TREATMENT AND ENHANCED DEGRADATION OF PETROCHEMICAL WASTEWATER BY CONTINUOUS STIRRED TANK REACTOR

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ABSTRACT

Currently, the world is facing two coexisting problems-1) the proper management of wastes generating from the industrial sectors, and 2) the scarcity for novel resources of gasoline to meet up energy demand of civilization. Anaerobic co-digestion, a sustainable green technology presents an outstanding opportunity both for energy conversion and pollution control. It has a wide variety of applications treating numerous wastewaters such as agro-agricultural, industrial, municipal, domestic sewage etc. Therefore, it has become a core method with meticulous attraction treating organic wastes on account of its economic benefits of energy generation. The continuous stirred tank reactor (CSTR) can be defined as a sealed-tank digester equipped with mixing facility. Chemical pretreatment coupled with anaerobic co-digestion technology was applied on petrochemical wastewater using CSTR focusing on enhanced hydrolysis and methanogenesis. Particularly, batch experiments were performed, with applied H_2O_2 doses of 0.5, 1 and 1.5% for contact times of 5, 10 and 15 min. Results revealed that 1% H_2O_2 dose (1.0mM Fe^{3+}) for 5 min exposure elevated biodegradability index (BOD/COD) up to 35%. Catalase activity scavenged the toxicity on microbes. Subsequently, batch experiments were employed, with various mixing proportions of petrochemical wastewater (PWW): dairy cattle manure (DCM): beef cattle manure (BCM), such as 25: 37: 38, 40: 30: 30, 50: 25: 25, 60: 20: 20, and 75: 12: 13. Results revealed that PWW: DCM: BCM ratio (50: 25: 25) provided maximum methane production. Hence, CSTR was operated with this specific feed ratio. Effect of temperature and organic loading was also verified. Batch test operation was also performed for ammonium bicarbonate (NH_4HCO_3) dosing avoiding volatile fatty acid (VFA) accumulation. Specific dosing limit was selected up to 40 mg/L. A 10 mg/L of NH_4HCO_3 dosing was proved suitable. Although methane production is considered to get introverted by VFA accumulation leading to reactor instability during anaerobic digestion, the co-digestion of PWW together with BCM and DCM caused 50% enhancement in methane production, followed by a 98±0.5% reduction in chemical oxygen demand at 10 days hydraulic retention time. No VFA buildup was identified, demonstrating that reactors were not running at stress-overloading situations. In comparison with the digestion of PWW alone, methane yield increased by 50–60% under mesophilic conditions and 50–65% under thermophilic conditions due to co-digestion. This was induced by an optimum C: N ratio (30:1) of the feed stock ensuring microbial growth and buffering capacity. This study provides guidelines for kinetic analysis of the viability of transforming PWW to bioenergy.

ABSTRAK

Kini, dunia sedang menghadapi dua permasalahan utama iaitu: 1) pengurusan bahan buangan dari sector industri secara tidak sesuai, dan 2) ketidakcukupan sumber bahan bakar yang baru untuk memenuhi permintaan tenaga di seluruh dunia. Melalui proses ko-penghadaman secara anerobik, adalah merupakan satu cara untuk mengekalkan teknologi hijau yang menawarkan potensi yang tinggi pada kedua-dua aspek penukaran tenaga dan pengawalan pencemaran. Justeru, ia telah menjadi satu kaedah yang penting dengan kebolehan yang tersendiri dalam merawat sisa organik dan pada masa yang sama mampu untuk menjana tenaga yang boleh diperbaharui. 'Continous Stirred Tank Reactor' (CSTR) adalah merupakan tangki pemprosesan yang tertutup serta dilengkapi dengan bilah pengadun untuk meningkatkan lagi tindakbalas kimia. Pra-rawatan kimia serta teknologi ko-penghadaman anerobik ini telah diaplikasikan pada air kumbahan industri petrokimia menggunakan CSTR yang memberi pemfokusan pada hidrolisis dan metanogenesis. Secara khususnya, eksperimen secara berkelompok telah dijalankan, dengan menggunakan H_2O_2 pada dos 0.5,1 dan 1.5% dengan kawalan masa tindak balas 5,10, dan 15 minit. Keputusan menunjukkan 1% dos H_2O_2(1.0Mm Fe^{3+}) pada kawalan masa tindak balas 5 minit, kadar indeksi biodegradasi (BOD/COD) telah menunjukkan peningkatan sehingga 35% dan ketoksinan mikrob diserap kesan daripada tindakbalas katalase. Seterusnya, eksperimen berkelompok dijalankan dengan perbezaan kadar adunan air buangan dari industry petrokimia(PWW): baja lembu susu (DCM) : baja lembu daging (BCM), dengan kadar 25: 37: 38, 40: 30: 30, 50: 25: 25, 60: 20: 20, dan 75: 12: 13. Keputusan menunjukkan kadar PWW: DCM: BCM (50: 25: 25) memberikan hasil metana yang tertinggi. Seterusnya, CSTR telah di aplikasikan pada kadar imput yang telah dispesifikasikan. Perubahan suhu yang berbeza keatas muatan organic juga turut dikaji. Kajian operasi berkelompok juga telah di jalankan dengan meggunakan ammonia bikarbonat (NH_4HCO_3) yang mempunyai kadar dos yang optimum bagi mengelakkan berlakunya penggumpulan asid lemak yang mudah meruap. Kadar dos yang telah dipilih adalah sehingga 40mg/L dan dos yang telah dibuktikan keberkesanannya adalah10 mg/L NH_4HCO_3. Walaupun penghasilan metana boleh terhasil daripada penggumpulan asid lemak teruwap (VFA) yang boleh menyebabkan ketidakstabilan reaktor semasa AD, ko-penghadaman PWW bersama dengan BCM dan DCM akan menyebabkan 50% peningkatan dalam penghasilan metana yang mana diikuti dengan kadar pratusan penurunan 98±0.5% dalam penggunaan oksigen pada masa pengekalan hidrolik pada hari ke 10. Daripada kajian,VFA telah dikenalpasti tidak terhasil, rentetan reaktor tidak berfungsi pada tekanan yang berlebihan. Berbanding dengan penghadaman PWW, penghasilan metana meningkat sehingga 50-60% pada kondisi mesofilik dan 50-65% pada keadaan termofilik dan ini adalah disebabkan oleh proses ko-penghadaman.

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A	Cross-sectional area
AD	Anaerobic digestion
AFBR	Anaerobic fluidized bed reactor
AHMPR	Anaerobic hydrogen and methane production reactor
ASB	Activated sludge biomass
ASBR	Anaerobic sequencing batch reactor
ASCD	Anaerobic semi continuous digester
BCM	Beef cattle manure
BOD	Biochemical oxygen demand
BOD_5/COD	Bio-degradability index
BDOC	Biodegradable dissolved organic carbon
CA	Catalase activity
CBCTT	Chemical and biological coupled treatment technology
C/N	Carbon to nitrogen ratio
COD	Chemical oxygen demand
COD_{in}	Influent chemical oxygen demand
CSTR	Continuous stirrer tank reactor
DCM	Dairy cattle manure
DOC	Dissolved organic carbon
F/M	Food to micro-organism ratio

FAFBR	Flocculant-anaerobic fluidized bed bioreactor
FSAD	Full scale anaerobic digester
HRT	Hydraulic retention time
H_2O_2	Hydrogen peroxide
IBR	Integrative biological reactor
MSW	Municipal solid waste
OLR	Organic loading rate
OHP	Oxidation by hydrogen peroxide
PWW	Petrochemical wastewater
Q	Flow rate
SD	Standard deviation
SRT	Sludge retention time
SS	Suspended solids
TKN	Total Kjeldahl nitrogen
TN	Total nitrogen
TOC	Total organic carbon
TP	Total phosphorous
TSS	Total suspended solids
UASB	Upflow anaerobic sludge blanket
UASSR	Upflow anaerobic solid state reactor
VFA	Volatile fatty acid
VSS	Volatile suspended solids
˚ C	Degree Celsius

KM	Kilometer
min	Minute
cm	Centimeter
cm^2	Square centimeter
d	Diameter
g	Gram
H	Height
h	Hour
Kg	Kilogram
L	Liter
M	Micro mole
m^3	Cubic meter
V	Velocity
µ	Micro (10^{-6})
P	Phosphorous
N	Normality
TS	Total solids
NH_4HCO_3	Ammonium bicarbonate
MFBR	Mesh filter bioreactor
SAMR	Submerged anaerobic membrane reactor
SMAR	Self-mixing anaerobic reactor
SCR	Semi continuous reactor

CHAPTER 1

INTRODUCTION

1.1 INTRODUCTION

At starting of 21st century, the world is affronting environmental contingency of wastewater management and global warming, due to population rise, industrialization, solid waste generation, urbanization and unplanned waste management. Integrating these into whole generates huge untreated industrial and domestic wastewater which is carcinogenic to environment. Particularly, Wastewater generating from petrochemical industries is a complex mixture of polycyclic aliphatic and aromatic petroleum hydrocarbons (Shahrezaei et al., 2012, and Delia et al., 2010) in which aromatic portion cannot be easily digested by commonly practiced methods. Petrochemical wastewater, possessing much oxygen undermining potential (COD 1-60 g/L) as industrial sewage becomes conspicuous challenges to meet up the progressively strict environmental guidelines (Francine et al., 2012; Patel et al., 2002 and Parilti, 2010). The deficiency of wastewater management absolutely affects natural divergence of the aquatic ecosystems, disordering the elementary integrity of total ecosystems. So, the prevention of continuous pollution caused by petrochemical effluents is obligatory. Anaerobic digestion (AD) presents an outstanding opening for energy conversion and pollution minimization mutually (Shanmugam et al., 2009).

The conventional treatments include gravitational separation, centrifugation, ozonation, and wet oxidation, application of coagulants, flocculants, flotation, ultra filtration or sorption on organic minerals, advanced treatment process (Parilti, 2010 and

Monal et al., 2012). The anaerobic digestion (AD) system among all treatment options had been accepted as the fundamental one of a progressive mechanism for environmental safeguard (Latif et al., 2011). To meet up growing requirement for energy and financially-advantageous treatment strategy, AD system has become the motivation of universal consideration (Hanssan et al., 2001). In comparison with former technologies, the main benefits of AD system are minor sludge yield, minimum budget, great energy feedback and process severity. Besides, it provides an optimistic environmental influence accommodating waste management with net energy generation. The technology also permits the utilization of effluent as compost. Numerous researchers have been studied concerning anaerobic digestion since the last decade. Among them were those by Bipro et al. (2012); Paterakis et al. (2012); Rani et al.(2012); Chandra et al. (2012); Zhen et al. (2012); Xiao et al. (2012); Babu et al. (2010); Najafpour et al. (2006), and Borja et al. (1996). Nevertheless, despite these benefits, anaerobic digestion is not practiced widely in PWW treatment due to its slow reactions, leading to long hydraulic retention time (HRT), volatile fatty acid (VFA) accumulation, and poor process stability. Hence; this study on this basis is focused.

Anaerobic digestion is accomplished via three basic mechanisms; namely hydrolysis, acidogenesis and methanogenesis (Rasi et al., 2007, and Alrawi et al., 2011). Notable that hydrolysis is considered to be a rate-defining stage in AD; specifically, due to recalcitrant substrates. Fatty acids in wastewater have an inhibitory impact on many microorganisms, which makes biological degradation difficult (Ahmad et al., 2003, and Babu et al., 2010). Pretreatment might play a role in improving biochemical degradation efficiency (Chaiprapat et al., 2011). Many pretreatments aspire to solubilize or hydrolyze the compounds to improve degradability in biotic reactors. Those consist of physical dimension reduction, thermal hydrolysis, ultrasonic treatment, chemical treatment by acid or alkali, and ozonation and oxidation by H_2O_2. H_2O_2 is a versatile, vigorous oxidative agent that reacts via a hydroxyl radical mechanism with an oxidizing potential of 2.6V, which reduces chemical oxygen demand (COD), produces H_2O and CO_2, and enhances biodegradability of organic matters.

Even if there were widespread application of AD, the methane generation would be squat and related to elevated nitrogen and lignocellulose content (Mladenovska et al., 2003). Hence, co-digestion of pretreated PWW with beef cattle manure (BCM) and dairy cattle manure (DCM) could offer an efficient solution, with marked reduction in volatile fatty acid (VFA) accumulation and improved reactor stability. In this study, we focused on the consequence of various mixing proportions on methane generation latent and stability of continuous stirred tank reactor (CSTR) under different conditions.

A CSTR can be defined as a closed-tank digester equipped with mixing facility. Mechanical instigator renders much area of contact between substrate and microorganisms thus ameliorating gas production (Poh et al., 2009). Over and above feeding of furthermost anaerobic digesters are amalgamated to assure competent transmission of organic compound for the active bacteriological biomass, to discharge gas bubbles grabbed in the system and to avoid precipitation of heavier coarse substance (Ward et al., 2008).

1.2 CHEMICAL PRETREATMENT AND ANAEROBIC CO-DIGESTION IN CSTR

The application of H_2O_2 as an oxidizing auto catalyst is already proved treating halogenated hydrocarbon endures in waste water treatment (Muganlinskii et al., 1985; Adeyinka et al., 1996, and Adeyinka et al., 1997). To degrade various variety of hazardous wastes in situ chemical oxidation (ISCO) has been used as an encouraging inventive technique (ITRC, 2001, and ITRC, 2005). H_2O_2 oxidation mechanism might be made of a struck via OH radicals on the carbon-hydrogen chain of fatty acids. OH radicals possess muscular capability to breakdown the aromatic ring fixed to hydroxyl groups exists in fatty acids. These accelerate development of water-soluble complexes through cogitation of hydrogen and addition of oxygen atoms through contribution of ferrous or ferric ions. This process generates minor aliphatic compounds, resulting from infringement of lengthier hydrocarbon chains of fatty acids and lastly provokes mineralization of preliminary organic matters. In combination of biological treatment, make oxidation by hydrogen peroxide (OHP) an innovative alternative for advanced waste water treatment (Jeworski and Heinzle, 2000).

Habitually, in industrial effluents, fraction of digestible COD which may be symbolized by BDOC is relatively low (Tripathi et al., 2011). Hence, to enhance the treatment productivity, an evocative oxidant that enhances BDOC of raw wastewater is obligatory. H_2O_2 can transubstantiate several refractory organic compounds to biodegradable ones, i.e., BDOC that can be eliminated simply via biodegradation. Primitive researchers reported that H_2O_2 might enhance biodegradability of organic waste products producing most effective intermediates like OH- radicals in presence of Fe2+ (Long et al., 2007, and Babu et al., 2010). Scientists reported that OH radicals produced via Fenton-like mechanism are proficient of oxidation of plentiful organic matters, including diesel (Kong et al., 1998; Ferguson, 2004; Yeh et al., 2008, and Prabir et al., 2011), chlorinated ethylenes (Yeh et al., 2003), aromatic hydrocarbons (Yeh et al., 2008, and Ahad et al., 2008), 2,4-dichlorophenol (Zhou et al., 2008), and 4-chlorophenol (Zhou et al., 2008).

Catalase, an antioxidant can break down of H_2O_2 into water and oxygen (Milton, 2008). To split H_2O_2 into molecular O_2 and H_2O, Catalases use a two-electron transfer mechanism (Guwy et al., 1999). One unit of catalase activity corresponds to disintegration of 1 µmole of H_2O_2 per minute at standardized conditions, providing a gas flow of 11.2 µl of O_2/min at STP (Guwy et al., 1999). To neutralize H_2O_2 toxicity effect on activated microbial biomass catalase activity has been employed before anaerobic co-digestion.

Methane yield of AD system might be enriched by Co-digesting sewage sludge together with agro agricultural wastes or municipal solid waste (MSW) (Bolzonella et al., 2006; Gomez et al., 2006, and Romano and Zhang, 2008) and has shortly been studied (Alatriste-Mondragon et al., 2006). Moreover, co-digestion of cattle manure and MSW (Callaghan et al., 1999, and Hartmann and Ahring, 2005) provided to increase methane yield. A predominantly resilient cause for co-digestion of wastes is the appropriate fixation of carbon-to-nitrogen (C: N) ratio. The optimal C: N ratio of 25–30:1 is usually been utilized by microorganisms. Nonetheless C: N ratios may frequently be significantly lesser than this, for instance the C: N ratio of sewage sludge is around 9:1 (Kizilkaya and Bayrakli, 2005). Wastewaters can differ extensively in C: N values. The two-stage reactor through biomass retention has been investigated to be reflected the proficient of dependable performance having C: N ratios less than 20 certainly (Mata-Alvarez, 2002). The ideal C: N ratio may be achieved by Co-digesting low and high C: N ratio wastewater like as biomass. In a view to increase methane production compared to the conventional method co-digestion has been chosen in this study.

Temperature plays a significant role as operational parameter for AD method. The effect of temperature on bacterial growth and degradation frequency may be demonstrated by Arrhenius equation (Batstone et al., 2002; Hao et al., 2002, and Siegrist et al., 2002). AD at thermophilic conditions presents numerous benefits like as enhanced reaction frequency and ameliorated bio-digestibility of organics (Rintala, 1997, and Kim et al., 2002). Noticeable that an alteration from mesophilic to thermophilic conditions is conducted by a remarkable (over 80%) and prolonged (over 4 days) reduction in methane yield because of acclimatization of methanogens to thermophilic state (Van Lier et al., 1992, and Visser et al., 1993). Nonetheless, mesophilic methanogens were exposed to bear short-range temperature rise (Speece and Kem, 1970 and Ahn and Forster, 2002) or sludge interchange between mesophilic and thermophilic digesters (Song et al., 2004). Therefore, both conditions were executed to study the performance of CSTR.

This study also proposes the application of ammonium bicarbonate (NH_4HCO_3), due to its buffering capability opposite to acidity throughout operational period and also to maintain bacteriological population balance. So, significant roles will be performed by NH_4^+ as the recommended microbial nutrient for nitrogen and buffering capability in an anaerobic reactor (Gerardi, 2003). Nonetheless, excessive NH_4HCO_3 concentrations create free ammonia toxicity particularly for methanogensis (Sawayama et al., 2004).

Hence, the optimal dosage for NH_4HCO_3 applied as supplementation in AD system should be investigated.

1.3 PROBLEM STATEMENT

Anaerobic digestion is being used effectively in the numerous fields such as petrochemical industries, POME industries, distillery industries, olive-oil industries, piggery wastewater, dairy wastewater, fishery wastewater, municipal wastewater, and slaughterhouse wastewater to protect environmental pollution and energy generation as well (Latif et al., 2011). Particularly for petrochemical wastewater investigations reported that after lengthy acclimatization, aldehydes, acids, alcohols, and esters might be employed for methane yield (Chen et al., 2007). The existence of hydroxyl groups and a growing carbon chain decreased the toxicity of complexes to the digester microflora. Adaptations to aromatic ring and double-bond compounds are time consuming. The most common design applied in AD is continuous stirred tank reactor (CSTR). The major problem of the reactor is prolonged retention time and minor gas yield. Presently, anaerobic digestion is facing following impairments:

i. sluggish reactions, that need lengthier HRT and indigent system stability in commonly practiced designs
ii. operational failure is caused by an abrupt drop of pH & accumulative concentration of VFA
iii. insufficient buffering control & distraction of bacterial population stability between non-methanogen & methanogen to transform carbonaceous organic to CH_4

Patel et al. (2001) anticipated an approach for acidic petrochemical wastewater treatment in single and multi-chamber fixed film anaerobic reactor. The objective was to compare the performance of fixed film anaerobic reactor with single and multi-chamber strategies. They separated acidogenesis from methanogenesis in order to achieve better project stability and increased biogas production. But ultimately their approach outstripped in a real sense due to high volatile fatty acid (VFA) accumulation, process instability and low methane production. Moreover, multi-chamber strategy was not successful treating petrochemical wastewater. Single stage strategy proved better performance over that of multi-chamber in terms of COD removal and CH_4 production. Nonetheless, the sustaining problem with anaerobic treatment remained unsolved.

Patel et al. (2002) introduced an approach treating petrochemical wastewater in anaerobic up-flow fixed-film reactor. The goal of their method was to investigate the effects of temperatures and organic loading rates on bio-methane production of the same. They selected temperature range from mesophilic to thermophilic and organic loading rate from 3.60-27.20 kg COD/ m^3 d. It took a prolonged startup period of 80 days. However, this strategy achieved 98% COD removal and 0.37 m^3/ kg COD d at 15 days HRT. Then fact was that at organic loading rate of only 6.66 kg COD/ m^3 d the total system was failed due to vigorous VFA accumulation. Ultimately the sludge washed out from reactor. So, this approach was also unable to solve the burning problem with anaerobic digestion process.

In 2006, Jafarzadeh et al. studied petrochemical wastewater treatment in anaerobic Hybrid reactor. Two stage operations in mesophilic condition were implemented. At the end of 39 weeks when the acclimatization of the microbs to the petrochemical wastewater was done, COD reduction achievement was only 70% at HRT of 18 days and OLR of 2 kg/ m^3 d. That was an unproductive result again. So, pollution control with energy production strategy of anaerobic digestion process still facing stability challenge and retention time challenge.

1.4 OBJECTIVES OF RESEARCH

This research focuses on the anaerobic co-digestion of petrochemical wastewater with beef and dairy cattle manure in CSTR having chemical pretreatment strategy. Anaerobic co-digestion is proposed based on the biodegradation technique to avoid slow reaction, prolonged startup, volatile fatty acid accumulation, reactor failure, sludge washout and to enhance methane production capability of CSTR. This research framework combines chemical and biological treatment system much effectively. It can be applied in petrochemical industries, POME industries, distillery industries, olive-oil industries, slaughterhouse wastewater etc. Therefore, it meets up the energy demand cost effectively.

The objectives of this research are projected below:

i. ‘To study the effect of H_2O_2 pretreatment and biological co-digestion on continuous stirred tank reactor during petrochemical wastewater treatment’
ii. ‘To reduce the VFA accumulation during anaerobic co-digestion of Petrochemical wastewater treatment using continuous stirred tank reactor’
iii. ‘To enhance methane production during anaerobic co-digestion of Petrochemical wastewater treatment using continuous stirred tank reactor’

1.5 SCOPES OF RESEARCH

The scopes of this research are as follows:

i. Application of chemical & biological coupled treatment technology which will investigate effective H_2O_2 dosing, enhancement in biodegradable dissolved organic carbon (BODC), Catalase activity activation neutralizing H_2O_2 toxicity effect prior to anaerobic digestion, enhancement of biodegradability index, COD & TOC removal achievement.

ii. Application of co digestion method which will investigate the balance of nutrients at an appropriate C: N ratio and a stable pH necessary for enhanced CH_4 yield the effect of temperature and organic loading rate on the rate of CH_4 generation & reduce HRT, reduction in VFA accumulation.

iii. Application of supplementation of ammonium bicarbonates which will investigate the optimal NH4+ dosing ensuring the process stability of anaerobic digestion enhancing CH4 production as well.

1.6 ORGANIZATION OF THESIS

The current research has been organized to provide features on the particulars, observations, logics, interpretations and ways to meet the objectives. Chapter 1 commonly provides the momentary background of anaerobic degradation, problem statement, objectives and scope of the research. Chapter 2 describes the literature review of H_2O_2 pretreatment, biodegradable dissolved organic carbon formation, catalase activity, anaerobic degradation and anaerobic co-digestion. Chapter 3 explains the framework of the proposed chemical and biological coupled treatment technology (CBCTT). Different stages and mechanism of the same and definition of the notation have been described. Chapter 4 reports the implementation of CBCTT framework and compares the performance with other techniques. The conclusions of current research are summarized in Chapter 5. Ideas and recommendations for future work have also been projected in this chapter.

CHAPTER 2

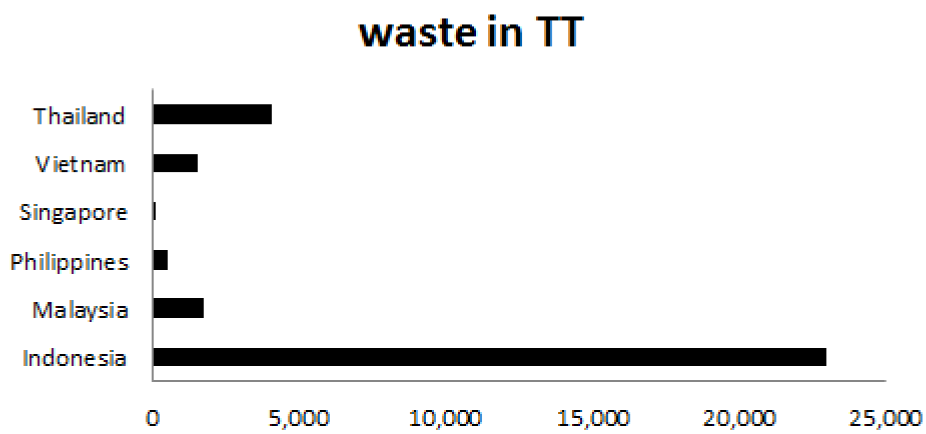
LITERATURE REVIEW

2.1 INTRODUCTION

This chapter brings out a short review on fundamental concept of chemical and biological coupled treatment technology treating petrochemical wastewater. The review covers characterization of petrochemical wastewater, effect of chemical pretreatment and catalase activity, working principle of anaerobic digestion, different types of anaerobic reactor setup for enhanced biogas production, assessment of reactor performance, investigation of factors affecting system off-set and model development on anaerobic co-digestion process. The need of pretreatment and working principle of anaerobic digestion is obligatory to understand the back ground of anaerobic system. The contribution of catalase activity is a must to bridge the gap between chemical and biological combined treatment technology. In case of anaerobic reactor setup, emphasis will be provided to continuously stirred tank reactor (CSTR) and high rate anaerobic reactors with their benefits and limitations. This will explain the reason why chemical and biological treatment has been coupled together. Investigation of factors affecting system off-set will highlight the effect of temperature, organic loading, hydraulic retention time, VFA accumulation, pH, C: N ratio. This investigation will help a lot to analyze the experimental out comes. An abridged review on model construction of chemical and biological coupled treatment technology will illustrate a fundamental overview for the construction of mathematical modeling projected in this research.

2.2 PROPERTIES OF PETROCHEMICAL WASTEWATER

Malaysia has the world's 23rd crude oil reserves inclusive condensates (5.52 billion barrels). Malaysia also possesses the world's 14th natural gas reserves (14.66 billion barrels). The 2010 projected hazardous waste generation per annum of particular ASEAN Countries is provided in Figure 2.1 (source: Hernandez, 1993; UNEP, 1994; United Nations, 1995 and Nelson, 1997).



	Indonesia	Malaysia	Philippines	Singapore	Vietnam	Thailand
Series1	23,000	1,750	530	135	1,560	4,120

Figure 2.1: 2010 projected hazardous waste generation per annum of particular ASEAN Countries

Malaysia stated approximately 345 thousand tons (TT) of hazardous wastes accumulation in 2000. Out of that particularly, 24 % comes from chemical, 6% comes from gas industry (UNEP, 2002). Organization of Petroleum Exporting Countries (OPEC, 2011) reported that, energy needs has risen from 55 million barrels of oil equivalent/day (mboe/day) in 1960 to 227 mboe/day in 2008. Energy needs will be increasing with economy expansion, the world population growth, and living standards improvement.

Wastewater discharged from petroleum refinery comprising of excessive aliphatic and aromatic petroleum hydrocarbons that might cause vigorous pollution on earth and water bodies (Dsikowitzky et al. 2004a; Dsikowitzky et al. 2004b, and Shahrezaei et al. 2012). Refineries produce contaminated effluent, comprising COD concentration about 11000 mg/L, pH ranges between 2.5-8.75, total fatty acid concentration approximately 9000 mg/L comprising (m/v) acetic acid- 70%, propanoic acid- 16%, isobutyric acid- 2.5%, n-butyric acid- 7-9%, iso-valaric acid- 1%, n-valaric acid- 2-3% (Britz et al., 1983; Patel et al., 2002, and Parilti, 2010). According to the previous researchers report physic-chemical properties of petrochemical wastewater are projected below (Table 2.1):

Table 2.1: Physico-chemical characteristics (PWW)

Parameter*	**Patel et al. (2002)**	**Gasim et al. (2010)**
pH	2.5-2.7	6
BOD	30-32	-
COD	50-60	1.06
TS	0.02-0.3	0.19[a]
SS	-	0.06[a]
TN	0.05-0.212	0.023
Oil and Grease	0.012-0.013	-

* Entire parameters are in g/L except pH

The amount and properties of effluent produced depend on the system configuration (Shahrezaei et al., 2012).