Paper ID # 28 Addition of Cow Urine and Cheese Whey as Nitrogen Source on the Biogas Production from Cow Manure

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Biogas is a potential renewable energy source due to its high methane content and caloric value. Cow manure is a good substrate to produce biogas. In this research work the addition of nitrogen source from cow urine and cheese whey in the production of biogas from cow manure was observed. The purpose of this research was to investigate the effect of the addition of the nitrogen sources to the quantity and the quality of biogas generated. The experiments were conducted in batch reactor and substrate composition was varied. The biogas and methane yield and some volatile fatty acids concentration were used as the main observed parameters, while analysis was also performed to investigate the pH change and COD removal in the residual substrate. The research result showed 37.9% COD reduction was reached. The obtained biogas yield were in the range of 13.7 – 150.4 liter/(kg VS), while the methane yield was in the range of 1.23 – 14.92 liter/(kg VS). The volatile fatty acids detected in the biogas, which consist of butyric, acetic and propionic acid, showed a low concentrations and found the concentration of acetic acid is the highest. A relatively high decrease in pH was observed in the mixture with relatively high C/N ratio.

Keywords: anaerobic; biogas; cow manure; cow urine; cheese whey

1 Introduction

About 13 TW of energy was consumed all over the world recently, in which approximately 80% portion comes from burning of fossil fuels. The over dependency on the fossil fuels poses risks such as depletion of fossil fuel resources, excessive greenhouse gases emission, and global climate changes due to increasing the CO_2 levels in the atmosphere. The trends regarding the CO_2 levels and the atmospheric temperature was shown on Table 1 [1,2]. This situation have worldwide increased people's attention and effort, in order to achieve sustainable development, utilize renewable resources, reduce energy consumption, and produce efficient energy. Biogas become an alternative clean energy with great potential for energy conservation. Biogas is referred as a gas produced by microbial degradation of organic matter through anaerobic process. The potential of biogas as one of the alternative energy source related to the high content of methane that has implications for the high calorific value. Biogas is colorless, relatively odorless and flammable. It is also stable and non-toxic. It burns with a blue flame and has a calorific value of 4500–5000 kcal/m3 when its methane content ranges from 60% to 70% [3]. Anaerobic digestion of animal wastes for production of biogas is a widely studied. It has been one of the most widely used processes for treating these wastes and represents an attractive method for biogas production. Properly functioning biogas systems can yield a whole range of benefits for its applications, including production of heat, light, and electricity, transformation of organic waste into high-quality fertilizer, improvement of hygienic conditions through reduction of pathogens, reduction of work for firewood collection and cooking, and environmental advantages through protection of soil, water, air, and woody vegetation [4].

Table 1 Trends of atmospheric CO_2 and average temperature

Year	Atmospheric CO_2 concentration (ppm)	Average atmospheric temperature (^oC)
1800	280	15
1870	280	15
1950	305	15.2
1970	325	15.2
1988	350	15.5
2000	360	15.8
2006	375	16.0
2050*	~550	Up to 17.2
2100*	Up to ~800	Up to 19.2

*: Forecasted values

Domestic biogas plants convert animal manure and various other organic materials into combustible methane gas known as biogas. Biogas consists primarily of methane (CH_4) and carbon dioxide (CO_2). The methane is a valuable product as it is an efficient energy carrier that has a wide range of uses, from simple gas stoves for cooking to lamps for lighting. The slurry left over from this process is easily collected and can be used as organic fertilizer to improve crop yields. The CO_2 produced is equivalent to the amount of CO_2 captured when the biomass was created. Biogas is therefore a CO_2 neutral source of energy i.e. a renewable energy [5]. The uncontrolled decomposition of organic material can result in large-scale contamination of soil, water, and air. Decomposition of one metric ton of organic material can potentially release 50–110 m^3 of carbon dioxide and 90–140 m^3 of methane into the atmosphere. If the organic component of the solid waste is converted into energy through anaerobic digestion, it will reduce the adverse impact on the environment and contribute to reduction in consumption of fossil fuel [6]. In this research work the addition of nitrogen source from cow urine and cheese whey in the production of biogas from cow manure substrate was observed. The objective of this research was to investigate the effect of the addition of the nitrogen sources to the quantity and the quality of biogas generated.

2 Materials and Methodes

The cow manure was obtained from cows fed with rice straw, and the urine was obtained from the same cow. Both were taken from Babat District, East Java, Indonesia. Meanwhile, the whey was taken from yogurt and mozzarella cheese factory located in Batu District, East Java, Indonesia. The process of anaerobic digestion was carried out in 2 liter bottle schott which was connected to respirometer using silicone hose. The respirometer consisting of a combination of 2 liters and 0.5 liter graduated plastic cylinders. A gas drain hole, which was used to release the gas when the respirometer was fully charged, was installed at the base of the 0.5 liter cylinder. This hole was closed with a rubber stopper. The 2 liter cylinder was filled with water and then the 0.5 liter graduated cylinders was placed upside down in the 2 liter cylinder. A thermometer was fitted inside the respirometer to observe the temperature of the gas. Meanwhile, the ambient temperature was observed by install a thermometer in the room where the anaerobic digestion was held. Equipment arrangement of the anaerobic digester used in this work was shown in Fig. 1. In this work the C/N ratio of the substrate was varied by applying a different composition of the substrate which was a mixture of cow manure, cow urine, cheese whey, and water. Analysis of total carbon (Walkley & Black method) and total N (Kjeldahl method) were performed to measure the C/N ratio in the substrate.

Figure 1 Equipment arrangement of the anaerobic digester used in this work

The measured parameters include: biogas volume, analysis of methane gas content, and analysis of VFA (Volatile Fatty Acids: butyric acid, acetic acid, and propionic acid) content in gas, COD (Chemical Oxygen Demand) removal, and pH. All measurement we carried out with two replications and the average value was used.

3 Theory and Principles of Anaerobic Digestion

Anaerobic digestion in biogas plants is an alternative way to handle bio-waste, which includes animal and human waste. Anaerobic digestion produces methane (biogas), reduces odor, and the digested residues may be used as fertilizer in agriculture [7]. The anaerobic biological conversion of organic matter occurs in three steps. The first step involves the enzyme-mediated transformation of insoluble organic material and higher molecular mass compounds such as lipids, polysaccharides, proteins, fats, nucleic acids, etc. into soluble organic materials, i.e. to compounds suitable for the use as source of energy and cell carbon such as monosaccharide, amino acids and other simple organic compounds. This step is called the hydrolysis and is carried out by strict anaerobes such as Bactericides, Clostridia and facultative bacteria such as Streptococci. In the second step, acidogenesis, another group of microorganisms ferments the break-down products to acetic acid, hydrogen, carbon dioxide and other lower weight simple volatile organic acids like propionic acid and butyric acid which are in turn converted to acetic acid.

In the third step, these acetic acid, hydrogen and carbon dioxide are converted into a mixture of methane and carbon dioxide by the methanogenic bacteria (acetate utilizers like Methanosarcina spp. and Methanothrix spp.; hydrogen and formate utilizing species like Methanobacterium and Methanococcus, etc.) [8]. A typical flow sheet for the anaerobic process is shown in Fig. 2 [9,10]. Then, it was clear that the principal gases produced during the anaerobic digestion process are methane and carbon dioxide. Small amounts of hydrogen sulphide is also produced which may be noticeable in terms of the odor characteristics of the digester gas [1]. Typical details about the biogas are given in Table 2 [3]. The stability of the anaerobic process and the rate of gas production are both depend on organic loading rates [11,12]. Long retention times are required for manure digestion, not only due to the presence of complex organic compounds, but also due to the high concentration of ammonia nitrogen, which affects anaerobic decomposition [13]. The current practice in unheated biogas plant in India, for example, is to use a retention time of about 30 days in warm climates and up to 55 days in the colder hilly regions [14]. The effect of increasing the pressure in the anaerobic digestion has been addressed by several researchers. The prime effect relates to the increasing carbon dioxide concentration in the liquid phase caused by an increased pressure. Ref. [15] reports an increasing methane content in a digester with higher pressure. Carbon dioxide is 40 times more soluble in water than methane, and a high digester pressure therefore results in high concentration of carbon dioxide in the substrate, which drives the methane producing reactions forward and stimulates methane production.

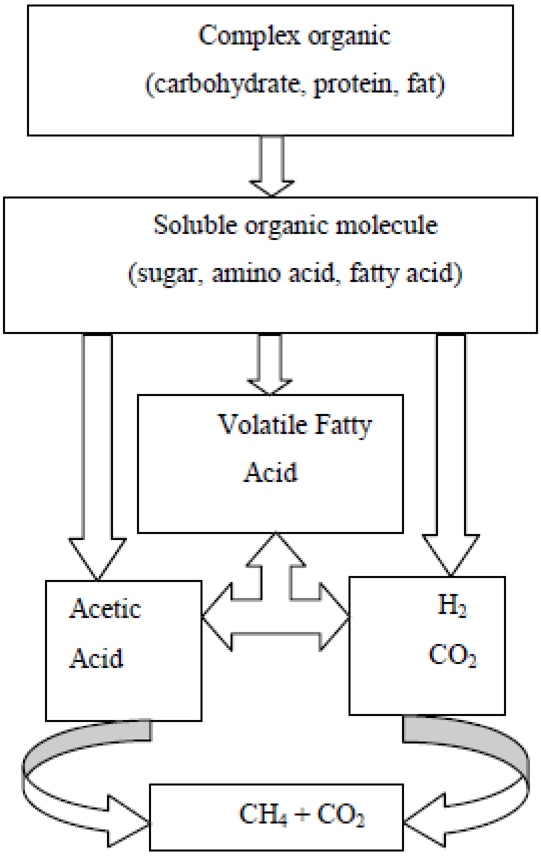

Figure 2 Typical flow sheet for anaerobic digestion process

Table 2 The Composition of Biogas

Component	Composition (% v)
Methane (CH_4)	55 - 75%
Carbon dioxide (CO_2)	30 - 45%
Hydrogen sulphide (H_2S)	1 - 2%
Nitrogen (N_2)	0 - 1%
Hydrogen (H_2)	0 – 1%
Carbon monoxide (CO)	Trace
Oxygen (O_2)	Trace

By changing the total gas pressure of the anaerobic digester toxicity effects can be avoided. An increase of CO_2 partial pressure will decreases the pH value, and reduces the non-ionized ammonia concentration. On the other hand, a decrease in CO_2 partial pressure will increases the pH level, and reduces the non-ionized hydrogen sulfide concentration [16]. Anaerobic digesters are typically designed to operate in the mesophilic (20–40 °C) or thermophilic (above 40 °C) temperature zones. Sludge produced from the anaerobic digestion of liquid biomass is often used as a fertilizer [17].

4 Result and Discussion

4.1 C/N Ratio of the Substrate

Analysis of total carbon and total nitrogen content was carried out to the original substrate including cow manure, cow urine and cheese whey before mixing. The results of the analysis and calculation of C/N ratio of each substrate was shown in Table 1. The table showed that nitrogen content of cow urine and cheese whey higher than it content of cow manure, which indicates that both substrates are suitable for use as a source of nitrogen. The carbon content of cheese whey, however, is so large that its value of C/N to be high.

Meanwhile, the composition of mixed substrate and its C/N ratio value, which were used in this experimental works, was shown in Table 2. The control, labeled as CTR, was equal part mixture of cow manure and water. Control was a representative of substrate which was prepared without addition of any nitrogen source. The C/N ratio of mixed substrate was obtained by develop simple mass balance to count total carbon and nitrogen content in the mixture.

Table 2 C/N Ratio of the Original Substrate

Substrate	Total C (% b/v)	Total N (% b/v)	C/N ratio
Cow manure	7.31	0.65	11.3
Cow urine	1.93	0.69	2.8
Cheese Whey	14.42	0.73	19.8

Table 2 C/N Ratio of the Mixed Substrate

Mixed substrate	Composition	C/N ratio
A	50%w : cow manure 50%w : cow urine	7.0
B	50%w : cow manure 35%w : cow urine 15%w : water	7.8
C	50%w : cow manure 15%w : cow urine 35%w : water	9.3
CTR	50%w : cow manure 50%w : water	11.2
D	50%w : cow manure 10%w : whey 40%w : water	12.7
E	50%w : cow manure 30%w : whey 20%w : water	14.4
F	50%w : cow manure 50%w : whey	15.5

The mixture of cow manure and cow urine (mixed A, B and C) resulted in C/N ratio lower than the control, while the mixture of cow manure and cheese whey (mixed D, E and F) resulted in C/N ratio higher than the control but still lower than range of C/N ratio for effective anaerobic digestion. Biomass with a carbon: nitrogen ratio between 20 and 30 has been reported to produce optimized biogas composition [18].

4.2 Biogas and Methane Yield

In all of experiments, the bottle schott digester was filled out with substrate which consist of as much as 0.9 liter cow manure and mix with cow urine or whey and water to reach 1.8 liter volume of mixture. The anaerobic digestion was carried out at 25 ^{o}C for 40 days. The volume of biogas was measured every 5 days base on the change of water level difference in the respirometer. The evolution of biogas volume was shown on Figure 3. After 40 days digestion, the biogas volume produced by all substrate mixture were in the range of 0.4 – 4.4 liter. To calculate how much biogas be produced per kg VS (volatile solid), a typical average value of volatile solid in the mix substrate 32.5 g VS/L was used [19], then the biogas yield by all substrate mixture were in the range of 13.7 – 150.4 liter/(kg VS). The obtained biogas yield is comparable to those given in the literature for anaerobic digestion of animal manure i.e.: 114 liter/(kg VS) for 16 days, 173.2 liter/(kg VS) for 14 days and 134 liter/(kg VS) for 26 days biogas production from cow manure and whey mix [20]; between 208 and 267 liter biogas/(kg VS) produced from anaerobic digestion of maize and dairy cattle manure[21]; 444 liter biogas/(kg VS) for 5 days anaerobic digestion of mix of whey and cow manure with composition was 2:1 ratio [22].

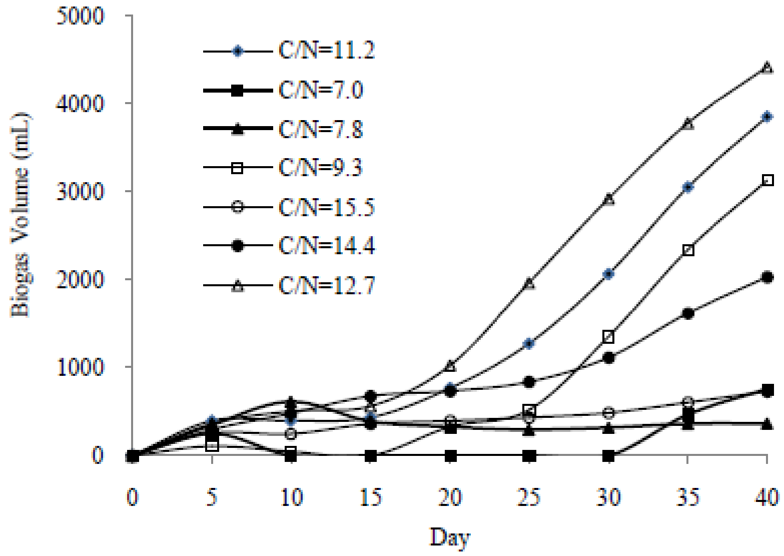

Figure 3 Evolution of biogas volume produced during anaerobic digestion

From Fig. 3, it could be seen that biogas production was actually slow at starting of observation. This is predicted because biogas production rate in batch condition is directly equal to specific growth of methanogenic bacteria [23]. The result of analysis methane content in the biogas at the end of experiment showed the methane yield in the range of 1.23 – 14.92 liter methane/(kg VS). This result was higher than that reported by [23] during the anaerobic digestion of cow manure using a laboratory scale 10 liter batch bioreactor which provide methane yield of 0.15 liter/(kg VS), but comparatively lower than yield obtained from anaerobic digestion of cow manure reported by [4] which reach 6.40 – 33.57 liter/(kg VS) and by [20] which reach 33.57 liter/(kg VS). The low yields obtained could be attributed to the quality of the VS in the manure and the low temperature during the digestion process. In addition, the low C/N ratio of the substrate used in this work, which mean excessive nitrogen content, could be the reason behind the low methane yield. Substrates with either excessive carbon or nitrogen can result in poor bioreactor performance and biogas with high carbon dioxide content [17].

4.3 COD Removal

COD represent the organic material contained in the substrate which could be cellulose, hemicelulose, lignin, protein, fat, biomass, organic acids, and othe organic substances. The measured COD in the cow manure was 62 g/liter which was comparable to [24] which reported value of 34 – 58 g/liter. While, the measured COD in the whey substrate was 171 g/liter which was higher than the value reported by [25], 60 – 80 g/liter. The COD removal, which was measured after 40 days digestion, was shown on Figure 4. The COD removal was monitored, in order to verify efficiency. The average initial COD of the substrate was 104 g/l. Meanwhile, the average value of the COD removal was 37.9%. This average value was comparatively lower than the commonly obtained COD removal from cow manure anaerobic digestion (45 - 47%) [20, 22].

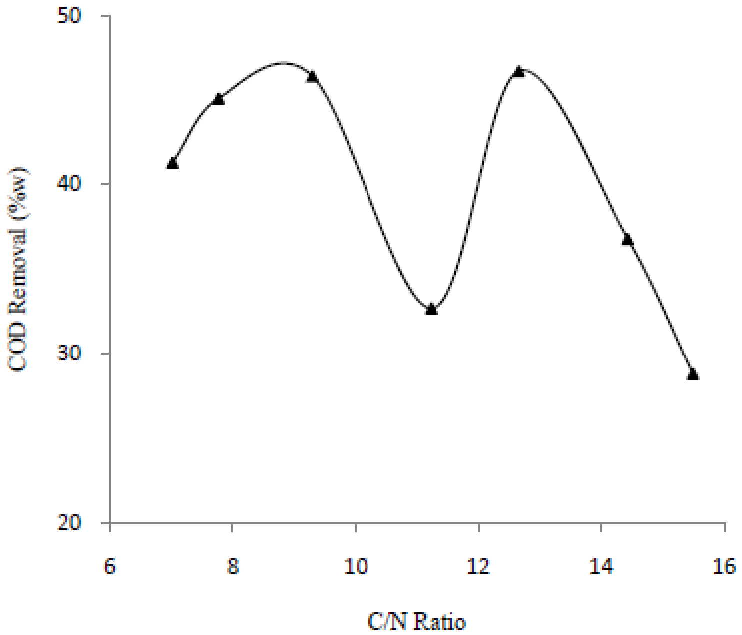

Figure 4 Profile of COD removal expressed as percent weight as a function of C/N ratio in substrate

In this work the highest C/N ratio result in the lowest COD removal, this result was believed to be due to the high C/N ratio of the substrate. If the organic substrate is available in very excessive, then the performance of the metabolism of microorganisms in it also becomes un-optimal [26]. This condition happen due to the increasing number of substrates available in the environment, then they create a large concentration gradient between the outside and inside the cell which caused an osmosis to be occurred. This osmosis can cause cells to become dehydrated (water out of the cell).

4.4 Volatile Fatty Acid Concentration

The analysis of volatile fatty acid was conducted using Gas Chromatography. The result of analysis of the volatile fatty acid concentration in the biogas at the end of the experiment was shown on Figure 5. Compare to butyric and propionic acid, the concentration of acetic acid is the highest.

Volatile fatty acids (VFA) detected in the biogas showed low concentrations. This is because of the low vapor pressure of the volatile fatty acids, then most of the volatile acids are in a state of liquid in the slurry. Evaporation of a small portion of VFA probably due to be carried away by methane and CO_2 gas.

4.5 The pH Change

The pH measurement was carried out to the substrate at the initial and the end of the digestion process and was intended to determine the decrease in pH. The result of pH measurements were presented in Table 3. In each experiment variation, at the beginning of fermentation the pH value was approximately neutral, and at the end of fermentation showed a decrease in pH. A relatively high decrease in pH was observed in the mixture with relatively high C/N ratio, this could be due to high volatile fatty acid formation [27], and it was met with volatile fatty acid concentration profile in biogas as was presented in Fig. 5.

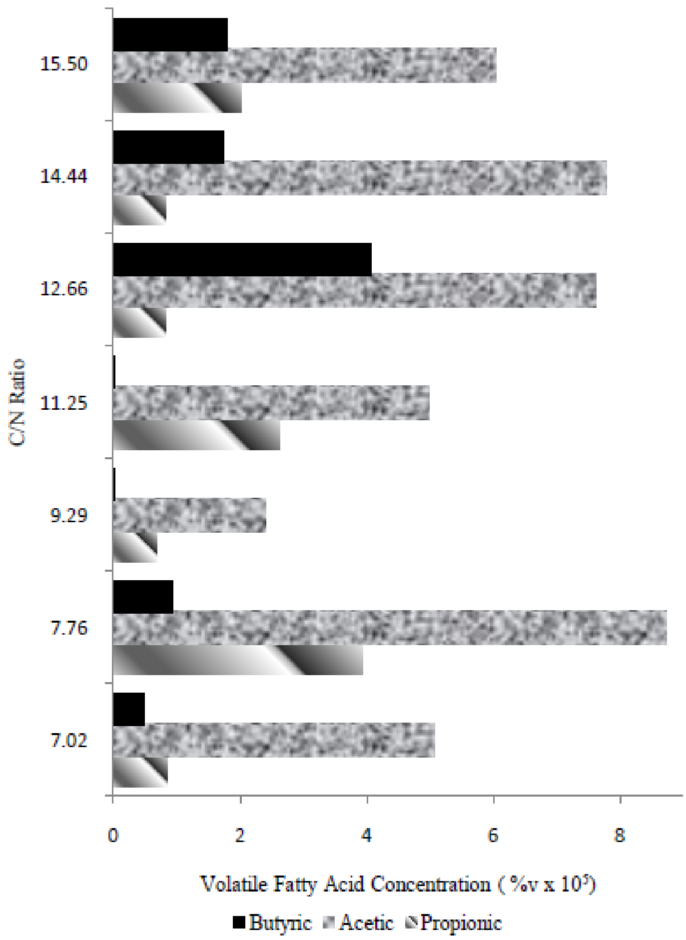

Figure 5 The volatile fatty acid concentration profile as function of C/N ratio in substrate

The high volatile fatty acid formation was leading to excessive accumulation of the acid. The main cause is an unbalance rate of breaking of chemical bonds that occurs at the stage of acidogenesis and methanogenesis, in which lactose contained in whey is a substrate that is easily degraded by acidogenic microorganisms that cause acid inhibition [28]. Because acidogenic bacteria grow faster than methanogens, acid will accumulate. Breakdown product of lactose is a short chain fatty acids (propionic acid, butyric acid, acetic acid) and lactic acid [29]. If there are too many volatile acids present, acetogenic bacteria (especially heteroacetogen producing hydrogen) and methanogens can not metabolize the acid (butyric acid, propionic acid, acetic acid) at fairly quick rate and cause the acid accumulation, so that the pH drops suddenly.

Table 3 The Initial and Final pH of the Substrate

C/N ratio	Initial pH	Final pH	Decreasing pH
7.02	8.02	7.68	0.34
7.76	7.86	7.45	0.41
9.29	7.55	7.15	0.40
11.25	7.78	7.07	0.71
12.66	7.13	6.77	0.36
14.44	7.04	4.97	2.07
15.50	6.66	4.74	1.92

5 Conclusions

This study investigated the effectiveness of cow urine and cheese whey addition as nitrogen source for biogas production from cow manure and presented the performance characteristics of the anaerobic digestion in 2 liter batch bioreactor. Under this condition the substrate mixture digestion reach 37.9% COD reduction. The obtained biogas yield by all substrate mixture were in the range of 13.7 – 150.4 liter/(kg VS), while the methane yield was in the range of 1.23 – 14.92 liter methane/(kg VS). Volatile fatty acids detected in the biogas, which consist of butyric, acetic and propionic acid, showed a low concentrations and found the concentration of acetic acid is the highest. A relatively high decrease in pH was observed in the mixture with relatively high C/N ratio, which could be due to high volatile fatty acid formation.

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The official conference language is English.

No translation service will be provided.

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Thursday, March 28	6:00 PM – 8:00 PM
Friday, March 29	9:00 AM – 9:30 AM

Internet Access

No Internet Service is available inside conference rooms.

Conference Structure and Events

Program

The technical program includes invited plenary lectures, oral sessions and poster presentations.

Oral Presentations

Oral presentations are scheduled for 15 minutes of presentation and 5 minutes of Q&A.

All presentations should be in PowerPoint or PDF formats. A laptop and LCD projector will be available in all sessions. Each presenter is requested to bring the presentation in a USB storage device and upload it to the laptop before the session begins. All presentations will be destroyed at the end of the session.

We urge all presenters to use the provided laptop for presentation so as to minimize changeover times.

Since we have a very tight and fully packed program, we request all the delegates to be punctual and respect the allocated timeslots.

In case of absence of some presenter, next presenter will be called for presentation.

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The dimensions of the poster board will be 594 mm (Width) x 841 mm (Height) (or equivalently 23.3 in (W) x 35 in (H)). This corresponds to A1 Size in portrait layout. Posters are to be put up according to the assigned Paper IDs shown in the detailed program. The posters can be put up from Thursday afternoon 6:00 PM, and must be removed after the poster session. Posters left on the boards will be taken down and disposed of.

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Full registration guests may receive a complimentary Kuala Lumpur City Tour. Special tourism bus can be arranged for easy commutation. Presenters are requested to make a mention of their consent to join the city tour at the registration desk.

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Detailed Program

Day-1; Mar 29, 2013

Registration (9:00 – 9:30 am)

Opening Ceremony (9:30 – 11:00 AM)

Welcome Address: (Conference Chair, ICCNSE-2013)

Plenary Speech(es): *Prof. Dr. Said S. E. H. Elnashaie*
(Chemical and Environmental Engineering Department, University Putra Malaysia(UPM), Serdang, 43400, Malaysia.)
Plenary Speaker 2

Tea/Coffee Break (11:00 - 11.30 AM)

Paper ID	*Oral Session A1 (11:30 AM - 1:00 PM)* *CHEMICAL* *Chair:* *Secretary:*
11	SYNTHESIS OF HELICAL CARBON NANOTUBES BY THERMO CATALYTIC DECOMPOSITION OF METHANE OVER Co/Al_2O_3 CATALYST *Sushil Kumar Saraswat*
22	SYNTHESIS OF ALUMINUM CHLORIDE BY REACTION WITH RECYCLED IRON CHLORIDE *Dong-Won Lee*
28	ADDITION OF COW URINE AND CHEESE WHEY AS NITROGEN SOURCE ON THE BIOGAS PRODUCTION FROM COW MANURE *Puguh Setyopratomo*
30	MATHEMATICAL MODEL DEVELOPMENT OF MASS TRANSPORT IN DIRECT FORMIC ACID FUEL CELLS *Nur Hidayah Maslan*
39	EXTRACTION OF METAL IONS THROUGH SUPERCRITICAL CO_2 *Pradeep Kumar*

45	2D/3D SIMULATIONS OF MASS TRANSFER IN CIRCULAR MICROCHANNELS FOR LIQUID-LIQUID SLUG FLOW *Abhishek Kumar Chandra*
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	Chair: ***Dr. Moon Ki Kim*** ***Secretary:***

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49	REDOX-ACTIVE INJECTABLE GEL FOR RHEUMATOID ARTHRITIS TREATMENT *Magdalena Bednarowicz*
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