



Hydrothermal liquefaction of separated dairy manure for production of bio-oils with simultaneous waste treatment

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ARTICLE INFO

Article history:

Received 13 June 2011

Received in revised form 2 November 2011

Accepted 12 December 2011

Available online 21 December 2011

Keywords:

Thermochemical conversion

Dairy waste

Waste utilization

Biomass

Biooils

ABSTRACT

A bench scale hydrothermal liquefaction (HTL) system was tested using dairy manure to explore biooil production and waste treatment potential. Carbon monoxide was used as the process gas and sodium carbonate (Na_2CO_3) as catalyst. At a 350 °C process temperature, the HTL unit produced 3.45 g (± 0.21) of acetone soluble oil fractions (ASF), with an average Higher Heating Value of 32.16 (± 0.23) MJ kg⁻¹. A maximum ASF yield of 4.8 g was produced at a process temperature of 350 °C and 1 g of catalyst. The best ASF yield corresponded to 67.6% of energy contained in the raw manure. GC–MS analysis of ASF indicated that the highest quantities of phenolic compounds were formed when 1 g catalyst was used. Chemical Oxygen Demand (COD) reduction in the dischargeable slurry was as high as 75%. The results point to an alternative dairy waste treatment technology with a potential to generate transportable biooils.

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1. Introduction

Hydrothermal liquefaction (HTL), a widely researched thermochemical conversion process, also known as direct liquefaction, involves high temperature, increased pressure, and an oxygen deprived environment to produce oil and gas products from biomass feedstocks. The thermochemical liquefaction was first reported by Berl in 1940s (Berl, 1944), who suggested that cornstalks, corn cobs, sugar cane, bagasse, seaweed, algae, sawdust, Irish moss, molasses, sorghum, and grasses could be converted into petroleum-like products.

More recently, by heating spruce wood powder to 377 °C, an oil yield (wt.% of water, extractive and ash free oil) of 49% was achieved (Demirbas, 2005), and Higher Heating Values (HHV) of up to 34.9 MJ kg⁻¹ were obtained from beech wood. HTL converting microalgae in the presence of alkaline catalysts such as Na_2CO_3 have also been explored (Shuping et al., 2010; Biller and Ross, 2011) and HTL of swine waste was studied in some detail (He et al., 1998, 2000a,b, 2001a,b). Studies with the latter feedstock indicated that, contrary to earlier beliefs, reducing process gases (CO and H_2) are not crucial for oil production and both reducing and inert gases (CO_2 , N_2 , and compressed air) can be used as a process gas (He et al., 2001a). Despite these experimental results, the exact role and reaction mechanism of a process gas still remain to be elucidated.

The role of catalysts in HTL is also not well understood. It is known that carbonates and hydroxides of water soluble bases (sodium, calcium, and potassium) increase the production of oil (Yokoyama et al., 1987; Karagoz et al., 2004, 2006; Demirbas et al., 2005; Xu and Lad, 2008; Shuping et al., 2010; Biller and Ross, 2011) and a mechanism for carbonate-catalyzed liquefaction in the presence of CO has been proposed (Appell, 1967). However, oil production in the presence of other catalysts such as Ni , FeSO_4 , CH_3COOH , and HCOOH (Fang et al., 2004; Xu and Lad, 2008; Ross et al., 2010; Biller and Ross, 2011) and other process gases, especially inert and non-reducing gases has not been explained.

The overall objective of the present research was to identify a treatment process which has a potential to simultaneously generate value-added products (energy/biooils) from dairy manure. This feedstock is of interest because concentrated animal feeding operations (CAFOs), such as dairy industry, generate enormous quantities of wet manure (~8% of body weight per day), with water content as high as 88% (Burke, 2001). As the HTL process does not require dewatering or drying, energy efficiency advantages are possible (Peterson et al., 2008). The HTL process has a very versatile chemistry and can hydrothermally transform the components of the manure which typically contains 31% cellulose, 12% hemicellulose, 12.2% lignin, 12.5% starch, and 12.5% crude protein (Stafford et al., 1980). HTL delivers biooils with more desirable properties than those produced from fast pyrolysis. Compared to pyrolysis biooils, the HTL oils have lower oxygen (12% versus 36%) and moisture (5% versus 25%) contents. The HTL oils also have lesser quantities of undesirable polar organic compounds and have

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higher HHVs than pyrolysis oils (35.7 versus 22.6 MJ kg⁻¹) (Elliott and Schiefelbein, 1989).

The HTL process can also simultaneously treat the dairy wastes and completely sterilize the liquid wastes and inactivate biotoxins. As dairy manure contains numerous human and animal pathogens such as *Salmonella* spp., *Escherichia coli* O157:H7, *Listeria monocytogenes*, *Mycobacterium avium*, *Cryptosporidium parvum*, and *Giardia* spp. (Pell, 1997), the importance of complete sterilization cannot be overstated.

Specifically, the current study assessed the potential of HTL in converting separated dairy manure to biooils, determined the effect of Na₂CO₃ catalyst on the quantity and chemical make-up of biooil, and explored the potential of using HTL as a dairy waste treatment alternative.

2. Experimental

2.1. HTL processor

A bench top 300 ml stainless steel reaction pressure vessel from Autoclave Engineers (Erie, PA, USA) was used for HTL experiments. A schematic of the HTL processor is illustrated in Fig. 1. The vessel could be operated at extreme conditions of 350 °C and 38 MPa. Agitation was achieved using a magnetic drive coupled to a motor and controller with a propeller designed for liquid and gas mixing. Agitation speed of the propeller was maintained at a constant rate (200 RPM) throughout all experiments. Carbon monoxide (CO) was chosen as a process gas, because of its successful application in earlier studies (He et al., 2000a,b, 2001a,b). CO was introduced to the vessel through a high-pressure inlet valve and tubing. A cylindrical electric heater with an outer ceramic insulator/liner was used for heating the HTL unit. A temperature controller provided by Autoclave Engineers was used to control operating temperatures. The controller was equipped with a Proportional-Integral-Differential (PID) control and safety features to prevent overheating. Temperatures were maintained within 5 °C of set conditions. A stainless steel liner (a hollow cylindrical sleeve with a flat bottom) was used to allow for easy transfer of pre and post-processed slurries since

the vessel was not equipped with a drain port. DASyLab 9.0 software was used to log temperature and pressure during operation through the use of a Type-K thermocouple and a pressure transducer, connected to a USB based hardware system (Measurement Computing Corp., Norton, MA, USA). A water loop was installed for rapid cooling upon completion of the heating cycle. A pressure relief valve and rupture disc were used for safety reasons and to prevent damage to the vessel in case the temperatures or pressures exceeded the maximum rated values. The entire system was enclosed in a steel box with a hinge door. This metal enclosure provided an extra level of safety for the personnel working on the unit in case the rupture disc failed or the safety relief valve was triggered.

2.2. Feedstock preparation

Dairy manure was collected from the Louisiana State University AgCenter's on-campus Dairy. Manure flushed from concrete feeding paddocks was separated by an inclined gravity screen. The solid manure separated from the screen physically resembled wet, chopped-up straw. To minimize the variability in feedstock, manure was collected one time from the pile of separated solids. The collected manure was characterized for moisture content, volatile solids, and HHV, which were 84.3%, 83.2%, and 11.9 MJ kg⁻¹, respectively. The manure solids were dried at 105 °C to remove all moisture and then ground to a fine powder to ensure a homogeneous sample. Dry powdered manure was stored in freezer bags at 4 °C and was used as needed. The total and volatile solid contents of the manure were measured before loading it into the reaction vessel. Additionally, CHN (Carbon, Hydrogen, Nitrogen) and Inductive coupled plasma (ICP) analyses were done to determine nutrient content and elemental composition of feedstock before reaction. Based on this information, the HHV of the raw manure was computed. For each run, 80 ml of de-ionized water was added to 20 g (dry) of powered manure to bring the total solids to 20%. The resulting slurry was loaded into the stainless steel liner, which was lowered into the reaction vessel.

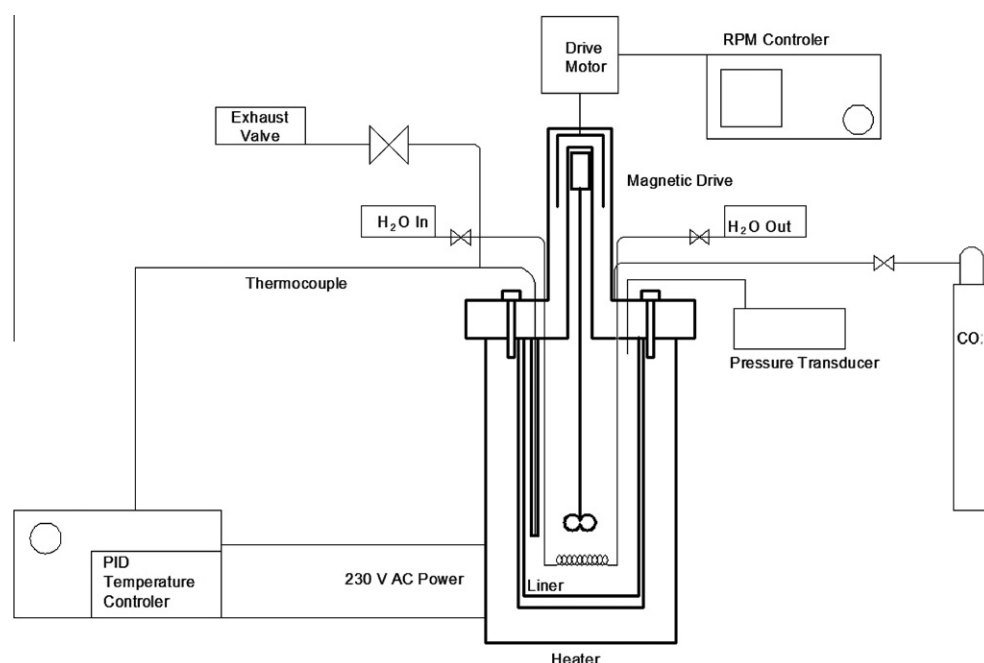


Fig. 1. A sketch of the 300 ml vessel used for hydrothermal liquefaction (HTL) experimentation is shown. Also shown are a controller, propeller, cooling loop, thermocouples, pressure transducer and valves.

2.3. Experimental procedure

In order to prevent gas leaks and contamination during the HTL process, all equipment and seals were thoroughly washed before each new trial. The dry manure, water, and catalyst (if needed) were first added to the stainless steel (SS) liner and mixed thoroughly. The pH was recorded and the SS liner containing the slurry mixture was placed into the vessel. The top of the vessel, containing the cooling loop, agitation drive, propeller, and thermowells was attached. Six bolts were then tightened in the specified sequence to the recommended torque. The vessel was purged continuously for 10 min with process gas (CO) to eliminate air. After passing a minimum of five vessel volumes or purge cycles the vessel was charged to the desired initial pressure (2.068 MPa) and tested for leaks using a spray of soapy solution. The CO lines were disconnected from the vessel after the initial charge. The thermocouples and pressure transducer were attached and the rpm of the propeller was set. The door for the safety metal enclosure was shut, and the vessel was then heated to the desired temperature for a set amount of time, after which the contents were rapidly cooled using the water cooling loop. Once the vessel temperature returned to the pre-run temperature, the process gas was collected, the vessel was opened, and its contents were processed.

2.4. Process parameters

The parameters that were studied for this research were operating temperature and catalyst quantity. The operating range was 250–350 °C, with corresponding pressures of 5.1–20.5 MPa. The catalyst used was anhydrous sodium carbonate (Na_2CO_3). Amounts of 0, 1, 2, 3 and 4 g of catalyst were tested with each operational temperature of 250, 275, 300, 325, and 350 °C, yielding a total of 25 experimental runs. Na_2CO_3 was used as a catalyst because it is one of the most widely used HTL catalyst (Demirbas, 1998, 2000; Fang et al., 2004; Ross et al., 2010; Biller and Ross, 2011). The loaded mixture had 20% total solids (TS), of which approximately 85% were volatile solids (VS). The retention time (RT, time material remained at set process temperature) for all experiments was 15 min. The 15-min retention time was based on results from prior research (He et al., 2000a). The initial pH of all slurries was recorded but was not controlled. The pH of raw manure in slurry (no catalyst) was approximately 6.5 and increased to 10.5 with the addition of 4 g of Na_2CO_3 to the slurry.

A separate reproducibility study was done in triplicate using the HTL setup. These experiments were conducted at 350 °C without any catalyst to evaluate the reproducibility of the HTL process and compute the statistical parameters.

2.5. Analysis

The total solid content was measured by ASTM E1756-01 (ASTM, Standard Test Method for Determination of Total Solids in Biomass). Volatile solids were measured according to ASTM E1755-01 (ASTM, Standard Method for the Determination of Ash in Biomass). 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 biooil and the heating content of gases is known to be insignificant (Goudriaan et al., 2001). The gaseous products were separated from the post-processed slurry through a gas relief valve immediately after the vessel returned to the initial temperature and the final pressure and temperature were recorded. The liner containing the post-processed water (solids and liquid) was removed from the vessel. The solid residue remaining after the reaction was composed of char, tar-like organic compounds, and non-volatile solids. The liquid included post-

processed water, very fine suspended solids passing the glass fiber filter, and water soluble hydrocarbons. Fig. 2 shows the protocol used to collect and quantify the produced oils. A 0.7- μm (pore size) glass fiber filter (Fisher Scientific, Pittsburgh, PA) was used to separate the solids from the post-processed water. The filtered water was combined with ACS grade ethyl ether anhydrous ($(\text{CH}_3\text{CH}_2)_2\text{O}$) in a 1:1 ratio. The mixture was thoroughly shaken for 2 min in a gravimetric funnel to allow for extraction of 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. The solids retained on the filter paper, liner, and cooling loop coils were mixed with 250 ml of ACS grade acetone to extract oil-like compounds. After mixing using a magnetic stirrer for 15 min, the acetone mixture was again filtered. The liquid passing the filter (0.7 μm pore size) was labeled as acetone soluble fraction (ASF). The remaining solids from the filter paper were named acetone insoluble fraction (AINF). The ASFs and AINFs were dried at 60 and 105 °C, respectively, to evaporate any remaining acetone or moisture. All fractions were allowed to dry in a desiccator for 24 h before gravimetric quantification. The AINF fraction was further tested for volatile solids by igniting at 550 °C. Carbon, hydrogen, and nitrogen (CHN) analysis were performed on all four fractions to determine heating values. A GC-MS and a National Institute of Standards and Technology (NIST) database was used to identify the individual compounds in the ASF. Chemical oxygen demand (COD) of the feedstock slurry and dischargeable end products were quantified to assess the waste treatment potential of the HTL process. The COD analyses were conducted as per Standard Methods 5220 (APHA, 2005).

2.6. Higher Heating Value computation and measurement

A modified Dulong's formula (Eq. (1)) (Demirbas et al., 1997) 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 weight percent of nitrogen is not used as a factor in this formula; it is only used to determine oxygen content. Table 1 shows sample CHN values and calculated HHV for the temperature runs using 2 g of catalyst:

$$\text{Higher Heating Value (MJ kg}^{-1}\text{)} = \frac{33.5 \times \text{wt.\%C}}{100} + \frac{142.3 \times \text{wt.\%H}}{100} - \frac{15.4 \times \text{wt.\%O}}{100} \quad (1)$$

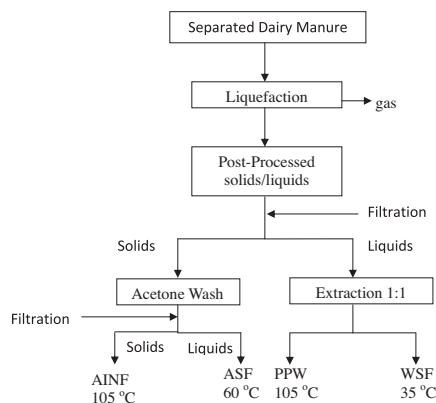


Fig. 2. Protocol used for separation and quantification of oil products. The final products include: AINF (Acetone Insoluble Fraction dried at 105 °C), ASF (Acetone Soluble Fraction dried at 60 °C), PPW (Post-Processed Water dried at 105 °C), and WSF (Water Soluble Fraction dried at 35 °C).

Table 1

Carbon, Hydrogen, Nitrogen (CHN) values for 2 g catalyst runs and their calculated Higher Heating Values (HHVs) (using modified Dulong's formula).

Temperature (°C)	Catalyst (g)	% C	% H	% N	% O ^a	HHV (MJ kg ⁻¹)
250	2	62.6	6.4	2.6	28.4	25.8
275	2	69.3	6.8	2.5	21.4	29.7
300	2	68.4	7.0	2.4	22.3	29.4
325	2	72.1	7.1	2.5	18.3	31.4
350	2	75.1	8.2	2.7	14.1	34.7

^a Calculated as the remainder from CHN.

For the reproducibility study, a 1341 Parr Oxygen Bomb Calorimeter assembly was used to measure the HHV of the ASF fraction for comparison to the theoretical values obtained by CHN analysis and modified Dulong's formula (Eq. (1)). The calorimeter was operated according to Parr manuals (Parr, No. 204 and 205).

3. Results and discussion

3.1. Temperature effect

Operating temperature is one of the primary control parameters of the HTL process. Temperature indirectly controls pressure of the closed system by properties of thermodynamics, corresponding to partial pressures of the mixture. Shown in Fig. 3 is a sample of the temperature and pressure data recorded from one trial. The increase in pressure (initial versus final) confirms that the process produces a gaseous product. Fig. 4 depicts the effect of process temperature on HHV and total energy content contained in the ASF at 0 g catalyst quantity. The total energy content (kJ) is computed by multiplying the HHV (kJ g⁻¹) with the corresponding mass of ASF (g). The HHV increased with an increase in processing temperature. However, the total energy content fluctuated, with a peak at 350 °C. From Table 2 (at 0 g catalyst), it can be seen that mass of the ASF had an increasing trend of 3.2–3.8 g between 250 and 350 °C. However, there was a drop in the mass of ASF at 325 °C. Xu and Lad (2008) experienced an initial increase in heavy oil mass (equivalent to ASF) up to 300 °C, followed by a continuous drop till 380 °C on their liquefaction runs without the presence of catalyst. They suggested that the drop was due to enhanced cracking and dehydration reactions (to form gases and water) and condensation reactions (to yield more solid products or char) at higher temperatures. Qu et al. (2003) who tested heavy oil yield between 280 and 360 °C, also experienced a similar trend. They indicated

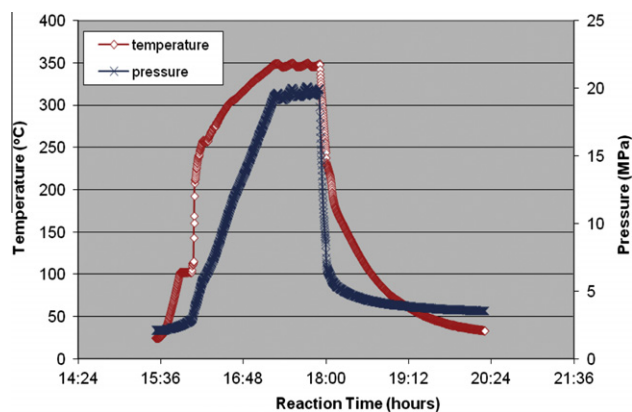


Fig. 3. Temperature and pressure response for 350 °C and 3 g of sodium carbonate catalyst. The initial, maximum, and final temperatures and pressures are shown (24.7, 348.5, 33.1) °C and (2.1, 20.0, 3.5) MPa, respectively.

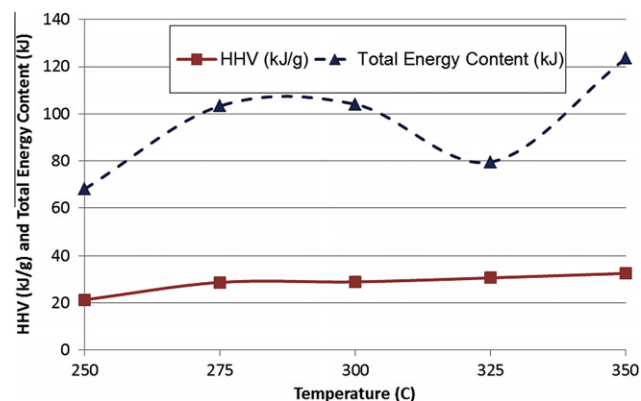


Fig. 4. Effect of process temperature on Higher Heating Value (HHV) and total energy content contained in the Acetone Soluble Fraction (ASF) at 0 g of catalyst. The operating conditions were initial CO pressure of 2.1 MPa, TS = 20%, and RT = 15 min. The corresponding pressures were 5.1–20.5 MPa.

Table 2

Effect of temperature and catalyst quantity on Acetone Soluble Fraction (ASF) mass and Higher Heating Value (HHV).

Temperature (°C)	Catalyst (g)	ASF (g)	HV (MJ kg ⁻¹)
250	0	3.2	21.3
250	1	3.8	21.8
250	2	3.1	25.8
250	3	3.8	19.0
250	4	4.2	21.6
275	0	3.6	28.7
275	1	3.4	29.4
275	2	4.0	29.7
275	3	3.5	24.5
275	4	3.2	27.5
300	0	3.6	28.9
300	1	4.5	30.0
300	2	3.4	29.4
300	3	3.4	29.5
300	4	3.1	29.9
325	0	2.6	30.6
325	1	4.0	28.5
325	2	3.5	31.4
325	3	3.7	33.4
325	4	4.2	32.5
350	0	3.8	32.5
350	1	4.8	33.5
350	2	4.4	34.7
350	3	3.4	33.4
350	4	4.3	33.0

that the initial increase in oil yield, followed by decreasing yield was due to two competing reactions involved in liquefaction, namely hydrolysis and repolymerization. They reported a peak yield between 320 and 340 °C for their test conditions. Despite a small variability, from a statistical stance, they indicated that the variation in heavy oil yield was not significant in the temperature range of 280–360 °C. The reason for the second increase in our ASF yields at 350 °C is not clearly understood. This high value (3.8 g) cannot be considered as an outlier as similar increases were noticed for several runs with different catalyst quantities (Table 2). One possible explanation for the double peak is the variability in feedstock. Zhang et al. (2008), who looked into thermal effects on the hydrothermal liquefaction process, concluded that the liquid product composition was linked to feedstock type more than to heating rate. With swine manure, a steep increase in oil yield was noticed around 280–285 °C; however, the oil yield remained almost steady thereafter (till 350 °C) (He et al., 2000a).

Despite setting the propeller exactly at 200 rpm and minimizing other process variations (except temperature), the end products had different consistencies including moisture content and texture (data not shown). It is not clear if the mixing patterns were similar inside the liner holding the wet biomass for all temperature runs. For example, a stuck propeller (or partially stuck propeller) is not visible from outside as the external magnetic drive pulley rotates at the set rpm, irrespective of the internal shaft rpm (due to magnetic drive slipping). Explanations for the observed double peak will have to await repetition of experiments using a larger high pressure vessel with large quantities of biomass, and preferably with some advanced sensors to monitor the mixing patterns inside the sleeve holding the biomass slurry. Larger sample sizes are anticipated to lower the variability introduced during the cleaning, collecting, and quantification.

Fig. 4 also shows the HHV (kJ g^{-1}) of ASF produced at different temperatures. It can be concluded that the HHVs gradually increased with increasing process temperatures. Demirbas (2005) also found a steady increase in HHV of acetone soluble fraction from 27.6 MJ kg^{-1} at 550°F (287.7°C) to 34.9 MJ kg^{-1} at 650°F (343.3°C). Despite the gradual increase in HHV, the total energy content in ASF (in Fig. 4) is linked primarily to the mass of ASF (Table 2, 0 g catalyst).

3.2. Catalyst effects

Table 3 shows quantities of ASF, PPW, AINF and ASF for trials conducted at 350°C with varying catalyst amounts. The added catalyst ended up in the PPW, which was evidenced by increasing PPW amounts with increasing catalysts amounts. The HHV of the ASFs for all five experiments conducted at 350°C (using 0–4 g catalyst quantities) were in the range of $32.5\text{--}34.7 \text{ MJ kg}^{-1}$ (Table 2). These values are in line with the 35.53 MJ kg^{-1} HHVs obtained for biooil produced from cattle manure (Yin et al., 2010). Table 2 also shows the catalyst quantities, HHVs, and ASF quantities. The ASF masses at 350°C varied between 3.4 and 4.8 g for the five catalyst quantities, with the highest value of 4.8 g resulting from the 1 g catalyst run (Table 2). Although similar variations in the recovered ASF mass were noticed at other reaction temperatures, there was no particular trend from 250 to 325°C . However, at 350°C , the average ASF quantity recovered was 4.14 g, compared to an average of 3.59 g from all other experiments at lower temperatures. The only pattern that is evident (although not 100% of the time) from the catalyst runs appears to be the initial increase in ASF masses from 0 to 1 g usage at or above 300°C , followed by a decrease in ASF quantities at higher catalyst amounts. As the WSF quantities are relatively small ($<0.25 \text{ g}$), it is assumed that the ASF fraction is the primary energy containing end product from the HTL process. This assumption is in line with Goudriaan et al. (2001) who looked into the heating content partitioning between bio-crude, aqueous organics, and combustible gases. From an energy content point-of-view, the best run (350°C , 1 g catalyst) yielded 4.8 g of ASF with a HHV of 33.5 MJ kg^{-1} . This relates to 67.6% energy conversion efficiency, when compared to the energy

content contained in the initial 20 g of manure (with a HHV of 11.9 MJ kg^{-1}).

The total energy content (g of ASF fraction multiplied by the corresponding HHV) in the ASF fraction for all the 25 catalyst runs are shown in Fig. 5. A catalyst amount of 1 g produced the highest energy at most temperatures (325°C being an exception). The uniqueness of the results from 1 g catalyst is likely due to a multitude of complex and intertwined processes. Alkali catalysts, such as sodium or potassium carbonate, can act as catalysts for hydrolysis of cellulose and hemicellulose macromolecules into smaller fragments (Chornet and Overend, 1985). 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 (Chornet and Overend, 1985). Russell et al. (1983) reported formation of aromatic compounds when cellulose was thermochemically converted in alkali solution. They suggested that the unstable intermediate compounds were converted to aromatic compounds by condensation and cyclization.

For the 350°C run, addition of catalyst higher than 1 g had a detrimental effect on the HHV of ASFs. To better understand the role of the catalyst, all ASF fractions at all catalyst quantities for the 350°C runs were analyzed using GC–MS. Table 4 compares the relative concentrations of 30 compounds with the largest peak areas of the chromatograms. ASF resulting from the dairy manure contained a mix of phenolic- and lipid-derived compounds, similar to those obtained by Vardon et al. (2011) and Xiu et al. (2010). The GC–MS analysis revealed that the most abundant compounds were phenols (35–47%). The phenolic compounds are likely derived from the carbohydrate and protein fractions, which have been identified during the HTL degradation of lignin (Demirbas, 2000) and protein compounds (Biller and Ross, 2011). Similarly, the fatty acids (4–27%) are likely derived from the crude lipid fraction, with fatty acids being observed during the decomposition of triglycerides under HTL conditions (Peterson et al., 2008; Biller and Ross, 2011).

With the exception of the sample treated at 275°C , the ASF total energy increased from 0 to 1 g of catalyst (Fig. 5). Compared to 0 g catalyst, the ASF yield increased by 20.8% with the use of 1 g catalyst at 350°C . This result was also evidenced by similar increases in total peak areas for all the compounds identified in the GC–MS chromatograms. Ogi et al. (1985) have reported that biooil yield decreased by 22.2 wt.% without any alkaline catalysts. However, increasing the catalyst amount beyond 1 g has no beneficial effect.

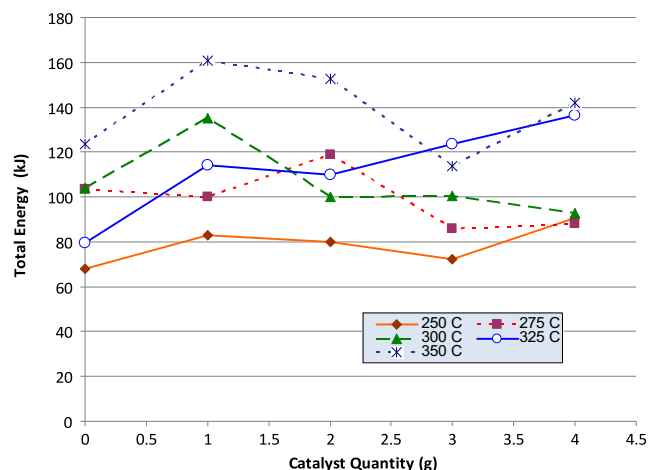


Fig. 5. The effect of temperature and catalyst quantity on the total energy partitioned to ASF. The total energy content was computed by multiplying the mass of ASF (g) with its corresponding Higher Heating Value (HHV) (kJ/g).

Table 3

Quantities of Acetone Soluble Fraction (ASF), Water Soluble Fraction (WSF), Post-Processed Water (PPW) and Acetone Insoluble Fraction (AINF) collected from experiments conducted at 350°C and 0, 1, 2, 3 and 4 g of sodium carbonate.

Catalyst (g)	WSF (g)	PPW (g)	AINF (g)	ASF (g)
0	0.33	1.38	6.67	3.77
1	0.29	2.21	4.72	4.76
2	0.17	3.48	5.00	4.40
3	0.11	3.93	5.00	3.42
4	0.14	5.87	5.47	4.34

Table 4

Top 30 compounds with the largest peak areas in the GC–MS chromatogram of Acetone Soluble Fractions (ASFs) generated at different catalyst quantities.

RT	Library/ID	CAS	Area				
			0 g	1 g	2 g	3 g	4 g
11.94	2-Nonene, (E) -	006434-78-2					2.45
12.14	Phenol	000108-95-2					2.87
13.24	2-Cyclopenten-1-one, 2,3-dimethyl	001121-05-7	1.93	3.05	1.81	2.7	3.27
14.83	2-Cyclopenten-1-one, 2,3,4-trimethyl	028790-86-5	1.9	4.01	0.13	2.02	2.89
15.11	Phenol, 4-methyl-	000106-44-5	12.61			2.94	2.46
17.40	Phenol, 4-ethyl-	000123-07-9		17.84	3.44	2.46	
17.45	Phenol, 4-ethyl-	000123-07-9			3.84	5.8	
17.73	Phenol, 4-ethyl-	000123-07-9		2.72	3.69		5.09
17.79	3-Heptyne, 5-methyl	061228-09-9				2.79	
17.81	Phenol, 3-ethyl-	000620-17-7		3.39	4.36		4.36
17.96	1,3-Cyclopentadiene, 1,2,5,5-tetramethyl	004249-12-1					5.15
18.03	Phenol, 2-methoxy-4-methyl	000093-51-6	1.56				
18.24	Cyclohexane, 1,3-dimethyl-2-methylene-, trans-	020348-74-7					2.75
19.45	Phenol, 2-ethyl-5-methyl-	001687-61-2		2.25		2.9	
20.04	Naphthalene, 2,7-bis(1,1-dimethylethyl)-	010275-58-8	2.77	4.64	4.24		2.35
20.05	2,3-Dimethylanisole	002944-49-2		2.93		2.44	
20.46	Phenol, 4-ethyl-2-methoxy-	002785-89-9	5.83				
22.38	Pyrazine, 2-methyl-3-(2-propenyl)-	055044-96-7		1.11	2.16		
22.49	Methanone, [4-(1,1-dimethylethyl)phenyl]([4-hydroxyphenyl]-	020294-32-0	1.86	1.24	2.32		
23.51	Ethanone, 1- (2,4-dimethylphenyl)-	000089-74-7	1.67	1.95	2.33	2.18	
24.55	Benzoic acid, 2,4-dimethyl-, (3,5-dimethylphenyl) methyl ester	055000-45-8	1.99	4.31	5.24	2.66	
26.34	4,5-Dimethyl-3H-isobenzofuran-1-on	1000188-08-0			2.62		
38.91	n-Hexadecanoic acid	000057-10-3	7.27				
22.12	Benzaldehyde	69770-23-6				0.55	0.77
22.49	Benzaldehyde	69770-23-7			2.32	1.52	2.14
24.55	Benzoic acid, 2,4-dimethyl-, (3,5-dimethylphenyl) methyl ester	055000-45-8					1.98
37.96	Hexadecanoic acid methyl ester	000112-39-0	1.23	1.42	0.76	0.33	1.01
41.99	Octadecanoic acid methyl ester	000112-61-8	1.14	1.3	0.64	0.41	1.16
43.08	Hexadecanoic acid butyl ester	000111-06-8	0.35	0.32	–	0.24	0.75
46.53	Octadecanoic acid butyl ester	000123-95-5	0.28	0.54	0.22	0.36	1.27
	Total		42.39	53.02	40.12	32.3	42.72
	Total phenols (% area)		20	23.95	15.33	11.2	14.78
	Total phenols (% of total area)		47%	45%	38%	35%	35%
	Fatty acids (% area)		10.27	3.58	1.62	1.34	4.19
	Total fatty acids (% of total area)		24%	7%	4%	4%	10%

The lower conversion efficiency experienced at higher catalyst quantities may be attributable to changes in process conditions or thermochemical and physical properties of organic and inorganic compounds. For instance, as the temperature increases from subcritical to supercritical temperatures, the water density can drop two orders of magnitude and can affect solvation power, degree of hydrogen bonding, polarity, dielectric strength, molecular diffusivity and viscosity (Peterson et al., 2008; Harvey and Friend, 2004). The excess salts may become insoluble, precipitate and interfere with the mixing inside the liner holding the biomass slurry. Fatty acids were reported to degrade in hydrothermal systems producing long-chained hydrocarbons (Watanabe et al., 2006). However, with addition of NaOH or KOH, decomposition increased significantly producing alkanes (Watanabe et al., 2006). In the current study, addition of Na₂CO₃ reduced the fatty acids yield.

Phenolic compounds which dominated the GC–MS spectra showed a marked increase in peak areas at 1 g catalyst when compared to the other catalyst loadings. Xiu et al. (2010) reported significant concentrations of phenols and its derivatives during hydrothermal co-liquefaction of swine manure and glycerol with base catalyst. Since recovery at the end of the process is an issue for homogenous catalysts, selecting the lowest catalyst quantity with the best conversion efficiency is the most logical approach. Based on the results obtained from the present study, it appears that 1 g of catalyst and a process temperature of 350 °C are optimum for converting dairy manure to biooils using the HTL process.

3.3. Reproducibility study

Results indicate that 3.45 g (±0.21) of ASF and 0.26 g (±0.05) of WSF were produced. The HHV for each of these ASFs were 32.16

(±0.24) and 24.96 (±0.19) MJ kg^{−1}, respectively. The HHVs for the WSF varied in a narrow range of 24.75–25.08 MJ kg^{−1}. The bomb analysis confirmed that the theoretical HHVs obtained by using the modified Dulong's formula (32.16 ± 0.23 MJ kg^{−1}) were consistent with bomb calorimetric analysis (32.30 ± 0.64 MJ kg^{−1}). The reproducibility study indicated that the ASF data from the HTL process were statistically valid, as indicated by low standard deviation and coefficient of variation (Tables 5 and 6). Results from the reproducibility study were also used to compute the partitioning of the energy contained in the feedstock to various energy products (ASF, WSF, PPW) (Fig. 6). The energy content imparted to the gaseous phase and energy lost due to mass losses (during the separation/quantification protocol, Fig. 2) were pooled and represented as “unaccounted”. The unaccounted portion is computed by difference. For comparison, the energy partitioning from the best HTL run (350 °C at 1 g catalyst) and values reported by Goudriaan et al. (2001) were also included in this figure. It is evident that the primary energy product from the HTL process is the acetone soluble fraction. By altering the HTL process conditions it is possible to maximize the energy partitioning to ASF.

3.4. Waste reduction

COD testing was conducted from two separate samples from the main batch of manure. The averaged COD for 20 g-dry dairy waste in 80 ml of de-ionized water (same concentration used in HTL vessel) was 74,914 mg/l. Only the PPW and AINF fractions of the post-processed slurry were measured for COD because they should be the only discharged/discarded portions. COD reduction varied from 54% to 75% with an average value of 62%. Improved extraction procedures and/or higher conversion to ASF and WSF would lead to an

Table 5

Results of the reproducibility experiment conducted at 350 °C with no catalyst.

Trial #	AINF (g)	ASF (g)	PPW (g)	WSF(g)	HHV of ASF (MJ kg ⁻¹)	HHV of WSF (MJ kg ⁻¹)
1	7.26	3.25	1.04	0.30	32.02	25.08
2	7.12	3.44	0.68	0.20	32.04	24.75
3	6.80	3.67	0.96	0.29	32.42	25.06
AVG	7.06	3.45	0.89	0.26	32.16	24.96
STDEV	0.24	0.21	0.19	0.06	0.23	0.19
CV	3.34%	6.09%	21.16%	20.91%	0.70%	0.74%

Table 6Bomb calorimeter Higher Heating Values (HHVs) obtained from the triplicate reproducibility study of Acetone Soluble Fractions (ASFs) compared to HHVs obtained by calculating theoretical values from the modified Dulong's formula (Eq. (1)). All values are shown in units of MJ kg⁻¹.

Trial #	ASF bomb run 1	ASF bomb run 2	ASF bomb run 3	Averaged values (Bomb)	Calculated values (Dulong)
1	52.62 ^a	31.71	30.83	31.27	32.02
2	32.82	34.00	31.79	32.87	32.04
3	32.04	33.33	32.95	32.77	32.42
AVG	x	33.01	31.86	32.30	32.16
STDEV	x	1.18	1.06	0.64	0.23
CV	x	3.57%	3.33%	1.98%	0.70%

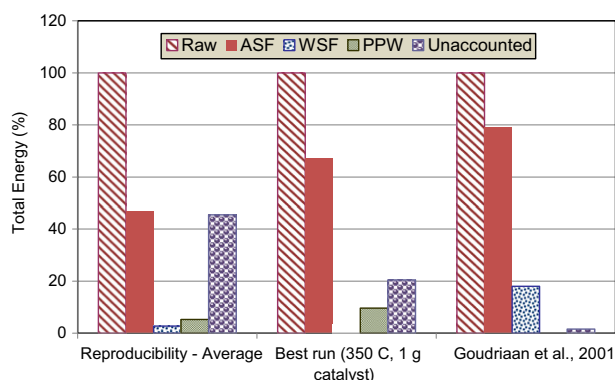
^a This run was not included in the averaged values.

Fig. 6. Partitioning of energy contained in the original feedstock to various energy end products (Acetone Soluble Fraction – ASF, Water Soluble Fraction – WSF, Post-Processed Water – PPW). The energy content imparted to the gaseous phase and energy lost due to mass losses (during the separation/quantification protocol, Fig. 2) were all pooled and represented as “unaccounted”. The unaccounted portion is computed by difference.

increase in the COD reduction percentages, thus improving the waste treatment potential of the process. Apart from major COD reductions due to HTL's extreme temperatures (which are much higher than a traditional sterilization autoclave temperature of ~121 °C), total sterilization in the post-processed water is possible.

4. Conclusions

The HTL process was successful in converting raw dairy manure into biooils, with energy conversion efficiencies as high as 67.8%. The process simultaneously lowered the COD in the dischargeable waters on average by 62%. Although not proven at a field-scale, the HTL process can be viewed as a practical alternative to anaerobic digestion, which primarily produces methane gas. The production of liquid end-products from the HTL process offers additional benefits in fuel portability and off-site usage. Future work should focus on gaining better understanding of HTL reactions and on development of continuous-flow systems with energy recovery features.

Acknowledgements

We thank LSU AgCenter's Callegari Environmental Center and the Environmental Sciences Department at LSU for analytical support. Special thanks are extended to Mr. Javed Iqbal for his assistance on elemental analysis and interpretation of GC–MS results and Ms. Buffy Meyer for GC–MS analyses and for compound identification using NIST database. Funding for this research was provided by the Department of Biological Engineering at LSU and a research grant from USDA/CSREES.

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