

ENVIRONMENT

Title: On-Site Biomethanol Production from Swine Waste Digester Methane **NPB# 05-131**

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Date Submitted: July 1, 2008

Industry Summary:

It is important to conserve and utilize valuable constituents in animal waste and implement environmentally superior technologies that are economically feasible. The economic feasibility of environmentally superior technologies being developed has become a major concern and thus emphasis is being directed to the development of marketable products that can offset their increased cost. Digester methane can be used to produce profitable products such as methanol. The current method to convert methane to methanol requires high temperature and pressure during processing. A direct conversion system utilizing light at different wavelengths was evaluated in this study. Conversions above 40% (higher than the 10% suggested for commercialization) were obtained for most reactions however the methanol produced could not be quantified due to small volumes produced. Optimization and scale up of the promising reaction conditions obtained in this study such as methane to air ratio, flow rate, and source of light can provide an economically feasible and environmentally superior technology to meet the increasing need to conserve and utilize valuable waste constituents as well as reduce odor, ammonia volatilization and greenhouse gas emissions. The end goal is to optimize and implement full-scale technology that shows the greatest potential to demonstrate the leadership of the swine industry to implement economically feasible environmentally superior technologies that conserve natural resources for future generations, meet social and regulatory goals, and protect environmental quality.

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These research results were submitted in fulfillment of checkoff funded research projects. This report is published directly as submitted by the project's principal investigator. This report has not been peer reviewed

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Scientific Abstract:

Sizeable amounts of methane can be produced on site by digestion of livestock waste. However its utilization is limited by cost justification for on-site electricity generation and challenges with the transportation of animal waste and/or methane to centralized facilities. It would thus be advantageous to convert methane into a liquid fuel such as methanol on-site so it can be easily transported using the existing petroleum pipelines and distribution systems. The objective of this research was to develop a low temperature on-farm alternative to Fisher Tropsch for direct conversion of methane to methanol. Studies were conducted to evaluate the performance of a photocatalytic process utilizing ultra violet light. Compressed methane:air gas mixtures of 100:0, 80:20 and 70:30 were sparged through water at 90°C and the effect of water vapor content in the feed gas studied by varying the flow rate from 35 – 45 ml/min during sparging. Moist feed gas at atmospheric pressure was fed to the photocatalytic reaction chamber, with a UV or UV-Vis light assembly, maintained at 100°C. An ice-cooled condenser at the downstream end was used to collect the methanol. The effect of hydrogen peroxide as free radical generator on conversion efficiency was investigated by adding 0 -1 ml/L H₂O₂ to the sparging water. Methane to methanol conversion in the presence of a catalyst (tungsten oxide (WO₃) in the photocatalytic reactor was also studied. Gas samples for chromatographic analyses were collected at intervals of 60 minutes to quantify methane, hydrogen, carbon monoxide, carbon dioxide and nitrogen. H₂, CO, and CO₂ were not detected during analyses. Methane conversions ranging primarily between 40-60% were obtained. Volumes of condensate collected at the end of each 3 hour run were measured and found to be less than 0.5 ml in most cases. It has been reported that for a direct process to be economically competitive with the conventional indirect process, 80% selectivity of methanol with a methane conversion of 10% is required. The results of this study indicate good conversion however further research is needed to determine selectivity for methanol. Hence, condensate composition needs be analyzed and the optimum gas ratio, flow rate, light source, and radical/catalyst combination determined.

Introduction:

Livestock waste can be a plentiful resource for renewable energy production through biological and chemical processing/anaerobic digestion. The tremendous amount of swine manure produced each year has the potential to be used as an alternative fuel source while our fossil energy reserves are depleting (Zhang et al., 1999).

Besides helping in odor control, anaerobic digestion of swine manure results in the release of a mixture of gases, referred to as biogas. Biogas is primarily composed of methane (CH₄ 50 – 80% by volume), carbon dioxide (CO₂ 20 – 50%), hydrogen sulfide (H₂S) and traces of carbon monoxide (CO), hydrogen (H₂), ammonia (NH₃), nitrogen (N₂) and nitrous oxide (N₂O) (US DOE, 2005). A number of factors affect the rate of digestion and biogas generation, including pH, water/solids ratio, carbon/nitrogen ratio, mixing of the digesting material, the particle size of the material being digested, size of digester and retention time. Anaerobic microorganisms can withstand temperatures in the range of sub zero to over 135°F; however, they perform best under mesophilic (98°F) and thermophilic (130°F) conditions (US DOE, 2005). The pH is generally self-regulating in an anaerobic digester. For a 150 lb hog, wet manure production is about 10 lbs per day of which about 9 lbs is water and only 0.7 lb per day is biodegradable (or volatile) solids (Gerardi, 2003). Usually only 40 – 60 % of the volatile solids (VS) are converted within a practical digestion time of 12 – 18 days. Biogas production through anaerobic digestion is between 10 and 25 ft³ per pound of volatile solids degraded (cu ft/lb VS) or 0.75 – 1.0 m³/ Kg VS (Gerardi, 2003) of which about 8 cu. ft. is methane.

Methane is a highly potent energy source with a heat value of approximately 1000 Btu/ft³ and can provide more energy compared to oil or coal due to the low C:H ratio in CH₄ (Gondal et al, 2003). However, the presence of carbon dioxide significantly reduces its heat value such that the heat value of raw biogas is 500 - 600 Btu/ft³. Besides, a CO₂ fraction in

biogas above 30% increases the acidity in the sludge causing the pH to drop below 7 and resulting in significant acid fermentation. Additionally, the inorganic gas, hydrogen sulfide (H_2S), produced in an anaerobic digester is highly undesirable. If biogas contains too much hydrogen sulfide the gas may damage digester equipment. It is therefore necessary to remove these gases in order to get maximum benefits of energy from biogas.

Removal of carbon dioxide, H_2S , trace gases and water vapor can be achieved by chemical means, yielding pipeline quality methane (Gerardi, 2003). Water vapor can be removed by frost-proof condensers and condensate traps to prevent corrosion in gas lines and to increase the calorific value of biogas. It is possible to achieve the complete removal of H_2S from biogas using an iron-scrubbing process, such as a column of iron impregnated chips, which operates at ambient temperature. The main advantage is the transformation of H_2S into S thereby eliminating the pollution potential of H_2S . Another process involves sparging biogas through a catalytic solution of Fe-Ethylene Diamine Tetra Acetic acid (EDTA) prepared using $FeBr_2$. This catalytic solution is quite effective in the removal of H_2S and is also able to absorb more CO_2 than pure water (Horikawa et al., 2004).

Although sizeable amounts of methane can be produced on site by swine waste digesters ranging from high tech to low tech its utilization is limited by cost justification for on-site electricity generation or insufficient availability of methane even from concentrated swine production areas. In a study of an engine - generator set by Williams and Frederick (2001) the efficiency of converting the energy in methane to electricity was found to be only 10%. Maintenance time required for on farm power generation poses another issue. It has also been reported that for on-farm electricity generation to provide positive cash flows from electricity selling price of more than \$0.10 per kWh are required (Scruton et al, 2004). Transportation/pumping of animal waste and/or methane to centralized facilities through pipelines is another challenge currently being faced by one large biomethanol production facility in the mid west. Methane requires a high pressure of 1160 psi (80 bar) along with refrigeration for transportation through pipelines (Gondal et al., 2003, Zhang et al., 2003). Yet recovery and utilization is critical because simply venting methane to the atmosphere discards its energy value and may contribute to global warming (US EPA, 2005). It would thus be advantageous to convert methane into liquid fuel such as methanol at the site of generation so that it can be easily transported using the existing petroleum pipelines and distribution systems besides helping overcome the need for expensive on-farm methane storage.

Methanol has a variety of applications including those as a fuel, feedstock for other chemicals and processes such as acetic acid production, and direct use as solvent, antifreeze, or inhibitor (Cheng and Kung, 1994). A methanol engine is 25% more effective than a gas engine and if methanol is dissociated into H_2 and CO in the automobile it can be up to 60% more efficient than gasoline (Cheng and Kung, 1994). In addition, methanol burns at lower temperatures than other fuels, making the design of engines simpler.

Industrially, methane is converted through Fischer-Tropsch chemistry by steam reformation to synthesis gas followed by catalytic conversion to methanol. A typical process involves the desulfurization of gas, steam reforming, methanol synthesis and purification by distillation with an overall efficiency of 75%. However, steam reforming is an energy intensive process requiring both high capital costs and high operating costs that account for 60 – 70% of the overall conversion.. It involves an endothermic reaction requiring high temperature (700 – 1100 °C) and pressure (43.5 – 363 psi or 3 – 25 bar) that could cause problems in the reactor operation and maintenance (Zhang et al., 2003). Methanol synthesis from syngas is an exothermic reaction and proceeds at 200 – 300°C and requires special catalysts. Therefore, for the conversion of methane to methanol to be economically and technologically feasible on farm/site, direct conversion methods need to be investigated. The direct conversion of methane to methanol offers a viable alternative to Fischer-Tropsch chemistry (utilizing synthesis gas) involved in thermo-catalytic processes such as those used at Circle Four Farms (Bestbiofuels, 2003).

A few techniques that have been investigated for direct conversion of methane to methanol include direct catalytic oxidation of methane, dielectric barrier discharge (DBD), photo-catalytic conversion by ultraviolet light or laser and microbial conversion by enzymes. Although the DBD method in which an ac or dc voltage is applied to the system has been found to be effective in the presence of a catalyst even at low gas temperatures, it requires high voltage inputs (higher than 50kV) for increasing methanol concentration. Photocatalytic methods allow direct conversion of methane to methanol with milder inputs and their selectivity for methanol (percentage of methanol in the conversion products) can be improved by optimizing the reaction conditions including temperature, pressure, methane:oxygen ratio, and gas flow rate/residence time (Zhang et al., 2003).

The development of a profitable low cost, low temperature, low maintenance and safe system for converting methane to methanol will have many benefits for society and especially the swine industry. These include the development of an economically feasible, environmentally superior technology and economic justification to convert lagoons to a covered unit to utilize methane and provide more controlled waste treatment for the conservation and off-farm marketing of valuable swine waste constituents and protection of environmental quality. The benefits of a covered in-ground ambient temperature digester which includes nitrogen conservation, and reduction of odor, ammonia and greenhouse gas have already been demonstrated for four years in North Carolina (Cheng et al, 2004).

It has been reported that for a direct process to be economically competitive with the conventional indirect process, 80% selectivity of methanol with a methane conversion of 10% is required (Zhang et al., 2003).

Objectives:

Preliminary review indicated that the laser/solar system has low conversion efficiency (< 5%), requires separation of methanol from a water-catalyst mix and is energy intensive. It was thus not the most economical option. Hence, as an alternative, a photo-catalytic conversion method was tested using UV light and UV-Visible light combination.

This study was undertaken to investigate technologies for direct conversion of methane to methanol. Two conversion methods were proposed for investigation at the bench scale: 1) an ultraviolet (UV) light conversion process that does not need a catalyst and can operate at significantly lower temperatures and pressures than Fischer Tropch steam reforming reactions and 2) a photo-catalytic conversion process using a constant wave laser or sun light (solar beam) and requiring small amounts of fairly inexpensive catalysts.

Materials & Methods:

Gas composition: A simulated biogas was generated by mixing compressed air and methane at the desired ratios.

Conversion of methane to methanol:

A conversion system that can employ either UV or UV-Visible lamps as light sources was designed and fabricated (Fig 1, 2). Direct conversion of methane to methanol was performed by subjecting the simulated biogas to a modified photo-chemical reactions using ultraviolet light (185 nm) and UV-visible light as light sources. Tests were conducted with and without an oxidant (free radical generator - hydrogen peroxide) and catalyst (tungsten oxide) for 3 hours

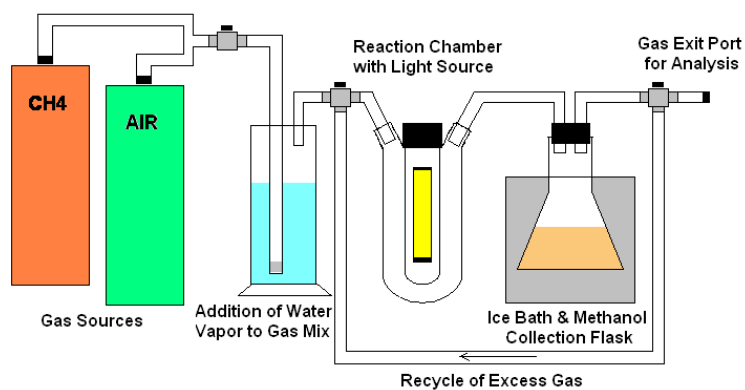


Figure 1: Schematic of the direct UV/UV-Vis conversion system



Figure 2: Direct UV/UV-Vis conversion system

The direct UV/UV-Vis conversion system can be used both in the batch and continuous modes and allows for the gas mixture to be recycled for enhanced conversion. It facilitates easy replacement of the light source and can be used with and without catalyst(s). Based on a statistical design of experiments, tests were conducted to study the effect of the following variables over a 3 hour reaction interval:

- i. Wavelength (UV or UV-Vis)
- ii. Ratio of methane:air (100:0, 85:15, and 70:30)
- iii. Gas flow rate (35, 40 and 45 ml/min)
- iv. Presence of catalyst in the reaction chamber (0, 1 g tungsten oxide)
- v. Presence of a free radical generator in the inlet gas mix (0, 0.5, 1 ml hydrogen peroxide/1 of sparging water)

During testing, compressed methane and air at gauge pressures of 15 psi were mixed to get the desired ratio by controlling the flow rates of the individual gases. The set flow rates were air- 13.5 mL/min, methane- 31.5 mL/min for 70:30, air- 9 mL/min, methane- 36 mL/min for 80:20 and air- 0, methane- 45 mL/min for 100:0.

Ultraviolet light conversion:

The mixture of gases, simulating biogas, was sparged through water at 90°C to increase its moisture content since the presence of water vapor is reported to enhance methane to methanol conversion. The warm and moist gas entered the UV/UV-Vis reaction chamber placed in an oil bath at 90°C. The flow rate of the gas controlled its residence time in the reaction chamber. At the end of the reaction, the exit gas passed through a condenser coil in an ice bath before being discharged into a fume hood. Initially coiled copper tube was used for condensate collection. However, the amount of condensate being generated was significantly small so the system was modified to allow condensation and collection of smaller samples by using a small diameter coil glass tube. The temperature drop in the condenser allowed the volatile gaseous components of the exiting gas to (presumably methanol) to condense into the collection flask as a liquid. An exit gas recycle system was tested initially but it resulted in back pressure in the system and was therefore not investigated further.

The reactGas samples for gas chromatography analyses were collected every hour to quantify methane conversion and by-product determination and quantification.

Photo-catalytic conversion:

Similar to the UV conversion, photo-catalytic conversion of methane to methanol was conducted in liquid phase by sparging the simulated biogas through 1 L water (at 90C) containing hydrogen peroxide (0.5, 1 ml /L) as free radical generator and catalyst (tungsten oxide (WO₃)). Amount of catalyst place in the reaction chamber was 1g. The flow rate of the gas was varied to study its effect on the conversion efficiency of two types of light beams: UV and UV-Vis.

All gas samples were taken with a gas tight syringe from sampling ports in the systems. The syringe was inserted through the septum and slowly filled and flushed three times before taking each sample. The samples were analyzed by gas chromatography immediately for methane, carbon dioxide, and hydrogen. Each syringe will be labeled with the run ID, time and replication number on tape.

The conversion system was operated as a batch reactor for 3 hours. Liquid product volumes were very small (typically less than 0.5 ml condensate) and hence could not be analyzed for composition.

Gas standards containing hydrogen, nitrogen, methane, carbon monoxide, and carbon dioxide were used to generate standard curves each time analyses were conducted. Prior to injection of samples air was injected as a blank.

Estimation of condensate volumes:

The condensate collected in the flask connected to the condenser coil was quantified using a pipette. The volumes were significantly small after the 3 hour runs and could not be analyzed in a GC for composition.

Economics:

Since the condensate volumes were very small a direct cost relation between methane conversion and methanol production could not be established. However, the components requiring establishment or operating cost were identified for the lab scale study.

Results: Report your research results by objective.

Effect of ultraviolet light and ultraviolet-visible light on the conversion of methane in the absence of a free radical or catalyst.

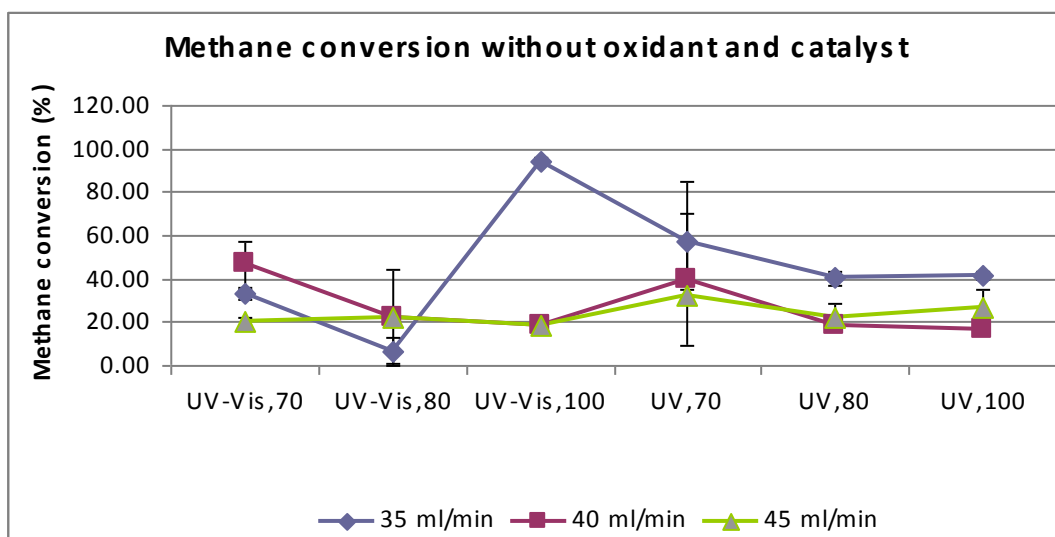


Figure 3. Methane conversion in the absence of oxidant and catalyst

Effect of ultraviolet light and ultraviolet-visible light on the conversion of methane in the presence of a free radical(oxidant).

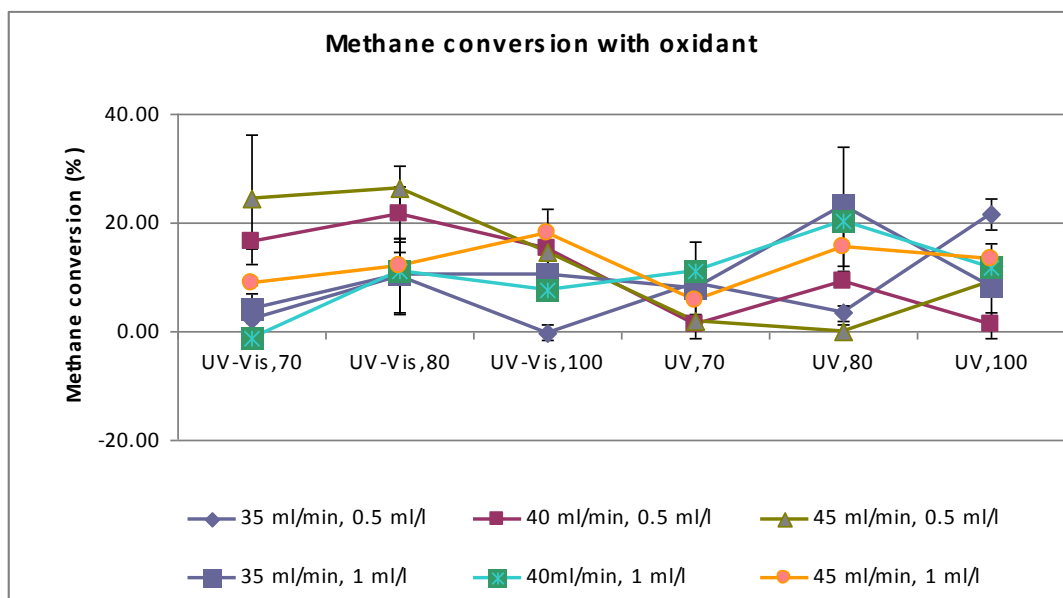


Figure 4. Methane conversion in the presence of oxidant

Effect of ultraviolet light and ultraviolet-visible light on the conversion of methane in the presence of a free radical(oxidant) and catalyst.

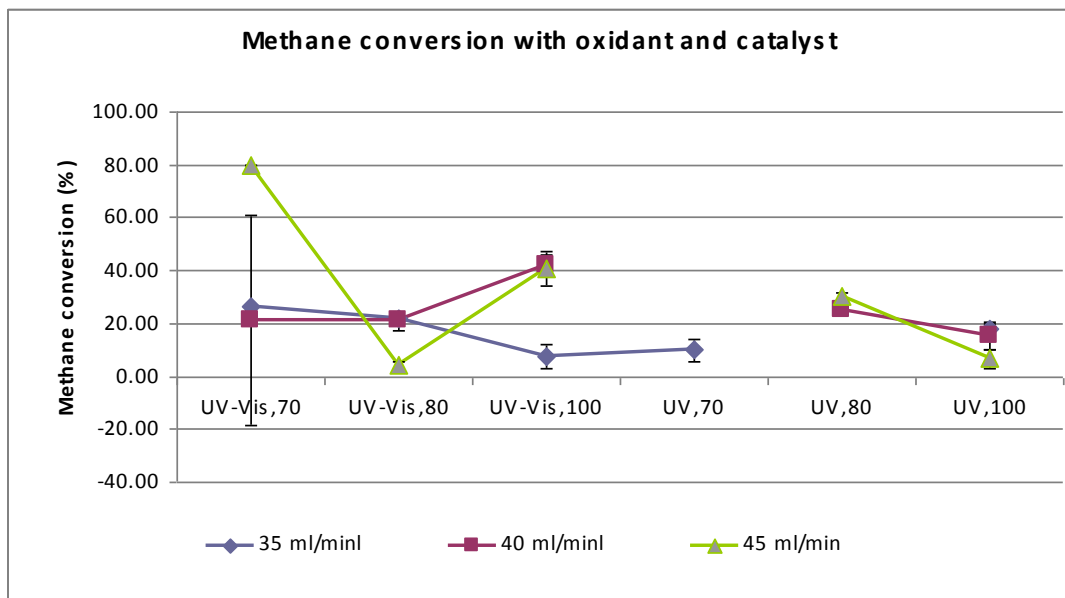


Figure 5. Methane conversion in the presenece of oxidant and catalyst

Table 1: Methane conversion data collected for various treatments and time intervals.

Flow rate (ml/min)	Light source	Oxidant (H ₂ O ₂ , ml/L)	Catalyst (WO ₃ , g)	Inlet Methane (%)	Outlet gases after 1h		Methane conversion	Outlet gases after 2h		Methane conversion	Outlet gases after 3h		Methane conversion
					Methane	Nitrogen		Methane	Nitrogen		Methane	Nitrogen	
35	UV-Vis	-	-	70	44.92	34.73	35.83	48.45	32.54	30.79	47.71	32.53	31.84
		-	-	80	77.15	19.16	3.56	69.21	24.58	13.49	77.04	19.26	3.70
		-	-	100	6.37	67.62	93.63	6.27	68.15	93.73	3.98	66.18	96.02
	UV	-	-	70	9.35	48.41	86.64	46.85	41.71	33.07	33.05	42.92	52.79
		-	-	80	49.26	36.78	38.43	45.21	38.25	43.49	49.10	35.34	38.63
		-	-	100	56.96	28.40	43.04	60.60	25.54	39.40	59.10	26.58	40.90
40	UV-Vis	-	-	70	32.35	46.57	53.79	46.11	46.11	34.13	33.54	46.57	52.09
		-	-	80	42.08	43.38	47.40	73.55	20.47	8.06	71.13	21.87	11.09
		-	-	100	84.93	10.31	15.07	82.11	10.16	17.89	78.23	10.06	21.77
	UV	-	-	70	59.79	22.61	14.59	18.26	30.47	73.91	47.89	30.05	31.59
		-	-	80	64.99	18.78	18.76	63.95	19.54	20.06	66.42	17.62	16.98
		-	-	100	85.19	2.95	14.81	84.90	3.16	15.10	78.77	7.04	21.23
45	UV-Vis	-	-	70	57.35	24.71	18.07	54.45	26.28	22.21	55.92	25.52	20.11
		-	-	80	62.21	21.58	22.24	62.89	20.89	21.39	62.73	20.71	21.59
		-	-	100	83.25	6.69	16.75	80.25	8.63	19.75	80.93	7.78	19.07
	UV	-	-	70	48.28	29.29	31.03	48.69	29.12	30.44	44.87	31.02	35.90
		-	-	80	67.11	16.96	16.11	63.17	23.04	21.04	56.68	22.12	29.15
		-	-	100	77.69	7.57	22.31	78.07	7.35	21.93	63.39	19.08	36.61
35	UV-Vis	0.5	-	70	69.34	23.79	0.94	70.08	23.39	-0.11	65.71	26.25	6.13
		0.5	-	80	77.25	18.63	3.44	72.16	23.66	9.80	66.26	23.24	17.18
		0.5	-	100	101.88	2.13	-1.88	98.93	4.13	1.07	99.85	3.50	0.15
	UV	0.5	-	70	57.63	29.64	17.67	66.98	23.20	4.31	66.98	24.61	4.31
		0.5	-	80	77.87	17.28	2.66	77.95	17.16	2.56	76.11	18.23	4.86
		0.5	-	100	76.96	14.02	23.04	81.65	11.73	18.35	76.68	14.32	23.32

Flow rate (ml/min)	Light source	Oxidant (H ₂ O ₂ , ml/L)	Catalyst (WO ₃ , g)	Inlet Methane (%)	Outlet gases after 1h		Methane conversion	Outlet gases after 2h		Methane conversion	Outlet gases after 3h		Methane conversion
					Methane	Nitrogen		Methane	Nitrogen		Methane	Nitrogen	
40	UV-Vis	0.5	-	70	57.91	30.80	17.27	58.34	21.54	16.66	59.32	29.60	15.26
		0.5	-	80	65.94	25.31	17.58	64.15	26.29	19.81	58.15	29.36	27.31
		0.5	-	100	86.25	9.68	13.75	87.15	9.06	12.85	81.02	13.00	18.98
	UV	0.5	-	70	69.14	23.36	1.23	68.73	23.63	1.81	69.60	23.08	0.57
		0.5	-	80	72.63	20.92	9.21	72.48	21.20	9.40	72.86	20.82	8.93
		0.5	-	100	99.83	2.86	0.17	100.50	2.52	-0.50	96.11	4.27	3.89
45	UV-Vis	0.5	-	70	61.54	28.15	12.09	44.98	31.73	35.74	52.37	27.36	25.19
		0.5	-	80	62.08	22.12	22.40	55.69	25.26	30.39	58.84	23.57	26.45
		0.5	-	100	89.27	7.20	10.73	84.98	8.36	15.02	81.59	10.31	18.41
	UV	0.5	-	70	68.15	24.15	2.64	68.19	24.13	2.59	69.45	23.26	0.79
		0.5	-	80	81.00	15.83	-1.25	78.82	16.99	1.48	80.09	16.41	-0.11
		0.5	-	100	95.18	5.06	4.82	94.07	6.07	5.93	82.69	13.82	17.31
35	UV-Vis	1	-	70	67.18	20.39	4.03	65.15	21.60	6.93	68.91	19.07	1.56
		1	-	80	77.76	14.77	2.80	70.52	18.84	11.85	66.90	19.67	16.38
		1	-	100	89.29	6.02	10.71	88.66	6.67	11.34	90.24	5.41	9.76
	UV	1	-	70	63.83	20.70	8.81	64.34	20.53	8.09	65.06	20.04	7.06
		1	-	80	51.91	27.82	35.11	68.68	17.83	14.15	64.09	19.51	19.89
		1	-	100	91.96	9.10	8.04	90.17	6.63	9.83	92.78	5.72	7.22
40	UV-Vis	1	-	70	71.77	17.69	-2.53	69.93	18.71	0.10	70.83	18.12	-1.19
		1	-	80	64.92	18.95	18.85	67.97	18.53	15.04	80.41	17.41	-0.51
		1	-	100	93.66	3.64	6.34	89.7	5.58	10.30	94.09	3.46	5.91
	UV	1	-	70	63.41	25.83	9.41	64.71	25.61	7.56	58.43	29.84	16.53
		1	-	80	65.44	22.85	18.20	66.25	22.12	17.19	59.8	27.2	25.25
		1	-	100	84.78	8.86	15.22	91.37	4.87	8.63	88.26	6.49	11.74
45	UV-Vis	1	-	70	63.51	22.25	9.27	64.02	21.96	8.54	63.89	22.16	8.73

Flow rate (ml/min)	Light source	Oxidant (H ₂ O ₂ , ml/L)	Catalyst (WO ₃ , g)	Inlet Methane (%)	Outlet gases after 1h		Methane conversion	Outlet gases after 2h		Methane conversion	Outlet gases after 3h		Methane conversion
					Methane	Nitrogen		Methane	Nitrogen		Methane	Nitrogen	
35	UV	1	-	80	69.56	17.04	13.05	72.75	15.83	9.06	68.79	17.51	14.01
		1	-	100	78.54	11.91	21.46	87.27	6.64	12.73	80.1	11.62	19.90
		1	-	70	60.3	26.21	13.86	68.11	26.35	2.70	69.39	26.39	0.87
		1	-	80	69.39	19.75	13.26	63.46	23.81	20.68	69.93	19.21	12.59
		1	-	100	87.52	5.94	12.48	86.37	6.81	13.63	86.05	6.93	13.95
	UV-Vis	1	1	70	50.81	33.84	27.41	52.03	32.73	25.67	52.09	32.82	25.59
		1	1	80	63.22	27.21	20.98	63.48	26.1	20.65	61.13	27.65	23.59
		1	1	100	97.42	4.01	2.58	90.25	7.42	9.75	88.95	8.24	11.05
		1	1	70	64.43	16.61	7.96	64.95	16.29	7.21	59.66	19.57	14.77
		1	1	80	-	-	-	-	-	-	-	-	-
40	UV-Vis	1	1	100	83.94	11.53	16.06	83.49	11.94	16.51	79.67	12.89	20.33
		1	1	70	70.91	59	-1.30	71.48	21.3	-2.11	23.21	21.62	66.84
		1	1	80	59.78	29.18	25.28	65.32	25.55	18.35	64.46	26.13	19.43
	UV	1	1	100	53.74	22.27	46.26	59.49	16.94	40.51	60.01	17.23	39.99
		1	1	70	-	-	-	-	-	-	-	-	-
		1	1	80	60.23	18.93	24.71	60.17	18.44	24.79	59.06	19.15	26.18
45	UV-Vis	1	1	100	79.18	15.13	20.82	89.19	8.36	10.81	86.36	10.35	13.64
		1	1	70	0	74.67	-	0	74.92	-	14.33	63.63	79.53
		1	1	80	77.38	14.89	3.28	75.52	16.09	5.60	76.79	14.73	4.01
		1	1	100	63.89	14.62	36.11	61.97	15.1	38.03	51.9	19.85	48.10
	UV	1	1	70	-	-	-	-	-	-	-	-	-
		1	1	80	56.05	20.85	29.94	54.44	22.25	31.95	56.65	21.15	29.19
		1	1	100	0	7.18	-	95.85	5.45	4.15	91.02	8.67	8.98

Condensate volumes produced during the 3 hour reaction runs

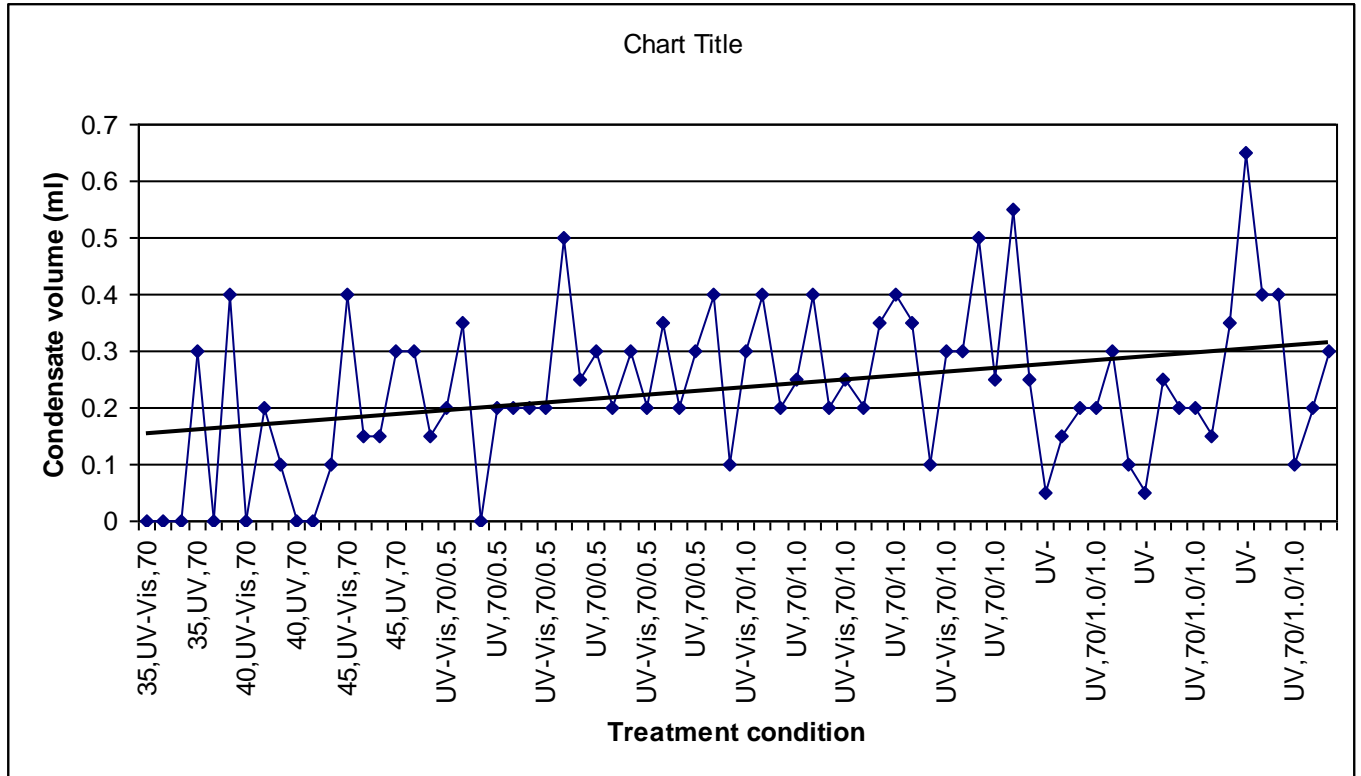


Figure 6: Condensate volumes collected during various runs

Discussion:

Results of this study indicated that methane gas to condensate conversion after 3 hour runs was extremely low. However, the effects of various parameters studied are discussed below.

Effect of flow rate:

Lower flow rates tended to give higher conversion efficiencies but overall there was not much difference in the conversion rates. The highest methane conversion was 94.5% but on average the conversions were below 60%. No H₂, CO or CO₂ was detected in the exit gas stream.

Effect of light source:

Wavelength of light did not necessarily increase conversion efficiency.

Effect of presence of oxidant:

The presence of hydrogen peroxide did not necessarily increase methane conversion but the efficiency was higher with 0.5 ml/L gave higher conversion at higher flow rates though statistically there was no significant difference in methane conversion.

Effect of presence of catalyst with oxidant

Presence of a catalyst along with the oxidant resulted in conversions similar to those without catalyst.

Condensate volumes:

The condensate volume was typically less than 0.6 ml with levels showing an increasing trend in the presence of the catalyst and/or oxidant.

Economics:

The primary cost components of this conversion system were the compressed air and methane tanks. Cost attributed to the oxidant and catalyst was minimal. Electricity consumed for heating the water and oil baths contributed to the operational costs.

Methane conversion primarily ranged between 40-60% which were higher than the 10% reported as being suitable for commercialization. However the condensate volumes were significantly smaller and the selective for methanol could not be quantified. Further studies in scaled up systems are needed to generate more condensate in shorter reaction times to determine the methanol production efficiency of the system.

Note:

Presentations made:

Ratna Sharma-Shivappa, Brian Belvin, Sara Dawson, Mike Boyette. Photocatalytic process for on-site conversion of methane to biomethanol. Poster # 083812. 2008 Annual meeting of the American Society of Agricultural and Biological Engineers. Providence, RI. June 29 – July 2, 2008.