PRELIMINARY CHARACTERIZATION OF RAW OIL PRODUCTS FROM THE THERMOCHEMICAL CONVERSION OF SWINE MANURE

B. J. He, Y. Zhang, Y. Yin, T. L. Funk, G. L. Riskowski

ABSTRACT. *In this study, the raw oil products from a thermochemical conversion process of swine manure were characterized based on elemental composition, benzene solubles, heating value, and water content. The analytical results of 78 samples showed that the raw TCC oil products had an average elemental composition of 71.1% carbon, 8.97% hydrogen, 4.12% nitrogen, 0.2% sulfur, and 3.44% ash. The water content of the raw oil varied from 11.3% to 15.8% by weight. The average high heating value of the oil products was 34,760 kJ/kg. These properties of the oil products are similar to those of oil products from the liquefaction of wood sludge and other biomass. The water content of the raw oil was less dependent on the operating parameters of the process. However, the viscosity and benzene solubles of the raw oil were greatly influenced by the TCC operating temperature and types of process gases. Further investigation on chemical composition is necessary before the full utilization of the oil products can be achieved.*

Keywords. Biomass, Renewable energy, Pyrolysis oils, Thermochemical conversion, Direct liquefaction, Swine manure.

I t is very important that biomass–derived oils are characterized in order to utilize them directly as fuel or for further upgrading. The chemical compositions of the biomass–derived oils are complicated and extensive numbers of compounds have been reported (Elliott et al., 1988; Pakdel and Roy, 1988; Piskorz et al., 1988; Maggi and Delmon, 1994; Sipila et al., 1998). The chemical and physical stability of the biomass–derived oils are also important for long–time storage (Adjaye et al., 1992). Rick and Vix (1991) proposed some requisite physical and chemical properties of biomass–derived oils for use as fuel in industrial plants, which included chemical composition, physical and thermal properties, viscosity, and the water content of the biomass–derived oils, and compared them with commercial fuel oils.

The elemental compositions of biomass–derived oils vary widely because of the diverse sources of feedstock. Boyles (1984) stated that a typical pyrolysis oil from biomass is composed of 58% carbon, 7.6% hydrogen, and 33.4 % oxygen. The heating value was 24 MJ/kg. According to the analyses of Piskorz et al. (1988), the composition of the oils obtained by fast pyrolysis of four different wood feedstocks was very similar, and contained about 54% carbon and 6.9% hydrogen. The water content of the pyrolytic liquids ranged from 18% to 20% by weight. Elliott et al. (1988) analyzed and compared the elemental compositions of several liquefaction oils from different high–moisture (90%–95%) biomass feedstocks. Their results showed that the process yields varied from 19.2% to 34.7% and the biomass–derived oils had a similar carbon and hydrogen content of 75% and 9%, respectively. Klass (1998) compared a few properties of liquid oils created by flash pyrolysis and by direct liquefaction of different biomass. His results showed that the carbon, hydrogen, and oxygen contents were about 53%, 6.2% and 40%, respectively, for flash pyrolysis oils, and about 79%, 8% and 14%, respectively, for direct liquefied oils. The oxygen content indicates a large difference in the energy content, or the heating values, of the oils, which were about 22 MJ/kg and 34 MJ/kg for flash pyrolysis and direct liquefied oils, respectively.

Our previously reported research showed that oil products were produced by a thermochemical conversion process of swine manure and the process converted 62% or more of the volatile solids in the feedstock into a raw oil product (He et al., 2000a). The process parameters affecting the process, including the TCC operating temperature, retention time, initial process gas to feedstock volatile solids ratio, feedstock pH, feedstock total solids content, and different types of process gases, were also investigated previously (He et al., 2000b, 2001a, b). The experimental results showed that the operating temperature and retention time were the key parameters. It is critical that a process gas, either a reducing gas or an inert gas but not water vapor, is added to the process in order to yield an oil product. The objective of this study

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was to preliminarily characterize the elemental composition and some physical properties of the TCC oil products.

MATERIALS AND METHODS

A batch TCC reactor made of T316 stainless steel with a capacity of 1.8 liters (0.5 gal) was used in this study. The TCC reactor could be operated at extreme conditions of 375°C (700°F) and 34.5 MPa (5000 psi) (Parr Instruments Co., Moline, Ill.). Parameters studied in the TCC process included the operating temperature, retention time, process gas initial pressure, solids content, and pH. The operating temperature was controlled by a controller that features a three–term Proportional–Integral–Differential control. The operating temperature range in this study was 275 to 350°C. The corresponding operating pressures were in the range of 5.5 to 18 MPa (800 to 2600 psi), which was coupled with the operating temperatures under the equilibrium of water vapor and the water slurry. Retention time varied from 5 to 180 minutes for different conditions. Process gases tested in this study included carbon monoxide, nitrogen, carbon dioxide, hydrogen, and compressed air. The initial pressure of the process gases ranged from 0.34 to 2.76 MPa (50 to 400 psi). The total solids content of the feedstock was adjusted from 10% to 25% by weight. The pH of the feedstock was at 4, 7, and 10. Because of the presence of abundant minerals and carbonates, some of which, although unclear, played catalytic roles in the process, no extra catalysts were added throughout the experiments.

The raw TCC oil products were characterized to determine their elemental composition, viscosity, thermal properties, and heating values. The elemental composition of carbon, hydrogen, and nitrogen in the raw TCC oil products was analyzed using a Carbon–Hydrogen–Nitrogen (CHN) Analyzer (Exeter Analytical, Inc., N. Chelmsford, Mass.). The detection limit of the CHN Analyzer was 0.1%. Sulfur content was measured using a coupled plasma–optical emission spectrometer (Perkin–Elmer, Norwalk, Conn.). Its detection limit for the measurement of sulfur was 1 ppm. The ash content of the TCC oils was measured according to the Standard Methods for the Examination of Water and Wastewater (Clesceri et al., 1989).

The water content in the raw TCC oil products was measured by solvent rectification following the procedure of ASTM Standard D95 (ASTM, 1999a) in a batch distillation assembly. Benzene (ACS Certified grade, Fisher Chemicals) was selected as the solvent. A raw TCC oil sample (60 to 80 g) was dissolved in the benzene solvent (80 to 100 ml) in a flask and distilled until no water was visible in any part of the apparatus except in the receiver. The water content of the oil products was defined as follows:

$$\text{Water content} (\%) = \frac{\text{Water collected in receiver (g)}}{\text{Weight of raw oil sample (g)}} \times 100 \quad (1)$$

The benzene solubles in the TCC oil products is another indicator of the TCC oil quality. It was defined as the percentage of the TCC oil that dissolved in benzene solvent. The modified method was based on the ASTM method for petroleum product measurement (ASTM, 1999b), by replacing the solvent toluene with benzene. The benzene solubles was measured in a 125–ml flask by adding 2 to 2.5g of the raw TCC oil sample to 25 ml benzene. The mixture was then oscillated on a shaker for 1 h at room temperature (22°C). The insoluble residue was then separated from the solubles through vacuum filtration (filter size 2–5 μm, W&R Balston Ltd., England). The insoluble residue was dried at 105°C for 12 to 15 h before it was weighed. The benzene solubles was calculated by the following equation:

$$\text{Benzene solubles} (\%) =$$
$$(1 - \frac{\text{Dried insoluble residue (g)}}{\text{Weight of raw oil sample (g)}}) \times 100 \quad (2)$$

The thermogravimetric analysis (TGA) of the raw TCC oil products was performed using a thermo–gravimetric analyzer (Perkin–Elmer, Norwalk, Conn.). The temperature range of the TGA analysis was 20°C to 800°C, and the rate at which temperature increased was 20°C/min. Nitrogen was used as an inert gas to prevent the sample from oxidizing and as a carrier gas to remove the gaseous products during the analytical process. Viscosity of the raw TCC oil was measured using a Synchro–Lectric viscometer (Brookfield Engineering Laboratories, Stoughton, Mass.) according to the ASTM Standard D5018 (ASTM, 1999c). The viscometer was calibrated with glycerin (Certified ACS grade, Fisher Chemicals) at 26°C. The relative error between the measured data and the data in the literature (Lide, 1999) was within 5%. The samples were measured at 65°C maintained by a water bath and the spindle speed was set at 20 rpm.

The high heating value (HHV) or the heat of combustion of a substance is the amount of heat evolved by the complete combustion of a unit amount of a substance and is usually measured experimentally with a standard calorimetric method. When the elemental composition is known, the heating value of a substance can also be estimated by the heat of formation of the elements contained in it (Kotz and Treichel, 1996). It is convenient to estimate the heating value when the substance is a mixture of organic matters and the exact heating value is not crucial. Due to the unavailability of calorimetric equipment, the HHVs of the TCC oil products, Ht (kJ/kg), were not measured experimentally in this study. Instead, they were calculated using an equation derived by the author based on the complete oxidation of carbon, hydrogen, nitrogen, and sulfur. The negative effect of oxygen content in the TCC oils on the HHV was taken into consideration in the equation, which is completely empirical (He, 2000):

$$Ht \text{ (kJ/kg)} = f \cdot (32{,}792 \cdot C + 142{,}900 \cdot H)$$
$$+ 9{,}275 \cdot S - 2{,}371 N \quad (3)$$

and

$$f = 1 - \frac{7}{8} \cdot \frac{2 \times moles\ of\ element\ oxygen}{(4 \times moles\ of\ element\ carbon) + moles\ of\ hydrogen}$$
$$(f \leq 1) \quad (4)$$

where C, H, S, and N are the mass fractions of carbon, hydrogen, sulfur, and nitrogen in a raw TCC oil product, respectively, and f is a correction factor defined by equation 4. The heating values calculated by equations 3 and 4 were validated using 20 compounds of known heating values that contain carbon, hydrogen, oxygen, and nitrogen. Results showed that the standard deviation of errors of the predicted heating values was 3.12% and the average of the errors was

+2.41%. Comparing to the Dulong's equation, which was used by other researchers for estimating heating values of coal and biomass–derived oils (Selving and Gibson, 1945; Sawayama et al., 1996), equation 3 gave a smaller standard deviation than the Dulong's equation on heating values of the same 20 compounds. The low heating value (LHV) is based on the definition by Rick and Vix (1991) at the reference temperature of 25°C:

$$LHV = HHV - 217.9H - 24.42 \cdot W \text{ (kJ/kg)} \qquad (5)$$

where H is the hydrogen percentage by weight, and W is the water percentage by weight.

RESULTS AND DISCUSSIONS

ELEMENTAL COMPOSITION AND HEATING VALUES

The typical oil yield in wood and moist–biomass liquefaction found by previous researchers was 25% to 35% (Figueroa et al., 1982; Elliott et al., 1988). The oil yield of the TCC process was 60%–65% on the volatile solids input with the highest yield of 80% (He et al., 2000a). The raw TCC oil was readily separated by gravity from the post–processed water that contained some water–soluble components from the feedstock and from the depolymerization of swine manure. Organic solvent extraction, which was usually used for the recovery of liquefaction oils from some biomass conversion processes (Boocock et al., 1980; Elliott et al., 1988), was not necessary for the TCC process.

Seventy–eight oil samples produced by the TCC process using CO as the process gas and under different operating conditions were analyzed to determine the elemental composition of carbon, hydrogen, nitrogen, and sulfur. The average carbon content in the raw TCC oil samples was 71.1%, hydrogen 9.0%, nitrogen 4.1%, and sulfur 0.2%. Ash residues were determined to be 3.4%. By difference, the oxygen content plus all the other traceable compounds in the TCC oils was calculated to be about 12% with a standard deviation of 5%. Experimental results showed that the water content in the raw TCC oils was affected less by the operating parameters, varying from 11.3% to 15.8%.

Comparison of the above results to those of typical pyrolysis and liquefied oils is summarized in table 1.

The elemental composition of TCC oils was very similar to that of liquefied oil obtained from kelp (Elliott et al., 1988). This means that both processes underwent a similar chemical mechanism except that the liquefied oil from kelp was obtained under much harsher operating conditions and the oil yield was much lower (about 20%) than that in the TCC process (62%–65%). The TCC oils contained higher carbon and hydrogen content and lower nitrogen content than pyrolysis oils (Rick and Vix, 1991). The water and ash content of TCC oils were similar to those of pyrolysis oils. However, the sulfur content of TCC oils was much higher due to the high sulfur content in the swine manure, which was 0.38%. Further treatment is needed in order to utilize the TCC oil directly as fuel. This factor should also be considered in selecting upgrading processes because both nitrogen and sulfur in oils are major air pollution concerns. The average calculated HHV of 78 TCC oil samples was 34,760 kJ/kg with a standard deviation of 2,317 kJ/kg. The corresponding LHV was 32,500 kJ/kg. This value is about 86% of that of

Table 1. Characteristics of the TCC oils and other biomass–derived oils.

Properties	TCC process		Pyrolysis oil[c]	Liquefied oil[d]
	Feedstock[a]	TCC oil[b]		
Composition, % wt.				
Carbon	45.67 ±1.12	71.1 ±4.5	50 – 67	76.7
Hydrogen	6.45 ±0.21	9.0 ±0.5	7 – 8	8.9
Nitrogen	3.45 ±0.38	4.1 ±0.4	8 – 10	3.5
Sulfur	0.38 ±0.06	0.2 ±0.03	<0.01	n/a[e]
Oxygen	31.33[f]	12.2 ±4.8[g]	15 – 25	9.9
Ash	12.72 ±1.27	3.4 ±3.1	0.4 – 10	n/a
Water, %	—	13.5 ±2.2[h]	10 – 14	n/a
Heating value (LHV), MJ/kg	—	32.5 ±2.3[I]	21.1 – 24.7	n/a

[a] Dry matter basis.
[b] Averaged from 78 different oil samples with CO as the process gas.
[c] Summarized from different pyrolysis and liquefaction processes (Rick and Vix, 1991).
[d] Extracted from kelp liquefaction product obtained at 350°C and 27.3 to 35.5 MPa, CO initial pressure was 5 MPa (Elliott et al., 1988).
[e] n/a = not available.
[f] By difference, O = 100 – C – H – N – S – ash.
[g] Based on 4 measurements. Each measurement was conducted on the mixed sample of several oil products from different runs.
[h] Calculated using equation 3.

heavy fuel oil (40,200 kJ/kg) and about 30% higher than that of some pyrolysis oils (Rick and Vix, 1991).

The results of process gas effects on the elemental composition of the TCC oil products are summarized in table 2. Based on the variance analysis of multiple–populations for the mean at 95% confidence level, the elemental compositions of carbon, hydrogen, nitrogen and sulfur between different process gases were not significantly different. The carbon content stayed at an average level of 72%. Although the difference between the carbon content of the oils with CO_2 and H_2 as process gases was 6.6%, it was insignificant because of the large variations of the measurements. When CO was added as the process gas, the hydrogen content in the oil was 9.6%, which was higher than when other process gases were used (about 8.8%). This 0.8% (by weight) difference is very important to the energy content of the TCC oil products. Nitrogen was high in all measurements, ranging from 4.1% to 4.6%. It was slightly lower when CO was added, and stayed at about the same level of 4.4% when other process gases were added. The sulfur content also stayed at about the same level (0.2%) among the oils with different process gases. When hydrogen was used as the process gas, the sulfur content appeared lower. Due to the large standard deviation of 0.08%, however, this value did not significantly differ from the others based on variance analysis at 95% confidence level for the mean.

Unlike other elements, the oxygen content of the oil products varied significantly based on the statistical analysis. It happened that when CO_2 was used as the process gas, the oxygen content was 15.2%, the highest among the five process gases. A possible explanation is that the oxygen elimination from biomass was hindered by the high CO_2 partial pressure present and no reaction mechanisms could be expected between the highly oxidative CO_2 and the oxygen–containing groups in the biomass. On the other hand, the oxygen content was lowered when the reductive CO and H_2 were added (7.7% and 6.7%, respectively). A high oxygen

Table 2. Effect of alternative process gases on elemental content of the TCC oil products. The operating conditions were: 305ºC, RT = 120 min, TS = 20%, p_{ini} = 0.69 MPa, feedstock pH = 6.1. The corresponding TCC operating pressure was 10.5 MPa. The error terms are standard deviations. The oxygen content of the oil products with CO_2 as the process gas (treatment A) was significantly different from the rest (treatment B) at 95% confidence level for the means.

	Process gas				
	CO	N_2	CO_2	H_2	Air
Yields, % wt	57.1 ±8.3	64.9 ±6.4	60.8 ±8.0	77.7 ±0.7	70.2 ±5.0
Element content, %					
Carbon	69.69 ±3.61	75.50 ±2.55	67.20 ±0.57	73.84 ±0.11	71.36 ±2.11
Hydrogen	9.58 ±0.34	8.97 ±0.38	8.90 ±0.71	8.88 ±0.42	8.81 ±0.33
Nitrogen	4.06 ±0.13	4.58 ±0.05	4.24 ±0.22	4.50 ±0.53	4.44 ±0.01
Sulfur	0.23 ±0.05	0.22 ±0.01	0.21 ±0.02	0.12 ±0.08	0.20 ±0.01
Oxygen	7.67 ±1.31[B]	9.41 ±0.11[B]	15.22 ±0.55[A]	6.70 ±0.77[B]	10.28 ±2.61[B]

content leads to a lower heating value of an oil product. Therefore, the addition of a reducing gas is desirable for obtaining an oil product with a high heating value.

BENZENE SOLUBLES

The solubility of TCC oils in an organic solvent is another indication of oil quality. Based on the "like dissolves like" principle, a higher solubility of the TCC oils in benzene implies that it contains more oil–like compounds. The benzene solubles are affected by many factors. The most important one is the TCC operating temperature. Figure 1 depicts the effect of the operating temperatures on the benzene solubles of the TCC oils when CO was used as the process gas. It was found that the benzene solubles increased with the operating temperatures in the range of 285°C to 310°C and slightly decreased in the range of 310°C to 350°C. The benzene solubles was 80% at 285°C and increased to 93% at 335°C. When the temperature increased to 350°C, the benzene solubles decreased to 89.1%. It was also found that solid char formed at 350°C. Some char was contained in the oil products and did not dissolve in the benzene; therefore, the benzene solubles were lowered. The formation of solid char was caused by the high temperature and long retention time (120 min in this case), i.e., once the oil product formed, it underwent an over–oxidation process where it was thermally "chopped" into smaller molecules and eventually became char.

The benzene solubles was also affected by the addition of different process gases. Figure 2 shows the effect of alternative process gases on benzene solubles. Each column represents the average of four different measurements and the error bars are standard deviations. The highest benzene solubles of the oil products occurred when CO was added as the process gas. The benzene solubles were 88.6% with a standard deviation of 1.6%. The benzene solubles with all the other process gases were at approximately the same level of 73%. The statistical analysis of variance for multiple population means showed that the benzene solubles with CO as the process gas was significantly different from the other gases tested at 95% confidence level (fig. 2).

VISCOSITY

Viscosity is one of the most important criteria for the differentiation of oil grades. A lower viscosity indicates a higher light–oil content in oil samples. Figure 3 presents the viscosity of raw TCC oils measured at 65°C as a function of the TCC operating temperature. The results indicated that the viscosity of the raw TCC oil samples dramatically decreased
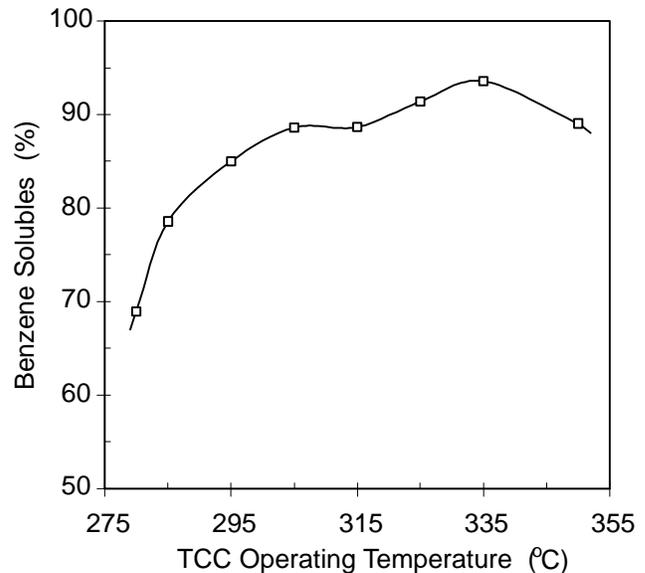

Figure 1. Effect of TCC operating temperatures on the benzene solubles of TCC oil product. The oil samples were obtained with CO as the process gas and under the operating conditions of $p_{ini, CO}$ = 0.69 MPa, TS = 20%, RT = 120 min, and feedstock pH = 6.1. The corresponding TCC operating pressures were 7 to 18 MPa.

from 15.5 Pa·s to 0.843 Pa·s as the TCC operating temperature increased from 285°C to 315°C. When the TCC operating temperature further increased to 350°C, the viscosity decreased gradually to 0.51 Pa·s. It was assumed that the decomposition rate of the organic polymers in the feedstock increased as the operating temperature increased in the range of 285°C to 315°C. When the TCC operating temperature was above 315°C, the viscosity did not change substantially. This was possibly because most decomposition of organic polymers had occurred below 315°C during the 120 min retention time. The viscosity of crude petroleum oil at the same measurement temperature (65°C) was 0.02 Pa·s (Beckman, 1981). This comparison shows that raw TCC oils had a much higher viscosity than that of typical crude petroleum oil.

The stability of the TCC oil products under an ambient environment is one of the most important considerations for its upgrading and utilization. The more the oil properties change, the less stable the oil is. In this study, the viscosity change of the TCC oils was measured as the oil samples were stored in non–airtight containers. Figure 4 shows the change of the TCC oil viscosity versus storage time at ambient
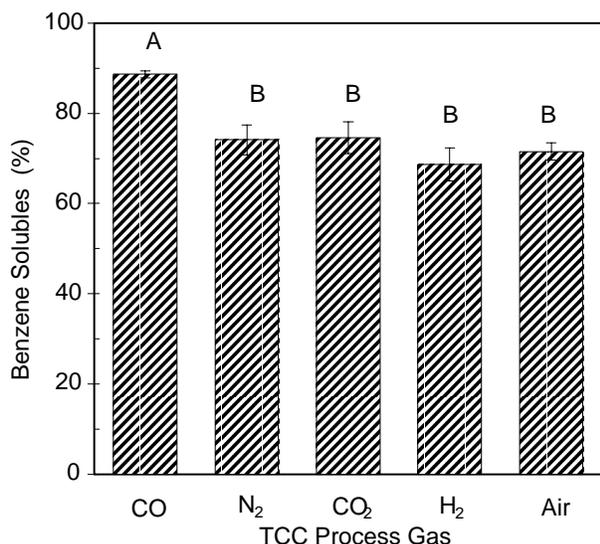
Figure 2. Effect of alternative process gases on benzene solubles. The TCC operating conditions were: T = 305°C, process gas initial pressure p_{ini} = 0.69 MPa, RT = 120 min, TS = 20%, feedstock pH = 6.1. The corresponding TCC operating pressure P = 10.5 MPa. The error bars are standard deviations. The difference between treatments A and B was statistically significant at 95% confidence level.
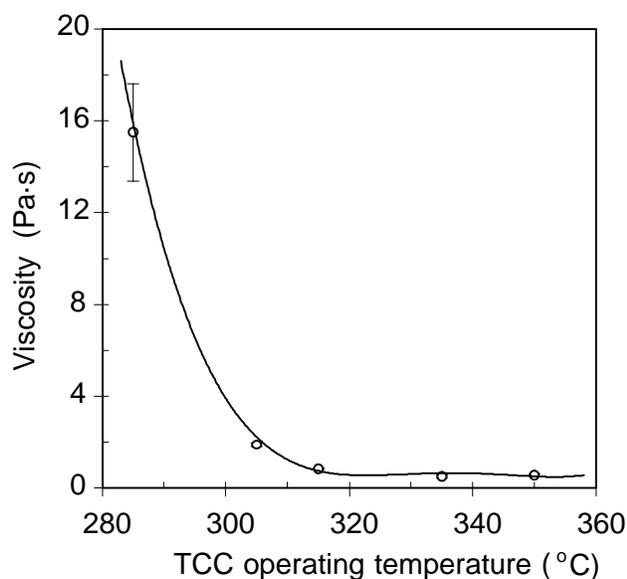

Figure 3. Effect of TCC operating temperatures on the raw TCC oil viscosity. The oil samples were obtained with CO as the process gas and under the operating conditions of $p_{ini, CO}$ = 0.69 MPa, TS = 20%, RT= 120 min, and feedstock pH = 6.1. The corresponding TCC operating pressures were 7 to 18 MPa. The viscosity measurements were conducted at 65°C. The error bars are standard deviations.

temperature (about 22°C). The TCC oil samples were obtained under operating conditions of 315°C with 0.69 MPa CO as the process gas and measured at 45°C. Each data point was an average of six measurements. The viscosity of raw TCC oils increased from 9 Pa·s to about 13 Pa·s in the first 15 d of storage and did not substantially change over the rest of the 60 d storage time (fig. 4), which agreed with the observations by Adjaye et al. (1992). This oil–aging phenomenon can be explained by the oxidization reactions that occurred when the reactive components of the TCC oil,
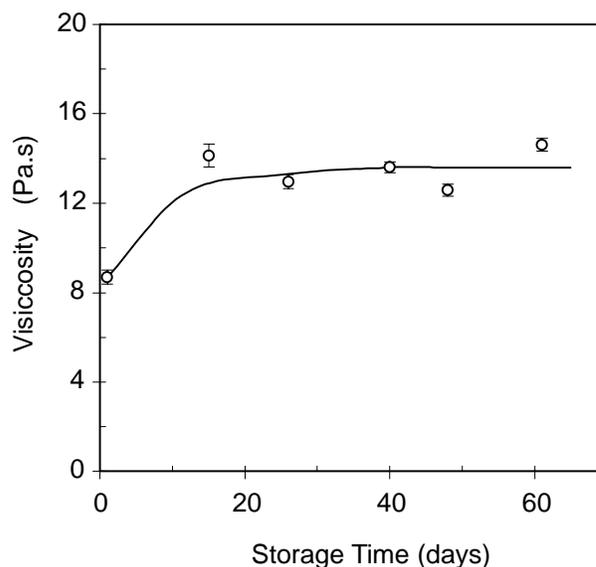

Figure 4. Viscosity change of raw TCC oil products versus storage time when stored in non–airtight containers at ambient temperature. The oil samples were obtained with CO as the process gas and under the operating conditions of $p_{ini, CO}$ = 0.69 MPa, T = 315°C, RT = 120 min, TS = 20%, and feedstock pH = 6.1. The viscosity measurements were conducted at 45°C. The error bars are standard deviations.

such as the unsaturated bond–containing compounds, were exposed to air. This change in viscosity should be considered during the TCC oil upgrading and utilization.

The oil viscosities with different process gases differed considerably. Figure 5 shows the effect of alternative process gases on TCC oil sample viscosity. Each column represents the average of three to five different measurements and the error bars are standard deviations. Based on the statistical analysis of variance for multiple population means, the differences between the viscosities with the five process gases were significant at 95% confidence level. Under the given operating conditions, the lowest viscosity occurred when CO was applied as the process gas. The TCC oil with CO_2 had the next lowest viscosity of 14.4 Pa·s. The oil viscosity with hydrogen as the process gas was the highest (50 Pa·s). The dramatic difference in viscosity between the oil samples with CO as the process gas and H_2 as the process gas was unexpected. A possible explanation is that the structures of the oil products obtained with H_2 as the process gas did not change extensively from polymers to smaller oil–like molecules due to the inactivity of hydrogen at 305°C and lack of proper catalysts. However, this explanation is hardly applicable to the situations with CO_2, nitrogen, or compressed air as process gases, in which the viscosities were lower than that with hydrogen as the process gas.

THERMOGRAVIMETRIC ANALYSIS

Thermogravimetric analysis (TGA) is one of the most commonly used analytical techniques for measuring the thermal characteristics of carbonaceous materials. It can determine the decomposition weight loss, combustion analysis, and temperature stability of oil samples. The cumulative weight loss includes the volatile components that evaporate at temperatures below 300°C and the components that are thermally cracked during the process. The residues after measurement at certain temperatures are considered "non–
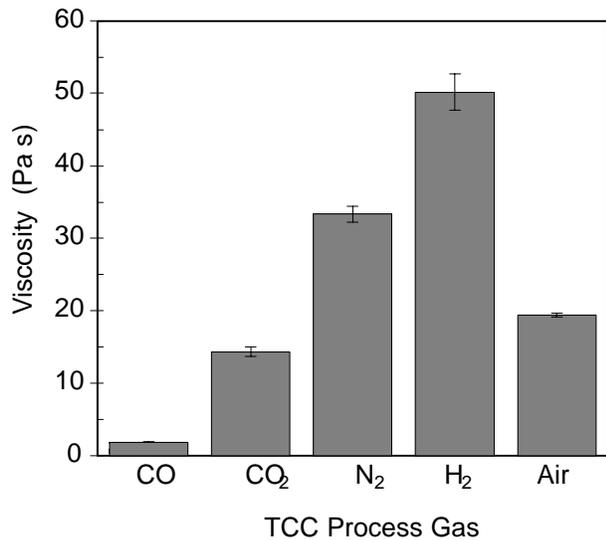
Figure 5. Viscosity of oil products with different process gases. The viscosities were measured at 65°C. The TCC operating conditions were: 305°C, p_{ini} = 0.69 MPa, RT = 120 min, TS = 20%, and feedstock pH = 6.1. The corresponding TCC operating pressure was 10.2 MPa. The error bars are standard deviations. Based on the statistical analysis of variance for multiple population means, the differences between the five process gases were all statistically significant at 95% confidence level.

volatile" components. In the case of biomass analysis, the non–volatile residues are mainly char and minerals. Therefore, TGA can characterize the quality of a TCC oil product based on its weight loss and the rate of weight loss. In this study, the TGA analysis was conducted on selected TCC oil samples and the cumulative weight loss and the rate of weight loss were measured as a function of temperature. Two examples of the weight loss and weight loss rate are presented in figure 6. Sample #1 was obtained at a TCC operating temperature of 325°C and sample #2 at 285°C. Both had a retention time of 120 minutes and CO was used as the process gas.

The overall cumulative weight loss of the oil products increased as the TGA operating temperature increased. At different temperatures, the weight loss rates were different, shown by the number of surge peaks. In both samples, a peak occurred between 100 and 200°C. The rates of weight loss were about 4%/min. This peak was caused by the lightest components of the oil products. Water content in the oil sample possibly contributed to this weight loss surge. The weight loss under the peak was about 3% wt for sample #1 and 5% for sample #2. The second peak of the weight loss rate occurred at about 300°C. The weight loss rate of sample #1 was as high as 25%/min, and the cumulative weight loss was about 50% under this surge weight loss peak (fig. 6a). The weight loss rate in the same temperature range was nearly 22% for sample #2. The cumulative weight loss was about 50% under this surge weight loss peak (fig. 6b). The similarity of the two samples up to 350°C indicates that the two samples contained about the same amount of volatile components at 100~200°C. When the TGA operating temperature increased to 600°C, the weight loss of samples #1 and #2 reached 79% and 83% of their initial sample weights, respectively. In other words, the volatile components contained in the two samples were still at a similar level at temperatures up to 600°C, although the weight loss rates

differed slightly. Subsequently the weight loss rate of sample #2 dropped and the cumulative weight loss leveled off. When the temperature increased to 800°C, the total cumulative weight loss of sample #2 increased to 85.2%, or about 15% residues. Sample #1, on the other hand, continued to lose its components and the cumulative weight loss of sample #1 reached about 99.7%, indicating that the high boiling–point components continued to be cracked into volatile compounds under such high temperatures. The residues were less than 0.3% as the temperature increased to 800°C. Based on the TGA results, it is evident that the oil sample #1, which was obtained at higher TCC operating temperature, had more oil–like compounds and less char than the oil sample #2. The results showed that thermogravimetric properties of the TCC oil samples were different from those of biomass such as rice husks (Mansaray and Ghaly, 1998), which had more than 30% of the residues left. On the other hand, it indicated that the light fraction of the raw oil was low and refining without further upgrading may not yield a good quality oil product.
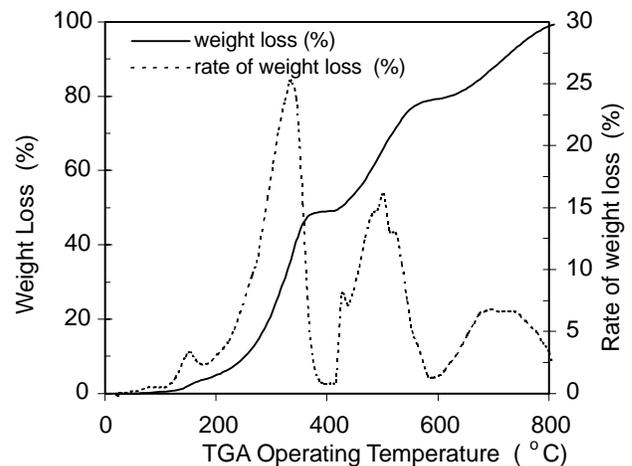
(a) Sample #1
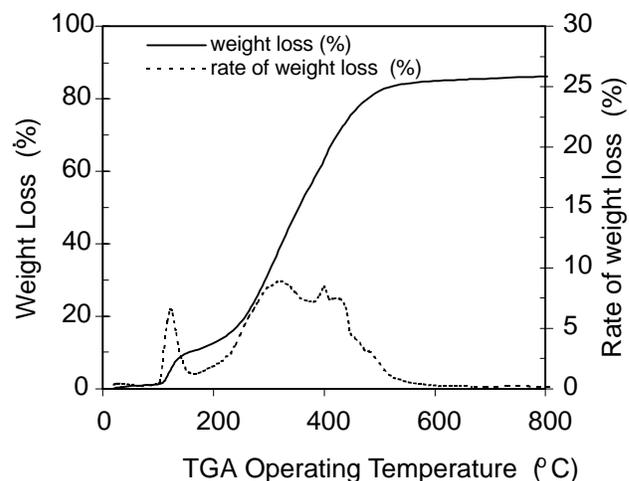
(b) Sample #2

Figure 6. Examples of the thermogravimetric analysis (TGA) results on raw TCC oil products: weight loss and weight loss rate versus temperature. TGA operating conditions were: 20°C to 800°C, temperature increasing rate = 20°C/min, headspace gas was nitrogen. Sample #1 was obtained from TCC process at 325°C and sample #2 at 285°C. Both had a retention time of 120 minutes and CO was the process gas.

CONCLUSION

The results of this study showed that the raw TCC oil products from the thermochemical conversion of swine manure had an elemental composition similar to other biomass–derived liquefaction oils. The benzene solubles of the TCC oils were as high as 95% and the calculated heating value averaged 34,740 kJ/kg. The viscosity of raw TCC oils was high compared to crude petroleum oil and changed verses storage time when exposed to the atmosphere. The light fraction of the raw oil was relatively low. Direct rectification of the TCC oils would not achieve a high light oil yield. Since the TCC process of swine manure originated as an alternative process for waste treatment, the utilization of the TCC oils as fuel to offset energy consumption is promising. However, the high nitrogen and sulfur content in swine manure led to high nitrogen and sulfur content in the raw oil products. Utilization of the TCC oils as fuel will require further treatment in order to reduce the emissions of NO_x to the atmosphere. It is also necessary to upgrade the raw TCC oil to enhance its utilization value. A continuous–flow TCC process is desirable for producing more composition–consistent TCC oils from a scaled–up process. Further analyses, e.g. qualitative and quantitative chemical composition, are needed in order to fully explore the possible utilization of the TCC oils. Utilization of such biomass–derived oils for the production of adhesives for use in the manufacture of engineered wood products and phenol–formaldehyde–type resins is possible (Stoikos, 1991). Different specialty chemicals from the TCC oils are also possible after further processing and separation.

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