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Properties of Fractionated Poultry Litter

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Abstract. *Due to environmental issues with the use of poultry litter for land application, alternative means for its value added utilization need to be identified. One possible solution is the fractionating of poultry litter into a nutrient rich fine fraction that can be used as fertilizer and a coarser fraction that has the potential of being used as bioenergy feedstock. In this study, physical properties relevant to storage, handling and processing of poultry litter that were separated into three fractions (with average diameters of 0.396, 0.708 and 1.181 mm) were determined. The densities (bulk, particle and tap) of the fractions increased with fraction size. The fine fraction was the most compressible and was the dominant contributor to the compressibility of unfractionated poultry litter. Coarse fraction was the least compressible. The flow index values of the coarse, middle and fine fractions were 16.1, 13.2 and 11.5 respectively and were significantly higher than the flow index of unfractionated poultry litter (3.6). The heating value, the carbon content and the rate of thermal decomposition of the fractions increased with increase in particle size of the fractions. Maximum thermal decomposition rates of 0.107 min^{-1}, 0.126 min^{-1}, 0.154 min^{-1} were obtained for the fines, middle and coarse fractions respectively.*

Keywords. Bound water, specific heat, melting point, enthalpy, pyrolysis

Introduction

Poultry litter is a combination of accumulated chicken manure, feathers and bedding materials. The bedding materials are typically wood shavings, sawdust, wheat Triticum aestivum L.) straw, peanut (Arachis hypogaea L.) hulls or rice (Oryza sativa L.) hulls [1]. The type of bedding material used is highly dependent on the available agro-processing residue in the poultry production area. For example, wood shavings and peanut hull are respectively used in Northern part and Southern part of Alabama. Rice hull is traditionally used in Arkansas.

Close to 11 million tons of poultry litter is produced in United States annually [2]. Due to its excellent N:P:K (nitrogen:phosphorous:potassium) ratio [3], and due to high cost that will be incurred in transporting low density poultry litter, this waste material has been traditionally used to fertilize lands that are close (< 10 miles) to poultry producing regions in the country. Since poultry production typically occur in small concentrated areas, the prolonged application of poultry litter on the neighboring agricultural lands has resulted in a buildup of N and P in the soil on these lands [4]. Ground water and surface water problems have also been created as excess nutrients run off the land or leach into ground water supplies [5,6].

Due to the environmental problems associated with the prolonged use of poultry litter, various studies have been carried out on the value-added utilization of poultry litter. An example is the fractionating of poultry litter into a nutrient rich fine fraction that can be used as fertilizer and a coarse fraction that has the potential of being a better feedstock for energy production when compared to the whole litter [7]. Coloma [8] found that the bulk density of poultry litter retained on #5, #10, #18 and #20 screens (equivalent screen openings of 4 mm, 2 mm, 1 mm and 0.85 mm) were significantly lower than the bulk density of the untreated poultry litter. No other physical properties were measured by these authors. The value-added use of fractionated poultry litter will require that appropriate equipment and facilities be designed and selected to store, handle, and transport the fractions [9,10], hence the need to quantify their physical and flow properties. Physical and flow properties that are relevant to the handling, storage and processing of biological materials include bulk density, particle density, porosity and compressibility and flow index [10,11,12]. A detailed description of the importance of these properties can be found in Fasina [10].

Pyrolysis is one of the promising thermal approaches that can be used to convert biomass to energy [13]. Thermogravimetric (TG) analysis is the preferred technique for obtaining thermal events and quantifying thermal decomposition kinetics during pyrolysis. This is because of the relative ease and straightforward manner for obtaining mass loss data that is needed for determination of pyrolysis kinetics [14,15]. Knowledge of the pyrolysis kinetics during the thermal decomposition of biomass materials is needed for the design, operation and control of thermochemical conversion units such as gasifiers and pyrolysis reactors [16].

Therefore, the objectives of this study were to: (a) quantify the physical (bulk density, particle density, tap density, compressibility), and flow properties of fractionated poultry litter, and (b) determine the influence of fractionating on the pyrolysis characteristics of poultry litter.

Materials and Methods

Poultry litter sample (with wood shavings bedding) used in this study was obtained from a local poultry farmer in Lee County, Alabama. A vibrating screen separator (Vibro-Separator, Model

LS-450-A-N10, CE International Group Corp., Miami FL) was used to separate the sample into three fractions: (a) coarse fraction - particles retained on a standard 25 mesh screen (0.710mm), (b) fine fraction - particles that passed through a standard 50 mesh screen (0.300 mm) and (c) middle fraction - particles that passed through a 25 mesh screen but retained on a 50 mesh screen. The choice of sieve size was based on preliminary study on the particle size distribution of raw poultry litter (see results and discussion section).

After fractionating, physical (bulk density, particle density, porosity, compressibility, tap density), and flow (cohesion and angle of internal friction) properties of the fractions were carried out according to the procedure detailed in Fasina [9]. In addition, the particle size distributions of the raw and fractionated samples were carried according to the ASABE Standard S319.3 [17].

Pyrolysis of poultry litter (raw and fractionated samples) was carried out in a Pyris 1 TGA - thermogravimetric analyzer (Perkin-Elmer, Shelton, CT). Before use, the samples were ground in a Wiley mill to pass a 40 mesh screen. A sample mass of 5 mg was used for TGA experiments. The sample was heated from $25^{o}C$ to $800^{o}C$ at a heating rate of $20^{o}C/min$. Nitrogen was used as carrier gas at a flow rate of 20 ml/min.

Carbon, nitrogen, ash and heating values of the fractionated and raw samples were also determined. A Leco TruSpec analyzer (Leco Corp., St. Joseph, MI) was used to determine carbon and nitrogen contents. Heating value was obtained with an IKA C200 calorimeter (IKA Works, Wilmington, NC). Ash determination was carried out according ASTM Standard D5142 [18].

Statistical Data Analysis

Collection of all data in this study was carried out in triplicate. Testing of process variable for statistical significance was carried out by means of analysis of variance in SAS Statistical Software [19] using 95% confidence interval.

Results and Discussion

Particle size distribution

Data from screen analysis showed that the particle size distribution of raw poultry litter has two peaks (Figure 1). This indicates that poultry litter can be separated into three different fractions based on these peaks. Figure 2 shows the resulting particle size distribution graphs for the three fractions obtained after the fractionating process. As expected, the distribution of each fraction was unipeak. There was also skewness (to the left) of each distribution curve. This is a feature expected of naturally occurring particle populations (i.e. log-normal distribution) [20]. Similar skewness was reported for alfalfa, wheat straw, barley straw and corn stove grinds [21,22]. The analysis procedure outlined in ASABE Standard S319.3 [17] was then used to obtain the geometric mean particle size and geometric standard deviations of the samples (Table 1).

Bulk, particle and tap density

In general, fractionating significantly affected (P< 0.05) the bulk, particle and tap densities of poultry litter, with the densities reducing with increase in size of the fractions (Table 1). This is an indication that a high percentage of the minerals in the raw poultry litter ended up in the fine fraction (hence higher density – see results of compositional analysis), while the coarse fraction had higher content of biological portion (e.g. hardwood chips). It should be noted that the measured densities of the fractions (> 500 kg/m^3) were considerably higher than the values that have been typically reported for agricultural materials (< 200 kg/m^3) [23-26]. This is because of the relatively high amount of minerals (ash) present in poultry litter [9].

The porosity of poultry litter significantly increased (P<0.05) from 0.666 to 0.729 as the size of the fractions increased due to the fact that bulk larger sized particles generally have more pore volume than the smaller particles [21]. The average porosity of spherical particles is 0.4 while irregular shaped particles have higher porosity values [27]. Therefore, the porosity values in Table 3 indicate that the fractions became less spherical with increase in size. This confirms the observation that a major part of the hardwood bedding material separated into the coarse fraction. As expected and based on the values of Hausner ratio (defined as ratio of tap density to bulk density), the flow behavior of the poultry litter improved with increased in size of fraction [28].

Compressibility

Figure 3 shows that the fine fraction of poultry litter was the most compressible while the coarse fraction was the least compressible. The compressibility of the middle fraction was close to but significantly higher (P<0.05) than the compressibility of the coarse fraction within the pressure range used in this study. When compared to the compressibility of the raw sample, it is obvious that the fine fraction of poultry litter is the dominant contributor to the compressibility of poultry litter. This is in contrary to previous studies on effect of particle size on compressibility that generally found that compressibility increases with increase in particle size [9,29]. One possible reason is that the coarser fraction has more spread of particle size ranges (see Fig. 2) which therefore promoted the filling of voids with particles of the same or smaller size during the compression process. At consolidating pressures greater than 12 kPa, fine fraction and raw poultry litter changed from being having excellent flow properties to good flow properties when the flowability prediction criterion of Fayed and Skocir [30] was applied to the compressibility data. The medium and coarse fractions had excellent flow irrespective of consolidating pressure. This supports the results obtained from tap density measurement that showed the flow behavior (based on reduction in Hausner ratio) of poultry litter improved with increased in size of fraction.

Flow Properties

The flow function plots (or the plot of the ultimate yield stess – UYL versus the major consolidating stress - MCS) for the different fractions is shown in Figure 4. The flow index values (the slope of the plots in the figure), hence the flowability of the coarse, middle and fine fractions were 16.1, 13.2 and 11.5 respectively, and are considerably higher than the flow index of raw poultry litter (3.6). In raw litter, the smaller particles filled the voids of the bigger particles thereby causing more resistance to flow [28]. In the fractionated samples, the sizes of particles in each fraction are close. Therefore, the amount of particles that have sizes small enough to fill the voids will be smaller. The increase in flow index values with increase in size of fraction supports the results obtained from tap density and compressibility measurements. Using the classification of Jenike [31], fractionating improved the flowability of poultry litter from good to excellent.

Heating value and composition

Table 2 shows the results from composition analysis carried out on raw and fractionated poultry litter. As hypothesized, the energy value of the fractions significantly increased with increase in size. This is confirmed by the reducing ash content and increasing carbon content with increase in particle size. Therefore based on heating value and composition, fractionating may be an effective way of increase the value added utilization of poultry litter as both an energy feedstock and as fertilizer. As expected the values of the properties in Table 2 for raw litter falls between the values for the coarse fraction and the fine fraction.

Pyrolysis study

Observed thermal behavior (TG curve) of fractionated and raw poultry litter during pyrolysis is shown in Fig. 5. There was an initial decrease in the weight (about 15%) of the samples between 30^{o}C and 150^{o}C due to the release of moisture in the samples. The figure also shows that a significant loss of sample mass (25% of original weight) occurred within the temperature range of 150^{o}C and 350^{o}C, and that thermal decomposition was essentially complete at 600^{o}C. Similar to the results obtained for the ash content of the fractions, the char yield (residual sample mass after pyrolysis) decreased with increase in particle size.

Figure 6 shows the mass loss rate curves (derivative thermograms – DTG curves) for the poultry litter samples within the temperature range (150 to 800^{o}C) at which thermal decomposition of the samples occurred. The mass loss rate (a) was obtained as follows:

$$\alpha = \frac{m - m_o}{m_f - m_o} \qquad (1)$$

There was a clear difference between the thermograms of the samples with the mass loss rate (and hence the amount of reactivity) increasing with increase in particle size. We attribute this to the increase in energy and carbon contents of the sample with particle size, which implies increasing amount of fraction available for combustion, hence the increase in mass loss rate. As typically reported for thermal decomposition of biomass, all the samples produced two overlapping peaks – a single peak and a shoulder peak on the left of the single peak [32,33].

Based on studies that have been carried on biomass feedstocks, the shoulder at the left side corresponds to hemicellulose decomposition while the higher temperature peak represents the degradation of cellulose [14,32]. The flat tailing section of the DTG curves at higher temperatures corresponds to the decomposition of lignin, the pyrolysis of which is known to occur in an wide temperature range [14,34].

The highest mass loss rates occurred at temperature of about 335^{o}C. The values of the highest mass loss rates for the fine, medium and coarse fractions and for the raw poultry litter were 0.107 min^{-1}, 0.126 min^{-1}, 0.154 min^{-1} and 0.115 min^{-1} respectively. Based on the closeness of the thermal decomposition of the raw poultry litter to the fine fraction, we hypothesize that the fine fraction play a more significant role in determining the pyrolysis characteristics of the raw fraction, hence the importance of separating the fine fraction from poultry litter in situations where the waste material is to be used for bioenergy applications. The values of the mass loss rates are within the range that has been obtained for other biomass wastes (olive kernel, forest residue, cotton residue [14]; coconut and cashew nut shells [32]; rice husk and cotton straw [35]).

Pyrolysis kinetics

As discussed in the previous section, the DTG curves of biomass frequently contain partially overlapping peaks. This is an indication that more than one reaction occurred during pyrolysis of the fractions [35]. Mathematical models are typically used for the deconvolution of these overlapping peaks in the DTG curves. Most authors that have studied the kinetics of biomass pyrolysis have assumed three parallel independent reactions, with each reaction corresponding to the decomposition of the constituent pseudo-components hemicellulose, cellulose and lignin [36,37]. The pyrolysis rate for three independent reactions is described as follows:

$$\frac{d\alpha}{dt} = \sum_{i=1}^{3} c_i \frac{d\alpha_i}{dt} \qquad (2)$$

where c_i is a measure of the relative contribution of the partial processes to the overall mass loss.

The separate conversion α_i for each component is given by:

$$\alpha_i = \frac{m_i - m_{o,i}}{m_{f,i} - m_{o,i}} \qquad (3)$$

where $m_{o,i}$, m_i and $m_{f,i}$ are the initial sample mass, the actual sample mass and the final yield of component i, respectively. The components are all assumed to decompose individually according to the nth order reaction equation:

$$\frac{d\alpha_i}{dt} = A_i \exp\left(-\frac{E_i}{RT}\right)(1-\alpha_i)^{n_i} \quad (4)$$

where A_i, E_i, R and n_i denote the frequency factor, activation energy, gas constant and reaction order respectively.

The ForK (Formal Kinetic Models) software (ChemInform Ltd, SaintPetersburg) was used to estimate the kinetic parameters from the above set of equations. This involved the use of non-linear optimization and Runge-Kutta numerical integration scheme. The values of the estimated parameters for the raw and fractionated poultry litter are given in Table 3. Figure 7 shows that the pyrolysis of poultry litter is well described by the three independent nth order parallel reactions model as seen by the good fit of predicted to experimental data for coarse poultry litter fraction (R^2 >0.986 and standard error of estimate < 0.00416). Similar fits were obtained for all the other samples. The first pseudo-component corresponded to hemicellulose, which was reactive at temperatures between 180C and 365^oC., the second component corresponded to the cellulose fraction that decomposed between 300 and 460^oC while the third component was for the decomposition of lignin within a broad temperature range of 180 and 800^oC. For all the samples, cellulose and lignin had the highest and lowest activation energies respectively (175 to 187 kJ/mol for cellulose, 29 to 34 kJ/mol for lignin). These values are within the range that have been reported for biomass samples [33,35,37].

Conclusions

In this study, poultry litter was fractionated into three sizes. The physical and pyrolysis characteristics of the fractionated poultry litter were thereafter. The conclusions drawn from this study are:

- The physical attributes of the fractions are different. Densities (bulk particle and tap) of the fractions increased with fraction size. Fine fraction was the most compressible and contributed most to the compressibility of raw poultry litter. Fractionated poultry litter has better flow properties than raw poultry litter.
- The heating value, carbon content and rate of thermal decomposition of the fractions increased with particle size. The thermal decomposition of poultry litter occurred within a temperature range of 150^oC to 800^oC and occurred in three stages – hemicellulose decomposition (180^oC to 365^oC), cellulose decomposition (300 to 460C) and lignin decomposition (180^oC to 800^oC).
- Kinetic modeling showed that the thermal decomposition of raw and fractionated poultry litter can be described by means of three independent n^{th}-order parallel reactions.

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Table 1: Physical properties of poultry litter fractions

Property	Fine fraction	Middle fraction	Coarse fraction	Raw poultry litter
Geometric mean (mm)	0.396	0.708	1.181	0.841
Geometric standard deviation	0.219	0.171	0.343	0.252
Bulk density	553.7[a]	443.7[b]	419.3[c]	542.5[a]
Particle density	1656.5[a]	1601.5[b]	1547.4[c]	1554.4[c]
Porosity	0.666[a]	0.723[b]	0.729[b]	0.649[a]
Tap density	663.3[a]	517.3[b]	439.3[c]	579.5[d]
Hausner ratio	1.198[a]	1.166[b]	1.048[c]	1.071[d]

Values are means of duplicates. Means with different letters in a row are significantly different ($P<0.05$).

Table 2: Composition and heating value of poultry litter fractions

Property	Fine fraction	Medium fraction	Coarse fraction	Raw poultry litter
Nitrogen (%, d.b.)	5.34[a]	4.21[b]	4.36[b]	4.65
Carbon (%, d.b.)	25.92[a]	28.23[b]	32.47[c]	28.83
Ash (%, d.b.)	42.44[a]	42.81[a]	31.53[b]	40.96
Energy (MJ/kg)	11.83[a]	13.10[b]	15.12[c]	13.11

Values are means of duplicates. Means with different letters in a row are significantly different ($P<0.05$).

Table 3: Estimate of parameters of the three independent nth order parallel reactions (Eqns. 2 to 4).

	Fractions			
Parameter	**fine**	**middle**	**coarse**	**raw**
Ln A_1	23.203	24.841	23.140	20.596
E_1 (kJ/mol)	124.457	131.383	124.370	113.330
n_1	1.303	1.079	1.081	1.023
c_1 (%)	16.341	16.771	16.334	17.170
Ln A_2	31.222	31.419	33.436	33.634
E_2 (kJ/mol)	175.361	178.956	186.771	186.746
n_2	2.124	1.649	1.578	1.903
c_2 (%)	29.487	31.777	34.020	30.272
In A_3	0.206	0.223	0.257	0.156
E_3 (kJ/mol)	36.611	34.685	34.488	36.747
n_3	4.366	4.252	3.951	4.424
c_3 (%)	73.968	69.789	72.468	75.179
R^2	0.986	0.993	0.994	0.994
s.e.*	0.00416	0.00286	00.00256	0.00349

*R^2 is the coefficient of determination. An R^2 of 1 indicate a perfect fit. s.e. is standard error of estimate - the average deviation between experimental and fitted data. The lower the s.e., the better the fit.

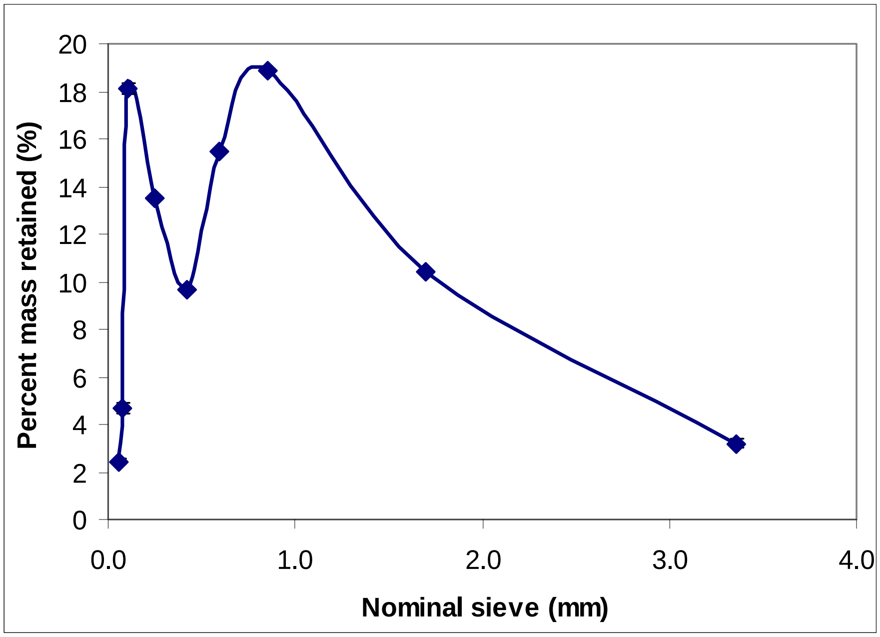

Figure 1. Particle size distribution of raw poultry litter

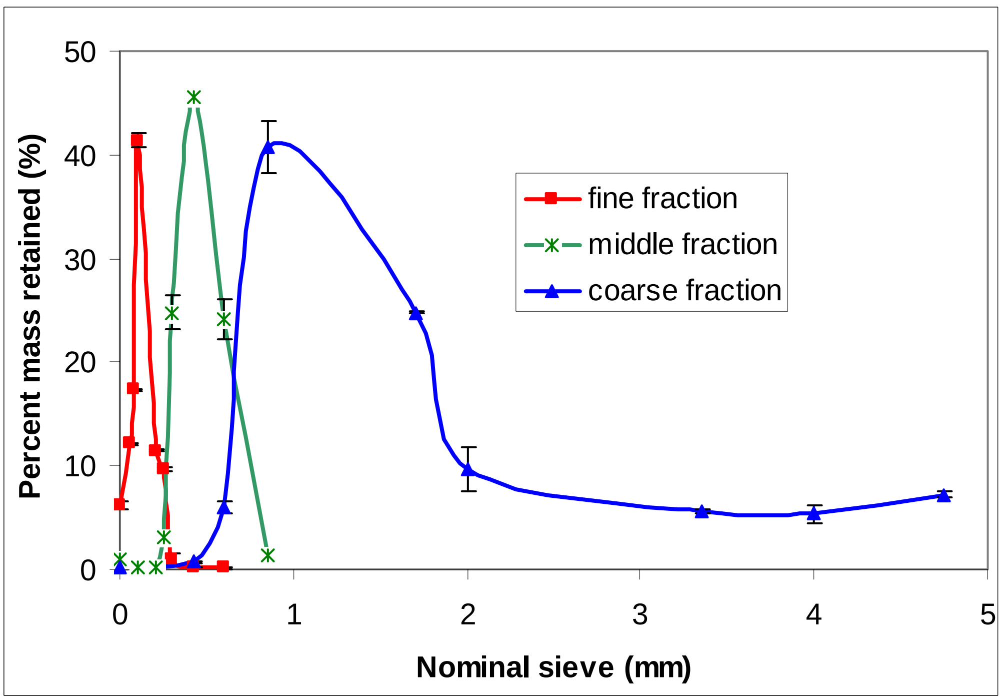

Figure 2. Particle size distribution of fractionated poultry litter

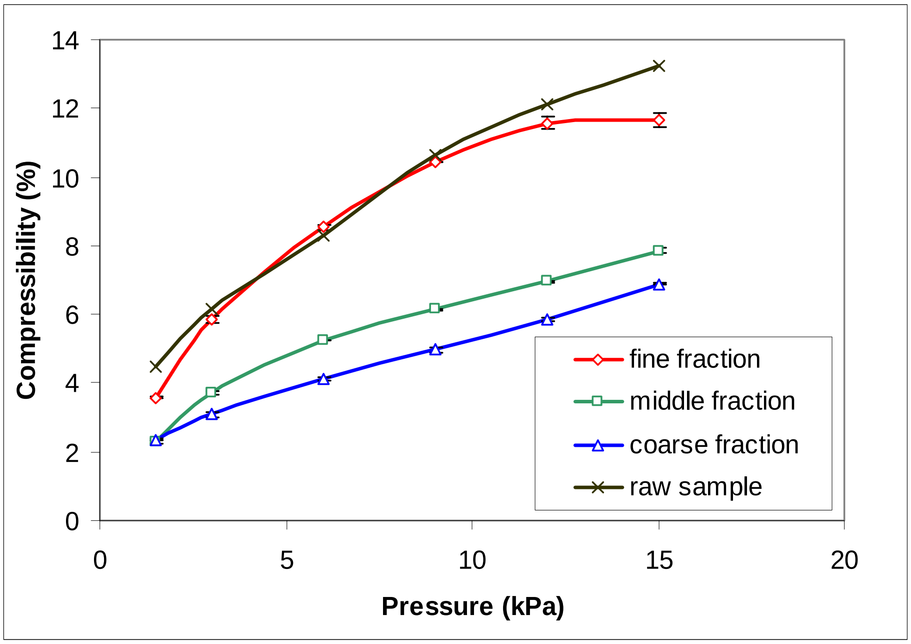

Figure 3. Compressibility of fractionated poultry litter

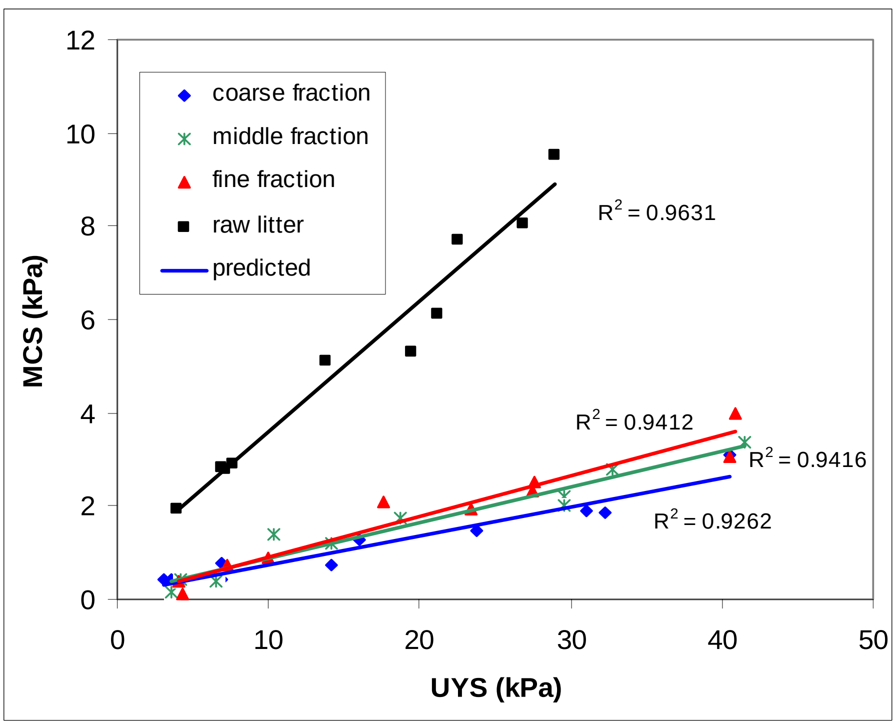

Figure 4. Flow properties of fractionated poultry litter

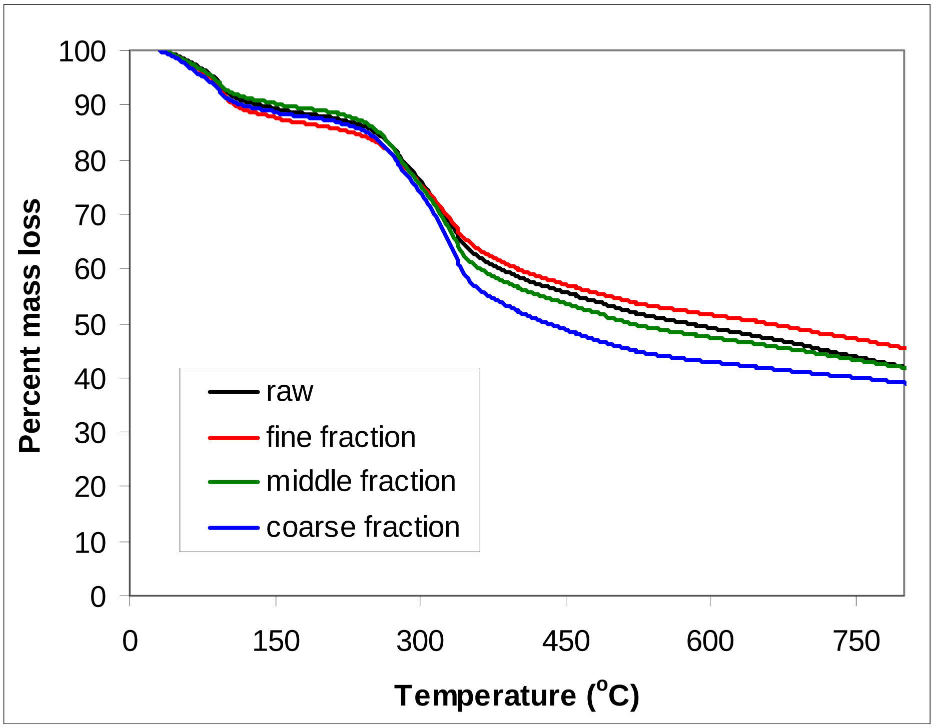

Figure 5. Mass loss from the thermal decomposition of raw and fractionated poultry litter. Mass loss was defined as percent ratio of mass of sample at a temperature divide b the original mass of sample.

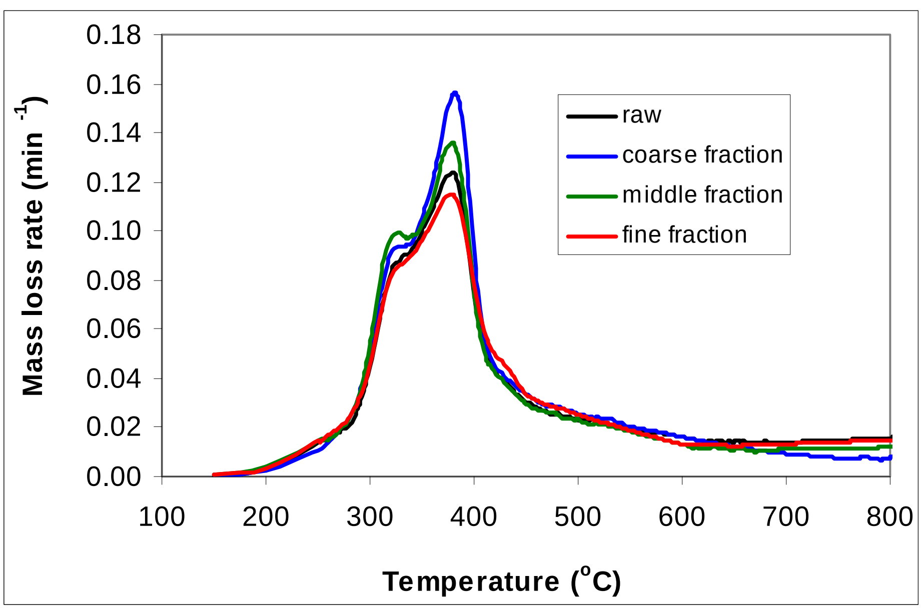

Figure 6. Mass loss rate from the thermal decomposition of raw and fractionated poultry litter.

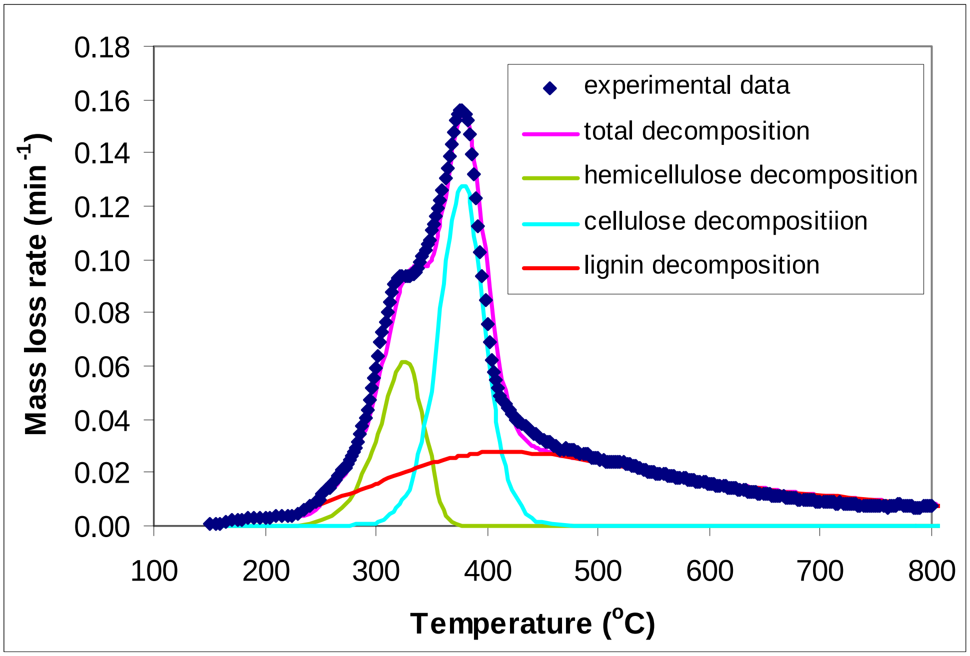

Figure 7: Predicted decomposition of the pseudo-components in coarse poultry litter fraction.