

HYDROTHERMAL PROCESSING OF SWINE MANURE TO OIL USING A CONTINUOUS REACTOR SYSTEM: EFFECTS OF OPERATING PARAMETERS ON OIL YIELD AND QUALITY

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ABSTRACT. A continuous-mode hydrothermal process (CHTP) reactor was developed to convert swine manure into oil. The effects of operating parameters on oil yield and quality were investigated to determine the optimal condition for the continuous-mode process. Operating temperature, pressure, residence time, and the use of carbon monoxide as a process gas were all found to affect oil yield. Results showed an interaction between the operating temperature and pressure. Oil yield increased with hydraulic residence time, but a diminishing benefit was observed beyond 60 min. A slight decrease in yield was found when carbon monoxide was used. The highest oil yield of 70% (of volatile solids) was in the region where temperature was about 300°C and pressure was 10 MPa. Increasing the temperature from 285°C to 305°C was found to increase the carbon content, heating value, and benzene solubility of the oil. However, increasing the pressure negatively affected both the carbon content and heating value of the oil. The addition of carbon monoxide was found to be beneficial in increasing the carbon content of the oil by 7.4% and improving its solubility to benzene. The hydrogen, nitrogen, and sulfur content of the oil were relatively constant for all test cases, with values of $9.6 \pm 0.4\%$, $3.9 \pm 0.3\%$, and $0.3 \pm 0.1\%$, respectively.

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

Technological developments in the area of thermochemical conversion present new ways to reduce pollution potential while extracting valuable energy and fertilizer from swine manure. 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. Batch-mode (He et al., 2000a) and continuous-mode (Ocfemia et al., 2006) process studies have shown that swine manure can be thermochemically converted into an oil product via hydrothermal processing at high temperature and high pressure for a certain residence time in the presence of liquid water, catalysts, and reducing gas to convert organic material into oil. The oil product could be used on-farm as a fuel for boilers during winter heating or serve as a starting material for petroleum-based products such as lubricants and asphalt.

The mechanisms and kinetics of the thermochemical conversion process are very complex and are not sufficiently known yet. Some researchers (Chornet and Overend, 1985; Vasilakos and Austgen, 1985) have suggested that the sequence of structural and chemical changes in the process

involves 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, and C–O and C–C bond ruptures; and hydrogenation of functional groups.

The conversion of organic wastes to oil via the hydrothermal process has been of interest for several decades, considering its environmental and economic benefits. The Bureau of Mines has experimented with various feedstocks, including urban refuse, agricultural wastes, sewage sludge, and bovine manure (Appell et al., 1980; Appell et al., 1985). The experiments were done by reaction with carbon monoxide at operating temperatures of 250°C to 400°C and pressures of 1,500 to 4,000 psig in the presence of catalysts. Oil yields of 40% to 60% were obtained. Itoh et al. (1994) studied direct thermochemical liquefaction of sewage sludge into heavy oil. At 300°C and 10 MPa, they were able to convert 48% of the organic materials in the sludge into heavy oil. A research team at the National Institute for Resources and Environment, in Onogawa, Japan, also tested a variety of feedstocks, including ethanol fermentation stillage (Minowa et al., 2003), Indonesian biomass residues (Minowa et al., 1998), and simulated garbage (Minowa et al., 1995). Oil yields obtained from the tests ranged from 20% to 60%. More recently, Changing World Technologies, Inc., developed a commercial-scale plant in Missouri that could convert turkey offal into oil using a two-stage thermochemical conversion process (Adams et al., 2004; Roberts et al., 2004).

Currently, hydrothermal processing of swine manure is at its early developmental stage. Most of the work has been

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done in laboratory-scale batch-mode experiments (He, 2000). With the long-term goal of developing a full-scale hydrothermal process unit, a small-scale continuous-mode process reactor unit was developed (Ocfemia, 2005). This unit was successfully operated continuously for 16 h, not including start-up and shut down. To optimize the process, the effects of the different operating conditions need to be evaluated. This re-evaluation is necessary considering the change in the mode of process from batch to continuous. This article presents the effects of operating parameters including temperature, pressure, hydraulic residence time, and use of carbon monoxide on the yield and quality of the oil produced from the continuous-mode process.

MATERIALS AND METHODS

TEST CONDITIONS

Experiments using the continuous hydrothermal process (CHTP) consisted of 21 test conditions, as shown in table 1. The effects of temperature, pressure, hydraulic residence time, and use of CO as process gas were investigated because they are the most important parameters in the thermochemical conversion process (Kucuk and Demirbas, 1997). Although the effects of most of these parameters have already been investigated in the batch-scale process (He et al., 2000b), it was necessary to re-evaluate their effects in the continuous-mode process.

Three temperature settings were investigated: 285 °C, 305 °C, and 325 °C. These temperatures were chosen based on the results obtained from the batch experiments, in which the optimal conditions for oil yield and oil quality were in a narrow temperature range spanning a few degrees above and below 305 °C.

The effect of pressure was not independently investigated in the batch study but was considered as a factor coupled with temperature (He, 2000). In this continuous-mode process study, the effect of pressure was investigated. At the operating temperatures used in this study, pressure may not have a significant effect on the properties of liquid water, but properties such as the solubility of gases in the reactor may have a significant impact on the reaction processes involved in the production of oil. At the operating temperature of 285 °C, three pressure settings were investigated: 9.0, 10.3, and 12.1 MPa. The pressure settings for the operating temperatures of 305 °C and 325 °C were constrained as dictated by the properties of water. In the hydrothermal process, most of the water needs to be kept in the liquid phase. Therefore, the minimum operating pressure should be above the vapor pressure of water at the operating temperature.

Table 1. Experiment test conditions.

Use of CO	Temp. (°C)	Pressure (MPa)	Hydraulic Residence Time ^[a]			
			40 min	60 min	80 min	
No	285	9.0	TC 1	TC 2	TC 3	
	285	10.3	TC 4	TC 5	TC 6	
	285	12.1	TC 7	TC 8	TC 9	
	305	10.3	TC 10	TC 11	TC 12	
	305	12.1	TC 13	TC 14	TC 15	
	325	12.1	TC 16	TC 17	TC 18	
	Yes	305	10.3	TC 19	TC 20	TC 21

^[a] TC = test case.

Three hydraulic residence times were investigated: 40, 60, and 80 min. These residence times were chosen based on a theoretical calculation for producing a significant amount of oil (He, 2000). The slurry flow rate for each of the test cases was computed from the required mean residence time and total mass that can be held inside the reactor. The required slurry input rate (\bar{M}) was computed as follows:

$$\bar{M} = \frac{V/v}{RT} \quad (1)$$

where v is the specific volume of water at the operating temperature, V is the total liquid volume that can be held inside the reactor, and RT is the mean residence time. The flow rate of feedstock ranged from 14.7 to 33.6 g/min.

The effect of the addition of CO gas at a rate of 100 mL/min was investigated to determine how much improvement in oil yield and quality could be gained. The batch experiment results showed that addition of CO is not necessary for the production of oil, but certain improvements in the characteristics of the oil were observed (He, 2000).

EXPERIMENT SETUP AND TEST PROCEDURE

Figure 1 is a schematic of the continuous hydrothermal process (CHTP) reactor system. The system is composed of a high-pressure slurry feeder, a process gas feeder, a continuously stirred tank reactor, a product separation vessel, and process controllers. The development and operation were described in detail by Ocfemia et al. (2006).

In a typical test run, fresh swine manure was collected from the pen floors of the Swine Research Center growing facility in the University of Illinois at Urbana-Champaign. To make the manure pumpable, the fresh manure was slurried using a commercial blender. The slurry was passed through a high-shear mixer (model L4RT, Silverson Machines, Inc., Longmeadow, Mass.) to further reduce the size of large particles. A commercial strainer was then used to remove particles larger than ~1 mm in diameter. Particle size reduction was important to avoid clogging, especially at the suction side of the slurry feeder. The total solids content of the slurry was adjusted down to 20% by adding deionized water. The slurry was placed into a reservoir and pressurized to 0.4 MPa, enough to force the viscous slurry into the suction side of the pump. An initial batch of slurry was also placed inside the reactor before the reactor head was sealed. The reactor, including the separation vessel, was flushed with N₂ to remove as much air in the airspace as possible. After flushing, the system was pressurized to 6.9 MPa (1,000 psi). 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 started for 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 at a temperature of ~50 °C. The oil was easily separated from the aqueous fraction by decanting. Samples of the different product streams were collected, quantified, and analyzed.

PRODUCTS ANALYSES

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

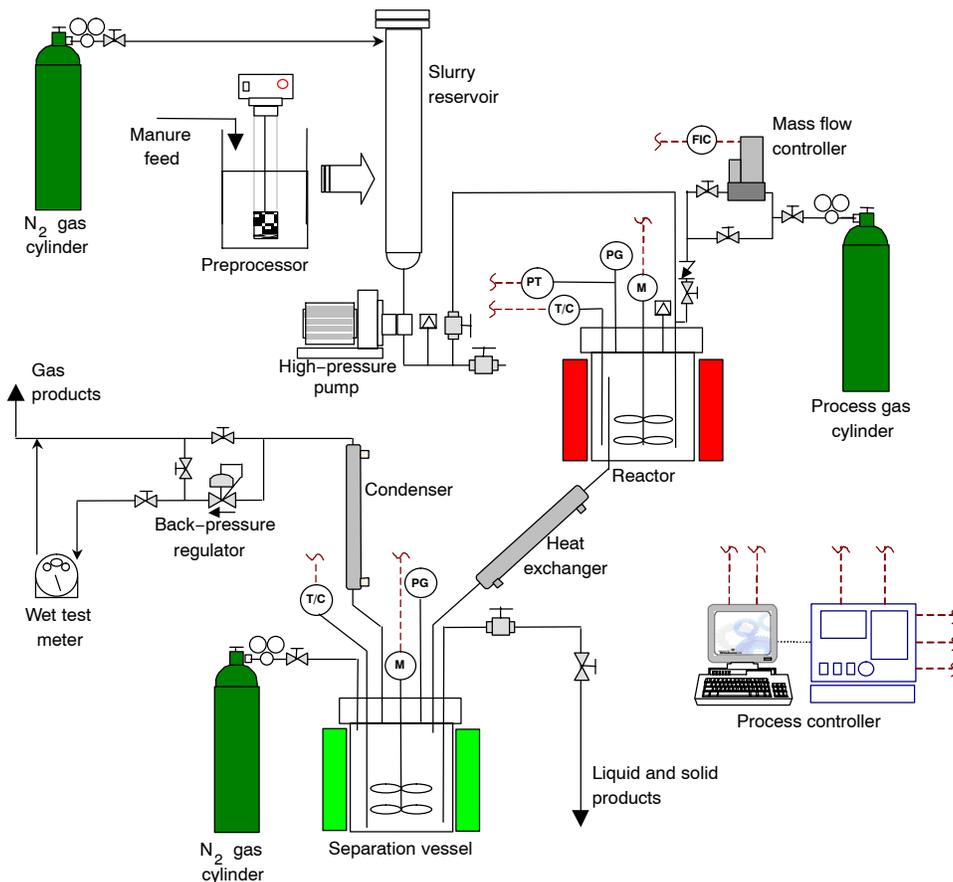


Figure 1. Schematic of the continuous hydrothermal process (CHTP) reactor system.

Oil yield (%) =

$$\left[\frac{\text{total oil product (g/min)}}{\text{total volatile solids input (g/min)}} \right] \times 100\% \quad (2)$$

Elemental analysis of the oil was conducted. 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 the 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 (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.

Carbon and hydrogen mainly dictate the heating value of the oil. The ratio of hydrogen to carbon gives an idea of the level of saturation of the hydrocarbons in the oil. Nitrogen and sulfur are undesirable constituents of oil. Nitrogen forms nitrogen oxides that negatively impact the environment. In addition, the decomposition of nitrogen compounds in catalytic cracking and hydrocracking processes forms am-

monia and cyanides that can cause corrosion. Nitrogen also has deleterious effects on refinery catalysts. Sulfur in the form of sulfides, thiophenes, benzothiophenes, and dibenzothiophenes is detrimental because it can act as a catalytic poison and can contribute to corrosion and atmospheric pollution. Hydrogen sulfide can also evolve from sulfur-containing oil during the refining process. Production of hydrogen sulfide is undesirable because it is corrosive and toxic.

The oil products were 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 using equation 3:

Benzene solubility =

$$\left[1 - \frac{\text{weight of undissolved residue (g)}}{\text{weight of oil sample (g)}} \right] \times 100\% \quad (3)$$

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.

RESULTS AND DISCUSSION

EFFECTS OF OPERATING PARAMETERS ON OIL YIELD

The four operating parameters (hydraulic residence time, temperature, pressure, and the addition of carbon monoxide) were all found to affect oil yield. Interestingly, the yields obtained from all of the tests were higher than what was expected from using a continuously stirred tank reactor, consistent with what was observed in a previous study (Ocfemia et al., 2006).

Effect of Hydraulic Residence Time

Figure 2 shows the effect of hydraulic residence time on oil yield. The yield increased with the increase in hydraulic residence time. The yield curve plateaus at longer residence times for most cases. With an operating temperature of 305 °C and most cases. With an operating temperature of 305 °C and pressure of 10.3 MPa, increasing the residence time from 40 min 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. Similarly, for the case involving 285 °C and 12.1 MPa, an oil yield gain of 6.8% was achieved when residence time was increased from 40 min to 60 min, while only 0.9% was gained when residence time was increased further to 80 min. For the tests involving 305 °C and 12.1 MPa, oil yield increased by 4.1% when residence time increased from 40 to 60 min, and a gain of 0.6% was achieved when residence time was increased by an additional 20 min. At 325 °C and 12.1 MPa, oil yield increased by 1.6% by increasing residence time from 40 to 60 min; only 0.6% increase was obtained when residence time was increased from 60 to 80 min. The trend can be observed for most of the tests, except for those involving 285 °C at 9.0 MPa and 10.3 MPa. For the tests involving 285 °C and 9.0 MPa, the change in yield was 1.2% and 2.6% for increasing residence time from 40 to 60 min and from 60 to 80 min, respectively. At 285 °C and 10.3 MPa, oil yield did not show any noticeable change across the residence times tested.

Apparently, there was not much increase in oil yield after increasing residence time beyond 60 min. Operating a reactor system at a shorter residence time is favorable because the rate of production will be higher and heat loss per unit mass of oil produced could be significantly lower for a fixed reactor volume, making the process more energy efficient.

Effect of Temperature

The effect of temperature on oil yield is shown in table 2. The results have been grouped by residence time. The yields obtained from tests involving 285 °C and 305 °C show no significant difference. However, oil yield obtained from tests involving 325 °C was significantly lower than those from 285 °C and 305 °C. Raising the temperature by 20 °C from 305 °C decreased oil yield by 22.3% wt, 24.9% wt, and 25.3% wt for tests involving 40, 60, and 80 min, respectively. The standard deviation of oil yield for 285 °C and 305 °C ranged from 4.8% to 9.5%.

Effect of Pressure

For test cases in which the expansion and vaporization of water could not attain the desired operating pressure, N₂ gas was injected into the system. Nitrogen gas is chemically inert

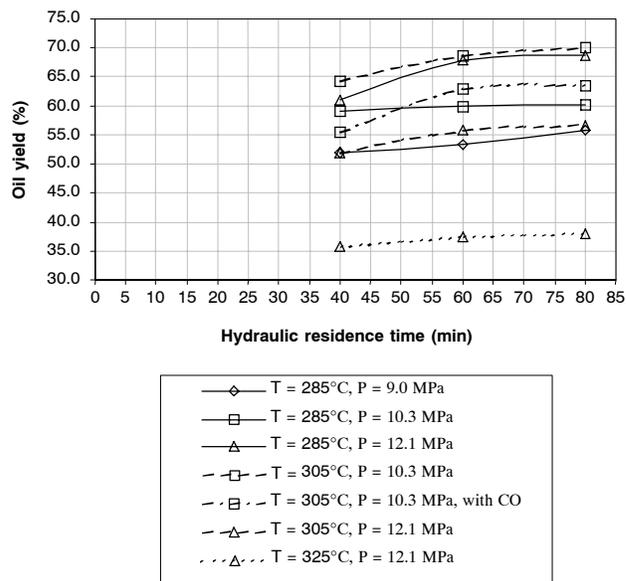


Figure 2. Effect of hydraulic residence time on oil yield.

and believed to be inactive in the process, considering the operating temperatures and pressures involved. If trace amounts of H₂ are produced from the reaction process, then formation of ammonia from N₂ is negligible, as the operating temperature is far below 450 °C (Haber process). Thus, the role of N₂ was only to keep the operating pressure at the desired level. Water is produced from the dehydration of carbohydrates in the manure, but its contribution to the total pressure is expected to be less than that of the carbon dioxide that is produced from the process. Carbon dioxide is believed to originate from the water-gas shift reaction or from the decomposition of organic molecules (Appell et al., 1975). Other gases, including carbon monoxide, gaseous hydrocarbons, and other volatile organic materials, are also formed from the process, but their contribution to pressure was considered negligible.

The results shown in table 3 were obtained from experiments in which the operating pressure was set well over the vapor pressure of water. Because of this, the partial pressure from water was constant throughout the range of operating pressures tested. The difference in pressure was almost entirely due to N₂. Using a residence time of 40 min, oil yield increased by 7.2% when pressure was raised from 9.0 to 10.3 MPa. An additional increase of 1.9% was achieved when pressure was raised from 10.3 to 12.1 MPa. Increases in oil yields were also observed for tests involving 60 and 80 min residence times. When a residence time of

Table 2. Effect of temperature on yield at different residence times.

Residence Time (min)	Temperature (°C)	Pressure Range (MPa)	Oil Yield (% wt, mean \pm s.d.)
40	285	9.0-12.1	57.4 \pm 4.8
	305	10.3-12.1	58.1 \pm 8.8
	325	12.1	35.8
60	285	9.0-12.1	60.3 \pm 7.4
	305	10.3-12.1	62.3 \pm 9.0
	325	12.1	37.4
80	285	9.0-12.1	61.6 \pm 6.6
	305	10.3-12.1	63.3 \pm 9.5
	325	12.1	38.0

Table 3. Effect of pressure on oil yield.

Residence Time (min)	Pressure (MPa)	Oil Yield (% wt)	
		285°C	305°C
40	9.0	52.0	--
	10.3	59.2	64.3
	12.1	61.1	51.8
60	9.0	53.2	--
	10.3	59.9	68.6
	12.1	67.9	55.9
80	9.0	55.8	--
	10.3	60.2	70.0
	12.1	68.8	56.5

80 min was used, oil yield as high as 68.8% was achieved when the operating pressure was 12.1 MPa. It also appeared that better quality oil was produced at high pressures. Visual observation showed that a less viscous oil was produced when using high pressures. However, at an operating temperature of 305 °C, an opposite trend was observed; the oil yield dropped when pressure was increased. At a residence time of 40 min, oil yield dropped by 12.5% when pressure was increased from 10.3 to 12.1 MPa. In the case of 60 and 80 min residence times, oil yield dropped by 12.7% and 13.5%, respectively. Apparently, increasing pressure by a certain degree was only beneficial to oil yield when a low operating temperature was used.

Effect of Carbon Monoxide Addition

The addition of carbon monoxide to the reaction media at 100 mL/min showed a slightly lower oil yield. Figure 3 shows a 6.9% decrease in average oil yield when an operating temperature of 305 °C and an operating pressure of 10.3 MPa were used. It appears that the addition of carbon monoxide is detrimental to oil production, but this decrease in yield is explained by the changes in the quality of the oil product. With the addition of carbon monoxide, more of the elemental oxygen is removed from the oil, causing a mass weight reduction in the oil produced per unit time. Visual observation also indicates that the oil produced when adding carbon monoxide was less viscous at room temperature.

OPTIMAL CONDITION FOR OIL PRODUCTION

From the results presented above, it was found that there was an interaction between temperature and pressure during the process. To show optimal conditions for the process, 3-D surface plots of the oil yield with respect to temperature and pressure are shown in figure 4. The data within the operating temperature and pressure ranges used in the tests were

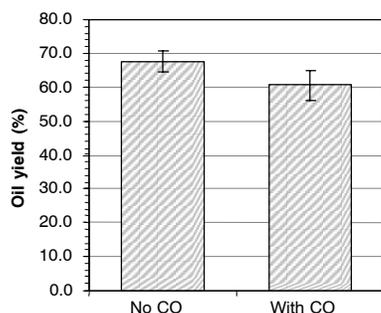


Figure 3. Effect of carbon monoxide addition at 100 mL/min to oil yield.

interpolated and plotted using Mathematica ver. 5.1 (Wolfram Research, Inc., Champaign, Ill.). Oil yield was set to zero when operating conditions would not allow a consistent liquid phase in the reactor. This assumption is valid, considering that mostly char, instead of oil, is produced at these conditions. The lightest surface on the plots represents the optimal range for oil production, while the darkest region represents conditions in which oil production is low. The plots are generally dome-shaped, with the best yields on top. The light region can be seen to spread more with increased residence time. Results indicate that the highest oil yields can be obtained at ~300 °C and ~10.5 MPa, irrespective of residence time.

EFFECTS OF OPERATING PARAMETERS ON OIL QUALITY

Table 4 shows the elemental composition, heating value, and benzene solubility of the oil from the different test cases. Among these oil characteristics, only hydrogen, nitrogen, and sulfur concentrations were found to be at relatively constant levels for all test cases. Hydrogen had an average concentration of 9.6% and a standard deviation of 0.4%. The average concentration of nitrogen was 3.8% with a standard deviation of 0.2%. The high nitrogen content in the oil most likely originated from the organic nitrogen and ammonia in the swine manure feedstock. A study by Inoue et al. (1999) showed that ammonia in the feedstock improves oil production but also tends to increase nitrogen content in the oil product. Sulfur was found to be low, with a value of 0.3% and a standard deviation of 0.1%. Low sulfur content is desirable, as sulfur has negative impacts on processing and utilization of the oil.

Effects of Hydraulic Residence Time

No significant changes or particular trends in elemental composition, heating values, and benzene solubilities were found within the range of residence times used. Except for the test case involving 305 °C and 12.1 MPa, the changes in heating value with respect to residence time were well within the range of error that was expected for this analysis, indicating that increasing the residence time from 40 to 60 min had no influence over the heating value of the product. Extending the residence time was found to have more influence on the quantity rather than the quality of oil produced.

Effects of Temperature

The effect of operating temperature on elemental composition of the oil was primarily on carbon content. On the average, carbon content increased 10.4% when the temperature was raised from 285 °C to 305 °C. By mass balance, carbon content is inversely proportional to the oxygen content of the oil when considering constant hydrogen, nitrogen, sulfur, ash, and water percentages. Given this, the increase in carbon content is the direct result of increased elemental oxygen removal at higher operating temperatures. High temperature promoted reactions such as decarboxylation that effectively eliminated oxygen from the organic compounds in the manure. For the test case involving 325 °C, however, the average carbon content was a low 55.2% because of the unusually high water content of the oil.

As expected, the effect of temperature on oil heating values was in accordance with the oil's elemental composition. Note that the heating value of the oil is primarily

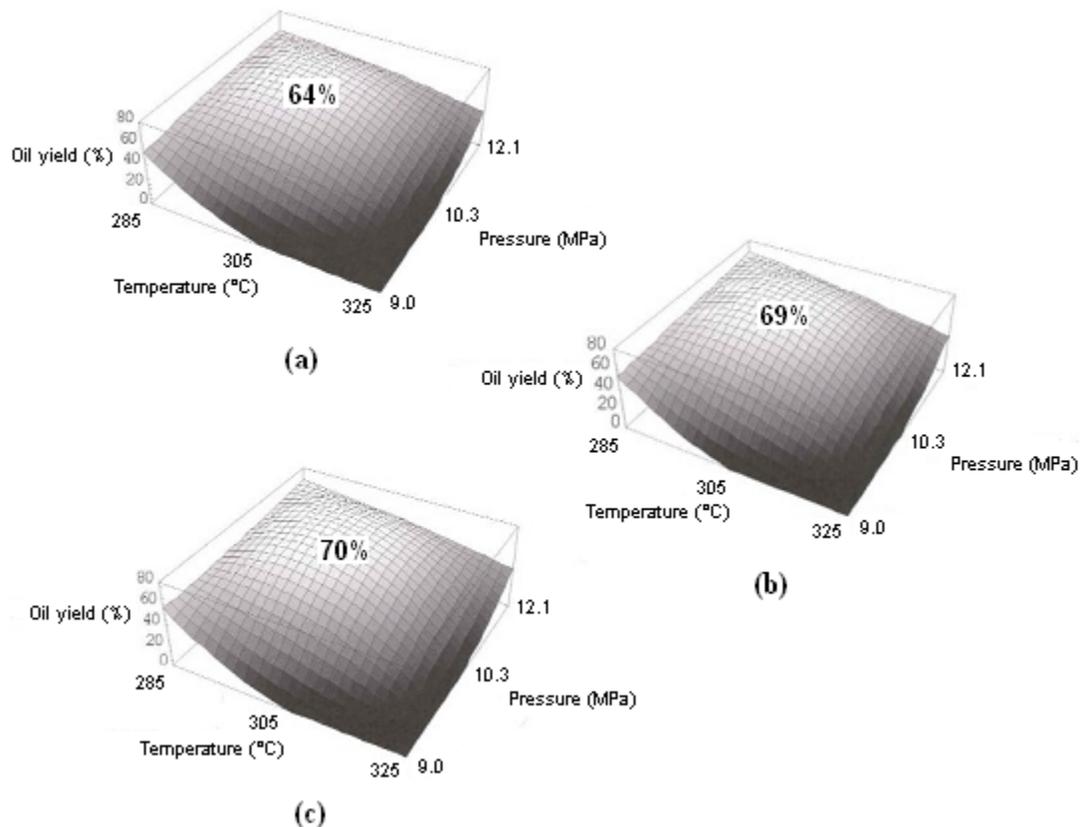


Figure 4. Effect of temperature and pressure on oil yield: (a) RT = 40 min, (b) RT = 60 min, and (c) RT = 80 min.

Table 4. Elemental composition, heating value, and benzene solubility (mean \pm s.d.) as affected by process operating parameters.[a]

Process Gas	Temp. (°C)	Pressure (MPa)	RT (min)	C (% wt)	H (% wt)	N (% wt)	S (% wt)	Heating Value (MJ/kg)	Benzene Solubility (%)
None	285	9.0	40	63.6 \pm 0.2	9.5 \pm 0.1	4.1 \pm 0.0	0.3	29.3	78.2 \pm 1.4
None	285	9.0	60	62.8 \pm 3.2	9.4 \pm 0.1	3.9 \pm 0.2	0.3 \pm 0.1	28.8 \pm 0.7	82.5 \pm 3.5
None	285	9.0	80	65.4 \pm 1.2	9.1 \pm 0.1	3.7 \pm 0.2	0.3	28.3	80.1 \pm 1.9
None	285	10.3	40	57.7 \pm 0.5	9.5 \pm 0.3	3.8 \pm 0.0	0.3	29.0	81.7 \pm 2.9
None	285	10.3	60	60.0 \pm 0.7	9.3 \pm 0.2	3.9 \pm 0.1	0.3 \pm 0.1	27.9 \pm 1.1	83.4 \pm 1.5
None	285	10.3	80	64.4 \pm 0.2	9.6 \pm 0.0	4.4 \pm 0.3	0.3	29.0	84.2 \pm 1.6
None	285	12.1	40	55.1 \pm 0.3	9.5 \pm 0.1	3.9 \pm 0.1	0.3	26.4	82.4 \pm 1.3
None	285	12.1	60	60.6 \pm 1.5	10.1 \pm 0.0	3.9 \pm 0.1	0.2	27.5	82.8 \pm 0.3
None	285	12.1	80	53.1 \pm 0.4	9.1 \pm 1.1	3.5 \pm 0.0	0.5	26.2	84.4 \pm 1.8
None	305	10.3	40	65.9 \pm 3.4	9.4 \pm 0.3	4.0 \pm 0.1	0.3 \pm 0.0	30.3 \pm 2.5	87.5 \pm 2.4
None	305	10.3	60	66.4 \pm 3.5	9.6 \pm 0.1	3.7 \pm 0.4	0.4 \pm 0.1	30.7 \pm 1.6	86.3 \pm 1.0
None	305	10.3	80	69.0 \pm 0.2	9.2 \pm 0.0	4.1 \pm 0.0	0.3 \pm 0.0	31.1 \pm 0.1	87.2 \pm 1.3
None	305	12.1	40	60.8 \pm 0.9	10.0 \pm 0.0	4.0 \pm 0.1	0.3	29.0	86.1 \pm 0.9
None	305	12.1	60	63.2 \pm 0.5	9.6 \pm 0.0	3.9 \pm 0.1	0.3	29.5	86.0 \pm 0.2
None	305	12.1	80	51.0 \pm 3.3	9.3 \pm 0.3	3.5 \pm 0.2	0.3	27.4	88.7 \pm 1.8
None	325	12.1	40	55.2 \pm 0.4	10.0 \pm 0.2	3.5 \pm 0.1	0.6	27.9	88.3 \pm 0.0
None	325	12.1	60	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
None	325	12.1	80	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
CO	305	10.3	40	73.3 \pm 0.4	10.3 \pm 0.2	4.5 \pm 0.1	0.3	25.2	88.4 \pm 0.1
CO	305	10.3	60	69.3 \pm 0.8	10.0 \pm 0.0	4.4 \pm 0.0	0.3	28.6	87.9 \pm 0.7
CO	305	10.3	80	73.6 \pm 0.8	10.2 \pm 0.1	4.5 \pm 0.0	0.4	25.8	89.0 \pm 0.1

[a] n.d. = not determined.

dictated by the carbon and hydrogen percentages. Heating value improved by 7.3% when the temperature was increased from 285 °C to 305 °C. No further improvement was found beyond 305 °C.

The average benzene solubility of the oil product increased from 82.4% to 88.3% when the temperature was increased from 285 °C to 325 °C. This indicates that better quality oil was obtained at higher operating temperatures.

This is in agreement with the results of the batch experiments (He, 2000).

Effects of Pressure

Results showed that increasing pressure had a negative effect on the carbon content of the oil. At an operating temperature of 285 °C, the average carbon content dropped from 64.0% to 60.7% when pressure was increased from 9.0 to 10.1 MPa. At 12.1 MPa, the average carbon content dropped further to 56.3%. Because the carbon content of the oil decreased with pressure, the H:C ratio increased consequently. It was perhaps because of this increased carbon saturation that the oil produced at higher operating pressures was less viscous. Consistent with results for carbon content, operating pressure had a negative effect on the heating value of the oil (on the assumption that residence time had no effect on heating value). At a temperature of 285 °C, no significant change in heating value was found when pressure increased from 9.0 to 10.3 MPa. However, when pressure was increased to 12.1 MPa, heating value decreased by 2,162 kJ/kg. A similar trend was found for the test cases involving 305 °C, in which heating value dropped by 2,415 kJ/kg. For the range of operating pressures used, results showed that pressure had no direct influence on benzene solubility.

Effects of Carbon Monoxide Addition

The test case involving the addition of carbon monoxide showed the highest carbon content in the oil, reaching as high as 73.6%. The increased carbon content was a result of the elemental oxygen removal from the organic compounds that were converted to oil. Carbon monoxide may have participated in the removal of elemental oxygen in two ways. Carbon monoxide produced hydrogen (via the water-gas shift reaction) that reacted with carbonyl and hydroxyl groups to form water, in effect removing elemental oxygen. Carbon monoxide could have also directly reacted with elemental oxygen to form carbon dioxide. It was expected that higher heating value oil would be produced when additional carbon monoxide is added to the reaction media. Bomb calorimetry results, however, showed otherwise. This cannot be explained at this time and needs to be further investigated.

CONCLUSIONS

The operating parameters temperature, pressure, residence time, and the use of CO were all found to affect oil yield. The interaction between operating temperature and pressure was evident. A surface plot was created to show the optimal oil yield as affected by temperature and pressure. The highest yield of 70% (based on volatile solids content of the manure feedstock) was found to be in the region where temperature was about 300 °C and pressure was 10 MPa. Yield was found to increase with hydraulic residence time. However, the benefit of increasing hydraulic residence time beyond 60 min was minimal. The addition of carbon monoxide to the process did not improve the oil yield.

Results indicated that hydraulic residence time did not influence the quality of the oil, at least for the range of residence times used in this study. Apparently, hydraulic residence time has more impact on yield than on the quality of the oil. Operating temperature, on the other hand, showed a significant influence on oil quality. For a particular operating pressure, carbon content, heating value, and

solubility to benzene were all found to increase with temperature. The increase, however, was found to be more evident when temperature was increased from 285 °C to 305 °C. Increasing the operating pressure negatively affected both carbon content and heating value of the oil. The addition of carbon monoxide was found to be beneficial in increasing the carbon content of the oil and improving its solubility to benzene.

The hydrogen, nitrogen, and sulfur content of the oil were relatively constant for all test cases, with values of $9.6 \pm 0.4\%$, $3.9 \pm 0.3\%$, and $0.3 \pm 0.1\%$, respectively. The high nitrogen content is undesirable. Results indicate that the nitrogen content could not be controlled by altering the operating condition and, thus, may need to be reduced by post-processing.

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