HYDROTHERMAL PROCESSING OF SWINE MANURE INTO OIL USING A CONTINUOUS REACTOR SYSTEM: DEVELOPMENT AND TESTING

K. S. Ocfemia, Y. Zhang, T. Funk

ABSTRACT. *Hydrothermal processing of swine manure is a novel technology that has shown very promising results in treating waste and producing oil. A batch hydrothermal process system that was previously developed at the University of Illinois at Urbana−Champaign successfully converted up to 70% of swine manure volatile solids into oil and reduced manure chemical oxygen demand by up to 75%. Since a continuous system is more applicable for scale−up operations, a small−scale continuous hydrothermal process (CHTP) reactor system was developed to evaluate the technical feasibility of the continuous−mode process. The CHTP reactor system was composed of a high−pressure slurry feeder, a process gas feeder, a continuous stirred tank reactor, a product separation vessel, and process controllers. It had a capacity to process up to 48 kg of manure slurry per day. The CHTP reactor system was successfully operated continuously for up to 16 h per test. Oil yields ranging from 62.0% to 70.4% were achieved. The heating value of the oil product ranged from 25,176 kJ/kg to 31,095 kJ/kg with the highest value at T = 305°C, P = 10.3 MPa, and RT = 80 min.*

Keywords. Hydrothermal process, Thermochemical conversion, Swine manure, Waste treatment.

Over the years, animal production in the U.S. has evolved to fewer producers, larger average herd or flock sizes, and higher concentration of animals and production facilities. One major problem in this scenario is that intensive animal production facilities produce more livestock manure waste than is needed to maintain the nutrient cycle balance in traditional agricultural systems on the nearby farmland. Livestock manure can also be viewed as an underutilized resource. Technological developments in the area of thermochemical conversion (TCC) present new ways to reduce the pollution potential of manure while extracting valuable energy and fertilizer resources.

Thermochemical conversion is a chemical reforming process in which depolymerization and reforming reactions of organic matter occur in a heated, pressurized, and oxygen−limiting enclosure. Some researchers (Chornet and Overend, 1985; Vasilakos and Austgen, 1985) suggested that the sequence of structural and chemical changes in the process would involve at least the following steps: cracking and reduction of polymers such as lignin and lipids, hydrolysis of cellulose and hemicellulose to glucose, hydrogenolysis in the presence of hydrogen, reduction of amino acids, new molecular rearrangements through dehydration,

decarboxylation, C−O and C−C bond ruptures, and hydrogenation of functional groups. However, the mechanisms and kinetics of the process are very complex and are not yet sufficiently known. The products of thermochemical conversion include gas, oil, solids, and tar. The amounts of these products are dependent on the characteristics of the raw material and the process operating parameters, which include temperature and pressure.

Research on thermochemical conversion of biomass into renewable energy began in the 1970s (Jones and Radding, 1978). Several researchers investigated biomass conversion mechanics and kinetics, product analysis, and products upgrading (Meier and Faix, 1999; Zabaniotou, 1999; Demirbas, 1998; Cundiff et al., 1996; Bridgewater, 1994; Solantausta et al., 1992; Grassi, 1991; Hayes, 1991; Solantausta and Sipila, 1991; Alen et al., 1989; Soltes and Milne, 1988; Overend et al., 1986; Beckman and Elliot, 1985; Labazuy et al., 1985; Klass, 1981; Jones and Radding, 1980). Most research focused on the pyrolysis of materials with high lignin and cellulose content, such as wood. However, there were also a number of studies that attempted to make use of biomass with low contents of lignin and cellulose. Use of municipal sewage sludge, industrial and food processing wastes, and agricultural wastes as feedstock for the conversion process has been investigated (He et al., 2000a, 2000b; Raymond and Kieffer, 1995; Itoh et al., 1994; Williams and Besler, 1992; Yokoyama et al., 1987; Suzuki et al., 1986; Kranich, 1984; Kreis, 1979; White and Taiganides, 1971).

Among the various methods to thermochemically convert organic material, hydrothermal processing appears to be most suited for use with swine manure. It requires no pre−drying of the feedstock and is advantageous in several ways. Since a closed system is involved, pollution problems caused by leaking and/or runoff of the manure to the ground and surface waters, commonly associated with biological

The authors are **Kim S. Ocfemia, ASABE Member,** Post-Doctoral Research Associate, **Yuanhui Zhang, ASABE Member Engineer,** Professor, and **Ted Funk, ASABE Member Engineer,** Extension Specialist and Assistant Professor, Department of Agricultural and Biological Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois. **Corresponding author:** Kim S. Ocfemia, 1304 W Pennsylvania Ave., Urbana, IL 61874; phone: 217-333-5243; fax: 217-244-0323; e-mail: ocfemia@uiuc.edu.

treatment in lagoons, can be prevented. Nuisance odor emission to the atmosphere that may otherwise come from manure storages can be substantially reduced. All pathogens in the manure are eliminated because high pressure and high temperature are involved. In addition to the environmental benefits, the process can be economically viable. From batch experiments, the energy consumption of the process was found to be less than one third of the energy in the oil product. Utilization of the oil product as raw material could also substantially add to the value of the process.

Thermochemical conversion of swine manure into oil has already been shown to be feasible in batch mode. In a study by He (2000), a bench reactor was used to process swine manure at operating temperatures ranging from 275°C to 350°C, which corresponded to pressures ranging from 5.5 MPa to 18 MPa. Oil yield based on the conversion of total volatile solids to oil was as high as 76.2%. The chemical oxygen demand of the raw manure was effectively reduced by as much as 75.4%. This earlier work showed that the technology has potential to treat manure effectively and can be used as a method to produce a liquid biofuel.

The next logical step was to design and build a continuous−mode hydrothermal process (CHTP) system where swine manure is fed continuously into the reactor and products are continuously withdrawn. In the large scale, a continuous−mode process has the advantage of avoiding excessively long warm−up and cool−down periods, which are associated with batch processing. Moreover, heat exchange/recycling can be easily integrated in a continuous mode system, which can reduce the energy consumption associated with heating. At this point, a small−scale CHTP system will provide a larger amount of oil sample per run compared to the previous batch setup. The larger amount of oil will allow a more extensive characterization of the oil product. Alternative utilization of the oil can be explored. In addition, a small−scale CHTP system will aid in determining the technical feasibility, economical viability, and environmental soundness of a pilot plant. This article describes the design and operation of a bench−scale continuous hydrothermal process reactor system that can convert swine manure into oil.

MATERIALS AND METHODS
EXPERIMENT PROCEDURE
Fresh swine manure was collected from the pen floors of the Swine Research Center grower facility at the University of Illinois at Urbana Champaign. The manure was slurried using a commercial blender and a high−shear mixer (model L4RT, Silverson Machines, Inc., Longmeadow, Mass.). To prevent clogging of the pump suction side, the slurry was filtered using a commercial strainer. The solids content was then adjusted to 20%. The slurry was placed into a reservoir and pressurized to 0.4 MPa, enough to push the viscous slurry into the suction side of the pump. An initial batch of slurry was also placed inside the reactor before it was sealed. The reactor, including the separation vessel, was flushed with N_2. After flushing, the system was pressurized to 6.9 MPa (1,000 psi), checking for any leaks along the way. The reactor was then heated to the desired operating temperature. The initial charge of manure slurry was left to reside in the reactor for 15 min. After this, the high−pressure pump was turned on

to start continuous feeding of the manure slurry. All parameters including pressure and temperature were monitored and recorded continuously. Liquid product samples were collected from the separation vessel, after which the oil was separated from the aqueous fraction by decanting. Samples of the different product streams were collected, quantified, and analyzed.

PRODUCT ANALYSIS
The oil yield represents the amount of organic material in the manure that was converted into oil. It was computed as follows:

$$\text{Oil yield (\%)} = \left[\frac{\text{total oil product (g/min)}}{\text{total volatile solids input (g/min)}}\right] \times 100\% \qquad (1)$$

The heating value of the oil was determined by bomb calorimetry in accordance with ASTM standard D240−02. An automated isoperibol oxygen bomb calorimeter (model 1281, Parr Instruments, Moline, Ill.) was used in the determination of the heating value. The sample was combusted in an oxygen−filled bomb, and the temperature rise was measured. Corrections for the sulfur and acid were entered into the microprocessor, and the final heating value was calculated and printed. The calorimeter was standardized based on the combustion of benzoic acid tablets.

The carbon, hydrogen, and nitrogen (CHN) content of the oil were determined using a CHN analyzer (model CE440, Exeter Analytical, Inc., North Chelmsford, Mass.). The instrument is specific for detection of these three elements. The process involves oxidizing the carbon, hydrogen, and nitrogen into CO_2, H_2O, and N_xO_y at 980°C. These gases are then carried to a detector with He gas as carrier. The detector then compares the measurement with a known standard. The results are reported in weight percentage. Sulfur content was measured using a Leco SC−32 (Leco Corp., St. Joseph, Mich.) following ASTM Standard Method D−1552−03 (ASTM, 2004). In the instrument, the oil sample was fully combusted to convert all sulfur into SO_2. After moisture and dust were removed with traps, SO_2 was then measured with a non−dispersive solid−state infrared detector. A commercial calibration standard was used to calibrate the instrument.

The oil products were also characterized based on solubility to benzene. In the procedure, about 2 to 3 g of oil sample was mixed with 25 mL of benzene (ACS grade). The mixture was shaken for 1 h, and the insoluble residue was separated by vacuum filtration. The residue was then dried in a laboratory oven at 105°C for 24 h and weighed. The benzene solubility was computed as follows:

$$\text{Benzene solubility} = \left[1 - \frac{\text{weight of undissolved residue (g)}}{\text{weight of oil sample (g)}}\right] \times 100\% \qquad (2)$$

RESULTS AND DISCUSSION
CHTP DEVELOPMENT
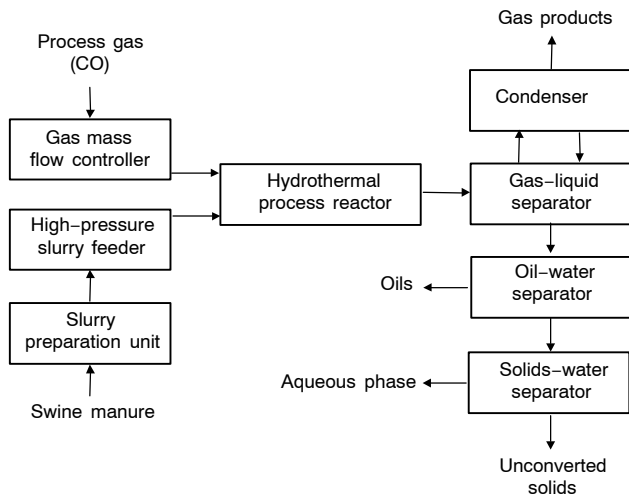Figure 1 shows a simple flowchart describing the continuous−mode process to convert swine manure into oil.

Figure 1. Continuous thermochemical conversion process.

At this stage of the research, a simple linear process was developed to assess the performance of using a single reactor in continuously converting swine manure into oil. No heat recovery was integrated into the system at this point.

In developing the CHTP system, choosing the appropriate reactor was of utmost importance. A previous design for a similar type of application involved the use of screw−type reactor (Eager et al., 1983). Plugging, deterioration of reactor parts, and backflow were some of the problems encountered. These issues were carefully considered in the selection and design of the system components in this research. A CSTR was selected over a plug−flow type reactor because it has the advantage of easy temperature control throughout the reaction vessel.

Since the reactions and kinetics involved in the hydrothermal process of swine manure to oil are still not fully known, it is difficult to accurately predict the oil yields that can be obtained from a continuous−mode process using a CSTR. An estimate of oil yield, however, can be made by coupling the oil yield results from batch experiments with the residence time distribution of the volatile solids (VS) in the manure. The residence time distribution can be derived from a washout experiment. Assuming perfect mixing, a mass balance on the volatile solids is:

$$V \frac{dc_{sys}}{dt} = Qc_{in} - Qc_{out} \qquad (3)$$

where
V = volume of reactor (L)
c_{in} = steady inlet VS concentration (g/L)
c_{sys} = VS concentration in the reactor (g/L)
c_{out} = outlet VS concentration (g/L)
Q = volumetric flow rate (L/s).
Dividing through each side by V yields:

$$\frac{dc_{sys}}{dt} = \frac{c_{in}}{\bar{t}} - \frac{c_{out}}{\bar{t}} \qquad (4)$$

where $\bar{t}$ is the theoretical mean residence time (s).

In perfect mixing, the contents of the system are homogeneous and, therefore, $c_{out} = c_{sys}$. In the washout experiment, the inlet, outlet, and interior concentrations are the same prior to $t = t_0$, and the inlet concentration goes to zero at $t = t_0$. Therefore, if we consider the system response for $t \geq t_0$ only, we can say that $c_{in} = 0$:

$$\frac{dc_{out}}{dt} = -\frac{1}{\bar{t}} c_{out} \qquad (5)$$

Although the inlet concentration is zero after $t = t_0$, we can fix the initial condition in the system as $c_{sys} = c_{out} = C_0$ at $t = t_0$. Rearranging and integrating yields:

$$\int \frac{dc_{out}}{c_{out}} = -\int \frac{dt}{t} \qquad (6)$$

$$\frac{c_{out}}{C_0} = \exp\left(-\frac{t}{\bar{t}}\right) \qquad (7)$$

The cumulative residence−time distribution function, $F(t)$, is easily obtained using the following equation:

$$F(t) = 1 - \frac{c_{out}}{C_0} \qquad (8)$$

The fractions of volatile solids that reside for a certain length of time in the reactor can be calculated from the cumulative residence time distribution (eq. 8). Figure 2 shows the residence time distribution when the hydraulic residence time is 60 min. The figure indicates that 8.0% of the volatile solids resides in the reactor for 5 min, 7.4% resides for 10 min, and so on following a decreasing trend with time. This trend is characteristic of single CSTRs. The oil yield results from the batch process study by He (2000) are also shown in figure 2 to show the yields that could be obtained from each of the fractions. The total fractional yield represents the predicted yield. Thus, for the test case involving 60 min hydraulic residence time at 305°C and 10.2 MPa, an oil yield of about 54.8% is expected. By coupling yield data from batch experiments with residence time distributions of volatile solids at different hydraulic residence times, a plot of predicted yields can be obtained (fig. 3).

The reactor was a modified 2 L T316SS vessel. It was fitted with a magnetically driven stirrer. The stirrer has two 6−blade impellers spaced 8 cm apart with the lower impeller located 2 cm from the bottom of the reactor. A type−J thermocouple was inserted into the thermowell to monitor the reactor temperature. A pressure gauge and a pressure transducer were installed to monitor the reactor pressure. The
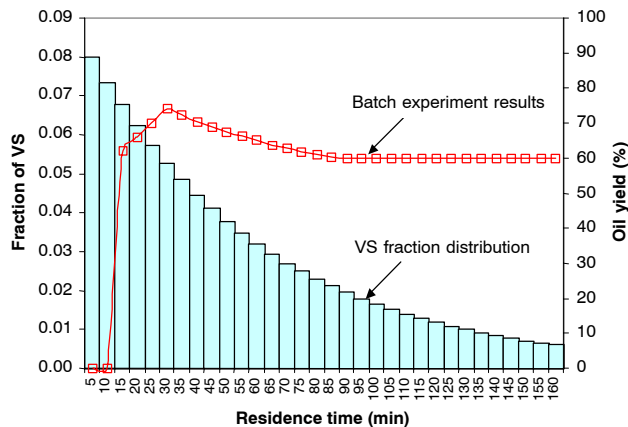

Figure 2. Residence time distribution and batch experiment results to predict oil yield for the continuous−mode process using a single CSTR.
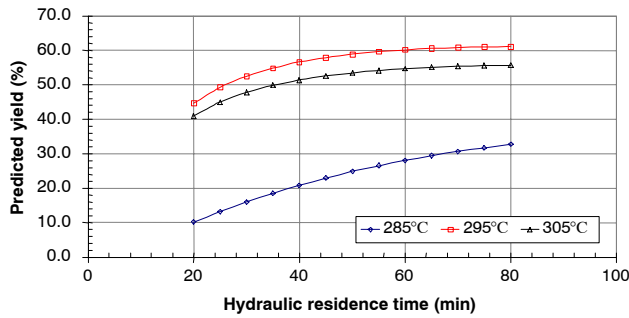
Figure 3. Predicted oil yields with respect to hydraulic residence time.

reactor was externally heated with an electric furnace. The operating temperature was controlled using a PID controller (model 4842, Parr Instruments, Moline, Ill.). A serpentine cooling coil was installed inside the reactor for cooling purposes. A rupture disk, set to 17.2 MPa (2,500 psi), was placed on top of the reactor as a precautionary measure against overpressurizing the vessel. A dip tube from the top of the reactor served as the entry point for the manure slurry. The tip of the dip tube was located at about 11 cm below the liquid surface, close to the upper impeller. This was to make sure that the fresh slurry did not bypass to the overflow. Placing the entry point close to the impeller also ensured that the fresh manure was quickly mixed into the reaction media. The process gas,

on the other hand, was fed with the feed slurry, allowing it to be bubbled through the reaction media. An overflow tube was used to maintain a fixed volume of liquid material inside the reactor. Both liquid and gas products exited through this overflow tube.

Procuring a high−pressure pump was the most time−consuming and challenging task in completing the system. Aside from the fact that the manure slurry needed to be pumped from atmospheric pressure to a pressure of up to 12 MPa (1750 psi), the slurry contained solid particles and was very viscous (~32,000 cp). This was further complicated by the fact that a low flow rate was needed for the process scale. A special high−end metering pump was needed.

Inquiries to various pump companies led to two options: use of a piston−diaphragm pump, or use of a valveless rotary piston pump. Piston−diaphragm pumps incorporate check valves on both suction and discharge. These check valves may be troublesome, considering the characteristics of swine manure slurry. Pig hair or any flaky particle in the manure can cause the valve to seat improperly, which may cause blockage and unwanted backflow. By contrast, rotary piston pumps are valveless, so problems associated with valve seating are avoided. A valveless rotary piston pump (model DRb 15/7, Prominent−Orlita, Giessen, Germany) was the logical choice for the process because it met all the pumping requirements of the system.
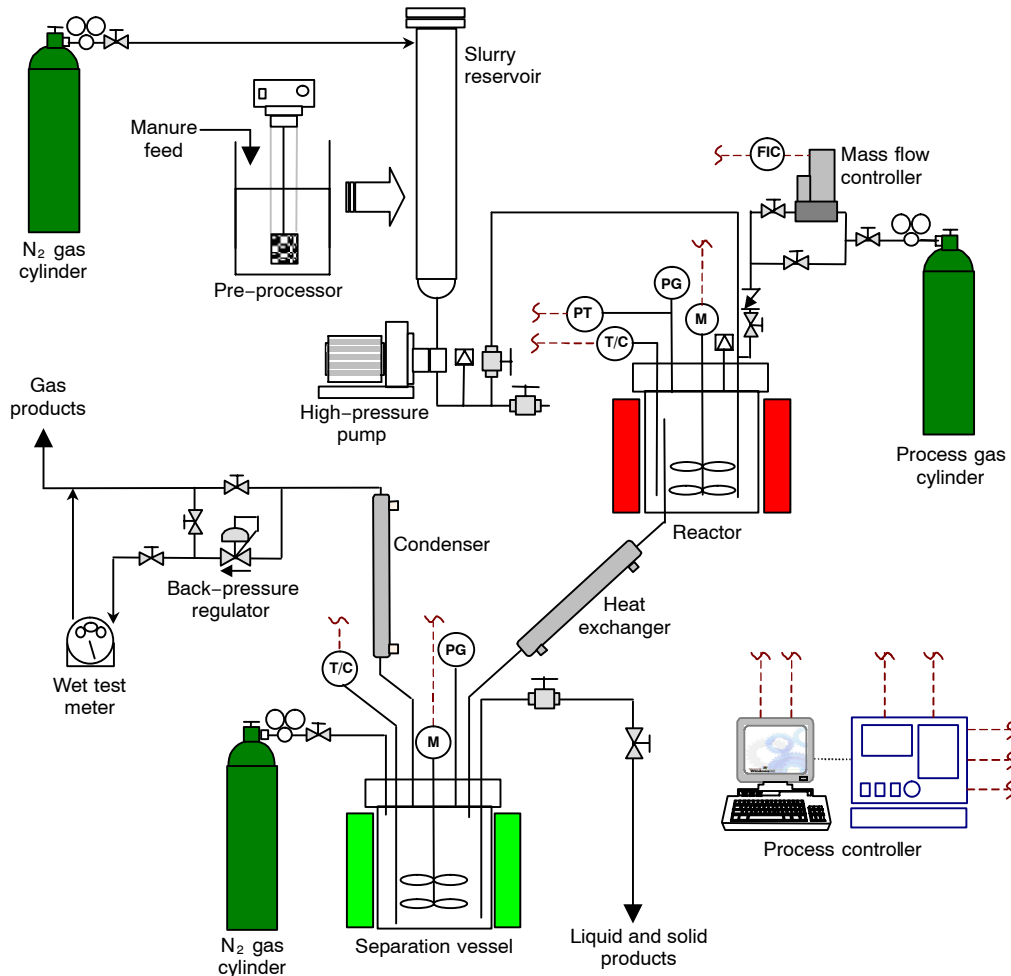

Figure 4. Schematic of the continuous hydrothermal process (CHTP) reactor system.

Figure 5. Photo of the CHTP reactor system setup.

A Brooks SMART Series mass flow controller (model 5850S, Brooks Instrument, Hatfield, Pa.) was used to control the flow of process gas (CO) into the reactor. The unit has a ±0.7% of rate plus ±0.2% of full−scale accuracy. It was interfaced with a PC via a D−connector (RS−232 cable). The process gas (99.9% purity) was supplied from commercially available high−pressure cylinders. A high−pressure piston regulator maintained the required 345 kPa pressure difference across the mass flow controller.

The separation vessel was a 1.8 L T316 stainless steel cylinder rated to withstand 34.5 MPa at 375°C. The vessel was also equipped with two 6−blade impellers that were magnetically driven. Mixing was necessary in the separation vessel to maintain a near−homogeneous bulk product. This allowed consistent product withdrawal. A well−regulated product flow from the separation vessel was achieved using a ball valve in series with a needle valve.

A schematic of the CHTP reactor system is shown in figure 4. All connections and fittings were made of stainless steel to prevent corrosion. Pressure relief valves and rupture disks were placed in several points in the system to avoid overpressurization in case of blockages.

CHTP REACTOR SYSTEM TESTING

Figure 5 shows a photo of the completed CHTP system. The temperature and pressure response of the system was determined to assess how long it takes to start−up the process and how well operating conditions were held.

Figure 6 shows a typical reactor temperature profile. The temperature response curve shows no overshoot, indicating sufficiently good temperature control by the PID controller. In certain cases, where the operator found through experience that the temperature might rise or drop far beyond the

required operating temperature, the temperature setpoint was adjusted accordingly. In maintaining the operating temperature, the average standard deviation was 2.3°C. The fluctuations in temperature were most likely due to the slow heat transfer across the thick reactor wall, which resulted in response delays.

The pressure in the reactor was monitored and recorded every 5 min. In certain instances, the back−pressure regulator setting had to be changed in order to maintain the required operating pressure. Figure 6 shows typical variations in operating pressure that were observed in the test runs. Before heating was started, the reactor was initially pressurized to 6.9 MPa (1,000 psi). In test cases involving 9.0 MPa (1,300 psi) and 10.3 MPa (1,500 psi) operating pressure, heating the slurry was enough to raise pressure to the desired operating pressure. For test cases involving 12.1 MPa,
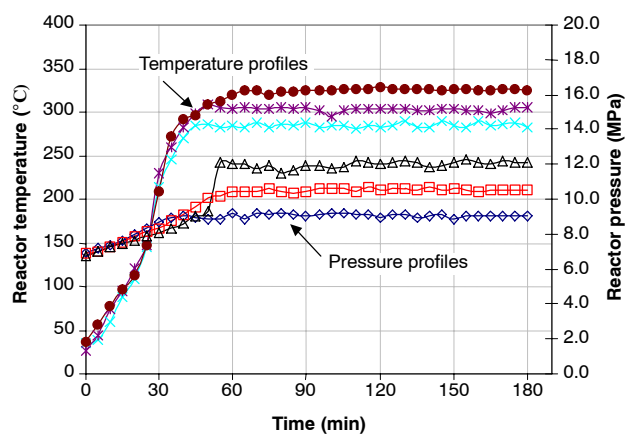

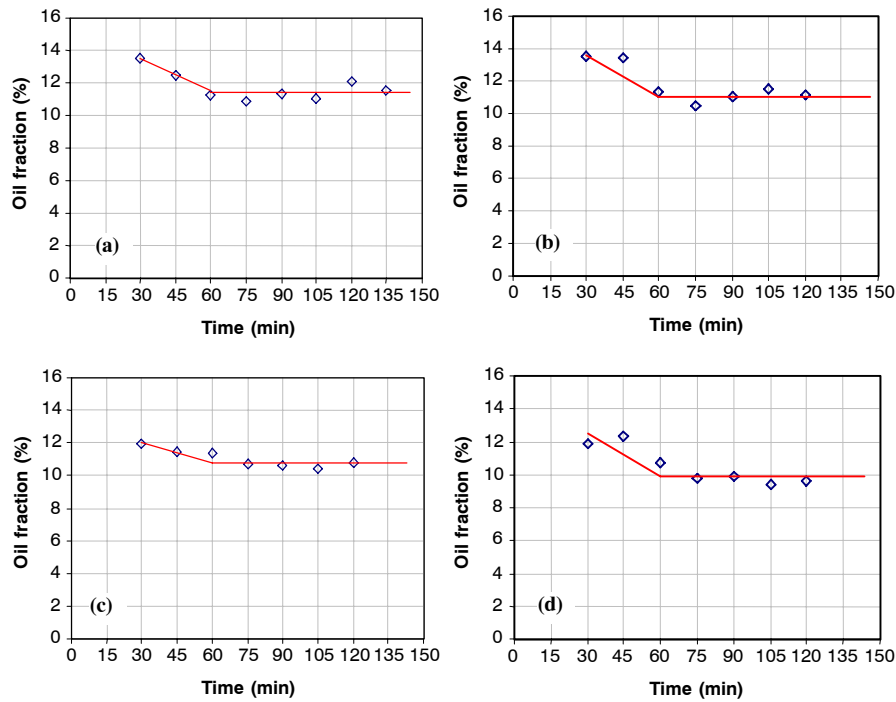**Figure 6. Typical temperature and pressure profiles during experiments.**

Figure 7. Oil fraction in liquid product: (a) T = 305°C, P = 10.3 MPa, RT = 60 min; (b) T = 305°C, P = 10.3 MPa, RT = 40 min; (c) T = 285°C, P = 10.3 MPa, RT = 60 min; and (d) T = 285°C, P = 9.0 MPa, RT = 80 min.

additional pressurization using N_2 was needed once operating temperature was reached.

Steady state was determined by monitoring the products concentration during a 3 h test run. Results show that it took about 60 min for the solids and oil concentration to settle to a constant value (fig. 7). The solids contents of the 15 min aqueous samples were also determined to verify the results obtained from oil fraction measurements. Figure 8 shows the solids contents of the samples for tests involving 305°C, 10.3 MPa, and 40 and 60 min residence times. As was expected, the fraction of the fixed solids in the aqueous product stream did not vary with time. This was an indication that material did not accumulate in the reactor. In agreement with the oil yield results, the total solids were also found to stabilize after 60 min. Although oil yields stabilized after 60 min, it was very possible that the composition of the products was still approaching steady state. Therefore, samples that were used for characterization and analyses were obtained after 120 min of starting the pump.

The reactor system was successfully operated continuously for up to 16 h without any problems. However, a pump durability issue was encountered after several experiments. The piston and sleeve wore out quickly, allowing only about 30 h of operation per set. It appeared that the slurry was very abrasive, causing an increase in the clearance between the piston and sleeve surfaces. As a result, beyond 20 h of operation, a noticeable reduction in flow rate was observed. In one extreme case, material backflow occurred that caused blowoff from the suction side of the pump. Experiments where a noticeable change in flow was observed were discontinued and the results disregarded.

EXPERIMENT RESULTS

The oil yield results obtained from the experiments are shown in figure 9. The highest oil yield was 70% (based on volatile solids in the manure slurry). Apparently, the hydraulic residence time has a strong influence on oil yield, but the effect diminishes as residence time goes beyond
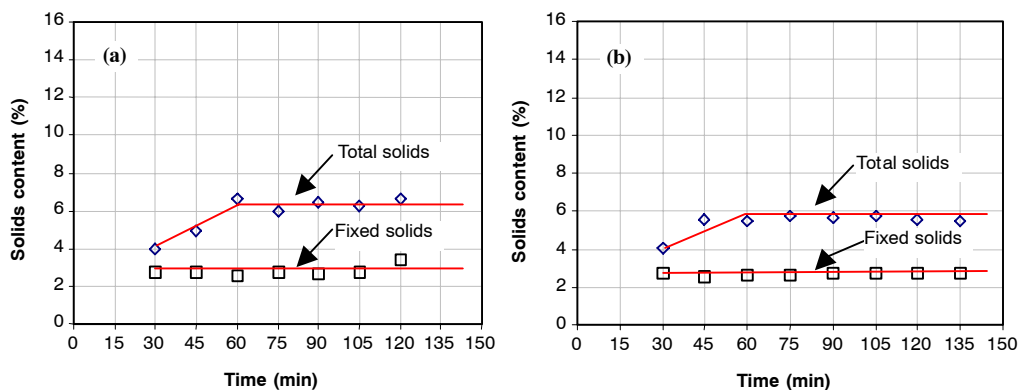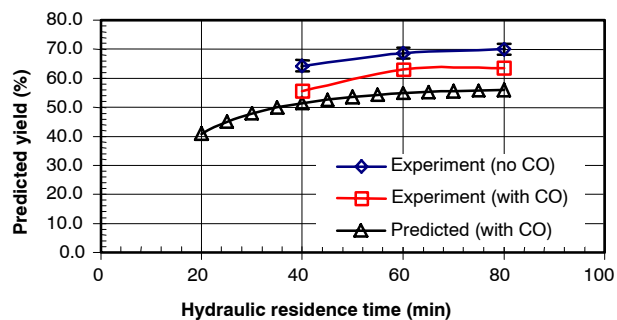

Figure 8. Solids content of aqueous product: (a) T = 305°C, P = 10.3 MPa, RT = 40 min; and (b) T = 305°C, P = 10.3 MPa, RT = 60 min.

Figure 9. Comparison of experiment and predicted yields (at an operating temperature of 305˚C, pressure of 10.3 MPa, and with or without CO at 100 mL/min).

60 min. Consider the test case where an operating tempera–ture of 305˚C and 10.3 MPa was used. Increasing the residence time from 40 to 60 min increased the oil yield by 4.3%. However, further increasing the residence time to 80 min only gained an additional 1.4% in oil yield. The diminishing benefit from increasing residence time was more evident in the test case involving CO. Oil yield increased by 7.4% when residence time was increased from 40 to 60 min but only increased by 0.4% when residence time was increased from 60 to 80 min.

Figure 9 shows a comparison of the predicted yield and actual yield for the CHTP system. Interestingly, the actual yields obtained from the experiments were higher than the predicted yields and followed the same trend. Several factors may have contributed to the high yields obtained in the continuous–mode experiments. Note that the predicted yields were based on the results of the batch tests done by He (2000). Distinct differences in how the tests were done may give some explanation. In the batch tests, the manure was not homogenized. Bulk manure was placed in the reactor with water (to achieve the desired solids content) and was manually mixed. In this study, the manure was macerated and slurried before processing. By breaking down the large particles and slurrying the manure, better heat and mass transfer were achieved. It may have been that catalysts had better access to the structure of the organic material in the manure, resulting in higher yields. By physically decreasing the particle sizes, the surface area at which the reactions could occur was increased. The minerals (i.e., alkali metals) and NH_4^+ that were already present in fresh swine manure are suspected to be the catalysts for the conversion reactions. These catalysts and their role in the thermochemical conversion process have been studied and presented in previous works (Sealock et al., 1996; Inoue et al., 1999).

The rate of heating was also different. In the batch study, the manure feedstock was heated slowly to reach the operating temperature, typically taking about 60 min. In the continuous process, it took only about 2 min to heat the feedstock from room temperature to the operating tempera-ture. Another factor was that, with the use of a CSTR, fresh incoming feed immediately came into contact with inter-mediates of the hydrothermal process. Without the need for any initiation step, the fresh feedstock immediately under-went reactions leading to the formation of oil. The results indicate that the use of batch data coupled with volatile solids residence time distribution is insufficient to accurately predict the oil yield. Better prediction could be made if reaction pathways and reaction rates are known.

Table 1 shows some of the characteristics of the oil products, including heating value, elemental composition, and benzene solubility. Due to a pump problem, no replications were done for the tests involving CO. The heating values of the oil obtained from the tests not involving CO showed no significant difference within the range of hydraulic residence times that were used. No particular trend in oil heating value was observed for the tests involving CO. However, the heating values of the oil products from the test cases without CO addition were consistently higher than those achieved with CO. No explanation can be made yet, given the limited number tests conducted in this part of the study. It was interesting to find that the oil product with the highest heating value was found in the test case that also gave the highest oil yield: T = 305˚C, P = 10.3 MPa, and 80 min residence time.

The results show a significant increase in the carbon and hydrogen content of swine manure after undergoing hydro-thermal processing. Carbon content and hydrogen content increased by as much as 27.9% and 3.9%, respectively. This gives an indication of how much oxygen element was removed from the organic compounds in the manure after the hydrothermal process. It was interesting to find that the carbon content and hydrogen content of the oil was significantly higher when CO was used than when it was not added. This result does not seem to be in agreement with the result that oil from tests not involving CO had a higher heating value. It is possible that the oil heating value results for the tests involving the use of CO were inaccurate. This will be further investigated. Note that these are preliminary results and, in certain test cases, no replications were made. No significant difference was found for the carbon and hydrogen contents within the hydraulic residence times used in the tests.

The oil had a high average nitrogen content of 4.2%. Nitrogen in crude oil is undesirable because nitrogen forms

Table 1. Characteristics of the oil products (test condition @ T = 305˚C and P = 10.3 MPa) and the swine manure feedstock.

CO (mL/min)	RT (min)	Heating Value (MJ/kg)	Elemental Composition (% wt)				Benzene Solubility (%)
			C	H	N	S	
No	40	30.3±2.5	65.9±3.4	9.4 ±0.3	4.0 ±0.1	0.3 ±0.0	87.5
No	60	30.7±1.6	66.4±3.5	9.6 ±0.1	3.7 ±0.4	0.4 ±0.1	86.3
No	80	31.1±0.1	69.0±0.2	9.2 ±0.1	4.1 ±0.0	0.3 ±0.0	87.2
Yes[a]	40	25.2	73.3	10.3	4.5	0.3	88.4
Yes[a]	60	28.6	69.3	10.0	4.4	0.3	87.9
Yes[a]	80	25.8	73.6	10.2	4.5	0.4	89.0
Swine manure (dry basis)			45.7±1.1	6.4 ±0.2	3.4 ±0.4	0.4 ±0.1	–

[a] No replications due to pump problem.

nitrogen oxides, which negatively impact the environment. In addition, the decomposition of nitrogen compounds in catalytic cracking and hydrocracking processes forms ammonia and cyanides, which can cause corrosion. Nitrogen also has deleterious effects on refinery catalysts. Thus, the oil product from swine manure may need to be upgraded by a post-process that could reduce its nitrogen content. The sulfur in the oil product is also undesirable because it can contribute to corrosion and atmospheric pollution, but it was in very low amounts, about 0.3% on the average. Hydraulic residence time was found not to significantly affect the nitrogen and sulfur content of the oil for the range of residence times used in the tests.

The benzene solubility of the oil was used as an indicator of quality based on the principle that "like dissolves like." High solubility in benzene indicates that the oil contains more hydrocarbon-like components and, therefore, has good quality. The average benzene solubility of the oil products obtained from the tests was 87.7%. This shows that the crude oil product contained some impurities that may consist of char and other non-soluble components that were mixed with the oil. Note that, in the tests, a decanting method was used to separate the oil and aqueous product. The purity of the oil will vary depending on the separation method (e.g., extraction, distillation, or centrifugation).

Figure 10 shows the product distribution when using 20% solids content swine manure feedstock. The operating conditions were 305°C, 10.3 MPa, and 60 min hydraulic residence time. The product was primarily water, which accounted for 80.7% of the total product. The oil accounted for 11.9%, and gases (primarily CO_2) accounted for about 2.6%. The remaining amount was solids, accounting for 4.8%.

SUMMARY AND CONCLUSIONS

A small-scale continuous reactor system that can convert swine manure into oil was designed and built. It was composed of a high-pressure slurry feeder, a process gas feeder, a continuous stirred tank reactor, a product separation vessel, and process controllers. The reactor system was successfully operated with a continuous running time of up to 16 h excluding startup and shutdown. No clogging or accumulation was experienced in using the continuous stirred tank reactor. There was, however, a pump durability issue where the piston and sleeve wore out quickly. The high-pressure pump needs modification, or a different type of
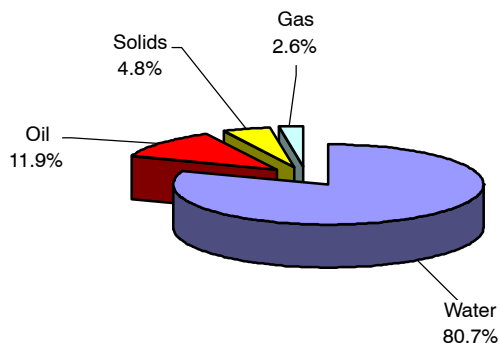

Figure 10. Product mass distribution when using a temperature of 305°C, 10.3 MPa, and 60 min hydraulic residence time.

feeder needs to be used. Continuous-mode operation of the reactor showed that steady state could be achieved in about 60 min, given that an initial batch of material is processed before starting continuous flow.

The oil yield for the continuously mixed process was calculated using the volatile solids residence time distribution combined with previous batch test results. For each of the hydraulic residence times used in the tests, the experiment yields were higher than predicted yields. An oil yield of 64.3% was reached in 40 min at 305°C and 10.3 MPa. Oil yield increased with residence time, with the highest value of 70% at 305°C, 10.3 MPa, and 80 min residence time.

The heating value of the oil products ranged from 25,176 to 31,095 kJ/kg. No significant change in heating value was observed with respect to hydraulic residence time. The addition of CO to the process resulted in a raw oil product with higher carbon and hydrogen contents (averages of 72.1% and 10.2%, respectively). The nitrogen and sulfur contents of the oil were relatively constant for all tests, with averages of 4.2% and 0.3%, respectively. The oil products on average were 87.7% soluble to benzene. The mass distribution of the products from 20% solids swine manure slurry was 80.7% water, 11.9% oil, 2.6% gas that was mostly CO_2, and 4.8% solids.

REFERENCES

Alen, R., P. McKeough, A. Oasmaa, and A. Johansson. 1989. Thermochemical conversion of black liquor in the liquid phase. *J. Wood Chem. and Tech.* 9(2): 265-276.

ASTM. 2004. D1552-03: Standard test method for sulfur in petroleum products (high-temperature method). West Conshohocken, Pa.: ASTM.

Beckman, D., and D. Elliott. 1985. Comparisons of the yields and properties of the oil products from direct thermochemical biomass liquefaction processes. *Canadian J. Chem. Eng.* 63: 99-104.

Bridgewater, A. V. 1994. *Advances in Thermochemical Biomass Conversion.* New York, N.Y.: Blackie Academic and Professional.

Chornet, E., and R. Overend. 1985. Biomass liquefaction: An overview. In *Proc. International Conference on Fundamentals of Thermochemical Biomass Conversion*, 967-1002. New York, N.Y.: Elsevier Applied Science.

Cundiff, J. S., E. E. Gavett, C. Hansen, C. Perterson, M. A. Sanderson, H. Sapouri, and D. VanDyne. 1996. Liquid fuels and industrial products from renewable resources. In *Proc. 3rd Liquid Fuel Conference.* St. Joseph, Mich.: ASAE.

Demirbas, A. 1998. Yields of oil products from thermochemical biomass conversion processes. *Energy Conversion Management* 39(7): 685-690.

Eager, R. L., J. M. Pepper, and J. F. Mathews. 1983. A small-scale semi-continuous reactor for the conversion of wood to fuel oil. *Canadian J. Chem. Eng.* 61: 189-193.

Grassi, G. 1991. The European energy from biomass programme. In *Biomass Pyrolysis Liquids: Upgrading and Utilization*, 1-10. A. V. Bridgwater and G. Grassi, eds. New York, N.Y.: Elsevier Applied Science.

Hayes, R. D. 1991. Overview of thermochemical conversion of biomass in Canada. In *Biomass Pyrolysis Liquids: Upgrading and Utilization*, 311-326. A. V. Bridgwater and G. Grassi, eds. New York, N.Y.: Elsevier Applied Science.

He, B. 2000. Thermochemical conversion of swine manure to produce oil and reduce waste. PhD diss. Urbana, Ill.: University of Illinois at Urbana-Champaign.

He, B., Y. Zhang, T. Funk, G. Riskowski, and Y. Yin. 2000a. Thermochemical conversion of swine manure: An alternative process for waste treatment and renewable energy production. *Trans. ASAE* 43(6): 1827-1833.

He, B., Y. Zhang, Y. Yin, T. Funk, and G. Riskowski. 2000b. Operating temperature and retention time effects on the thermochemical conversion process of swine manure. *Trans. ASAE* 43(6): 1821-1825.

Inoue, S., K. Okigawa, T. Minowa, and T. Ogi. 1999. Liquefaction of ammonia and cellulose: Effect of nitrogen/carbon ratio in the feedstock. *Biomass and Bioenergy* 16(5): 377-383.

Itoh, S., A. Suzuki, T. Nakamura, and S. Yokoyama. 1994. Production of heavy oil from sewage sludge by direct thermochemical liquefaction. In *Proc. IDA and WRPC World Conference on Desalination and Water Treatment* 98(1-3): 127-133.

Jones, J. L., and S. B. Radding. 1978. Solid waste and residue conversion by advanced thermal processes. Presented at the 175th meeting of the American Chemical Society. Washington, D.C.: American Chemical Society.

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

Klass, D. K. 1981. Biomass as a non-fossil fuel. ACS Symposium Series 144. Washington, D.C.: American Chemical Society.

Kranich, W. L. 1984. Conversion of sewage sludge to oil by hydroliquefaction. EPA-600/2-84-010. Washington, D.C.: U.S. Environmental Protection Agency.

Kreis, R.D. 1979. Recovery of by-products from animal wastes: A literature review. EPA-600/2-79-142. Washington, D.C.: U.S. Environmental Protection Agency.

Labazuy, C., N. Soyer, C. Bruneau, and A. Brault. 1985. Wood liquefaction with hydrogen or helium in the presence of iron additives. *Canadian J. Chem. Eng.* 63: 634-638.

Meier, D., and O. Faix. 1999. State of the art of applied fast pyrolysis of lignocellulosic materials: A review. *Bioresource Tech.* 68(1): 71-77.

Overend, R. P., T. A. Milne, and L. K. Mudge. 1986. Fundamentals of thermochemical biomass conversion. In *Proc. International Conference on Fundamentals of Thermochemical Biomass Conversion*. New York, N.Y.: Elsevier Applied Science.

Raymond, D. R., and J. A. Kieffer. 1995. Advanced biomass-to-energy conversion technologies for the pulp and paper industry. In *Proc. 2nd Biomass Conference of the Americas: Energy, Environment, Agriculture, and Industry*, 1741-1760. Golden, Colo.: National Renewable Energy Laboratory.

Sealock, Jr., L. J., D. C. Elliott, E. G. Baker, A. G. Fassbender, and L. J. Silva. 1996. Chemical processing in high-pressure aqueous environments: 5. New processing concepts. *Ind. and Eng. Chem. Research* 35(11): 4111-4118.

Solantausta, Y., and K. Sipila. 1991. Pyrolysis in Finland. In *Biomass Pyrolysis Liquids: Upgrading and Utilization*, 327-340. A. V. Bridgwater and G. Grassi, eds. New York, N.Y.: Elsevier Applied Science.

Solantausta, Y., D. Beckman, A. V. Bridgwater, J. Diebold, and D. Elliot. 1992. *Biomass and Bioenergy* 2(1-6): 279-297.

Soltes, E. J., and T. A. Milne. 1988. Pyrolysis oils from biomass: Producing, analyzing, and upgrading. ACS Symposium Series 376. Washington, D.C.: American Chemistry Society.

Suzuki, A., S. Yokoyama, M. Murakami, T. Ogi, and K. Koguchi. 1986. New treatment of sewage sludge by direct thermochemical liquefaction. *Chemistry Letters CMLTAG* 9: 1425-1428.

Vasilakos, N. P., and D. M. Austgen. 1985. Hydrogen-donor solvents in biomass liquefaction. *Ind. and Eng. Chem. Process Design and Development* 24(4): 304-311.

White, R. K., and E. P. Taiganides. 1971. Pyrolysis of livestock wastes. In *Proc. 2nd International Symposium on Livestock Wastes*, 190-194. St. Joseph, Mich.: ASAE.

Williams, P. T., and S. Besler. 1992. The pyrolysis of municipal solid waste. *J. Institute of Energy* 65: 192-200.

Yokoyama, S., A. Suzuki, M. Murakami, T. Ogi, K. Koguchi, and E. Nakamura. 1987. Liquid fuel production from sewage sludge by catalytic conversion using sodium carbonate. *Fuel* 66(8): 1150-1155.

Zabaniotou, A. A. 1999. Pyrolysis of forestry biomass by-products in Greece. *Energy Sources* 21: 395-403.