

*Full Length Research Paper*

# **Pilot-scale recovery of low molecular weight organic acids from anaerobically treated palm oil mill effluent (POME) with energy integrated system**

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**Low molecular weight organic acids such as acetic acid, propionic acid and butyric acids generated from partial anaerobic treatment of palm oil mill effluent (POME) were recovered using pilot scale filtration and evaporation system. Mechanical filter press (14 L) was used for removing solid fractions and fraction distillation unit (40 L) for evaporation and clarification of concentrated acid from POME. Clarification using rotary evaporator was found to be more suitable than distillation column. Due to the presence of more than 90% of water in POME, the final clarified product comprises only 7% of the total volume. The material balance for the overall process was estimated and integrated system for the bioconversion of organic acids into polyhydroxyalkanoates (PHA) was proposed. The recovery of organic acids has a significant and economical impact, since around 50% cost of PHA production is believed to be associated with the substrate itself.**

**Key words:** Acidogenesis, anaerobic treatment, organic acid, palm oil mill effluent, recovery.

## **INTRODUCTION**

Anaerobic wastewater treatment technology is being widely used for the treatment of high-strength wastewater streams from food, beverage, paper pulp, palm oil mill and petrochemical industries (Liu et al., 2002). Palm oil mill generates large quantities of liquid wastes which are commonly referred to as palm oil mill effluent (POME). In Malaysia, various treatments have been proposed to treat POME in order to meet the discharge standard. The most common practices for the treatment of POME are the ponding system, open tank digester, extended aeration system and land application system. Considering the highly organic character of POME, anaerobic process is the most suitable approach for its treatment (Zinatizadeh et al., 2007).

Anaerobic digestion is the breaking down of organic

materials biologically by a complex group of acid-forming and methanogenic bacteria producing end products of water, methane, carbon dioxide and stabilized solids in the absence of oxygen. Several researchers have claimed that optimization of both acidogenic and methanogenic phases would enhance the overall rate of waste stabilization if maintained in separate digesters in series: one for acid production and one for methane production (Yang et al., 2003). In acidogenic phase, organic particulates are transformed and fermented to volatile fatty acids (VFA) comprising mainly from acetic, propionic and butyric acids.

Acetic, propionic, butyric and valeric acids produced during anaerobic fermentation process can be recovered using several methods such as, liquid-liquid extraction of acetic and propionic acids (Solichien et al., 1995; Ozadali et al., 1996), permeation of acetic and propionic acid in a hybrid system composed of liquid and anion membranes (Wodzki and Nowaczyk 1997). Ingale and Mahajani (1994, 1996) used tributylphosphate as an extractant to

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recover acetic, propionic, butyric, valeric and caproic acids from waste stream. Lee et al. (2008) applied dual membrane process such as micro-filtration and reverse osmosis to concentrate the organic acid from fermented food waste. More recently, electrodialysis (ED) has been used for acetic acid recovery from wastewater (Yu et al., 2000) as well as for the recovery of organic acids from waste salt solution (Wang et al., 2006).

In the preliminary studies by Phang et al. (2003), a simultaneous process for POME treatment coupled with bioplastic production was developed using VFAs produced from fermentation of POME. Anaerobic fermentation of POME was studied by Nor'Aini et al. (1999) in 10 L fermenter. The continuous anaerobic treatment of POME at neutral pH at different retention time has been optimized. In the study, 9.53 g/L VFAs was produced at 5 days HRT. By using sludge recycle system, the HRT was reduced to 3.8 days with 10.4 g/L organic acids (Phang, 2001). Preliminary experiment using 50 L fabricated bioreactor and at 4 days HRT and pH 6.5 showed that, organic acids up to 15.36 g/L could be obtained (unpublished data).

Filtration and evaporation are commonly used to recover mixed volatile organic acids from wastewater. Despite of the high amount of energy required during distillation and evaporation, the process can be viable in the context of mill operation where steam is being continuously generated during the processing of oil extraction from Oil Palm. Moreover, it is more practical to use cheaper separation technologies that can be integrated with the existing unit operations in the conventional palm oil processing mill.

In this paper, a comparative study on the recovery of low molecular weight organic acids in pilot scale were undertaken and a material balance was developed for these to be used as a substrate for polyhydroxyalkanoates (PHA) biosynthesis. By using organic acids produced from acidogenic fermentation of POME for the production of PHA, production cost can be lowered down substantially.

## MATERIALS AND METHODS

### Palm Oil Mill Effluent (POME) and POME sludge

POME and POME sludge used for the treatment were obtained from Serting Hilir Palm Oil Mill, Negeri Sembilan, Malaysia. The bioreactor was located in the anaerobic treatment facilities of mill premises.

### Bioreactor set up

The height and diameter of the 50 L bioreactor was 71 and 30 cm, respectively. The top of the vessel was sealed with a transparent plastic plate. Mixing was accomplished by G.K. Heller motor model Glass-Col® precision stirrer agitated at 150 rpm and temperature was not controlled. Feeding of POME was accomplished by a circulating pump at a flow-rate of 12.5 ml/min. pH was controlled at 6.5 by using 10 M NaOH.

### Fermentation of POME for organic acid generation

Partial anaerobic treatment of POME was carried out to produce organic acids in a 50 L fabricated fermenter without sludge recycling. For the start-up operation, 20 L raw POME from holding tank and 20 L sludge from the settling tank were pumped into the bioreactor and were mixed for 20 min. After 4 days of acclimatization, 10 L of raw POME was fed daily and at the same time treated POME containing organic acids were collected and stored in cold room prior to recovery. Temperature of raw POME was recorded between 30 to 38°C and pH 4.2 to 4.8. The initial value of organic acids ranged between 1100 to 3900 mg/L. pH was recorded before and after adding raw POME and was manually adjusted by using 10 M NaOH to 6.5-7.0.

### Recovery of organic acids from treated POME

#### Filtration/solid separation

Treated POME containing organic acids was filtered using mechanical filter-press (14 L capacity) (Figure 1) to remove solid particles and sediments. Liquid sludge was pooled in a 75 L capacity stainless steel vessel and an amount of diatomaceous earth (Celite®) was added to the POME to facilitate the solubilization process. The effluent was then pumped to a filter press assembly that contains filter cloths, compression plates, 4-6 chamber plates. The compression plates and chamber plates were pressed together to hold the cloth in between them. During the filtration stage, as the liquid sludge was pumped through the cloth, water passed through the cloth, while the filter cloth trapped the solids.

When sufficient time has elapsed, compressed air was led into the diaphragm in the chamber plates to compress the solids sticking to the cloth. As a result of the squeezing, the sludge became dried to the consistency of modeling clay. The compression and chamber plates were then separated. The clay-like sludge were then separated from the cloth and were collected in bags and stored. The light brown liquid thus obtained was stored at 4°C until further use.

#### Distillation and evaporation

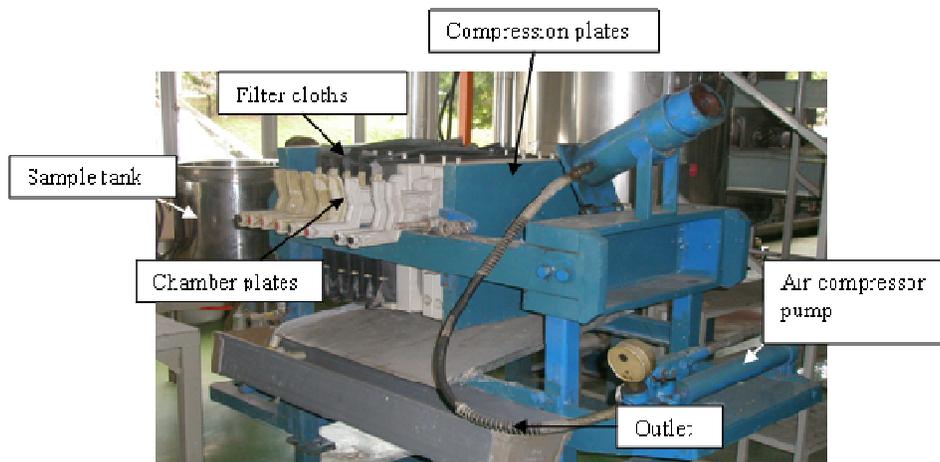
Two phases of distillation was required to get the final product: first phase comprises the dewatering and concentration of organic acid during the evaporation of filtered POME and the further recovery of clarified organic acids from the evaporator concentrate using sulfuric acid in the second phase.

A picture of the pilot plant distillation unit is shown in Figure 2. The pilot plant unit is composed of one round bottom sample flask (A) placed in a heating mantle (B)- 40 L capacity. It has three inlets, one outlet at the bottom and a side extension for temperature measurement (C). The unit has two condensers (D) fitted with a number of glass tunnels, tubings and joints. The sample outlet is connected to a vertical glass tube (E) which indicates the level or volume of sample in the flask. The final receiving flask (F) is 20 L capacity and G is the distillate outlet.

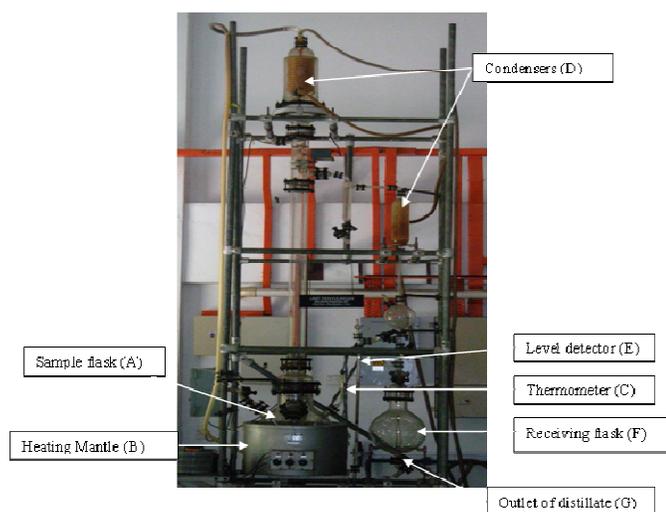
#### Pilot plant distillation operation in batch mode

Evaporation of filtered POME was carried out batch wise. At the beginning of each batch, 40 L of filtered POME was filled in the sample flask and evaporation was continued until the volume reduced to ten folds. The excess water distilled out was collected in the 20 L receiving flask and was checked for organic acid content. The resultant acid concentrate was taken out from the sample flask at the start of the next batch. This process was repeated for 6 times.

Once this recovery batch is completed, resulting organic acid concentrate underwent second phase distillation. Acid concentrate from each batch was pooled and poured in the sample flask. Upon



**Figure 1.** A Mechanical Filter Press used in the present study.



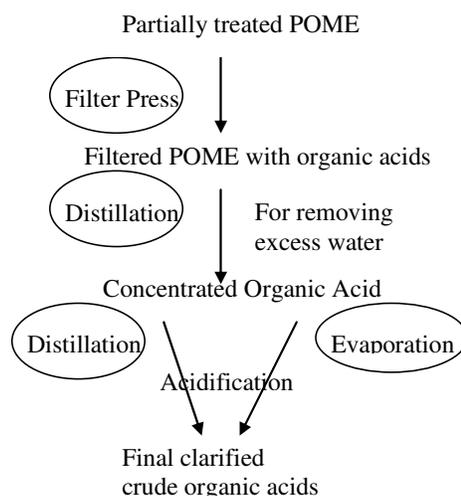
**Figure 2.** A pilot plant fraction distillation unit used in the present study.

acidification using sulfuric acid in a ratio of 8:1, a clear, colorless organic acids were distilled out in the receiving flask. The outline of the recovery stages are given in Figure 3.

A comparison was also made by operating first phase distillation in a semi-continuous manner where filtered POME was added to the vessel at different time intervals depending on the volume of water condensed out. Cooling water was circulated through the condenser to keep the temperature at 103°C. Moreover, during acidification stage, instead of distillation unit, rotary evaporator (Buchi Rotavapor R-220, 20 L capacity) was used to clarify the bioacids. The temperature was set at 97°C, with a rotation speed of 60 rpm and vacuum pressure was in between 345-370 mm Hg.

### Analyses

Organic acid content during the recovery steps was determined by high performance liquid chromatography (SPD-10A, UV-VIS Detector; LC-10 AS Liquid Chromatograph Shimadzu) using BIORAD-Aminex ion exclusion HPX-87H (300X7.8mm) by the methods



**Figure 3.** Recovery stages used in the study.

described by Hassan et al. (1997). Chemical Oxygen demand (COD) analysis was carried out based on standard method (APHA, 1985).

## RESULTS

Organic acids generated during partial anaerobic treatment of palm oil mill effluent for this study period varied from 5,000-14,000 mg/L. Acetic acid concentration was found to be higher than propionic acid followed by n-butyric acid. Traces amount of lactic, formic and iso-butyric acid were also detected in the treated POME which were not taken into consideration during recovery.

### Filtration/solid separation

Organic acid content of treated POME did not vary after

filtration. Solid removal accounted for 3-4% using filter press. COD value of filtered POME varied from 14,000-60,000 mg/L with total organic acid content of 10 g/L in average.

### Pilot plant distillation operation in batch mode

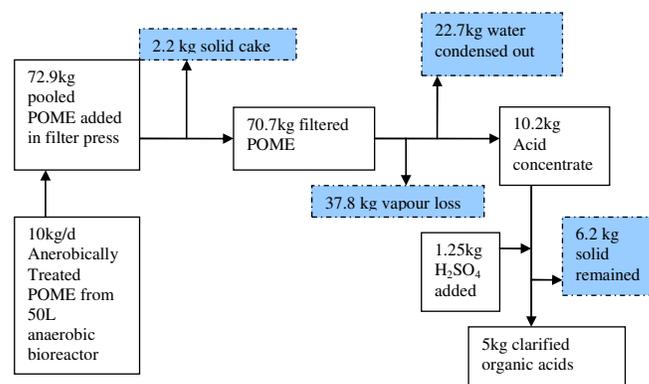
During the first phase distillation, each batch operation took about 6 days or 144 h at which approximately ten fold reductions in volume were achieved. When temperature above 105°C was used, condensed water contained 0.8 g/L to maximum of about 3.89 g/L of total organic acid. To reduce the loss of organic acid during dewatering process, operating temperature was maintained at 105°C by which the release of organic acid was reduced to 0.2 g/L. pH value of the water distilled out was acidic, ranged between pH 3.4-4.0 and COD value up to 28,000 mg/L was recorded. During first phase distillation, the volume removed in the form of water comprised approximately 27% of the total volume whereas 50-60% volumetric loss occurred as exhaust.

The second phase distillation and acidification process in full capacity (40 L) was stopped at day 8 at which 50% volume could be recovered as clarified acids. After that the temperature could not be controlled at 110°C and the rate of recovery slowed down from 125 ml/h to less than 1 ml/h. The solid particles in the acid concentrate reacted with sulfuric acid and settled down at the bottom resulting in the uncontrolled temperature. Concentration of pooled acids was 55 g/L wherein acetic acid comprises approximately 50% of the total organic acids, propionic acid approximately 25% and n-butyric acid constituted approximately 24%.

### Pilot plant distillation operation in semi-continuous mode

During semi-continuous operation, approximately six fold concentrations were achieved within 30 days; 69% of water was condensed out as distillate and the rest (approximately 15%) was evaporated through exhaust. Even though the time taken for distillation could not be shortened by semi-continuous feeding of POME, the percentage vapour loss can be substantially reduced. Moreover, the water distilled out was devoid of organic acids. The concentrated acid was clarified using a pilot scale rotary evaporator 20 L capacity.

In the rotary evaporator, the recovery rate was 270 ml/h which is two times higher than that of distillation unit. Moreover, the sample was continuously rotating during operation which reduces the problem of settling/clogging. About 61% of the concentrated acid could be recovered as clarified acids. The concentration of bioacids in the solution was found to be 53.33 g/L (HAc- 30.71, HProp- 8.43, HButy- 14.19 g/L).



**Figure 4.** Material balance of integrated system of recovery and bioconversion of organic acids from POME.

### Material balance of the recovery process

The results of the overall separation process using distillation unit are given in Figure 4. The mechanical filtration separated 3-4% of the initial solid mass. Roughly 55% escaped as exhaust, 35% condensed as distillate and 13% fraction remained as concentrated acid. A 50% of the distillate during final recovery step was the final clarified product i.e., bioacids. The distillate contains 55 g/L of total acids which appear as a clear solution.

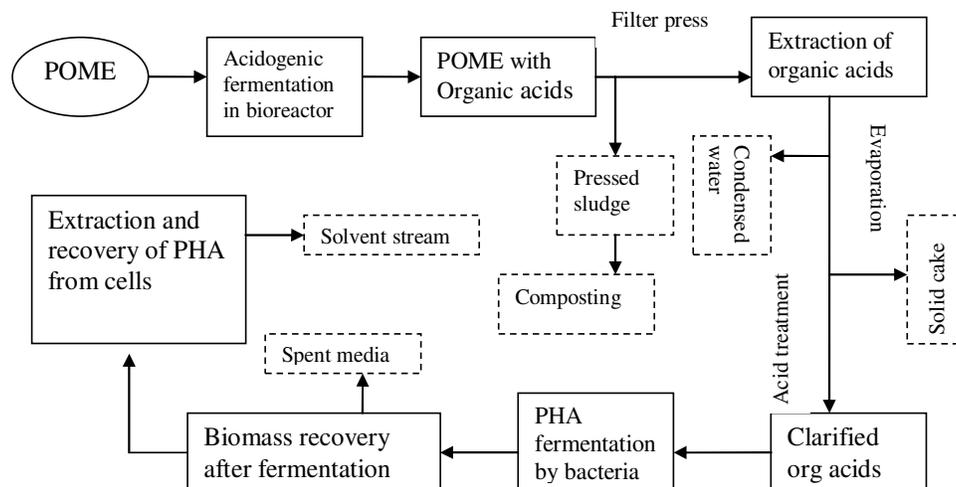
### Proposed strategy for the conversion of organic acids to PHA

Figure 5 shows the proposed strategy for the treatment and bioconversion of POME into PHA- a biodegradable thermoplastic. Our proposed strategy (Figure 5) would enable COD conversion of POME into PHA via organic acids, an environmentally friendly alternative to conventional plastics. Water in the POME can be recovered as distillate and later could be reused as boiler feed water or process water. Moreover, solids content (20–30% (w/v) produced during recovery process can be used as a fertilizer.

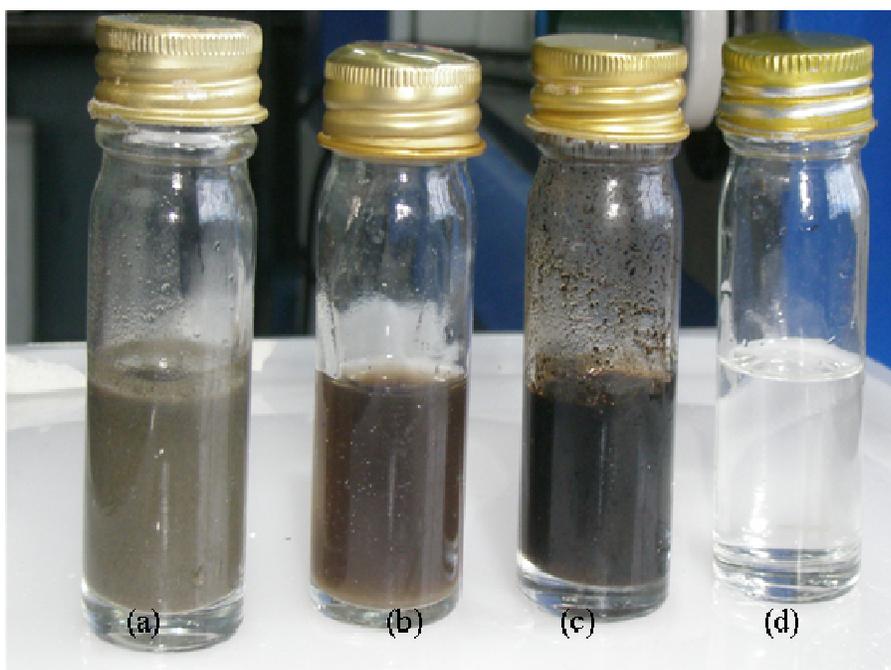
### DISCUSSION

There are currently about 265 active palm oil mills in Malaysia with a combined annual CPO production capacity of 13 million tonnes (<http://www.mpopc.org.my>). On an average, a standard palm oil mill, for each tonne of fresh fruit bunch (FFB) processed, generates about 1 tonne of liquid waste called palm oil mill effluent with biochemical oxygen demand (BOD) 37.5 kg, chemical oxygen demand (COD) 75 kg, suspended solids (SS) 27 kg and oil and grease 8 kg (Najafpour et al., 2005).

Taking account of this enormous quantity of wastewater, it is really needed to develop sustainable waste-



**Figure 5.** Proposed strategy for the treatment of POME and PHA production. Dotted line refers to waste stream.



**Figure 6.** Physical changes during the recovery of organic acids from treated POME: (a) treated POME; (b) filtered POME; (c) concentrated POME; and (d) clarified organic acids.

water treatment processes with a minimum of COD oxidation, CO<sub>2</sub> emissions and a maximum of waste utilization and COD conversion. Instead of being thrown away, this water after appropriate treatment can be reused to reduce the demand on the fresh water sources. In regions with water shortage, purified effluent could be a valuable resource.

Besides biogas/methane generation from anaerobic treatment of POME, POME can also be used to generate organic acids which are effectively used in a variety of

industrial process (Hassan et al., 2002). Several workers studied PHA production by mixed cultures using synthetic organic acids (Dionisi et al., 2005; Lemos et al., 2006; Bengtsson et al., 2008). In this paper, the conversion of palm oil mill effluent to low molecular weight organic acids and its subsequent recovery in pilot scale were described (Figure 6). The recovery process was further improved by using rotary evaporation system instead of distillation unit. Carrying out distillation using a vacuum (low pressure) allows use of lower temperatures and

attains higher product concentrations. The concentration of organic acids, however, in this study was found to be independent of the unit operation used during acidification stage. In both cases, the concentration of our final product was 53-55 g/L.

In order to recover organic acids from the treated waste stream, instead of organic solvent, inorganic acids like sulfuric acid was added to the concentrated treated POME to break sodium salts of organic acids and thus neutralize these organic acids (Ingale and Mahajani, 1996). These salts (acetate, propionate, butyrate) are formed during anaerobic treatment of POME to maintain the pH at 6.5. Optimization of concentrate to sulfuric acid ratio is useful for large scale recovery. Similar recovery studies carried out in lab scale by our research group yielded higher concentration (87.2 g/L) of organic acid (Sim, 2003). The relatively lower concentration of clarified acid obtained could be explained by the varied amount of organic acid content from batch to batch which again depends on the effluent characteristics. However, the clarified acid obtained in this study was found to be free of heavy metals. Concentration of most toxic metals like copper and zinc was below 1 ppm while chromium, cadmium, lead and nickel were undetectable (data not shown). This allows it to be a suitable substrate for PHA fermentation.

The concentration of clarified acids can be standardized by using membrane technology such as electro dialysis. Our future work will focus on the feasibility of electro dialysis in the overall recovery process of organic acid from palm oil mill effluent. The integrated system of utilizing waste streams in oil palm industries as being proposed here will create a good image of the oil palm industry whereby it helps to develop national economy and sustainability towards our environment.

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## REFERENCES

- APHA (1985). Standard Methods for the examination of water and wastewater 16<sup>th</sup> ed. American Public Health Association, NY USA.
- Bengtsson S, Werker A, Christensson M, Welander T (2008). Production of polyhydroxyalkanoates by activated sludge treating a paper mill wastewater. *Bioresour. Technol.* 99: 509-516.
- Dionisi D, Carucci G, Papini MP, Riccardi C, Majone M, Carrasco F (2005). Olive oil mill effluents as a feedstock for production of biodegradable polymers. *Water Res.* 39: 2076-2084.
- Hassan MA, Shirai Y, Umeki H, Yamazumi H, Jin S, Yamamoto S, Karim MIA, Nakanishi K, Hashimoto K (1997). Acetic acid separation from anaerobically treated palm oil mill effluent by ion exchange resins for the production of polyhydroxyalkanoate by *Alcaligenes eutrophus*. *Biosci. Biotechnol. Biochem.* 61(9): 1465-1468.
- Hassan MA, Nawata O, Shirai Y, Nor Aini AR, Phang LY, Ariff AB, Karim MIA (2002). A proposal for zero emission from palm oil industry incorporating the production of polyhydroxyalkanoates from palm oil mill effluent. *J. Chem. Eng. Jpn.* 35(1): 9-14.
- Ingale MN, Mahajani VV (1994). Recovery of acetic acid and propionic acid from aqueous waste stream. *Sep. Technol.* 4: 123-126.
- Ingale MN, Mahajani VV (1996). Recovery of carboxylic acids, C<sub>2</sub>-C<sub>6</sub> from a stream using tributylphosphate (TBP): Effect aqueous waste of presence of inorganic acids and their sodium salts. *Sep. Technol.* 6: 1-7.
- Lee JW, Kim JO, Jung JT (2008). Concentration of organic acid from fermented food wastes using a MF/RO process. *Mater. Sci. Forum* 569: 281-284.
- Lemos PC, Serafim LS, Reis MAM (2006). Synthesis of polyhydroxyalkanoates from different short-chain fatty acids by mixed cultures submitted to aerobic dynamic feeding. *J. Biotechnol.* 122: 226-238.
- Liu WT, Chan OC, Fang HHP (2002). Microbial community dynamics during start-up of acidogenic anaerobic reactors. *Water Res.* 36: 3203-3210.
- Najafpour GD, Zinatizadeh AAL, Mohamed AR, Isa MH, Nasrollahzadeh H (2005). High-rate anaerobic digestion of palm oil mill effluent in an up-flow sludge-fixed film bioreactor. *Proc. Biochem.* 41: 370-379.
- Nor Aini AR, Hassan MA, Shirai Y, Karim MIA, Ariff AB (1999). Production of organic acids from Palm oil mill effluent during continuous anaerobic treatment. *Asia Pacific J. Mol. Biol. Biotechnol.* 7(2): 179-184.
- Ozadali F, Glatz BA, Glatz CE (1996). Fed-batch fermentation with and without on-line extraction for propionic and acetic acid production by *Propionibacterium acidipropionici*. *Appl. Microbiol. Biotechnol.* 44(6): 710-716
- Phang LY (2001). Continuous production of organic acids from palm oil mill effluent and kitchen garbage. Masters thesis. UPM, Selangor, Malaysia.
- Phang, LY, Hassan, MA, Shirai Y, Wakisaka M, Karim MIA (2003). Continuous production of organic acids from palm oil mill effluent with sludge recycle by the freezing-thawing method. *J. Chem. Eng. Jpn.* 36(6): 707-710.
- Sim KH (2003). Utilization of organic acids from anaerobically treated Palm oil mill effluent with and without sludge recycle for polyhydroxyalkanoate production. MS thesis. Universiti Putra Malaysia, Selangor, Malaysia.
- Solichien MS, O'Brien D, Hammond EG, Glatz CE (1995). Membrane-based extractive fermentation to produce propionic and acetic acids: Toxicity and mass transfer considerations. *Enzyme Microb. Technol.* 17(1): 23-31
- Wang Z, Luo Y, Yu P (2006). Recovery of organic acids from waste salt solutions derived from the manufacture of cyclohexanone by electro dialysis. *J. Membr. Sci.* 280: 134-137.
- Wodzki R, Nowaczyk J (1997). Extraction and separation of propionic and acetic acid by permeation in a hybrid membrane system composed of liquid and ion-exchange polymers membranes. *Solvent Ext. Ion Exch.* 15(6): 1085-1106
- Yang K, Yu Y, Hwang S (2003). Selective optimization in thermophilic acidogenesis of cheese-whey wastewater to acetic and butyric acids: partial acidification and methanation. *Water Res.* 37: 2467-2477.
- Yu L, Guo O, Hao J, Jiang W (2000). Recovery of acetic acid from dilute wastewater by means of bipolar membrane electro dialysis. *Desalination.* 129(3): 283-288
- Zinatizadeh AAL, Mohamed AR, Mashitah MD, Abdulah AZ, Isa MH (2007). Optimization of pre-treated palm oil mill effluent digestion in an upflow anaerobic sludge fixed film bioreactor: A comparative study. *Biochem. Eng. J.* 35(2): 226-237.