

PRODUCT DISTRIBUTION AND IMPLICATION OF HYDROTHERMAL CONVERSION OF SWINE MANURE AT LOW TEMPERATURES

R. Dong, Y. Zhang, L. L. Christianson, T. L. Funk, X. Wang, Z. Wang, M. Minarick, G. Yu

ABSTRACT. *With the goal of utilization of agricultural wastes to produce valuable products, hydrothermal conversion of swine manure at 20% solids content was performed in a 2 L batch reactor at temperatures of 240 °C to 280 °C, 10 to 120 min reaction time, and 0.7 MPa initial pressure of nitrogen gas. Basically, four types of products (i.e., oil, aqueous product, solid, and gas) were collected from hydrothermal conversion of swine manure with primary material balance. Meanwhile, the raw oil product was distilled and extracted with toluene for accurately quantifying its oil, moisture, and solids content based on ASTM Standards. Results showed that oil yields from swine manure did not vary with reaction temperature and time used in this study, whereas the solid residue, aqueous product, and gas produced from swine manure changed as the temperature and reaction time increased. The results suggested that the hydrothermal conversion of swine manure to oil was a decarboxylation process with an oil yield of 33% by weight at 240 °C, which was mainly attributed to the presence of other components in the swine manure, such as lipids, rather than direct hydrothermal conversion of cellulose to oil.*

Keywords. *Bioenergy, Biofuels, Biomass, Hydrothermal, Liquefaction, Swine manure, Thermochemical.*

Concerns about environmental issues and foreign oil dependence have encouraged research on biofuel production to replace fossil fuels for the world's sustainable development and economic growth. Utilization of hydrothermal processes to produce liquid fuel from agricultural wastes has shown potential advantages over conventional biological processes for ethanol production from corn grain or cellulosic biomass in terms of feedstock cost, energy content of the biofuel, and the small footprint of the process (NSF, 2008). Generally, a hydrothermal process (HTP) converts organic material into a viscous and dark liquid (biofuel) as a major product in a hot-water environment under pressurized conditions. In the literature, similar processes are also known as liquefaction, hydroliquefaction, aqueous pyrolysis, hydropyrolysis, hydrothermolysis, aqueous thermolysis, or hydrothermal upgrading (HTU).

Because biofuel produced from hydrothermal processes resembles petroleum crude with similar heating values, about 30 to 40 MJ kg⁻¹ (Boocock et al., 1979; Goudriaan et al.,

2000), it is sometimes called bio-crude and can be further upgraded to diesel and gasoline via well-developed refinery processes (Elliott and Oasmaa, 1991; Gevert and Otterstedt, 1987). Results from a study indicated that the hydrothermal process was economically promising, with thermal efficiencies reaching 50% to 60% from biomass to gasoline and diesel (Elliott et al., 1990). The process had potential for further improvement with the advancement of research and development.

Hydrothermal processing of swine manure has been studied to produce valuable oil products and mitigate some of the environmental concerns associated with swine manure. It was reported for the first time that more than 60% yield of raw oil was produced from swine manure slurry (at 20% total solids content) in a batch reactor at temperatures of 295 °C to 305 °C, reaction time of 120 min, and 0.69 MPa initial pressure of carbon monoxide or nitrogen gas (He et al., 2000a, 2000b). As high as 90% fraction of the raw oil could be soluble in benzene, and the viscosity of the raw oil could be as low as 0.51 Pa·S as measured at 65 °C, depending on process temperature (He et al., 2001a, 2001b). Even with the presence of about 11% to 15% moisture, the raw oil product exhibited an energy content of about 34,940 kJ kg⁻¹ as a low heating value (He et al., 2000b). These results strongly imply that hydrothermal processing of agricultural wastes, particularly wet biomass such as swine manure, is technically and economically feasible. For a further technoeconomic assessment of hydrothermal processing of swine manure, more information is necessary, for example, the energy content of the moisture-free oil product.

These encouraging results deserved a detailed investigation of the operating conditions of the hydrothermal process, which can potentially improve the yield and quality of the biofuels produced from swine manure. It was found that the yield and quality of the raw oil product varied with the reac-

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tion time when swine manure at 20% solids content was converted in an aqueous environment with a pH of 6.1 (He et al., 2000a). For example, at 285 °C and with the presence of CO at an initial pressure 690 kPa, the raw oil yield increased from 10% to 60% as reaction time increased from 30 to 120 min. Similar to the yield, the benzene-soluble fraction of the raw oil product also increased with reaction time under the same conditions (He et al., 2000a). Based on these experiments, many plausible explanations for the oil formation from swine manure exist, according to the literature. However, due to difficulties in the product recovery from the reaction mixture, consistent information in the literature is very rare, and this makes it difficult to compare results from different studies. Therefore, more experimental data, collected with different approaches, might be helpful to clarify the disagreement in the literature and improve the understanding of the hydrothermal conversion of biomass.

Many different approaches have been used to quantify the HTP products derived from biomass or organic materials depending on the purpose of the individual study. Conventionally, an organic solvent is used to extract the oil product from the reaction mixture, followed by filtration and distillation. The organic solvents that have been commonly used include acetone (Karagöz et al., 2004; Minowa et al., 1995a; Nelson et al., 1984; Ogi et al., 1985; Qian et al., 2007), benzene (El-Saied, 1977; Fu et al., 1974), chloroform (Boocock et al., 1979; Goudriaan and Peferoen, 1990), dichloromethane (Barrows and Elliott, 1984; Bohlmann et al., 1999; Dote et al., 1996; Elliott et al., 1988; Inoue et al., 1999; Itoh et al., 1994; Minowa et al., 1995c; Suzuki et al., 1988; Yokoyama et al., 1987), diethyl ether (Boocock et al., 1979), and n-hexane (Faix et al., 1989; Matsui et al., 1997).

In order to accurately quantify product yields from hydrothermal conversion of swine manure, the experimental method was modified with the aim of improving the product recovery from a batch reactor. The material balance obtained by the modified experimental method was evaluated based on the dry weight of the swine manure in an attempt to justify the subsequent comparison of product yields from hydrothermal conversion of swine manure at different temperatures and reaction times. As hydrothermal conversion of swine manure proceeded with reaction time, the effect of reaction temperature on production distribution was examined at 240 °C to 280 °C. An attempt was made to explain the observed experimental phenomena, which might be valuable for further

research on the mechanism of hydrothermal conversion of swine manure to oil.

MATERIAL AND METHODS

MATERIALS

Swine manure was collected from pen floors of a swine grower house, pulverized with a commercial Waring blender (model MX1000, Waring Commercial, Torrington, Conn.) followed by homogenizing with a high-shear mixer (model L4RT, Silverson Machines, Inc., Longmeadow, Mass.), and then stored in a refrigerator below 4 °C. The swine manure was sent to Midwest Laboratories, Inc. (Omaha, Neb.) for analyses using methods defined by the Association of Official Analytical Chemists (AOAC). The analyses of the swine manure mainly included moisture content, crude protein, acid hydrolysis fat, acid detergent fiber, neutral detergent fiber, and ash.

EXPERIMENTAL PROCEDURE

The hydrothermal experiments were performed in a 2 L reactor (model 4534, Parr Instrument Co., Moline, Ill.) at reaction temperatures of 240 °C to 280 °C and reaction times from 10 to 120 min without adding any catalyst. A schematic of a similar reactor can be found in He et al. (2000b). In a typical experiment, 800 g of swine manure slurry, whose solids content was adjusted to 20% by weight by mixing with tap water, was loaded into the reactor. After sealing the reactor and flushing it with nitrogen gas, nitrogen was added to a pressure of 0.7 MPa. The reactor was then heated to the desired temperature (e.g., 280 °C \pm 1 °C) over a period of 40 min with stirring. The reactor was maintained at that temperature for a desired time (e.g., 60 min). Afterwards, it was rapidly cooled down to 30 °C in 10 min by allowing cooling water to pass through the cooling coil inside the reactor. A typical temperature profile is shown in figure 1. A J-type thermocouple was used in this study and calibrated with a dry block calibrator (model ETC400A, AMETEK Calibration Instruments, Allerød, Denmark). Gas products were vented to the atmosphere to gradually depressurize the reactor. Subsequently, the reactor was opened and well cleaned, including the internal structure (e.g., the cooling coils and thermocouple), with a spatula.

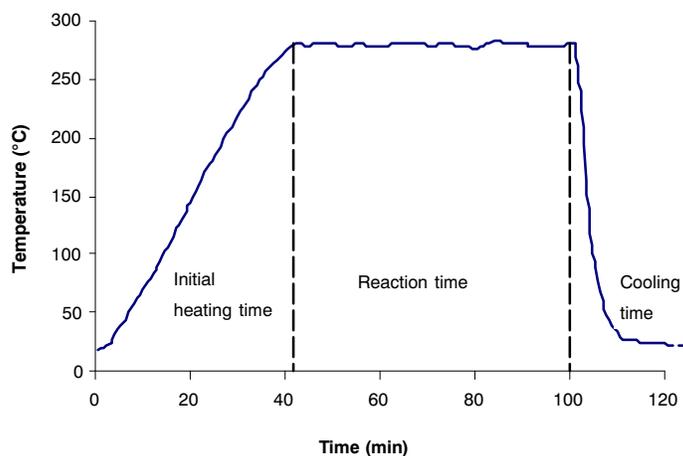


Figure 1. Representative temperature profile of the experiment at 280 °C for 60 min.

The total weight of the reactor with the reaction mixture was measured on a digital scale (model GP-20K, A&D Engineering, Inc., San Jose, Cal.) to estimate the amount of gas produced during the reaction. Usually, the net weight of the reactor was measured with the same digital scale at the beginning of experiments and subtracted from the total weight, so that the weight of the reaction mixtures could be obtained. The amount of gas formed in the reaction was assumed to be the difference between the weight of the original swine manure slurry loaded into the reactor and the weight of the remaining reaction mixtures. There was an assumption for this method that no leakage occurred during the reaction and that all products except the gas were collected in the reactor. To justify this assumption, a blank test was run with tap water and using the same procedures. The blank experiment was conducted with 500 g of tap water at 300 °C for 60 min with a stirring rate of 600 rpm and initial nitrogen pressure of 0.67 MPa. At 300 °C, the system pressure for the blank experiment increased to 9.76 MPa. When the reactor was cooled to room temperature and opened, 99.6% of the water was recovered, which indicated almost no leakage in the reactor system with proper sealing.

The product mixture that remained in the reactor contained two phases: the solid/oil phase and the aqueous phase. Some solids were suspended in the aqueous phase. The aqueous product was carefully poured out of the reactor and further filtered under vacuum. The suspended solids were obtained by drying in a convection oven at 105 °C for 2 to 3 h. The aqueous product was weighed, sampled, and analyzed. All remaining materials in the reactor were taken as the raw oil product. The raw oil product was then weighed and analyzed for moisture and sediment content. The aqueous product included the moisture in the filtered solids and the raw oil product. The yield of aqueous product was calculated by subtracting the initial amount of water input from the final aqueous product from the experiment to determine the best material balance based on the dry matter of the feedstock.

ANALYSES OF RAW OIL PRODUCT

The moisture content of the raw oil product was determined using a distillation apparatus based on ASTM Standard D95-99 (ASTM, 2004a). The sediment contents of the raw oil product were measured using a Soxhlet extraction apparatus with reference to ASTM Standard D473-02 (ASTM, 2004b) and ASTM Standard D4072-98 (ASTM, 2004c). Following ASTM Standards D473-02 and D4072-98, toluene

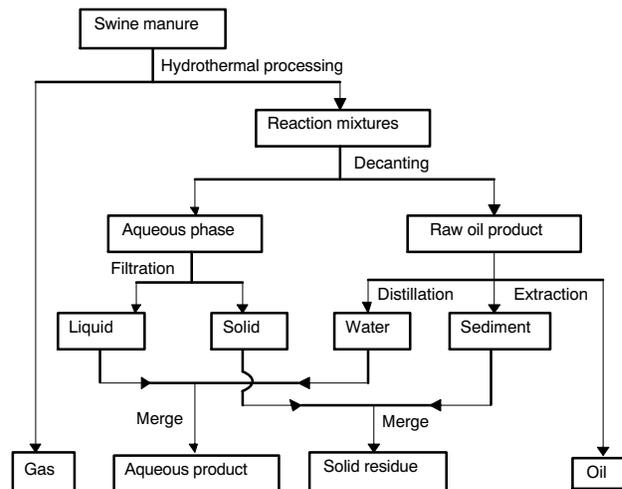


Figure 2. Procedures of product recovery.

was used as the organic solvent during the Soxhlet extraction to separate moisture and sediment contaminants from the HTP bio-oil. Cautious operation was paramount for maintaining the material balance within an acceptable range. The solids filtered from the aqueous phase were directly classified as solid residue in this study. No oil was further recovered from the solids filtered from the aqueous phase because the quantity of these solids was very small relative to the raw oil product. Moreover, the solids filtered from the aqueous phase showed apparently different color (yellowish earth) from the black color of the raw oil product, which implied that the solids might be a different substance from the raw oil product. Although the oil extraction was not further separated from the solution, the weight of the oil product could be calculated from the weight of the raw oil product by deducting the weight of the moisture and sediment, which were later considered part of the aqueous product and solid residue, respectively, to determine the material balance. In this study, a product yield based on dry matter was adopted since ash, as well as volatile solids, was loaded into the reactor and should therefore be considered in the material balance, particularly when the role of ash in a hydrothermal process is not very clear. The procedures for product recovery are summarized in figure 2, and the yields of the products are defined by the equations listed in table 1.

Table 1. Product yield equations.

Product	Equation
Raw oil yield (%)	$= \frac{\text{weight of raw oil product}}{\text{weight of dry matter of swine manure}} \cdot 100$
Oil yield (%)	$= \frac{\text{weight of (raw oil product - moisture - sediment)}}{\text{weight of dry matter of swine manure}} \cdot 100$
Gas yield (%)	$= \frac{\text{weight of (raw materials - reaction mixtures)}}{\text{weight of dry matter of swine manure}} \cdot 100$
Solid residue yield (%)	$= \frac{\text{weight of (filtration solid + sediment in raw oil product)}}{\text{weight of dry matter of swine manure}} \cdot 100$
Aqueous product yield (%)	$= \frac{\text{weight of (reaction mixture - solid residue - oil product - water input)}}{\text{weight of dry matter of swine manure}} \cdot 100$

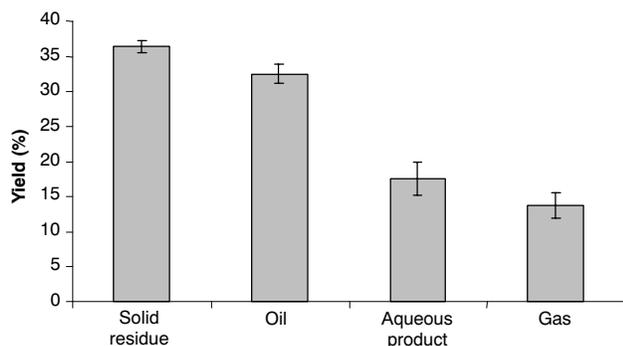


Figure 3. Product yield from triplicate experiments ($n = 3$) at 240°C temperature, 30 min reaction time, and 0.67 MPa initial pressure of nitrogen (error bars represent standard deviations).

RESULTS AND DISCUSSION

REPEATED EXPERIMENTS

Two sets of triplicate experiments were conducted with the swine manure (20% solids content by weight) at 240°C under 0.67 MPa initial pressure of nitrogen for 30 and 60 min reaction times, respectively. Figure 3 shows the repeated results obtained from the triplicate experiments with swine manure at 20% solids content, 240°C, 30 min, and 0.67 MPa initial pressure of nitrogen.

Based on the definition of product, the material balance was normalized to 100%, as shown in figure 3. The main factor that could lead to a poorer material balance was the recovery operation for the oil and aqueous product due to the high viscosity of the oil and the difficulty in accurate measurement of the moisture content of other products, i.e., the oil and solid residue. These factors could also result in fluctuations in product yields. As shown in figure 3, the average yields were 32.5% ± 1.4% (standard deviation) for oil, 14.2% ± 2.3% for aqueous product, 36.3% ± 0.9% for solid residue, and 13.7% ± 1.8% for gas with swine manure at 20% solids content and 240°C temperature for 30 min reaction time.

The relatively large deviations observed in the gas and aqueous product yields were due to limitations of the current experimental method. Particularly, under certain conditions (e.g., 260°C temperature and 30 min reaction time), a huge amount of foam could be produced in the experiment, which was difficult to collect and separate from the other products, thereby leading to relatively large deviations and poor material balance. It was also noted that the deviation in product yields shown in figure 3 might not be valid as experimental conditions change.

The example shown here demonstrated the repeatability of results from an experiment at typical conditions. Under typical conditions, the deviation relative to corresponding product yields was small and might not fundamentally compromise the reliability of the experimental results.

RAW OIL PRODUCT

The raw oil product collected from the hydrothermal experiments generally contained moisture and solids and was usually dark, viscous, and denser than the aqueous product. In addition, at short reaction times, the raw oil product appeared to consist of numerous small spherical particles of a homogeneous size. As temperature and time increased, the spherical particles disappeared and became a tar-like fluid with an estimated pour point higher than 80°C. Similar

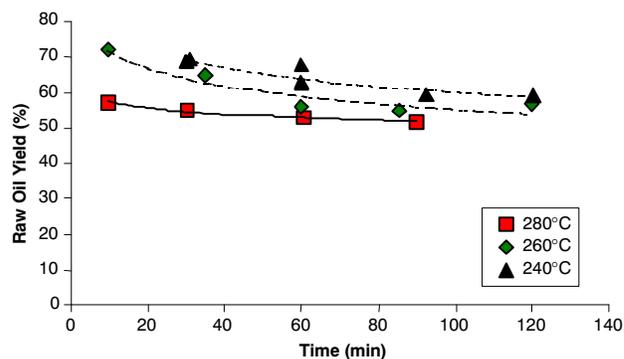


Figure 4. Raw oil yields from swine manure at temperatures of 240°C to 280°C for 10 to 120 min reaction time.

spherical structures were observed by Boocock and Kosiak (1988) with scanning electron microscopy (SEM) as a poplar stick was exposed to a steam/water temperature of about 290°C for an extremely short time in a tube reactor without agitation. The spherical particles were believed to indicate primary oil formation resulting from partial depolymerization of the biopolymers even while well-defined biomass structures are still present (Boocock and Kosiak, 1988).

Figure 4 shows the yield of raw oil product at temperatures of 240°C, 260°C, and 280°C for 10 to 120 min reaction time. Unexpectedly, the raw oil yield decreased rather than increased with the increase in reaction temperature and time. At extended times, the raw oil yield tended to level off at a certain value, e.g., about 50% by weight. According to the superficial appearance and yield trend of the raw oil product, it was reasonable to believe that the raw oil product contained partially unconverted biomass originating from the swine manure and might not be stabilized until these materials were depleted or separated. Otherwise, it was difficult to explain the yield of raw oil product with the general theory about chemical kinetics in this study. However, there were many non-oil substances, such as water and solids, mixed with the raw oil product. Therefore, a further separation of the raw oil product was necessary.

OIL PRODUCT

As described earlier, the oil product was defined as the toluene-soluble fraction of the raw oil product with reference to ASTM Standard D4072-98 (ASTM, 2004c). According to our observations, the toluene solvent changed from a colorless transparent solvent into the yellowish liquid after the swine manure was soaked in the hot toluene even for about 2 h. In addition, the swine manure could not form a homogeneous slurry in the hot toluene even when using mechanical stirring, which was apparently different from the behavior of swine manure in water and the behavior of raw oil product in toluene. Thus, a direct comparison of oil yields from swine manure before and after hydrothermal conversion, based on the same Soxhlet extraction process, might not be accurate.

Since it was very difficult to obtain a similar black toluene-extraction directly from swine manure before hydrothermal conversion, the toluene-soluble fraction of the raw oil product was believed to derive from the hydrothermal conversion of the swine manure. The oil yield was calculated from the weight of the raw oil product deducting the moisture and sediment content based on official methods used for evaluating petroleum products. Due to the inconsistency of the

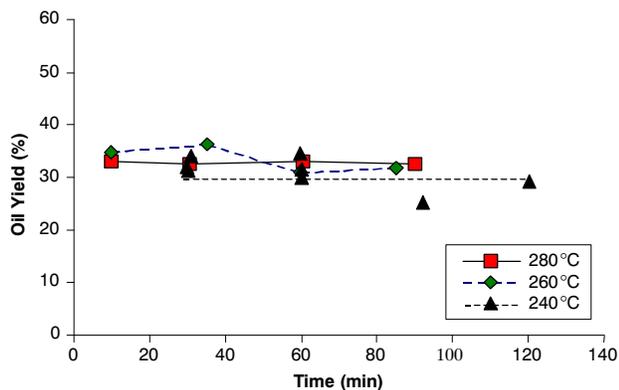


Figure 5. Oil yield from swine manure at temperatures of 240°C to 280°C for 10 to 120 min reaction time.

heterogeneous reaction mixtures and the multiple steps of the separation procedures, a relatively large deviation of oil yield occurred in this study. At 240°C temperature and 90 min reaction time, the oil yield appeared to deviate from the almost constant oil yield shown in figure 5, which is probably attributable to experimental error. Except for that data point, it is surprising that the oil yield remained almost constant at about 33% by weight (fig. 5) regardless of reaction temperature and time, which indicates that the oil product was stable under hydrothermal conditions and that the final yield did not depend on the reaction temperature and time. Under kinetically controlled reaction conditions, the product yield usually increases with reaction time (Masel, 2001). However, the oil yield as a function of time needs to be determined, which indicates that the process conditions used in this study were not within the kinetically controlled region. Under kinetically controlled conditions, it was possible to obtain 33% oil yield at a temperature below 240°C by extending the reaction time. In the future, to measure the kinetics of oil production from hydrothermal conversion of swine manure with the system used in this study, it will be necessary to further lower the reaction temperature.

For a reversible chemical reaction, the equilibrium yield of the final product generally varies with the reaction temperature, such as biodiesel production from a transesterification reaction (Čerče et al., 2005). If the oil from the hydrothermal conversion of swine manure was a product of a reversible reaction, then the equilibrium state should be achieved since no increase or decrease of oil yield occurred (fig. 5). However, the oil yield at equilibrium showed no remarkable discrepancy as the reaction temperature changed from 240°C to 280°C. This implies that the oil was probably produced by an irreversible reaction, and the final oil yield seemed to be determined only by the composition of the starting material under current experimental conditions.

Yokoyama et al. (1987) observed a similar trend of oil yield when they hydrothermally converted sewage sludge at 300°C temperature and 0 to 120 min reaction time under 120 MPa of nitrogen pressure with the presence of 5% sodium carbonate. The oil yield was constant at about 50% based on the weight of volatile solids and showed no marked difference at different reaction times. Similarly, Suzuki et al. (1990) showed that there was no statistically significant effect of temperature and reaction time on the yield of oil from hydrothermal processing of sewage sludge at temperatures of 250°C to 275°C and 0 to 60 min reaction time. The oil yield

from hydrothermal conversion of garbage at temperatures of 250°C to 340°C and 0.1 to 2 h reaction time was also independent of reaction time (Minowa et al., 1995c). With reference to the composition of sewage sludge (Yokoyama et al., 1987) and swine manure (Hrubant et al., 1978), it was noticed that, except for differences in the amount of fiber, both feedstocks contained significant amounts of crude fat and crude protein, which could be one of the major reasons leading to the higher oil yield at a relatively lower temperature.

It was possible that some particular components in the swine manure, such as crude fat and crude protein, made major contributions to the oil formation, and that the quantity of these components eventually determined the oil yield. Analyses of the swine manure by Midwest Laboratories, Inc., showed that the swine manure slurry collected from the pig house contained about 29.2% dry matter, 7.4% crude protein (Kjeldahl), 4.8% acid hydrolysis fat, 4.3% acid detergent fiber, 10.3% neutral detergent fiber, 4.2% ash, and a small amount of minerals based on the weight of a wet sample. Suzuki et al. (1988) reported that crude fat was nearly linearly related to the dichloromethane-soluble oil content originally existing in the starting materials. If most of the oil content present in the starting materials could completely convert or directly appear in the oil product under experimental conditions, then the oil yield would be linearly proportional to the crude fat fraction of the swine manure. Minowa et al. (1994) compared the oil yield from sweet potato, barley, rice, and buckwheat at temperatures of 250°C to 350°C with a presence of 0% to 5% sodium carbonate for 0 to 30 min reaction time under nitrogen pressure. They found that the yield of oil (which was extracted with dichloromethane from the reaction mixture) from buckwheat was significantly higher than the yield from the other feedstocks under similar hydrothermal conditions. The high oil yield was attributed to the high crude fat content in the starting material, since the fat was able to directly dissolve in dichloromethane (Minowa et al., 1994). Then again, if the oil was generated by an irreversible reaction, as hypothesized for the oil derived from swine manure, then the oil yield would be dictated by the stoichiometry of the feed stream, i.e., the oil yield would be proportional to some specific compositions of feedstock. In addition to the crude fat, the protein and carbohydrates could also participate in the oil formation under proper hydrothermal conditions (Minowa et al., 1995b). In hydrothermal processing of protein-containing biomass, the high nitrogen content of the oil product was found to be directly correlated to the nitrogen in the feedstock (Dote et al., 1996; Elliott et al., 1988). Swine manure usually has up to 16.8% crude fat and 15.1% amino acids based on dry matter (Hrubant et al., 1978), which coincides with the average 33% oil yield by weight obtained from the swine manure in this study. Although this study might not completely exclude the carbohydrate contribution to the oil yield, more experiments with the presence of crude fat and protein probably would provide evidence to further understand the origin of oil during hydrothermal processing of swine manure.

SOLID RESIDUE

Solid residue dispersed in both the aqueous product and the raw oil product in this study. Superficially, the solid residue collected from the aqueous product was different from that separated from the raw oil product by extraction and filtration. The solid residue collected from the aqueous prod-

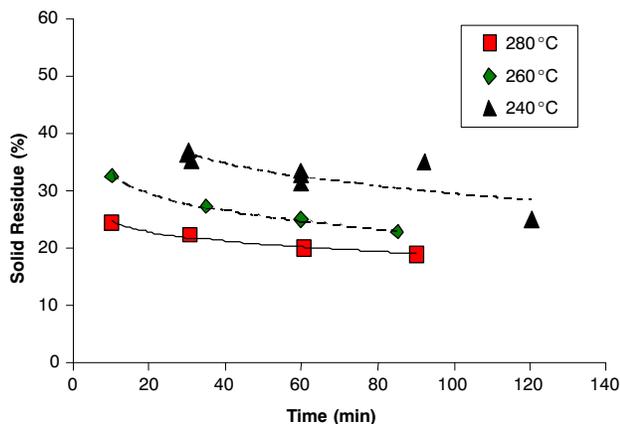


Figure 6. Yield of solid residue derived from swine manure at temperatures of 240 °C to 280 °C for 10 to 120 min reaction time.

uct looked like mud when moisture was present. In contrast, the solid residue present in the raw oil product was similar to black carbon or charcoal. The physical and chemical properties of the solid residue were not further investigated, since only the weight of the solid residue was considered for the oil yield calculation.

Figure 6 shows that the yield of solid residue decreased with increasing reaction temperature and time, tending to level off at about 20% by weight at 280 °C: the higher the temperature, the less solid residue remained. The decrease of solid residue with respect to time implies a decomposition process of biomass in the aqueous and gaseous phases (Funazukuri et al., 2000; Lin et al., 1992; Saeman, 1945; Sasaki et al., 1998; Xiang et al., 2003). Theoretically, it is reasonable to speculate that the solid residue was composed of unconverted volatile solids from the swine manure plus inorganic ash, part of which was insoluble in water. In the absence of a catalyst, hydrothermal degradation of cellulose in the aqueous phase is slow; more than 50% of the cellulose remained in the solid residue at 274 °C after 10 min reaction time (Bobleter, 1994). About 60% of crystalline cellulose was even recalcitrant to decompose at 290 °C when exposed to compressed hot water (Sasaki et al., 1998). Therefore, it is possible that fibrous components in the swine manure, such as cellulose, remained in the solid residue under the current process conditions.

The solid residue might contain char derived from intermediates of the hydrothermal processing of swine manure. Mok et al. (1992) showed that charcoal formation from biomass was favored by the presence of water in a sealed reactor. The radicals that formed from intermediates released into the water phase were thought to be able to condense and repolymerize to form a solid mass during the solubilization of biomass (Minowa et al., 1998b). The random recombination of the intermediate compounds could also lead to char formation (Chornet and Overend, 1985). If char derived from intermediates dominated the solid residue, then one should expect to observe an increase in the yield of solid residue with reaction time. Therefore, the slightly decreasing trend in solid residue, shown in figure 6, is not the result of char formation by the condensation and repolymerization of intermediates.

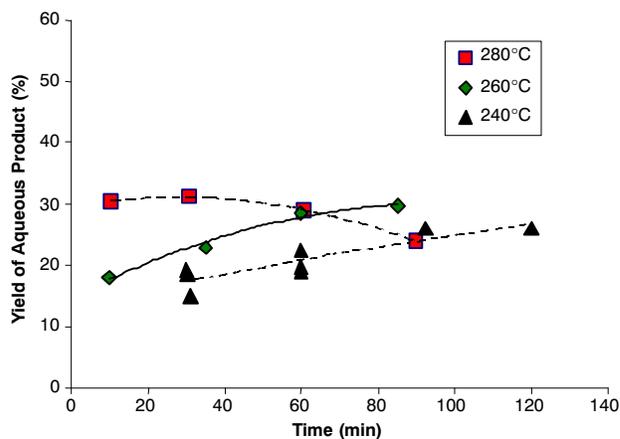


Figure 7. Yield of aqueous product from hydrothermal processing of swine manure at temperatures of 240 °C to 280 °C for 0 to 120 min reaction time.

AQUEOUS PRODUCT

The aqueous product exhibited an increase followed by a decrease while the oil product remained constant during the hydrothermal processing of swine manure. Therefore, the formation and decomposition of the aqueous product might not necessarily lead to the oil product when swine manure is exposed to hydrothermal conditions. At temperatures of 240 °C and 260 °C, the yield of aqueous product increased with reaction time but decreased after reaching a maximum of 280 °C, as shown in figure 7. A similar trend was observed in the intermediate yield from a consecutive reaction, e.g., hydrolysis of biomass to sugar and then decomposition to other products (Church and Wooldridge, 1981; Lavarack et al., 2002; Lee et al., 1999; Saeman, 1945). In that consecutive reaction, the biomass hydrolyzed to sugars and then decomposed to other products, such as HMF, furfurans, and even gases (Kruse and Faquir, 2007; Sinag et al., 2003). Both the experiment and theoretical model indicated that the sugars, as intermediates from the hydrolysis of the biomass, experienced a maximum yield with respect to time (Church and Wooldridge, 1981; Lavarack et al., 2002; Lee et al., 1999; Saeman, 1945), which is the same trend shown in figure 7 for the aqueous product from the hydrothermal conversion of swine manure. However, as the aqueous product was converted at 280 °C for more than 30 min reaction time (fig. 7), the oil yield from hydrothermal conversion of swine manure did not increase but remained constant (fig. 5). In contrast to the oil yield from swine manure, the gas yield increased at 280 °C, as will be shown later. Therefore, it is believed that the aqueous product derived from hydrothermal processing of swine manure decomposed to gas at a high temperature, but did not necessarily result in an oil product based on the law of the conservation of mass.

Minowa et al. (1998c) showed that it was possible for oil to form via intermediates in the aqueous phase during hydrothermal processing of cellulose because a similar oil product was obtained from glucose under the same conditions. Under a catalyst-free condition, the oil derived from cellulose and glucose and the product yields from cellulose and glucose had similar trends (Minowa et al., 1998c). Particularly, it was noted that the oil produced from hydrothermal conversion of cellulose was not stable in the absence of a catalyst, and initially increased and then decreased with temperature (Mino-

wa et al., 1998c). However, the oil from the hydrothermal conversion of swine manure was stable at the same temperatures, as shown in figure 5, which implies that the oil derived from swine manure was probably different from the oil derived from cellulose and glucose in the absence of a catalyst. In addition, a significant amount of oil was produced from hydrothermal conversion of swine manure below 250 °C, but very little oil was obtained from cellulose and glucose under the same conditions (Minowa et al., 1998c). This suggests that oil production from swine manure probably followed a different pathway from that of hydrothermal conversion of cellulose and glucose to oil in a catalyst-free environment. Although the aqueous product could be the intermediate for oil formation, direct conversion of glucose and its derivatives from hydrolysis of cellulose might not completely explain the course of oil production from swine manure. Therefore, a more important factor or reaction network could contribute to oil formation under hydrothermal conditions, since the 33% oil yield (on dry matter basis) from swine manure at 240 °C was much higher than the 25% oil yield (on carbon basis) from cellulose and glucose under the most preferred conditions. Factors that might have significant effects on oil formation during hydrothermal processing of swine manure could be a catalyst, pH, and components in the swine manure, (e.g., fat and protein).

Under the effect of sodium carbonate, the hydrothermal process was able to generate stable oil from cellulose with a similar yield as that from glucose (Minowa et al., 1997), which strongly implies that the oil formation was probably through aldol condensation of the intermediates derived from hydrolysis of cellulose with the catalysis of alkaline (Nelson et al., 1984). It was reported that about 20% of the oil yield was obtained from glucose at 300 °C with the presence of 5% sodium carbonate, which was the same as that from cellulose under the same hydrothermal conditions (Minowa et al., 1997). Since swine manure contains a significant amount of minerals (Hrubant et al., 1978), the cellulose components of swine manure and its derivatives could be potentially converted to oil under the effect of those alkaline minerals during the hydrothermal process. However, the 33% oil yield from swine manure obtained in this study was significantly higher than that from pure cellulose and glucose under the similar conditions. Therefore, it is speculated that the oil from hydrothermal conversion of swine manure might not derive from direct conversion of decomposition products, such as glucose, from hydrolysis of cellulosic components in swine manure. In addition, a significant amount of oil could be produced from swine manure at 240 °C (fig. 5) with an increase of the aqueous product (fig. 7), while at such temperatures (below 250 °C) the decomposition of cellulose was slow and little oil was produced, even when using 5% of sodium carbonate as a catalyst (Minowa et al., 1997; Nelson et al., 1984). This implies that it is almost impossible to convert glucose to oil under the conditions used in this study for hydrothermal conversion of swine manure. At 180 °C, it was reported that little oil was obtained from hydrothermal conversion of glucose when using an alkaline catalyst (Minowa et al., 1997). Other than that, little information is available in the literature about oil formation from hydrothermal conversion of glucose with the presence of an alkaline catalyst. Therefore, it is thought that hydrothermal conversion of cellulose to oil might not explain the complete reaction that occurs during hydrothermal processing of swine manure to oil,

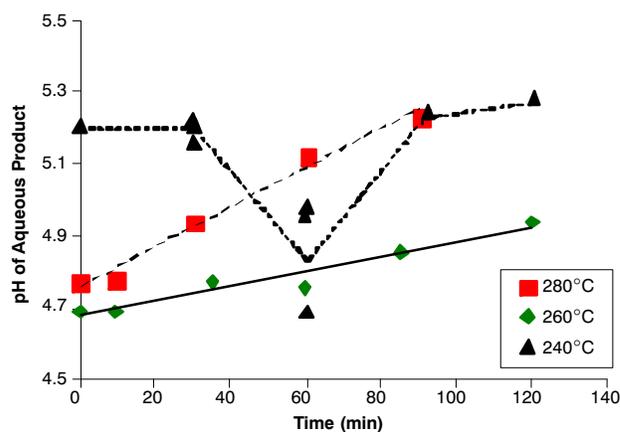


Figure 8. The pH of aqueous product from hydrothermal processing of swine manure at temperatures of 240 °C to 280 °C for 0 to 120 min reaction time.

and a relatively complicated reaction network could exist. Other components in swine manure might make a significant contribution to oil formation, and further research is needed to understand the mechanism of hydrothermal conversion of swine manure.

It is also interesting to note that the pH of the aqueous product from hydrothermal processing of swine manure experienced a drop followed by an increase with time (fig. 8). Naturally, swine manure slurry had a pH of about 5.8 to 6.6 (He et al., 2001c; Hrubant et al., 1978). The pH measured as the hydrothermal process reached the desired temperature showed a rapid decrease, from 5.2 to about 4.7 at 240 °C. Since the hydrolysis of biomass could occur below 240 °C, the pH of the aqueous phase very likely started to decrease during the heating-up stage. Subsequently, the pH of the aqueous product increased to 5.3 as the conversion progressed at 240 °C. To confirm that the pH drop was not due to experimental error, triplicate experiments were conducted at 240 °C and 30 min reaction time, while duplicate experiments were repeated with swine manure from a different batch at 240 °C and 60 min reaction time. As shown in figure 8, the pH of the aqueous product showed a small standard deviation of 0.03 at 240 °C and 30 min reaction time and a dramatic decrease in pH at 240 °C and 60 min reaction time where a relatively large fluctuation was observed, mainly due to the variation in feedstock. As long as the initial swine manure had a pH of 5 to 7, the aqueous product from the hydrothermal process very likely experienced a pH drop following an increase. At temperatures of 260 °C and 280 °C, only the increasing phase of pH could be observed. Measuring the pH of the aqueous product during the heating-up period might show a gradual decrease in pH as the temperature increased to 260 °C and 280 °C, which eventually led to the initial low pH at 0 min in figure 8.

It is common for the pH of the aqueous phase to decrease and then increase during hydrothermal processing of biomass. In hydrothermal conversion of cellulose with sodium carbonate at 300 °C for 1 h under 10.3 MPa of nitrogen, it was noted that the pH of the reaction mixture decreased from 11 to 4 (Nelson et al., 1984). In a continuous hydrothermal process using wood slurry with 13% solids content prepared by mixing with neutral water, the pH of the processed water ended up at 3 to 5 under conditions of 350 °C, 6 min residence

time, and 180 bar nitrogen pressure (Goudriaan and Peferoen, 1990). With 0% to 20% sodium carbonate present in the starting material (sewage sludge), Yokoyama et al. (1987) confirmed that the pH of the aqueous product was the lowest at about 5.4 and maximum at about 8.6 at temperatures of 250 °C to 340 °C, zero holding time, and 12 MPa nitrogen pressure. According to a study of pH changes during pyrolysis of rice husk by Maiti et al. (2006), the destruction of biomass could generate organic acids and phenolic substances under hydrothermal conditions, which lowered the pH of the aqueous product, thus making it acidic. As the reaction continued, the alkali salts began to separate from the organic matrix of the biomass, and the pH of the aqueous product increased. Eventually, the pH of the aqueous product could become constant as all the alkali salts released from the biomass and organic acid were stabilized under the experimental conditions.

GAS PRODUCT

A significant amount of gas was generated during the hydrothermal conversion of swine manure to oil. The gas yields were around 15% and changed slightly with time at temperatures of 240 °C and 260 °C, but a nearly linear increase was observed from 12% for 10 min reaction time to 24.7% for 90 min reaction time at 280 °C (fig. 9). Compared with the gas produced from hydrothermal processing of other biomass types (Itoh et al., 1994; Karagöz et al., 2006; Minowa et al., 1998b; Suzuki et al., 1988; Yilgin and Pehlivan, 2004; Yokoyama et al., 1987), the gas produced from the swine manure not only increased with reaction temperature and time but also exceeded 10% by weight depending on the process conditions (fig. 9). Although the composition of the gas product is not reported here, it was estimated that carbon dioxide generally dominated the gas product, according to the gas composition in the hydrothermal processing of other biomass types under similar conditions (Goudriaan and Peferoen, 1990; Itoh et al., 1994; Nelson et al., 1984).

In this study, an increase in gas yield with time at 280 °C seemed not related to the oil formation or decomposition but rather was a result of decomposition of the aqueous product that derived from decomposition of the solid residue. Originally, it was believed that the oil product was unstable and decomposed to gas, since the gas yield increased as the oil yield decreased during hydrothermal processing of cellulose (Minowa et al., 1997). Unexpectedly, the oil yield from hydro-

thermal conversion of swine manure did not decrease but remained constant (fig. 5) with the increase in gas yield (fig. 9), which implies that the increase in gas yield at 280 °C might not be caused by oil decomposition. The increase in gas yield was more likely due to decomposition of the aqueous product, since the yield of aqueous product decreased with time (fig. 7) as gas yield increased at 280 °C. A similar study by Minowa et al. (1998a) showed that the gas yield increased with the decomposition of the aqueous product while the oil yield was almost constant at temperatures of 300 °C to 350 °C during hydrothermal conversion of cellulose with the presence of sodium carbonate. Therefore, it is possible for gases to be generated from decomposition of the aqueous product derived from hydrothermal processing of the swine manure in this study.

At temperatures of 240 °C and 260 °C, the gas yield changed slightly with time (fig. 9), while the solid residue decreased (fig. 6) and the aqueous product increased with time (fig. 7), which excluded the possibility of direct gasification of solid residue but supported the pathway of decomposition of the aqueous product to gases. Theoretically, the relationship of solid residue, aqueous product, and gases could be described by a kinetic model similar to that of sugar from cellulose hydrolysis, if this pathway existed and if sufficient and qualitative data were available. On the other hand, it was also noticed that the slope of the gas yield at temperatures of 240 °C and 260 °C in figure 9 was very small, which indicates that the rate of decomposition of the aqueous product to gases was very slow at 240 °C and 260 °C. The decomposition rate of the aqueous product was so slow that it was impossible to generate so much gas (10% by weight in yield) in 30 min at temperatures of 240 °C to 260 °C. Extrapolating the gas yield at 240 °C and 260 °C to the zero time in figure 9 does not pass through the origin point, which implies that a significant amount of gas had already formed at the beginning of the hydrothermal conversion of swine manure in this study. In other words, the gas yield of 10% by weight observed at the initial stage in figure 9 might not derive entirely from decomposition of the aqueous product; there must be some other reaction that generates a significant amount of gas at relatively low temperature and in a short time during conversion of the swine manure. Since the formation of oil was also completed (fig. 5) when a significant amount of gas had been produced at the beginning of the reaction (fig. 9), it is postulated that the gas probably accompanied oil formation as a byproduct during hydrothermal conversion of the swine manure. A previous study (Appleford, 2004) showed that the major component of the gas product was CO₂, which was consistent with the role of the decarboxylation reaction in liquefaction proposed by Chornet and Overend (1985). This means that the oil formation from the hydrothermal processing of swine manure was probably a decarboxylation process.

SUMMARY

A reliable experimental method was used to obtain the yields of oil, solid residue, aqueous product, and gas from hydrothermal conversion of swine manure using a batch reactor. It was found that the oil yield from the hydrothermal conversion of swine manure was not influenced by temperatures of 240 °C to 260 °C and 10 to 120 min reaction time in this study, while the solid residue was very likely converted to an

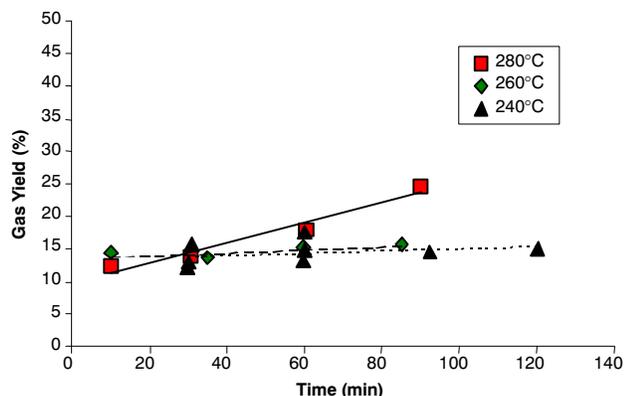


Figure 9. Gas yield from hydrothermal conversion of swine manure at temperatures of 240 °C to 280 °C for 0 to 120 min reaction time.

aqueous product that further decomposed to gases under hydrothermal conditions. In this study, the oil production from hydrothermal conversion of swine manure was not under kinetically controlled reaction conditions. Under the investigated conditions, the hydrothermal conversion of the cellulose component in the swine manure might not directly result in the formation of oil in high yields. The significant amount of oil produced from the swine manure at a low temperature and in a short reaction time was probably related to a decarboxylation reaction involving some components present in the swine manure (e.g., the fat and protein).

The equivalent amount of oil collected at 240°C implies that the thermal efficiency of the hydrothermal processing of swine manure could be further improved by lowering the reaction temperature. To accurately quantify the products from swine manure and evaluate the hydrothermal process, more sophisticated equipment and experiment skills are necessary. With a batch reactor similar to that used in this study, it will be necessary to collect more data at reaction temperatures below 240°C. Alternatively, a similar study could be carried out using a continuous unit to explore chemical reactions at high temperatures, high pressures, and very short reaction times.

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