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Research Paper

Bio-Methane Potential of Biological Solid Materials and Agricultural Wastes

Nuntiya Paepatung [1,*], Annop Nopharatana [1] and Warinthorn Songkasiri [2]

[1]Pilot Plant Development and Training Institute (PDTI), King Mongkut's University of Technology Thonburi (KMUTT), Bangkhuntien, Bangkok 10150 Thailand

[2]National Center for Genetic Engineering and Biotechnology (BIOTEC), Biochemical Engineering and Pilot Plant R&D Unit (BEC), Bangkok, 10150 Thailand

*Author to whom correspondence should be addressed, email: nuntiya@pdti.kmutt.ac.th

Abstract: This research studied the bio-methane potential of biological solid materials as alternative sources for biogas production. An agricultural residue (rice straw), wastes from four agro-industries, (cassava pulp, pineapple peel, decanter cake and empty fruit bunches) and two weeds (cat-tail [*Typha angustifolia L.*] and water hyacinth [*Eichlornia crassipes Solms*]) were evaluated as substrates for biogas production. The methane potential assays varied from 0.34 to 0.40 m^3 CH_4 kg^{-1} VS_{added}. The maximum specific methane production rates comparing extent and digestibility of each material in a descending order were that of pineapple peel of 36.77 ml CH_4d^{-1}, cassava pulp of 36.57 ml CH_4 d^{-1}, decanter cake of 32.86 ml CH_4 d^{-1}, empty fruit bunches of 13.48 ml CH_4 d^{-1}, cat-tails of 11.63 ml CH_4 d^{-1}, water hyacinth of 11.57 ml CH_4 d^{-1}, and rice straw of 10.98 ml CH_4 d^{-1}. *Rm* values depended upon the substrates readily degradable composition and proportions, including lignocellulosic compounds. All experiments on biogas productivity were conducted for more than 90 days to reach the final yield. The experimental results revealed that bio-solids could be potential sources for biogas production, while further improvement of biogas yield and process flexibility in terms of various feedstocks is necessary.

Keywords: biogas, substrates, digestion, rice straw, cassava, pineapple, decanter cake, oil palm, cat tail, water hyacinth, BMP, Thailand

Introduction

The rising prices of traditional energy sources and the global warming problem have led to a large effort to promote renewable energy. In Thailand, a 'Strategic Plan for Renewable Energy Development' has been established since 2003. It aims to increase the share of renewable energy from 6.4%, or 4,237 kilo tons of crude oil equivalent (ktoe) per year, in 2008 to 20.3% of the commercial primary energy, or 19,700 ktoe per year, by the year 2022 [1].

Biogas can be categorized as one solution for this renewable energy promotion scheme as well as an alternative for reduction of greenhouse gases emissions. Currently, approximately 2,300 biogas systems exist in Thailand [2]. Overall annual biogas production is approximately 234 million m^3 with an equivalent energy content of 165 ktoe or equal to 2,012 GWh of electricity [3]. Although Thailand is an agricultural country with a large volume of potential biogas feedstocks, only two major sources are currently utilized for biogas production. These are wastewaters from cassava starch factories and pig farms [3].

This research studied biogas potential of alternative feedstocks, i.e., bio-solids such as wastes from agro-industries and agricultural weed residues, to increase biogas potential production in Thailand. The major agricultural residue (rice straw), solid wastes from four agro-industries (cassava pulp, pineapple peels, and decanter cake and empty fruit bunches from palm oil mills), and two weed residues (cat-tail/elephant grass (*Typha angustifolia L.*) and water hyacinth (*Eichlornia crassipes Solms*)) were evaluated as substrates for biochemical methane potential (BMP) experiments. The study provided preliminary results for governmental biogas promotion plans and policies in the country.

Materials and Methods

Selection of Potential Feedstock for Biogas Production

Rice straw

Thailand is one of the world's biggest rice producers with widespread cultivation throughout the country. According to data provided by the Office of Agricultural Economics, in 2007, the estimated cultivation area was 11.2 million hectares, with a production capacity of 33 million tons of paddy [4]. An annual generation of rice straw (excluding stubble) was estimated by multiplying the residue coefficient of 0.447 by the rice product yield [5]. It was estimated to be 14.75 million tons in 2008. In general, around 90% of rice straw is used as animal feed or as material for mushroom cultivation [6]. The rest, which is abundant, is left and burnt in paddy fields to prepare the fields for a next crop cycle. The annual residue of rice straw is normally estimated by multiplying the residue coefficient of 0.047 to the rice product yield to be approximately 3.11 million tons of excess rice straw residues.

Cassava pulp

Cassava pulp is considered as the main solid waste from the extraction process in cassava starch factories. During starch production, each ton of dry starch can generate 0.95-2.86 tons of cassava pulp [7]. There are approximately 70 cassava starch factories in the country, producing 3-4 million tons of dry starch every year [3]. It is estimated that approximately 6-7 million tons of cassava pulp is generated annually, with 50% of starch (dry basis) and approximately 80% of moisture content (see Table 1). Although they contain a high level of starch, the main usage of large quantities of cassava pulp has been limited to low value animal feed and fertilizer. It is usually sold for around Baht 200-300 per ton (wet basis) or Baht 2,000-3,000 per ton (dry basis) [3].

It is considered that cassava pulp has potential as a carbohydrate source for biogas production. The pulp has a chemical oxygen demand (COD) value of 1,251 g/kg dry and volatile solids (VS) of 98%.

Empty fruit bunches and decanter cake from palm oil mills
Approximately 60 crude palm oil factories in Thailand produced approximately 1.24 million tons of crude palm oil from 6.4 million tons of fresh fruit bunches (FFB) in 2007 [3, 4]. The production process generates a large amount of biomass residues namely fibre, shells, empty fruit bunches (EFB) and decanter cake. Chavalparit *et al.*, [8] reported that average values of waste generation rate (per ton FFB) from palm oil mills in Thailand were 140 kg of fibre, 60 kg of shells, 240 kg of EFB and 42 kg of decanter cake. The production of fibre, shells, EFB and decanter cake were estimated to be 0.894, 0.13, 1.53, and 0.27 million tons a year, respectively. Nevertheless, fibre is mostly used in boilers as solid fuel in the palm oil mills, while shells are sold at Baht 1,500-1,700 per ton as solid fuel to other industries, e.g. cement factories [3]. EFB, with a high moisture content of 60-70%, are difficult to use as fuel for power boilers. Partial EFB and decanter cake are currently utilized as fertilizers and soil cover materials in palm oil plantation areas, whilst the rest of EFB is dumped in areas adjacent to the mill because of the high generation rate along with its limitations for current utilization.

Pineapple peels
Canned pineapple has been one of Thailand's main exports of canned fruit products. In 2007, approximately 522,145 tons of pineapples provided the raw materials for canned pineapple production [9]. However, the fruit canning process usually generates a huge amount of solid wastes, such as pulp, peels and pineapple cores. Pineapple peels were estimated to be approximately 28% of fresh pineapple weight (wet basis) [10]. In 2008, Thailand produced approximately 2.18 million tons of pineapple, simultaneously generating 0.62 million tons of pineapple peels [4]. Dried pineapple peels can be used as animal feed. The Department of Industrial Works reported that fuel oil used for process pineapple canning is about 22 litres per ton of product [10]. With a high requirement for energy consumption, biogas from pineapple peels may be an alternative source of renewable energy for the canned fruit industry.

Water hyacinth
In 1913, the Water Hyacinth Control Act was promulgated with the objective to prevent further spread of water hyacinth in rivers [11]. However, this objective has not been met successfully, due to its extremely high growth rate. In Thailand, maximum biomass of water hyacinth is produced during the month of April. Annual production is 1.87 tons (dry basis) per hectare or approximately 5 million tons (wet basis) [12]. Water hyacinths have attracted much attention as potential for animal feed, materials for craftworks and as wetland for water treatment.

Biogas production from water hyacinth could be one alternative solution because it has rich protein content that is easily biodegradable. This protein content varies from 6 to 17 % on a dry-weight basis [13].

Cattail/ Elephant grass
Cattail or elephant grass is a perennial aquatic plant growing in many natural wetlands, marshes, shallow areas, fertile lakes and ditches [14, 15]. The total annual productivity of cattail grass is estimated to be approximately 56.6 tons per hectare. The biomass above ground and below ground is in the range of 3.8-52.7 and 9.7-101.4 tons per hectare, respectively [14].

Biochemical Methane Potential (BMP) experiments

BMP batch experiments were performed using a serum vial technique and carried out at a ratio of 3:1 of inoculum to substrate. Nutrient broth of trace elements was supplied for stable digestion. Temperature was controlled at 37°C in pentalicate using 120-ml serum bottles. A working volume of 65 ml was used in each serum vial. The vials were flushed with gas mixture of 70% N_2 and 30% CO_2 before sealing. All cumulative biogas productions were measured via displacement method [16]. Biogas composition was determined using gas chromatography (Shimadzu 14B), with Porapak-N column connected with a thermal conductivity detector [16]. The experiments were conducted for 90 days with an assumption of maximum specific methane production rate. The modified Gompertz equation, employed to fit the cumulative methane production data, is shown as follows [17].

$$M = P \times \exp\{-\exp[\frac{Rm \times e}{P}(\lambda - t) + 1]\} \tag{1}$$

where M is cumulative methane production (ml); e is exp(1) Rm=The maximum specific methane production rates (ml d-1); P is methane production potential (ml); and λ is lag phase time (days).

Total solid (TS), volatile solid (VS), chemical oxygen demand (COD), total nitrogen content (TKN), and ammonia nitrogen content (NH4+-N) were analyzed according to standard methods [16]. Moisture content, cellulose, lignin and ash content were determined using AOAC methods [18].

Seed sludge was taken from stable plug-flow anaerobic digesters of a pig farm in Ratchburi province. All samples of selected feedstock were collected during the year 2007. Rice straw, cassava pulp and pineapple peels were obtained from a paddy field in Nakhon Sawan province, a cassava starch factory in Chonburi province and a fruit canning factory in Prachuapkhirikhan province, respectively. EFB and decanter cake were obtained from a palm oil mill in Suratthani province. Water hyacinth and cattail grass were obtained from wetlands in the Bangkok area. All of the samples were crushed in a blender so that particle sizes were smaller than 5 mm. Table 1 presents the determined characteristics of selected potential feedstock for biogas production.

Table 1. Characteristics of selected feedstock.

Parameter	Unit	rice straw	cassava pulp	EFB	decanter cake	pineapple peel	water hyacinth	cattail
Moisture	%	8.70	81.60	65.7	76.7	91.0	91.27	85.97
Vol. Solids	% dry basis	86.53	98.07	92.5	83.4	93.6	84.33	86.96
COD	g/kg dry	1,011	1,251	1,107	880	1,194	1,011	1,067
TOC	g/kg dry	395	ND	405	470	416	390	311
Carbon	% dry basis	40.4	44.68%	46.4	43.6	40.8	39.8	42.3
Hydrogen	% dry basis	5.6	6.31%	5.90	5.79	5.94	5.7	5.59
Nitrogen	% dry basis	0.6	1.85%	0.43	2.21	0.99	3.0	0.96
Oxygen	% dry basis	39.6	46%	39.6	31.7	31.8	34.9	37.3
Sulphur	% dry basis	0.43	0.13%	0.21	0.15	> 0.00	0.93	0.80
Cellulose	% dry basis	37.34	12.56	29.08	ND	18.11	30.49	35.33
Lignin	% dry basis	5.70	1.86	23.30	ND	1.37	5.58	8.86
TKN	g/kg dry	7.35	2.76	6.41	21.50	12.03	21.33	11.79
NH_3-N	g/kg dry	0.07	0.58	0.22	0.69	1.16	0.63	0.17
Oil & Grease	% dry basis	ND	ND	1.99	4.62	ND	ND	ND
Starch	% dry basis	ND	50	ND	ND	ND	ND	ND

ND: not determined

Results and Discussion

Biomass Potential

Tables 2 and 3 show the potential of biological solid materials and crop residues as an alternative source of biogas production, with 12.31 million tons per year of the total potential from rice straw and agro- industrial waste. The water hyacinth and cattail grass produced annually are estimated at 20.76 and 10.4 tons per hectare, respectively. The major obstacle for rice straw, water hyacinth and cattail grass to produce biogas is widespread distribution, resulting in difficulties for harvesting, including escalated collection and transportation costs. Such obstacles continue to provide a challenge for economic recovery of this potential energy source. The low waste load of decanter cake and pineapple peel in each factory may not be sufficient to make a biogas plant cost-effective. Co-digestion of decanter cake/pineapple peel with other wastes offers some interesting alternatives such as, decanter cake co-digestion with EFB in palm oil mills and pineapple peel co-digestion with wastewater or other bio-wastes in fruit canning.

Table 2. Potential of Biological Solid Materials in Thailand.

Feedstock		Biomass Potential in 2007 (mt/pa)
Agricultural residue	Rice straw (exclude. stubble)	3.11
Agro-industrial waste	Cassava pulp	6.6
	EFB	1.53
	Decanter cake	0.27
	Pineapple peel	0.62
Total		**12.31**

Table 3. Potential of Weed Crops in Thailand.

Crop	Unit	Potential
Water hyacinth	tons per hectare a year	20.76
Cattail grass	tons per hectare a year	10.4

Bio-Methane Potential (BMP)

Figure 1 shows cumulative methane productions from rice straw, cassava pulp, EFB, decanter cake, pineapple peel, water hyacinth and cattail grass. The methane potential as maximum specific methane production rates (*Rm*), ultimate methane yield and biodegradability are shown in Table 4. The most rapid decrease of readily biodegradable fraction occurred during the first 5-10 days for pineapple peel and cassava pulp, which are mainly composed of easily degradable sugar and starch. The *Rm* of pineapple peel and cassava pulp were 36.77 and 36.57 ml d^{-1}, respectively. The decanter cake as selected feedstock had rapid initial methane production rate, with *Rm* of 32.86 ml d^{-1} due to hydrolysis of oil compounds (4.62% dry basis) present in the cake contents. Neves *et al.* [19] review that the substrate with an excess of carbohydrate (starch) and lipid presented hydrolysis rate constants (0.2-1.08 and 0.1-0.7 d^{-1}, respectively) higher than the substrate with an excess of cellulose (0.12-0.18 d^{-1}) which requires the highest retention time. Rice straw, EFB, water hyacinth and cattail grass contain high levels of cellulosic fraction (~30-50% at dry basis) which gave an *Rm* of 10.98, 13.48, 11.51 and 11.63 d^{-1}, respectively, resulting in a slower initial methane production rate than that of pineapple peel, cassava pulp and decanter cake of ~15-18% at dry basis.

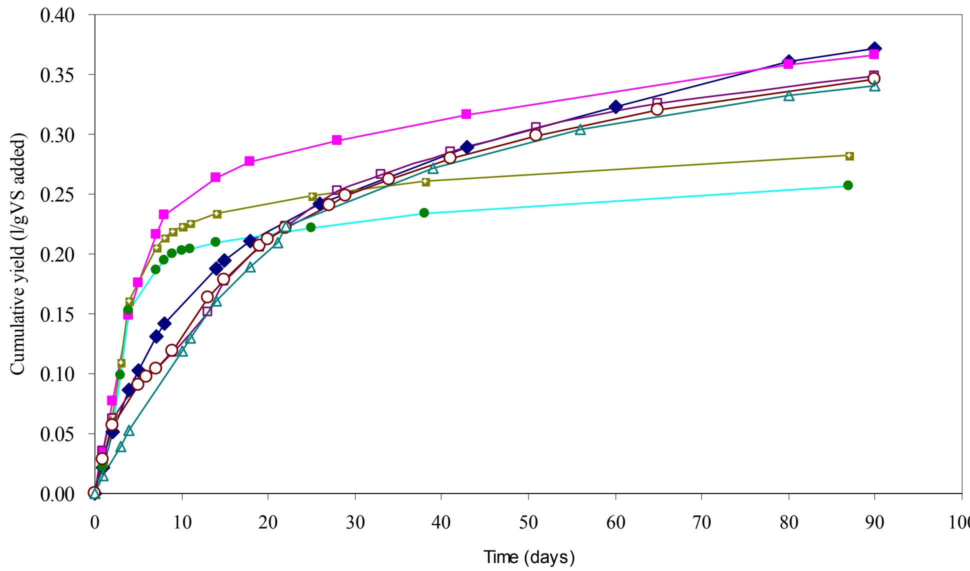

Figure 1. Cumulative methane production from selected feedstock.
(◆, EFB; ■, decanter cake; ◘, pineapple peel; ●, cassava pulp; □, water hyacinth; ○, cattail grass; Δ, rice straw)

Table 4. *Rm* and ultimate methane yield of each selected feedstock.

Feedstock	Ultimate methane yield 90 days (l g−1 VS added)	*Rm*; maximum specific methane production rates (ml d^{-1})	Biodegradability (%)
Rice straw (exclude. stubble)	0.34	10.98	66
Cassava pulp	0.37	36.57	76
EFB	0.37	13.48	66
Decanter cake	0.37	32.86	60
Pineapple peel	0.40	36.77	66
Water hyacinth	0.35	11.51	66
Cattail grass	0.35	11.63	63

The ultimate methane yield of all samples varied from 0.34 to 0.40 m^3 CH_4 kg^{-1} VS_{added} and 60 to 70%, respectively. The biodigestibility of each material for 90 days, in descending order, were cassava pulp of 76%, rice straw, EFB, pineapple peel and water hyacinth of 66%, cat-tail of 63% and decanter cake of 60%. These values depended upon the substrate composition and proportion of readily degradable, non-degradable organic compounds, including cellulose, hemi-cellulose and lignin, which are refractory to decomposition under anaerobic conditions even at long residence time [20]. The pattern for the average biodegradability of rice straw, EFB, water hyacinth and cattail grass appeared to increase gradually, while methane production from pineapple peel and cassava pulp were observed to slow down after 10 days due to a slow degradation of complex materials and degradation of remaining readily biodegradable material. Reters, *et al.* [21] reported that the remaining readily biodegradable material is probably entrapped within cells by cell walls that contain cellulose and are thus not accessible to microbial degradation until the cellulose is degraded. Parawira *et al*. [22]

suggested that more easily degradable compounds were digested before degradation of complex material taking place after that period.

Tables 5 and 6 provide an estimation of the methane potential from bio-solids and bio-crops calculated from the experimental data and BMP assay as renewable energy sources. The biogas potential from rice straw, cassava pulp, EFB, decanter cake and pineapple peel were estimated to be 675, 343, 145, 16 and 17 ktoe, respectively or 251, 127, 54, 5.6 and 6 MWe of electricity equivalent, respectively. This renewable source of energy may replace 689, 350, 148, 16, and 17 million litres of fuel oil, respectively. Rice straw has the highest biogas potential compared to the other tested feedstocks. However, this study does not take the cost of collection and transportation of rice straw into consideration.

Table 5. Potential for Biomethane Production.

Feedstock	Methane potential (million m^3 per year)	ktoe	MWe	Fuel oil (million litres)
Rice straw	836	675	251	689
Cassava pulp	425	343	127	350
EFB	179	145	54	148
Decanter cake	19	16	5.6	16
Pineapple peel	21	17	6	17
Total	**1,480**	**1,196**	**443.6**	**1,220**

The potential for methane production from water hyacinth was appoximately 553 m^3 methane per hectare (ha) a year, with an equivalent energy content of 0.43 toe or 0.16 kWe, or 440 litres of fuel oil per hectare a year. The potential for biogas production from cat-tail grass was 440 m^3 methane per hectare a year, and 0.36 toe or 0.13 kWe, or 363 litres of fuel oil per hectare a year.

Table 6. Potential of Bio-crops for Biogas Production.

Feedstock	Methane potential (m^3 per ha a year)	toe per ha	kWe per ha	Fuel oil (litres per ha)
Water hyacinth	553	0.43	0.16	440
Cattail grass	440	0.36	0.13	363

Conclusion

This research estimated biomass potential of selected feedstock for biogas production from BMP experiments. Cassava pulp, pineapple waste, pineapple peel and palm oil empty fruit branches (EFB) demonstrate the most promising potential for industrial biogas production, in descending order. Rice straw and bio-energy crops, e.g., water hyacinth and cattail grass, with a high content of cellulose, hemicellulose and lignin, require further research studies on pre-treatment processes and hydrolysis stage for enhancing of biogas yield, together with a closer study of economic viability.

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