RESEARCHREPORT
ENVIRONMENT

Title: Thermochemical Conversion Process to Produce Oil from Swine Manure – **NPB #06-102**

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Industry Summary

Laboratory scale tests show that more than 60% of the volatile solids in swine manure can be converted to bio-crude oil using a thermochemical conversion (TCC) process. The process can work with manure pulled from shallow pits up to 40 days old with minimal decline in the oil yield or quality compared to that from fresh manure. It is not known how well the process will work with older manure (e.g., from deep pits or lagoons), but it is known that there is some loss of volatile solids with time, so the potential yields are lower.

Our research team was able to produce oil with blends of swine manure and sawdust and swine manure and corn stalks. We also produced oil when a separation process was used to concentrate the manure solids.

The scope of this research was not to track the nutrient flow. However, the researchers noted that the most valuable nutrients (nitrogen, phosphorus and potassium) are not consumed in the TCC process, and thus remain available for use as fertilizer.

The scope of this research was also not economic and cost-benefit analyses. However, based on the measured oil yields, the manure from a hog from birth to market will produce 1/4 to 1/3 barrel of bio-crude oil. And the TCC process kills pathogens in swine manure.

III. Scientific Abstract

Thermochemical conversion (TCC) is a chemical reforming process of organic polymers in a heated enclosure, usually in an anoxic or very low oxygen environment. The products are liquid oil, char, and gases, depending on operating conditions. Unlike pyrolysis, which requires dried feedstock, the TCC process in this study treats the manure slurry directly. The major end product in this process is liquid oil. TCC technology has been studied using feedstock such as coal and wood sludge since the oil crises in the 1970's, but the technology was not sustained due to the low fossil oil prices and high cost of the feedstock. The TCC process, has been applied to the processing of livestock manure − a costless feedstock, not only for renewable energy production but also for waste reduction and treatment.

In our first stage research, a batch TCC reactor was developed and a systematic investigation on process parameters, including operating temperature, type and initial pressure of process gases, retention time, total solids content and feedstock pH levels, was conducted. The process was evaluated in terms of oil production efficiency and waste reduction efficiency, and the oil product was analyzed for its benzene solubility, elemental composition, and heating values. The key factors of the TCC process were found to be the operating temperature, the retention time, and the addition of a process gas. Processed with carbon monoxide between 15-30 minutes at temperatures of 295°C to 305°C an average of 62% wt of the volatile solids (or 54% wt of the total solids) was converted to oil product, COD was reduced by 60 to 70%. At optimum operating parameters, 80% wt of volatile solids (or 70% wt of total solids) were converted to oil, of which 80% had a heating value between 32,000 and 36,700 kJ/kg.

Biomass conversion studies in the early 1970's showed that conversion of wood sludge into renewable energy was technically sound, but not economical (Jones and Radding, 1980), primarily due to the low price of fossil oil and high cost of feedstock (wood sludge). Economic evaluations by the University's licensee for commercialization of the technology suggest that the TCC technology may be economically feasible once the design and operations are perfected for production scale applications.

Introduction

Swine manure is both a challenge and opportunity for pork producers. With increasing fertilizer prices globally over the last few years, the value of the nutrient content (primarily nitrogen, phosphorus and potassium) has become increasingly important.

While the hydrocarbons contained largely in the volatile solids fraction of the manure also have value as a soil amendment, they appear to have greater value as a potential source of renewable bio-fuel. At crude oil prices in the $100/barrel range, and discounting for being a heavier crude oil, the bio-crude produced can have a value of $15 to $20/hog marketed.

There are also important environmental benefits from the TCC process. Methane is converted to a bio-fuel and emissions of methane, a more critical factor than carbon dioxide in global warming, are minimized. Odor in the swine manure is also largely eliminated and the lower biological oxygen demand of the post TCC by-products reduces environmental risks.

The ultimate goal of the proposed project is to commercialize the thermochemical conversion (TCC) process as a method to treat swine manure and to produce bio-oil. At this stage, we investigated how swine manure type, source, and age affect oil yield and quality. Practical application of TCC to convert swine manure to oil is more likely if the process can be adapted to current manure handling and storage facilities.. Since feedstock composition is an important factor in the TCC process, it is important to assess any changes that may result from variations in swine manure composition. The results from this proposed work provide critical information on how to integrate a farm-scale TCC unit to an actual swine farm and how to best process the manure generated from the farm.

Objectives

Our primary objective was to determine the effects methods of storage, handling and pre-processing swine manure had on oil yield and quality. Information on how to best process a particular type of swine manure will prove useful in the development of the farm-scale unit. The specific objectives of the completed work are listed below.

1. Investigate the oil yield and quality that can be obtained when using different types and sources of swine manure. This is important for economic feasibility studies to guide the design of farm-scale TCC systems.

2. Determine the optimal operating conditions for oil production as a factor of swine manure feedstock composition. Variability in composition of the feedstock affects the process as a whole. Thus, information on which operating conditions are optimal for a particular feedstock is valuable.

3. Characterize and analyze the composition of by-product streams. Other components were identified that may add value to the process. In addition, information was gained on the need for further treatment of and opportunities to generate value from product streams.

Materials and Methods

Objective 1 – Batch TCC tests using different swine manure types and sources

Batch TCC experiments using different types of swine manure feedstock were conducted following the protocol that was developed for previous batch TCC tests (He, 2000).

We tested the oil yields that derived from processing fresh swine manure collected from two sources: (1) pen floors and (2) pits (including shallow and deep pit. The effect of manure age on oil production and yield was investigated for deep pit manure. The manure samples were obtained from a local swine producer that we have worked with previously.

This project was conducted at the Bioenvironmental Engineering Section of the University of Illinois at Urbana-Champaign (UIUC). The groups who collaborated in the previous studies, including the University's Swine Research Center, Department of Animal Sciences, MicroAnalysis Laboratory of the School of Chemical and Life Sciences, and the Illinois Geological Survey Laboratory located on the UIUC campus, will be continuously involved in the project.

Objective 2 – Process optimization

The optimal condition for each type of feedstock was determined by evaluating oil yields and oil quality at different operating conditions. We conducted tests at different operating temperatures (280-320°C), pressures, and residence times (15-60 minutes). The effect of catalyst additions was also investigated. Optimizing the process requires operating the reactor under several parameter combinations around the optimums determined in the batch process study and also evaluating the impacts and costs of processing the bio-fuel for optimal burning characteristics.

Objective 3 – Products characterization

Samples from each product stream were analyzed separately. The procedures and instrumentation for the analysis of the feedstock and end products were established and followed in all analytical analyses.

Oil product: Samples were analyzed using several ASTM procedures for the characterization of petroleum products. Tests include:

D240-02	Standard Test Method for Heat of Combustion of Liquid Hydrocarbon Fuels by Bomb Calorimeter; Elemental Analysis using CHN Analyzer

D-1552	Standard Test Method for Sulfur
D473-02	Standard Test Method for Ash from Petroleum Products
D-4124	Standard Test Method for Saturates, Aromatics, Resins, and Asphaltenes/Benzene Solubility
UOP389-86	Trace Metals in Oils by Wet Ash/ICP-AES

Knowing the properties and composition of the oil product is very important to determine potential markets and to estimate the value of the oil product. Also, based upon the results of the above characterization tests, we assessed the potential for upgrading of the crude oil. We expect that further upgrading will greatly increase the value of the oil product.

Aqueous product: From our previous work, we have found that most of the fertilizer value of the original manure feedstock is retained in the aqueous product and in readily usable forms. Given this, we determined the NPK content of the aqueous product so we can determine its potential for direct use as a fertilizer.

Using the federal EPA effluent standards for wastewater quality as a benchmark, aqueous samples were tested for various compounds using standard methods. Specific tests include:

SM2540	Standard Method for the Determination of Total Solids, Volatile Solids, and Fixed Solids
EPA 160.3	Determination of Total Suspended Solids in Water and Wastewater
SM4110C	Anions in Water by Ion Chromatography

Gases: The composition of the product gas was determined using ASTM D2650-99 Standard Test Method for Chemical Composition of Gases by Mass Spectrometry.

The above analyses helped us determine the economic value of end-products and evaluate the necessity of further treatment for farm-scale systems to protect the environment. The optimal combination of variables and processing methods requires further in-depth study.

Results and Discussion

Objective 1. Evaluation of effects of manure handling system and pig ages on oil yields.

We tested the oil yields derived from the swine manure collected from two sources: (1) pen floors and (2) pits (including shallow and deep pit). Also, different stages of production were investigated as a factor affecting oil yield. The effect of manure age on oil production and yield was investigated for pit manure.

A summary of the batch test results for various manure feedstocks is shown in Table 1.The operating conditions used in these tests are subjected to the TCC process at optimal operating conditions found for fresh swine manure. The conditions are listed as: Temperature, 305°C; Retention time, 30-60 min; operation pressure, ~1500-1700Psi; process gas (N_2 or CO) with a 100 Psi initial pressure. Effect of catalyst addition was also investigated which depends on individual samples. Based on previous study in our lab, repeatability of the system is reliable (as one but not the only evidence, triplicate tests were run with 14d swine manure, raw oil yield is 68.6%±1.9%), so not all tests were repeated three times.

Table 1: Batch test results for various manure feedstocks

Run	*Feedstock*	*Description*	*Separation method*	*Catalyst added*	*Temp (°C)*	*Pressure (MPa)*	*RT (min)*	*Raw Oil yield (%)*
1	Fresh manure	Grower/ Finisher	floor	none	305	10.3	60	up to 70%
2	Fresh manure	Nursery manure (SRC/IL)	floor	none	305	11.9	30	53.9
3	Fresh manure	Sow manure one day old (WWBE)	floor	Na_2CO_3 (1.0%)	305	1700Psi (CO)	60	No oil[#]
4	Pit manure	Sow manure (over 30 years in pit, SRC*/IL)	N/A	none	305	11.2	30	No oil
5	Pit manure	shallow pit (SRC/IL)	gravitational settling + drying	none	305	10.3	60	24.94
6	Pit manure	shallow pit (SRC/IL)	gravitational settling + drying	none	305	10.3	60	32.50
7	Pit manure	shallow pit (SRC/IL)	gravitational settling + drying	none	305	10.3	30	34.91
8	Pit manure	deep pit (Winston-Simpson/MO)	centrifuge	none	305	10.3	60	No oil
9	Pit manure	deep pit (Winston-Simpson/MO)	centrifuge	none	305	10.3	30	No oil
10	Pit manure	deep pit (Winston-Simpson/MO)	centrifuge	none	285	10.3	60	No oil
11	Pit manure	deep pit (Winston-Simpson/MO)	centrifuge	none	285	10.3	30	No oil
12	Pit manure	deep pit (John Green-wood /MO)	centrifuge + filter	none	305	12.1	30	No oil
13	pit manure	deep pit (John Green-wood /MO)	centrifuge + filter	Na_2CO_3 (0.8%)	305	12.1	30	No oil
14	Pit manure	deep pit (John Green-wood /MO)	centrifuge + filter	$(NH_4)_2SO_4$ (0.8%)	305	12.1	30	No oil
15	Pit manure	Deep pit (WWBE**)	Belt press with polymer	N/A	305	9.65	30	No oil
16	Pit manure	Deep pit (WWBE)	Belt press	N/A	305	11.7	60	Invisible oil
17	Pit manure	Deep pit (WWBE)	Belt press	Na_2CO_3 (1.0%)	305	1500Psi (CO)	60	19.4
18	Pit manure	Deep pit (WBE)	Belt press	Na_2CO_3 (1.0%)	305	11.7	60	29.8

* SRC - Swine Research Center, UIUC

** WWBE - WorldWide BioEnergy Company

[#] No oi l- No visible oily product (which is described as 0% raw oil yield sometime), but it is not necessarily true that there is no toluene/benzene soluble fractions in the solid product

Oil products were obtained from nursery, grower and finisher swine manure, and there was no raw oil yield found for sow manure. When oil product was found, products after the TCC process were distributed into four different portions: aqueous product, including raw oil product and post-water, gaseous product, and solid product, the raw oil product floated on top of the reactor vessel, the post-water in the middle and the solid product settled on the bottom of the reactor. The solid product contained dirt, char and some heavy oil, and a small amount of minerals. After the other tests without obvious oil product, only aqueous product was found, which is dark in color, almost black. Some solids settled immediately and were black in color.

Oil production was used to measure the TCC efficiency. Benzene/acetone solubility of oil product was used as an indicator of oil product quality. The higher benzene/acetone solubility of oil products, the higher oil quality. The results of oil product and solid product were typically shown in Table 2.

Table 2: Oil yield and benzene solubility to pit manure and fresh manure by TCC process

Materials	*Oil yield, %*	*Benzene solubility of oil, %*
Fresh manure	65	76
Shallow pit manure	34.91	89.0
Deep pit after Belt press	29.8	29.2
Deep pit centrifuge	0	--
Deep pit belt press with polymer	0	--

The difference in composition may explain why crude oil could or not be produced from different feedstocks. Basically, manure samples which produced oil present a much higher volatile solid composition of the manure samples that cannot produce oil. It also can be found that the higher lignin content, the lower the oil yield. These results are also in agreement with the literature. However, other factors, such as interactions between the component fractions, catalytic actions by the mineral matter content, and inhibitors that could prevent the formation of oil, also play a role in the formation of oil and we do not understand that yet.

Prior to this research period, we established that swine manure handling systems which separate the feces from the urine shortly after excretion (e.g., some Y-gutter systems, and the Agri-Marche system), and stored separately, work well for the TCC process. Urine and waste water can be blended back with the feces and more than 70 percent of the volatile solids in the manure can be converted to crude oil.

In this project, we determined that swine manure from shallow pull-plug systems up to 40-day-old manure works well in the TCC process. This is important because large numbers of U.S. swine farms have such systems, and management practices with such systems typically mean the manure is from 0-21 days old when the system pits are drained. Thus, the TCC process can be adapted to shallow pit systems with no building modifications and minimal modifications of operating practices.

Different aged swine manure samples were collected from shallow pit and air dried when necessary to adjust the total solid content to ~20%. Raw oil yields are consistently around 65% for all manures aged from 0-39 days. Comparison of raw oil yields is shown in Figure 1. Comparison of refined oil yields and product compositions are shown in Figure 2. The refined oil yields of different aged manure are quite consistent at around 35% (wt% of TS). There is no strong evidence to show that manure age between 0-39 days is a significant factor affecting the refined oil yield or product compositions of the TCC process, which swine manure age may probably not influence the TCC process or composition of TCC products.

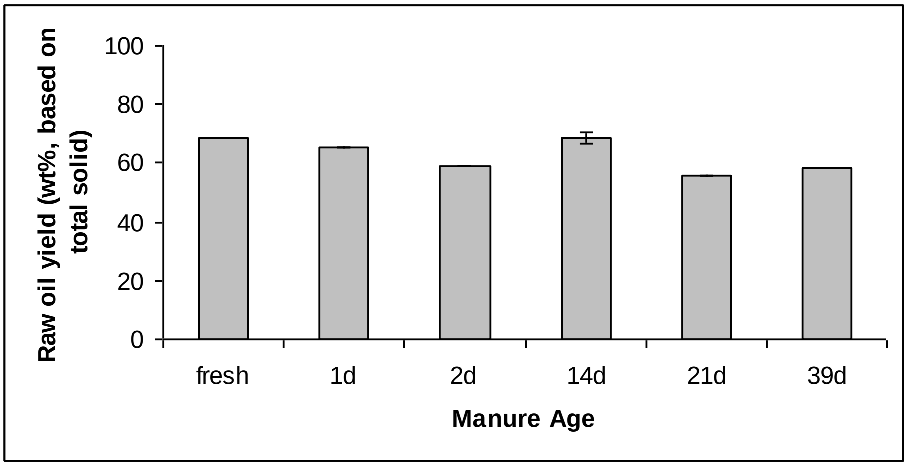

Figure 1: Effect of manure age on raw oil product

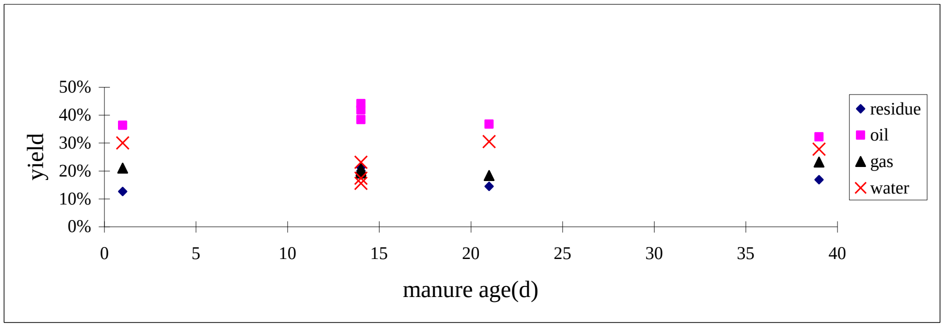

Figure 2: Effect of manure age on the composition of TCC products

Objective 2. Process optimization.

It was determined that we have two alternatives for obtaining the desired liquids/solids ratio for swine manure from the pits. One method is manure separators, with a portion of the liquid fraction added back to the swine manure before TCC processing. The second method is blending high solids content residues (e.g., sawdust, corn stalks) to the swine manure without a separation process. There is more work needed to determine the range of crop/wood residues which can be blended with swine manure and to learn the most effective and economical combination (based on cost and availability of the residue as well as overall oil yield and oil quality).

A screw/screen separator and a centrifuge which has a maximum 3000 rpm speed were used to concentrate the feedstock. The screw/screen separator could consistently increase the total solid content of swine manure from around 15% to 35%. After the screw/screen separator, the centrifuge was used to continue concentrating the liquid fraction, and the solid fraction after this centrifuging process could also reach a solid content of about 35%. TCC tests were run with the concentrated solid fraction. No raw oil product was found. Compared to the results that we did get oil from, the same swine manures treated by air drying, we concluded that the loss of some crucial components in the supernatant fraction caused the results of no raw oil yield. To concentrate the pit swine manure without losing important components, the air drying method was utilized. Five to seven days or longer was needed to increase the solid content from ~5% to above 20% at room temperature.

With the centrifuging method, when some of the supernatant fraction was added back to the solid fraction and the mixture was taken as feedstock, oil product was found and a raw oil yield of 62.1% was obtained.

Effects on raw oil yield of adding different cellulosic materials into 14-day-old pit swine manure are shown in Table 3. From the result, cases of adding either rice straw or cornstalk into 14-day-old manure (TS =

12.9%) could not make oil products. However, when sawdust was added to the same feedstock we did make an oily product. Furthermore, adding sawdust into 14-day-old manure of a lower total solid content (TS = 5.7%) did not make an oily product, which implies that there is a limited amount of sawdust that can be added.

Table 3: Effect of adding different cellulosic materials on raw oil yield

#	*Feedstock*	*TS (%)*	*Loaded (g)*	*Raw oil yield (%)*
1	Rice straw	93.1		0
	14d manure	12.9		
	Mixture	20.4	801.4	
2	Cornstalk	91.8		0
	14d manure	12.9		
	Mixture	20.3	801.8	
3	Sawdust	90.5		58.3
	14d manure	12.9		
	Mixture	20.4	800.2	
4	Sawdust	90.5		
	14d manure	5.7		
	Mixture	19.7	799.8	0
5	14d manure after air drying	17.8	802.6	69.1

Note: All tests were run with an initial N_2 pressure of 100 psi, a reaction temperature of 305ºC and a retention time of 30 minutes. Zero raw oil yields do not necessarily mean no toluene soluble components in the products.

<u>Objective 3 – Characterize and analyze the by-product streams.</u>

Specific properties of by-product streams were analyzed and listed here, all tests used fresh manure as feedstock due to its relatively-small variation of characteristics compared to other kinds of manure feedstocks.

The nitrogen content of aqueous products is shown in Table 4. No particular trend with respect to operating conditions was found for the total nitrogen content of the aqueous products. The average total N was 6,099 mg/L with a standard deviation of 1,941 mg/L. This result indicates that almost all of the original nitrogen in the manure slurry remains in the aqueous product after the process. The average N content of the swine manure was 3.4% on a dry basis. Given this, the total nitrogen recovery was about 76.2%.

Table 4: Total nitrogen, ammonia, and nitrate content of the aqueous products

Temperature (°C)	*Pressure (MPa)*	*Residence time (min)*	*Total N (mg/L)*	*N-NH_3 (mg/L)*	*NO_3^- (mg/L)*
285	9.0	40	8,352	1,940	1.7
285	9.0	60	7,119	2,270	0.1
285	9.0	80	4,631	1,860	0.1
285	10.3	40	8,071	2,055	1.1
285	10.3	60	6,093	2,610	0.1
285	10.3	80	2,463	2,530	2.0
285	12.1	40	3,455	2,495	0.9
285	12.1	60	3,418	2,820	1.8
285	12.1	80	4,536	2,100	2.2
305	10.3	40	2,389	3,953	0.1
305	10.3	60	7,790	3,743	0.4
305	10.3	80	6,642	3,270	2.0
305	12.1	40	6,824	3,790	1.9
305	12.1	60	6,337	2,540	0.1
305	12.1	80	4,996	3,380	2.0
325	12.1	40	6,947	4,555	0.2
325	12.1	60	8,652	6,740	0.8
325	12.1	80	7,921	7,070	1.7
*305	12.1	40	7,068	3,750	0.8
*305	12.1	60	6,580	3,860	0.8
*305	12.1	80	7,799	3,760	0.8

Note: *CO was used at a rate of 100 mL/min.

Table 5 shows the PO_4^- concentration of the aqueous samples. Considering all of the tests that were conducted, the average PO_4^- concentration of the aqueous product was 971 mg/L with a standard deviation of 256 mg/L. From the data listed in

Table 5, operating temperature showed a relatively greater influence on PO_4^- concentration as compared to residence time, operating pressure, and addition of CO. No sufficient explanation can be given from this study due to lack of information on other forms that phosphorus may take after the reaction process.

Table 5: Phosphate content of the aqueous products

Temperature (°C)	*Pressure (MPa)*	*Residence time (min)*	*PO_4^- (mg/L)*
285	9.0	40	1,130
285	9.0	60	1,274
285	9.0	80	1,240
285	10.3	40	1,285
285	10.3	60	1,436
285	10.3	80	1,310
285	12.1	40	1,049
285	12.1	60	1,090
285	12.1	80	1,249
305	10.3	40	1,062
305	10.3	60	710
305	10.3	80	895
305	12.1	40	1,052
305	12.1	60	1,306
305	12.1	80	786
325	12.1	40	161
325	12.1	60	149
325	12.1	80	94
*305	12.1	40	1,218
*305	12.1	60	1,196
*305	12.1	80	690

Note: *CO was used at a rate of 100 mL/min.

The aqueous K content of some of the aqueous products is shown in Table 6. The average concentration was 1,482 mg/L with a standard deviation of 839 mg/L. The large variation from the average was primarily due to the low levels found in the aqueous samples from tests involving 325°C.

Table 6: Aqueous K concentration of aqueous products

Temperature (°C)	*Pressure (MPa)*	*Residence time (min)*	*Aqueous K (mg/L)*
285	9.0	60	1,893
285	10.3	40	2,061
285	10.3	60	2,176
285	10.3	80	2,411
285	12.1	60	1,784
305	10.3	40	2,271
305	10.3	60	1,545
305	10.3	80	1,154
325	12.1	40	856
325	12.1	60	92
325	12.1	80	56

The volatile organic compounds that were detected in the aqueous product samples are shown in Table 7. Among the compounds detected, acetone had the highest concentration followed by 2-butanone and ethanol. On the average, acetone had a concentration of 700 mg/L. The average concentration of 2-butanone and ethanol were 354 mg/L and 133 mg/L, respectively. The presence of the aromatic hydrocarbons and ether in the aqueous product was a result of incomplete separation of the oil product and aqueous product. Trace amounts of the oil got left behind in the aqueous fraction after separation. Results show that a considerable amount of organic compounds in swine manure were directly or indirectly converted into ketones and ethanol.

There was a large difference between the measured quantities of volatile organic compounds in the two samples. The concentrations of water-soluble organic compounds in Sample 2 (T=325°C and P=12.1 MPa) were consistently higher and for the most part almost double that of Sample 1 (T=305°C and P=10.3 MPa). This suggests that temperature has a large influence on the quantity of material that gets converted into water-soluble organic compounds. It is very possible that some of the oil constituents undergo reactions leading to the formation of ketones and alcohols. This is in agreement with the result where lower oil yields were obtained from a test involving 325°C.

Table 7: Volatile organic compounds in the aqueous product samples

Compound Name	*Concentrations (ug/L)*	
	Sample 1	*Sample 2*
Acetone	456,000	944,000
2-Butanone (MEK)	200,000	508,000
Ethanol	126,000	140,000
Ethylbenzene	934	-
2-Hexanone	2,680	5,680
4-Methyl-2-pentanone (MIBK)	5,190	9,030
Styrene	767	1,090
Tetrahydrofuran	-	6,080
Toluene	4,370	4,670

Notes: Sample 1 – T=305°C, P=10.3 MPa, and RT=60 min; Sample 2 – T=325°C, P=12.1 MPa, and RT=60 min.

Table 8 is the list of bases, neutrals and acids that were identified in the aqueous product. A variety of compounds were found in both samples, but all were not necessarily present in both. The nitrogen containing compounds (i.e., pyrazine and pyrroles) were most probably formed from the reaction of ammonia with compounds that resulted from the decomposition of lignocellulosic material in the manure. In a study by Inoue et al. (1999), it was found that the liquefaction of cellulose with ammonia resulted into the formation of nitrogen containing heterocyclic aromatic organic compounds such as pyrazine and indoles. The amides may have been a result of the reaction of amines and/or ammonia with the carboxylic acids in the reaction media.

Table 8: Base, neutral, and acids in the aqueous product

Compound Name	*Concentrations (ug/L)*	
	Sample 1	Sample 2
1, 3-Diazine	14.7	1,950.0
Pyrazine	14.7	1,950.0
Pyrazine, 2,5-dimethyl-	-	3,770.0
Pentanoic acid	3,320.0	-
Butanoic acid	-	443.0
Butanoic acid, 2-methyl	3,320.0	-
Compound Name	*Concentrations (ug/L)*	
	Sample 1	Sample 2
Acetamide, N-ethyl-	928.0	561.0
Butanamide	4,160.0	2,370.0
Propanamide, 2-methyl-	-	538.0
Cyclopentanone	-	443.0
2-Cyclopenten-1-one, 3 meth	467.0	-
Cyclopentanemethanol, .alph	1,080.0	-
2,3-Dimethylcyclopent-2-en	1,080.0	-
2,5-Pyrrolidinedione, 1-met	-	2,440.0
2-Pyrrolidinone, 1 methyl	991.0	1,840.0
2-Isopropylpyrrolidine, 1-met	1,680.0	-
1H-Pyrrole-2-acetonitrile,	1,680.0	-
Pyrrolidine, 1-acetyl-	340.0	-
L-Proline, 1-acetyl	1,650.0	-
Piperidinone	1,650.0	1,840.0
Benzeneacetic acid	1,650.0	
1-Pentadecene	-	4,000.0
Hexadecanoic acid (palmitic)	-	1,890.0
Oleic acid	-	1,890.0
Octadecanoic acid (stearic)	-	1,890.0
Dodecanamide	-	1,890.0
A-Norcholestan-3-one, 5-eth	-	4,000.0
Unknown	-	2,290.0

Notes: Sample 1 – T=305°C, P=10.3 MPa, and RT=60 min; Sample 2 – T=325°C, P=12.1 MPa, and RT=60 min.

Gas analysis was also done on selected samples and listed in Table 9. In the test case involving 325°C, O_2 was detected in the gas sample. It was expected that all of the O_2 would be spent through oxidation to CO_2 and H_2O as was exhibited the analytical results for the test case involving 285°C. The O_2 detected may have been brought about by contamination during sampling. The sample collection involved collecting gases in Tedlar bags. At one point in the collection of the sample involving 325°C, the bag broke loose from the connector while filling and had to be reattached. This may have introduced some ambient air into the sample.

Table 9: Fixed gases composition of selected gas samples

Component	*Measured percentages (%)*		*Corrected percentages (%)*	
	Sample 1	Sample 2	Sample 1	Sample 2
CO_2	15.0	18.1	97.7	97.9
CO	0.4	0.4	2.3	2.1
N_2	85.6	82.2	-	-
O_2	-	2.4	-	-

Notes: Sample 1 – T=305°C, P=10.3 MPa, and RT=60 min; Sample 2 – T=325°C, P=12.1 MPa, and RT=60 min.

The measured average CO_2 concentration was 16.6% but after applying the corrections, the gas product had an average CO_2 concentration of 97.8% (Table 9). Carbon monoxide was also consistently detected in the gas samples with a corrected average value of 2.2%. The presence of CO in the gas product shows that it was produced in excess of what may have been needed in the shift reaction. Note that the samples used in Table 9 were from test cases where CO was not introduced into the reaction. From this, it was very possible that the CO produced from the decomposition of the organics in manure participated in the deoxygenation of the organic structure. This may explain why additional CO was not necessary in the production of oil.

Using EPA Method TO-14 (U.S. EPA, 1999a), only four volatile organic compounds were detected in the gas product samples (Table 10). Benzene, ethylbenzene, styrene, and toluene were found to have average concentrations of 0.54 ppmv, 1.4 ppmv, 0.82 ppmv, and 14.95 ppmv, respectively. The presence of these toxic organic compounds indicates that the gas product needs to be treated before discharging to the atmosphere.

Table 10: Volatile organic compounds in the gas product

Component	*Concentration (ppmv)*	
	Sample 1	Sample 2
Benzene	0.4	0.6
Ethylbenzene	1.6	1.3
Styrene	0.9	0.7
Toluene	12.8	17.1
THC as Gas	167.0	288.0

Notes: Sample 1 – T=305°C, P=10.3 MPa, and RT=60 min; Sample 2 – T=325°C, P=12.1 MPa, and RT=60 min.

Based on the samples analyzed, the total hydrocarbon in the gas product had an average concentration of 227.5 ppmv (Table 0). Methane, ethane and ethane mainly comprise the total gas hydrocarbon that was produced (Table 11). The average methane concentration was 192.0 ppmv. The ethane and ethene average concentrations were 91.1 and 58.8 ppmv, respectively.

Table 11: Methane, ethane, and ethene in the gas product

Component	*Concentration (ppmv)*	
	Sample 1	Sample 2
Ethane	74.1	108.0
Ethene	48.9	68.8
Methane	173.0	211.0

Notes: Sample 1 – T=305°C, P=10.3 MPa, and RT=60 min; Sample 2 – T=325°C, P=12.1 MPa, and RT=60 min.

We have also developed a comprehensive analysis of feedstocks – swine manure, swine manure blended with catalysts, swine manure blended with crop/wood residues, swine manure post separation for various types of separators (e.g., screw, inclined screen, centrifuge), human (i.e., municipal sewage) sludge, food processing sludges and various primarily cellulose plant materials (e.g., corn stalks, rice straw, corn processing byproducts) and primarily lignin plant materials (e.g., various types of wood wastes). This characterization of alternative feedstocks is enabling us to identify key ingredients needed for the TCC reaction to be efficient and to have a system for adapting the TCC process to a wider range of swine manures by knowing what, if any, ingredients are needed to supplement the swine manure for the TCC process to work well.

We have characterized the oil as similar to No. 6 grade petroleum oil for most combinations of TCC parameters. Blending plant materials with swine manure varies the oil characteristics, but appears not to affect the conversion of the swine manure volatile solids to oil.

Figure 3 shows the results of adding sawdust into swine manure as additives. With the increase of proportion of swine manure in the mixture, the refined oil yield kept increasing. When KOH was added as catalyst, it increased the refined oil yield, especially when the amount of sawdust fraction was predominant. There is a linear regression, which implies that there is no interaction between conversion of manure fraction and sawdust fraction.

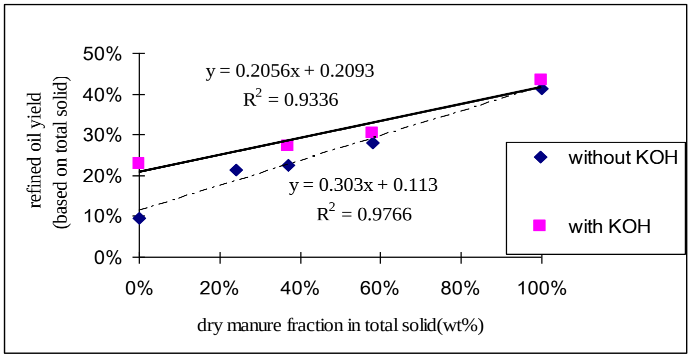

Figure 3: Effect of adding sawdust to swine manure as additives

We have a follow-up research project with the focus on determining how and which crop residues can be blended with swine manure to minimize or eliminate the need for liquid/solid separation prior to the TCC process. Preliminary tests verify that blending plant residues may eliminate the need for liquid/solid separation, which is expensive in initial costs, operational costs and maintenance. Eliminating the need for manure preparation beyond blending with low cost crop residues makes the process more economically attractive to swine producers and provides an additional value-added opportunity.

Citations

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