



**MARMARA UNIVERSITY**  
**INSTITUTE FOR GRADUATE STUDIES**  
**IN PURE AND APPLIED SCIENCES**



**SEPARATION OF VOLATILE FATTY  
ACIDS FROM LEACHATE VIA  
COMPOSITE PERVAPORATION  
MEMBRANES**

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**ÇAĞLAR KÜLLÜ**

**MASTER THESIS**

Department of Environmental Engineering

**ADVISOR**

Assoc. Prof. Dr. A. Evren TUĞTAŞ

ISTANBUL, 2018

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**INSTITUTE FOR GRADUATE STUDIES**  
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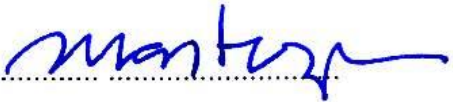
**MARMARA UNIVERSITY**  
**INSTITUTE FOR GRADUATE STUDIES IN**  
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## **ABSTRACT**

### **SEPARATION OF VOLATILE FATTY ACIDS FROM LEACHATE VIA COMPOSITE PERVAPORATION MEMBRANES**

Every year about 1.3 billion tons of food is wasted globally, which can be fermented and used for the production of commodity chemicals such as volatile fatty acids (VFAs). VFAs that were produced biological ways should be separated from the fermentation system to prevent their inhibitory effect on fermentation and thus to increase their production rate. Recent studies have focused on separation of VFAs through pressure, electrical, or concentration gradient/vapor pressure driven membrane processes. Among the recently used membrane processes, vapor pressure driven pervaporation process is rapidly gaining attention in separation of VFAs from fermentation broths as it provides a pure and concentrated permeate with high separation factor. The main aim of this study was to investigate the effect of VFA separation from anaerobically fermented organic solid wastes on overall VFA production and separation efficiency. Anaerobic fermentation process was carried out in leach bed reactors (LBRs) using organic fraction of municipal solid waste as a feed. In addition, in order to investigate the effect of membrane type on VFA separation efficiency of the pervaporation process; polydimethylsiloxane (PDMS) membranes with different compositions were manufactured, characterized and tested. The results of the study revealed that the optimum separation factor ( $2.13 \pm 0.02$ ) and total acid flux ( $7.04 \pm 1.08\text{g}/(\text{m}^2\cdot\text{h})$ ) was observed in 0.1% hydrophilic nano-silica filled low molecular weight PDMS-OH membrane. The optimum membrane composition (0.1% hydrophilic nano-silica filled low molecular weight PDMS-OH membrane) was used in “Integrated Leach Bed Reactor – Vapor Pressure Membrane Contactor – Pervaporation (LBR-VPMC-PV) System”. LBR-VPMC-PV system separated 94.04% of the total VFAs-COD which were produced from test reactor and 7.74% of the separated VFAs were purified. And finally the integration of VPMC process to system test reactor had 2.06 fold VFA production efficiency over control reactor. This study is believed to add new and valuable information to the carboxylate platform studies.

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## ÖZET

### UÇUCU YAĞ ASİTLERİNİN KOMPOZİT PERVAPORASYON MEMBRANLARI İLE SIZINTI SUYUNDAN AYRILMASI

Her yıl dünya çapında fermentasyon ile uçucu yağ asitleri (UYA) gibi ticari kimyasallar üretilen yaklaşık 1,3 milyar ton yiyecek çöpe atılmaktadır. Biyolojik yollar ile üretilen UYA'lar inhibisyon etkilerinden ve bu etkiye bağlı olarak UYA üretim hızlarını düşürdüklerinden dolayı fermentasyon sistemlerinden uzaklaştırılması gereklidir. Yakın geçmişteki araştırmalar UYA'ları ayırmak için basınç farkı, elektriksel potansiyel farkı, konsantrasyon veya buhar basıncı farkı ile işleyen membran tekniklerine yoğunlaşmıştır. Günümüzde kullanılan membran ile ayırma teknikleri arasında buhar basıncına dayalı pervaporasyon işlemi sayesinde yüksek ayırma faktörleri ile saf ve konsantre süzüntülerin elde edilebiliniyor olması; fermentasyon sıvılarından UYA'ların ayırımı alanında pervaporasyon işlemine olan ilgiyi hızla artırmaktadır. Sunulan bu çalışmanın amacı UYA ayırımının anaerobik fermantasyon işlemi üzerine etkisini incelemektir. Anaerobik fermantasyon işlemi evsel katı atıkların organik kısımlarının besin olarak kullanıldığı süzülen yataklı anaerobik reaktör (SYAR)'da gerçekleşmiştir. UYA ayırımının, UYA üretim verimliliği üzerine etkisi araştırmak amacı ile değişik kompozisyonlarda polidimetilsiloksan (PDMS) membranlar laboratuvar koşullarında üretilmiş, karakterize edilmiş ve test edilmiştir. Çalışmanın sonucunda; 0,1% hidrofililik nano-silika dolgulu düşük moleküler ağırlıklı PDMS-OH membran ile optimum ayırım faktörü ( $2,13 \pm 0,02$ ) ve toplam asit akısı ( $7,04 \pm 1,08 \text{ g}/(\text{m}^2 \cdot \text{h})$ ) elde edilmiştir. Optimum verimin elde edildiği membran (0,1% hidrofililik nano-silika dolgulu düşük moleküler ağırlıklı PDMS-OH membran), süzülen yataklı anaerobik reaktör- buhar basıncı membran kontaktörü- pervaporasyon (SYAR-BBMK-PV) sisteminde kullanılmıştır. Entegre SYAR-BBMK-PV sisteminin sonucunda test reaktöründe üretilen UYA'ların %94,04 sistemden ayırılmış ve %7,74 kadarı saflaştırılmıştır (KOİ cinsinden). Ayrıca test reaktörü kontrol reaktörüne göre 2,06 kat daha fazla UYA üretmiştir. Bu çalışmanın karboksilat platform çalışmalarına ışık tutacağı düşünülmektedir.

Mart, 2018

Çağlar KÜLLÜ

## SYMBOLS

<b>A</b>	: Area (m <sup>2</sup> )
<b>C</b>	: Concentration (mgL <sup>-1</sup> or kgm <sup>-3</sup> )
<b>CaO</b>	: Calcium Oxide
<b>Ca(OH)<sub>2</sub></b>	: Calcium Hydroxide
<b>cm</b>	: Centimeter
<b>cm<sup>2</sup></b>	: Square Centimeter
<b>cm<sup>3</sup></b>	: Cubic Centimeter
<b>CH<sub>3</sub>COOH</b>	: Acetic Acid
<b>CH<sub>3</sub>CH<sub>2</sub>COOH</b>	: Propionic Acid
<b>CH<sub>3</sub>(CH<sub>2</sub>)<sub>2</sub>COOH</b>	: Butyric Acid
<b>CH<sub>3</sub>(CH<sub>2</sub>)<sub>3</sub>COOH</b>	: Valeric Acid
<b>CH<sub>3</sub>(CH<sub>2</sub>)<sub>4</sub>COOH</b>	: Caproic Acid
<b>d</b>	: Day
<b>gr</b>	: Gram
<b>H<sub>2</sub></b>	: Hydrogen Gas
<b>hr</b>	: Hour
<b>J</b>	: Flux (g.m <sup>-2</sup> hr <sup>-1</sup> )
<b>KCl</b>	: Potassium Chloride
<b>kg</b>	: Kilogram
<b>L</b>	: Liter
<b>m</b>	: Mass (g)
<b>M</b>	: Molarity (molL <sup>-1</sup> )
<b>min</b>	: Minute
<b>mL</b>	: Milliliter
<b>mm</b>	: Millimeter
<b>m<sup>2</sup></b>	: Square Meter
<b>m<sup>3</sup></b>	: Cubic Meter
<b>mg</b>	: Milligram
<b>rpm</b>	: Revolution per Minute
<b>t</b>	: Time (Day or Hour)

<b>T</b>	: Temperature (K or °C)
<b>TiO<sub>2</sub></b>	: Titanium Dioxide
<b>wt. %</b>	: Percentage by Weight
<b>%</b>	: Percentage
<b>α</b>	: Separation Factor
<b>-COOH</b>	: Carboxyl Group
<b>°C</b>	: Degree Celsius
<b>μm</b>	: Micrometer
<b>Ø</b>	: Diameter (mm)

## **ABBREVIATIONS**

<b>AA</b>	: Acetic Acid
<b>BA</b>	: Butyric Acid
<b>CA</b>	: Caproic Acid
<b>COD</b>	: Chemical Oxygen Demand
<b>ESEM</b>	: Environmental Scanning Electron Microscope
<b>GC</b>	: Gas Chromatography
<b>ID</b>	: Inner Diameter
<b>LBR</b>	: Leach Bed Reactor
<b>OD</b>	: Outer Diameter
<b>PA</b>	: Propionic Acid
<b>PAN</b>	: Polyacrylonitrile
<b>PB</b>	: Polybutadiene
<b>PEBA</b>	: Polyether-Block-Polyamide
<b>PEI</b>	: Polyetherimide
<b>PDMS</b>	: Polydimethylsiloxane
<b>PDMS-OH</b>	: Hydroxyl Terminated Polydimethylsiloxane
<b>PDMS-Vinyl</b>	: Vinyl Terminated Polydimethylsiloxane
<b>PP</b>	: Polypropylene
<b>PSI</b>	: Pervaporation Separation Index
<b>PTFE</b>	: Polytetrafluoroethylene
<b>PV</b>	: Pervaporation
<b>PVA</b>	: Polyvinyl Alcohol
<b>SEM</b>	: Scanning Electron Microscope
<b>TEOS</b>	: Tetraethylorthosilicate
<b>TDDA</b>	: Tridodecylamine
<b>TOA</b>	: Trioctylamine
<b>TOPO</b>	: Tri-n-octylphosphine Oxide
<b>UK</b>	: United Kingdom
<b>US</b>	: United States
<b>VA</b>	: Valeric Acid
<b>VFA</b>	: Volatile Fatty Acid

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# 1. INTRODUCTION

## 1.1. Scope and Objective of the Study

Solid waste generation in Turkey has reached to 28,011 thousand tons per year in 2014 (Turkish Statistical Institute 2014). In Turkey, the majority of the solid wastes are landfilled or dumped and only 0.4% of the solid waste is composted (Turkish Statistical Institute 2014). Managing solid waste via dumping or landfilling has become an economical problem and also an ecological problem due to large amount of land requirement and possible hazardous effects on the environment. Organic fraction of municipal solid waste is valuable and according to Ministry of Environment and Forestry of Turkey in 2006, organic fraction of municipal solid waste (OFMSW) changes between 55.9% and 76.9% in different seasons (Çevre ve Orman Bakanlığı 2006). In current global situation, where resource limitations are increasing, OFMSW can be considered as a raw material rather than a waste if proper methods such as anaerobic digestion can be applied (Tugtas 2014).

Anaerobic digestion is a process, which organic compounds such as carbohydrate, protein, and fat are biochemically converted into a biogas, which is a mixture of methane, carbon dioxide and a small portion of hydrogen sulphur. For a long time, biogas has been considered as the only valuable product of anaerobic digestion process. However, in addition to biogas, volatile fatty acids are being produced as intermediates and VFAs can also be considered as important products of anaerobic fermentation process. As a result of skipping the methane forming step of the anaerobic digestion process, valuable products such as acetic, propionic, butyric, valeric and caproic acids or solvents such as ethanol can be produced through anaerobic fermentation process (Dogan and Demirer 2009, Olsson and Hahn-Hägerdal 1996, Vandák et al. 1997, Wang et al. 2003). Acetic, propionic, butyric, valeric and caproic acids are categorized as volatile fatty acids (VFAs) and are considered as important chemical compounds according to the book “The 100 Most Important Chemical Compounds” (Myers 2007). VFAs are used in several industries such as food and beverage, pharmaceutical, chemical and fuel industries (Lee et al. 2014, M. Gryta and M. Barancewicz 2011, Y. M. Lee et al. 2001, Zacharof and Lovitt 2013). However, when the methane producing

step of anaerobic digestion process (methanogenesis) is skipped, VFA production does not present a sustainable system. Accumulated VFAs can be self-inhibitory to fermentative microorganism and can decrease the cytoplasmic pH causing decreased enzymatic activity (Pind et al. 2003, Zoetemeyer et al. 1982). Therefore, VFAs should be separated/recovered from anaerobic fermentation system for sustainable VFA producing system then the separated VFAs can be purified for further use (Tugtas 2014, Yesil et al. 2014). VFA separation can be achieved via different methods such as chemical precipitation, electro-dialysis, solvent extraction, adsorption, and/or membrane processes (Alkaya et al. 2009, Eggeman and Verser 2005, Evangelista and Nikolov 1996, Qin et al. 2003, Wasewar and Pangarkar 2006). Among all these methods, membrane separation seems to be the most promising method for dilute VFA solutions such as fermentation broth (Qin et al. 2003, Thongsukmak and Sirkar 2007).

Pervaporation is a membrane process that is considered as a safe, eco-friendly and economic for the separation and purification of azeotropic mixtures (Bennett et al. 1997). In pervaporation process, volatile compounds become vapour and adsorbed to a membrane, travel through the membrane via diffusion then desorb from the other side of the membrane, this mechanism is called sorption-diffusion mechanism (Dogan and Hilmioglu 2010). Feed is recirculated continuously on one surface of the membrane at an atmospheric pressure and vacuum is applied to the other (permeate) side of the membrane, creating constant vapour pressure difference between the feed and permeate sides of the membrane (Vane 2005). In the literature, various membranes were used in pervaporation studies such as polytetrafluoroethylene (PTFE) (Qin et al. 2003), polyaniline (PANI) (Huang et al. 1998), polyvinyl alcohol (PVA) (Isiklan and Sanli 2005), acrylonitrile (Alghezawi et al. 2005), and polydimethylsiloxane (PDMS) (Bennett et al. 1997). Furthermore, to enhance the separation performance of polymeric membranes, inorganic fillers, such as nano-silica (Sun et al. 2013), zeolite (Li et al. 2010), TiO<sub>2</sub> (Yang et al. 2009), and carbon black have been used (Panek and Konieczny 2007) It has been reported that nano-silica filling, enhances the membrane separation efficiency of organics (VOCs such as chloroform) from water in pervaporation systems (Guo et al. 2007, Sun et al. 2013).

In this study, hydrophilic and hydrophobic nano-silica filled vinyl terminated and hydroxyl terminated PDMS membranes were manufactured in different compositions.

These membranes were characterized and were investigated in terms of flux and separation factor via synthetic fermentation broth. Best performing membrane was used in an integrated leach Bed Reactor/Pervaporation system and an integrated Leach Bed Reactor/ Vapour Pressure Membrane Contactor System /Pervaporation system to determine the VFA separation efficiency of these systems.

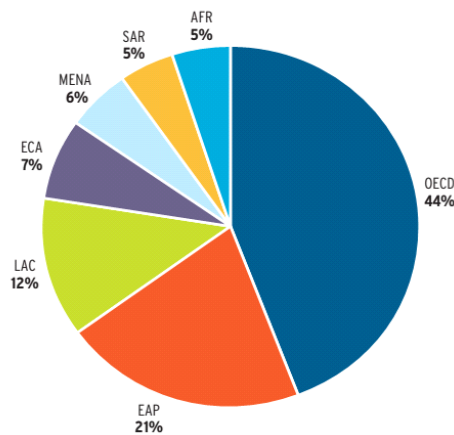
## **1.2. General Background**

### **1.2.1. Municipal solid waste**

Municipal solid waste (MSW) can be defined as wastes that are generated by public with everyday items such as papers, cardboards, glasses, bottles etc. in urban society. MSW can be generated from houses, commercial centres, shops, markets, hotels, schools or hospitals. Furthermore, waste management became an urgent case of exponential growth of city life. Conventionally, MSWs are being handled with mostly in landfills, combustion or incineration (Ostrem et al. 2004). It is quite obvious that landfills are an efficient way for handling waste with the limited land in urban life. Another disadvantage for landfill is low contribution on recycle, reuse, and suitability.

#### **1.2.1.1. Municipal solid waste generation in the world**

Solid waste management is the one thing just about every city government provides for its residents. While service levels, environmental impacts and costs vary dramatically, solid waste management is arguably the most important municipal service which serves as a prerequisite for other municipal actions. Currently, world cities generate about 1.3 billion tons of solid waste per year. This volume is expected to increase to 2.2 billion tons by 2025 (Hoornweg and Bhada-Tata 2012). Waste generation rates are being expected to double over the next twenty years in countries with lower income (Hoornweg and Bhada-Tata 2012). By the estimation, solid waste management costs will globally increase from today's annual \$205.4 billion to about \$375.5 billion in 2025 (Hoornweg and Bhada-Tata 2012). The significant increase in per capita waste generation rates is expected to move from 1.2 to 1.42 kg/person/day in the next fifteen years (Hoornweg and Bhada-Tata 2012).



**Figure 1. Global waste outcome per region (Hoornweg and Bhada-Tata 2012)**

The OECD countries generate 572 million tons of solid waste per year (Hoornweg and Bhada-Tata 2012). The per capita values range from 1.1 to 3.7 kg/person/day with an average of 2.2 kg/capita/day (Hoornweg and Bhada-Tata 2012). In South Asia, approximately 70 million tons of waste is generated per year, with per capita values ranging from 0.12 to 5.1 kg/person/day and an average of 0.45 kg/capita/day (Hoornweg and Bhada-Tata 2012). As it can be seen on the figure 1 which illustrates global waste generation per region, where OECD countries make up almost half of the world's waste with a 44 percent rate, EAP countries are being the second in place on waste generation, while Africa and South Asia are the regions that produce the least waste with 5 percent each (Hoornweg and Bhada-Tata 2012).

#### 1.2.1.2. Characteristics of municipal solid waste

Municipal solid waste may contain organics (food scraps, yard waste, wood process residues), paper, plastics, glass, metal, and other (textiles, leather, rubber, e-waste, appliances, ash, other inert materials etc.) (Hoornweg and Bhada-Tata 2012).

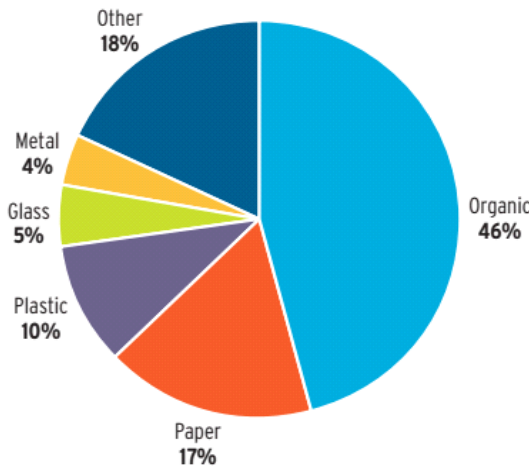
**Table 1.** Current estimates on the waste outcome (Hoornweg and Bhada-Tata 2012)

Income Level	Current Estimates					
	Organic (%)	Paper (%)	Plastic (%)	Glass (%)	Metal (%)	Other (%)
Low Income	64	5	8	3	3	17
Lower Mid. Income	59	9	12	3	2	15
Upper Mid. Income	54	14	11	5	3	13
High Income	28	31	11	7	6	17

**Table 2.** Year 2025's estimates on the waste outcome (Hoornweg and Bhada-Tata 2012)

Income Level	2025 Estimates					
	Organic (%)	Paper (%)	Plastic (%)	Glass (%)	Metal (%)	Other (%)
Low Income	62	6	9	3	3	17
Lower Mid. Income	55	10	13	4	3	15
Upper Mid. Income	50	15	12	4	4	15
High Income	28	30	11	7	6	18

Waste composition changes by many factors such as development level of the country, cultural norms or climate (Hoornweg and Bhada-Tata 2012). Generally, organic fraction is ranged between 40-80% of municipal solid waste in low and middle income regions (Hoornweg and Bhada-Tata 2012). However, in high income regions paper, plastic, glass and metal waste generation is much higher (Hoornweg and Bhada-Tata 2012).



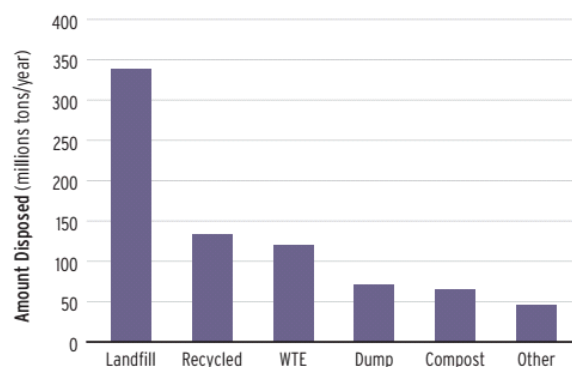
**Figure 2.** Waste variance in low income countries. (Hoornweg and Bhada-Tata 2012)

Figure 2 illustrates the waste outcome in the countries with low income. In low income countries 46% of total waste is organic (Figure 2) (Hoornweg and Bhada-Tata 2012).

### 1.2.1.3. Municipal solid waste management

Solid waste generation is increasing day by day and solid waste management already became a major issue due to environmental problems. Solid waste management hierarchy can be classified from the least preferred to the most preferred option as controlled dump, incineration, landfill, recover, recycle, reuse, and reduce (Bagchi

2004). Most desired option for waste management is to reduce the possible generation of waste by reducing initial source, such as less packaging or reusing materials (Bagchi 2004). Also after products were used and became a waste, there is a huge portion of the wastes that can be recycled such as glass, metal, plastic, or paper and repurpose into other products. Organic fraction of solid waste can also be recovered or repurposed after some processes such as being used as fertilizer (by composting) (Gallardo-Lara and Nogales 1987), valuable organic acids (by anaerobic fermentation) (Dogan and Demirer 2009) or energy (by anaerobic digestion and incineration) (Murphy and McKeogh 2004).



**Figure 3.** Amount of waste disposed by million tons per year and disposal methods (Hoorweg and Bhada-Tata 2012)

If solid wastes cannot be reduced, recycled or recovered, at least its toxicity can be taken under control and reduced by volume with a process such as incineration (Brunner 1994). In the light of the figure 3, it can be seen that even though it is the least preferred method, most commonly used solid waste management method is landfilling (Hoorweg and Bhada-Tata 2012).

#### **1.2.1.4. Pre-treatment technologies prior to landfill**

Landfill practices are widely used around the world due to its simple and cheap operation; on the other hand, dumping of solid waste on lands has severe impacts on the environment. Decomposition of solid wastes would release gases which contribute to greenhouse effects, and also some liquid phase with organic soluble content (leachate) can be leaked to surface and ground water resources; which can cause toxicity, alter the habitat, and even damage the ecosystem (Beaven and Walker 1997, Belevi and Baccini

1989). Therefore, a pre-treatment is essential before landfill disposal for reducing greenhouse effects and activity of solid waste through optimized and controlled conditions (Komilis et al. 1999, Zach et al. 2000).

There are three main categories for the treatment of solid waste before dumping to landfills; physical, chemical, and biological (Eliyan 2007). Grinding, drying, and separation techniques are in physical category, whereas incineration can be found in chemical category, and last of the treatment category is biological methods such as aerobic or anaerobic digestion (Zach et al. 2000). Biochemical treatment of municipal solid wastes having high organic content are driving attention (Zach et al. 2000).

A soil conditioner with high nutrient levels for plants can be made via aerobic digestion. Aerobic microorganism need oxygen for biodegradation of organic fraction of solid waste therefore, solid waste must be aerated for a measured period of time for different composition of waste (Haug 1986). Aerobic digestion has an energy consumption due to aeration therefore aerobic digestion is not the most suitable way due to economic reasons, and also with considerable gas emissions, it is not the best ecological way either (Hartmann and Ahring 2006).

Anaerobic digestion is a method for producing methane, which can be used to produce energy from and there is no need for aeration in this process, therefore there is lower energy consumption in this method (Baldasano and Soriano 2000, Hartmann and Ahring 2006). Also it is a better way to handle wet wastes when comparing aerobic and anaerobic digestion. Generally anaerobic digestion is a treatment method for organic solids, in addition it is more economical and environmental compared to that of other methods at the same time.

### **1.2.2. Anaerobic Digestion**

Anaerobic digestion is a naturally occurring biochemical process, which involves microorganisms such as bacteria and archaea (Tabatabaei et al. 2010). In this processes organic matters such as organic fraction of solid wastes (OFSW), which contains complex organic matter such as carbohydrates, proteins and lipids are converted into methane, carbon dioxide, ammonia and a little fraction of hydrogen sulphide under anaerobic conditions via several bio-chemical steps (Tugtas 2011). The sum of these

several steps are metabolic pathway of anaerobic digestion (Pavlosthatis and Giraldo-Gomez 1991). Hydrolysis, fermentation (acidogenesis), acetogenesis, and methanogenesis are the main processes in metabolic pathway (Pavlosthatis and Giraldo-Gomez 1991). The first process of anaerobic digestion is hydrolysis, which carbohydrates, proteins and lipids in the complex organic matters are hydrolyzed into monomers; monosaccharides, amino acids and fatty acids by extracellular enzymes produced by fermentative bacteria (Nayono 2009). Monomers that are small enough to pass through a cell membrane are converted to propionic, butyric, and valeric acids as intermediate products in acidogenesis step (Rittmann and McCarty 2001). Intermediate products are oxidized into carbon dioxide, hydrogen gas, and acetic acid through acetogenesis (Rittmann and McCarty 2001). Acetate and hydrogen are very important for methane production because methanogenic microorganisms are using acetate and  $H_2$  as a substrate to produce methane (Tchobanoglous et al. 2003).

Methanogens are archaea; a sub group of microorganisms that produce methane using simple carbon sources and  $H_2$  (Tchobanoglous et al. 2003). Acetoclastic methanogens bio-synthesize methane via acetate and carbon dioxide, through this hydrogenotrophic methanogens produce methane with hydrogen and carbon dioxide (Nayono 2009). Acetoclastic methanogens are responsible of the production of 66% of  $CH_4$  while 34% of  $CH_4$  is formed by carbon dioxide-reducing (hydrogen utilizing) methanogenic archaea (Nayono 2009). Every step of anaerobic digestion has different limiting factors and optimum operational conditions. Anaerobic digestion can be effected by temperature, pH, substrate characteristics, and inhibitory substances. Temperature affects reaction rates and also the diversity of microorganisms. Mesophilic microorganisms live optimally at  $35^\circ C$ , whereas  $55^\circ C$  is optimum for thermophilic microorganisms (Mata-Alvarez 2002). Mesophilic reactor are preferred due to low energy requirement levels and lower investment cost compared to that of thermophilic reactors, although thermophilic reactors can operate with higher organic load, higher degradation level, and higher yield of biogas with smaller reactor designs (Mackie and Bryant 1995). Value of pH is an indicator for the balance of alkalinity and volatile fatty acid production which is very important for microbial efficiency. However the enzymes of bacteria and archaea have different optimum pH values that they are inhibited (Veeken et al. 2000, Zoetemeyer et al. 1982).

Solid waste characteristic is a key element of a successful anaerobic digestion. Biodegradable part of solid waste such as carbohydrates, proteins, and lipids are substrates for anaerobic digestion systems. Biogas yield and efficiency of anaerobic reactors are affected by substrate composition, for instance a high content of lipids as substrate for anaerobic digestion process can be good due to higher methane yield compared to other organic materials (Nayono 2009). However, lipids may also cover the surfaces that enzymes and slow down the hydrolysis process (Neves et al. 2008).

#### **1.2.2.1. Volatile fatty acid production from OFSW via anaerobic fermentation**

Aim of first three steps of anaerobic digestion is producing the substrate of methanogens. However, methane is not the only valuable product that can be produced; intermediate products such as alcohol, propionic, butyric, valeric, caproic, and acetic acid (which is the final product along with H<sub>2</sub> and direct substrate of methanogens) are also produced in anaerobic fermentation as a step of anaerobic digestion. For instance acetic acid is a volatile fatty acid (VFA) and one of the most important compounds that are used in several industries such as food, beverage, pharmaceutical, and chemical industries (Aydin et al. 2018, M. Gryta and M. Barancewicz 2011, Y. M. Lee et al. 2001, Yesil et al. 2014, Zacharof and Lovitt 2013). Volatile fatty acids (VFAs) are molecules with low molecular weight, short chain organic acids and as their name implicates they can vaporize or evaporate at atmospheric pressure (Gerardi 2003). While non-volatile fatty acids have two carboxyl group (-COOH), volatile fatty acids have one carboxyl group in their chains (Tugtas 2011). In anaerobic digestion systems, acetic and butyric acids are predominant organic acids among the other volatile fatty acids (Wang et al. 2014). Production of high levels of VFAs are possible by modification of reactor and inhibition of methanogenic step of anaerobic digestion (Yesil et al. 2014). Inhibition of methanogenic step can be achieved easily by reducing pH below 6.5 where VFA production continues and even enhances due to reducing methanogen activity (Fang and Liu 2002, Yuan et al. 2006). Also accumulation of VFAs can help the pH adjustment for inhibition of methanogens but undissociated forms of VFAs can easily pass into cell and cause a self-inhibitory effect on fermentation bacteria (Tugtas 2014). Therefore, VFAs should be continuously separated

from anaerobic digestion systems to prevent inhibition during fermentation processes (Tugtas 2014).

#### **1.2.2.2. Separation of volatile fatty acids**

As mentioned in the previous sections, if methanogens are to be inhibited in an anaerobic fermentative system, VFAs (primarily acetic and butyric acid) should start to build up in the system. Factors like pH and temperature will affect the production efficiency. In some research, it is being mentioned that the separation of the VFAs will affect positively in the process of VFA production, even this can help to maintain the pH values in the controlled system by helping the sustainability (Cavdar et al. 2011, (Yesil et al. 2014)). Other than the positive effect on the system, separated VFAs can be purified to be used in industrialized areas as commodity chemicals. In the literature, VFA separation/recovery methods such as chemical precipitation, electro dialysis, solvent extraction, adsorption, and membrane separation have been used.

##### **1.2.2.2.1. Chemical precipitation**

Being one of the oldest methods, chemical precipitation, is still being broadly used. Calcium hydroxide or calcium oxide transforms the VFAs into salt form, therefore makes them easier to be collected through precipitation, however there has to be a further process for the VFAs to be able to be in use as commodity chemicals (Li et al. 2010). Carboxylic salts which have been formed by the chemical precipitation process must be filtered from leachate. VFAs are obtained in unionized forms with  $H_2SO_4$ , by this  $CaSO_4$  is obtained as side a product (Kertes and King 1985). After acidification, unionized VFAs should be purified via a method such as adsorption or ion exchange processes. In the following, VFAs are concentrated and crystalized for commodity purposes (Tugtas 2011). Furthermore, unionized and free forms of formic, acetic, and lactic acids are very soluble in water above  $0^\circ C$  and pH values between 1 and 14. Therefore, chemical precipitation is very difficult to operate to separate/recover VFAs from leachate (Li et al. 2010).

#### 1.2.2.2.2. Adsorption

Adsorption is a surface phenomenon when the gas, liquid or a dissolved solid create adhesion on a surface in form of atoms, molecules or ions (Schlegelmilch et al. 2005). This method is widely used for the treatment of hazardous waste, cleaning the odour, colour or bacteria from drinking water. Adsorption level is effected mostly from polarity and surface active area (Freitas et al. 2007). Adsorbent must be similar with the targeted matter in terms of polarity; polar target matter is adhered on polar adsorbent and nonpolar target matter is adhered on non-polar adsorbent. VFAs can be considered as mostly polar molecules but when the molecular chain of VFAs get longer, they get more nonpolar characteristic. Therefore, higher molecular weight VFAs are less polar so they can adhere on nonpolar adsorbents such as activated carbon easily than lower molecular weight VFAs (Freitas et al. 2007). Activated carbon, montmorillonite clays, commercial adsorbents and anionic exchange resins have been used in some studies of VFAs adsorption (Freitas et al. 2007, Garcia 1991, Hassan et al. 1997).

**Table 3.** Some similar studies in the literature

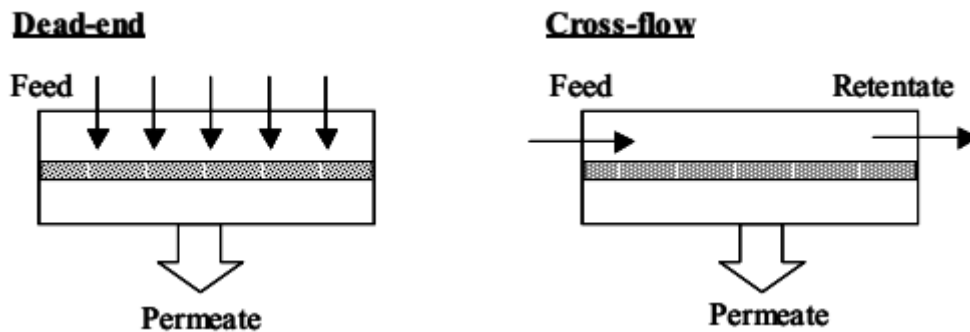
Feed Composition	Recovery Efficiency	Reference
0.5 M AA	9%	(Hassan et al. 1997)
250 mg/g AA, PA and BA	70%	(Freitas et al. 2007)

Surface area is another important factor; VFAs can be removed from solutions with adsorbent with high surface area per volume such as activated carbon. However, adsorption is not a selective removal method, if the adsorbent is similar with another matter in terms of polarity, the other matter than the target matter will be also adsorbed to adsorbent and also adsorption need further treatments to recover VFAs. In the literature recovery efficiencies can be changed 9% to 70% (Table 3) (Freitas et al. 2007, Hassan et al. 1997)

#### 1.2.2.2.3. Membrane Separation Processes

Membrane process is another method for VFA separation and purification (Qin et al. 2003). There are different membrane contactor applications for wastewater treatment, VOC removal, protein extraction, and fermentation processes (Stanojevic et al. 2003).

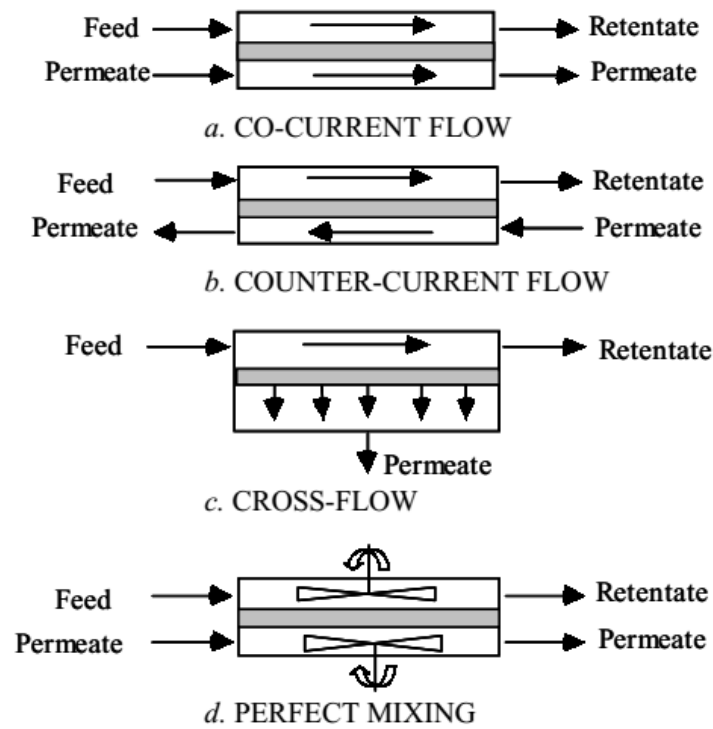
In the membrane contactor two phases are created by a membrane; a feed and permeate (Kocherginsky et al. 2007). Mass transfer of target compound from feed to permeate through membrane can be achieved by one or more driving forces such as concentration gradient, pressure difference, temperature difference or electrical potential (Stanojevic et al. 2003). And in the literature, there are various applications of membranes and membrane contactor designs (Stanojevic et al. 2003). Membrane contactor designs can be different due to membrane type and application. Membrane contactors can be operated in different operation modes; dead-end and/or cross-flow operation (Figure 4).



**Figure 4.** Two different operation form of membrane contactors (Stanojevic et al. 2003).

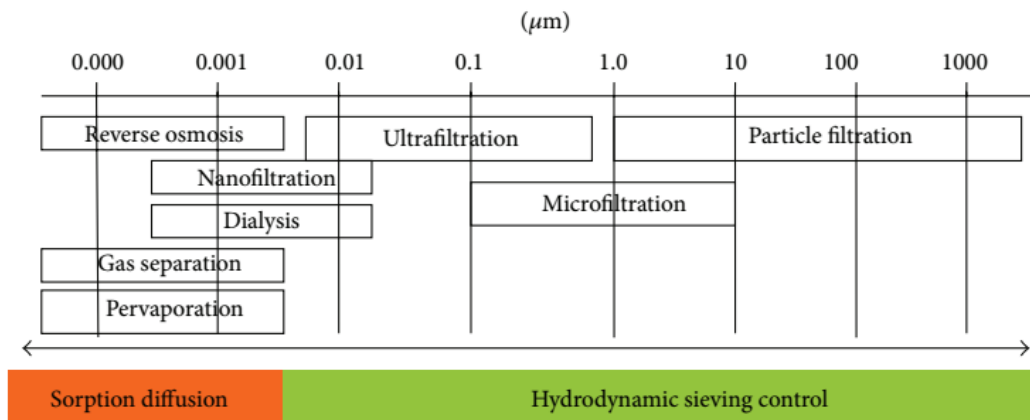
In dead end application, all the feed is forced to pass through membrane. In cross-flow membrane, operation a small portion of target compound passes through membrane with the velocity of feed. Different types of cross-flow types can be listed best performance to least; counter current > cross-flow > co-current flow > perfect mixing (Mulder 1997, Stanojevic et al. 2003).

Different types of membranes can be used in membrane contactors; for instance, membranes can be separated due to tendency of water such as hydrophobic, hydrophilic or can be separated due to porosity such as porous, dense or composite.



**Figure 5.** Principle flow patterns used in cross-flow operation (Stanojevic et al. 2003).

And also even membranes can be differentiated flat sheet, hollow fiber, rotating annular, and spiral wound (Stanojevic et al. 2003).



**Figure 6.** The choice of membrane with respect to the size of particles encountered (Jyoti et al. 2015).

Separation also can be categorized by pore sizes and the membranes got their characteristic names as microfiltration, ultrafiltration, and nanofiltration membranes (Figure 6) (Jyoti et al. 2015). Nanofiltration was successfully applied for removal of

hazardous compounds such as metals or endocrine disruptors of waste effluents as well as for the recovery of low molecular weight chemicals including enzymes and proteins (Kimura et al. 2009, Koyuncu 2002, Zacharof et al. 2016, Zhou et al. 2013). And also in the literature VFA separation via nanofiltration can be found (Zacharof and Lovitt 2014, Zacharof et al. 2016, Zhou et al. 2013).

**Table. 4** Some results for NF separation of VFAs in the literature

Feed Composition	Recovery Efficiency	Reference
2000 mg/L AA to 10000 mg/L AA	55% - 58%	(Zhou et al. 2013)
3000 mg/L AA and 6000 mg/L BA	72.2% - 69.7%	(Zacharof et al. 2016)
1266 mg/L AA and 1393 mg/L BA	45.18% - 72.23%	(Zacharof and Lovitt 2014)

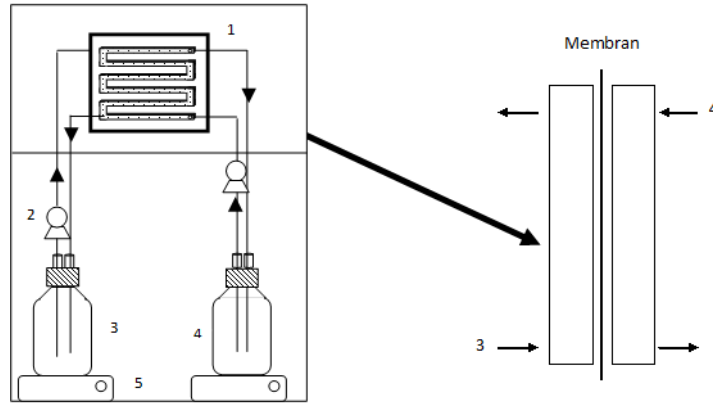
In the literature VFA recovery efficiency results were changed between 45.18% to 72.23% (Table 4) (Zacharof and Lovitt 2014, Zacharof et al. 2016, Zhou et al. 2013).

And membrane separation types can be categorized based on driving forces such as electrical potential differences (electro-dialysis), vapour pressure difference/concentration gradient driven processes (pervaporation and vapour permeation membrane contactors (VPMC)).

#### 1.2.2.2.3.1 VPMC Systems

There are two aqueous phases which separated from each other by a microporous hydrophobic membrane in VPMC systems (Albrecht et al. 2005, Aydin et al. 2018, Han et al. 2005, Yesil et al. 2014). Even though microporous hydrophobic membranes are used in VPMC systems, VPMC systems are different from microfiltration systems (Aydin et al. 2018). VPMC is not based pressuring on one side of the membrane and ions/liquids cannot pass through membrane like in microfiltration systems (Aydin et al. 2018, Tugtas 2014, Yesil 2013). Only volatile species or dissolved gases can pass through the microporous hydrophobic membranes in VPMC systems (Aydin et al. 2018). The partial pressure difference and concentration gradient are the main separation principles in VPMC system (Aydin et al. 2018, Tugtas 2014, Yesil 2013). Volatile species such as VFAs would be transferred from feed to permeate side until the concentration or partial pressure of volatile species reaches an equilibrium and as consequence driving force reaches to zero and mass transfer will be stopped (Han et al. 2005). Concentration gradient in both sides of the membrane should be maintained to

keep driving force constant by converting unionized volatile fatty acids or carboxylic acids into ionized forms (carboxylates) in permeate side (receiving solution) through a reaction (Aydin et al. 2018, Tugtas 2014, Yesil 2013).



**Figure 7.** Schematic of a typical VPMC system. Membrane contactor (1), feeding pump (2), feed solution (3), receiving solution (4) and magnetic stirrer (5)

VFAs in vapour form can diffuse from feed side through the membrane pores and absorb into receiving solution where VFAs will simultaneously transform into ionic forms and as a result concentration/vapour pressure of VFAs to be zero in the permeate side of the membrane, creating constant driving force (Tugtas 2014) (Figure 7). In addition, ionized VFAs (carboxylates) in the reactive permeate will not be able to pass backward through the membrane to the feed side thus back diffusion will be prevented (Aydin et al. 2018). PTFE membranes have high chemical resistance, good thermal stability and poor surface hydrophilicity, therefore, PTFE is preferred in membrane applications, where hydrophobicity is required (Zhang et al. 2013). However, when used in membrane contactors, PTFE membranes may also allow the diffusion of alcohols, water vapour, ammonia and other volatile species causing decreased selectivity towards VFAs (Qin et al. 2003, Thongsukmak and Sirkar 2007).

In the literature VFA recovery from landfill leachate was similar to that of fermentation broth, as about 45% acetic acid recovery and more than 86% of propionic, butyric, valeric, and caproic acid recovery was achieved (Aydin et al. 2018). In another study with fermentation broth the recovery efficiencies of acetic, propionic, butyric, valeric, and caproic acids were 3.3, 1.8, 7.2, 10.8, and 8.5%, respectively (Yesil et al. 2014).

### 1.2.2.2.3.2 Electro-dialysis

Electro-dialysis (ED) is a method based on, the ions' movement towards less concentrated regions using membranes with electro potential difference (Bazinet et al. 1998). In this method, a continuous direct current electric resource, ion exchange membrane, electrodes and solvents are being used. On the anode and cathode, substances are being ionized by oxidation/reduction reaction and being carried by the driving force, created by direct current (Tugtas 2011). Anion-cation and bipolar membranes are mostly used for electro-dialysis process. Electro-dialysis systems can be applied with membrane processes which are driven by pressure (reverse osmosis, nano-filtration, microfiltration, ultrafiltration, etc.), chemical unit operations (adsorption, extraction, electrolysis, stripping, ion exchange, etc.), or biochemical unit processes (fermentation and membrane bioreactors) (Xu and Huang 2008). In the literature, there are several different methods that have been used for VFA separation with electro dialysis. Some of the research are on synthetic solutions and either with mixed VFAs in a mixture or a single VFA in a mixture has been tested, and 80% to 90% recovery rates has been shown (Vertova et al. 2009).

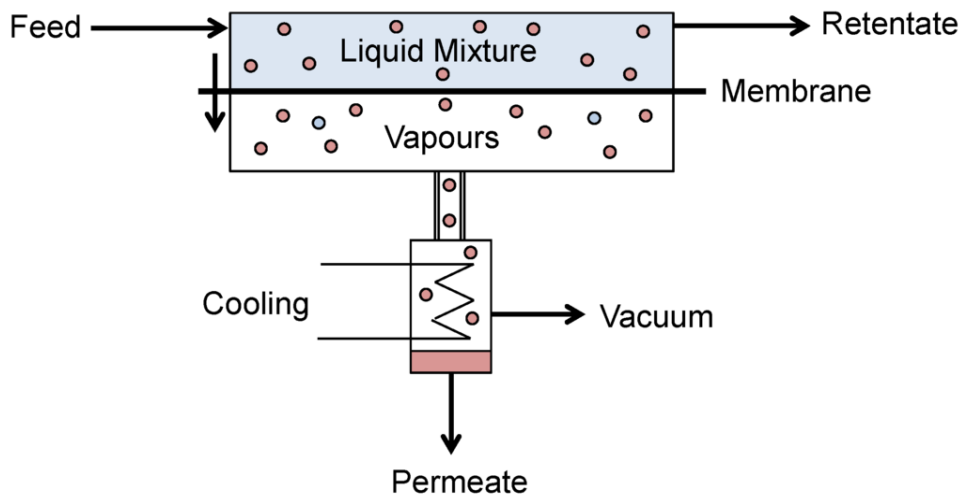
**Table 5.** Some studies of ED in the literature

<b>Feed Composition</b>	<b>Target Compound</b>	<b>Recovery Efficiency</b>	<b>Reference</b>
(C1–C6) carboxylic acids	(C1–C6) carboxylic acids	50%	(Vertova et al. 2009)
Fermentation broth	Acetic acid	93% - 96%	(Kim and Moon 2001)
Fermentation broth	Propionic and Acetic Acids	75% - 83%	(Weier et al. 1992)

Whereas the other research is usually reports data with fermentation broth and 75% to 96% recovery rates have been noted where propionic and acetic acids were separated. (Kim and Moon 2001, Weier et al. 1992), even though the recovery rates were high; due to membrane clogging, concentration polarization, reverse carriage of the ions from the membrane, high membrane costs and energy consumption , this system has not been widely used.

Among all the types of membrane systems, pervaporation is accepted as an ecological and economical choice which has been used for binary or multicomponent azeotropic

liquid mixtures such as VFA-water mixtures (Thongsukmak and Sirkar 2007). Pervaporation term was first proposed by Kober in 1917 as combination of the words permeate and evaporation (Kober 1917). In pervaporation systems cross-flow designs are used. Membrane divides membrane contactor into two sides, feed and permeate. At feed side, feed flows on membrane target compound or compounds pass through membrane via sorption - diffusion - desorption mechanism, beneath the membrane target compound as permeate in gaseous or vapour phase is carried out with vacuum or gas purge (Dogan and Demirel 2009, Vane 2005).



**Figure 8.** Schematic of a typical pervaporation process.

In this system, permeate constantly carried out from one side of the membrane and this factor causes a concentration gradient by itself. Polytetrafluoroethylene (PTFE), polydimethylsiloxane (PDMS) and polyvinylalcohol (PVA) membranes are mostly used for VFA separation in pervaporation systems (Lipnizki et al. 1999, Sun et al. 2013, Ten and Field 2000). However PTFE membranes with hydrophobicity, resistant to chemicals and heat qualities and PDMS membranes with organic acid affinity and separation factor are providing advantages for VFA separation (Qin et al. 2003, Thongsukmak and Sirkar 2007).

**Table 6.** Overview of membrane performance parameters of different pervaporation systems

System	Feed Composition	Membrane	Temperature (°C)	Flux (g/m <sup>2</sup> .h)	Separation Factor	Reference
Water/isobutyl acetate	50 wt %	PDMS	70	4429	1.421	(Korkmaz et al. 2011)
Isobutyl acetate/water	-	Cross-linked PDMS	60	3700	1.4	(Korkmaz et al. 2009)
Fermentation broth	0.5 g/L AA <sup>a</sup> 1.7 g/L BA <sup>b</sup>	PDMS	37	0.46 <sup>a</sup> – 1.6 <sup>b</sup>	-	(Setlhaku et al. 2012)
Synthetic Mix	5% AA	Zeolite membrane	30 – 70 – 90	230 – 470 – 490	2.2 – 6 – 7.7	(Sun et al. 2009)
Synthetic Mix	5% AA	Silicate	30	350	0.75	(Sun et al. 2009)
Synthetic Mix	0.3% AA	Zeolite membrane	70	60	1.9	(Sun et al. 2009)
AA /water	15% Vol. AA	Silicate	30	38	2.6	(Sano et al. 1997)
AA /water	2.5% mol AA	Carbon molecular sieve-filled PDMS (CMS=20%)	45	10	2.2	(Li et al. 2004)
AA /water	5.2 % mol AA	Carbon molecular sieve-filled PDMS (CMS=0%)	30 – 45	30 – 40	2.43 – 2.07	(Li et al. 2004)
AA /water	5% wt AA	PDMS	25	40 – 45	1.25 – 1.55	(Lu et al. 2000)
Synthetic Mix	AA: 0.5 g/L PA: 0.25 g/L BA: 6 g/L VA: 0.5 g/L	PEBA Graphene (0.75% wt)	70	AA=1 PA=1.5 BA=38 VA=5	AA=9 PA=15 BA=32 VA=45	(Choudhari et al. 2015)
Synthetic Mix	BA = 6 g/L	PEBA Graphene (0.75% wt)	40 – 70	60 – 180	29 – 38	(Choudhari et al. 2015)
Synthetic Mix	AA = 2 g/L PA = 2 g/L BA = 2 g/L VA = 2 g/L CA = 2 g/L	PDMS (50%)	35	AA: 0,14±0.08 PA: 0,22±0.12 BA: 0,28±0.16 VA: 0,23±0.13 CA: 0,09±0.03	AA: 1.68±0.02 PA: 2.60±0.03 BA: 3.31±0.02 VA: 2.62±0.01 CA: 1.28±0.38	(Taner 2016)

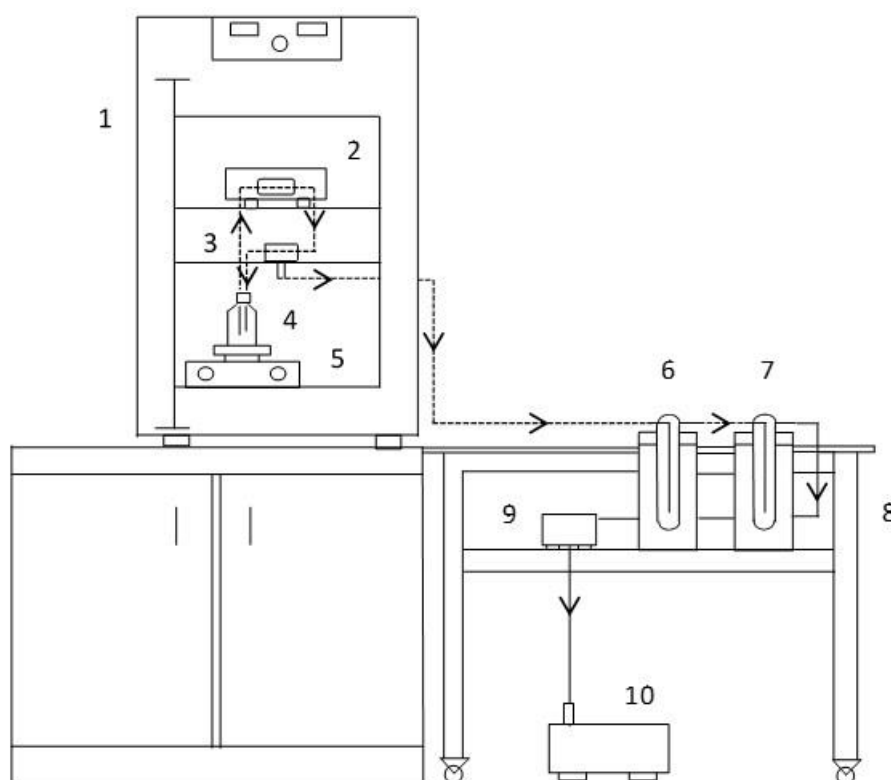
In the literature pervaporation system was used for purification and separation purposes. In different two studies to enhance performance of esterification, pervaporation was used and a form of acetate was separated with fluxes were 4429 and 3700 g/m<sup>2</sup>.h and separation factors were around 1.4 (Korkmaz et al. 2011, Korkmaz et al. 2009). Also there were studies with the aim of separation of VFAs from synthetic mixture and the results were changing between 0.14 to 490 g/m<sup>2</sup>.h as flux and 1.25 to 38 as separation factor (Table 6) (Choudhari et al. 2015, Korkmaz et al. 2011, Korkmaz et al. 2009, Li et al. 2004, Lu et al. 2000, Sano et al. 1997, Setlhaku et al. 2012, Sun et al. 2009, Taner 2016). However in a study with fermentation broth the results of separation factor were 0.46 and 1.6 for acetic and butyric acid respectively which showed a lower performance compare to synthetic studies (Setlhaku et al. 2012).

In pervaporation systems generally efficiency of these membranes is calculated over in terms of flux (J), separation factor ( $\alpha$ ) and pervaporation separation index (PSI). Per mass passing through per area of membrane in per time is called flux. Separation factor defines the ability of membrane how much target compound is selected. Pervaporation separation index (PSI) has been identified as a relative measure of the separation ability of a membrane. This index can be used to select a membrane with an optimum combination of separation factor and flux (Kariduraganavar et al. 2005).

## 2. MATERIALS AND METHODS

### 2.1. Pervaporation studies with Synthetic Fermentation Broth

Synthetic VFA separation experiments were conducted with a pervaporation setup for understanding of separation efficiencies of pervaporative membranes (Figure 9). A lab scale two-pieced stainless steel pervaporation module (membrane contactor) was designed to be used in pervaporation studies. The module contained two stainless steel parts, one part contained entrance and exit sections along with O-rings to avoid leakage.



**Figure 9.** (1) Temperature-controlled cabinet, (2) Peristaltic pump, (3) Laboratory scale membrane contactor, (4) Feed bottle (5) Magnetic stirrer, (6) Inline cold trap, (7) Protector cold trap, (8) Pervaporation table, (9) Vacuum regulator and (10) Vacuum pump.

The other side of the contactor was equipped with a vacuum entrance connection. Pervaporative membranes were placed into the membrane contactor which separated the feed and the permeate sides. In the membrane contactor, pervaporative membranes had  $12.56 \text{ cm}^2$  active membrane areas and were supported by a  $10\text{-}16 \text{ }\mu\text{m}$  porous glass

support (Borucam G4, İstanbul, Turkey) to prevent any damage from vacuum to membrane.

Feed concentration was chosen as a VFA mixture of acetic, propionic, butyric, valeric, and caproic acids each with a concentration of 2000 mg/L and de-ionized water as VFA mixture. In a previous study, pervaporation setup was tested under 55°C with a VFA mixture (2000 mg/L each of acetic, propionic, butyric, valeric and caproic acids) and flow rate were ranged between 20.8 L/d to 502.8 L/d (20.8 L/d, 102.3 L/d, 212.6 L/d, 376.1 L/d and 502.8 L/d). The optimum flow-rate for this setup was found 300 L/d (Taner 2016). In this study, the feed was fed with a peristaltic pump (Watson Marlow 323, Cornwall, UK) to system as cross-flow with constant 300 L/d flow rate which was pre-determined with the previous study (Taner 2016). Permeate was collected from downstream into cold traps (KGW Isotherm 17202 KF 29-GL-Z, Karlsruhe, Germany) under 3 bar pressure with help of vacuum pump (Edward 1.5 Crawley, England) and pressure was controlled by a regulator (J-KEM Sceintific-300, USA). The cold traps were connected in series and were kept in liquid nitrogen. Samples were taken from feed and permeate every two hours and an experiment period is six hours and the experiments were done under constant 35°C with a temperature-controlled cabinet (WTW TS606 G/2i, Weilheim, Germany). Composite membranes with different compositions were manufactured in laboratory and used in this system.

## **2.2. Manufacturing Composite membranes**

First step of understanding the best membrane for non-synthetic fermentation broth assay was manufacturing composite membranes that were going to be assessed in terms of separation factor and acid flux. The manufactured membranes can be categorized in two segments; vinyl terminated PDMS membranes and hydroxyl terminated PDMS membranes.

### **2.2.1. Vinyl terminated PDMS membranes**

Vinyl terminated PDMS (PDMS-vinyl) (Xiameter RBB 2100-30, Dow Corning Co., Midland, Michigan, USA) were crosslinked with dicumyl peroxide (Merck 8201630250, Millipore Co., Billerica, Massachusetts, USA). Hexane (Acros 197360010, Thermo Fisher Scientific, Geel, Belgium) was used as solvent for

manufacturing non-filled PDMS-vinyl composite membranes. Predetermined ratios of PDMS-vinyl, hexane and dicumyl peroxide were mixed with help of a magnetic stirrer (Heidolph MR Hei-Mix L, Germany) at 6.98 as G value for 24 hours in a glass bottle. After 24 hour hours the mixture was treated with an ultra-sonic bath (Bandelin, Sonorex DK 156 BP, Germany) in order to disperse homogeneously and release remaining hexane bubbles for an hour closed to atmosphere and another hour open to atmosphere. The polymeric membrane mixture was poured into a Teflon pan and slightly tilted to opposite side of pouring to achieve same thickness for a membrane. The PDMS-vinyl mixture was left for 24 hours so hexane can vaporize. After 24 hours the PDMS-vinyl membrane was treated with heat gradually to 200°C in six and a half hours.

In our group's previous study polymer/hexane ratios from 10% to 75% were used to manufacture non-filled PDMS-vinyl membranes (Table 7, (Taner 2016)). Polymer mixture could not be homogenized at/above polymer/hexane ratios of 50% and therefore, polymer/hexane ratios above %50 were not used (Taner 2016).

As PDMS-vinyl polymer's molecular weight is unknown, PDMS-vinyl/dicumyl peroxide ratio was assayed between 0.5-6 percent (Taner 2016).

**Table 7.** The membranes which is prepared for understanding the effect of polymer ratio and cross-linker ratio (Taner 2016)

Membrane No	Polymer Ratio (%)	Cross-linker Ratio (%)
PDMS-V-1	20	2
PDMS-V-2	20	3
PDMS-V-3	20	4
PDMS-V-4	20	5
PDMS-V-5	10	3
PDMS-V-6	10	4
PDMS-V-7	10	5

When manufacturing non-filled PDMS-vinyl membranes 10% and 20% PDMS-vinyl/hexane ratio with combination of 2%,3%,4% and 5% ratio cross-linker (dicumyl peroxide) were used as shown in Table 6 (Taner 2016).

Membrane mixture which was predetermined polymer, hexane and cross-linker ratio was poured onto a Teflon pan and was gradually heated up to 200°C.

In this study Hydrophilic (Aldrich 718483, Silicon Dioxide 12 nm) and hydrophobic (Aerosil R812 Evonik Industries) nano-silica was used as filling materials for increasing VFA separation efficiency via pervaporation system. Silica nanoparticles were added to hexane at predetermined ratios. Similar procedures as in non-filled membranes were used for the manufacturing of filled membranes, the only difference was the addition of silica to filled polymeric membranes. Hydrophilic and hydrophobic silica ratios were changed between 0% and 10% and membranes are showed in Tables 8 and 9. Some of the membranes were manufactured twice to assess repeatability and consistence of the manufacturing process.

**Table 8.** PDMS-vinyl membranes with hydrophilic nano-silica filling.

Membrane No	Polymer ratio (%)	Silica ratio (%)
PDMS-V-8	20	0.1
PDMS-V-9	20	0.5
PDMS-V-10	20	2.5
PDMS-V-11	20	5.0
PDMS-V-12	20	10.0

**Table 9.** PDMS-vinyl membranes with hydrophobic nano-silica filling.

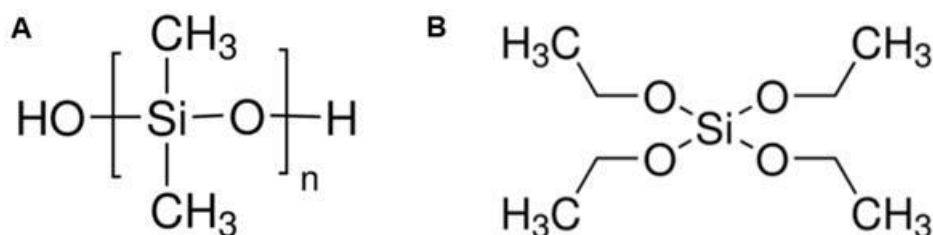
Membrane No	Polymer ratio (%)	Silica ratio (%)
PDMS-V-13	20	0.1
PDMS-V-14	20	0.5
PDMS-V-15	20	2.5
PDMS-V-16	20	5.0
PDMS-V-17	20	10.0

### 2.2.2. Hydroxyl terminated PDMS membranes

Two different polymers with different molecular weights were used for the manufacturing of hydroxyl terminated non- filled PDMS membranes. First of these polymers was low molecular weighted PDMS-OH with 550 g/mol molecular weight and 25 cSt viscosity. The other polymer had the viscosity value ranging between 1800-2200 cSt as given by the producer, the molecular weight of the polymer could not be assessed, however in the literature molecular weight of PDMS-OH with 2200 cSt viscosity was found to be 36000 g/mol (Cho et al. 2012).

Low and high molecular weight PDMS-OH membranes manufactured via solvent casting method on a porous (0.2  $\mu\text{m}$ ) PTFE membrane as support layer. The polymeric solvent was prepared with low molecular weight PDMS-OH polymer (Aldrich 432989, St. Louis, Missouri, USA) or high molecular weight PDMS-OH polymer (Aldrich 481939, St. Louis, Missouri, USA), a crosslinker tetraethyl orthosilicate (TEOS) (Acros 157810010, Thermo Fisher Scientific, Geel, Belgium) and a solvent hexane (Acros 197360010, Thermo Fisher Scientific, Geel, Belgium). And also dibutyltin dilaurate (Acros 382690050, Thermo Fisher Scientific, Geel, Belgium) was used as a catalyst to enhance the reaction rate. Predetermined ratios of PDMS-OH, hexane, TEOS, and dibutyltin dilaurate were mixed in a glass bottle for 24 hours with the help of a magnetic stirrer (Heidolph MR Hei-Mix L, Germany) at 250 rpm and room temperature. The homogeneous solution was casted on a PTFE membrane with a stainless steel casting knife (Gardco Universal blade applicator, USA) at a thickness of 254  $\mu\text{m}$ . PDMS-OH membrane solution which was casted on PTFE membrane was left for 24 hours at room temperature to vaporize hexane. After 24 hours of drying, the membrane was treated with heat gradually until 100  $^{\circ}\text{C}$ . The vulcanization process was carried out in a stepwise manner as, half an hour at 30 $^{\circ}\text{C}$ , half an hour at 60 $^{\circ}\text{C}$ , half an hour at 75 $^{\circ}\text{C}$ , half an hour 90 $^{\circ}\text{C}$  and finally 22 hours at 100 $^{\circ}\text{C}$ .

Crosslinker amount was calculated from stoichiometric ratios due PDMS-OH molecular weights so ratio of PDMS-OH / crosslinker was calculated as 20% for low molecular weight PDMS-OH and 0.3% for high molecular weight PDMS-OH (Figure 10).



**Figure 10.** Molecular structure of (A) PDMS-OH and (B) TEOS

Catalyst ratio was constant (2%) for low molecular weight non-filled PDMS-OH and polymer ratio of membrane was chosen as 50% considering previous studies of our group (Taner 2016).

Two of high molecular weight non-filled PDMS-OH membranes were manufactured to determine the effect of catalyst ratio on separation of VFAs. The membranes had constant polymer ratio of 30% and the catalyst ratio changed from 0.5% to 1% (Table 10).

**Table 10.** The membranes manufactured to determine the effect of catalyst ratio on VFA separation efficiency.

Membrane No	Polymer Ratio (%)	Catalyst Ratio (%)
PDMS-OH-18	30	0.5
PDMS-OH-19	30	1.0

In addition, to determine the effect of polymer ratio on membrane characteristics, polymer ratio was ranged from 20% to 35% as the catalyst ratio was kept constant 1% (Table 11).

**Table 11.** Non-filled high molecular weight PDMS-OH

Membrane No	Polymer Ratio (%)	Catalyst Ratio (%)
PDMS-OH-20	20	1.0
PDMS-OH-21	25	1.0
PDMS-OH-19	30	1.0
PDMS-OH-22	35	1.0

Two different silica-nano filling (hydrophilic and hydrophobic) were used for increasing the VFA separation efficiency. Nano-silica particles were mixed with hexane and the same procedure was followed as for non-filled PDMS-OH membranes. Polymer ratio was kept constant at 50% with 20% cross linker and 2% catalyst ratio for nano-silica filled low molecular weight PDMS-OH membranes.

**Table 12.** The nano-silica filled low molecular weight PDMS-OH membranes for understanding efficiency on VFA separation

	Membrane No	Polymer ratio (%)	Nano-silica Ratio (%)
Hydrophilic nano-silica	PDMS-OH-9	50	0.1
	PDMS-OH-10	50	0.5
	PDMS-OH-8	50	2.5
	PDMS-OH-11	50	5.0
	PDMS-OH-12	50	10.0
Hydrophobic nano-silica	PDMS-OH-13	50	0.1
	PDMS-OH-14	50	0.5
	PDMS-OH-15	50	2.5
	PDMS-OH-16	50	5.0
	PDMS-OH-17	50	10.0

Separation factor of high molecular weight PDMS-OH membrane filling material was based on efficiency of filled low molecular weight PDMS-OH membranes. Hydrophilic silica nano-particles were added to hexane polymer solution at designated ratios (Table 12) and followed same procedure for non-filled PDMS-OH membranes.

**Table 13.** The hydrophilic nano-silica filled high molecular weight PDMS-OH membranes

Membrane No	Polymer ratio (%)	Nano-silica Ratio (%)
PDMS-OH-23	30	0.1
PDMS-OH-24	30	0.5
PDMS-OH-25	30	2.5
PDMS-OH-26	30	5.0
PDMS-OH-27	30	10.0

### 2.2.3. Characterization of membranes

Characterization of membranes have to be determined in order to understand the manufactured membrane behaviours against volatile fatty acid solutions and also characterizations are extremely helpful for evaluating performance results of manufactured membranes when the characterizations are considered as a parameter or a reference to the case.

### **2.2.3.1. Contact Angle**

Contact angle values of all membranes were assessed to determine the hydrophilicity/hydrophobicity of each membrane. Contact angles were measured in Marmara University Chemistry Department via Krüss FM41 (A.Krüss Optronic GmbH, Hamburg, Germany) and Kocaeli University Engineering Faculty Chemical Engineering Department via KVK Attention brand tool.

### **2.2.3.2. SEM analysis**

Topographic and inner nano-silica distribution and structure of pervaporative membranes were investigated with a scanning electron microscope (SEM) (JEOL JSM 5919LV, Peabody, Massachusetts, USA) in Marmara University Engineering Faculty Environmental Engineering Department and with an ESEM (Philips, XL30 ESEM-FEG/EDAX Model, Eindhoven, Netherland) in Bogazici University.

### **2.2.3.3. Tensile Strength**

Physical endurance of prepared PDMS-vinyl membranes was tested via tensile strength measurement, which was conducted at Marmara University Chemistry Department with a Zwick Roell 500N (Zwick GmbH & Co., Ulm, Germany). Elasticity module factors were obtained from 30 mm / minute pulling velocity to membranes.

### **2.2.3.4. Swelling/Sorption Test**

Membrane and feed interactive relation was explained with swelling test. Dry weighted membrane samples were kept in VFA solution for 24 hours and at 35°C. Wet weight of membranes was measured and calculated percentage of change in mass with dry weight. Found results were reported as swelling/sorption values.

## **2.3. VFA Production via Leach Bed Reactor**

VFA production in laboratory conditions was a need to assay the manufactured membranes under realistic conditions. A leach bed reactor (LBR) was used to produce VFAs from organic fraction of municipal solid wastes and was manufactured by outsource. The LBR was ensured that worked under anaerobic conditions.

### 2.3.1. Preparation and characterization of solid wastes

Solid wastes were obtained from ISTAC A.S., which operates Istanbul Kemerburgaz Compost and Recycling Facility. In the facility; plastics, metal, glass and other inorganic fractions were separated from organic fraction of municipal solid waste (OFMSW) mechanically. Organic fraction of municipal solid waste was obtained from Kemerburgaz Kompost Facility on two different seasons (40 kg OFMSW) (Figure 11A and 11B).



**Figure 11.** Municipal wastes which were obtained from Kemerburgaz Compost Facility (A) (Yesil 2013) winter season (B) summer season

Small inorganic materials in both summer and winter season wastes were separated manually in the laboratory (Figure 11A). Two wastes with high organic content were splintered with a 1000 W food processor and were mixed together.



**Figure 12.** Separation of municipal waste (A) inorganic waste (B) organic fraction of winter waste (C) organic fraction of summer waste (Yesil 2013).

The organic fraction of two wastes was prepared as homogenous as possible (Figure 12). Composite of winter and summer wastes were wrapped into two kilogram packages and were kept at  $-4^{\circ}\text{C}$  until used.



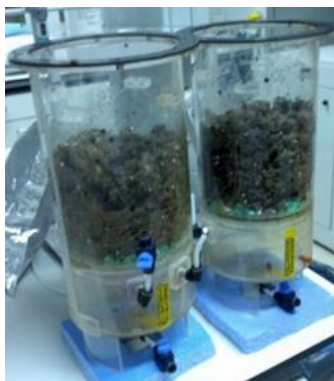
**Figure 13.** Composite organic municipal waste

Carbon, nitrogen, phosphorous ratios, total solid and water content of organic waste in LBR were measured beginning and end of operation.

### **2.3.2. Operation of leach bed reactor**

VFA production from prepared organic waste through anaerobic fermentation was conducted in two 7 L acrylic laboratory scale LBRs. Design of LBRs was exactly the same and one of the LBRs was used for control and the other was used for VFA separation via pervaporation. Separation effect was investigated on VFA production by measuring total VFAs in two LBRs.

The leach bed reactor was equipped with 1 L headspace, 4 L solid waste compartment, and 2 L cone-bottomed leachate collection systems (Figure 14). A stainless steel mesh was placed on top of the leachate collection compartment, which separated solid waste and leachate sections, and was supported by plastic pebbles to prevent clogging of the mesh screen during operation (Figure 14). Two packages (4kg) of organic solid wastes were taken into room temperature from  $-4^{\circ}\text{C}$  for melting. Organic solid wastes were taken out of the freezer and adjusted to ambient temperatures overnight then were equally placed into reactor (2 kg each) (Figure 14).



**Figure 14.** Organic solid wastes were placed in LBRs.

1.5 liter of tap water was poured on each LBRs that is showed in Figure 15.



**Figure 15.** Addition of tap water to control and test reactors.

Inoculum was not added to LBRs to prevent methanogenic activity, which would come with the seed. Anaerobic condition was maintained by flushing LBRs with nitrogen gas before sealing the reactors. LBRs were then placed into incubator at 35°C. Double capped peristaltic pumps were used for leachate recirculation (Figure 16).

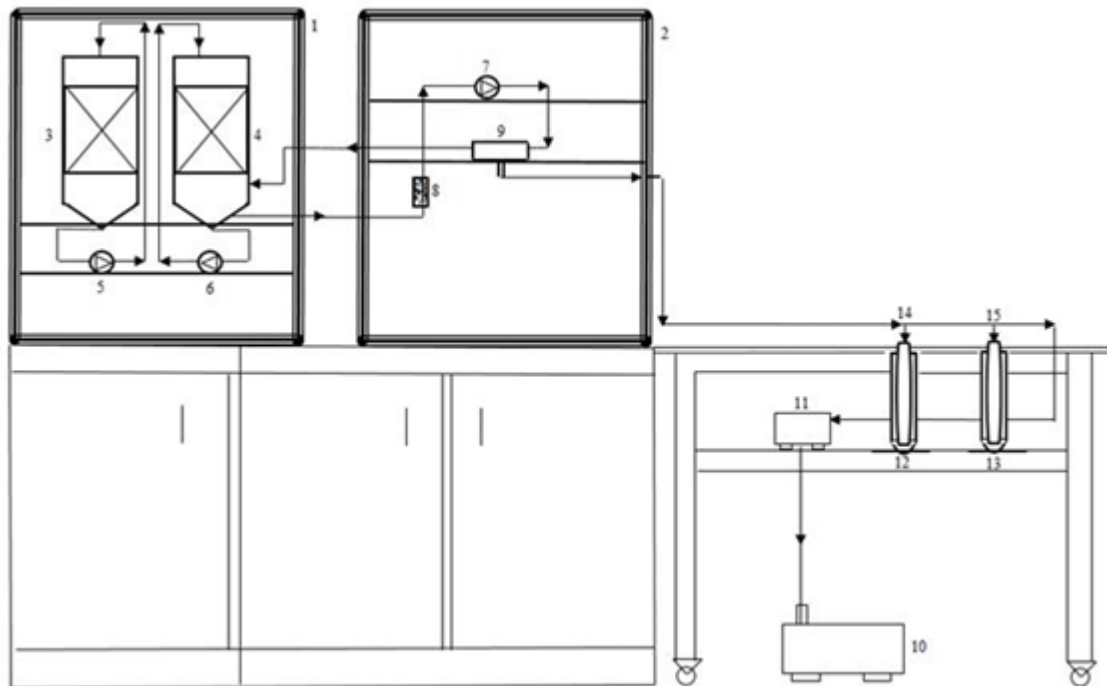


**Figure 16.** Control and Test LBRs in an incubator

## 2.4. Pervaporation studies with Fermentation Broth

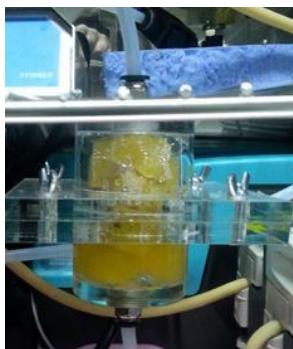
### 2.4.1. Integrated leach bed reactor via pervaporation

Pervaporation system was integrated to one of the LBRs as shown in Figure 17. (Figure 17). Leachate collection chamber was used as a feed bottle in synthetic pervaporation system and all necessary connections were done on recirculation line. Leachate collection chamber was used as a feed bottle in synthetic pervaporation system and all necessary connections were done on recirculation line. A filter unit also was added to design for eliminate solid particle which may clog membrane (Figure 18).



**Figure 17.** Integrated LBR-pervaporation system: (1 and 2), control LBR (3), test LBR (4), peristaltic pumps (5, 6 and 7), filtration unit (8), pervaporation membrane contactor (9), vacuum pump (10), vacuum regulator (11), Dewar containers (12 and 13) and cold traps (14 and 15)

Filtration unit was tested before integrated system with leachate and observed that the unit is very effective for preventing clogging on membrane. Filtration unit was placed on feed line (leachate outline) to pervaporation system.



**Figure 18.** The filtration unit which was placed before pervaporation system

Control and test reactors were started to operate after organic solid waste and tap water were placed into the reactor at 35°C. Sample collection from control and test reactors was done twice a day as in the morning and in the afternoon. After leaching and sampling, leachate in test reactor was transferred with a peristaltic pump first to filtration unit then pervaporation system. Pervaporation system was operated under 35°C, 300L/day recirculation rate with a membrane (PDMS-OH-9).

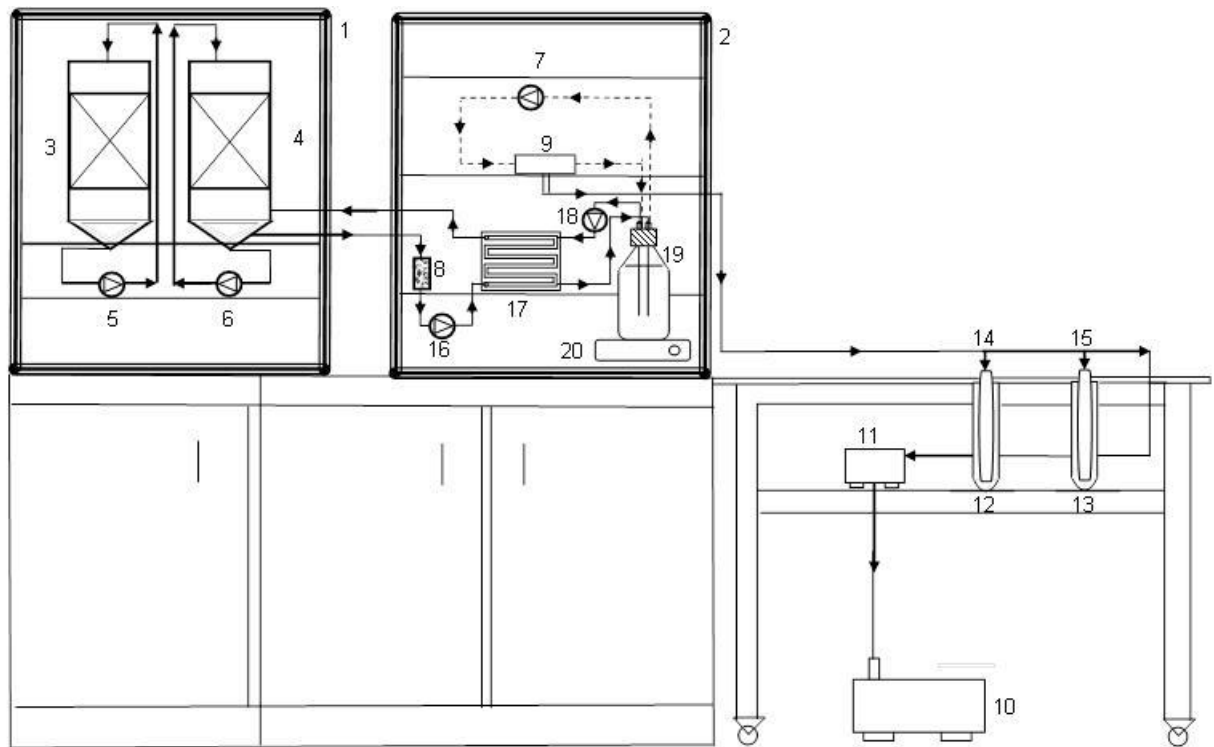
pH of leachate was measured before feeding to pervaporation system and was adjusted with concentrated HCl to keep the pH below 4 to increase the non-ionized VFA species in the leachate. VFA separation via pervaporation was done for 8 hours in a day. Samples were taken from cold traps by washing cold traps with 6 ml H<sub>2</sub>SO<sub>4</sub> (8mM) and necessary analyses were done. Pervaporation and leachate recirculation did not work simultaneously. Pervaporation system was operated for 8 hours' during the day time then the pervaporation system was shut off. Leachate recirculation was performed for the remaining 16 hours of the day with a total volume of 20L (20L/ 2 days). pH adjustments to maintain microbiological activities was done with NaHCO<sub>3</sub>.

pH, conductivity, VFA concentration, soluble and total chemical oxygen demand (COD), and ammonia nitrogen (NH<sub>4</sub>-N) concentrations were checked periodically in the leachates of control and test reactors. pH, conductivity and total COD measurements were done without filtration but all the other parameters were checked with filtrated samples which filtration was done via hydrophobic PTFE syringe filter.

VFA concentration values from samples from cold traps were measured without any other filtration process. Gas compositions were measured from samples in gas collection chambers.

## 2.4.2. Integrated leach bed reactor, vapour pressure membrane contactor and pervaporation system

In the light of VFA separation results, which were obtained from synthetic VFA separation experiments along with the pervaporation system and integrated LBR-pervaporation system, it was observed that, increased VFA concentration in the feed enhances the VFA separation efficiency of the pervaporation system. For this reason, vapor pressure membrane contactor system (VPMC) was used for concentrate VFAs in feed solution. At 20th day of this assay VPMC system also integrated to LBR-pervaporation system (Figure 19). Operational condition was found in previous studies.



**Figure 19.** LBR- VPMC -pervaporation integrated system: incubator (1 and 2), control LBR (3), test LBR (4), peristaltic pumps (5, 6 and 7), filtration unit (8), pervaporation membrane contactor (9), vacuum pump (10), vacuum regulator (11), Dewar containers (12 and 13), cold traps (14 and 15), VPMC feed pump (16), VPMC system (17), VPMC alkali receiving solution pump (18), alkali receiving solution (19) and magnetic stirrer (20)

Leachate collection chamber of test reactor was used as feed container for vapour pressure membrane contactor system and all necessary connections were made on the

recirculation line (Figure 19). The filter unit, which was used in the previous integrated system was placed before the VPMC system (Figure 19). VPMC system and receiving solution bottle were placed in another incubator and operated at night for 16 hours.

Similar to the pervaporation system, pH of the feed solution is very important for VFA separation efficiency of the VPMC system. pH values were adjusted with HCl and kept between 4.2 – 4.5 before being used in the VPMC system. In addition, 0.5 N ve 1 N NaOH were used as a receiving solution. VFAs were concentrated in 100 ml receiving solution (0.5 N or 1.0 N NaOH) around 4-5 days. After the operation of VPMC, collected permeate in NaOH solution was fed to the pervaporation system after the adjustment of pH below 4. Feed pH was adjusted to below for before being fed to the pervaporation system. Purification of VFAs in the pervaporation setup in receiving solution was done for 8 hours a day. Samples were collected after operation and the cold traps were washed with 6 ml de-ionized water to collect all the droplets attached to the walls of the trap then the samples were analysed. LBR- VPMC -pervaporation integrated system was tested with 1L/d and 10L/day recirculation flowrates. After 8 hours of pervaporation process, VPMC system restarted.

Sampling of control and test reactors was done twice a day in the morning (after VPMC process was stopped and before recirculation starts) and in the afternoon (before VPMC process was started and recirculation stopped). Samples from receiving solution of VPMC system and cold traps were taken once a day. In a day pervaporation process was used for 8 hours and VPMC process was used for 16 hours.

## **2.5. Analytical Methods**

### **2.5.1. Sampling**

#### **2.5.1.1. Sampling during operation of VFA production via LBR**

Leachate samples were directly taken from the leachate recirculation line two times a day in VFA production assay. During sampling, primarily recirculation pump was stopped and then sampling valve was opened and all other valves were closed. Approximately 5 ml sample was taken in the sampling line was discarded before sampling. After sampling, recirculation pump was started again. Leachate samples were

analysed for pH, conductivity, volatile fatty acids, chemical oxygen demand and  $\text{NH}_4\text{-N}$ . At the beginning of the experiment, gas composition was analysed each day and gas samples were directly taken from headspace of the anaerobic reactor to check elimination of methanogenic phase via the composition of produced gas in the reactor. After ensuring absence of methanogenic activity, gas sample was not taken up to end of the study.

#### **2.5.1.2. Sampling during operation of VFA separation via membrane contactor and pervaporation systems**

VFA solution samples were taken from receiving solution and cold traps after cold traps reach to room temperature and washed with 6ml of water. VFA solution samples were analysed for pH, conductivity, volatile fatty acids, chemical oxygen demand and  $\text{NH}_4\text{-N}$ .

At the end of the study, 500 mg of fermented solid waste was separated for further analyses and characterization of OFMSW.

#### **2.5.2. pH and conductivity**

pH measurement of the samples was done via WTW Sentix 940 pH electrode equipped WTW 9310 pH meter (WTW GmbH, Weilheim, Germany). Conductivity was measured with a conductivity meter (Delta, HD2106.1).

#### **2.5.3. Chemical oxygen demand**

Chemical oxygen demand was measured via the Closed Reflux Colorimetric Method (Standard Method, 5220 D). COD was measured with COD Reactor Model 45600 and DR/890 Colorimeter (HACH Company, Colorado, USA). The measurement range of the method was 0 – 1000 mg/L. Therefore, dilution of samples was done with deionized water considering this range.

#### **2.5.4. Ammonia**

$\text{NH}_4^+\text{-N}$  concentrations were analysed using the Nessler Method (Method 8038), which was adapted from Standard Methods 4500- $\text{NH}_3$  B & C with HACH DR/2000

spectrophotometer using Mineral Stabilizer, Polyvinyl Alcohol and Nessler Reagent, for the samples of fermentation experiment. The measurement range of the method was 0 – 2.50 mg/L. Therefore, samples were diluted with deionized water considering this range.

#### **2.5.5. Volatile fatty acids**

Samples for VFA analysis was acidified with 1% phosphoric acid and kept at -20°C until measurement. GC-2014ATF (Shimadzu GC-2014ATF, Kyoto, Japan) with FID detector and capillary column TRB-FFAP (Teknokroma TRB-FFAP 30m x 0.32 mm x 0.50 µm Sant Cugat del Vells, Spain) was used for VFA concentration measurement. Samples for gas composition was taken by a 10 ml syringe and was measured via TCD detector and Restek MS-13X (Restek MS-13X 45/60, length: 2.74 m, inner diameter: 2.0 mm, Bellefonte, USA) equipped Shimadzu GC-2014ATF (Shimadzu GC-2014ATF, Kyoto, Japan) under 70 kPa and injection, column and detector temperatures were 150°C, 40°C and 150°C respectively.

#### **2.5.6. Total solids and volatile solids**

Solids content of organic solid waste was measured accordingly to Standard Methods chapter 2540 B. Water content of organic solid waste was calculated from solid content of the waste. 103-105°C furnace (Philip Harris Ltd., UK) for the total solids measurement. Volatile solid content of solid waste was found through procedures from Standard Methods (Standard Methods 2540 E). Muffle furnace (Lenton ECF 12/6, Derbyshire, UK) was used for measuring volatile solid content of solid waste.

#### **2.5.7. Total nitrogen and total phosphorus**

Nitrogen content was measured through Macro-Kjeldahl method and Total Kjeldahl Nitrogen (TKN) (Standard Methods 4500–Norg B). For this assay a thermo-reactor (Gerhardt, Turbotherm, Germany) was used for disintegration process and then a distillation tool (Gerhardt, Vapodest 30s, Germany) was used. Concentrations were measured by a spectrophotometer (WTW GmbH, PhotoLab 6100 VIS, Weilheim, Germany). Ammonia concentration was measured via Nessler method (Standard Methods 4500-NH<sub>3</sub> B & C). Samples were diluted for 30 times with deionized water.

The measurement range of the method was 0 – 2.50 mg/L. Therefore, samples were diluted with deionized water considering this range.

Solid waste samples were firstly digested for the measurement of the phosphorus content (Standard Methods 4500-P B.4). Vanado Molibdo Phosphoric Acid Colorimetric method (Standard methods 4500-P C) was used for Orthophosphate concentration which is formed after the digestion of of solid wastes. Vanado Molibdo Phosphoric methods' calibration range was changed from 0 to 30 mg PO<sub>4</sub>-P/L and samples were diluted 30 times for this range. Spectrophotometer (HACH, DR 2500, Colorado, US) was used for both total nitrogen and total phosphorus measurement.

### **3. RESULTS AND DISCUSSION**

#### **3.1. Operation of pervaporation system with Composite membranes**

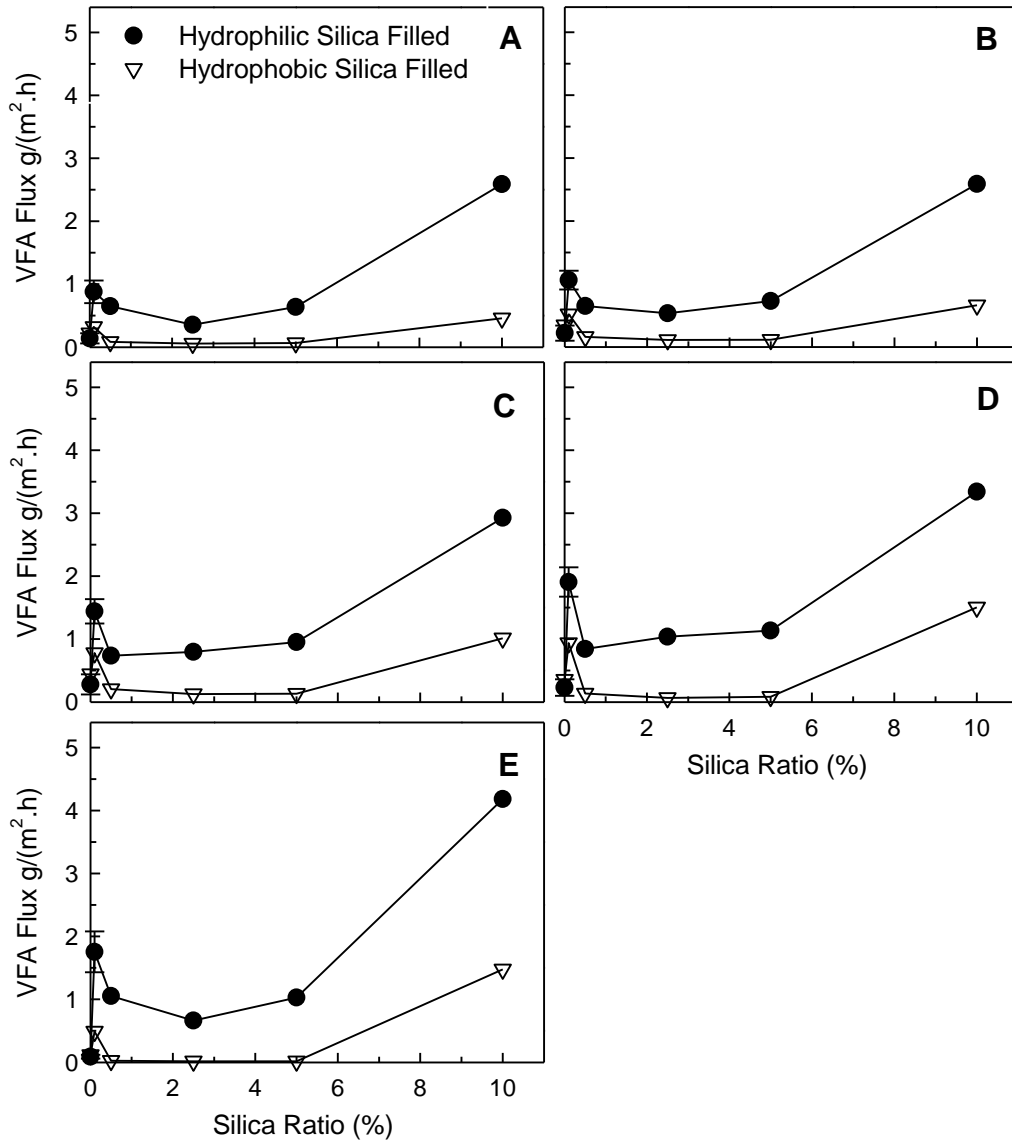
Composite membranes were manufactured with two different polymers; hydroxyl terminated polydimethylsiloxane (PDMS-OH) and vinyl terminated polydimethylsiloxane (PDMS-vinyl). Two different molecular weight PDMS-OH polymers (550 and 36000 g/mol) were used to manufacture PDMS-OH membranes. Also the effect of filling material was investigated by using hydrophilic and hydrophobic nano-silica as filling materials for manufactured PDMS-OH and PDMS-vinyl membranes. Each VFA with a concentration of 2000 mg/L (acetic, propionic, butyric, valeric and caproic acids) were used as a feed VFA mixture, 300 L/day feed recirculation rate, 3 torr vacuum and temperature of 35°C were chosen as operational conditions as a result of our previous studies (Taner 2016). Some of the best performing membranes were also tested in pervaporation system under the operational temperature of 45°C.

##### **3.1.1. Hydrophilic and Hydrophobic Silica Filled 550 g/mol weight (Low molecular weight) PDMS-OH membranes**

Silica filled low molecular weight PDMS-OH membranes were manufactured in the composition of 50% PDMS (w/w with hexane) as polymer, 20% tetra orthosilicate (TEOS) (w/w with PDMS) as cross linker, 2 % (w/w) dibutyltin dilaurate as catalyst, hexane as solvent and pre-designated hydrophilic or nano-silica in values of 0.1%, 0.5%, 1%, 2.5%, 5% and 10% (all w/w with PDMS). All PDMS-OH membranes were casted on PTFE support membrane. All the synthetic assays were conducted with 10-16 glass support, 300 L/day, under 35°C and 3 torr vacuum.

Addition of 0.1% hydrophilic nano-silica to low molecular weight PDMS-OH membranes resulted in an increase of acid flux compared to that of non-filled PDMS-OH membranes which were investigated in a previous study (Taner 2016) (Figure 20). Generally, with the increase of aliphatic groups, acid flux of VFAs was also increasing (Figure 20). Acetic acid flux was increased 1.45 fold and caproic acid flux was increased 4.14 fold (Figure 18). However, 0.5%, 2.5% and 5% hydrophilic nano-silica

filled low molecular filled PDMS-OH membranes had lower acid flux compare to that of 0.1% hydrophilic nano-silica filled low molecular PDMS-OH membrane (Figure 17). When the hydrophilic nano-silica ratio was increased to 10%, acid flux of all acids was increased between 2 to 12 fold (Figure 1).

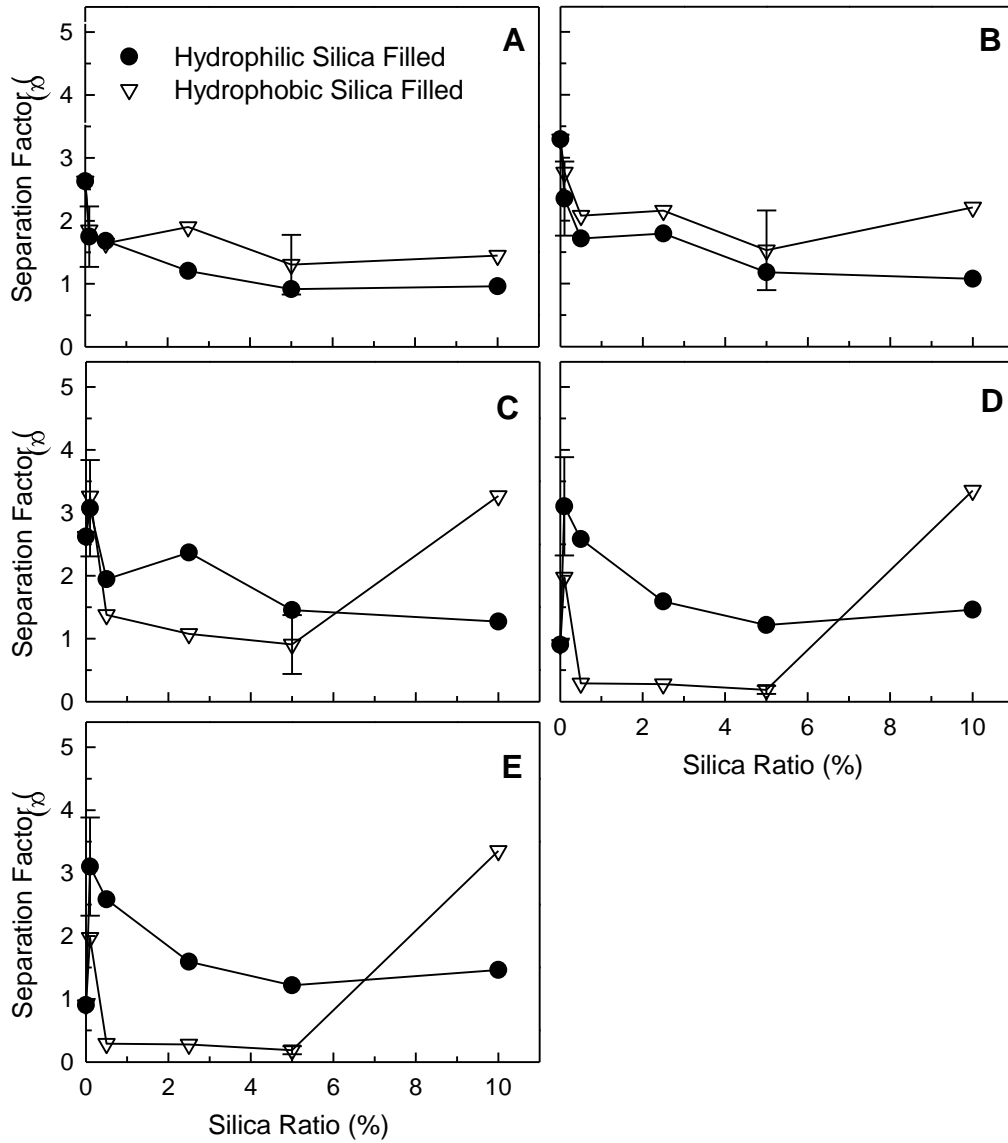


**Figure 20.** Effect of silica type and ratio on VFA flux values for low molecular weight PDMS-OH membranes (50% PDMS-OH/hexane, 2% catalyst, 20% cross-linker): acetic (A), propionic (B), butyric (C), valeric (D) and caproic acids (E) ( non-filled results was taken from (Taner 2016).)

In order to determine the effect of hydrophilic nano-silica addition on VFA separation efficiency of composite membranes, 0.1%, 0.5%, 1%, 2.5%, 5% and 10% of hydrophilic

nano-silica (w/w with PDMS) was added to PDMS-OH membrane. 0.1% hydrophilic nano-silica filled low molecular PDMS-OH membrane was showed an increase on acid flux for all VFAs (Figure 20). Lowest acid flux was observed for acetic acid as 0.88 g/m<sup>2</sup>.h and highest result was observed for valeric acid as 1.91g/m<sup>2</sup>.h (Figure 20). When non-filled low molecular weight PDMS-OH and 0.1% hydrophilic nano-silica filled low molecular weight PDMS-OH membrane acid flux are compared; 0.1% hydrophilic nano-silica filled low molecular weight PDMS-OH membrane appeared to perform higher results compared to other ones. The least increase was on propionic acid flux with 3 fold and highest increase of acid flux was observed on caproic acid with an increase of 15 fold (Figure 20). Therefore, hydrophilic nano-silica filed low molecular weight PDMS-OH membranes showed dramatic flux increase when compared to non-filled low molecular PDMS-OH membranes. PDMS-OH membranes filled with 0.5%, 2.5% and 5% hydrophilic nano-silica showed lower acid fluxes compare to that of 0.1% hydrophilic nano-silica filled low molecular weight PDMS-OH membranes (Figure 20). However, when the nano-silica ratio was increased to 10% acid fluxes reach to 2.59 g/m<sup>2</sup>.h, 2.58 g/m<sup>2</sup>.h, 2.93 g/m<sup>2</sup>.h, 3.34 g/m<sup>2</sup>.h and 4.18 g/m<sup>2</sup>.h for acetic, propionic, butyric, valeric and caproic acids respectively (Figure 20). Therefore, 10% hydrophilic nano-silica filled low molecular weight PDMS-OH resulted in high acid flux increases that were ranged from 6 fold to 36 fold compared to non-filled low molecular weight PDMS-OH (Figure 20). Total VFA flux of  $0.97 \pm 0.52$  g/m<sup>2</sup>.h was obtained when non-filled low molecular weight PDMS-OH membrane was used. The total VFA flux was increased to 5.11 g/m<sup>2</sup>.h when 10% hydrophobic nano-silica filled low molecular weight PDMS-OH membrane was used. Total VFA fluxes were  $7.04 \pm 1.08$  g/m<sup>2</sup>.h and 15.63 g/m<sup>2</sup>.h for 0.1% and 10% hydrophilic nano-silica filled low molecular weight PDMS-OH membranes, respectively. In the literature higher acid fluxes can be seen; according to Sun et al. (1997), acid flux reached to 350 g/(m<sup>2</sup>.h) at 30°C for acetic acid (5% by volume) through pervaporation with Silicalite-1 membrane which was manufactured in lab with a crystallization technique of Silicalite and ZSM-5 (SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio of 300) on a porous support layer and in another study only 38 g/(m<sup>2</sup>.h) could be managed with the same conditions of Sun et al. except in that study Sano et al. used 15% acetic acid by volume (Sano et al. 1997, Sun et al. 2009). On the

other if the amount of acetic acid is considered with our study which is around 0.019% by volume, low acid fluxes is reasonable compare to literature.



**Figure 21.** Effect of silica type and ratio on separation factor values for low molecular weight PDMS-OH membranes (50% PDMS-OH/hexane, 2% catalyst, 20% cross-linker): acetic (A), propionic (B), butyric (C), valeric (D) and caproic acids (E) ( non-filled results was taken from (Taner 2016).)

Separation factor of acetic acid for hydrophilic and hydrophobic nano-silica filled low molecular weight PDMS-OH membranes were similar (Figure 21). However, hydrophobic nano-silica filled low molecular weight PDMS-OH membrane separation factor values of propionic and butyric acid were higher compare to that of hydrophilic

nano-silica filled low molecular weight PDMS-OH membranes (Figure 21). Acetic acid separation factor of 0.1% hydrophilic and hydrophobic nano-silica filled low molecular weight PDMS-OH membranes were calculated to be around  $1.3 \pm 0.1$ , however acid fluxes decreased with the increase of the nano-silica ratio (Figure 21). Nevertheless, butyric acid separation factor for 10% hydrophobic nano-silica filled low molecular weight PDMS-OH reached to 2.2 (Figure 21). Higher separation factor values were observed for valeric and caproic acids via 5% and lower ratio of hydrophilic nano-silica filled low molecular weight PDMS-OH membranes in comparison to 5% and lower ratio of hydrophobic nano-silica filled low molecular weight PDMS-OH membranes (Figure 21). However, higher separation factor values were reached via 10% hydrophobic nano-silica filled low molecular weight PDMS-OH membrane when the results were compared with hydrophilic nano-silica filled low molecular weight PDMS-OH membranes regardless of the silica ratio (Figure 21). Sano et al. (1997) reported separation factor of 2.6 for acetic acid separation factor value and Sun et al. (2009) observed only 0.75 separation factor value for acetic acid at 30°C with synthetic mixture of acetic acid (5% by volume for Sun et al., 15% for Sano et al.) via pervaporation with Silicalite-1 membrane which was manufactured through crystallization of Silicalite and ZSM-5 ( $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio of 300) on a porous support layer (Sano et al. 1997, Sun et al. 2009).

In conclusion, optimum separation factor values for hydrophilic nano-silica fillings were observed via 0.1% hydrophilic nano-silica filled low molecular weight membrane. Separation factor values were 1.4, 1.7, 2.4, 3.1 and 3.1 for acetic, propionic, butyric, valeric and caproic acids respectively via 0.1% hydrophilic nano-silica filled low molecular weight PDMS-OH membrane. When 10% hydrophobic nano-silica filled low molecular weight PDMS-OH membrane was used, 1.1, 1.4, 2.2, 3.3 and 3.4 separation factor values were observed for acetic, propionic, butyric, valeric and caproic acids, respectively.

### **3.1.2. Hydrophilic Silica Filled and non-filled high molecular weight (36000 g/mol) PDMS-OH membranes**

PDMS/Hexane ratio of 20%, 25 %, 30% and 35% were used for manufacturing non-filled high molecular weight PDMS-OH membranes. Pervaporation efficiency of the

non-filled high molecular weight PDMS-OH membranes were assayed under operational conditions of 35°C temperature, 300L/day recirculation rate and 10-16 µm pore sized glass support. Among all the tested polymer/hexane ratios, membrane manufactures using PDMS/hexane ratio of 30% was the only membrane, which was stable in 6 hours of pervaporation experiments. Other membranes were ruptured or deformed causing decreased separation efficiencies. The effect of catalyst (dibutyltin dilaurate) on pervaporation efficiency was assayed by using 0.5% and 1% catalyst/PDMS ratio for manufacturing non-filled high molecular weight PDMS-OH membranes. Cross-linker (TEOS) ratio was constant at 0.3% due to stoichiometry for non-filled high molecular weight PDMS-OH membranes.

**Table 14.** Effect of catalyst ratio on VFA flux for high molecular weight PDMS-OH membranes

Catalyst Ratio	Total VFA Flux g/(m <sup>2</sup> .h)	Water Flux g/(m <sup>2</sup> .h)	VFA Flux g/(m <sup>2</sup> .h)				
			AA	PA	BA	VA	CA
0.5	1.45	149.8	0.17	0.27	0.36	0.41	0.24
1	2.79	88.8	0.40	0.44	0.49	0.65	0.80

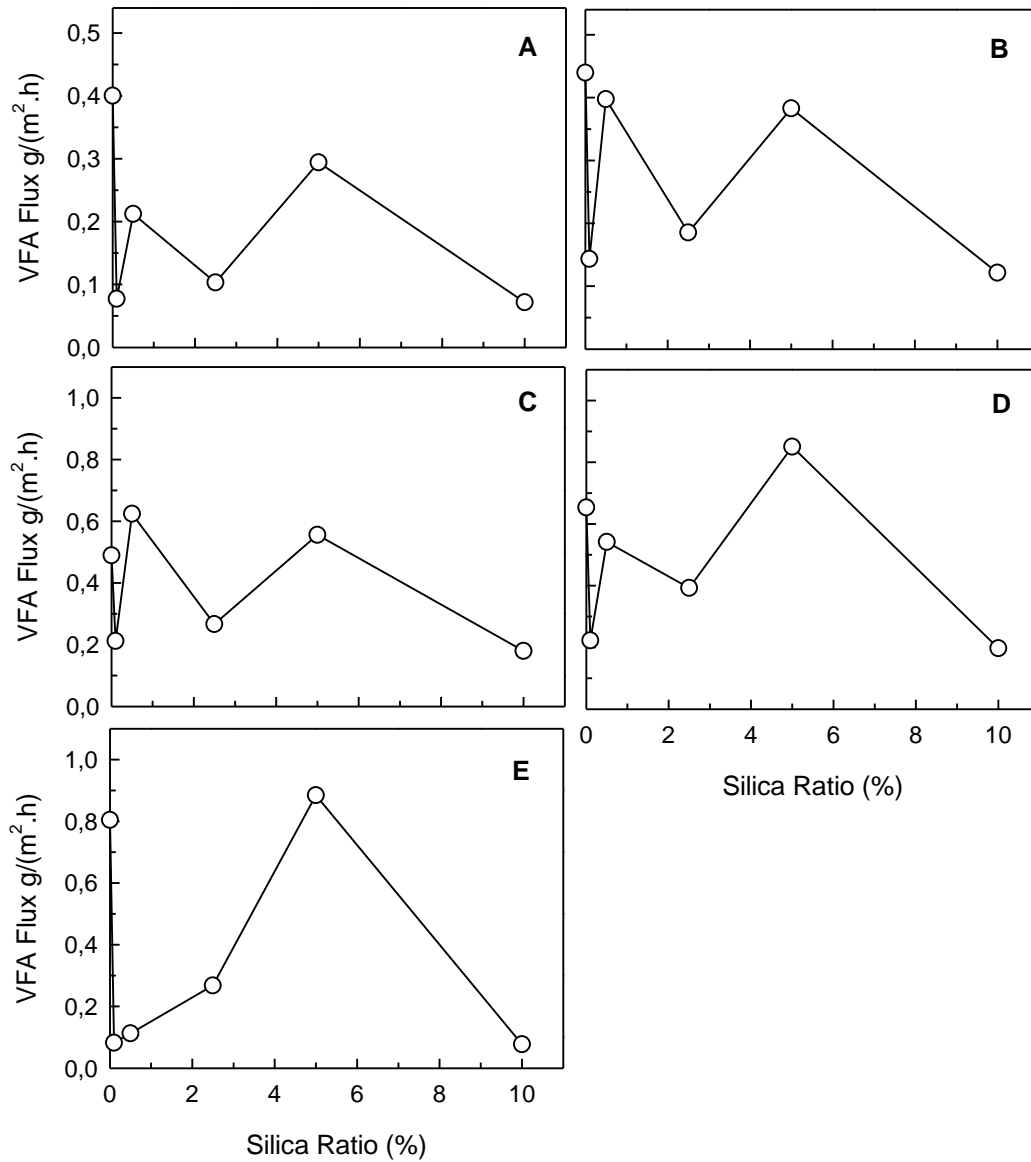
When catalyst ratio was increased from 0.5% to 1%, water flux was decreased and VFA fluxes were increased therefore, separation factors of VFAs were increased (Table 14 and Table 15). Accordingly, optimum composition of non-filled high molecular weight PDMS-OH membrane was 30% PDMS-OH, 1% catalyst and 0.3% cross-linker and same composition was used for all nano-silica filled high molecular weight PDMS-OH membranes.

**Table 15.** Effect of catalyst ratio on separation factor for high molecular weight PDMS-OH membranes

Catalyst Ratio	Separation factor ( $\alpha$ )				
	AA	PA	BA	VA	CA
0.5	1.49	2.27	3.29	3.62	2.21
1	2.03	2.32	2.75	3.57	4.54

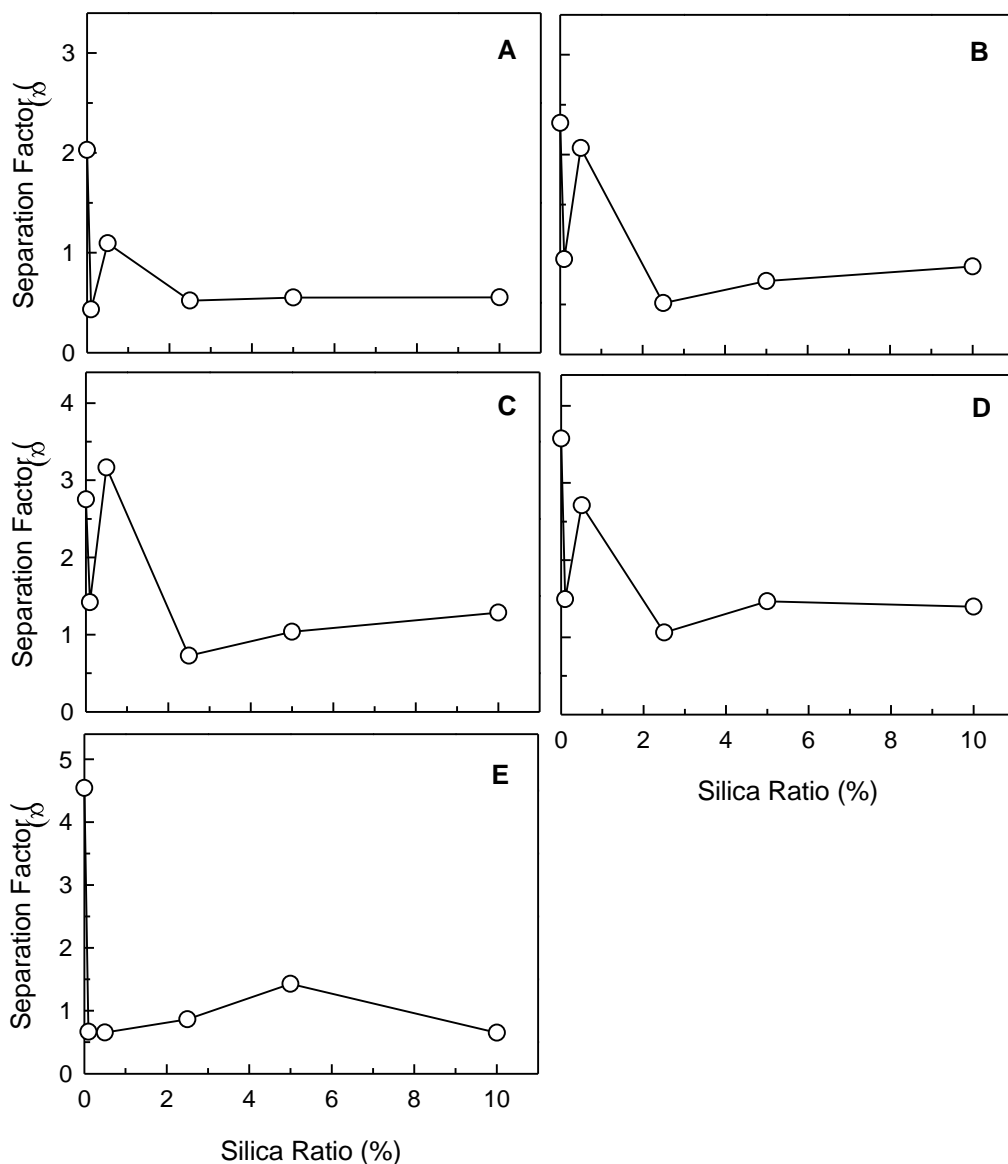
Results obtained through previous silica filled experiments revealed that hydrophilic silica filling resulted in better VFA separation efficiencies in pervaporation system

compared to that of hydrophobic nano-silica filling. Therefore, high molecular weight PDMS-OH membranes were filled only with hydrophilic nano-silica. Hydrophilic silica to PDMS ratio was changed between 0 to 10 % when hydrophilic nano-silica filled high molecular weight PDMS-OH membranes were manufactured. Hydrophilic nano-silica filling resulted in a decrease of acid flux for acetic and propionic acids and similar results were shown for butyric, valeric and caproic acids with the results are compared with hydrophilic nano-silica filled low molecular weight PDMS-OH membranes (Figure 20). Non-filled and 5% hydrophilic nano-silica filled high molecular weight PDMS-OH membranes were shown highest acid flux values compared to that of other membranes (Figure 21). Pervaporation separation efficiency of non-filled and hydrophilic nano-silica filled high molecular weight PDMS-OH membranes was lower when the results of non-filled and hydrophilic nano-silica filled low molecular weight PDMS-OH membranes were compared (Figure 20 and 22).



**Figure 22.** Effect of silica ratio on VFA flux for hydrophilic nano-silica filled high molecular weight PDMS-OH membrane (30% PDMS-OH/hexane, 1% catalyst, 0.3% cross-linker): acetic (A), propionic (B), butyric (C), valeric (D) and caproic acids (E)

Hydrophilic nano-silica filled high molecular weight PDMS-OH resulted in 0.65 to 2.97 g/m<sup>2</sup>.h acid fluxes, whereas 3.39 to 15.63 g/m<sup>2</sup>.h acid flux values were reached via hydrophilic nano-silica filled low molecular weight PDMS-OH membranes (Figure 20 and 22).

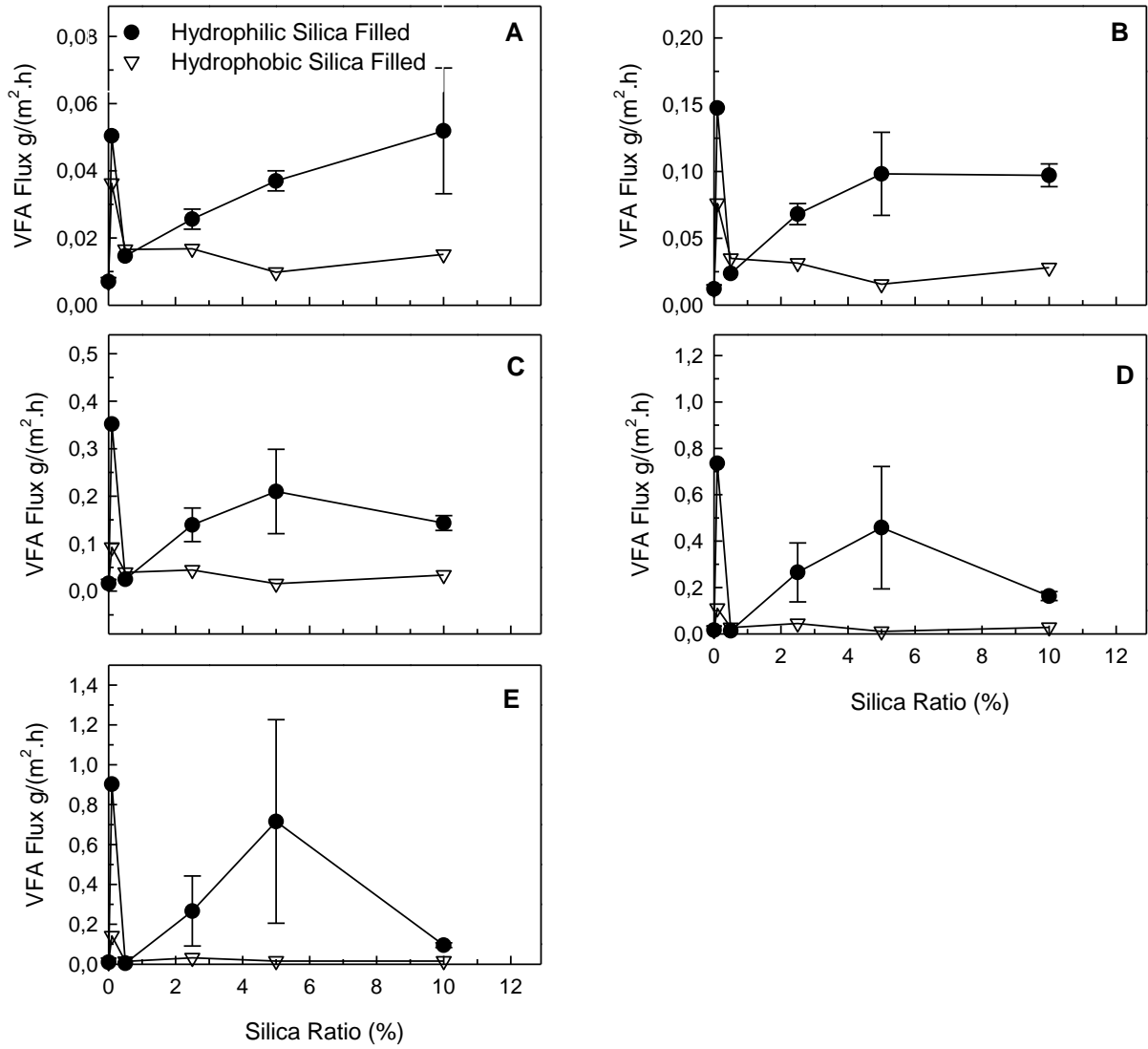


**Figure 23.** Effect of silica ratio on separation factor for hydrophilic nano-silica filled high molecular weight PDMS-OH membrane (30% PDMS-OH/hexane, 1% catalyst, 0.3% cross-linker): acetic (A), propionic (B), butyric (C), valeric (D) and caproic acids (E)

Hydrophilic nano-silica filling was generally caused a decrease in separation factor values due to increase in water flux (Figure 23). Total separation factor value of non-filled high molecular weight PDMS-OH was 3.21 (Table 21). High molecular weight PDMS-OH membrane separation factors of VFAs were lower when the results were compared with low molecular weight PDMS-OH membranes.

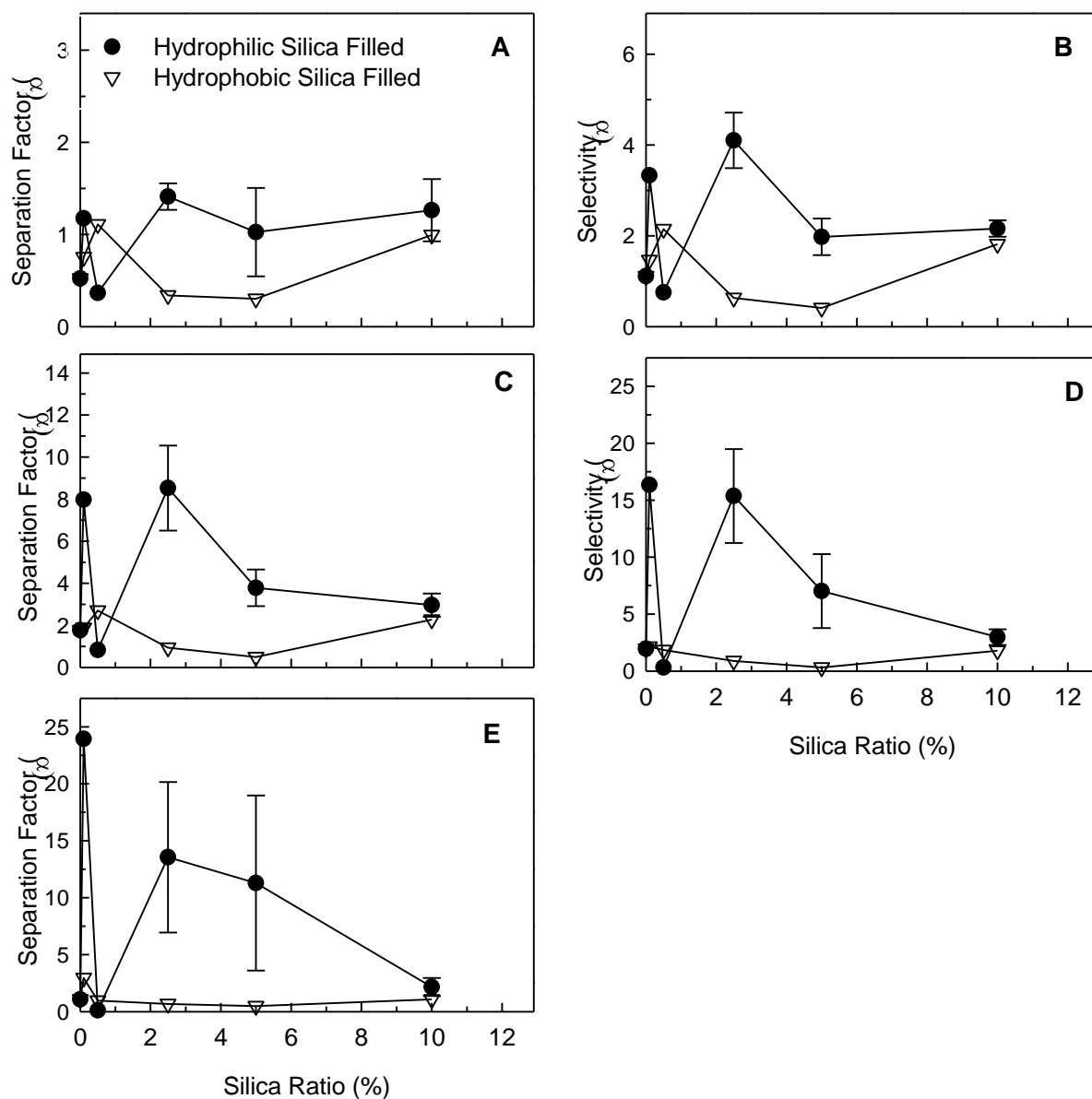
### 3.1.3. Hydrophilic and Hydrophobic Silica Filled vinyl terminated PDMS membranes (PDMS-vinyl membranes)

PDMS/hexane ratio of 20% and 4% cross linker ratios were kept constant for all manufactured silica filled PDMS-vinyl membranes. 0.1%, 0.5%, 1%, 2.5%, 5% and 10% nano-silica ratios were used for manufacturing hydrophilic and hydrophobic nano-silica filled PDMS-vinyl membranes.



**Figure 24.** Effect of silica type and ratio on VFA flux values for PDMS-vinyl membranes (20% PDMS-vinyl/hexane and 4% cross-linker): acetic (A), propionic (B), butyric (C), valeric (D) and caproic acids (E) ( non-filled results was taken from (Taner 2016).)

Highest total VFA flux ( $2.2 \text{ g/m}^2 \cdot \text{h}$ ) was reached via 0.1% hydrophilic nano-silica filled PDMS-vinyl membrane among all silica filled PDMS-vinyl membranes. Lowest acid flux was observed for acetic acid; however acid fluxes were increasing when aliphatic chains of VFAs got larger (Figure 24).



**Figure 25.** Effect of silica type and ratio on separation factor values for PDMS-vinyl membranes (20% PDMS-vinyl/hexane and 4% cross-linker): acetic (A), propionic (B), butyric (C), valeric (D) and caproic acids (E) ( non-filled results was taken from (Taner 2016).)

All hydrophobic nano-silica filled PDMS-vinyl membranes, except for 0.1% hydrophobic nano-silica filled PDMS-vinyl membrane, showed lower result when they

were compared with non-filled PDMS-vinyl membranes (Figure 25). Highest total VFA flux was  $0.46 \text{ g/m}^2\cdot\text{h}$  when 0.1% hydrophobic nano-silica filled PDMS-vinyl membrane was used compared to all hydrophobic nano-silica filled PDMS-vinyl membranes. In the literature there is a study similar to our study, in that study acetic acid was separated from a synthetic mixture (mixture composition: Ethanol, acetic acid, lactic acid, glycerol, succinic acid and acetic acid concentration was changing 2700 - 9000 mg/L) via pervaporation with PDMS membrane under  $35^\circ\text{C}$  (Yi et al. 2010). According to Yi et al. (2010), acid flux of acetic acid was  $0.5 \text{ g/(m}^2\cdot\text{h)}$  for 2700 mg/L acetic acid concentration and  $1.7 \text{ g/(m}^2\cdot\text{h)}$  for 9000 mg/L acetic acid concentration (Yi et al. 2010). If the acid results were compared with the literature, the acid flux results (Highest total VFA fluxes  $2.2 \text{ g/(m}^2\cdot\text{h)}$  and  $0.46 \text{ g/(m}^2\cdot\text{h)}$  for 0.1% hydrophilic nano-silica filled PDMS-vinyl membrane and 0.1% hydrophobic nano-silica filled PDMS-vinyl membrane respectively) are higher especially when the fact ,that literature's concentration values were higher than our study and concentration is an important parameter for separation, is considered.

In conclusion, comparison of total VFA flux efficiency for PDMS-vinyl membranes were as follows in decreasing order: 0.1% hydrophilic nano-silica filled PDMS-vinyl membrane > 0.1% hydrophobic nano-silica filled PDMS-vinyl membrane > non filled PDMS-vinyl membrane. Hydrophilic silica filling positively affected the VFA flux values 0.5% hydrophilic nano-silica filled PDMS-vinyl membrane (Figure 25). Highest separation factor results were shown for acetic, propionic and butyric acids via 2.5% hydrophilic nano-silica filled PDMS-vinyl membrane and for valeric and caproic acids via 0.1% hydrophilic nano-silica filled PDMS-vinyl membrane (Figure 25). A positive relationship was observed between longer aliphatic groups of VFAs and separation factor via hydrophilic nano-silica filled membranes therefore, caproic acid separation factor was the highest and acetic acid separation factor was the lowest among all the VFAs (Figure 25).

Highest separation factor values were observed for acetic, propionic and butyric acids via 0.5% hydrophobic nano-silica filled PDMS-vinyl membrane when the results were compared with non-filled PDMS-vinyl membrane for the effect of nano-silica ratio of hydrophobic silica filled PDMS-vinyl membranes in addition highest separation factor values for valeric and caproic acids were observed via 0.1% hydrophobic nano-silica

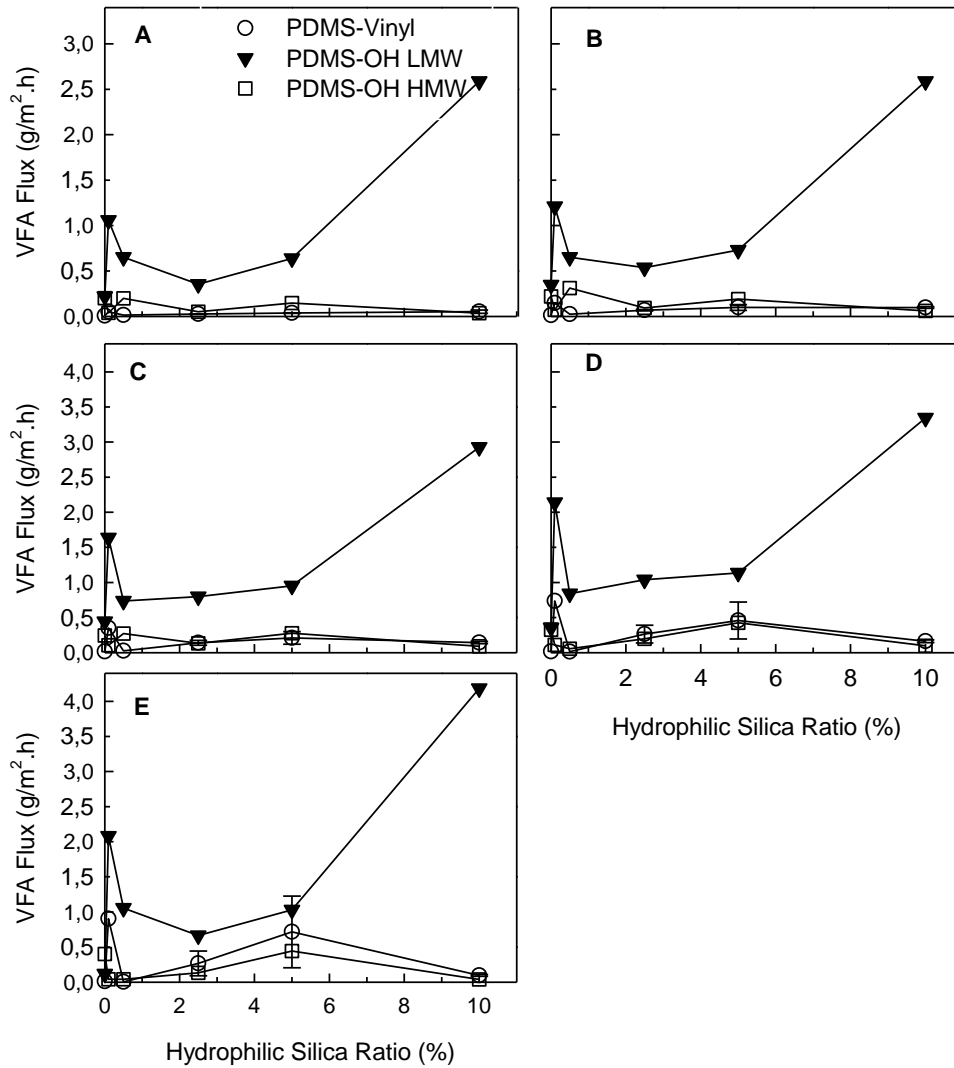
filled PDMS-vinyl membrane (Figure 25). However, 0.1% hydrophobic nano-silica filled PDMS-vinyl membrane was shown highest increase of separation factor among all hydrophobic nano-silica filled PDMS-vinyl membranes (Figure 25).

In conclusion, comparison of separation factor for nano-silica filled and non-filled PDMS-vinyl membrane for acetic, propionic and butyric acids were in decreasing order as follows: 2.5% hydrophilic nano-silica filled PDMS-vinyl membrane > 0.1% hydrophobic nano-silica filled PDMS-vinyl membrane > non-filled PDMS-vinyl membrane and for valeric and caproic acids comparison was changed as ; 0.1% hydrophilic nano-silica filled PDMS-vinyl membrane > 0.1% hydrophobic nano-silica filled PDMS-vinyl membrane > non-filled PDMS-vinyl membrane.

#### **3.1.4. Comparison of VFA separation efficiencies of composite membranes**

Efficiency assays were conducted under optimum parameters; temperature of 35°C , 300L/day recirculation rate, 3 tor of vacuum, 10-16 µm pore sized glass support and a mix VFA solution (2000mg/l of each acetic, propionic, butyric, valeric and caproic acids). The membranes which were analysed for VFA separation efficiency and the affecting parameters are listed as follows:

- Hydroxyl terminated PDMS:
  - Effect of polymer's molecular weight (550 g/mol or 36000 g/mol)
  - Effect of cross-linker ratio
  - Effect of hydrophilic nano-silica ratio
  - Effect of hydrophobic nano-silica ratio
- Vinyl terminated PDMS:
  - Effect of cross-linker ratio
  - Effect of hydrophilic nano-silica ratio
  - Effect of hydrophobic nano-silica ratio



**Figure 26.** Effect of hydrophilic nano-silica filling ratio on VFA flux for PDMS-vinyl (20% PDMS-vinyl/hexane and 4% cross-linker), low molecular weight (LMW) PDMS-OH (50% PDMS-OH/hexane, 2% catalyst, 20% cross-linker) high molecular weight (HMW) PDMS-OH membranes: acetic (A), propionic (B), butyric (C), valeric (D) and caproic acids (E) ( non-filled results was taken from (Taner 2016).)

Similar VFA flux values were observed for same nano-silica ratios of filled high molecular weight PDMS-OH membranes and filled PDMS-vinyl membranes (Figure 26).

**Table 16.** VFA separation efficiencies of membranes via pervaporation (35°C temperature, 300 L/day recirculation rate, 3 torr vacuum, 10-16 µm porous glass support) (non-filled results was taken from (Taner 2016).)

Polymer Type and Ratio	Nano Silica Type	Filling Ratio (%)	VFA Separation Factor <sup>d</sup>	Total VFA Flux (g/(m <sup>2</sup> .h))
LMW <sup>a</sup> 50	-	-	1.86 ± 0.36	0.97 ± 0.52
<b>LMW 50</b>	<b>Hydrophilic</b>	<b>0.1</b>	<b>2.13 ± 0.02</b>	<b>7.04 ± 1.08</b>
LMW 50	Hydrophilic	0.5	1.34	3.94
LMW 50	Hydrophilic	2.5	1.66	3.39
LMW 50	Hydrophilic	5	1.15	<b>4.49</b>
LMW 50	Hydrophilic	10	1.18	<b>15.63</b>
LMW 50	Hydrophobic	0.1	<b>2.33</b>	3.04
LMW 50	Hydrophobic	0.5	1.25	0.61
LMW 50	Hydrophobic	2.5	1.24	0.37
LMW 50	Hydrophobic	5	1.43	0.41
<b>LMW 50</b>	<b>Hydrophobic</b>	<b>10</b>	<b>2.48</b>	<b>5.11</b>
HMW <sup>b</sup> 30	-	-	3.21	2.79
HMW 30	Hydrophilic	0.1	1.08	0.74
HMW 30	Hydrophilic	0.5	<b>2.02</b>	1.89
HMW 30	Hydrophilic	2.5	0.75	1.22
HMW 30	Hydrophilic	5	0.93	2.97
HMW 30	Hydrophilic	10	1.01	0.65
Vinyl <sup>c</sup> 20	-	-	<b>3.21</b>	0.06
Vinyl 20	Hydrophilic	0.1	<b>11.53</b>	2.19
Vinyl 20	Hydrophilic	0.5	0.71	0.08
Vinyl 20	Hydrophilic	2.5	<b>8.19 ± 3.07</b>	0.77 ± 0.35
Vinyl 20	Hydrophilic	5	<b>2.94 ± 0.66</b>	1.52 ± 0.90
Vinyl 20	Hydrophilic	10	<b>2.85 ± 0.09</b>	0.55 ± 0.07
Vinyl 20	Hydrophobic	0.1	<b>2.27</b>	0.46
Vinyl 20	Hydrophobic	0.5	1.79	0.13
Vinyl 20	Hydrophobic	2.5	0.74	0.17
Vinyl 20	Hydrophobic	5	0.41	0.07
Vinyl 20	Hydrophobic	10	1.62	0.12

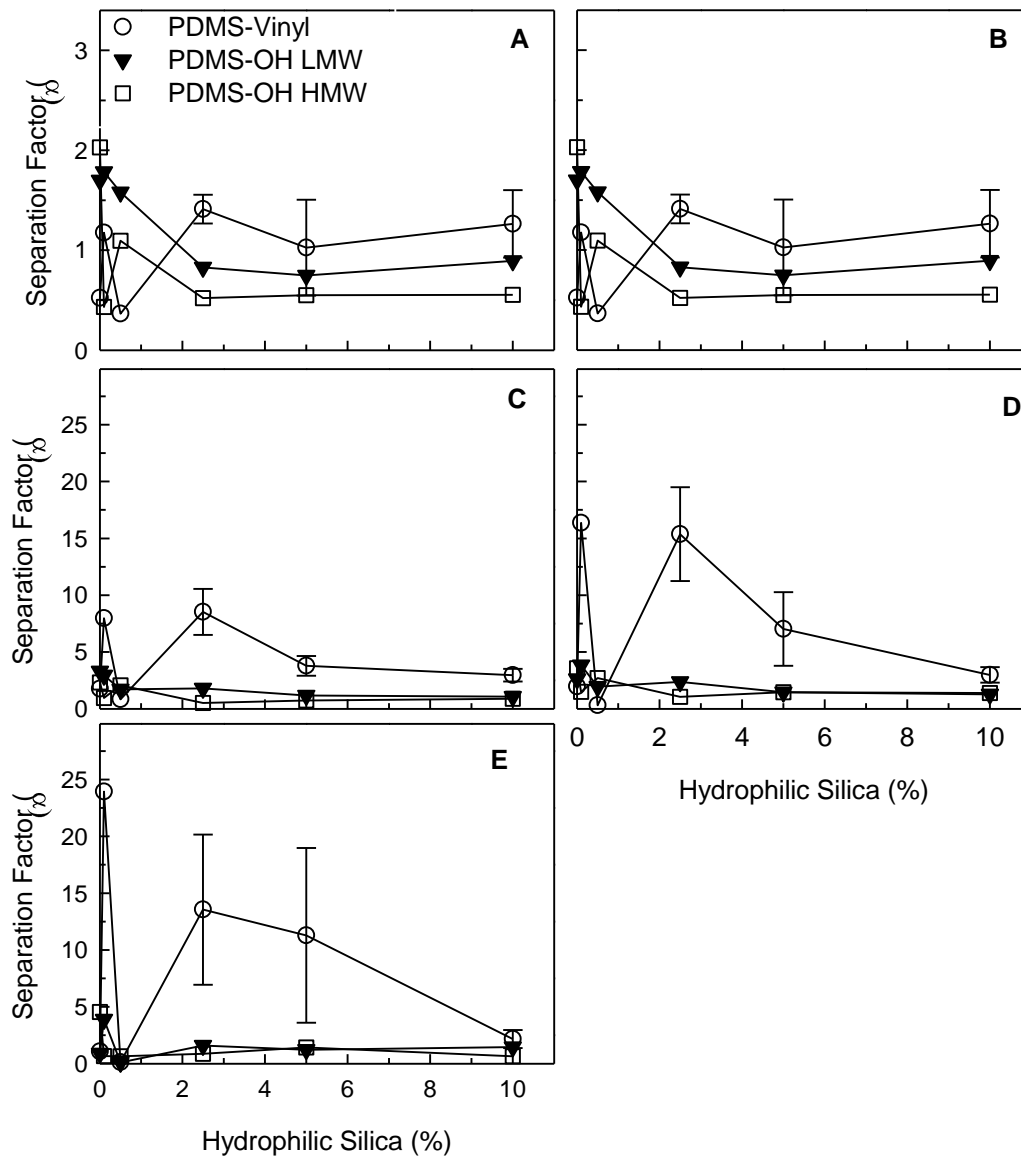
<sup>a</sup> LMW: 550 g/mol PDMS-OH membrane (low molecular weight)

<sup>b</sup> HMW: 36000 g/mol PDMS-OH membrane (high molecular weight)

<sup>c</sup> Vinyl terminated PDMS membrane

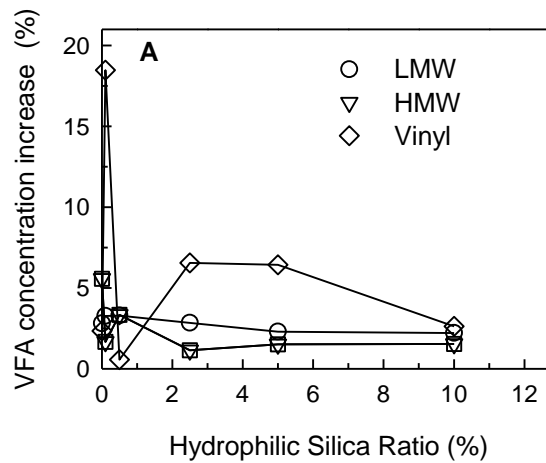
<sup>d</sup> Total separation factor values were calculated on total VFA-COD

Highest acid fluxes were observed via filled low molecular weight PDMS-OH with 0.1% and 10% hydrophilic nano-silica filled low molecular weight PDMS-OH membranes. Total VFA fluxes of 0.1% and 10% hydrophilic nano-silica filled low molecular weight PDMS-OH membranes are 7.04 and 15.63 g/m<sup>2</sup>.h respectively (Table 16).



**Figure 27.** Effect of hydrophilic nano-silica filling ratio on separation factor for PDMS-vinyl (20% PDMS-vinyl/hexane and 4% cross-linker), low molecular weight (LMW) PDMS-OH (50% PDMS-OH/hexane, 2% catalyst, 20% cross-linker) high molecular weight (HMW) PDMS-OH membranes: acetic (A), propionic (B), butyric (C), valeric (D) and caproic acids (E)

Highest total VFA-COD flux value was observed via 10% hydrophobic nano-silica filled low molecular weight PDMS-OH membrane among all hydrophobic nano-silica filled low molecular weight PDMS-OH membranes (Table 16). Total VFA-COD flux values were lower than  $0.46 \text{ g/m}^2 \cdot \text{h}$  for all hydrophobic nano-silica filled PDMS-vinyl membranes (Table 16). When the separation factor values of PDMS-vinyl membranes, low molecular weight PDMS-OH membranes and high molecular weight PDMS-OH membranes had been compared, most performing membrane was 0.1% hydrophilic nano-silica filled PDMS-vinyl by the mean of separation factor for acetic, propionic, butyric, valeric and caproic acids with the separation factor values of 1.18, 3.33, 7.97, 16.36, and 23.94 respectively (Figure 26).



**Figure 28.** Permeate VFA concentration increase values for hydrophilic silica filled PDMS-vinyl (20% PDMS-vinyl/hexane and 4% cross-linker), low molecular weight (LMW) PDMS-OH (50% PDMS-OH/hexane, 2% catalyst, 20% cross-linker) high molecular weight (HMW) PDMS-OH membranes: acetic (A), propionic (B), butyric (C), valeric (D) and caproic acids (E)

Total VFA separation factor was calculated in terms of COD as 11.53 for 0.1% hydrophilic nano-silica filled PDMS-vinyl (Table 16). Highest total separation factor value was 2.27 as COD via 0.1% hydrophobic nano-silica filled PDMS-vinyl among all the hydrophobic nano-silica filled PDMS-vinyl membranes (Table 16). VFA concentration increase was from 1% to 20% with 0.1% hydrophilic nano-silica filled PDMS-vinyl after pervaporation process (Figure 27). In non-filled low and high molecular weight membranes, maximum VFA concentration increase was 5% (Figure 28).

### 3.2. The Effect of Operational Temperature on VFA separation

Efficiency assays were conducted under optimum parameters; 35°C temperature, 300L/day recirculation rate, 3 tor of vacuum, 10-16 µm pore sized glass support and a mix VFA solution (2000mg/l of each acetic, propionic, butyric, valeric and caproic acids). In addition, some of the manufactured membranes were also tested at 45°C to determine the effect of the temperature on pervaporative separation efficiency via composite membranes. Four membrane compositions were selected as listed below:

- Low molecular weight (550 g/mole) 0.1% hydrophilic nano-silica filled PDMS-OH membrane (PDMS-OH/Hexane ratio: 50%, catalyst/PDMS-OH ratio: 2%, cross-linker/PDMS-OH ratio: 20%)
- High molecular weight (36000 g/mole) non-filled PDMS-OH membrane (PDMS-OH/Hexane ratio: 30%, catalyst/PDMS-OH ratio: 1%, cross-linker/PDMS-OH ratio: 0.3%)
- 0.1% hydrophilic nano-silica filled PDMS-vinyl membrane (PDMS-OH/Hexane ratio: 20%, cross-linker/PDMS-OH ratio: 4%)
- 2.5% hydrophilic nano-silica filled PDMS-vinyl membrane (PDMS-OH/Hexane ratio: 20%, cross-linker/PDMS-OH ratio: 4%)

VFA fluxes decreased with the increase of operational temperature from 35°C to 45°C with 0.1% hydrophilic nano-silica filled low molecular weight PDMS-OH membrane. Similarly, increase of the temperature caused a dramatic decrease in water flux. Both water and VFA flux decrease may be an indication of changes in membrane structure as a result of increase in temperature. Increase of temperature resulted in increase of propionic, butyric and valeric acids separation factor values, meaning the 0.1% hydrophilic nano-silica filled low molecular weight PDMS-OH membrane became more selective towards VFA, which is also supported by the decrease of water flux. Increase of butyric and valeric acid fluxes and decrease of acetic, propionic and caproic acid fluxes were observed with the increase of the temperature with non-filled high molecular weight PDMS-OH membrane. However single acid fluxes were below 0.9 g/m<sup>2</sup>.h and were within the statistical error ranges, therefore, a net increase or decrease may not be asserted through this result. In that case VFAs except for acetic and caproic acids were remained unaffected through temperature increase via pervaporation process

with non-filled high molecular weight PDMS-OH membrane. And in terms of separation factor propionic, butyric and valeric acid separation factor values for non-filled high molecular weight PDMS-OH membrane were increased and, acetic and caproic acid separation factor values were decreased with the increase of the temperature.

Acid fluxes of VFAs were decreased with the increase of the temperature 35°C to 45°C for 0.1% hydrophilic nano-silica filled PDMS-vinyl membrane. On the other hand, acetic, propionic and butyric acid fluxes were increased and, valeric and caproic acid fluxes were decreased due to increase of the temperature for 2.5% hydrophilic nano-silica filled PDMS-vinyl membrane. All the observed flux values smaller than 1 g/m<sup>2</sup>.h therefore, increase of the fluxes may be accepted as negligible. Membrane separation factor was generally lower for both 0.1% and 2.5% hydrophilic nano-silica filled PDMS-vinyl membranes with the increase of the temperature.

### **3.3. Membrane Characterization**

#### **3.3.1. Contact Angle**

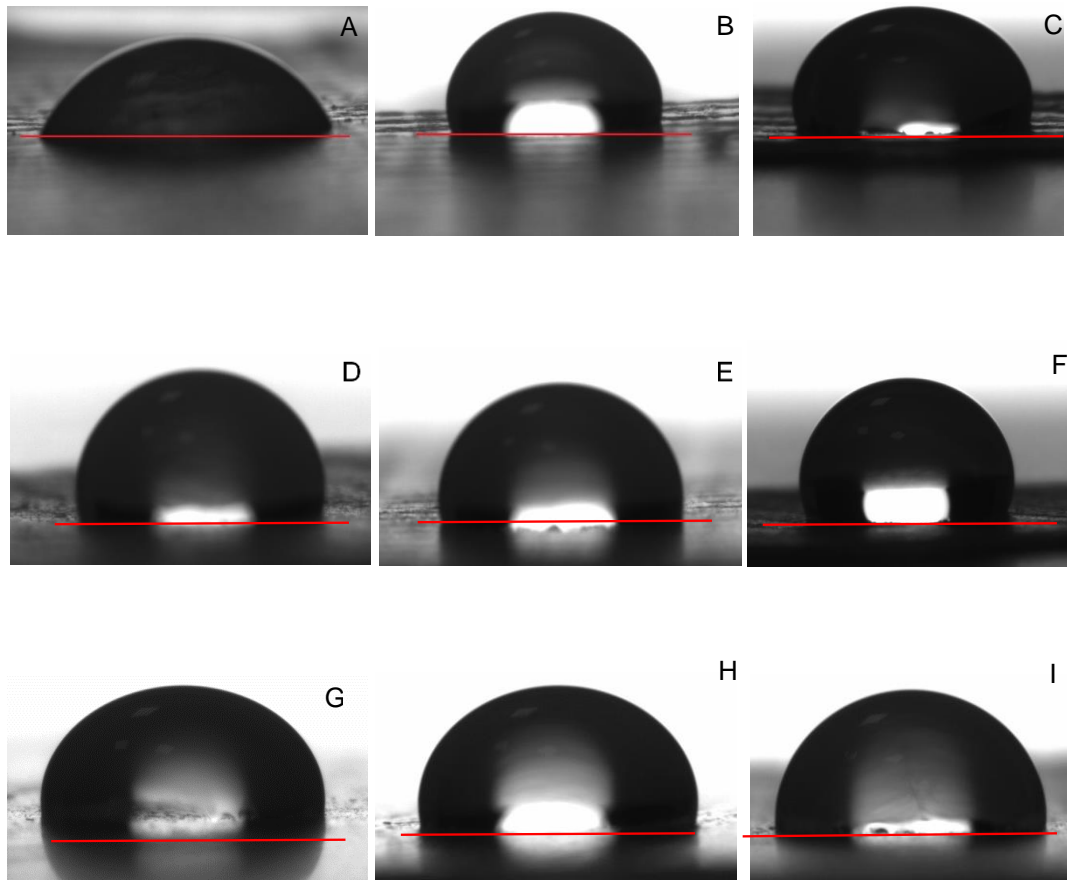
Contact angles of all the membranes that were used for pervaporation or integrated system were measured (Table 17). Samples were measured for three times each of the right and left side to ensure the repeatability of the results.

Non-filled and filled low molecular weight PDMS-OH membranes were hydrophobic because the contact angle values were greater than 90°, which is the limit value for hydrophilicity (Li et al. 2010) (Table 17). In the literature, PDMS membranes reported as hydrophobic with contact angle values ranging from 100° to 115° (Chakrabarty et al. 2010). Contact angle of non-filled high molecular weight PDMS-OH membrane was similar to low molecular weight non-filled PDMS-OH membrane and both were in the range of the literature (Figure 29C).

**Table 17.** Contact angle values of membranes were used in integrated systems

Molecular Weight (g/mol)	Membrane composition	Contact Angle (°) (Average ± Standard Error)
	PTFE	143±0.1
550 g/mol	%50 PDMS-OH (non-filled)	105 ± 1.7
	%50 PDMS-OH (0.1% hydrophilic silica)	103 ± 2.3
	%50 PDMS-OH (0.5% hydrophilic silica)	104 ± 1.3
550 g/mol	%50 PDMS-OH (2.5% hydrophilic silica)	104 ± 1.4
	%50 PDMS-OH (5.0% hydrophilic silica)	101 ± 2.2
	%50 PDMS-OH (10.0% hydrophilic silica)	103 ± 2.1
	%50 PDMS-OH (0.1% hydrophobic silica)	98 ± 0.3
	%50 PDMS-OH (0.5% hydrophobic silica)	101 ± 1.3
550 g/mol	%50 PDMS-OH (2.5% hydrophobic silica)	102 ± 3.1
	%50 PDMS-OH (5.0% hydrophobic silica)	102 ± 1.2
	%50 PDMS-OH (10.0% hydrophobic silica)	102 ± 1.7
36000 g/mol	30% PDMS-OH (non-filled)	108 ± 5.8
	30% PDMS-OH (0.1% hydrophilic silica)	115 ± 4.0
	30% PDMS-OH (0.5% hydrophilic silica)	106 ± 2.3
36000 g/mol	30% PDMS-OH (2.5% hydrophilic silica)	104 ± 8.0
	30% PDMS-OH (5.0% hydrophilic silica)	119 ± 0.8
	30% PDMS-OH (10.0% hydrophilic silica)	103 ± 1.5
>500000 g/mol	20% PDMS-vinyl (non-filled)	97 ± 2.5
	20% PDMS-vinyl (0.1% hydrophilic silica)	104 ± 1.5
	20% PDMS-vinyl (0.5% hydrophilic silica)	107 ± 5.1
>500000 g/mol	20% PDMS-vinyl (2.5% hydrophilic silica)	91 ± 1.0
	20% PDMS-vinyl (5.0% hydrophilic silica)	99 ± 0.4
	20% PDMS-vinyl (10.0% hydrophilic silica)	98 ± 4.3
	20% PDMS-vinyl (0.1% hydrophobic silica)	95 ± 3.0
	20% PDMS-vinyl (0.5% hydrophobic silica)	100 ± 3.9
>500000 g/mol	20% PDMS-vinyl (2.5% hydrophobic silica)	104 ± 1.7
	20% PDMS-vinyl (5.0% hydrophobic silica)	96 ± 0.8
	20% PDMS-vinyl (10.0% hydrophobic silica)	92 ± 0.4

Hydrophilic and hydrophobic nano-silica filling to PDMS-OH changed the contact angle between 99-106° and 98-106° degrees respectively. These values were lower than non-filled low molecular weight PDMS-OH but hydrophobicity was maintained (Table 17, Figure 29D and Figure 29E). This phenomenon may be caused by increasing surface roughness due adding silica nano particles (Nourani et al., 2014). According to Wenzel correlation increasing surface roughness may be caused lowering contact angle on hydrophobic surfaces on the other hand on hydrophilic surfaces surface roughness may be caused to increase contact angle (Nourani et al., 2014).



**Figure 29.** Contact angle images of composite membranes: PTFE-TDA (A), non-filled LMW PDMS-OH (B), non-filled HMW PDMS-OH (C), 5% hydrophilic nano-silica filled LMW PDMS-OH (D), 5% hydrophobic nano-silica filled LMW PDMS-OH (E), 5% hydrophilic nano-silica filled HMW PDMS-OH (F), non-filled PDMS-vinyl (G), 5% hydrophilic nano-silica filled PDMS-vinyl (H) and 5% hydrophobic nano-silica filled PDMS-vinyl (I)

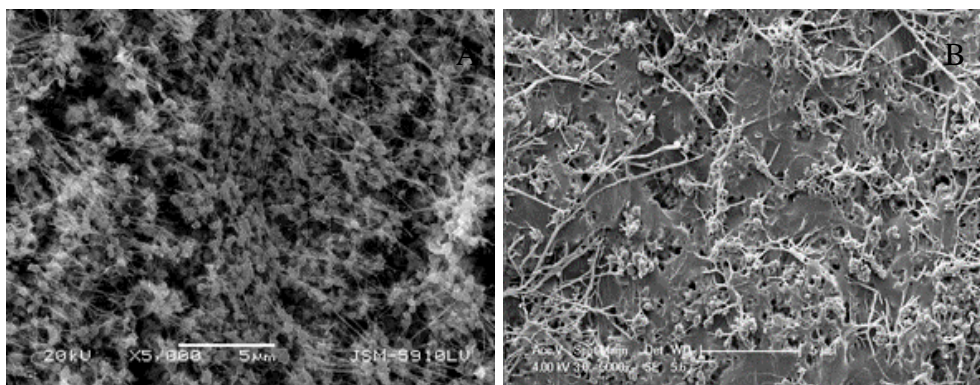
Addition of the hydrophilic nano-silica to high molecular weight PDMS-OH membranes resulted in increase of contact angle values, especially for 0.1% and 5% hydrophilic silica ratios, for these membranes contact angle values were increased to 115° and 119° respectively (Table 17, Figure 29F). The change of contact angle for other hydrophilic silica ratios was negligible (Table 17).

On the previous study contact angle value of non-filled PDMS-vinyl was changed in the range of 94-99° and membrane was maintain its hydrophobic character (Table 17, Figure 29G, (Taner 2016)). Contact angle values of hydrophilic and hydrophobic nano-silica filled PDMS-vinyl membranes were 90-112° and 92-106° and these values are higher than non-filled PDMS-vinyl membrane (Table 17, Figure 29H and Figure 29I).

The correlation between non-filled PDMS-vinyl and silica filled PDMS-vinyl membranes seemed to be the opposite of the correlation between non-filled low molecular weight PDMS-OH and silica filled low molecular weight PDMS-OH membranes. The reason of this situation is based on again Wenzel correlation that was explained as on hydrophilic surfaces increasing surface roughness is caused increasing contact angle (Nourani et al., 2014).

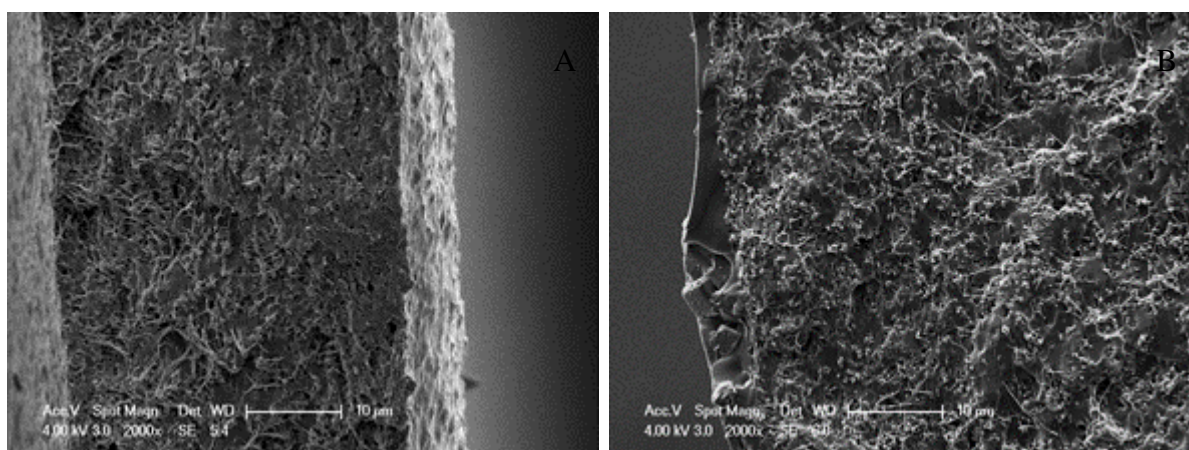
### **3.3.2. Scanning Electron Microscope**

Both surface and cross section of some manufactured membranes was observed via scanning electron microscope (SEM) images for understanding surface morphology and nano-silica dispersal. Hydrophilic nano particles (bright and white spheres) and polymeric solution were observed as filled into PTFE support layer in the SEM images of 0.1% hydrophilic nano-silica filled low molecular weight PDMS-OH membrane (Figure 30). Also a tiny amount of polymeric solution was got over the pores of PTFE support and was remained on the surface of composite membrane (Figure 30B). Hydrophilic nano particles were shown a homogenous dispersion in the polymeric solution of 10% hydrophilic nano-silica filled PDMS-OH membrane (Figure 32).



**Figure 30.** Cross section SEM images of PTFE (5000x) (A) and non-filled LMW PDMS-OH membranes

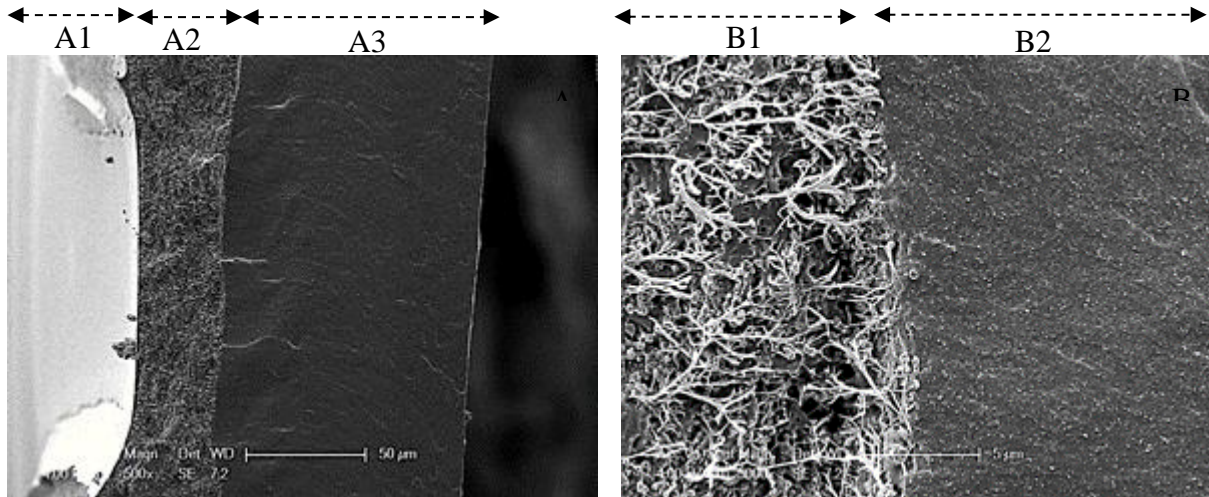
However, it was observed that the polymeric solution was filled only a small amount into PTFE support pores when the SEM images were compared with only PTFE support SEM images (Figure 29A and 31, (Taner 2016)). This case may be caused by a possible resistance on the PTFE support and was led to a thick layer of remaining polymeric solution of the PTFE support. surface area of particles was also increased by the increase of nano particles, and that may be led to accelerate of hexane vaporization was deliberated when 0.1% and 10% hydrophilic silica filled low molecular weight PDMS-OH membranes were compared (Figure 30B and 31).



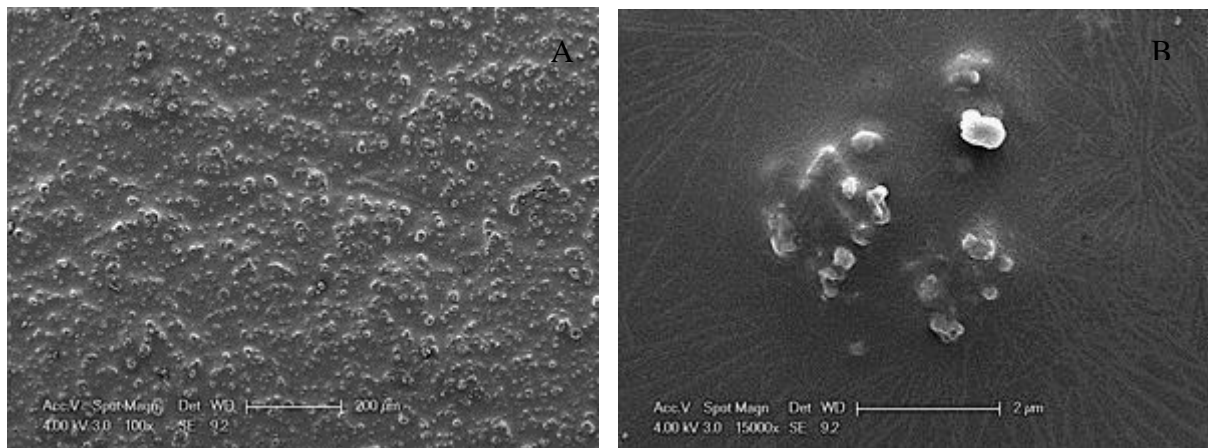
**Figure 31.** Cross section SEM images of non-filled LMW PDMS-OH membrane (2000x) (A) and 0.1% hydrophilic nano-silica filled membrane (2000x) (B)

Hexane expanded as it vaporized, which may have obstructed filling of the polymeric solution into the PTFE support and may have caused the formation thick polymeric layer on the surface of the PTFE support. The hydrophilic nano-silica particles were

dispersed homogeneously on the surface of the composite membrane as the surface SEM image of 0.1% hydrophilic silica filled low molecular weight PDMS-OH membrane was shown (Figure 32). Dispersed nano-silica particles resulted in the formation of a rough surface (Figure 32).



**Figure 32.** Cross section SEM images: 10% hydrophilic nano-silica filled LMW PDMS-OH (500x) (A) and 10% hydrophilic nano-silica filled LMW PDMS-OH (5000x) (B) (A1: Polyethylene support fabric, A2 and B1: PTFE support membrane and, A3 and B2: 10% hydrophilic nano-silica filled LMW PDMS-OH polymeric solution)

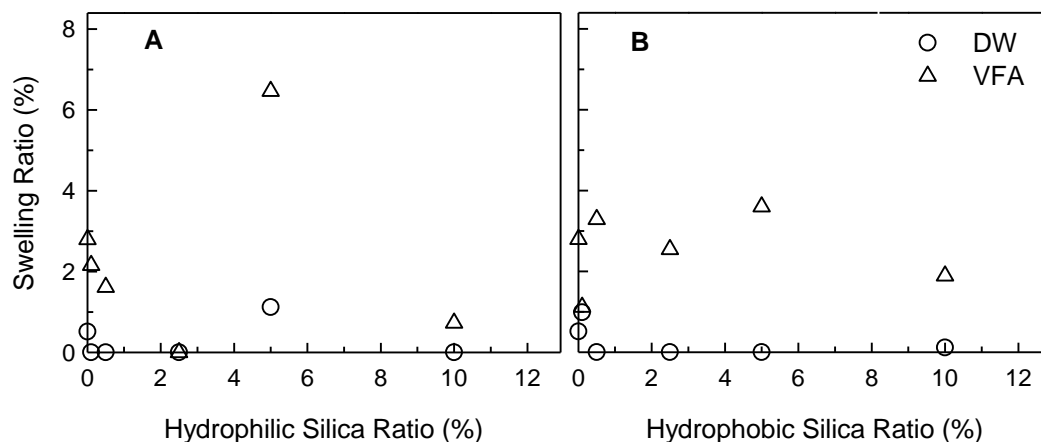


**Figure 33.** Surface SEM images: 0.1% hydrophilic nano-silica filled LMW PDMS-OH membrane: 100x (A) and 15000x (B)

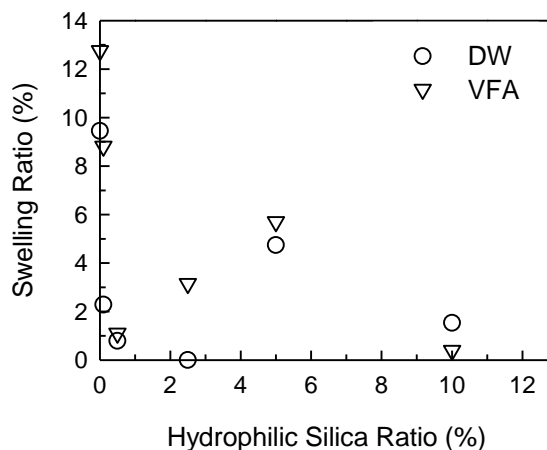
Surface SEM images were supporting the surface roughness and the hydrophobicity correlation was mentioned before as Wenzel correlation.

### 3.3.3. Swelling/Sorption Tests

Swelling tests were done to understand the behaviour of the VFA mixture and the composite membranes. The swelling behaviours of PDMS-OH and PDMS-vinyl membranes were observed at 35°C in both deionized water and standard VFA mixture that was used for generally for the VFA separation assays.



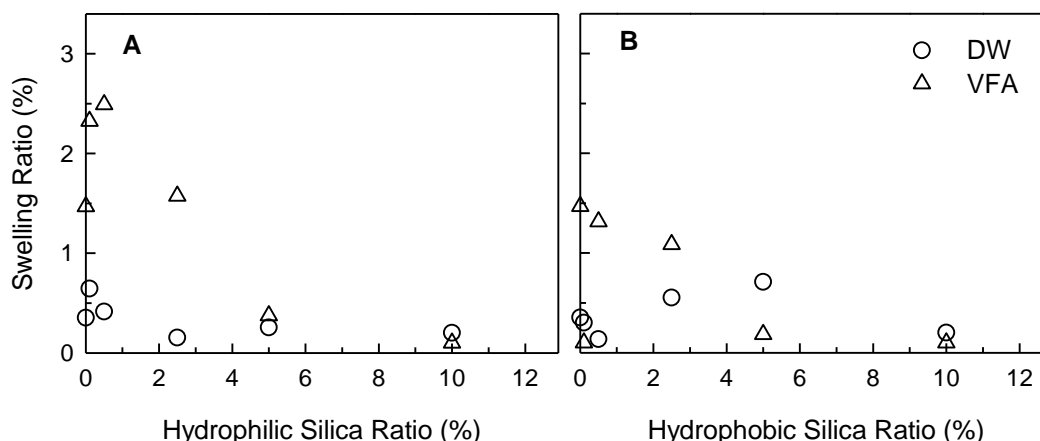
**Figure 34.** Swelling ratios of low molecular weight PDMS-OH: hydrophilic silica (A) and hydrophobic silica (B)



**Figure 35.** Swelling degrees of hydrophilic nano-silica filled high molecular weight PDMS-OH membranes

Both hydrophilic and hydrophobic nano-silica filled low molecular weight membranes were drawn less water and more VFA regardless of the silica type (Figure 34A and 34B). This shows VFA attraction to membranes was greater than water attraction to membranes. The attraction of VFAs to hydrophilic nano-silica filled low molecular weight PDMS-OH membranes were less than non-filled low molecular weight PDMS-OH membranes (Figure 34A). However hydrophobic nano-silica filling did not cause a perceivable change in attraction of VFAs to membrane (Figure 34B).

All the hydrophilic nano-silica filled high molecular weight PDMS-OH membranes were measured heavier after VFA solution phase and deionized water phase except 10% hydrophilic nano-silica filled high molecular weight PDMS-OH membrane (Figure 34). This shows that VFAs were more attracted to manufactured high molecular weight PDMS-OH membranes than water.



**Figure 36.** Swelling degrees of PDMS-vinyl membranes: hydrophilic silica (A) and hydrophobic silica (B)

Most of the PDMS-vinyl membranes were attracted by VFAs rather than water however, some of the membranes were attracted by water when the behavior of hydrophilic and hydrophobic nano-silica filled PDMS-vinyl membranes were compared in deionized water and VFA solution (Figure 36A and 36B). No significant effect on water attraction to membranes was observed with the addition of hydrophilic or hydrophobic nano-silica particles (Figure 36A and 36B). VFA attraction to filled PDMS-vinyl membranes decreased with the increase of the silica ratio regardless of the silica type (Figure 36A and 36B). However, VFA attraction to membranes was higher

with hydrophilic nano-silica filled PDMS-vinyl membranes than hydrophobic nano-silica filled PDMS-vinyl membranes (Figure 36A and 36B).

In conclusion, non-filled high molecular weight PDMS-OH membrane gained more mass with in both deionized water and VFA mixture than non-filled PDMS-vinyl and low molecular weight PDMS-OH membranes (Figure 33A, 34 and 35A). Similarly, water and VFA attraction to hydrophilic nano-silica filled low molecular weight PDMS-OH membrane was more than non-filled PDMS-vinyl and low molecular weight PDMS-OH membranes (Figure 33A, 34 and 35A).

### 3.4. Integrated Fermentation VFA Separation System

#### 3.4.1. Characterization of Organic Solid Waste

Carbon ratio, nitrogen ratio, phosphate ratios, total solid matter and water mass of organic solid waste were determined before the start-up of leach bed reactor. Characteristics of organic solid waste were shown at Table 18. Starting COD: N: P ratio of organic solid waste was proper values for anaerobic fermentation system (Table 18).

**Table 18. Starting and ending organic waste characterization**

Parameters	Starting <sup>a</sup>	Ending <sup>b</sup>	
	Control & Test LBR	Control LBR	Test LBR
Water content (%)	67.2 ± 0.4	59.4 ± 2.5	64.5 ± 4.4
Total solid compound (%)	32.8 ± 0.4	40.6 ± 2.5	35.5 ± 4.4
Volatile solid compound (%) (w/w of dry total solid compound)	69.6 ± 0.9	70.4 ± 3.3	63.1 ± 0.8
Total COD (g O <sub>2</sub> /kg dry solid weight)	490.4 ± 70.0	117 ± 18.0	133 ± 12.0
Total nitrogen (g N/kg dry solid weight)	9.6 ± 0.4	1.2 ± 0.1	1.4 ± 0.2
Total phosphorus (g P/kg dry solid weight)	3.9 ± 0.6	NE <sup>c</sup>	NE
COD/N	51/1	98/1	95/1
COD/N/P	~500/9/4 ~125/2.5/1	-	-

<sup>a</sup> Triple repetition for total solid compound and water content and 5 repetitions for total COD and nitrogen

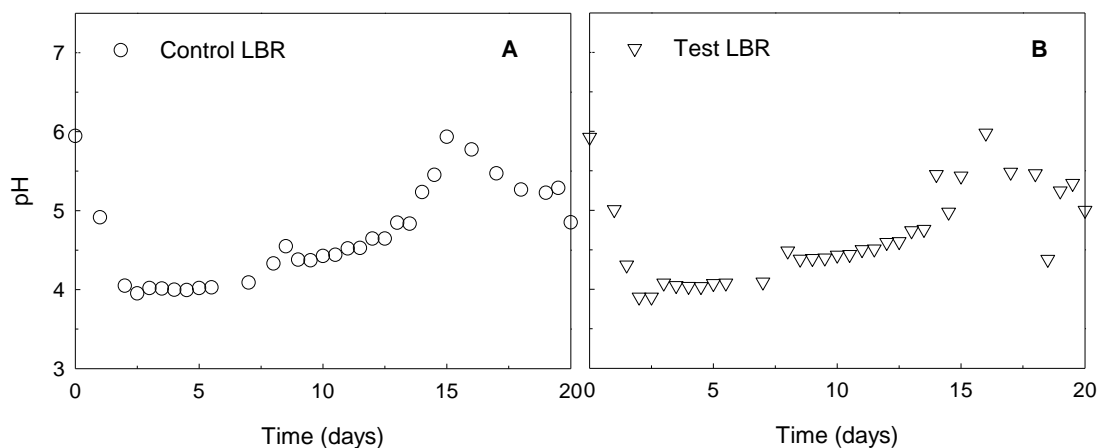
<sup>b</sup> 4 repetition for total solid compound and water content; 5 repetitions for total COD and nitrogen

<sup>c</sup> NE: Nonexistence

Ending COD: N: P ratio of both control and test reactors' organic solid waste were given separately (Table 18). COD values of solid organic waste decreased at the end of the anaerobic fermentation process for both control and test reactors (Table 18). Decreasing total COD values were indicated hydrolyzed/dissolved organic matters and VFAs that were produced via fermentation were passed to leachate. At the same time total nitrogen values in solid wastes were decreased in both control and test reactors by hydrolyzing of organic nitrogen and increasing ammonia values in leachate (Table 18).

### 3.4.2. Integration of Pervaporation system to Leach Bed Anaerobic Reactors

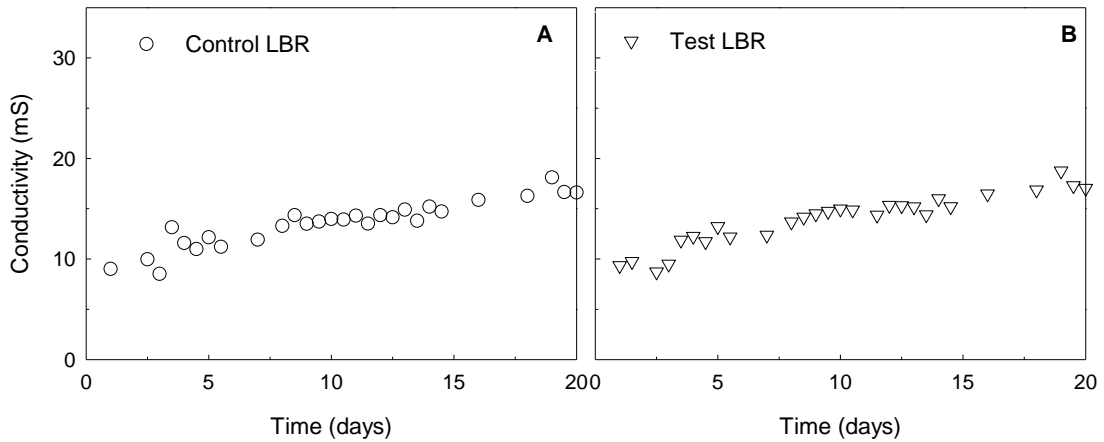
Pervaporation system was integrated to leach bed reactor (LBR) for the separation of VFAs that were produced from organic solid waste by anaerobic fermentation. The pervaporation system integrated LBR was named as "Test LBR" and the LBR system that had no separation system were named as "Control LBR". Integrated LBR-pervaporation system was operated at 35°C, 10L/day recirculation rate for fermentation process and 35°C, 10L/day recirculation rate and 0.1% hydrophilic nano-silica filled low molecular weight PDMS-OH membrane was used for pervaporation process. 0.1% hydrophilic nano-silica filled low molecular weight PDMS-OH membrane was selected to be used in integrated LBR-PV system because this composition was optimum for VFA separation in previous assays.



**Figure 37.** pH values of Control (A) and Test (B) LBRs for 19 days.

At this point explaining "the optimum membrane" is necessary; in theory acid flux of the membrane should be high enough to maintain VFA separation for avoiding VFA's

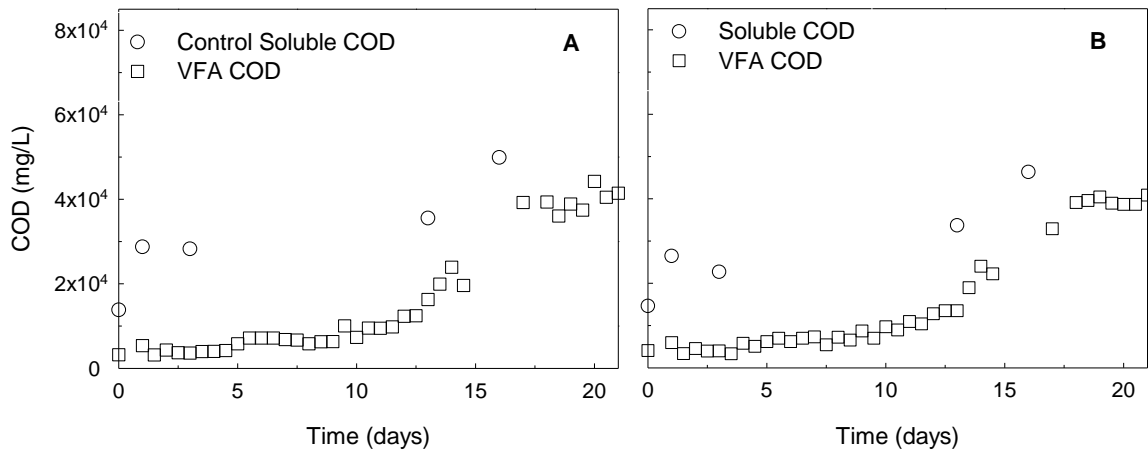
inhibitory effects on anaerobic system and separation factor should be also high enough to maintain water level and separate/purify VFAs efficiently.



**Figure 38.** Conductivity values of Control (A) and Test (B) LBRs for 19 days.

However, increasing separation factor may cause decreasing in flux or vice versa. Therefore, an optimum membrane should maintain enough acid flux and separation factor to be used in an efficient LBR-PV system. Integrated LBR-pervaporation system was started with addition of tap water and the VFA separation efficiency was observed for 19 days. Leachate pH values of first samples that were taken from control and test reactors after addition of tap water on the organic solid waste were measured as 5.9 for both the control and test reactors. (Figure 38). Both pH values of reactors were measured around of 5 at the end of the first day due to production of acids (Figure 38A). Pervaporation is a separation system that is based on gaseous or vapour form of matters following adsorption/diffusion/desorption steps through non-porous membranes. Therefore, free VFA percent of leachate of test reactor would directly affect the VFA separation efficiency of the pervaporation system. Free form of VFAs in the leachate are related with pH values (Yesil et al. 2014). Percentage of non-ionized VFAs is 85% and 36% for the leachate pH values of 4 and 5 respectively.

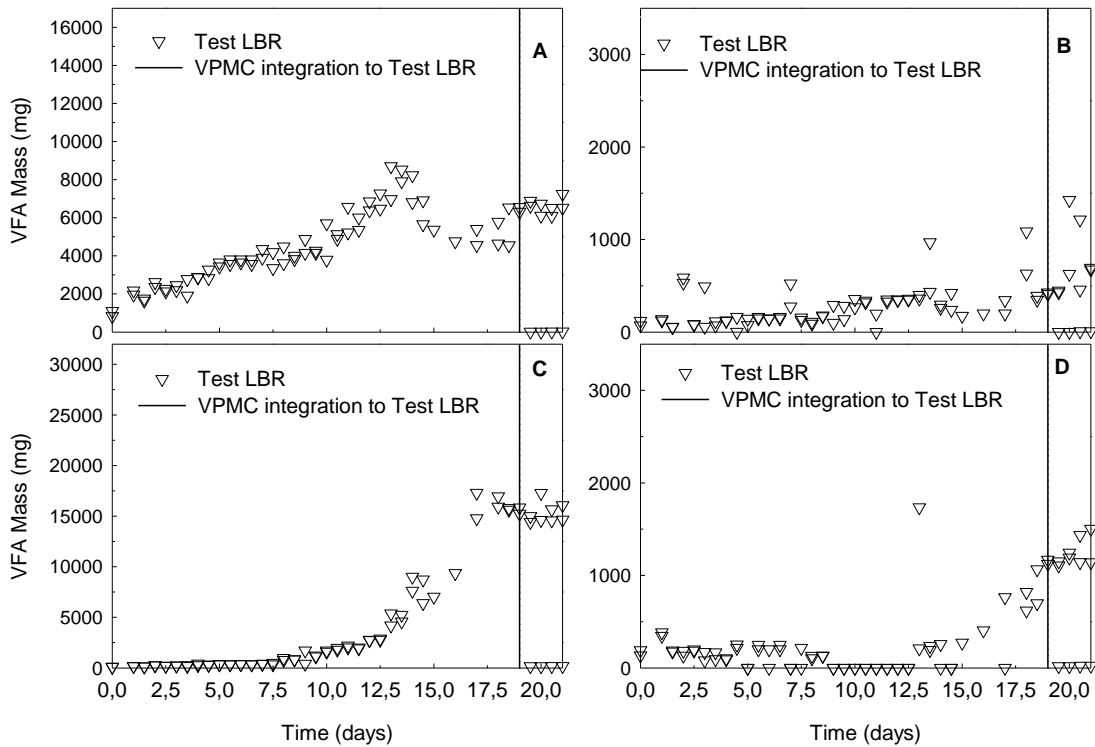
Leachate pH value must be around 4 for an efficient pervaporation separation process. Therefore, leachate pH values of control and test reactors were decreased below 4.0 respectively by pH adjustment with acid at the initiation of the experiment (Figure 38A). No significant COD concentration changes were observed between control and test reactors for 19 days of integrated LBR-pervaporation system (Figure 39A and 39B).



**Figure 39.** VFA and Soluble COD values of Control (A) and Test (B) LBRs for first 19 days.

Soluble COD values of control and test reactors were 14604 mg/L and 13819 mg/L as initial values but COD equivalent of measured VFAs was 3264 mg/L and 2574 mg/L, respectively (Figure 39A and 39B). The differences between soluble COD and VFA-COD were indicated the presence of another soluble organic matter in leachate. High levels of lactic acid concentration were observed in first 10 days and the main source of soluble COD rather than VFA was proven to be lactic acid. The lactic acid concentrations were increased in control and test reactors for 10 days then it gradually decreased until completely depleted on 17<sup>th</sup> day. In the literature, production of lactic acid in first days of fermentation (2 to 10 days) was also reported (Komemoto et al. 2009, Yesil et al. 2014). However lactic acid depletion was taken for long time compare to literature with 17 days. The reason of these phenomena was thought as by adjusting pH values to 4 and both of the reactors were operated at 4 pH for 10 days. Alkalinity was added at NaHCO<sub>3</sub> form in both leachates of control and test reactors to make VFA production more dominant than lactic acid. Chemical adjustment of pH was not done until 16<sup>th</sup> day. At the 16<sup>th</sup> day of integrated system operation leachate pH values of control and test reactors were 5.8 and 5.9 respectively (Figure 39A). After pH values were increased, VFA-COD concentrations began to increase and a fast decrease was observed at lactic acid concentrations (Figure 39A and 39B).

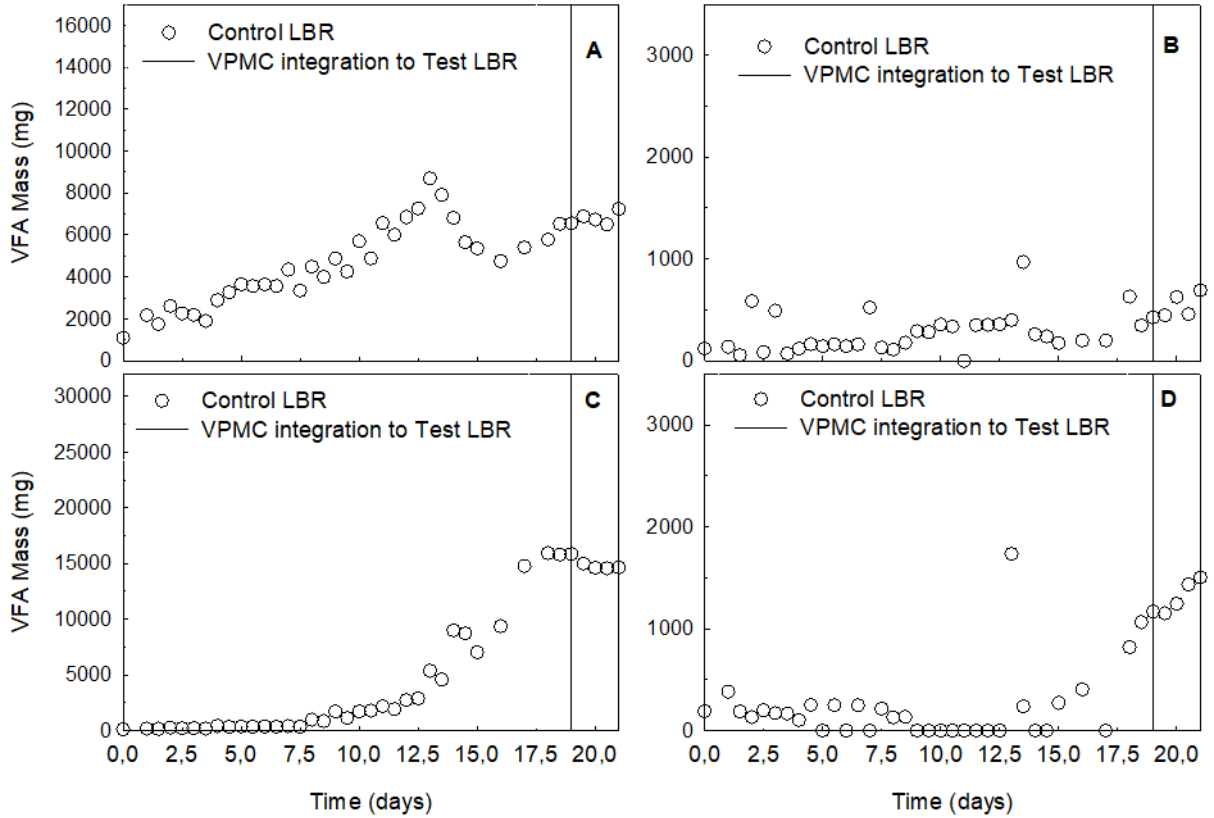
Soluble COD concentrations of control and test reactor were 46325 mg/L and 49885 mg/L and VFA-COD concentrations of control and test reactors were 25319 mg/L (55% of Soluble COD) and 30790 mg/L (62% of Soluble COD) respectively at the 17<sup>th</sup> day of the operation of integrated system (Figure 37A and 37B). However high pH values would result in the formation of ionized VFAs, which would negatively affect the VFA separation efficiency of the pervaporation system so leachate pH values of control and test reactor were decreased to 5.4 pH adjustment were continued until the end of 19<sup>th</sup> day (Figure 34A). Acetic, propionic, butyric and caproic acid were produced as VFAs in control and test reactor and valeric acid production was not observed all 19 day of integrated LBR-pervaporation system operation time (Figure 40).



**Figure 40.** VFA production in test LBR via integrated LBR-PV system: acetic acid (A), propionic acid (B), butyric acid (C) and caproic acid (D).

Acetic and caproic acids were produced in both control and test reactors in first 7 day of integrated system after 7th day butyric acid production began (Figure 40). Butyric acid production by butyric acid transformation from caproic acid was reported by Pind et al. (2003). Butyric acid could be produced dominantly at the pH range of 5-7 according to literature (Horiuchi et al. 2002). The reason of butyric acid deficiency at first 7 days of

operation may be operating the system at 4 pH and lack of caproic acid – butyric acid transformation at this pH (Figure 38A and 38C). Additionally, caproic acid that could not be transformed into butyric acid, accumulation was observed in the leachate at first 7 days (Figure 40D).



**Figure 41.** VFA production in control LBR via integrated LBR-PV system: acetic acid (A), propionic acid (B), butyric acid (C) and caproic acid (D).

VFA masses of control and test reactors in each 1.5L leachate for were; acetic acid 3347-4184 mg, propionic acid 129-156 mg, butyric acid 332-493 mg and caproic acid 200-215 mg respectively at 7<sup>th</sup> day (Figure 41). Leachate pH values decreased with the production of acetic, propionic and butyric acids until 13<sup>th</sup> day and caproic acid was completely depleted in both reactors (Figure 41). Butyric acid mass was constant and acetic, propionic acid masses were significantly decreased between 13<sup>th</sup> and 16<sup>th</sup> days (Figure 41A, 41B and 41C). Only caproic acid mass continued to increase after 16<sup>th</sup> day (Figure 41D). The gas samples from control and test reactors were measured and H<sub>2</sub> 14-24%, CO<sub>2</sub> 60-61% and N<sub>2</sub> 15-26% were calculated respectively at 13<sup>th</sup> day. At 16<sup>th</sup> day gas percentages were measured as; H<sub>2</sub> 32%, CO<sub>2</sub> 57% and N<sub>2</sub> %1. Accumulation of

hydrogen gas may be caused inhibition of fermentation and affected VFA production negatively. Therefore, both reactors were washed with nitrogen gas and gas percentages were measured again at 17<sup>th</sup> day.

The results of control and test reactor were; 2-4% (H<sub>2</sub>), 6-10% (CO<sub>2</sub>) and 86-91% (N<sub>2</sub>). Butyric acid mass was dramatically increased and caproic acid mass was increased between 16<sup>th</sup> and 19<sup>th</sup> after control and test reactors were washed with nitrogen gas (Figure 41C and 41D). However, in the same time acetic acid mass in control reactors was increase but acetic acid mass was constant in test reactor (Figure 41A). COD-VFA equivalents of leachate in control and test reactors were 29957 mg/L (37594 mg COD-VFA) and 31121 mg/L (37509 mg COD-VFA) at 19<sup>th</sup> day of integrated LBR-pervaporation system operation (Figure 40). Highest mass in control and test reactors was measured as butyric acid with 27239-27686 mg COD-VFA respectively, lowest mass was observed as propionic acid with 619-674 mg COD-VFA (1.6%- 1.8%) (Figure 39).

**Table 19. Last day measurements for LBR-PV**

Parameter	Control LBR	Test LBR
pH	5.3	5.3
Conductivity (mS/cm)	16.7	17.3
Soluble (mg COD/L) <sup>a</sup>	46325	49885
Total VFA-COD Percentage (%) <sup>b</sup>	64.7	62.4
Total VFA-COD (mg VFA-COD)	37794	37509
NH <sub>3</sub> -N (mg/L)	422	360
VFA (mg/L)		
Acetic acid	5294	5041
Propionic acid	342	327
Butyric acid	11525	12183
Caproic acid	885	899
VFA (mg)		
Acetic acid	6882 (7343) <sup>c</sup>	6302 (6724) <sup>c</sup>
Propionic acid	445 (674) <sup>c</sup>	409 (619) <sup>c</sup>
Butyric acid	14983 (27239) <sup>c</sup>	15229 (27686) <sup>c</sup>
Caproic acid	1150 (2538) <sup>c</sup>	1124 (2480) <sup>c</sup>

<sup>a</sup> There were no measurement for 19<sup>th</sup> day for soluble COD and 16<sup>th</sup> day measurement was given at table

<sup>b</sup> Total VFA-COD percent = (total VFA-COD/soluble VFA-COD)\*100

<sup>c</sup> VFA mass values were given as mg-COD equivalence in parenthesis.

In conclusion, VFA production in control and test reactors were similar during the 19 days of operation of both reactors (Figure 39). VFA-COD values in control and test LBRs were 37794 mg VFA-COD and 36341 mg VFA-COD respectively via integrated system at 19<sup>th</sup> day (Figure 39). Additionally, at the end of the 19<sup>th</sup> day pH values of leachates were around 5.3 for both reactors and conductivity values were reached maximum value (around 17 ms/cm) (Figure 36A, 36B and Table 19).

**Table 20. COD mass relations for LBR-PV**

Parameter	Initial	Day 19
Total COD (g O <sub>2</sub> / kg dry waste)	490.4 ± 70.0	-
Total COD (g for dry waste)	980 ± 140.0	-
Soluble (g COD)	13.819	49.885
Total VFA-COD (g COD)	2.789	37.550
Separated VFA-COD (g COD)	0	0.028
Produced VFA-COD per g of Total COD %	0.2%	3.83%
Separated VFA-COD (g COD) per g Total VFA-COD %	0%	0.07%

At day 19 total COD could not be measured because of the anaerobic condition concerns. But table 17 shows that most of the produced soluble COD transformed into VFAs. And 3.83% of the total COD was converted into VFA-COD. However only 0.07% percent of the VFA-COD could separate via PV system (Table 20).

Ammonia concentration of 19<sup>th</sup> day in both control and test reactors were 422 mg NH<sub>3</sub>-N/L and 360 mg NH<sub>3</sub>-N/L which were far less than inhibition level (Table 19). And only 28 mg VFA-COD was separated from system via integrated LBR-pervaporation system for 19 operation days (Figure 40). This amount was only 1.6% of predicted VFA-COD which was calculated from synthetic studies before. The reasons of under achievement of VFA separation via integrated LBR-pervaporation system can be listed as below:

- (1) leachate pH (4-6) of integrated system was above of synthetic VFA mixture's pH (2-3),
- (2) Particles in leachate were clogged physically the active area of pervaporative membranes and active area of membranes were decreased dramatically,

- (3) The laminar flow regime in the pervaporation unit were caused concentration polarization on the surface of the membrane which may be led to decrease in driving force of VFAs through membrane.

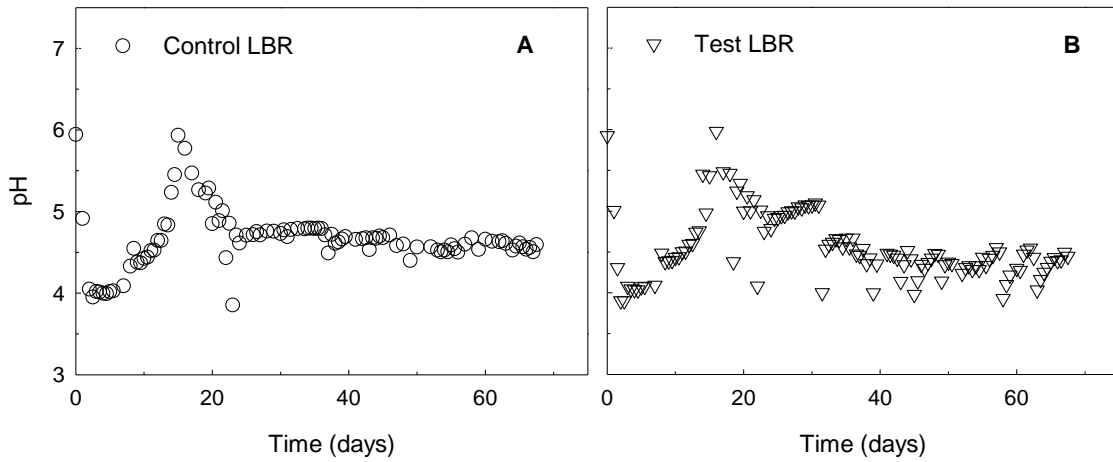
VFAs were produced from integrated LBR-pervaporation system via anaerobic fermentation was far more than VFAs were separated from system via pervaporation system. And it is known that VFAs must be removed from system to prevent accumulation of VFAs and thus possible inhibition of fermentation system. Therefore, a vapour pressure membrane contactor system process which was optimized for VFA removal before was also integrated to system as a modification. Thus it was aimed that integrated-LBR- vapour pressure membrane contactor system -pervaporation system could be achieved an efficient VFA separation and also VFAs that were separated system would be pure and concentrated.

### **3.4.3. Integrated Leach Bed Reactor – Vapour Pressure Membrane Contactor – Pervaporation (LBR-VPMC-PV) System**

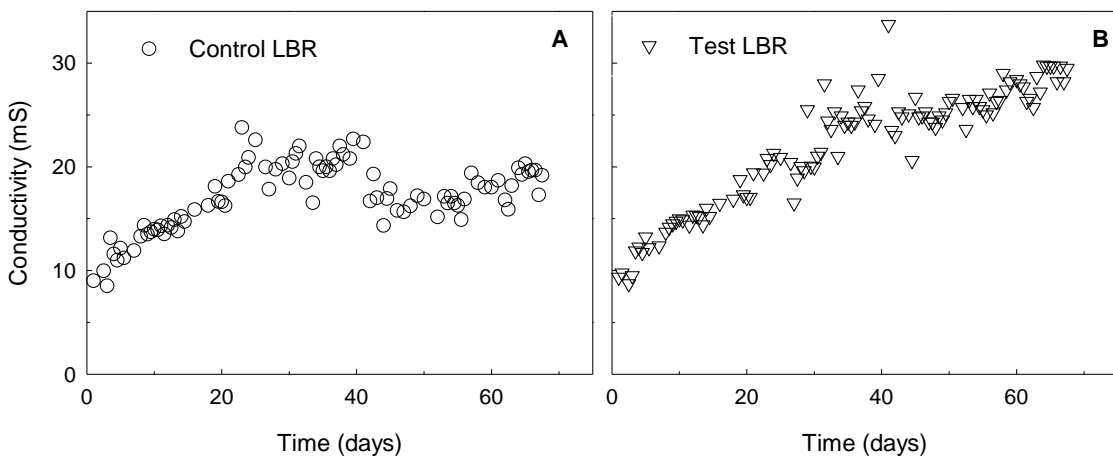
VPMC system was placed between fermentation and pervaporation systems and VFA separation was observed for 48 days (Total LBR operation time was 68 day with 19 days of LBR-pervaporation) via integrated leach bed reactor – vapour pressure membrane contactor – pervaporation (LBR-VPMC-PV) system. VPMC system was placed on recirculation line and leachate in test reactor was used as a feed to the VPMC system. Filtration unit that was used before for LBR-pervaporation system was placed before VPMC system. VPMC system was operated at 38°C with receiving solution at 0.5 or 1 N NaOH, 50L/day recirculation rate and 16 hours' operation hours. PTFE membrane for VPMC and pervaporative membranes in integrated LBR-VPMC-PV were changed with new ones approximately once a week. VPMC is a process that is depended on gas or vapour transfer as pervaporation system therefore pH value is very important for efficiency. Thus pH of both control and test reactors were adjusted with HCl until 35<sup>th</sup> day. After 35<sup>th</sup> day only test reactors pH was adjusted until end of the assay at 67<sup>th</sup> day. Permeate of the VPMC (the receiving side) was pH adjusted before it was fed to pervaporation system as feed solution. Leachate recirculation in fermentation and pervaporation system were operated in days and VPMC system was operated at nights in integrated LBR-VPMC-PV system.

Leachate pH values of control and test reactors were measured and were changed between 4.6 – 5.3 in integrated LBR- vapour pressure membrane contactor system - pervaporation (LBR-VPVC-PV) in between 20<sup>th</sup> and 67<sup>th</sup> days (Figure 43A). Leachate pH values of test reactor were analysed in beginning and end of each day. Leachate pH values were kept between certain values for maintain high VFA separation efficiency;

- (1) Feed solution pH values were changed between 3.9 and 4.4 in Vapour Pressure Membrane Contactor (VPVC) system (Figure 43). This way increasing free VFA concentration in leachate that was fed to VPVC was aimed.
- (2) Leachate pH values of test LBR were changed between 4.5 and 5.3 (Figure 42). Therefore, recirculated control and test leachate values were kept similar (Figure 41A).



**Figure 42.** pH values of Control (A) and Test (B) LBRs for 67 days.



**Figure 43.** Conductivity values of Control (A) and Test (B) LBRs for 67 days.

Conductivity values of control and test reactors were observed as increased between 20<sup>th</sup> and 42<sup>nd</sup> day in integrated LBR-VPMC-PV (Figure 43). Around 600 mL of leachate was lost from each control and test reactors at 42<sup>nd</sup> day of integrated LBR-VPMC-PV. 600 mL tap water was added in to both control and test reactors instead of lost leachates.

Addition of tap water at 42<sup>nd</sup> day was caused a decrease of VFAs in LBR reactors. However, conductivity values were increased from 42<sup>nd</sup> day to 67<sup>th</sup> day (Figure 43). Conductivity values were very similar at 35<sup>th</sup> day both control and test reactors, after 35<sup>th</sup> day conductivity values of control and test reactors were differentiated due to adjust of pH values in test reactor with HCl (Figure 43). Conductivity values of control and test reactors were reached at highest 19.2 mS/cm and 29.5 mS/cm respectively.

**Table 21.** Last day measurements of integrated LBR-VPMC-PV system

Parameter	Control LBR	Test LBR	Receiving Solution
pH	4,59	4,45	-
Conductivity (mS/cm)	19,18	29,5	-
Total COD (mg COD/L)	41723	26782	-
Soluble COD (mg COD/L)	28336	12093	-
Soluble COD percent (%) <sup>a</sup>	67,9	45,1	-
Total VFA-COD (mg VFA-COD/L)	24166	3712	49780
Total VFA-COD percent (%) <sup>b</sup>	85,3	30,7	-
Total VFA-COD (mg VFA-COD)	26582	31799	47352
		52980 <sup>c</sup>	
NH <sub>3</sub> -N (mg/L)	405	402	-
VFA (mg/L)			
Acetic acid	4643	814	8824
Propionic acid	315	0	2500
Butyric acid	8836	1175	22952
Caproic acid	1210	321	2995
VFA (mg)			
Acetic acid	5107	692	7060
Propionic acid	347	0	2001
Butyric acid	9720	999	18361
Caproic acid	1331	273	2396

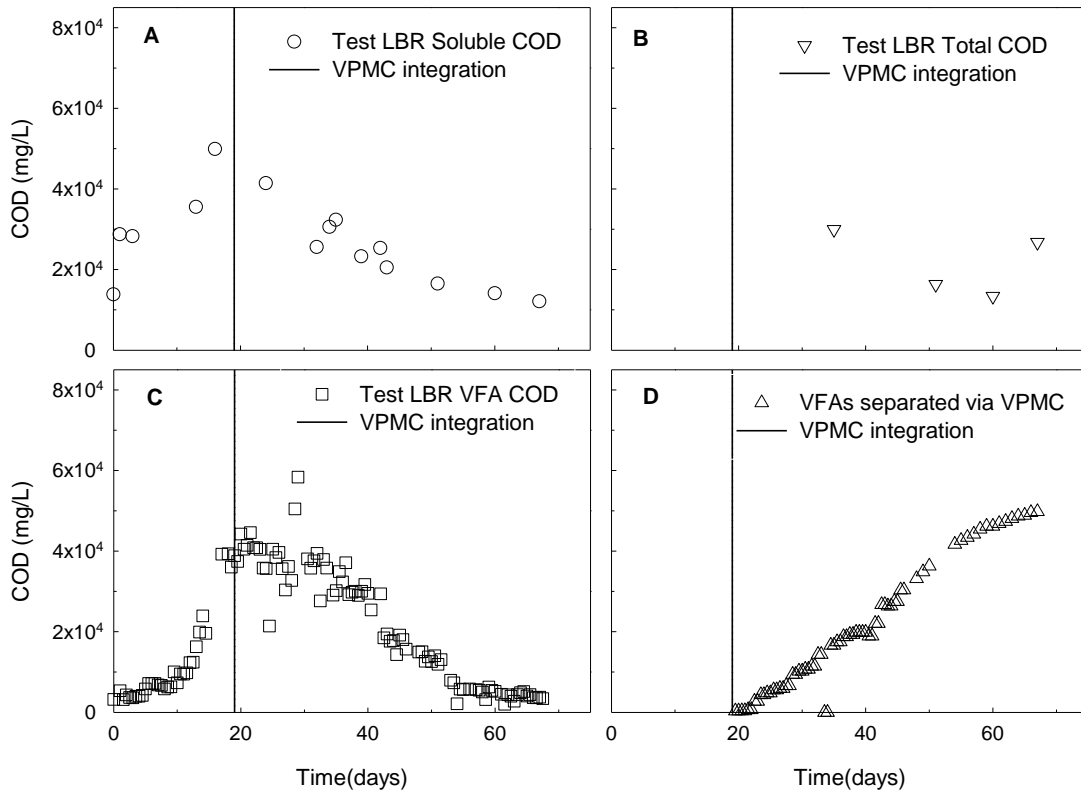
<sup>a</sup> Soluble COD percent = (soluble COD / total COD)\*100

<sup>b</sup> Total VFA-COD percent = (total VFA-COD / soluble COD)\*100

<sup>c</sup> VFA mass that was produced in test reactor = VFA mass in leachate + total VFA mass in receiving solution

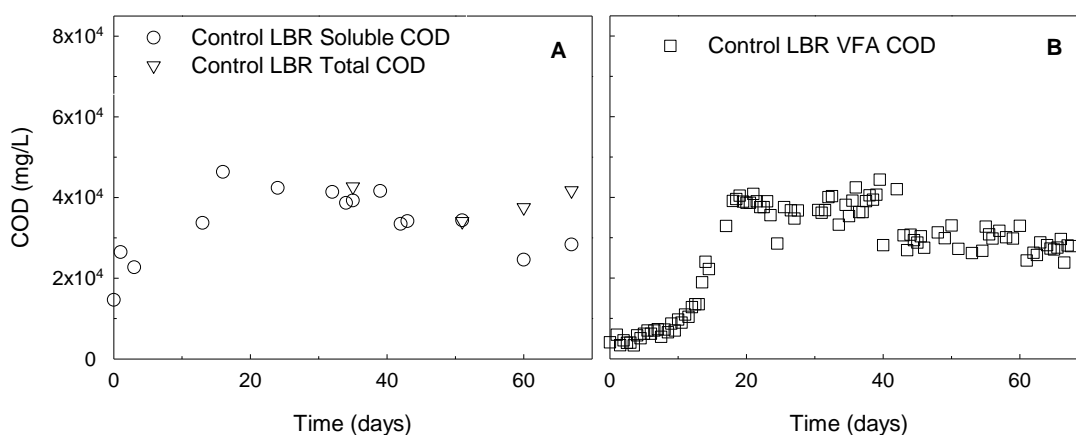
Ammonia concentrations in leachate were measured periodically at whole period of integrated LBR-VPMC-PV operation. Highest ammonia concentration level was observed for both control and test reactors at 39<sup>th</sup> day with concentrations of 491 mg NH<sub>3</sub>-N/L and 525 mg NH<sub>3</sub>-N/L respectively. However, at 67<sup>th</sup> day ammonia levels were observed 405 mg NH<sub>3</sub>-N/L and 402 mg NH<sub>3</sub>-N/L for control and test reactors respectively with the tap water addition at 42<sup>nd</sup> day. Ammonia concentrations were under inhibitory levels (Table 21).

COD and VFA-COD concentrations were measured after the integration of the VPMC system to fermentation reactors between 20<sup>th</sup> and 67<sup>th</sup> days. At 67<sup>th</sup> day COD concentration was sourced mostly by VFAs (85.3%) in control reactor (Figure 39A and Table 20). However, VFA-COD concentration in test reactor decreased due to separation via VPMC process and VFA-COD was only 30.7% of soluble COD at 67<sup>th</sup> day of operation (Figure 43A and Table 21).



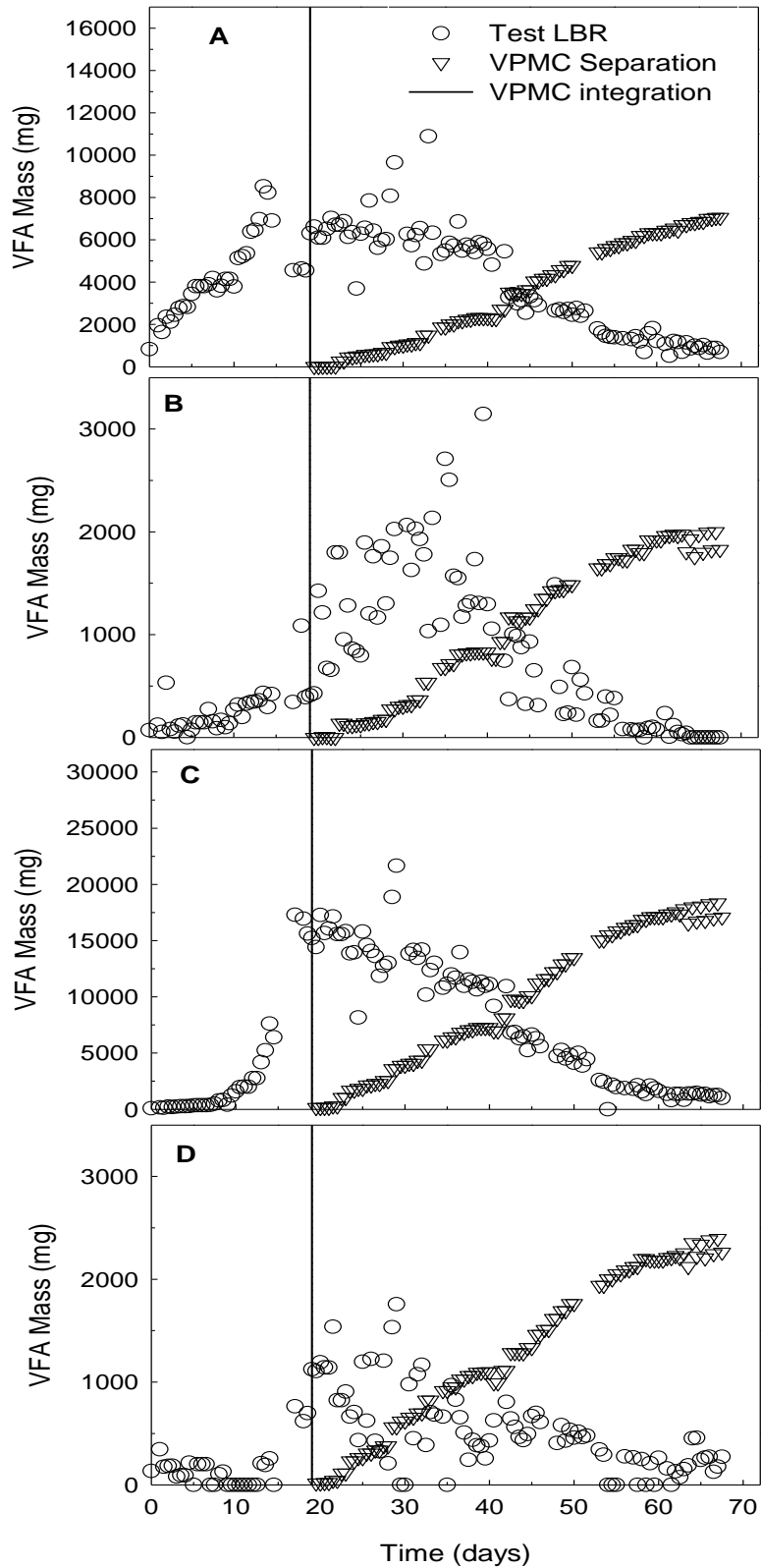
**Figure 44.** Values of soluble COD (A), total COD (B), VFA-COD (C) and VPMC VFA-COD (D) in test LBR via integrated LBR-VPMC-PV system

Total COD concentration was measured alongside soluble COD after 35<sup>th</sup> day. According to COD measurements ratio of soluble COD to total COD values were observed as 67.9% and 45.1% for control and test reactors respectively. This difference of total COD and soluble COD was resulted from particles in leachate. VFA-COD concentration was measured as 29957 mg/L at 19<sup>th</sup> day (Figure 39A). However, after 19<sup>th</sup> day VFAs were not produced significantly and no big difference was observed at the end of the operation for control reactor (Figure 40A). At 42<sup>nd</sup> day VFA-COD was seem decreased to 23499 mg/L due to add tap water and concentration was kept nearly constant till 67<sup>th</sup> day with the concentration 24166 mg/L (Figure 45).



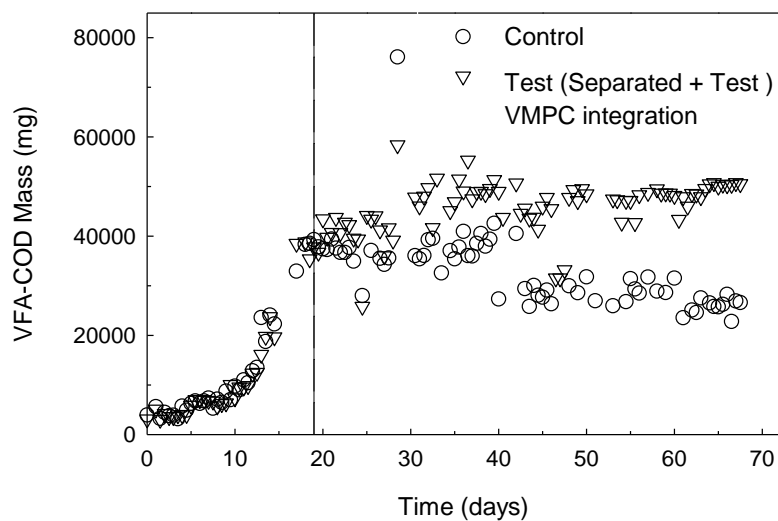
**Figure 45.** Values of soluble COD, total COD (A) and VFA-COD (B) in control LBR in total 67 days.

First day of LBR- VPMC-PV VFA-COD concentration was measured as 31121 mg/L for test reactor and last day of LBR-VPMC-PV VFA-COD concentration was measured as 3712 mg/L (Figure 46). VFAs in test reactor were passed through PTFE membrane and were trapped into NaOH solution via VPMC process which was operated night time in LBR-VPMC-PV. 0.5N NaOH solution was used for first three days of VPMC integration (20<sup>th</sup> day to 22<sup>nd</sup> day). However, pH values of NaOH were not kept above 12 and efficiency was dropped because VFAs were rapidly accumulated in NaOH solution. Therefore, after 4<sup>th</sup> day of operation (23<sup>rd</sup> day) receiving solution concentration was changed into 1 N NaOH until end of the integrated LBR-VPMC-PV operation. After receiving solution concentration was changed from 0.5N to 1N, VFA separation became stable throughout the operation (Figure 46). VFA-COD concentration in 1N NaOH solution was observed as 49780 mg/L on the 67<sup>th</sup> day (Figure 46).



**Figure 46.** Mass values of acetic acid (A), propionic acids (B), butyric acid (C) and caproic acid (D) in test LBR and separated from test LBR via integrated LBR-VPMC-PV system

Acetic, propionic, butyric and caproic acids were main VFAs in both control and test reactors (20<sup>th</sup> day to 67<sup>th</sup> day) (Figure 44 and 45). VFA mass was measured in test reactor as 6302 mg acetic acid, 409 mg propionic acid, 15229 mg butyric acid and 1124 mg caproic acid at 20<sup>th</sup> day of the process (Table 17). All VFA masses were decreased with the integration of VPMC system and VFA measurements were acetic acid 692 mg, 999 mg butyric acid and 273 mg caproic acid at 67<sup>th</sup> day (Figure 46A, 46C and 46D). All propionic acid in the test reactor leachate was transferred to receiving solution (Figure 46). Butyric acid separated with highest efficiency and propionic acid was separated with the lowest efficiency compared to that of other VFAs (Figure 46). Butyric acid was the most concentrated VFA and propionic acid was the least concentrated VFA in the leachate that was fed to VPMC system. Therefore, VFA concentration obviously affected the VFA separation efficiency of VPMC and 18361 mg butyric acid with the highest VFA concentration was transferred to receiving solution (Figure 46C). After the 19<sup>th</sup> day of operation VFA production was completely stopped in the control reactor whereas VFA production was continued to be observed in the test reactor, suggesting that VFA separation through VPMC-PV system increased the VFA production efficiency of the LBR reactor whereas control reactor was completely inhibited (Figure 45). Total VFA-COD produced in control LBR was 26582 mg and total VFA-COD produced and separated via VPMC system was 52936 mg VFA-COD (Table 20). Therefore, with the integration of VPMC process to system test reactor had 2.06 folds' efficiency over control reactor (Figure 47 and Table 20).



**Figure 47.** VFA-COD mass in control and test LBRs.

VFAs were separated from LBR and were trapped into receiving solution in salt form such as sodium acetate or sodium butyrate via VPMC process. High efficiency was achieved at VFA separation from leachate via VPMC process however, VFAs that were separated and trapped in salt form cannot be used for commodity purposes due to NaOH and water content. VFAs in receiving solution were needed a purification process. Therefore, VFAs that were trapped in receiving solution via VPMC were fed to pervaporation system. Integrated LBR-VPMC-PV system was started at 20<sup>th</sup> day however first feeding of receiving solution to pervaporation was on 27<sup>th</sup> day. The reason of this delay was firstly 0.5N NaOH receiving solution usage at first three days (20<sup>th</sup> – 22<sup>nd</sup>) thus unstable VFA separation and secondly after concentration change of receiving solution 0.5 to 1N, around 4 days were needed for the receiving solution got concentrated for feeding to pervaporation system. Therefore, VPMC system and pervaporation system were started working together at 27<sup>th</sup> day and were kept working together until end of 67<sup>th</sup> day.

Particles in test reactor leachate was clogged the membrane in integrated LBR-VPMC-PV system due to physical blockage time to time and this was led to decrease in efficiency of VFA separation via VPMC. Therefore, the PTFE membrane was changed with a new one time to time. Also 1N NaOH solution as receiving solution was changed time to time when its pH value was fewer than 12. PTFE membrane of VPMC was changed for 4 time and receiving solution was changed for 8 time between 20<sup>th</sup> and 67<sup>th</sup> days. 19.25 cm<sup>2</sup> active membrane area and 800 mL of 1N NaOH solution were used for separating 49780 mg VFA-COD via VPMC system. Highest VFA flux was owned by butyric acid with 12.4 g/m<sup>2</sup>.h and lowest VFA flux was with propionic acid 1.4 g/m<sup>2</sup>.h acid flux via VPMC system.

Total VFA-COD flux of PTFE membrane was calculated as 32.7 g/m<sup>2</sup>.h. Composite membranes in pervaporation module were also changed every 10 days a total 4 membranes for entire integrated LBR-VPMC-PV operation. 3779 mg of VFA-COD was passed through pervaporative membrane and was trapped in cold traps via LBR-VPMC-PV system and 12.56 cm<sup>2</sup> active membrane area was used for VFA purification and separation. Total VFA flux was calculated as 9.4 g VFA-COD/m<sup>2</sup>.h via pervaporation process. Butyric acid has the Highest VFA flux with 4 g/m<sup>2</sup>.h and lowest VFA flux was with 0.1 g/m<sup>2</sup>.h for caproic acid.

**Table 22.** Mass relations of integrated LBR-VPMC-PV system for test reactor

Parameter	Initial	Day 67
Total COD (g O <sub>2</sub> / kg dry waste)	490.4 ± 70.0	133.120
Total COD (g for dry waste)	980 ± 140.0	266.240
Soluble (g COD)	13.819	12.092
Total VFA-COD (g COD)	2.789	52.935
Separated VFA-COD (g COD)	0	49.780
Produced VFA-COD per g of Total COD %	0.2%	5.40%
Separated VFA-COD (g COD) per g Total VFA-COD %	0%	94.04%

At 67<sup>th</sup> day 266.24 g COD of 980 ± 140.0 g total COD was left in Test LBR. 713.76 g COD was consumed however only 49.780 g of VFA-COD was separated and 12.092 of Soluble COD was left in Test LBR. 651.88 g of COD was consumed in other paths (Table 22).

According to results changing LBR-PV into LBR-VPMC-PV was helped to solve out some of the problem with LBR-PV; (1) VFA pH can be adjusted into desired amounts (around pH 3) and (2) particles in leachate were filtered via PTFE membrane in the VPMC system before they were reached to non-porous membrane of pervaporation. Therefore, system became more efficient in both separation and purification.

## CONCLUSIONS

The aim of the study was to investigate VFA recovery from anaerobically fermented organic-rich municipal solid waste through pervaporation. In order to reach this aim, polymeric membranes with different characteristics were manufactured and tested for their VFA separation efficiency through flux and separation factor analysis. In addition, VFA separation from anaerobic digestion systems is important in terms of preventing VFA concentrations to reach inhibitory levels, therefore the effect of VFA separation on VFA production efficiency of anaerobic digestion systems were also investigated. Composite membranes with different characteristics were manufactured and characterized to be used in the pervaporation system. Manufactured composite membranes were (a) 550 g/mol molecular weight (low molecular weight) poly dimethylsiloxane (PDMS-OH) membranes with hydrophobic and hydrophilic nano-silica filling, (b) 36000 g/mol molecular weight (high molecular weight) non-filled and hydrophilic nano-silica filled poly dimethylsiloxane (PDMS-OH) membranes and (c) hydrophilic and hydrophobic silica filled vinyl terminated PDMS (PDMS-vinyl) membranes. VFA separation efficiency of all manufactured membranes were determined in terms of VFA flux and separation factor in pervaporation system.

Main conclusions drawn from the study are;

- Optimum VFA separation efficiencies through pervaporation was obtained through 0.1% nano-silica filled high molecular weight PDMS-OH (30% polymer, 1% catalyst (dibutyltin dilaurate) and 0.3% cross-linker (TEOS)) membrane.
- 0.1% hydrophilic nano-silica filled low molecular weight PDMS-OH membrane was considered as optimum membrane composition for VFA separation with flux and separation factor values of 7.04 g/m<sup>2</sup>.h and 2.13, respectively. The membrane was used in integrated fermentation/membrane separation system.
- Generally, increase of operational temperature from 35°C to 45°C resulted in decreased separation flux and separation factor.
- Integrated system was operated as fermentation and pervaporation system for the first 19 days of operation. However, pervaporation behaved more like a purification step and resulted in only 28 mg VFA-COD separation in 19 days.

Therefore, a new configuration was designed including vapor pressure membrane contactor system (LBR-VPMC-PV system) in order to increase VFA separation efficiency and thus VFA production efficiency of the integrated system.

- VPMC process separated 49780 mg VFA-COD of total VFAs were produced (52936 mg VFA-COD) from test fermentation reactor within 47 days of operation of LBR-VPMC-PV system.
- VFA fluxes were measured as 32.7 g VFA-COD/m<sup>2</sup>.h for VPMC process and 9.4 g VFA-COD/m<sup>2</sup>.h for PV process. 3156 mg VFA-COD was purified.
- Integrated system resulted in enhanced VFA production in the fermentation step as the produced VFAs were separated by VPMC and PV systems before reaching inhibitory levels. In addition, efficient VFA separation and purification was achieved.

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