ORIGINAL PAPER

Assessing Feedstocks and Catalysts for Production of Bio-Oils from Hydrothermal Liquefaction

Jason. S. Midgett · Benjamin E. Stevens ·
Adam J. Dassey · James J. Spivey ·
Chandra. S. Theegala

Abstract A bench-scale hydrothermal liquefaction (HTL) process was utilized to convert several readily available biomass feedstocks into bio-oils that could potentially be converted to renewable liquid fuels. Bio-oils produced from dairy manure, poultry litter, pine sawdust, tallow seeds, switchgrass, peanuts, and vegetable oil were compared based on heating values and product yields. Catalysts tested in the HTL process were sodium carbonate (Na_2CO_3), potassium carbonate (K_2CO_3), and sodium hydroxide (NaOH). Operating parameters included 350 °C processing temperature with a corresponding pressure of $\sim$20.5 MPa. Carbon monoxide was used as the process gas with an initial pressure of 2.1 MPa for all trials. Quantification of oils was achieved by using an acetone and ethyl ether extraction. Bio-oils from acetone soluble fractions (ASF) showed the highest heating values ranging from 31.1 to 35.4 MJ kg^{-1}. The effect of the catalysts on ASF was not clearly evident from these studies, although sodium carbonate catalyst appeared to improve conversion efficiency, measured by overall energy value, at 1–2 g catalyst quantities. The feedstock study indicated that the highest energy recovery of 70.8 % was possible from dairy manure. GC–MS results indicated that oily feedstocks produced fewer compounds, while feedstocks that have high lingo-cellulosic contents produced significantly higher number of compounds at relatively lower concentrations. Results indicated that high oil content was not necessary for effective energy conversion in the HTL process; therefore, from an economic perspective, feedstocks with high lipid concentrations do not offer major advantages over low-value (economic) cellulosic or waste feedstocks.

Keywords Thermochemical conversion · Liquefaction · Biomass · Bio-oils · Renewable energy · Catalyst

Introduction

Biomass is the most abundant renewable energy resource available and the fourth largest energy source worldwide, following coal, oil, and natural gas (excluding nuclear energy). Currently, biomass meets 10–14 % of the world's energy needs primarily through direct burning. However, direct burning is extremely inefficient due to high moisture contents and naturally low heating value [1]. Theoretically, biomass has the capacity to provide all of the world's energy requirements; however, current production approaches and use of biomass for energy are not sustainable [2]. Additionally, many biomass sources are treated as waste products and cause increased pollution locally. The effective use of biomass feedstocks for alternative energy production would generate additional revenue for certain agricultural sectors, while alleviating waste disposal problems, especially for animal production facilities.

Biomass conversion technologies are steadily improving and biomass energy production is increasing throughout the US and world. Thermochemical conversion technologies (TCC) are currently being studied to utilize biomass as a source of energy. TCC technologies include, but are not limited to, gasification, liquefaction, pyrolysis, direct combustion, and supercritical fluid extraction. Hydrothermal liquefaction (HTL), also known as direct liquefaction, is a high pressure/high temperature TCC process with no

Jason. S. Midgett · B. E. Stevens · A. J. Dassey ·
J. J. Spivey · Chandra. S. Theegala (✉)
Biological and Agricultural Engineering Department, Louisiana
State University AgCenter, 149 E.B. Doran Bldg,
Baton Rouge, LA 70803, USA
e-mail: ctheegala@agcenter.lsu.edu

added oxygen in which biomass is converted into (a) a liquid phase consisting of a bio-crude fraction and a water fraction with some polar organic compounds, (b) a gaseous phase consisting primarily of steam and light gases such as $CO/CO_2/CH_4$, and (c) a solid residue [3]. In HTL, a process gas (reducing or non-reducing) and catalyst (alkali and/or metal) are often used to increase the yield of desired products and the reaction rate. A major problem with commercializing HTL processes for biomass conversion is that it remains uneconomical when compared to the costs of diesel or gasoline. More specifically, the high costs associated with transportation of bulky, low-density biomass, and poor conversion efficiencies, coupled with a lack of understanding of complex reaction mechanisms has prevented widespread acceptance of the HTL process commercially. In the late 70s and early 80s the Lawrence Berkeley Laboratory conducted research on biomass liquefaction, confirming the process' ability to convert various biomass sources to oil products [4]. However, the low cost of fossil fuels in the 1980s limited major technological and commercial advances in this area. More recently, HTL has received greater attention as conventional liquid fuel sources have become more expensive [5, 6].

Due to sporadic HTL research, several fundamental questions still remain un-answered. For example, extensive studies were conducted by researchers at the University of Illinois at Champaign [7–11], who focused on oil production from swine waste. Results showed a minimum temperature of 285 °C and a 15–30 min retention time were required for oil production. Temperatures beyond 335 °C lead to higher solid char formation. Their initial research assumed the need for reducing gases (CO and H_2). However, their later research indicated that reducing process gases are not crucial for oil production. He and co-workers indicated that both reducing gases and inert gases (CO_2, N_2, and compressed air) can be used as a process gas [10]. As of now, the exact role and reaction mechanisms of a process gas still remain to be clarified.

Another area that is not clearly understood is the role and exact mechanism of a catalyst in the HTL process. Demirbas and co-workers concluded that the use of sodium hydroxide increases quantities of oils produced by 33 % for *Picea orientalis* (oriental spruce tree) at 377 °C [6]. Heating values of 33 MJ kg^{-1} were obtained by Yokoyama and colleagues when using sodium carbonate as a catalyst with sewage sludge [12]. The most recent wave of catalyst assisted HTL research was initiated at various parts of the world, ranging from the US to Japan and from Canada to China [13–17]. In general, it can be concluded that the catalyst use increases the quantity and quality of oil produced. Except for a few exceptions, there has been little description about the roles that a catalyst plays in the liquefaction process [18]. The mechanisms that were originally proposed by Appell and coworkers in the 1960s [19]

are still being cited [18]. These mechanisms are based on sodium carbonate-catalyzed liquefaction in presence of carbon monoxide. However, the proposed reactions do not explain oil production from other catalysts and other process gases, especially inert and non-reducing gases.

The focus of this study was to evaluate the effectiveness of three catalysts on improving bio-oil production from a sample biomass feedstock (dairy manure) and assess the conversion efficiencies from several readily available biomass and bio-waste feedstocks.

Materials and Methods

HTL Processor

A bench-top 300 mL stainless steel reaction pressure vessel from Autoclave Engineers was used to conduct the HTL experiments. All experiments were carried out as batch tests. DASYLab 9.0 software was used to log temperature and pressure during operation through the use of a K-type thermocouple and a pressure transducer, connected to a USB-based hardware system (Measurement Computing Corp). The vessel was equipped with a Proportional-Integral–Differential (PID) control and safety functions to prevent overheating and to control heating rates. Temperatures were maintained within 5 °C of set conditions. A rupture disc was used to prevent damage to the vessel if operation exceeded the maximum rated conditions. A stainless steel liner provided by Autoclave Engineers® was used to facilitate easy transfer of pre and post-processed slurries since the vessel was not equipped with a drain port. Additional system setup details can be found in earlier work by Midgett and Theegala [20]. To facilitate easy understanding of the processor and the experiments, a schematic of the HTL processor is illustrated in Fig. 1.

Preparation of Feedstocks

Feedstock sources were compared for resulting heating values of oils extracted from the HTL process. The feedstocks used in this study were dairy manure, poultry litter, pine sawdust, tallow seeds (both ground and whole), switchgrass, peanuts, and vegetable oil. All but two of the solid feedstocks (vegetable oil and tallow whole) were ground to a fine powder and homogenized using a blender prior to HTL processing (Table 1). All feedstocks except for raw vegetable oil were then dried in an oven at 105 °C for 24 h prior HTL processing. The total solids and volatile solids of the feedstocks were measured according to APHA [21]. Carbon, hydrogen, and nitrogen (CHN) analysis was conducted on all pre-processed feedstocks so that higher heating values (HHV) could be calculated and compared to
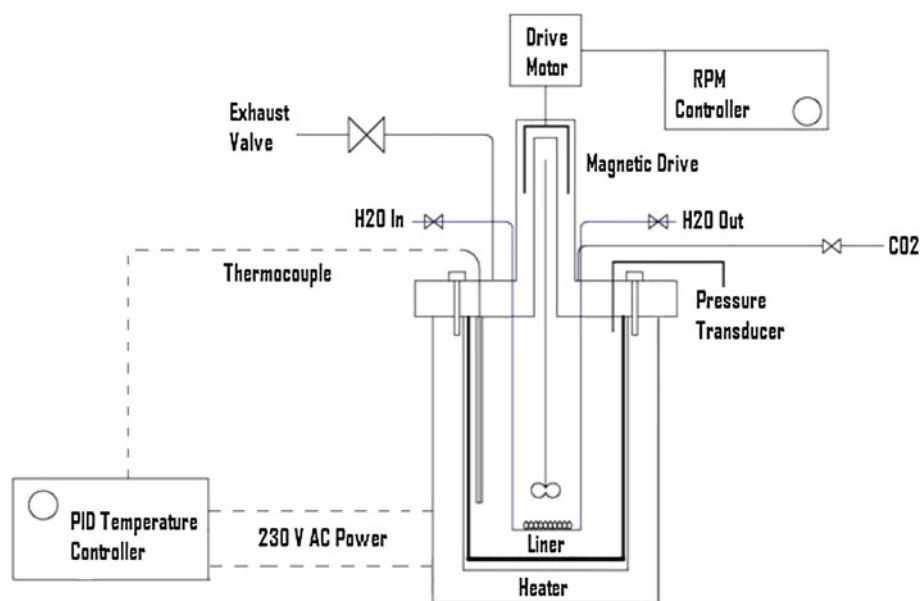
those of the post-processed oils obtained in the HTL process. The LSU AgCenter's Callegari Environmental Center conducted all CHN analyses using procedures developed by Elementar under guidelines from APHA [21]. A modified Dulong's formula (eq.1) [22] was used to calculate HHV based on the percent of carbon (C), hydrogen (H), and nitrogen determined by CHN analysis and assuming the remainder percent to be oxygen (O). The composition of nitrogen is not used as a factor in the modified Dulong's formula; it is only used to determine oxygen content (which is computed by difference).

Higher heating value $(MJkg^{-1})$

$$= \frac{33.5 * wt\%C}{100} + \frac{142.3 * wt\%H}{100} + \frac{15.4 * wt\%O}{100} \quad (1)$$

All solid feedstocks except switchgrass and pine sawdust were combined with deionized water to yield a 20 % total solid solution (by weight) to be used as the pre-processed slurry. Switchgrass and pine sawdust were difficult to agitate in the HTL processor using the same solution concentration as the other feedstocks; therefore, 10 g of solids to 80 mL of de-ionized water were used to yield an 11.1 % solid slurry. The energy values for switchgrass and sawdust were later doubled for comparison with the other feedstocks. The raw vegetable oil was processed as-received with 20 mL oil to 80 mL de-ionized water. Table 2 shows the samples masses, volatile solids (VS), and HHV values (computed using the modified Dulong's formula) for all feedstocks used in this study.

Experimental Setup and Process Parameters

The 100 mL feedstock and water slurry, along with the catalyst, were first added to the stainless steel liner and

Table 1 Acquisition and preparation details of feedstocks used for the HTL study

Feedstock	Acquired location	Preparation
Dairy manure	LSU dairy center	Screened and solar dried to 3 % moisture content
Poultry litter	LSU poultry farm	Dried and ground
Pine sawdust	LSU biological engineering woodshop	Dried
Tallow seeds	Chinese tallow tree on LSU campus during spring after first bloom	Left whole for tallow-whole
		Ground up for tallow-ground
Switchgrass	LSU Ag center's hill farm experiment station	Stalks and leaves were ground
Peanuts	Raw, uncooked, grocery store	Peanuts were peeled from shell and ground
Vegetable oil	Grocery store	No modifications

mixed thoroughly. This liner was placed inside the HTL processor. Agitation speed of the propeller was maintained at a constant rate (200 RPM) throughout all experiments. Carbon monoxide (CO) was used as the process gas with initial pressure of 2.1 MPa for all experiments. CO was selected because of its successful application in earlier studies [7–11]. Additionally, out of all the process gasses, only a mechanism for carbonate-catalyzed liquefaction in the presence of CO has been proposed [19].

To ensure use of a procedure that has been shown to produce desirable products, most processing parameters

Table 2 Raw feedstock sample sizes and feedstock characteristics

	Dairy	Poultry	Sawdust	Tallow-whole	Tallow-ground	Switch grass	Peanuts	Vegetable oil
Sample size (g or mL)	20 g	20 g	10 g	20 g	20 g	10 g	20 g	20 mL
VS (g)	16.6	16.7	10	19.5	19.5	9.5	19.4	19.9
VS (%)	83.2	83.3	99.9	97.5	97.5	95.3	97	99.3
Elemental analysis								
C%	38.8	36.5	45.1	59.1	59.1	45.1	53.9	77.8
H%	5.1	5.5	5.9	8.3	8.3	6.1	7.9	11.1
N%	1.3	4.4	0.07	2.3	2.3	0.8	4.6	0.05
O%	54.7	53.7	48.9	30.4	30.4	48.0	33.6	11.1
HHV (MJ g^{-1})	11.9	11.7	16.0	26.9	26.9	16.4	24.1	40.1

chosen were the same as those used in an extensive study conducted by researchers at the University of Illinois at Champaign dealing with oil production from swine waste [9–11]. In short their tested parameters and ranges were: (1) swine manure tested at 275–350 °C using 1.8 L pressure vessel, operated under a batch mode, (2) process gases tested were CO, H_2, CO_2, N_2, and compressed air, (3) feedstock pH ranged from 4 to 10, (4) operating pressures ranged from 5.5 to 18 MPa, (5) retention time was varied from 5 to 180 min, (6) heating rate was set at 5–10 °C/min, (7) total solids was between 10 and 25 %. The operating temperature of the present HTL process for all feedstocks was set at 350 °C, which elevated the vessel pressure to ∼20.5 MPa. The retention time for all experiments was 15 min. Although the heating rate was set at 10 °C/min, the vessel took significantly longer time to heat to 350 °C (approximately 1 h 45 min.). This was primarily due to heat losses and variable heating rates as dictated by the PID controller. Once the vessel was heated, it was maintained at 350 °C for 15 min., after which the heater was turned off and the cooling water loop was initiated to cool the vessel back to pre-run conditions. Once the cooling loop was initiated, the vessel temperature dropped down to approximately 250 °C within the first 5 min. The next drop to 150 °C took approximately 20 min. The final drop from 150 to 50 °C took even longer, approximately 65 min.

A 1341 Parr oxygen bomb calorimeter assembly was used to conduct a calorimetric study on the ASF fraction for comparison to the theoretical values obtained by CHN analysis and the modified Dulong's formula. The calorimeter was operated according to parr manuals No. 204 and 205 [23], which include procedures for proper calibration.

Catalysts Comparisons

Catalyst types and quantities were studied for their effects on oil quality and quantity from the HTL process using only the dairy manure feedstock. Base catalysts have been indicated to increase water soluble hydrocarbons and decrease solid residue [24]. Three catalysts were tested: anhydrous sodium carbonate (Na_2CO_3), anhydrous sodium hydroxide (NaOH), and anhydrous potassium carbonate (K_2CO_3). Catalyst concentrations were varied at 1, 2, 3 and 4 g for each of the 3 catalysts tested.

Post-processing and Product Analysis

The liner containing the post-processed slurry (solids and liquid) was removed from the vessel. The post–processed slurry consisted of char, organic solids, water, and water soluble hydrocarbons. The protocol used for collecting and quantifying the various oils was discussed in an earlier paper [20]. However, to assist the reader in understanding the various terms, it is depicted in Fig. 2.

A 0.7-micron glass fiber filter (Fisher Scientific, Pittsburgh, PA) was used to separate any solids from the post-processed water. The filtered water was combined with ACS grade ethyl ether anhydrous (($CH_3CH_2)_2O$) in a 1:1 ratio and thoroughly shaken for 2 min. in a gravimetric funnel to extract light oils. The bottom layer contained water, which was drained and labeled PPW (post-processed water). The remaining top layer, containing light oils and ether, was drained and labeled WSF (water soluble fraction). Moisture was evaporated from the PPW at 105 °C and ether from the WSF at 35 °C (slightly above boiling point of ether). The remaining solids on the filter paper, liner, and cooling loop coils were washed with 250 mL of ACS grade acetone (C_2H_6O) to extract oil-like compounds. The acetone mixture was again filtered and labeled ASF (acetone soluble fraction). The remaining solids from the filter paper were named AINF (acetone insoluble fraction). The ASF and AINF fractions were dried at 60 and 105 °C, respectively, to evaporate any moisture or acetone remaining. All fractions were allowed to dry for 24 h and then any remaining solids or oils were quantified. The AINF fraction was further tested for volatile solids by igniting at 550 °C.
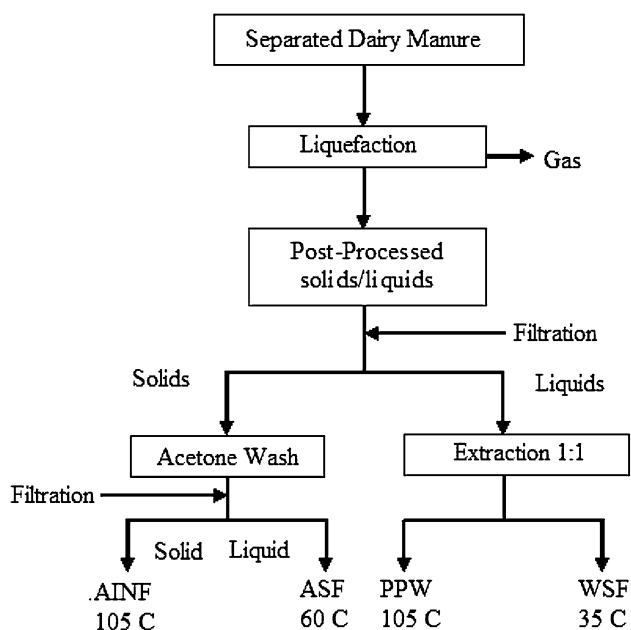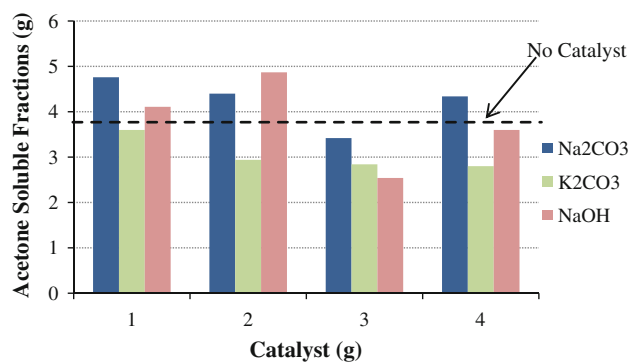
Fig. 2 Procedure for the separation of oil products. The final products include: AINF (acetone insoluble fraction or char dried at 105 °C), ASF (acetone soluble fraction dried at 60 °C), PPW (post-processed water dried at 105), and WSF (water soluble fraction dried at 35 °C [20]

Fig. 3 Product quantities (g) of acetone soluble fractions (ASF) obtained from dairy manure subjected to the HTL process while using the three different catalysts studied in quantities of 1, 2, 3, and 4 g of each catalyst. The result for a trial using no catalyst (0 g) is reported for comparison

CHN analysis was performed primarily on the ASF since this was the fraction having both the highest energy content (heating value) and the largest proportion of the overall product. The WSF fraction has the next highest heating value. Gases produced during the process, which contributed to the pressure increase during the temperature ramping-up stage, were quantified (volumetrically) but not analyzed since the primary target end product for the HTL process is bio-oil and the heating content of gases is known to be insignificant [20, 25]. A GC–MS (Agilent 7890A GC/Agilent 5975C Inert XL MSD) with an Agilent 7683B Injector and Restek column (Rxi-5 ms, 30 m × 0.25 mm × 0.25 micron film) were used for ASF oil characterization. National Institute of Standards and Technology (NIST) database was used to identify the individual compounds in the ASF samples.

Results and Discussion

Catalyst Comparisons

The ASF and WSF were anticipated to contain the bulk of the energy from the biomass. Results indicated that the ASF fraction remained the most important fraction since the WSF continued to yield very low quantities (<0.5 g or <2.5 % of raw biomass weight). It has to be kept in mind that even if the ASF masses are significantly lower than the

raw feedstock mass, the energy density is significantly higher. Shown in Fig. 3 is the comparison of ASF product quantities obtained from the HTL process while using the three different catalysts studied in quantities of 1, 2, 3, and 4 g of each catalyst. Dairy manure was the feedstock used for the comparison.

Based on the results, it was difficult to determine the single best catalyst. The highest ASF fraction (4.87 g) was obtained using 2 g of sodium hydroxide (NaOH), but 1 g of sodium carbonate (Na_2CO_3) was not significantly less (4.76 g of ASF). No difference was detected in product quantity between these two catalysts using t testing with an alpha level of 0.05. T testing between the control and each of the 1–4 g trials only indicated that (K_2CO_3) was significantly worse than no catalyst at all and provided no benefit. Potassium carbonate did not yield a higher ASF fraction when used as a catalyst at any concentration. Using more than 2 g of any catalyst is not recommended as ASF fractions obtained from processing did not improve in most instances. The excess catalyst ended up in the PPW, which was evidenced by increasing PPW amounts with increasing catalysts amounts [20].

The HHVs in the ASF using various catalyst concentrations are provided in Fig. 4. There was no statistically significant difference ($P > 0.05$) in HHVs among the three catalysts. The highest HHV (34.7 MJ kg^{-1}) for the ASF fractions was obtained using 2 g sodium carbonate (Na_2CO_3), which consistently yielded the highest ASF energy density value except when using 4 g of catalyst. NaOH yielded the highest heating value with 34.6 MJ kg^{-1} at 4 g concentration. All heating values obtained were similar to the heating value of 33 MJ kg^{-1} obtained by Yokoyama and colleagues when using sodium carbonate as a catalyst with sewage sludge [12]. From a HHV point-of-view, none of the catalysts, however,
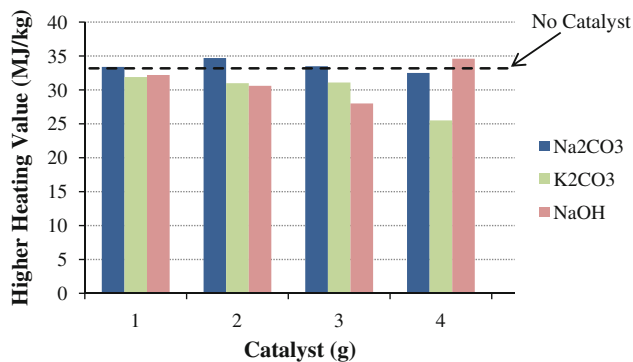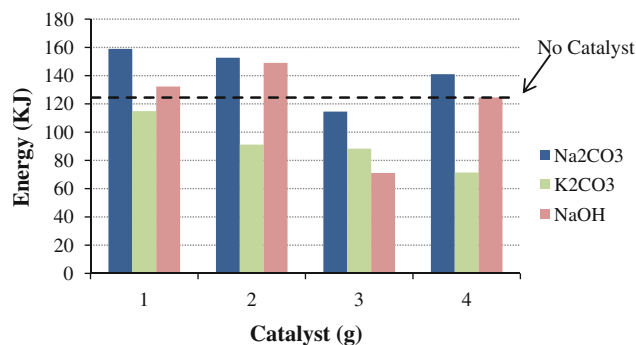
Fig. 4 Higher heating values (MJ kg^{-1}) of acetone soluble fractions (ASF) obtained from dairy manure subjected to the HTL process while using the three different catalysts studied in quantities of 1, 2, 3, and 4 g of each catalyst. The result for a trial using no catalyst (0 g) is reported for comparison

Fig. 5 Total energy values (KJ) from the mass of acetone soluble fractions (ASF) obtained from dairy manure subjected to the HTL process while using the three different catalysts studied in quantities of 1, 2, 3, and 4 g of each catalyst. The result for a trial using no catalyst (0 g) is reported for comparison

indicated any significant advantage in energy density ($P > 0.05$) when compared no catalyst.

The ASF masses obtained in Fig. 3 were multiplied with the ASF heating values obtained in Fig. 4 to produce the total energy values seen in Fig. 5. Potassium carbonate produced no energy gain compared to no catalyst. At 1 and 2 g catalyst quantities, sodium carbonate appeared to produce slightly higher energy values, while sodium hydroxide had no significant effect ($P > 0.05$).

This research, although demonstrated the advantages of using 1–2 g of sodium hydroxide catalyst, failed to cast light on the underlying mechanisms. As this research was not aimed as a fundamental research, justifying the results was not attempted as it would be unsubstantiated and speculative.

The uniqueness of the 3 g catalyst quantity and the exact reasoning behind its corresponding low energy value (Fig. 5) is not clearly evident from this research. Pinpointing the exact reason is very difficult due to the multitude of complex and intertwined processes. Alkali catalysts, such as sodium or potassium carbonate, can act as catalysts for hydrolysis of cellulose and hemi-cellulose macromolecules into smaller fragments [26]. These fragments are further degraded to smaller compounds by dehydration, dehydrogenation, deoxygenation, and decarboxylation. Once produced, these compounds rearrange through condensation, cyclization, and polymerization, leading to new compounds [26]. Apart from the complex and intertwined processes, the various catalyst quantities may also have led to the variations in end product consistencies. From the numerous experiments, it was observed that different catalyst amounts and process conditions produced end products with varied consistencies (such as moisture content and texture; data observed and not shown). The catalyst may have interfered with the propeller and mixing patterns within the liner holding the

wet biomass. The catalyst may also have interacted with the raw mineral content in the feedstock. All these unanswered questions clearly points to a need to clarify the role and mechanism of the catalyst.

Alkali or basic catalysts have been reported to limit char formation when used in HTL processes. This is beneficial because the available energy of the fuel is reduced proportionately to the magnitude of the ash content. The sample pH before the HTL run may also have an influence on the dehydration or other mechanisms. For example, the pH for dairy manure feedstock slurry with Na_2CO_3 catalyst increases from 5.95 (no catalyst) to: 8.34 at 1 g catalyst, 9.0 at 2 g, 9.25 at 3 g, and 10.45 at 4 g. However, the exact effect of pH on oil production is not assessed for the present study. Compared to no-catalyst runs, it can be generalized that all catalysts, with the exception of 4 g quantities, have a positive impact by reducing the acetone insoluble fractions (i.e., char) (Fig. 6). In the 2 g trials, potassium carbonate and sodium hydroxide reduced char formation (AINF) by 75 and 85 % respectively. However, increasing the catalyst concentrations to 3 and 4 g did not reduce the char formation further. The char yield for sodium carbonate was essentially constant at all catalyst quantities, averaging an AINF mass of 5.05 g, corresponding to significant ($P < 0.05$) reductions in AINF when compared to using no catalyst.

Although, there was significant variation in the ASF fraction produced with different catalysts and catalyst amounts, the overall results indicated that there was no significant difference ($P > 0.05$) in the percent recoverable energy from the ASF. Xu and Lad found that regardless of the presence of a catalyst or type of catalyst, the formation of total liquid organic products were temperature specific for various trials [15]. Additional trials under various temperatures would benefit the catalyst study. It was also determined that major variability was introduced into the
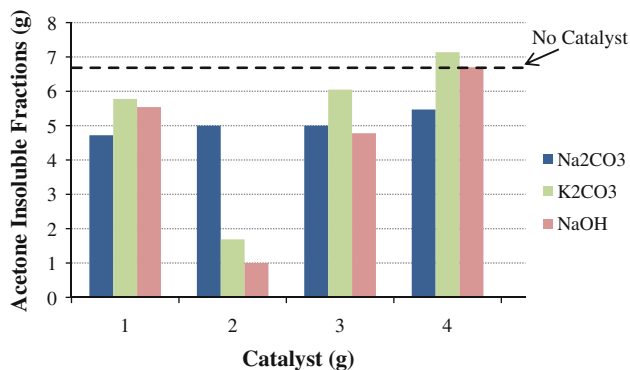
Fig. 6 Product quantities (g) of acetone insoluble fractions (AINF) obtained from dairy manure subjected to the HTL process while using the three different catalysts studied in quantities of 1, 2, 3, and 4 g of each catalyst. The result for a trial using no catalyst (0 g) is reported for comparison

results reported by various researchers due to factors such as the internal reactor surface, slurry mixing patterns, and sample volume.

Feedstock Results and Comparisons

The results for all feedstocks are summarized in Table 3, which compares the raw energy content of each feedstock and the total energy content (KJ) of the combined ASF and WSF fractions obtained during processing. These values were used to determine the conversion efficiency of the feedstocks.

Using the HTL process, 70.8 % of the energy in the dairy manure was recovered as liquid energy. This was unexpected considering that dairy manure had the lowest

organic content (VS%), comparable to poultry litter (Table 2). Yin and coworkers indicated that the maximum bio-oil yield under similar conditions was only 48.8 % [16], essentially equal to the yield for poultry litter (Table 3). With their lower organic contents, it was understandable that poultry litter would produce less bio-oil. Ash content of poultry litter at a particular location or farm varies widely due to soil contamination when the litter is removed from the dirt floor of broiler houses [27]. In comparison with the other feedstocks, the dairy manure and poultry litter produced the least amount oils (ASF + WSF) with 5.1 and 3.5 g respectively, while also producing some of the highest quantities of char (4.7 and 4.2 g of AINF, respectively). For each of the waste feedstocks tested here, the HTL process effectively converted the waste product with minimal raw energy into bio-oils with nearly three times the amount of energy.

The five remaining feedstocks all had energy recoveries between 57.8 and 65.5 %, falling in the range between those of dairy manure and poultry litter. The largest amount of bio-oils (ASF + WSF) came from vegetable oil (14.7 g), tallow seeds (9.1 g), and peanuts (7.6 g). These three products have relatively high initial oil content, as they are oils or oily seeds. The high oil contents in these feedstocks were also reflected in the high raw heating values (40.1, 24.1, 26.9 MJ/kg respectively), and were expected to produce the highest quantities of bio-oils. While these three feedstocks did produce marginally higher ASF heating values, the increases were not proportional to their raw HHVs. Looking at the percent energy recovery data, the advantages of using an oily feedstock is not clearly evident. This suggests that the HTL process is more cost-effective for producing bio-oils from low-value

Table 3 Feedstock study results are shown. All trials were conducted at 350 °C, with 15 min retention time and CO as process gas

Feedstock → parameter	Dairy manure	Poultry litter	Saw dust[a]	Tallow seeds	Switchgrass[a]	Peanuts	Veg. oil
Sample size (g or mL)	20	20	10 × 2	20	10 × 2	20	20
Raw HHV (MJ/kg)	11.9	11.7	16	26.9	16.4	24.1	40.1
ASF (g)	4.8	3.3	6.2	8.9	5.2	7.4	6.5
WSF (g)	0.3	0.2	0.4	0.2	0.6	0.2	8.2
AINF (g)	4.7	4.2	4.4	3.2	1.4	0.8	0.3
PPW (g)	2.2	3.6	1	2.3	7	4.4	0.3
ASF HHV (MJ/kg)	33.5	32.5	31.1	34.4	33.6	35.4	33.6
WSF HHV (MJ/kg)	25.3	23.8	25.8	24.6	31	28.7	37.4
Raw (kJ)	238	234	320	538	328	482	802
ASF + WSF (kJ)	168.4	112.0	203.1	311.1	193.3	267.7	525.1
% Energy recovery[b]	70.8	47.9	63.5	57.8	58.9	55.5	65.5

The agitation rate was set at 200-RPM and 1 g sodium carbonate was used as a catalyst

[a] Sawdust and Switch Grass values for (ASF, ESF, AINF, and PPW) were doubled in order to compare to other feedstocks

[b] Energy recovery was based on (ASF + WSF) KJ/Raw KJ, expressed as percent

(economic) biomass or pulp/residues (after oil extraction) rather than triglyceride-based oils or oil seeds.

Sawdust and switchgrass feedstocks had raw HHVs of 16 and 16.4 MJ/kg, respectively. The total oils produced by these feedstocks were 6.6 and 5.8 g with heating values of 31.1 and 33.6 MJ/kg for the ASF. In these cases the energy value of the bio-oil has doubled over the raw product. However, switchgrass appears to have one benefit over sawdust with lower AINF (1.4 compared to 4.4 g).

GC MS Analysis of ASF from Various Feedstocks

To better understand the reaction mechanisms and suitability as an alternative fuel, the ASF portions of all feedstocks were analyzed on a GC/MS. The analysis showed an expected wide range of oxygenates, with trace levels of nitrogen-containing compounds. Examination of the 20 most abundant compounds (as measured by peak areas) showed that the strongly polycyclic nature of many of these compounds would require significant catalytic hydrogenation to (a) remove oxygen (and nitrogen) and (b) to form new C–H bonds so that the resulting product more closely approaches the C/H ratio found in fuels ($\sim$1/2). In addition, conditions (and catalysts) required to promote hydrocracking (and hydrogenation) will be needed to reduce the chain length of the resulting hydrocarbons to the C5-C10 range (gasoline) or C10-C20 range (diesel). It is unlikely that any specific compound(s), regardless of their value as a pure product, could be separated from this complex mixture and purified in a cost effective process, meaning that liquid fuel is the most likely end use of this bio-oil.
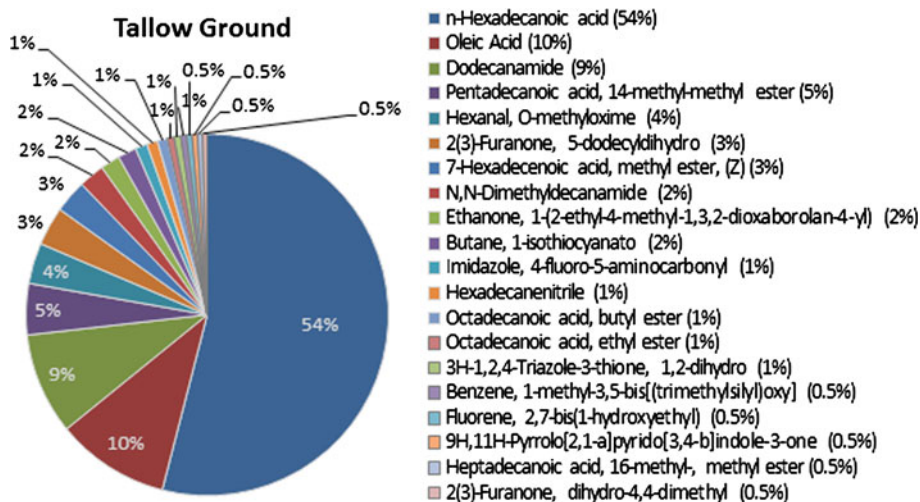
There were also compositional differences in the bio-oil produced from the various feedstocks. Within the non-oily feedstocks, the pine and dairy oils were relatively phenolic (with phenols comprising roughly an area of 23 and 25 %, respectively, of the analytes for these two products). Switchgrass and poultry, on the other hand, produced oils with no dominant class of compounds, while tallow oils (whole or ground) and peanut oils were relatively rich in carboxylic acids (62, 18, and 29 %, respectively). The high percent of hexadecanoic acid (or palmitic acid) content in the ASF from oily seeds is justifiable as it is the most common fatty acids found in plant-based oils. There were very few hydrocarbons in any of the oils, reflecting the expected reactivity of oxygen in this thermal process. To assist the reader, a sample of the top 20 compounds identified by the GC/MS in one non-oily and one oily feedstock are shown in Figs. 7 and 8.

Note that the somewhat arbitrary limitation of the GC/MS speciation analysis to the 20 most abundant compounds (by area) accounts for a quite different proportion of the total area for these different biomass feeds. In general, it can be concluded that oily feedstocks produced ASFs with fewer compounds and non-oily biomass feedstocks (with high cellulosic contents, such as pine and dairy manure) produced significantly more number of compounds. This is evident from the percentage of peak areas contributed the 20 most abundant compounds (Table 4). For tallow (whole or ground), these 20 compounds account for virtually all of the compounds produced, while for the other lingo-cellulosic feedstocks, between 47 and 81 % of the area is accounted for in this way.
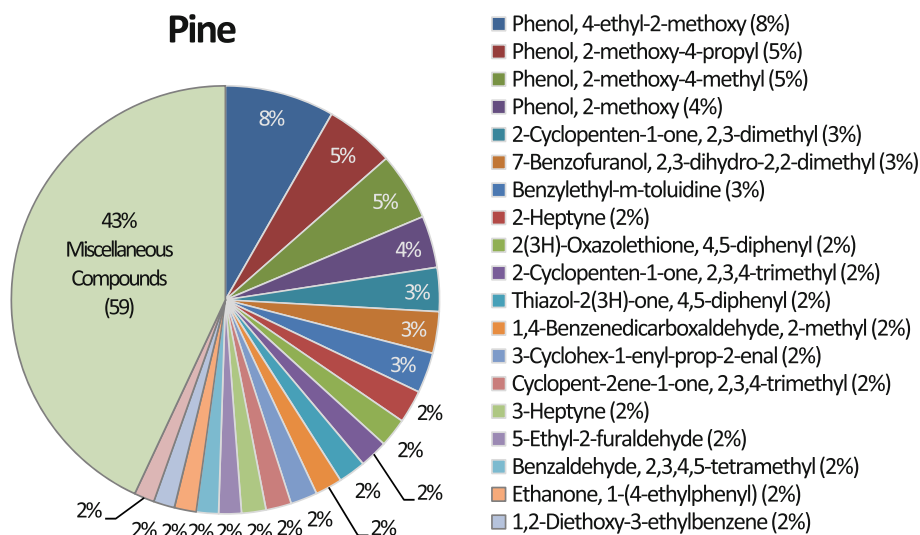
Given the significant difference in the composition of the bio oils produced from various feedstocks, it is surprising that the HHV density values (MJ/kg) based on the ASF portion of all oils is quite similar (Table 3). This may reflect the selective extraction of similar compounds from the raw bio oil, independent of the source of the oil.

Fig. 7 The top 20 most abundant compounds in the ASF produced from tallow ground accounted for 100 % of the area of the feedstock. The top 20 selection was based on the largest peak areas in the GC–MS chromatogram. All values are reported as weight percent

Tallow Ground

- n-Hexadecanoic acid (54%)
- Oleic Acid (10%)
- Dodecanamide (9%)
- Pentadecanoic acid, 14-methyl-methyl ester (5%)
- Hexanal, O-methyloxime (4%)
- 2(3)-Furanone, 5-dodecyldihydro (3%)
- 7-Hexadecenoic acid, methyl ester, (Z) (3%)
- N,N-Dimethyldecanamide (2%)
- Ethanone, 1-(2-ethyl-4-methyl-1,3,2-dioxaborolan-4-yl) (2%)
- Butane, 1-isothiocyanato (2%)
- Imidazole, 4-fluoro-5-aminocarbonyl (1%)
- Hexadecanenitrile (1%)
- Octadecanoic acid, butyl ester (1%)
- Octadecanoic acid, ethyl ester (1%)
- 3H-1,2,4-Triazole-3-thione, 1,2-dihydro (1%)
- Benzene, 1-methyl-3,5-bis[(trimethylsilyl)oxy] (0.5%)
- Fluorene, 2,7-bis(1-hydroxyethyl) (0.5%)
- 9H,11H-Pyrrolo[2,1-a]pyrido[3,4-b]indole-3-one (0.5%)
- Heptadecanoic acid, 16-methyl-, methyl ester (0.5%)
- 2(3)-Furanone, dihydro-4,4-dimethyl (0.5%)

Fig. 8 The top 20 most abundant compounds in the ASF produced from pine accounted for 57 % of the area of the feedstock. The top 20 selection was based on the largest peak areas in the GC–MS chromatogram. All values are reported as weigh percent

Pine

- Phenol, 4-ethyl-2-methoxy (8%)
- Phenol, 2-methoxy-4-propyl (5%)
- Phenol, 2-methoxy-4-methyl (5%)
- Phenol, 2-methoxy (4%)
- 2-Cyclopenten-1-one, 2,3-dimethyl (3%)
- 7-Benzofuranol, 2,3-dihydro-2,2-dimethyl (3%)
- Benzylethyl-m-toluidine (3%)
- 2-Heptyne (2%)
- 2(3H)-Oxazolethione, 4,5-diphenyl (2%)
- 2-Cyclopenten-1-one, 2,3,4-trimethyl (2%)
- Thiazol-2(3H)-one, 4,5-diphenyl (2%)
- 1,4-Benzenedicarboxaldehyde, 2-methyl (2%)
- 3-Cyclohex-1-enyl-prop-2-enal (2%)
- Cyclopent-2ene-1-one, 2,3,4-trimethyl (2%)
- 3-Heptyne (2%)
- 5-Ethyl-2-furaldehyde (2%)
- Benzaldehyde, 2,3,4,5-tetramethyl (2%)
- Ethanone, 1-(4-ethylphenyl) (2%)
- 1,2-Diethoxy-3-ethylbenzene (2%)

Table 4 Based on the GC–MS chromatogram, the oily feedstocks produced fewer compounds, which were reflected by the high percentage of areas accounted by the top 20 most abundant compounds

Feedstock	Oily feedstock	Area of most abundant 20 compounds (%)
Dairy manure	No	61.53
Poultry litter	No	60.01
Saw dust	No	56.92
Tallow ground	Yes	100
Tallow whole	Yes	99.98
Switchgrass	No	47.1
Peanuts	Yes	81.66

The cellulosic feedstocks produced as many as 79 compounds

Conclusions

Compared to an energy value of 124.4 kJ produced from no-catalyst runs, sodium carbonate catalyst produced higher energy values (159 and 152.7 kJ) at 1 and 2 g catalyst quantity. However, from a statistical perspective, potassium carbonate and sodium hydroxide catalysts did not produce significantly greater ($P > 0.05$) bio-oil yields in batch hydrothermal liquefaction of dairy manure than tests without a catalyst. The energy content (MJ/kg bio-oil) for these bio-oils was also statistically equal to that produce in the absence of a catalyst. However, the char yield was significantly reduced for NaOH and K_2CO_3 catalysts. Although the exact effect of pH elevation is not evident from this research, based on the results, it appears that the type and quantity of the alkali catalyst (and not high pH alone) had an effect on the bio-oil production. Except for catalyst types and quantities, no other process parameters were intentionally altered for the catalyst research. However, variations may have been introduced due to differences in the internal mixing patterns, which can have a major bearing on the gas–liquid mixing and end product quantities and properties.

All the feedstocks tested were converted to an oil product with a heating value of 31.1 MJ kg^{-1} or higher. This was approximately a 2–3 fold improvement for all feedstocks except vegetable oil, which lost energy through the HTL process. High oil content was not necessary for effective energy conversion in the HTL process; therefore, from an economic perspective, feedstocks with high lipid concentrations do not offer major advantages over low-value (economic) cellulosic or waste feedstocks. Dairy manure and poultry litter were effectively converted from low energy waste products to high energy bio-oils, but the high inorganic content in these feedstocks lead to high AINFs. Oil production from sawdust and switchgrass is particular promising from a bio-energy point-of-view as these feedstocks can be grown in a sustainable manner (as dedicated energy crops). Both were converted into bio-oil with twice the raw energy of the starting feedstock. Switchgrass produced less tars in the form of AINF than sawdust, making it the more appealing feedstock. The GC–MS analysis revealed that oily feedstocks produced ASFs with fewer compounds and non-oily biomass feedstocks (with high cellulosic contents, such as pine and dairy manure) produced significantly more number of compounds. Despite significant difference in the composition of the bio oils produced from various feedstocks, the HHV density (MJ/kg) based on the ASF portion of all oils is quite similar.

Further studies are needed to confirm these results by performing more replicates with the use of a larger conversion vessel capable of handling larger sample sizes. Larger sample sizes would limit the variability seen in small volumes of feedstock and minimize the effects of oil

masses lost to the vessel. Additionally, further studies should involve testing at varying temperatures (specifically higher ones) to potentially determine optimum temperatures for the conversion process of particular catalysts and feedstocks.

References

1. McKendry, P.: Energry production from biomass (part 1): overview of biomass. Bioresour. Technol. **83**, 37–46 (2002)
2. BiomassEnergyFacts. http://www.ecology.com/archived-links/biomassenergy/index.html. (2006) Accessed November 20, 2006
3. Biller, P., Ross, A.: Potential yields and properties of oil from the hydrothermal liquefaction of microalgae with different biochemical content. Bioresour. Technol. **102**, 215–225 (2011)
4. Figueroa, C., L.L.S., and Hubert G. Davis. LBL: Continuous bench-scale liquefaction unit, operation and results. Energy from Biomass and Wastes Conference, pp. 1097–1111. D. Klass, Institute of Gas Technology, Chicago, IL (1982)
5. Demirbas, A.: Fuel analyses and thermochemical processing of live residues. Energy Sources **26**, 731–738 (2004)
6. Demirbas, A.: Thermochemical converstion of biomass to liquid products in the aqueous medium. Energy Sources **27**, 1235–1243 (2005)
7. He, B.J., Zhang, Y., Riskowski, G.L., Funk, T.L.: Thermochemical conversion of swine manure, temperature and pressure responses. ASAE Paper No. 9844016. ASAE, St Jospeh, MI (1998)
8. He, B.J., Zhang, Y., Riskowski, G.L., Funk, T.L., Yin, Y.: Operating temperature and retention time effects on the thermochemical conversion process of swine manure. Trans. ASAE **43**(6), 1821–1825 (2000)
9. He, B.J., Zhang, Y., Riskowski, G.L., Funk, T.L., Yin, Y.: Thermochemical conversion of swine manure, an alternative process for waste treatment and renewable energy production. Trans. ASAE **43**(6), 1827–1833 (2000)
10. He, B.J., Zhang, Y., Riskowski, G.L., Funk, T.L., Yin, Y.: Effects of alternative process gases on the thermochemical conversion process of swine manure. Trans. ASAE **44**(6), 1873–1880 (2001)
11. He, B.J., Zhang, Y., Riskowski, G.L., Funk, T.L., Yin, Y.: Effects of feedstock pH, initial CO addition, and total solids content on the thermochemical conversion process of swine manure. Trans. ASAE **44**(3), 697–701 (2001)
12. Yokoyama, S., et al.: Liquid fuel production from sewage sludge by catalytic conversion using sodium carbonate. Fuel **66**, 1150–1155 (1987)
13. Fang, Z., Minowa, T., Smith Jr, R.L., Ogi, T., Kozinski, J.A.: Liquefaction and gasification of cellulose with Na_2CO_3 and Ni in subcritical water at 350°C. Ind. Eng. Chem. Res. **43**, 2454–2463 (2004)
14. Karagoz, S., Bhaskar, T., Muto, A., Sakata Y.: Hydrothermal upgrading of biomass, effect of K_2CO_3 concentration and biomass/water ratio on products distribution. Bioresour. Technol. **97**, 90–98 (2006)
15. Xu, C., Lad, N.: Production of heavy oils with high caloric values by direct liquefaction of woody biomass in sub/near-critical water. Energy Fuels **22**, 635–642 (2008)
16. Yin, S., Dolan, R., Harris, M., Tan, Z.: Subcritical hydrothermal liquefaction of cattle manure to bio-oil: effects of conversion parameters on bio-oil yield and characterization of bio-oil. Bioresour. Technol. **101**, 3657–3664 (2010)
17. Zhang, B., Keitz, M.v., Valentas, K.: Thermal effects on hydrothermal biomass liquefaction. Appl. Biochem. Biotechnol. **147**, 143–150 (2008)
18. Demirbas, A.: Mechanisms of liquefaction and pyrolysis reactions of biomass. Energy Convers. Manag. **41**, 633–646 (2000)
19. Appell, H.R.: The production of oil from wood waste. In: Anderson, L., Tilman, D.A. (eds.) Fuels from Waste, pp. 121–140. Academic Press, New York (1967)
20. Theegala, C.S., Midgett, J.: Hydrothermal liquefaction of separated dairy manure for production of bio-oils with simultaneous waste treatment. Bioresour. Technol. **107**, 456–463 (2012)
21. APHA, AWWA, WPCF: Standard Methods: for the Examination of Water and Wastewater, 21th edn. American Public Health Association, Washington, D.C. (2005)
22. Demirbas, A.: Yields of oil products from thermochemical biomass conversion processes. Energy Convers. Manag. **39**(7), 685–690 (1998)
23. Parr. 1108 Oxygen Bomb Instruction Manuel No 204 and 205. Parr
24. Karagoz, S., Bhaskar, T., Muto, A., Sakata, Y., Oshiki, T., Kishimoto, T.: Low-temperature catalytic hydrothermal treatment of wood biomass: analysis of liquid products. Chem. Eng. J. **108**(1–2), 127–137 (2005)
25. Goudriaan, F., van de Beld, B., Boerefijn, F., Bos, G., Naber, J., van der Wal, S., Zeevalkink, J.: Thermal efficiency of the HTU process for biomass liquefaction. In: Bridgwater, A. (ed.) Progress in Thermochemical Biomass Conversion, Tyrol, Austria, pp. 1312–1325. Blackwell, Oxford (2001)
26. Chornet, E., Overend, R.P.: Biomass liquefaction: an overview. In: Fundamentals of Thermochemical Biomass Conversion, pp. 967–1002. NewYork, Elsevier Applied Science, New York (1985)
27. Stephenson, A., McCaskey, T., Ruffin, B.: A survey of broiler litter composition and potential value as a nutrient resource. Biol. Wastes **34**, 1–9 (1990)