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ANAEROBIC DIGESTION OF MIXED CHEMICAL PULPING AND PALM OIL MILL EFFLUENT IN SUSPENDED GROWTH ANAEROBIC DIGESTER

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ABSTRACT

The feasibility of anaerobic digestion treating palm oil mill effluent (POME) with addition of chemical pulping wastewater (black liquor) was studied in semi-continuous fed digesters under thermophilic (55°C) condition. The anaerobic digestibility of POME with and without addition of black liquor (2.5% and 5% by volume) was compared. Black liquor is an effluent obtained from pulping processes and it has high toxicity level and poor biodegradability. The digesters contained POME without black liquor functioned as a control in this study. The chemical oxygen demand (COD) reduction for hydraulic retention time (HRT) of 5 days and 10 days were examined to evaluate the effect of HRT on the performance of the digesters. The results depicted that COD reduction could be achieved up to 87% in the digester without black liquor and 79% reduction in COD with black liquor added. Fourier Transform Infrared (FTIR) spectroscopy was used to identify the functional group of POME operated under thermophilic temperatures and with or without addition of black liquor. Differences in the functional group were depicted within ten days HRT for both conditions. The results of this work could be used as a basis to enhance the possibility of anaerobic digestion in treating the chemical pulping wastewater which is initially known difficult to degrade biologically.

Keywords

POME, black liquor, anaerobic digestion, thermophilic, COD, FTIR

1. INTRODUCTION

Malaysia is the world largest producer and exporter of palm oil. Approximately 13.98 million tonnes of crude palm oil (CPO) were produced in the year 2004 which increased by 4.7% from 13.35million tonnes in the year 2003 [1]. POME is considered as one of the most polluting agro-industrial residues due to its high organic load. The three main sources of POME are sterilizer condensate, hydrocyclone waste and clarifier sludge. The mixed POME is characterized by low pH (average 4.0), high chemical oxygen demand COD (60-90 g/L) and high suspended solid SS (20-40 g/L). For a well-controlled conventional oil palm mill, about 0.9 m3, 0.1 m3 and 1.5 m3 of sterilizer condensate, clarifier sludge and hydrocyclone waste are generated for each tonne of crude palm oil produced [2].

The biological ponding system is developed rapidly as a typical POME treatment system in Malaysia. This system consists of deoiling ponds, anaerobic, facultative and aerobic ponds. The anaerobic digestion systems are being increasingly used in wastewater treatment especially in agro-industry because they do not require high energy demanded as in aerobic biological treatment, produce less waste sludge and they can be easily restarted after months of shut down . The potential of producing methane, a biogas as a by-product make this method even more attractive.

Examples of various POME treatments were presented. POME treatment using membrane technology showed a reduction in turbidity, COD and BOD up to 100%, 98.8% and 99.4% respectively [4]. Two-stage up-flow anaerobic sludge blanket system could work efficiently up to 30g/liter/day COD whilst methane yield and COD reduction greater than 90% [2]. COD removal efficiencies greater than 94% obtained in single stage anaerobic tank digester and single stage anaerobic ponding system after 10 days of retention time [5]. A work carried out [6] showed COD removals higher than 90% in both anaerobic filter and anaerobic fluidized bed reactor at loading of 10 g/liter/day. 88% COD removal was obtained with 55h HRT using attached growth on a rotating biological contactor [7].

Pulping is the largest source of pollution in the paper making industry especially chemical pulping which generates high-strength wastewater [8]. The pulping wastewater is called black liquor contains high pH, COD, and dark in colour. In the present study, the anaerobic digestibility of POME with and without addition of black liquor was studied in semi-continuous single stage digester reactors with 5 and 10 HRT. The system performances were evaluated by COD removal.

2. MATERIALS AND METHODS

2.1 Samples

The POME used in this study was obtained from Malaysia Palm Oil Sdn Bhd. The samples were collected in 5L container and refrigerated. The black liquor (BL) derived from the chemical pulping of palm oil empty fruit bunch was collected from Division of Bioresource, Paper and Coating in School of Industrial Technology, USM.

2.2 Start-up and digestion condition

A total of four reactors with working volume 1000 ml each were used to study the anaerobic digestibility of POME at thermophilic temperature (55°C). Two reactors for raw POME with black liquor (A and B) and two reactors for POME as control (C and D). The reactors were seeded with digested POME from the anaerobic pond of above palm oil mill. The pH in each digester was controlled to an optimum pH range (6.8-7.8) by adjusted the pH with sodium bicarbonate $NaHCO_3$ (39g/L) and 1:1 hydrochloric acid HCl. Mixed liquor volatile suspended solid (MLVSS) analysis was carried out three times a week to monitor the microbial growth inside the digesters. After 100 days of acclimation, digestion of POME (as control) and POME with addition of black liquor (2.5%, 5%) was carried out at 5 and 10 days HRT. The substrates were purged with nitrogen gas prior to fed semi-continuously by means of a peristaltic pump. The reactors were kept at 55°C in water bath. Six runs of three set experiments were carried out in this study and there was a week of rest time within each run. Each set with two replicates in two reactors was carried out simultaneously.

2.3 2Analytical methods

The effluent COD from the digester was analyzed daily during the digestion period for each run experiment while the MLVSS was analyzed three to four times per run of experiment. COD in both the feed and effluent samples, MLSS and MLVSS were determined according to the Standard Methods [9].

2.4 Statistical Analysis

The effects of black liquor added on POME anaerobic digestibility were analyzed using two-way analysis of variance (ANOVA). Two-way ANOVA was used to detect any significant differences at $P = 0.05$ in effluent COD. All data were analyzed by SPSS (Statistical Package for Social Science) for Window Release 12.0 using an IBM Pentium PC.

3. RESULT AND DISCUSSION

3.1 pH trend during start-up and degradation process

Figure 1 shows the pH trends of reactors for raw POME with black liquor (A and B) and reactors for control (C and D) along the acclimation and degradation periods. The pH in each reactor was adjusted to a range of 6.8 to 7.8 to prevent methanogenesis inhibition. The lower pH during the start-up indicated that acidogenesis occurred where the substrates were hydrolyzed to form organic acids. The drop in pH directly caused the instability of the digesters [10]. A stable anaerobic digestion process was occurred concomitantly with the pH increased along the process.

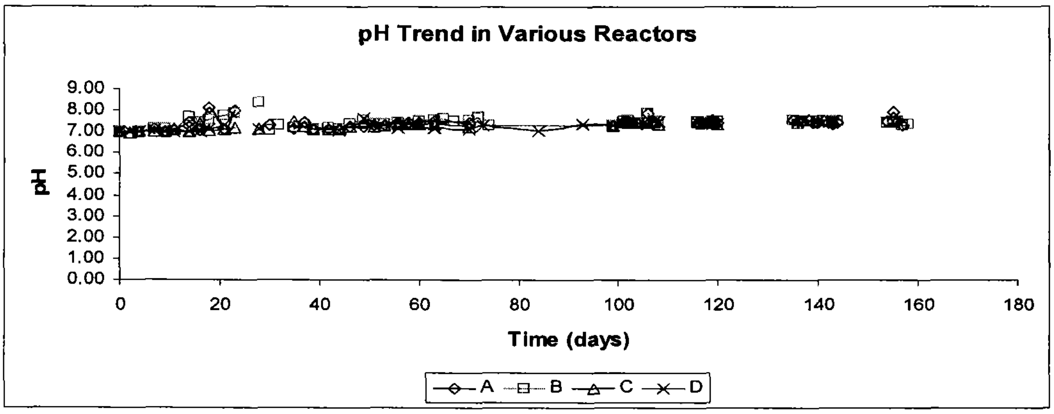

Figure 1 pH trends in various reactors

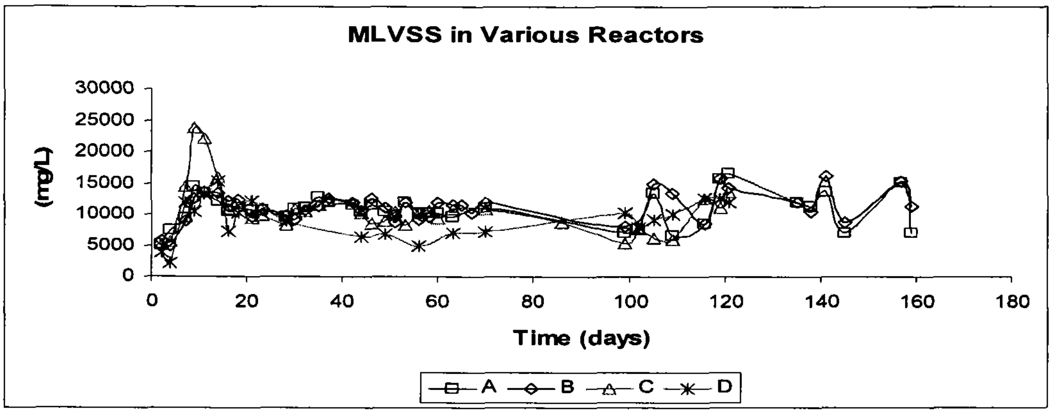

Figure 2 MLVSS concentration in various reactors

3.2 Microbial Growth During Start-up and Degradation Process

The biomass or microbial growth was measured by analyzing the MLVSS of mixed liquor sample in each reactor. The MLVSS was analyzed three times a week during acclimation period and three to four times during each run of digestion process. The MLVSS in various reactors was shown in Figure 2. The MLVSS in each digester was above 5000 mg/L.

3.3 COD Removal

The average feed COD for each run was tabulated in Table 1. The percent of COD removal in various reactors was tabulated in Table 2. Feed and HRT were found significantly (at 95% confidence level) affected the percentage of COD removal (Table 3).

Table 1 Average feed COD for different set experiments during degradation process with 5 and 10 days HRT

Feed	COD (mg/L)	
	5 HRT	10 HRT
POME (Control)	80570±5325	82370±8370
39 POME: 1 BL	82270±4236	81290±7925
19 POME: 1 BL	83440±3491	86694±4311

Table 2 Percentage of COD removal of the effluent in various reactors during degradation process with 5 and 10 days

Reactor	COD removal (%)	
	5 days	10 days
Control	83.3	87.7
Control	82.4	86.8
39 POME: 1 BL	76.9	76.3
39 POME: 1 BL	78.5	77.4
19 POME: 1 BL	73.4	80.3
19 POME: 1 BL	74.8	77.4

Table 3 P value denotes the significant differences among feed and HRT on COD removal by the Two-way ANOVA at P = 0.05.

Factors	COD Removal
Feed	0.000
HRT	0.006
Feed*HRT	0.023

Figure 3(a), (b) and (c) shows the effluent COD in various types of reactors for 5 HRT and Figure 3(d), (e) and (f) shows the effluent COD in various types of reactors for 10 HRT. The anaerobic microbial hydrolyzed the substrates into readily solubilized organic acids which can be easily consume by methanogenic to transform it to water, biomass, methane and carbon dioxide. After the acclimation period, the digesters were ready to perform a stable digestion process. The stability of the digestion process in each digester was shown in Figures 3(a) to 3(f). The daily effluent COD in each digester displayed the same trend with no big fluctuation thus indicated stable digestibility. The highest COD removal of 87% was achieved in control reactor at 10 days HRT. As for POME reactors with addition of black liquor, 79% COD removal was achieved in digester of POME with 5% black liquor at 10 days HRT as shown in Table 2. The COD removal efficiency of digesters with addition of black liquor was slightly lower than the digester without black liquor may because of some substances in black liquor such as lignin which is not easy to degrade. The COD removal efficiency for POME reactors with addition of 2.5% black liquor is 77% and 78% at 5 and 10 days HRT while there was a difference of 5% in COD removal efficiency in digesters with 5% black liquor at 5 and 10 days HRT. The digester with higher percent of black liquor may need longer HRT to achieve better COD removal. This was the same as for the totally POME digester achieved 83% and 87% COD removal at 5 and 10 days HRT.

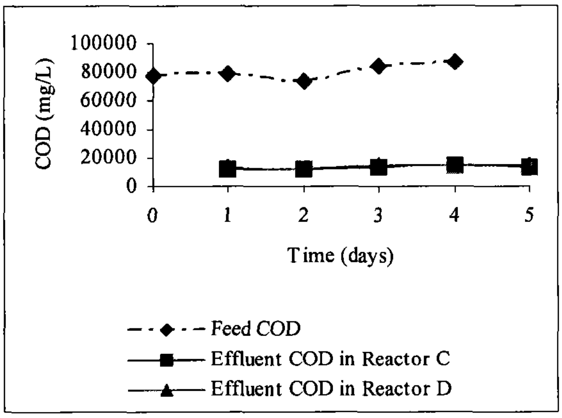

Figure 3(a) COD concentration of feed and effluent control reactors at 5 days

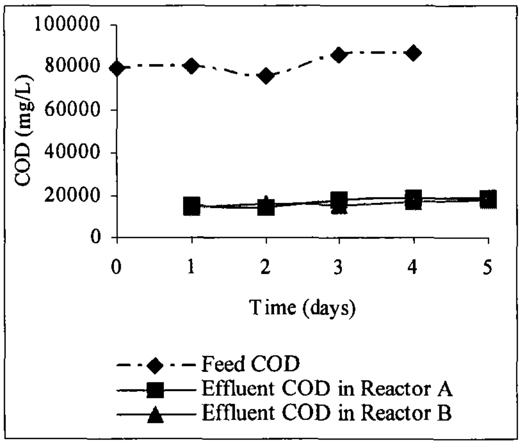

Figure 3(b) COD concentration of feed and in effluent in reactor A and B (39 POME: 1 BL) at 5 days

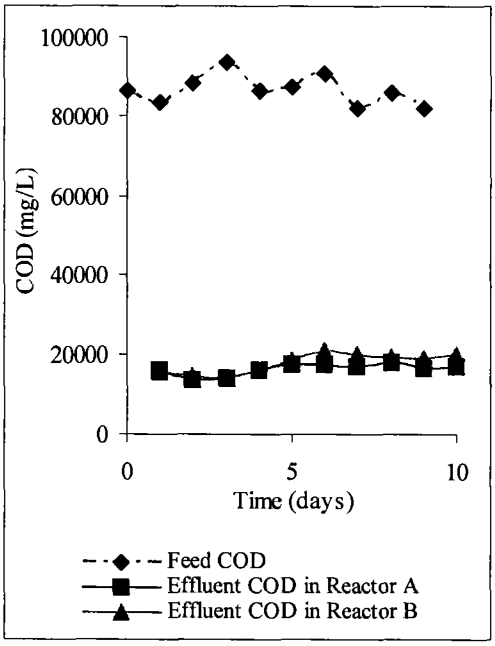

Figure 3(c) COD concentration of feed and effluent In reactor A and B (19 POME: 1 BL) At 5 days

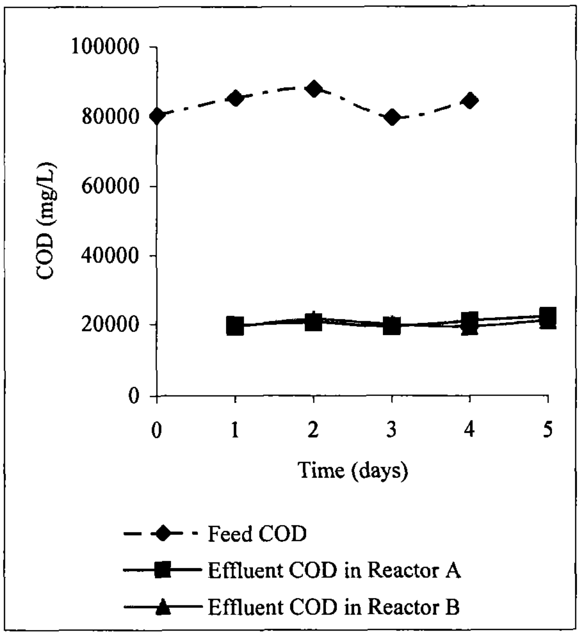

Figure 3(d) COD concentration of feed and effluent in control reactors at 10days

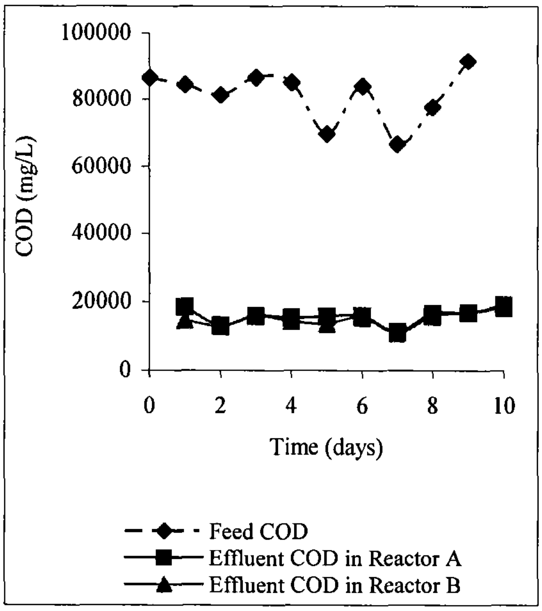

Figure 3(e) COD concentration of feed and effluent in reactor A and B (39 POME: 1 BL) at 10 days

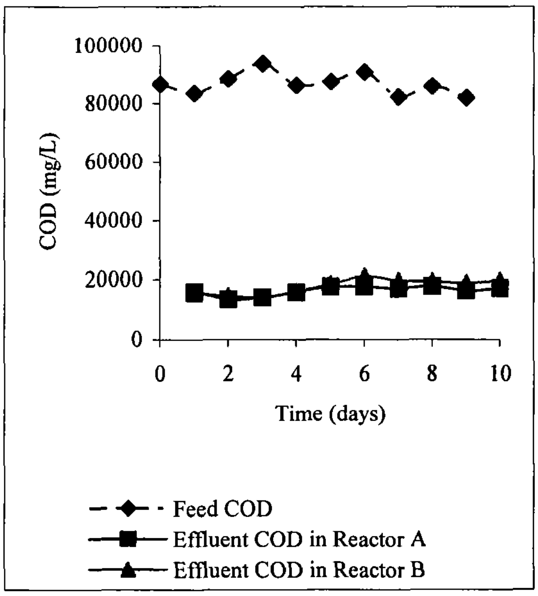

Figure 3(f) COD concentration of feed and effluent in reactor A and B (19 POME: 1 BL at 10 days

3.4 Data Analysis of POME Before Anaerobic Treatment

FTIR spectroscopy (4000-6000cm^{-1}) was used in this study to differentiate the functional group in the raw POME, raw POME with the addition of black liquor and the differences before and after anaerobic digestion at 55 °C under cultivation period of 10 days. Determination of functional group of the samples is reflected by the variations in their FTIR spectral patterns based on the correlation charts (Bellamy, 1966). Although raw POME with and without additional of black liquor have almost the same components but the quantity and distribution of the different functional groups vary. This statement is supported by Pokhrel and Viraraghavan (2004) where among the pulping processes, pulping generates a high-strength wastewater especially by chemical pulping. The wastewater contains wood debris and soluble wood materials. Besides that, wood consists of various compounds (lignin, carbohydrate and extractive) which are hard to biodegrade.

Figure 4 (4.1) and 5 (4.2) shows FTIR spectrum of raw POME and raw POME with addition of black liquor. Both of the samples obtained from the palm oil mills and no treatment has been carried out yet. Figures 6 (4.3) and 7 (4.4) shows the infra red (IR) spectra before and after anaerobic digestion of POME with black liquor operated under thermophilic (55°C) conditions.

All samples were analyzed using FTIR spectroscopy exhibit characteristic absorbance patterns at wavenumbers between 4000 and 1500 cm^{-1}. The results show that the sample has almost the same IR spectra with slightly differences. The IR spectrum of the samples, measured as liquid film, shows a strong band around 3300 cm^{-1} are strongly suggested that it is an OH group where mainly from the N-H stretching with contributions of the O-H stretching vibrations. Both of the group occurs in the hydrogen bonds and intermolecular H bonding (Cross and Jones, 1969).

For raw POME, the absorbance peaks around 2900-2800 cm^{-1} are mainly due to alkanes group (CH_2 and CH_3) asymmetric stretch whereas in the raw POME with addition of black liquor the peaks between these regions are not obvious. These functional groups are not obvious, since black liquors are concentrated wastewaters and it consists of lignin and other extractives from the wood which are hard to biodegrade (Pokhrel and Viraraghavan, 2004).

All Figures also showed an IR spectra for the region between 2110 and 2113 cm^{-1} which is from C≡C stretch. While the region of 1636 cm^{-1}, shows the functional group of Amide I with N-H stretching. The absorption bands around 1600-1700 cm^{-1} is originates from the C=O stretching vibration of the amide group weakly coupled to the N-H bending and the C-N stretching vibrations (Lefèvre and Subirade, 2001). Table 4 shows the major absorption band in the IR spectra for both raw POME and raw POME with the addition of black liquor.

Table 4 Major absorption in infrared spectra of raw POME and POME with black liquor added

Peak No.	Frequency (cm^{-1})	Definition of the Spectral
1	3345.89-3360.57	O-H and N-H group stretching vibration
2	2926.75	CH_2 asymmetric stretch
3	2857.34	CH_2 symmetric stretch
4	2110.48-2113.43	C≡C stretching
5	1636.00-1636.15	Primary amide with NH_2 stretching

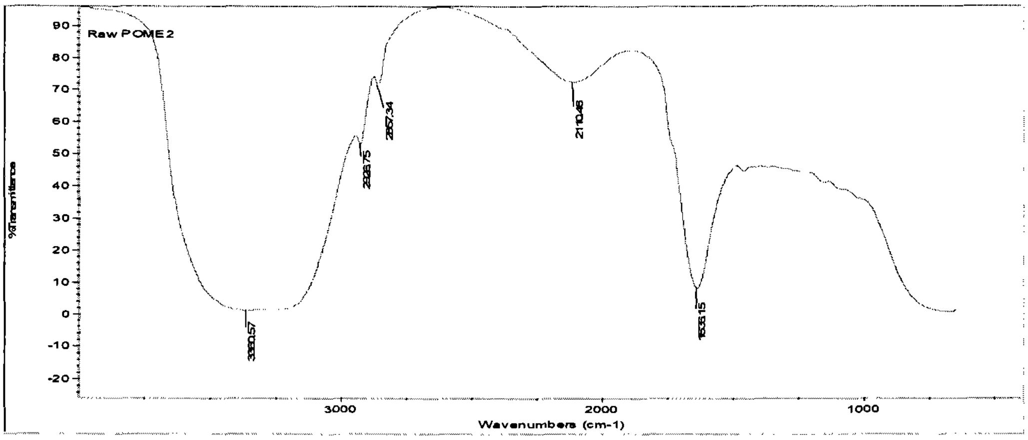

Figure 4 IR spectra of raw POME

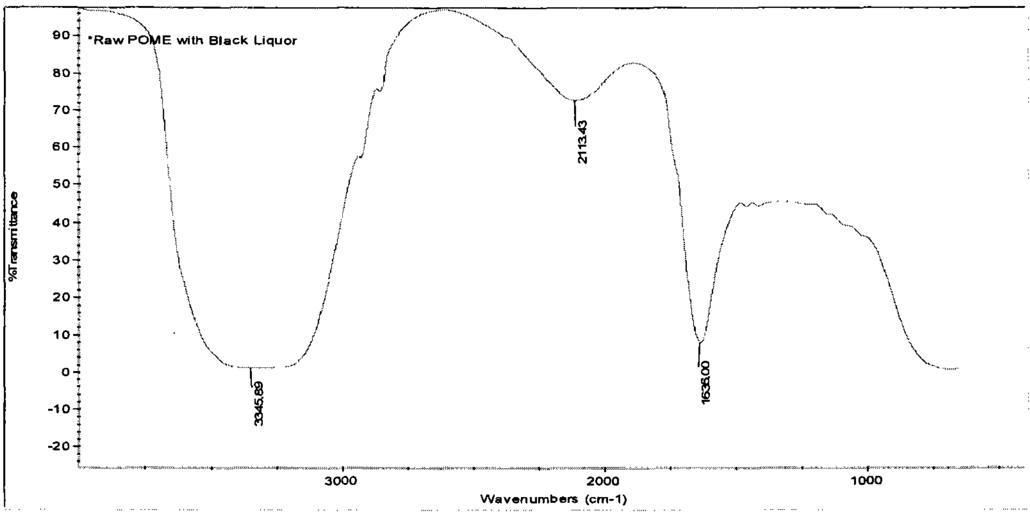

Figure 5 IR spectra of raw POME with black liquor

3.5 IR Spectra of Anaerobic Treatment under Thermophilic Conditions

As for the anaerobic digester cultivated for 10 days HRT at 55 °C, both Figure 6 and 7 represents the functional group of digested POME with black liquor added. The results shows almost no differences of both in functional group in before and after anaerobic treatment except there is a region around 1360 cm^{-1} exist in the IR spectra for before anaerobic treatment but absence after undergoing anaerobic digestion for 10^{th} day retention time. The region around 1360 cm^{-1} shows there is an alkenes group (C=C). The absence of this alkenes group after anaerobic digestion is because the wastewater undergoes hydrolysis and acetogenesis processes. According to Liu et al. (2004), hydrolysis process is the first step in anaerobic digestion of organic matter. In hydrolysis process, organic polymers was broke down into simpler products and the resulted product was further used in acetogenesis process. In acetogenesis process, the obligate hydrogen-producing acetogenic bacteria convert the resulted product into acetate, carbon dioxide and hydrogen.

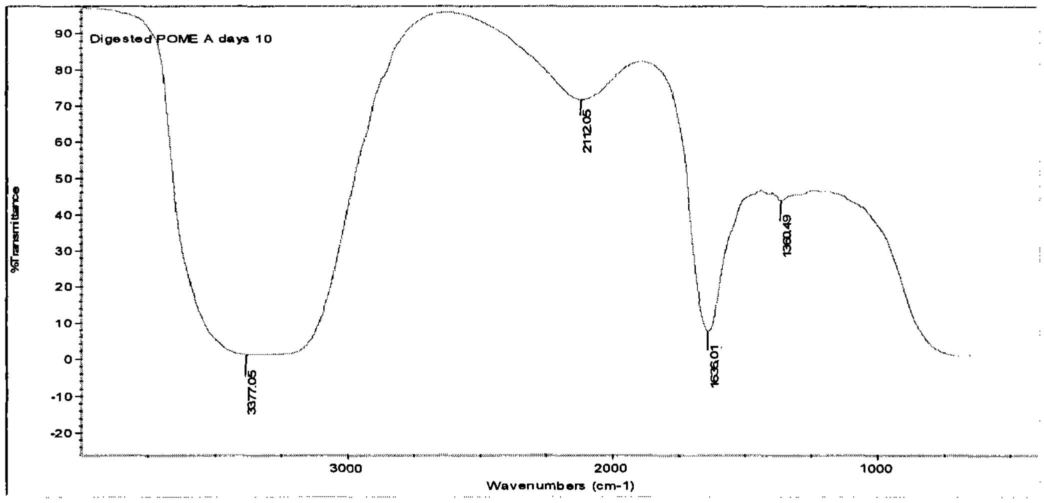

Figure 6 IR spectra of POME with black liquor on day 1 at 55°C (before anaerobic digestion)

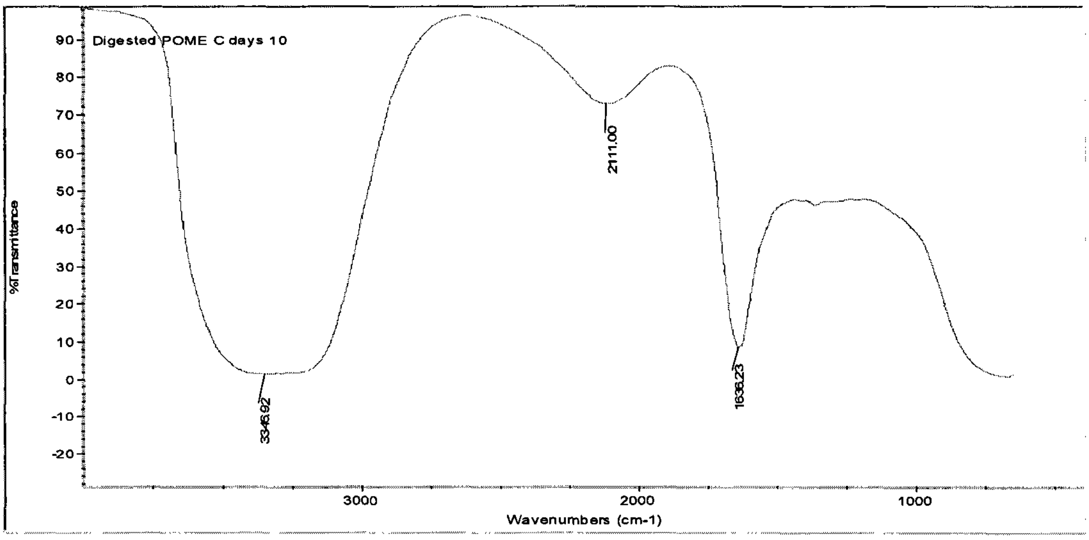

Figure 7 IR spectra of POME with black liquor on day 10 at 55°C (after anaerobic digestion)

A correlation of the various method discussed earlier can be obtained through FTIR results obtained for mesophilic temperatures. From the results obtained showed that during the 10th day retention time, the microorganisms are in acclimatization period and most of the organic and inorganic substances in POME are not completely degrade. Due to the slow growth rate of mesophilic anaerobic bacteria under mesophilic conditions, thus 10th day retention time is not sufficient to stabilize the wastewater. This can be represented in COD and BOD concentration chart against retention time.

The thermophilic anaerobic digestion process was found to be the most suitable condition for treating POME compared to mesophilic anaerobic digestion. This is due to the reduction efficiency for COD and BOD is higher at this temperature. The COD reduction efficiency for the digester with the addition of black liquor and without black liquor is 64.10 % and 80.01 %, respectively. Under mesophilic conditions, the COD reduction efficiency achieved by both digesters was 25.1% and 36.53%. Whereas, BOD reduction efficiency for both the digester 51.0 % and 68.12 % under thermophilic temperature which is higher if compared to BOD reduction efficiency under mesophilic temperatures (15.0% and 50.74%). From the result, it is evident that the anaerobic digestion process yield higher efficiency at thermophilic temperature.

Fourier Transform Infrared (FTIR) spectroscopy was also used to identify the functional group for the thermophilic and mesophilic anaerobic digestion for treating POME. The results of functional group available in IR spectra between 4000-6000 cm-1 and it can be used to differentiate the functional group in raw POME, raw POME with black liquor, before and after the anaerobic digestion treatment.

4. CONCLUSIONS

In this study it could be concluded that, feed and HRT were significantly affect the performance of POME anaerobic digestion. The addition of black liquor slightly affected the POME anaerobic digestion. The COD removal up to 79% in digesters with addition of 5% black liquor indicated that black liquor was treated by anaerobic digestion. The anaerobic digestion of POME with black liquor can reduce the environmental impact by reuse the black liquor.

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