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Optimizing Hydrogen and Methane Production from a MixALCO Process-Derived Sludge by Thermo-chemical Means

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Abstract

The mixALCO process collects and ferments heterogeneous organic waste materials into a mixture of alcohols. Considerable amounts of sludge rich in lignin and hemi-cellulose and dead bacteria are generated in this process. We have successfully used the response surface method (R.S.M.) as a statistical experimental design technique to optimize the pyrolytic production of hydrogen and methane for downstream use in the mixALCO process. With feedrate (lb of feed/minute) – modeled as auger R.P.M.- and temperature (degree Celsius) as main effect variables, only temperature appeared to be the significant variable determining gas production. Maximum hydrogen and methane volumetric yields of 45.4 and 20.0 % respectively were obtained at 750 and 770 C. The only oxide of carbon produced was carbon monoxide and energy efficiency decreased from 68.6 % at 630 to 43.4 % at 770 C. Irrespective of the efficiency, the process leaves no energy footprint.

Key words:: MixALCO process, sludge, pyrolysis, R.S.M., volumetric yields, efficiency, energy neutral.

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1 Introduction

Bioenergy constitutes an important part of the renewable energy mix deemed to significantly complement fossil fuels in the near term. Bioenergy has the potential to supply up to 11 % of world energy needs although the state of Texas consumed only 1.0 % of its total energy as bioenergy in 2003 [5,10].

Bioenergy is derived from carbon-based material and its environmental benefit is underpinned in its being carbon neutral – the carbon dioxide emitted during its combustion equals the amount consumed during carbon fixation in photosynthesis [2].

Bioenergy technologies are broadly classified as thermo-chemical, biochemical or physical. Thermo-chemical process involves combustion, gasification, and pyrolysis while biochemical process involves fermentation and anaerobic digestion. The physical process, especially esterification is the least feasible.

Since pyrolysis (the decomposition of organic matter under anaerobic conditions) offers more benefits such as higher energy efficiencies, flexible use of its fuel and is more environmentally benign over incineration, it is increasingly given attention especially at on-site energy use facilities. For example energy production from pyrolysis has become eligible for the Renewable Energy Obligation Certificates (ROCs) in the UK[7].

There are two types of pyrolysis: fast pyrolysis which favors bio-oil production and is operated at lower temperatures and slow pyrolysis operated at higher temperatures mainly for syngas production. The three products of pyrolysis are syngas, bio-oil and char.

The bio-oil, usually highly viscous has higher water and oxygen contents and is corrosive. This makes it an inferior fuel versus petroleum fuel. Hence it is recommended that it be upgraded into a second generation petroleum fuel ready for refineries [11-13]. The syngas typically contains hydrogen and oxides of carbon and lower hydrocarbons such as methane and trace amounts of ethane. Incineration of biomass leads to the recovery of only 10-25 % of stored chemical energy as thermal energy. This can be improved in a pyrolytic process when the bio-oil and syngas are used as energy carriers [1].

Although bioenergy production appears currently to be driven by dwelling fossil fuels and global warming concerns, regulatory, environmental and economic forces are also principal drivers in the industry [9]. When sludge is the feedstock for pyrolysis, water quality regulatory rigor will require its complete removal in the generation process. Hence its conversion into useful products such as hydrogen in a pyrolytic process will help meet not just regulatory and environmental requirements but also economic ones when the hydrogen produced is used as a feedstock in a downstream process to produce more value added products. More economic benefit is translated into carbon credits when the hydrogen and methane are used in a closed-loop system. Hence the objective of this work was to pyrolyze sludge from a mixALCO process (MAP) to optimize hydrogen and methane in the product stream for downstream use in the MAP.

2 Experimental

2.1 Experimental Overview.

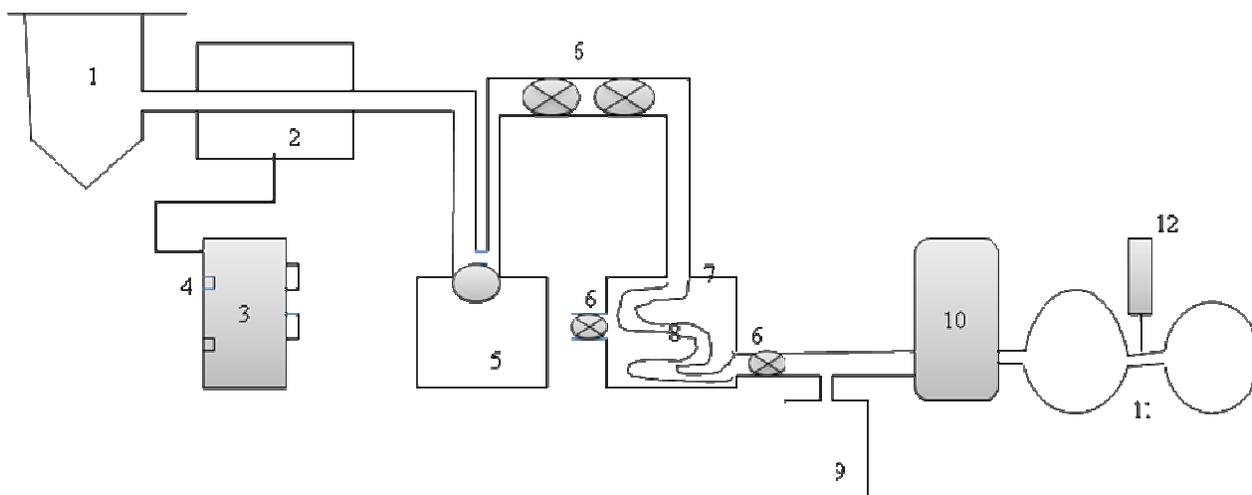
Fresh sludge from the mixALCO plant was collected and dewatered to a moisture content of < 10.0 % to minimize the water content of the bio-oil. Proximate and ultimate analyses together with heating values were determined using a Parr 6200 calorimeter (heating value of bio-oil and char determined at end of pyrolysis). Table 2.1 shows the results. MC (moisture content), VCM (volatile combustible matter), FC (fixed carbon).

Table 2.1 Proximate and Ultimate Analyses

														Heating value		
MC	VCM	FC	Ash	sludge	BioOil	Char										
%	%	%	%	Btu/lb	Btu/lb	Btu/lb										
7.2	66	3.3	23.7	5900	11000	4800										

Losses	C	H	N	S	Al	Ca	Fe	Mg	P	K	Si	Na	Ash
%	%	%	%	%	%	%	%	%	%	%	%	%	%
6.6	38	4.8	0.4	0.1	0.3	9.2	0.2	0.2	0.7	0.1	0.5	0.1	19

Between 6.5 to 7.5 pounds of dewatered feedstock was fed into the hopper of the pyrolysis system. Pyrolysis was carried out isothermally in a Thermoelectron Corporation/Centigrade Service Inc. furnace heated electrically by a Thermoelectron Corporation/Centigrade Service Inc. heater (70 amps capacity, 208/240 volts) at a preset temperature. Heating was done at 630, 680, 730, 750 and 770 C at auger federates (RPM) of 2.6, 3.0 and 3.4. The heater temperatures were measured by installed J-K type thermocouples. After feeding the hopper, it was sealed to create anaerobic condition and purged with nitrogen for 25 minutes. In the meantime, the condenser was properly iced to create appropriate condition for the separation of bio-oil from the syngas. Material in the hopper was passed into the furnace by an auger which was in turn turned by an electric Honey Well Inc motor (25 amps, 90 volts). The RPM of the motor was converted into an auger RPM by using a ratio of 500:1. At the end of each experiment, the char collected in the bin was removed and weighed and the value obtained was used for energy and mass balances (and efficiency) and yields calculations. The same parameters were determined for gases collected using a designed gas collection kit of 5 feet balloons purchased from Card and Party store, Bryan. Per cent composition (v/v) were determined by injection of 2.5 mL of gas sample collected through the latex tubing connecting both balloons. Injections were done in triplicate using an MG # 1 SRI series 8610 C GC, equipped with a TCD and an HID as detectors. The GC column temperature program maintained an initial column temperature of 60 °C for 5.0 minutes which was ramped to 220 °C with a ramp rate of 20 °C/minute. It was maintained at this temperature for 30 minutes before cooling to 60 °C in a column reconditioning subprogram. A gas standard of methane, hydrogen and carbon monoxide was used for GC calibration. The schematic of the pyrolysis process is shown in Figure 2.1.



1. Hopper 2. tube furnace 3. Furnace heater 4. J-K. type thermocouple 5. Char bin 6. Control valves
7. Condenser 8. Cooling fins 9. BioOil bottle 10. Gas filter 11. Gas collection balloons 12 gas collection needle.

Figure 2.1 Process Schematic.

2.2 Statistical Design.

The global kinetics model is used to study the kinetics of thermal decomposition of various feedstocks in a thermo-chemical process by thermo-gravimetric means. In this process, the rate of weight loss of the biomass at a given temperature is correlated with instantaneous qualitative and quantitative data on the gaseous process stream usually with the aid of an online GC, GC-MS system and the Fourier Transform Infrared Spectroscopy (FTIR) [8,9]. Kinetic parameters such as activation energy when determined can be fed in such empirical models and used to determine when (temperature and time) optimum gas production is possible. This requires huge resource deployment and a simpler and cost effective means of maximizing gas production by sheer statistical tools might be necessary. The response surface method is a technique that lends itself readily when proper adherence to experimental protocol and temporary-based system performance factors are considered.

Preliminary experiments were performed to gauge possible maxima (temperature, feedrate) for syngas production that can be considered as a center point in actual experiments. Each factor combination of temperature and auger R.P.M. was considered in triplicate for temperatures 730, 750 and 770 °C and R.P.M.s 2.6, 3.0 and 3.4. The combination (750 °C, 3.0) was considered as center point for a total of 15 runs. The temperature spread of 20 °C appeared insignificant for observable change in gas composition and R.P.M was shown to be “not significant” as a main effect necessitating a wider spread of 50 °C to include the temperatures 630 and 680 °C. The R.P.M was maintained at 3.0 for all these lower temperature runs. Runs at each temperature were in triplicate for a total of 6 additional runs.

2.3 Data Collection and Analysis

GC injections of gas standards were used to establish a coefficient for each gas. This was multiplied by the peak area of each gas in the chromatogram to get the per cent composition

(v/v) of the gas. Since the RPM was proved not to be the main effect variable the mean and standard error of the mean (SEM) of all injections were determined for each temperature.

The gas containing balloons were each approximated to a sphere and its volume determined. This together with per cent composition (v/v) was used to determine individual volume of each gas and the Ideal Gas Law was used to determine the density of the gas at the process temperature (70 °C). With these the mass of each gas could be calculated for mass/energy balance and efficiency purposes. Char and bio-oil weights together with energy values were determined as explained in Section 2.1. Volumetric gas productions, char and bio-oil yields, and material accounting were displaced in tables, bar graphs and flow diagrams. The % composition results were analysed by Design Expert® software to generate ANOVA tables, quadratic models and normal probability plot of the residuals.

3 Results and Discussion.

3.1 Syngas and the Quadratic ANOVA Model.

The per cent compositions (v/v) for the three gases detected – hydrogen, methane and carbon monoxide are displaced in Table 3.1.

Table 3.1 v/v Per cent Composition of Gas Product Stream.

temperature	hydrogen	methane	carbon monoxide
celsius	mean±SEM	mean±SEM	mean±SEM
630	20±0.2	19.6±0.6	22.9±1.0
680	31.0±1.4	15.5±0.6	22.0±1.3
730	42.8±0.5	19.2±0.1	26.3±0.3
750	45.4±0.9	20.0±0.2	29.5±0.8
770	44.7±0.3	19.4±0.2	31.1±0.1

The data shows good reproducibility with a maximum standard error of 1.4 %. Maximum hydrogen, methane and carbon monoxide productions of 45.4, 29.0 and 31.1 % respectively were obtained at 750 C for hydrogen and methane and 770 °C for carbon monoxide. Huang et al [6] had reported 55 and 10 v/v % respectively for hydrogen and methane using a microwave oven on rice straw owing to higher energy transfer capabilities; the highest so far reported in the literature.

More gas was produced as temperature was increased due to cellulosic decomposition by primary devolatilization. More of the liquid phase bio-oil produced at lower temperatures especially the phenolic compounds are converted into hydrogen and methane by catalytic secondary cracking [2, 5, 7]. The production of CO rather than the more oxidized form of CO₂ and the higher hydrogen produced at higher temperatures can be explained partly by highly anaerobic conditions and reactions such as methane gasification (reduction of methane by water to CO and H₂) and water gas reaction (water oxidation of carbon to CO and H₂) [4].

Table 3.2 shows the ANOVA data for hydrogen and the adequacy of the model for decision making is verified by the appropriate data fit of the normal probability of the residuals. The latter verified the normality assumption necessary for ANOVA statistical inferences. Similar data sets (not shown) for methane and carbon monoxide were obtained

Table 3.2 ANOVA Data for Hydrogen.

ANOVA for Response Surface Quadratic Model
Analysis of variance table [Partial Sum of Squares - Type III]

Source	Sum of squares	df	Mean square	F value	p-value prob > F	
Model	1419.34	5	283.87	27.17	< 0.0001	significant
A-temp	793.83	1	793.83	75.97	< 0.0001	
B-feedrate	0.08	1	0.08	0.01	0.9302	
AB	0.94	1	0.94	0.09	0.7684	
A ²	33.35	1	33.35	3.19	0.0942	
B ²	0.2	1	0.2	0.02	0.8928	
Residual	156.73	15	10.45			
Lack of Fit	29.6	1	29.6	3.26	0.0925	not significant
Pure Error	127.13	14	9.08			
Cor Total	1576.07	20				

The Model F-value of 27.17 implies the model is significant. There is only a 0.01% chance that a "Model Value" this large could occur due to noise

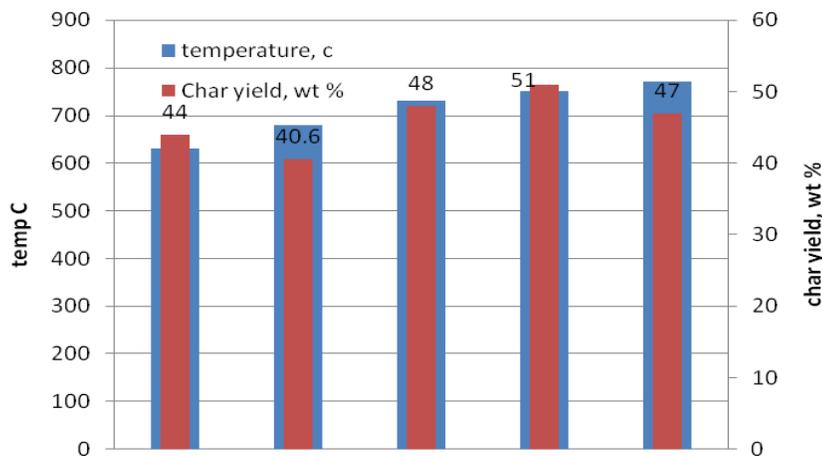


Figure 3.4 Char Yield, wt %

Increase in gas yield at higher temperature is mirrored by increase in total volume although this starts to drop at 770 C with decrease in energy efficiencies. Specific volumetric bio-oil is almost insignificant at at least 730 C with improved yields at lower temperatures (630 and 680 C) which contributed to improved energy efficiencies. No meaningful correlation existed between char yield and temperature although the bulk of biomass was converted to char.

3.3 Material Balances.

Material balances involved determinations flows of mass and energy into and out of the system boundary as shown in Figure 3.5 for a 4.7 lb of feedstock pyrolyzed at a temperature of 630 °C. Key parameters involved are shown in Table 3.4 with explanations of steps involved in calculations. Mass and energy efficiency calculations were determined at a temperature of 25 °C

and pressure of 1 atmosphere. The efficiency decreased with increased temperature and calculations showed the process to be energy neutral – leaving no energy footprint. This was in line with a study performed by Hossain et al [3] which showed both industrial and commercial sludge feedstocks to be energy neutral versus domestic sludge.

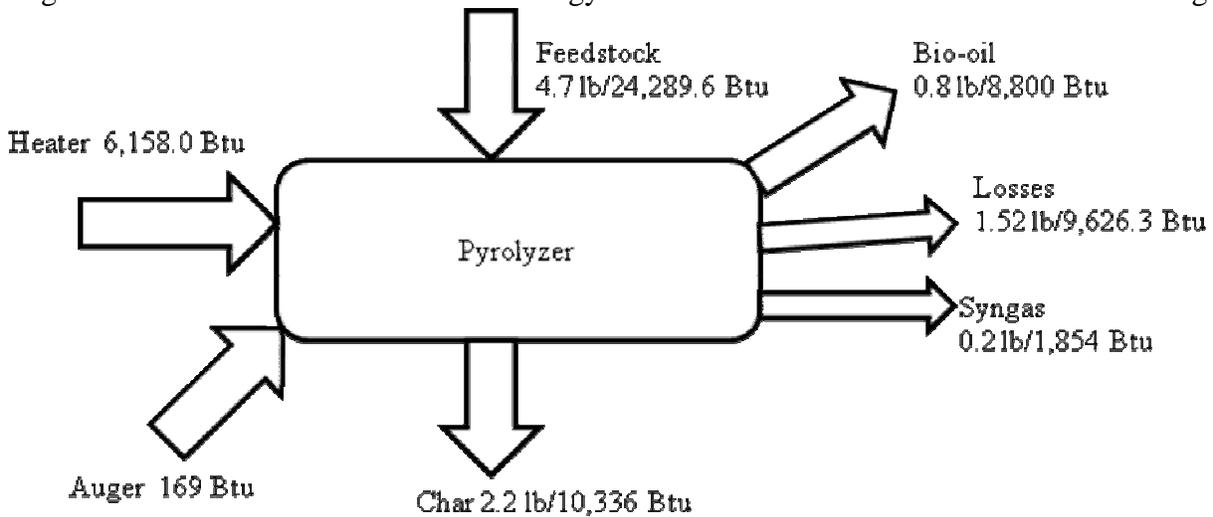


Figure 3.5 Material Flow for a pyrolysis temperature of 630 C

Table 3.4 Mass and Energy Balance Data (for 4.7 lb of feed at 630° C)

Mass (in) Pyrolyzed (lb) (mins)	Time	Input current and voltage				Mass (out) char (lb)	Mass (out) bio-oil (lb)	Total volume (out) gas (L)	
		Heater		Auger					
		Current (A)	Voltage (V)	Current (A)	Voltage (V)				
4.7	15	35	208	2.2	90	2.2	0.8	231	
Heating values (room temp and pressure) – Btu/lb				Density (lb/L)			Volume of gases (L)		
H ₂	CH ₄	CO	Bio-Oil	H ₂	CH ₄	CO	H ₂	CH ₄	CO
51,628	21,433	4,368	11,000	1.8×10 ⁻⁴	1.4×10 ⁻³	2.5×10 ⁻³	46.2	27.5	52.9
Energy in (Btu)				Energy out (Btu)					
feedstock	Heater	Auger	Sum	Char	Bio-oil	H ₂	CH ₄	CO	Sum
24,289.6	6,158.0	169	30,616.9	10,336	8,800	429.3	842.5	582.3	20,990.6

Calculations

$$volume\ gas\ produced = total\ volume\ (L) \times gas\ concentration\ \left(\frac{V}{V}\ \%\right)$$

$$\text{Density of gases } \left(\frac{\text{lb}}{\text{L}}\right) = \frac{\text{Pressure (atm)} \times \text{molecular weight (g)}}{R \times \text{temperature (K)}} \times 2.2 \times 10^{-3}$$

$$\text{Mass of gas produced (lb)} = \text{density } \left(\frac{\text{lb}}{\text{L}}\right) \times \text{volume (L)}$$

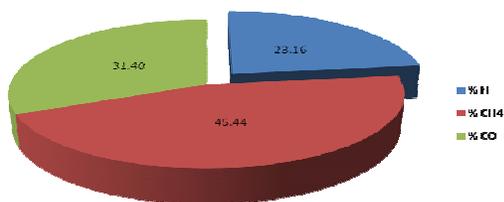
$$\text{Non - electrical energies (Btu)} = \text{Mass of material (lb)} \times \text{heating value } \left(\frac{\text{Btu}}{\text{lb}}\right)$$

$$\text{Electrical energy consumption (Btu)}$$

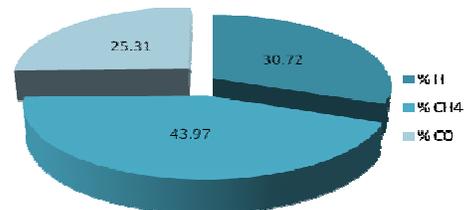
$$= \text{current (A)} \times \text{voltage (V)} \times \text{time (s)} \times 9.47 \times 10^{-4}$$

$$\text{Energy /mass efficiency (\%)} = \frac{\text{sum of energy /mass out}}{\text{sum of energy /mass in}} \times 100$$

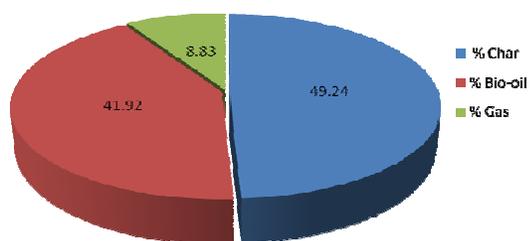
3.4 Energy Distribution



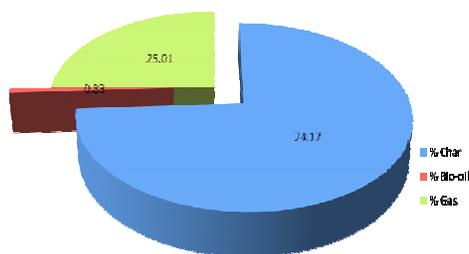
a) Product gases at 630 °C



b) Product gases at 770 °C



c) Char, Bio-oil and syngas (630 °C)



d) Char, Bio-oil and syngas (770 °C)

Figure 3.6 Energy Distribution

Figures 3.6 a) and b) show that the most energy is stored in methane than in hydrogen and carbon monoxide. Infact the total energy value of the methane produced is about equal to the combined energy values of hydrogen and carbon monoxide. This is because of the high heating value of methane compared to carbon monoxide. Hydrogen has a very high heating value but gravimetrically it is dwarfed by carbon monoxide and methane. The amount of hydrogen produced (lb) is only about 5.67 % of the total gas produced.

Figures 3.6 c) and d) show the most amount of input energy is captured in char. At higher the amount of energy in char is about 3 times that of bio-oil and syngas put together. As temperature is raised, this favors the production of gases since the bio-oil is converted into more gaseous product especially hydrogen. This explains the greater amount of energy distributed into the gas phase and consequent reduction the total energy of the bio-oil produced.

4 Conclusions and Recommendations.

Hydrogen and methane production can be maximized from sludge in a thermo-chemical process at higher temperatures in the range 735 to 770 C. Since energy efficiency is sacrificed at higher temperatures, lower temperature operation can lead to more bio-oil production whose energy value can increase the energy efficiency.

More insight on the process can be gained if this approach is coupled with GC-MS and FTIR capabilities. More research needs to be focused on the thermo-chemical process since it has more advantages over other technologies in the bioenergy industry. This should extend to cost effective large scale gas separation techniques to allow industrial operators to put the gases into economic use. The performance of the system will be improved with better gas collection system and operation in a continuous rather than batch mode.

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