inhibitors of the biogas formation process because it has antimicrobial properties. The use of membrane bioreactors (MBR) in the biogas production process is one way to overcome these inhibitors [3].

The membrane on the MBR plays a role as a selective barrier. Inhibitors in fruit waste are found to be hydrophobic so that the use of hydrophilic membranes in MBR allows the inhibitor to not enter the biogas production system. On the other hand, other organic compounds (nutrients for microbial biogas) contained in fruit waste can enter the system because it is hydrophilic. Therefore the selection of the right membrane is a supporting factor for the success of biogas production using MBR.

In this study two types of membranes were used, namely PVDF and PES. PVDF membrane is commonly used in a variety of studies related to MBR while the application of PES membrane in MBR is still
relatively new [4]. Some studies state that the performance of PES membranes is better than PVDF membranes. The advantages of PES membranes are higher filtration rates and lower fouling rates than PVDF membranes [5]. The use of PVDF membranes on bioreactor membranes can also reduce flux values faster than PES membranes [4].

D-limonene and xanthone were tested and modelled as inhibitors. D-limonene is naturally present in the orange fruit and xanthone is in mangosteen. While the substrates were modelled by glucose and acetic acid. Glucose is considered as monomer product of hydrolysis process and acetic acid is considered as intermediate product from acidification process.

The purpose of this study is to evaluate performance of the PVDF and PES membranes in retaining D-limonene and xanthone as inhibitors and to permeating glucose and acetic acid as substrate and intermediate product across through the membranes.

2. Experimental method

2.1. Material

The chemical materials used in this study were 97% xanthones and D-limonene p.a. standard obtained from Sigma Aldrich; glucose and n-hexane p.a. standard obtained from Merck; aquades and acetic acid obtained from the Laboratory of Chemistry, Food Biochemistry and Agricultural Products, Department of Food Technology and Agricultural Products, Gadjah Mada University. The membranes used in this study were PVDF and PES with both product code are VVLP09050 and GPWP09050, respectively and obtained from Merck.

2.2. Equipments

2.2.1. Membrane module

The simple membrane module was designed and used to fit with the membrane size. The membrane module material is acryllic without being processed using the laser cutting method. The material in the hose connection is a glass tube with a size of 6 mm. The membrane module is used as a place to attach the membrane. In the middle of the membrane there are barriers that are placed in such a way as to put pressure on the feed stream so that it can rise. At the four ends of the membrane module there are screws which are given rubber pads to tighten the module membrane. Rubber pads are used to reduce the screw pressure at the end of the membrane module so as not to break while leveling the pressure on all sides. The membrane module design can be seen in Figure 1.

![Membrane module design](image)

Figure 1. Membrane module design (a) Section of module passed by feed (b) Section of module passed by permeate [6]

2.2.2. The set of research equipments

The study used a membrane module, permeate holder, pump, feed beaker, hot plate and stirrer, and magnetic stirrer. The set of research equipments can be seen in Figure 2.
First, the one liter feed solution is prepared by dissolving D-limonene, xanthone, glucose or acetic acid into aquadest, depending on which solution is going to be determined. The concentration of D-limonene, xanthone, glucose or acetic acid in the feed solution are varies. The feed solution was put into a container and then flowed using a pump through the hose to the membrane module. The feed solution which penetrates the membrane (permeate) is accumulated in the permeate container while the feed solution which does not penetrate the membrane (retentate) is recycled to the feed container. The flux of permeate is determined by considering the time needed to obtain for each unit of the permeate volume. In this study the membrane is operated by cross flow.

2.3. Data Analysis

Analysis of D-Limonene concentration was carried out using the gas chromatography (GC) method (Shimadzu QC 2010 plus, Japan) with a FID detector (300 °C) in the OV-17 column (Shimadzu, Japan) dimensions of 30 m x 0.25 mm x 0.25 μm. The injector and detector temperatures are 260 and 350 °C, respectively. The carrier gas is He at a flow rate of 0.44 mL per minute with a pressure of 42.8 kPa. Analysis of xanthone concentration was carried out using High Performance Liquid Chromatography (HPLC). The configuration of xanthone was tested using HPLC refers to Walker's study [8]. Analysis of acetic acid concentration was carried out using Shimadzu GC: 8A, the column used is GP 10% SP 1200/1% H3PO4 on 80/100 Chromosorb WAW (length 2m, diameter 3mm), column temperature 150 °C, detector used is FID (temperature 250 °C), the carrier gas is N2 and the pressure used is 2 kg per cm². Analysis of glucose concentration was carried out using HPLC (Shimadzu Prominence LC-2030, Japan) method with the LC-2030 pump and RID-20A detector.

2.4. Flux and permeability calculations

Determination of the flux and permeability of compounds through the membrane is calculated using equations (1) and (2) as follows [9]:

\[
J = \frac{V}{At}
\]

\[
J_i = J_i x_i
\]

Where

- \(J\) is flux total, liter/(m² x hour)
- \(J_i\) is membrane permeability of \(i\) compound, kg/(m² x hour)
- \(V\) is volume of permeate, liter
- \(x_i\) is concentration of \(i\) compound in permeate, kg/liter
- \(A\) is surface area of the membrane, m²
- \(t\) is time, hour

3. Results and discussion

Membranes are widely used to various industrial applications, one of them is as a MBR in biogas production. Biogas can be produced from fruit wastes, cellulosic materials, animal and human dungs.
etc. In biogas production from fruit wastes, the presence of inhibitor such as D-limonene and xanthone, of course, inhibit the production process, therefore they have to be minimized or even blocked. While the substrate (glucose) and intermediate products (acetic acid) which are really needed for producing biogas have to be provided and available as feed.

Flux and selectivity of compound permeating through a membrane are important criteria in membrane separation process. In this study, the flux and selectivity of for compounds (D-limonene, xanthone, glucose and acetic acid) were tested on two hydrophilic membranes that are PVDF and PES. Concentration of compounds in the feed and permeate stream were analyzed to determine or evaluate the permeability of compounds and selectivity of membranes. Some results of flux permeating through the membranes, concentration of compounds in the feed and permeate stream are shown in the following tables and figures.

### Table 1. D-limonene permeability at various concentrations through PVDF and PES membranes

| D-limonene concentration in the feed stream, kg/m³ | D-limonene concentration in the permeate stream, kg/m³ | Total flux of permeate, L/(m²·hour) | D-limonene permeability, kg/(m²·hour) |
|---|---|---|---|
| PVDF | PES | PVDF | PES | PVDF | PES |
| 200 | ND | ND | 41.42 | 352.49 | ND | ND |
| 400 | ND | ND | 32.76 | 332.75 | ND | ND |
| 600 | ND | ND | 33.15 | 358.81 | ND | ND |
| 800 | ND | ND | 34.20 | 334.10 | ND | ND |
| 1,000 | ND | ND | 33.89 | 311.68 | ND | ND |

Note: ND is Not Detected

### Table 2. Xanthone permeability at various concentrations through PVDF and PES membranes

| Xanthone concentration in the feed stream, kg/m³ | Xanthone concentration in the permeate stream, kg/m³ | Total flux of permeate, L/(m²·hour) | Xanthone permeability, kg/(m²·hour) |
|---|---|---|---|
| PVDF | PES | PVDF | PES | PVDF | PES |
| 100 | ND | ND | 49.11 | 141.24 | ND | ND |
| 200 | ND | ND | 47.72 | 274.16 | ND | ND |
| 300 | ND | ND | 44.82 | 444.57 | ND | ND |
| 400 | ND | ND | 44.19 | 355.68 | ND | ND |
| 500 | ND | ND | 40.01 | 406.89 | ND | ND |

Note: ND is Not Detected

### Table 3. Glucose permeability at various concentrations through PVDF and PES membranes

| Glucose concentration in the feed stream, kg/m³ | Glucose concentration in the permeate stream, kg/m³ | Total flux of permeate, L/(m²·hour) | Glucose permeability, kg/(m²·hour) |
|---|---|---|---|
| PVDF | PES | PVDF | PES | PVDF | PES |
| 0.5 | 0.679 | 0.498 | 5.570 | 183.960 | 0.004 | 0.092 |
| 1.0 | 0.981 | 0.972 | 9.620 | 148.810 | 0.009 | 0.145 |
| 1.5 | 1.503 | 1.338 | 8.570 | 213.640 | 0.013 | 0.286 |
| 2.0 | 2.034 | 2.017 | 10.740 | 234.080 | 0.022 | 0.472 |
| 2.5 | 2.536 | 2.523 | 10.740 | 198.050 | 0.027 | 0.500 |
| 3.0 | 2.924 | 2.880 | 8.370 | 237.530 | 0.025 | 0.684 |
| 3.5 | 3.530 | 3.463 | 9.200 | 233.830 | 0.033 | 0.810 |
| 4.0 | 4.031 | 3.954 | 8.440 | 252.580 | 0.034 | 1.000 |

### Table 4. Acetic acid permeability at various concentrations through PVDF and PES membranes
In Table 1-4, PES membrane shows generally better performance than PVDF membrane in terms of amount of flux passing through the membrane. This may be due to the pore size of PES (0.22 μm) is larger than the pore size of PVDF (0.10 μm). The effect of inhibitor concentrations to the amount of flux tends to decrease however these trends are not uniform enough especially for separation of xanthone using PES membrane, the flux even tends to increase. Meanwhile the effect of substrate (glucose) and intermediate product (acetic acid) tends to increase however the increasing flux is slightly fluctuating. This is probably due to the inhibitors is hydrophobic while the substrate and intermediate product are hydrophilic.

As a comparison, Carvalho et al. [10] conducted separation of enzyme from pineapple juice. They obtained the value of flux in pineapple juice (pineapple juice with an enzyme clarification process) on PVDF and PES membranes of 35.7 and 57.5 L/(m² hour) at a pressure of 1.5 bar, respectively. In this study the PVDF membrane pore size was 0.30-80 μm while the PES membrane size was 0.3 μm. In addition, Hu et al. [11] showed a flux value of oil water solution (5%) of 85, 105 and 110 L/(m² hour) at successive flow rates of 0.5; 0.9 and 1.5 m/s. The test was carried out at pressure of 3 Mpa and temperature of 40 °C.

Hu et al [12] conducted experiments on the separation of water and oil through the ultrafiltration method using various types of membranes (PVDF, PES, and PAN (Polyacrylonitrile) as shown in Table 5. The process conditions were carried out at 3 bar pressure and 20 °C temperature.

### Table 5. Summary of the flux of PVDF, PES, and PAN membrane for different operating condition [7]

| Membrane | Material | MWCO (kD) | Water flux, L/(m² hour) | Max temperature, °C |
|-----------|----------|-----------|------------------------|---------------------|
| FS 102-05 | PES      | 10        | 550                    | 60                  |
| FS 202-09 | PES      | 20        | 700                    | 60                  |
| FF 502-04 | PVDF     | 60        | 1000                   | 60                  |
| CMF-DY-040 | PAN    | 40        | 700                    | 45                  |
| CMF-DY-010 | PAN    | 10        | 250                    | 45                  |
| CMF-DS-040 | PES    | 40        | 400                    | 95                  |
| CMF-DS-100 | PES    | 100       | 800                    | 95                  |
| FS 40PP   | PVDF     | 100       | 300-800                | 60                  |
| FS 50PP   | PVDF     | 50        | 300-700                | 60                  |

According to Pogodaeva and Sukhov [13] the xanthone compound has a log P value of 3.20 ± 0.05. The P log shows the lipophysical / hydrophobicity index. If log P positive value means that the solubility of the compound is greater in octanol (lipid cell membrane model) than water. It can be said that xanthone compounds are hydrophobic so that xanthone compounds cannot pass through hydrophilic membranes. One important difference between D-Limonene and glucose is the affinity of the two compounds for water. D-Limonene is hydrophobic while glucose is hydrophilic. This difference affects the solubility of compounds in water, where the solubility of D-Limonene is 13.8 mg/L (temperature 25 °C) while glucose has a solubility of 909 g/L (temperature 25 °C). The solubility of D-Limonene and glucose in water is an important factor because this study uses water as a solvent for both compounds.
In Table 1 and 2, the concentration of inhibitors in the permeate stream is not detected by GC and HPLC for all variation of both membranes. The phenomena indicates that the inhibitors may be retained by both PVDF and PES membranes, which is of course preferable, in term of the biogas production purpose. While glucose and acetic acid are able to permeate both PVDF and PES membranes as shown in Figure 3 and 4. Permeation of glucose and acetic acid through the membranes allows them to be feed to next step of biogas production. The ability of membrane to permeate glucose and acetic acid but to retain D-limonene and xanthone is in line with the purposes of utilizing the MBR system.

Figure 3. Correlation between fluxs and permeation time of the various concentrations of D-Limonene solution through (a) PVDF membrane and (b) PES membrane

Figure 4. Correlation between fluxs and permeation time of the various concentrations of xanthone solution through (a) PVDF membrane and (b) PES membrane

Figure 3 shows that the flux development of the various concentrations of D-limonene solution as a function of permeation time through the PVDF and PES membranes. While Figure 4 shows that the flux development of the various concentrations of xanthone solution as a function of permeation time through the PVDF and PES membranes. Both processes show that developing period is relatively short time, it takes not more than 5 minutes.

4. Conclusion
Biogas is a promising renewable energy in the future which can be produced from many wastes, one of them is from fruit wastes. The D-limonene and xanthone are natural inhibitor which is normally presence in the fruit wastes. The presence of these compounds in the biogas production, of course, inhibit the production process, therefore they have to be minimized or even blocked. While the substrate (glucose) and intermediate products (acetic acid) are really needed for producing biogas.

Two membranes PVDF and PES were used to retain D-limonene and xanthone and let glucose and acetic acid go across through the MBR. By analyzing the concentration of D-limonene and xanthone in
the permeate stream both for PVDF and PES membranes, it was found that concentrations of both compounds were so small and not identified by GC and HPLC. These mean that both membranes show the same performance to not permeate those compounds. Molecule size of D-limonene and xanthone are hydrophobic and larger than the size of membrane pore while both membrane are considered as hydrophilic. Positively, both membrane are able to permeate glucose and acetic acid which is, of course, preferable.

In term of flux and permeability, the membrane PES showed better performance that the membrane PVDP. The flux of the membrane PES is almost eight times then the flux of the membrane PVDP. This performance is caused of the pore size of PES is larger than the pore size of PVDP. The influence of concentration of inhibitor, intermediate and substrate in the system tend to reduce the flux, permeation through the membrane.

5. References
[1] Sanjaya A P 2013 The Presence of Inhibitors in Rotten Tropical Fruits for Biogas Production Master Thesis UGM Yogyakarta
[2] Wikandari R 2014 Effects Of Fruit Flavors On Anaerobic Digestion: Inhibitions and Solutions Doctoral Thesis University Of Boras Sweden
[3] Wikandari R, Ria M, Muhammad N C dan Mohammad J T 2014 Biogas Production from Citrus Waste by Membrane Bioreactor Membranes April pp 596-607 on www.mdpi.com/journal/membranes
[4] Chan N G S 2012 The Performance Study Of Membrane Bioreactor (MBR) Treating Synthetic Wastewater Universiti Tunku Abdul Rahman Malaysia
[5] Moce-Llivia L, Jofre J and Muniesa M 2003 Comparison Of Polyvinylidene Fluoride and Polyether Sulfone Membranes in Filtering Viral Suspensions. Journal of virological methods Vol 109(1) pp 99-101
[6] Kurniawan I G 2017 Pengujian Nilai Fluks dan Permeabilitas Senyawa D-Limonene dan Glukosa Melalui Membran Bioreaktor Polyvinylidene Difluoride dan PolyEthersulfone POLYETHERSULFONE Departemen Teknologi Pangan dan Hasil Pertanian Fakultas Teknologi Pertanian UGM Yogyakarta
[7] Prakosa M A 2017 Pengujian Nilai Fluks dan Permeabilitas Senyawa Xanthone dan Asam Asetat melalui Membran Polyvinylidene Difluoride dan PolyEthersulfone POLYETHERSULFONE Departemen Teknologi Pangan dan Hasil Pertanian, Fakultas Teknologi Pertanian, UGM, Yogyakarta
[8] Walker E B 2007 HPLC Analysis of Selected Xanthones in Mangosteen Fruit. J. Sep. Sci. 30, pp 1229–1234
[9] Mulder M 1996 Basic Principles of Membrane Technology, Second Edition Netherlands: Kluwer Academic Publisher
[10] Carvalho L M, Izabela M and Carlos A B 2007 A Study of Retention of Sugars in The Process of Clarification of Pineapple Juice (Ananas comosus, L. Merril) by Micro- and Ultra-Filtration Journal of Food Engineering Vol 87 pp 447–454
[11] Ha X, Bekassy-Molnar E, and Vatai G Y 2002 Analysis and Characterization of Membrane Fouling of Ultrafiltration Separation for Oil-in-Water Emulsion Chem. Pap. Vol 57 (1) pp 16-20
[12] Hu X, Vatai G, Bekassy-Molnar E, Meisz L, Oláh J 1999 The Study of Oil/water Separation in Emulsion by Ultrafiltration Membranes Chemische Technik Vol 50(3) pp 119 – 123
[13] Pogodaeva N N dan Sukhov B G 2011 Hydrophobicity Constants for Several Xanthones and Flavone Chemistry of Natural Compounds Vol 47 No 1 March

Acknowledgement
The authors would like to thank to
- Ministry of Research, Technology and Higher Education, Republic of Indonesia which partially give a financial support through the international collaboration research scheme
- Linnaeus-Palme Foundation which fully support the exchange student program for Sumeyya Dökümü, master student from Chalmers University of Technology, Gothenburg, Sweden