Title: Effect of Adding Sawdust and Corn Stover on Thermochemical Conversion of Swine Manure into Crude Oil – **NPB #08-076**

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Industry Summary

Our research team was able to produce bio-oil with blends of swine manure and cellulosic biomass. Laboratorial tests showed that adding cellulosic materials like sawdust and corn stover did not significantly affect the bio-oil formation from swine manure using the thermochemical process.

Most operation parameters for swine manure tests were also suitable for producing bio-oil from mixtures of swine manure and cellulosic biomass. Adding catalysts such as KOH could increase the refined oil yield.

A large portion of nutrients that have fertilizer value (nitrogen, phosphorus and potassium) remained in the post-process water, and thus, could be extracted as fertilizer with appropriate methods.

Based on the measured oil yields, the manure from a hog from birth to market will produce 1/4 to 1/3 barrels of bio-crude oil; and the TCC process kills pathogens and largely removes odors associated with swine manure. Adding cellulosic materials may help reduce the cost of dewatering or concentrating the swine manure.

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. 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 previous research work, 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 (He, 2000). Effects of manure storage time and sources were also investigated.

As swine manure on a swine farm usually has a high water content (90% or even higher), heating it directly may be a huge waste of energy. Dewatering or concentrating may also be expensive. On the other hand, cellulosic biomass, a large portion of which is produced as wastes, could be a choice to increase the solid content of feedstock for the TCC process.

Blending cellulosic materials with swine manure varies the oil characteristics, but appears not to affect the conversion of the swine manure volatile solids to oil. The process was evaluated in terms of refined oil production efficiency. When KOH was added as a catalyst, it increased the refined oil yield, especially when the amount of sawdust fraction was predominant. A large portion of nutrients that have fertilizer value (nitrogen, phosphorus and potassium) remained in the post-process water (2/3 for N, 1/3 for P and about 100% of K), and thus, could be extracted as fertilizer with appropriate methods.

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, 1978), primarily due to the low price of fossil oil and high cost of feedstock (wood sludge). Economic evaluations by the University of Illinois' 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.

Our ultimate goal is to research and aid development of thermochemical conversion (TCC) systems to produce bio-oil from swine manure. Doing this reduces odors and environmental risks from swine manure and enhances the economics of swine production.

One key remaining issue for commercial adaptation of this technology is optimizing the collection and preparation process for swine manure as a feedstock for the thermochemical conversion process. Blending low-cost, readily available crop residues is perhaps the most economical way to bring swine manure to the required 20% solids content needed for the TCC process to work.

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

As part of the development of a farm-scale unit, the objective of this proposed project is to determine the effect of readily available additives such as sawdust and corn stover to swine manure on oil yield and quality. Information on how best to process particular types of additives to swine manure will prove useful in the development of the farm scale unit. The specific objectives of the proposed work are:

Investigate the oil yield and quality that can be obtained when adding additives to swine manure at various storage times. By doing so, an economic feasibility study of a realistic farm-scale process can more accurately be made. Moreover, the results will aid with integrating a farm-scale design with existing swine facilities.

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 will be valuable.

Characterize and analyze the composition of by-product streams. Other components will be identified that may add value to the process. In addition, it will give information on what other unit processes may be needed to further treat product streams.

Materials and Methods

Objective 1 – Batch TCC tests using mixtures of swine manure and sawdust and swine manure and corn stover.

Batch TCC experiments using mixtures of swine manure and sawdust and swine manure and corn stover were conducted following the protocol that was developed for previous batch TCC tests (He, 2000).

The manure samples were obtained from a local swine producer that we worked with previously. Corn stover was collected from a local cornfield and dried. Sawdust samples were collected from a woodshop and were in the size range of 1 to 5mm.

This project was conducted by 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.

Reaction temperature is one of the most important operation parameters in the TCC process. Experiments were conducted to compare the refined oil yield of pure sawdust under 280^{o}C and 305^{o}C. Lower temperatures were not tested based on references and previous experiences. Other operation parameters followed previous tests. The effect of catalyst additions was also investigated.

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 included:

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

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 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.

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 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 the effects of adding organic matters to swine marure on oil yields.

Table 1: Effect of adding different cellulosic materials on raw oil yield

#	*Feedstock*	*TS (%)*	*Loaded (g)*	*Raw oil yield (%)*
1	Sawdust	90.5		
	1d manure	12.6		
	Mixture	18.6	802.6	56.7
2	Cornstalk	91.8		
	14d manure	12.9		
	Mixture	20.3	801.8	0
3	Sawdust	90.5		
	14d manure	12.9		
	Mixture	20.4	800.2	58.3
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 305°C and a retention time of 30 minutes. Zero raw oil yields do not necessarily mean that there are no toluene-soluble components in the products.

Blending cellulosic materials with swine manure varies the oil characteristics, but appears not to affect conversion of the swine manure volatile solids to oil. Table 1 shows the effect of adding different cellulosic materials on raw oil yield. When sawdust was added as an additive to 1d and 14d old swine manure of about 13% solid content, oily products were obtained. When manure of 5.7% solid content was used, no "oily" product was produced, but there was some toluene-soluble fraction in the product. Adding cornstalk did not yield oil, and the resulting product was powder-like. However, when the powder was extracted with toluene, there was a toluene-soluble fraction which could be considered as an oil product. As the sawdust showed a better performance than cornstalk in the thermochemical conversion, we used sawdust as a representative of cellulosic materials in an additional study.

Previous studies indicate that 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. Therefore, we used 14-day old manure as feedstock, and Figure 1 shows the refined oil yield change as the mixing ratio changed. From Figure 1, we could see as the manure fraction increased, the refined oil yield increased, and an obvious linear relationship was found. This implies that there was no significant interaction between sawdust and swine manure during the reaction.

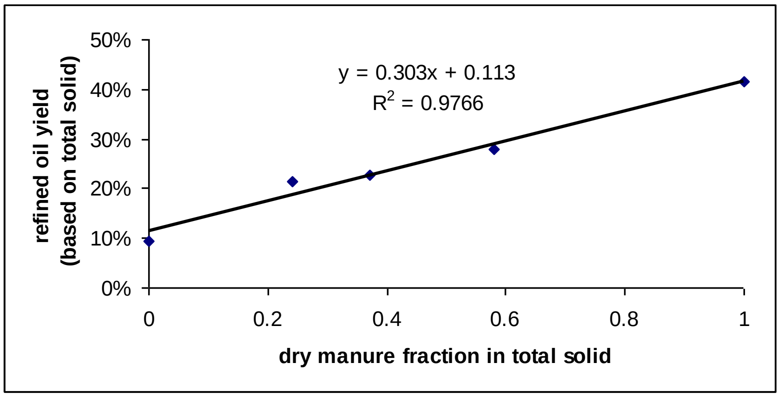

Figure 1: Effect of adding sawdust into swine manure as additives

Objective 2 – Determine the optimal operating conditions for oil production as a factor of swine manure feedstock composition.

Figure 2 shows the results of adding KOH as a catalyst to the mixture of swine manure and sawdust. With the increase of proportion of swine manure in the mixture, the refined oil yield kept increasing. When KOH was added as a 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 significant interaction between conversion of manure fraction and sawdust fraction.

Usually, swine manure in a pit has a solid content between 5-10%. When sawdust is added, an oil yield higher than 20% was achieved. Adding a catalyst may increase this oil yield by 5-10%. However, the increased cost was not calculated and whether adding a catalyst is economically feasible was not evaluated in this study.

Refined oil yields of 16% and 10% were obtained from tests under 280°C and 305°C for pure sawdust feedstock, respectively. Temperature did not show a very significant influence on the oil yield when it was higher than 280°C enough.

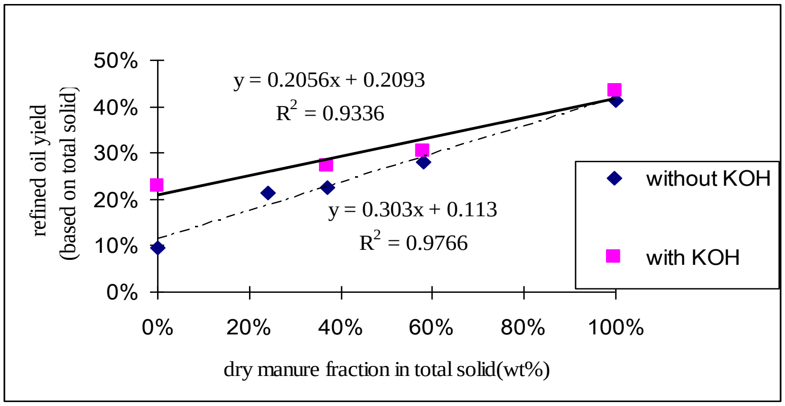

Figure 2: Effect of adding KOH as a catalyst into the sawdust/manure mixture

Objective 3 – Characterize and analyze the composition of by-product streams.

Table 2 shows the fertilizer-valuable nutrients distributed into post-TCC water in several selected tests. When a catalyst was not added, about 2/3 of the nitrogen and more than 1/3 of the phosphorus was transferred into the post-TCC water. On the other hand, no high phosphorus content was found in the bio-oil product, so it is reasonable to believe that other phosphorus may remain in the solid residue products, which could be recycled by some other means. The data of potassium transferred are greater than 100% due to measurement and calculation errors. But it is confirmed that most of the potassium remained in the post-TCC water. Adding KOH as a catalyst did not affect the nitrogen distribution too much, but it did decrease the phosphorus and potassium content in post-TCC water. When KOH was added and pH value of post-TCC water increased, phosphorus intended to be more in the state of PO_4^{3-} rather than H_2PO4^- and HPO_4^{2-}; therefore, it would be easier to participate as solid. More data and further study are needed to investigate the phenomenon.

Table 2: Nutrients distributed into post-TCC water

Test	Ratio of sawdust to dry manure	KOH added (wt% based on dry weight)	Nutrients remained in post-TCC water (%)		
			N	P	K
1	1.7:1	No	63	35	108
2	3.2:1	No	71	44	142
3	3.2:1	5	56	16	37
4	0.7:1	5	65	19	54

In the gaseous phase product, it is easy to understand that CO_2 is the dominant component, similar to previous results (Ocfemia, 2005). Other compounds included CO, CH4 and other organic gases, but in very low concentrations.

The bio-oil product definitely contains high value as fuel. However, the data indicates that we could also obtain extra values from the by-product like post-TCC water and solid residue left over rather than bio-oil.

Citations

He, B. 2000. Thermochemical conversion of swine manure to produce oil and reduce waste. PhD Dissertation. University of Illinois at Urbana-Champaign, Department of Agricultural and Biological Engineering, Urbana, IL.

Jones, J.L. and S.B. Radding. 1980. Thermal conversion of solid wastes and biomass. ACS Symposium Series 130. Washington, DC: American Chemistry Society.

Ocfemia, K. 2005. Hydrothermal process of swine manure to oil using a continuous reactor system. PhD Dissertation. University of Illinois at Urbana-Champaign, Department of Agricultural and Biological Engineering, Urbana, IL.