Pyrolysis of Energy Cane Bagasse and Invasive Chinese Tallow Tree (*Triadica Sebifera L.*) Biomass in an Inductively Heated Reactor

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ABSTRACT

The growing demand for energy and the increasing opposition to fossil fuels has given rise to the need for alternative fuels. The pyrolysis process is one viable option that converts lignocellulosic biomass into a liquid fuel. This study focuses, for the first time, on the use of an induction heating mechanism to pyrolyze biomass from energy cane (Saccharum complex) bagasse and invasive Chinese Tallow trees (Triadica sebifera L.). Energy cane and Tallow wood were pyrolyzed at 500, 550, 600, 650, and 700 °C at atmospheric pressure in a laboratory scale batch process with an initial loading of 15 g and 30 g for energy cane bagasse and CTT respectively. The results indicate that the highest liquid yield was obtained at 500 °C for both biomasses. The yields of char declined and the gas yields increased as the reaction temperature increased, as the biomass was more thoroughly decomposed at the higher reaction temperatures. GC-MS results show that the liquid product was rich in oxygenated compounds such as phenols, ketones and alcohols for biomasses at all temperatures. Bio-oil obtained from pyrolysis of Chinese tallow tree showed small concentration of fatty alcohols. Concentration of smaller compounds in the liquid product increased as the reaction temperature increased. Highest energy content and liquid yields (34 MJ/kg and 35.4 %) amongst the tested temperatures was obtained at 500 °C for both energy cane and tallow wood pyrolysis. Higher heating values were obtained for bio-oil from energy cane compared to tallow tree biomass.

Keywords: Biomass pyrolysis, Induction heating, Energy cane, Chinese tallow tree, Biofuel

1. Introduction

As the world's supply of fossil fuels continues to dwindle, and with large portions of these supplies located in politically unstable regions a strong interest has emerged in developing and utilizing alternative renewable energy resources. [1,2] Biomass can be used to produce biofuel using thermochemical treatments such as combustion, hydrothermal liquefaction, pyrolysis and gasification [3]. Each of these treatment methods are used for different reasons depending on the desired products and the available feedstock. Combustion involves burning the biomass in order to produce heat, which can then be used for a number of industrial processes [4]. Hydrothermal liquefaction and pyrolysis operate in an oxygen free environment to produce mostly a liquid product known as bio-oil [5]. While liquefaction uses high pressures (5 – 25 MPa) and moderate temperatures (250 – 550 °C)[6], pyrolysis is operated at higher temperatures (300 – 700 °C) but at atmospheric pressure to produce bio-oil.[3] . Gasification uses high temperatures (800 – 1000 °C) in a starved oxygen environment to mostly produce a combustible gas product.[7] Other methods including biomass and waste gasification [8] along with catalytic Fischer-Tropsch's reaction for gas to liquid fuel and direct liquefaction by solvolysis [9] has been recently developed however these processes involve high cost. Pyrolysis is one of the competitive methods for the production of transportation biofuel and has seen numerous recent advances in terms of bio-oil upgrading. [10]

To achieve high yields in a pyrolysis reactor, certain operating conditions need to be met: rapid heating rates, rapid transfer of heat to the biomass, precise control of the reactor temperature, low residence times for the pyrolysis vapors, and the rapid cooling of the pyrolysis vapors [3, 11]. While the most commonly used method for fast pyrolysis of biomass for high liquid yields is the fluidized bed reactor, this system uses a great quantity of carrier gas, typically nitrogen, and also

81 requires that a volume of carrier material (typically sand) be heated with the only purpose
82 increasing the heat transfer surface area [3]. By eliminating the carrier material from the process it
83 would allow for a reduced energy consumption and an increase in overall process efficiency.
84 Microwave pyrolysis would allow for the biomass to be heated directly[12], but there are certain
85 limitations associated with the use microwave heating. The most common problem is associated
86 with the fact that the majority of lignocellulosic biomasses have poor dielectric properties that
87 only allow a small fraction of the microwaves energy to be converted into heat [13]. Nonetheless,
88 this problem is, to certain extent, mitigated by the initial moisture content of the biomass as well
89 as by water produced during the reaction. Other techniques such as mixing char or other
90 microwave absorbing additives with biomass has also found to address this process limitation.
91 This work pursues another electromagnetic based method that directly heats the reactor chamber
92 walls via induction. This heating configuration allows for the biomass to be heated through
93 surface-to-surface conduction, which allows for rapid and more efficient transfer of heat from the
94 reactor to the biomass. Induction heating uses an alternating current through a conductive coil to
95 generate an alternating magnetic field, which induces eddy currents within the ferromagnetic
96 pyrolysis chamber, generating heat. Induction heating offers several features that make it
97 appealing for the use of pyrolysis such as rapid heating rates, uniform temperatures, precise
98 temperature control and high process efficiency[14]. Induction heating can uniformly heat a fixed
99 bed reactor's metallic components, eliminating the need for heat transfer materials typically used
100 in the fluidized bed [3]. However there are certain disadvantages associated with this method such
101 as high cost and energy requirement, less interchangeability and flexibility for process
102 modification, and potential issues during scale up. More thorough study to optimize is novel
103 process is required. Few studies on biomass fast pyrolysis using induction heating were found in

104 the literature. Tsai, Lee, and Chang used induction heating for pyrolysis of rice husk to examine
105 the effect of different pyrolysis parameters on product yields and their chemical compositions[15].
106 Characterization of the bio-oil product revealed highly oxygenated compounds in the oil
107 resulting in low pH and low calorific value. The same group also demonstrated the use of
108 induction heating for pyrolysis of rice straw, sugarcane bagasse, and coconut shell with
109 maximum bio-oil yield of 50% [11]. The most recent paper published on using induction heating
110 for pyrolysis experiments was on the pyrolysis of Napier grass, a non-forage and potential
111 energy crop. Using the induction heating system from previous work [16], the grass was tested
112 using the following parameters: a pyrolysis temperature starting at room temperature and heating
113 to around 500 °C, heating rates of 50, 100, 150, and 200 °C min^{-1}, and a holding time of 1.0
114 minute. The liquid yields of the Napier grass pyrolysis ranged from 12 - 35 %, and had a similar
115 chemical composition as previous experiments with high concentrations of hydrophilic and
116 carbonyl structures resulting in low pH values. The study concludes that due to the high water
117 concentration and numerous oxygenated compounds present that further processing would be
118 necessary before the bio-oil could be used as a fuel source [17]. Another study employed induction
119 heating for pyrolysis and upgrading of Pinewood sawdust which studied the effect of different
120 catalyst to biomass ratios and catalyst bed temperatures and concluded that induction heating is
121 an effective method for catalytic upgrading of pyrolysis vapors.[18]
122 Another factor that determines the yields of the pyrolysis reaction is the composition of
123 biomass that is pyrolyzed [19],[20]. This study explored the use of energy cane (*Saccharum* complex)
124 and Chinese tallow tree (*Triadica sebifera L.*) wood as potential energy crop feedstocks for
125 pyrolysis systems. Energy cane is a high fiber sugar cane hybrid of commercial and wild sugar
126 cane varieties. The cane yields much higher tonnage of biomass per hectare due to the high fiber

content of the bagasse, but this comes at the cost of decreasing the yield of fermentable sugars[21]. However, if the extra fiber could be used to create liquid fuels through pyrolysis, then growing energy cane instead of more typical sugarcane varieties could become profitable due to the significantly higher biomass yield per hectare[22]. Chinese tallow tree is an invasive species, which do not require dedicated resources for production. This species has been proposed as a potential dedicated energy crop for the production of biodiesel due to its high oil seeds[23]; while the wood can be utilized as a feedstock for pyrolysis.

While literature on induction heating pyrolysis is limited, numerous papers have investigated the effect of pyrolysis temperature on the yield and composition of pyrolysis products. Choi et al. pyrolyzed bald cypress sawdust in a bubbling fluidized bed reactor to study different pyrolysis parameters on the product yields [24]. The authors attained a maximum bio-oil yield of 57% at 500 ºC, while temperatures above 500 ºC favored formation of non-condensable gases. In another study, Zhou, Lei, and Julson examined the effect of reaction temperature and time on product yields from microwave pyrolysis of switchgrass[25]. The authors proposed a model to predict product yields as a function of reaction temperature and time. Furthermore, they concluded that the composition of the pyrolysis products is dependent on reaction temperature and residence time. Amutio et al. pyrolyzed pinewood sawdust in a conical spouted bed reactor in the temperature range of 400-600 °C [26]. The highest bio-oil yield of 75% was measured at 500 °C. On-line product analysis via chromatographic methods confirmed variation in product composition with temperature. Phenolic compounds in the bio-oil were namely guiacols at low temperatures and catechols at high temperatures. Lighter fractions were formed at higher temperatures due to cracking reactions. Heating value and surface properties of the char product improved with increasing pyrolysis temperature.

The aim of this study was to determine the potential of energy cane bagasse and Chinese tallow tree wood as pyrolysis feedstocks, and to understand the behavior of their yields as a result of changing reaction temperature. The objective was to test the use of novel advanced induction heating reactor for fast pyrolysis of these biomasses. To our knowledge, this is the first ever study to report the pyrolysis of these biomasses using a novel induction heating reactor. Product analyses were performed including total product yields, Karl-Fischer titration, CHN elemental analysis, gas chromatography-mass spectrometry (GC-MS), and higher heating value (HHV) calculations from CHN analysis to obtain useful data for the optimization of an induction heating pyrolysis reactor.

2. Materials and Methods

2.1. Materials

Energy cane bagasse was obtained from the Audubon Sugar Institute (Louisiana State University, Gabriel, LA). The cane had already been processed for sugar extraction which involves grinding and crushing of the cane, and had been further processed to remove any excess saccharides by washing the bagasse in hot water. The Chinese tallow tree biomass feedstock was collected in October 2013 from local trees around Baton Rouge, LA, as residue after harvesting of the tallow tree seeds. The woody biomass portion was then separated from the seeds and leaf material leaving a mixed assortment of twigs and small branches. Once received, both biomasses were dried overnight at 105°C to remove excess moisture from the biomass. The dried biomass was then ground into a fine particle size between 0.5 mm and 1.0 mm intermediate diameter length, and stored in sealed plastic bags at – 20 °C to prevent moisture absorption.

The moisture content of the biomass was determined using an LJ16 Moisture Analyzer (Mettler Toledo, Switzerland). The moisture content of energy cane was found to be 1.93 % by weight, while that of CTT was determined to be 3.5 % by weight. The dried biomass was then stored in sealed plastic bags at – 20°C to prevent moisture absorption until pyrolysis experiments were carried out. The composition of energy cane was 43% cellulose, 24% hemicellulose and 22% lignin[27] and that of CTT wood was similar to other woody biomass (40-42% cellulose, 30-33% Lignin and 20-25% hemicellulose).[27] The calorific value measured (LHV) for energy cane and CTT was 15.38 and 15.73 MJ/kg.

2.2. Equipment

The pyrolysis system used for the pyrolysis of the energy cane was a low frequency induction heater (RDO Induction L.L.C., Washington, NJ), used to heat a stainless steel reaction tube, which held the biomass (Figure 1). The power output for the heater was controlled using an infrared Omega iR2C PID controller (Omega Engineering, Inc., Stamford, CT), which used a 4 – 20 mA control signal to adjust the output power of the induction heater to achieve and then maintain the desired reactor temperature. The power output of the induction heater was monitored and recorded to be used in the energy analysis calculations. The RDO induction heater was a low frequency model that operated in the ranges of 35 to 100 kHz, and used a power supply of 5kW. The reaction tube was a 310-stainless steel tri-clamp tube, which was 419mm length with inner and outer diameters of 34.4 and 38.1 mm respectively. With an outlet located 29.4 mm from the end attached to the inlet air flow and which had an internal diameter of 16.5 mm. The induction coil used was a ten loop rubber coated copper coil with an overall length of 285 mm and an inner diameter of 59 mm. The actual reaction area was within these copper coils

where the heat was generated. The biomass was compactly packed within this area and an auger was used to mix the reactor.

Nitrogen gas was used both to purge the oxygen from the system prior to pyrolysis and as a carrier gas to move the pyrolysis vapors out of the reactor and into the collection system to be condensed and collected. The system used to collect and condense the pyrolysis vapors utilized an electrostatic precipitator (ESP) and a collection flask suspended in an ice bath. The ESP was built in house and operated at a 15 kV power level using a Gamma High Voltage power supply (Gamma High Voltage Research, Ormond Beach, FL) to control the power. The condensate was collected into the collection flask placed in an ice bath. For condensation of compound, an important thermodynamic property, dew-point should be taken into account to get maximum condensate.[28] Since the dew-point of pyrolysis vapors is low, a low temperature (-20 C) condensation system is sometimes employed for liquid collection[29]. To increase the product selectivity, a series of condensation columns maintained at different temperatures is also employed.[30] The temperature ranges on these condensers vary from 115 °C to -20 °C.[30] However, use of ice bath is also a common practice for bio-oil condensation[31] and thus was used for these experiments as using low temperature liquid nitrogen or acetone bath may be unfeasible at larger scales. The temperature surrounding the ice bath varied between 4 °C to 7 °C. All non-condensable gases and pyrolysis vapors which escaped the ESP were passed through ethanol and water bubble filters to remove any remaining soluble compounds before the non-condensable gases were vented.

2.3 Preliminary experiments

A metallic thermocouple cannot be operated within an induction heater and hence, reliability on the surface temperature is inevitable. In order to test the temperature gradient

within the pyrolysis reactor, preliminary experiments were conducted to determine the actual temperature of the biomass within the reactor as compared to the readout temperature on the controller. 25 g of bio char was loaded in the reactor and compactly packed. Bio-char from prior initial experiments was used to avoid the formation of pyrolytic gases. The reactor was heated to 500 °C in an induction heater. Once the target temperature was achieved the induction heater was powered off and k-type thermocouples were inserted into the char sample. The temperature was measured at two different locations where the char samples were packed; near the reactor wall and at the center of the reactor. Since the reactor is metallic and not insulated, the rate of cooling is higher, hence the thermocouples were inserted immediately to insure steady state temperature measurement. The experiment was repeated for two other temperatures 600 °C and 650 °C. The temperature recorded by the thermocouple was recorded using a PicoLog temperature data logger (TC-08 data logger, Pico Technology, Tyler, TX) and compared to the readout from the infrared remote sensor to identify any differences. The difference in the two reading was less than ± 5 °C (<1%), thus it was assumed for all subsequent experiments that the biomass temperature had negligible difference from that of the outside pipe temperature recorded by the infrared remote sensor for the given setup.

The time required for a complete reaction for each respective temperature was determined for the energy cane by performing pyrolysis experiments for different time lengths, spanned at 10 min intervals, and weighing the char residue. A 25 g biomass sample was heated in the induction heater at a particular temperature. The temperature was maintained for ten minutes and then the system was allowed to cool. The weight of the bio-char residue was recorded. This was repeated until the change in weight of the char residue was negligible. The

239 time, at which the char weight remained unchanged from the previous experimental run, was
240 considered the time required for a complete reaction at a given temperature.
241
242 *2.4. Experimental procedure*
243 Dried and ground energy cane biomass was tested in the batch induction pyrolysis system
244 (Figure 1) using five different reactor bed temperatures: 500, 550, 600, 650, and 700 °C. The
245 tests were performed in triplicates. Due to the difference in density and fixed volume reactor, the
246 energy cane biomass was tested in 15 g sample sizes and the Chinese Tallow wood in 30 g
247 samples sizes (unlike for preliminary experiments where 25 g sample was used), which were
248 weighed and inserted into the reaction chamber. Accurate liquid yields were obtained by
249 weighing the collection flask before and after the experiments. The flask was attached to the T-
250 joint which connected the pyrolysis chamber to the ESP and the collection flask. The collection
251 flask was suspended in an ice bath and the system was sealed using silicon vacuum grease at the
252 joints. Nitrogen gas was then flowed through the sealed system for 20 minutes at a flow rate of 1
253 $L \cdot min^{-1}$ to purge the system of oxygen and create the inert environment needed for pyrolysis
254 reactions.
255 Once the system had been purged of air the induction heater was powered on. The time
256 required to complete the experiment was temperature dependent and was based off of
257 preliminary data generated from section 2.3. The reaction time data was interpolated to
258 determine the time necessary for the different intermediate pyrolysis temperatures. During the
259 pyrolysis process, bio-oil vapors were produced along with non-condensable gases. These vapors
260 were all removed from the reaction chamber by the nitrogen carrier gas and passed into the
261 collection system, where the ESP cause the majority of the liquid vapors to be attracted to and

collected at the grounded, condensing and falling into the collection flask. Non-condensable gases and what few bio-oil vapors remained uncollected passed from the ESP and into the ethanol and water bubble filters, where any soluble compounds were removed. A gas sample was then collected from the outlet hose and the remainder of the gases was vented. Once the experiment had run its course, the pyrolysis chamber was allowed to cool and the collection flask was weighed. The difference between the initial and final weight of the collection flask was the yield of the liquid bio-oil fraction, which was placed into glass bottles and stored at – 20 °C to reduce degradation and secondary reactions. The char was removed from the reaction chamber and weighed, determining the char yield for the pyrolysis experiment, and the remaining mass unaccounted for was assumed to be the gas fraction.

2.5. Characterization and analysis

The products of the pyrolysis of energy cane biomass were analyzed to determine the characteristics of the char, liquid, and gas fractions. The solid char samples were analyzed for CHN content using a 2400 Series 2 CHNS/O elemental analyzer (Perkins Elmer, Inc., Waltham, MA). A 4 mg bio-char sample was weighed out and sealed in tin thimbles, which were then loaded into the machine for analysis.

The liquid fraction was analyzed using three different analysis techniques: Karl Fischer titrations to determine water content, CHN elemental analysis, and GC-MS. The Karl Fischer titration was performed in a Coulometric titrator (Karl Fischer titrator Metrohn Model 831 KF Coulometer, Riverview, FL), which gives the water content of the liquid samples on a percent mass basis. CHN analysis was performed on the liquid samples using the same device that was used for the CHN analysis of the bio-char. The sample preparation for the liquid samples differed from the char preparation, with glass-wool filter paper added to the bottom of the tin sample

286 thimbles to absorb the liquid and reduce sample evaporation. The liquid was well agitated and
287 4 μL of the bio-oil was placed onto the filter paper; the tin was then folded closed and the mass
288 of the liquid was recorded. The sample was then processed in the elemental analyzer and the
289 results were recorded.

290 The GC-MS of the liquid samples were performed to quantify the different compound
291 groups and their relative occurrence in the liquid samples, using a DCM extraction (5:1 V:V
292 ration DCM to bio-oil). The DCM-extracted samples were injected into a Varian Saturn 2200
293 GC-MS (Agilent Technologies, Santa Clara, CA). The operating conditions for the GC using a
294 DB-5 column with a flow rate of 1.0 $mL \cdot min^{-1}$were; the initial oven temperature was 40 °C
295 which was held for 6 minutes, then was heated at a rate of 4 $°C \cdot min^{-1}$ until a temperature of 240
296 °C was achieved, and then it was heated again at a rate of 20 $°C \cdot min^{-1}$ until the system was at
297 280 °C, for a total for 73 minutes per sample. The resulting GC plots were then analyzed to
298 identify compounds and their peak areas were integrated. The areas of different compound
299 groups were compared to determine their relative presence. The water soluble compounds were
300 not analyzed for composition due to laboratory limitations. These non-identified compounds may
301 include acids, ketones, alcohols, aldehydes and sugars.[32] Gas samples were analyzed with a SRI
302 8610C GC-MS (SRI Instruments, Torrance, CA) to determine the production of gases including:
303 CO, CO_2, and CH_4 which was used to determine the energy content of the gas products.

304 *2.6. Energy content*

305 The high heating value of char and liquid products from both biomasses was calculated
306 using the equation below. The CHNO content of bio-oil and bio-char was analyzed using Perkin
307 Elmer 2100 series elemental analyzer. The high heating value of gaseous product was not
308 calculated due to laboratory limitations. The energy content of the liquid and char products was

309 determined by the equation presented by Scholze and Meier (2001) which computes the higher
310 heating value (HHV) of the liquid product using the CHN analysis and Dulong's formula [33]:

311 $$\text{HHV(MJ/kg)} = \left[338.2 * C\ \% + 1442.8 * \left(H\ \% - \frac{O\ \%}{8}\right)\right] * 0.001$$

312

313 **3. Results and Discussion**

314 *3.1. Product yields*

315 The yields for energy cane and Chinese Tallow tree wood pyrolysis for the three
316 products, char, liquids, and gases, were studied to determine the behavior of the yields as the
317 reaction temperature for the pyrolysis experiments changed (Figure 2).

318 *3.1.1. Char Yields*

319 For the pyrolysis of energy cane (Figure 2a) char yields show a negative trend as the
320 reaction temperature increases from 25.5 % at 500 °C to 19.1 % at 700 °C, a net change of 6.4
321 %. The majority of the mass reduction occurs at lower temperatures, with a loss of 4.9 % of the
322 yield between 500 °C and 600 °C and the remaining 1.6 % yield loss occurring between 600 °C
323 and 700 °C (with only 0.5 % being lost in the final 50 °C temperature increase). These results are
324 consistent with results reported in the literature[11, 18, 34] which showed the majority of biomass
325 reduction to bio-char occurs in the initial stages of the pyrolysis reaction. Biomass thermal
326 degradation starts at lower temperatures of 300 °C, where cellulose is first broken down followed
327 by hemicellulose and lignin as the temperature increases. The degradation of cellulose is
328 governed by two important reactions; decomposition at lower temperatures up to 575 °C which
329 includes dehydration and charring and rapid volatilization at higher temperatures such as
330 cracking.[35] At lower temperature, a more stable anhydrosugars are formed and yields higher char
331 yields; thus, high char yields are achieved at lower reaction temperatures. At higher

temperatures, polymerization of cellulose and other components forms volatile products, decreasing the char yields. For fast pyrolysis, high heating rates suppresses the high char forming dehydration reaction and volatilization reaction is more dominant,[35] thus majority of char yield occurs at lower temperatures.

For the Chinese Tallow tree wood (Figure 2b), the char yields also followed a negative trend as the pyrolysis temperature was increased, with a maximum char yield of 33.7 % at 500°C similar to what is reported in literature from other feedstock and pyrolysis systems [11, 18, 32, 36]. The greatest net change in char mass was 3.3 % as the temperature increased from 650 °C to 700 °C; it occurred at a higher temperature than it did for energy cane bagasse (Figure 2). The higher temperature required for a significant change in bio-char is an indicator of the higher thermal stability of this biomass and its resistance to thermal decomposition compared to either pine sawdust [37] or energy cane bagasse. CTT wood has higher lignin content and lower hemicellulose content compared to energy cane baggase. Lignin is a complex cross linked organic polymer and has higher thermal stability[38] compared to cellulose and hemicellulose leading to high char yield. Moreover lignin has high fixed carbon yield which adds to the char yields. Lignin is the highest contributor to char yields compared to its counterparts. Since CTT displays higher lignin composition, greatest net change in char mass was observed at higher temperature and higher char yields were obtained for CTT pyrolysis compared to energy cane baggase.

3.1.2. Liquid Yields

The liquid yields from the pyrolysis of energy cane (Figure 2a) show a slight positive and then negative trend as the reaction temperature increase from 500 °C to 700 °C. The maximum yield was achieved at 550 °C with a liquid yield of 48.9 %. The liquid yield for 500 °C was very close at 47.9 % and with a standard deviation of ± 4.9 % and showing no statistical difference

using a t-test ($\alpha = 0.05$). After 550 °C there is a significant decline in the liquid yields as the yield decreases from 48.9 % at 550 °C down to 38.0 % at 700 °C. This significant loss of over 10 % liquid yields indicates that the production of bio-oil from energy cane is best performed at the lower operating temperatures 500 – 550 °C.

The liquid yields from the pyrolysis of Chinese Tallow tree wood (Figure 2b) initially follow an increasing linear trend ($y = 0.0133x + 0.341$, $R^2 = 0.99$ and then decreasing trend ($y = -0.0478x + 0.4283$, $R^2 = 0.98$) as the reaction temperature increased, with the maximum yields (38.1 %) achieved at the middle temperature tested, 600 °C (vs. energy cane bagasse at 550 °C). This is another indicator of the higher thermal stability of the biomass due to higher lignin content, and also gives the operating temperature to achieve the best pyrolysis results in terms of liquid yields. Since cellulose and hemicellulose are the highest contributor of overall liquid yields, higher liquid yields were obtained with energy cane pyrolysis compared to CTT wood. Since the operating conditions for all of the biomasses remained constant and the Chinese Tallow Wood retained much more of its initial mass even at the highest reactor temperatures, is a strong indicator that the Tallow wood has a higher inherent thermal stability.

3.1.3. Gas Yields

The gas yields from energy cane (Figure 2a), calculated as the difference from initial mass, were observed to follow a positive trend as the reaction temperature increased, as expected. The highest yield of gases occurred when the temperature of the pyrolysis reactor was 700 °C with a yield of 42.9 %. The gas yields increased most between the temperatures of 550 °C and 600 °C with a 6.4 % net increase in gas yields. The higher yield of gases is to be expected as the reaction temperature increases due to the biomass being more thoroughly broken down at the higher reactor temperatures [4, 36, 39]. Gas yield is mainly dominated by volatilization and

cracking reactions. As mentioned earlier, volatilization occurs above 575 °C, and as the temperature increases, the complex volatile molecules are broken down to simpler compounds such as CO, CH_4 and CO_2. Moreover at higher temperatures, char acts as a catalyst and enhances the deoxygenation reaction resulting in formation of CO, CO_2 and H_2O.[40]

The gas yield from Chinese Tallow wood (Figure 2b) was determined in the same manner as the energy cane yields. As expected, the gas yields show an overall increasing trend as the reactor temperature increases. The yield of the gas product showed no significant change between the operating temperatures of 500 °C to 600 °C, followed by a significant net increase of 14.1 % in the gas yields between 600 °C and 700 °C. This effect is also indicative of the higher resistance to thermal decomposition.

3.2. Water content of the liquid fraction

The water content of bio-oil was determined using Karl-Fischer titration, and was reported as a percentage of the total liquid yield (Figure 3). The water content of a liquid fuel has a significant impact on the heating value of the product, and it is therefore an important indicator of the quality of the fuel, [3] separately reported from the overall liquid yield (which includes both bio-oil and water). The declining trend seen in the water produced from the pyrolysis of energy cane indicated that the oils produced at higher temperatures have higher heating values. This phenomena, coupled with the high liquid yields, shows that the highest amount of bio-oil produced when the water is removed occurred at 550 °C with a bio-oil yield of 30.3 %.

For Chinese Tallow wood the water content of the liquids was shown to follow a slightly positive trend, leading to a decreased oil yield at the higher reaction temperatures. It can be concluded that for the pyrolysis of Chinese tallow tree wood the lower reaction temperatures, in the range tested for this study, yielded the highest quality liquid. However, with the highest

liquid yields were achieved at higher operating temperatures, this means reaction temperature chosen for the process will need to be determined based upon a cost benefit analysis which includes the removal of water from the liquid product. Since the overall water content from both biomasses was high, further processing of bio-oil is necessary before being used as a fuel additive.

3.3. Characterization of the char

The char fraction of the pyrolysis reactions was analyzed for carbon, hydrogen, and nitrogen content using an elemental analyzer; these results were compared to the analysis of the unprocessed energy cane biomass. The analysis of the CHN content of the char compared to the unburned energy cane, shown in Table 1 revealed a significant increase in the carbon content of the solids for both biomasses. The unpyrolyzed energy cane had a carbon content of 46.7 % of its total mass, after pyrolysis at 500 °C the carbon content increased to 71.9 %, a net increase of 25.2 %, the remaining mass can be mostly attributed to oxygen content that remains in the biomass due to the lower operating temperature; at higher temperatures the oxygen content of the bio-char is significantly decreased. The loss of mass coupled with the significant increase in carbon content can be attributed to the removal of oxygen (via volatile oxygenated species) from the biomass during the pyrolysis process. The carbon content follows a positive trend as the reaction temperature increases, but it shows stabilization at the higher temperatures (600 – 700 °C), indicating that the bio-char composition changes little above 600 °C. The hydrogen content of the char samples show a declining trend as the reaction temperature increases. This indicates that the hydrogen and oxygen are lost at a higher rate than carbon. As the dehydration and decarboxylation reactions proceeds, the volatiles are lost as a result of increasing temperature.[41]

Oxygen in char is in the the form of various functional groups such as –COO, -COH, -OH.[42] The oxygen present is in two major forms; labile and recalcitrant oxygen.[41] The labile oxygen form is lost easily as the temperature increases. However, the second form of oxygen is more stubborn and is left behind in the char.[41] This oxygen, at higher temperatures forms stable aromatic structural rings, lowering the C/O ratio.[41] This could be the reason for higher oxygen at 700 °C in both biomasses. The concentration of nitrogen in the char samples also follows a negative trend as the pyrolysis reactor temperature increases, indicating that, much like the hydrogen; the nitrogen is more readily removed from the biomass at higher reaction temperatures. The nitrogen is most likely be transformed into amine and amide compounds in the liquid or being volatilized into nitrogen based gases such as NO_x's. [43]

The carbon content in the unburned Chinese Tallow tree biomass was 48.7 %, and increased to 70.1 % in the bio-char obtained at 500 °C, a net increase of 21.4 %. Increase in carbon content as the biomass is broken down is an indication of the removal of oxygen and hydrogen, which both show declining trends as the reaction temperature was increased. The nitrogen concentration reduced slowly from 500 to 550 and 600 °C but remained unchanged at the higher reaction temperatures; this is an indication that the nitrogen is removed from Chinese tallow tree wood during pyrolysis as temperature increases but is independent of the reaction temperature at higher temperatures.

3.4. Characterization of the liquid fraction

The elemental analysis of the liquid product determined the content of carbon, hydrogen, and nitrogen in the bio-oil fraction, shown in Table 1. Using the assumption that the remainder of the chemical composition is oxygen, the effect of the reaction temperature on the chemical composition of the liquid fraction can be analyzed.

447 The GC-MS was performed on the DCM extracted liquid compounds, and the resulting
448 GC plots were integrated and the peaks identified by compound groups. The groups used (Table
449 2) were furans, ketones, aldehydes, alcohols, acids, phenols, polyaromatic hydrocarbons, fatty
450 alcohols, and other compounds that were unidentified. The relative content of phenols is for non-
451 aqueous fractions only as the composition of aqueous fraction was not tested, and hence the mass
452 fraction for phenols is higher for both CTT and Energy cane.
453 *3.4.1. Elemental Analysis*
454 For energy cane (Table 1) carbon to hydrogen ratio increases from 5.07:1 at 500 °C to
455 6.18:1 at 700 °C, and the proportion of carbon to oxygen decreases from 2.56:1 at 500°C to
456 1.96:1 at 700 °C. This change can be attributed to a decrease in the oxygenated functional groups
457 in the liquid yields as the reaction temperature increases; indicating that while the yield
458 decreased at higher temperatures (Figure 2) the quality and heating value of the oil improved [44].
459 Oxygen was removed at higher temperatures as CO and CO_2, as determined by the higher gas
460 yields of these two oxygenated products at elevated temperatures in correlation with a decreasing
461 oxygen content of the char. The nitrogen content of the liquids product was negligible compared
462 to carbon, hydrogen and oxygen values at all reaction temperatures in the case pyrolysis of
463 energy cane with no specific trend.
464 The composition of the liquid yield of the pyrolysis of the Chinese tallow wood (Table 1)
465 indicates that the nitrogen and hydrogen content of the liquid increased as the reaction
466 temperature increased. The carbon content, which coupled with the oxygen and hydrogen
467 content, can be used to determine the heating value of the liquid fraction [33]. With the assumption
468 that the oxygen content makes up the remainder of the liquid composition, the heating value is
469 highest in the liquid obtained at 700 °C. However, the low liquid yields and high water content at

this temperature would indicate that even though the bio-oil may be of a higher quality, the low quantity of oil negates the improved quality. Some discrepancies in the CHNO analysis could be due to machine error, or error due to mass changes. Many compounds in the bio-oil tend to volatize at room temperature; this fact made it rather difficult to maintain a constant weight for liquid samples during CHNO analysis.

3.4.2. GC-MS Analysis

The results from the GC-MS analysis of the energy cane and Chinese Tallow wood's liquid fraction (Table 2) show that the concentration of smaller furans compounds increased with increasing temperature, whereas larger compounds such as phenols and organic acids decreased, indicating that as the liquid products were broken down more thoroughly and into smaller compounds as was reported in other studies as well. [45] This phenomenon, paired with the decreasing oxygen content of the liquids at higher temperatures, would indicate that at higher temperatures the oils composition shifts from a tar rich, highly oxygenated mixture, to a lighter, less oxygenated one. Therefore the quality of the oil improved at the higher temperatures, at the expense of a decreased yield which may offset the slightly lower oil quality obtained at the lower temperatures.

From the Chinese Tallow wood's GC-MS results (Table 2) it can be observed that unlike the energy cane bagasse, at the same temperatures there is a large percentage of fatty alcohols from the pyrolysis of Chinese tallow wood. These compounds are wax like in nature, solids at room temperature, but soluble in the DCM solvent used for GC-MS. The presence of these compounds can be explained by two factors: 1. residual waxes and lipids from the tallow seeds may have been present and were pyrolyzed along with the wood, 2. the biomass itself may contain some wax like structures. The presence of these compounds was not identified in the

493 energy cane bagasse, and the Chinese tallow tree wood also generated less phenolic compounds
494 than the energy cane. The GC-MS analysis also indicates that all of the compounds identified are
495 oxygenated hydrocarbons; which coincide with the high oxygen content from the CHN analysis.
496 The presence of oxygen significantly reduces the heating value of the oil and therefore the oil
497 obtained may need to be upgraded via deoxygenation using a catalyst in order to improve its
498 overall quality as a fuel source.

499 *3.5. High heating value (HHV) of products*

500 HHV of bio-oil and char was calculated based on the CNHO content of products (Table
501 3). Knowledge of HHV is crucial in optimizing the process. The HHV of bio-oil was adjusted for
502 water content. The pyrolysis of energy cane biomass and Chinese Tallow wood in an induction
503 heater proved to be very successful in terms of both quantity and quality of the liquid yields,
504 indicating an increased energy density compared to the initial biomass. Highest heating value
505 was obtained for bio-oil from energy cane at 500ºC while Chinese tallow tree yielded the lowest
506 energy density at 550 ºC. Cellulose and hemicellulose is the highest contributor to the energy
507 density of bio-oil, simply, because they make up most of the biomass composition and is more
508 easily broken down compared to lignin. Since Chinese tallow tree had higher lignin content, the
509 energy content of bio-oil obtained from Chinese tallow tree was lower than energy cane.
510 Although the liquid yield is highest at 550 ºC, the yield at 500 ºC was only slightly lower but has
511 high energy content. Moreover, the energy cost to maintain a temperature of 500 ºC is lower than
512 550 ºC. Thus, 500 ºC would be an optimal temperature for high energy bio-oil production from
513 energy cane biomass. It must be noted that at 500 ºC, the water content of liquid product is
514 slightly higher compared to 550 ºC. For Chinese tallow tree bio-oil, although highest liquid yield
515 was obtained at 600 ºC, the energy content of the bio-oil obtained at this temperature was very

low. The highest energy content was obtained at 700 ºC but the liquid yields are low and water content of bio-oil from this temperature is high. An optimum temperature of operation for Chinese tallow tree pyrolysis would be 500 ºC which has more than average energy content and comparable liquid yields.

HHV values decreased as the pyrolysis temperature increased for both biomasses; however, HHV value for Chinese tallow tree bio-oil increased at 700°C. This could be because Chinese tallow tree wood contains high amount of long chain fatty alcohols and waxes (Table 2); at high temperature these heavy compounds are broken down more efficiently forming lower molecular weight compounds with higher energy density; higher temperatures may also enhance thermal cracking resulting in deoxygenation of oxygenated compounds.[46] Thus, higher pyrolysis temperatures (above 700°C) should be investigated for Chinese tallow tree bio-oil production.

Conclusions

The pyrolysis of energy cane biomass and Chinese Tallow wood was carried out for the first time in an induction heating reactor with results comparable with other induction-based pyrolysis for different biomasses. Highest liquid yield was obtained at 500 °C for both biomasses; the liquid product was rich in oxygenated compounds such as phenols, ketones and alcohols. Bio-oil obtained from pyrolysis of Chinese tallow tree showed small concentration of fatty alcohols. The low char yields showed that the energy cane more thoroughly breaks down under the investigated pyrolysis conditions than Chinese Tallow wood. The energy balance indicated that the higher energy content of the liquids was obtained at the pyrolysis temperature of 500 °C.

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672 **Captions of Figures and Tables**

673 **Figures**

674 Figure 1 The process flowchart showing the main components of the pyrolysis system and their
675 arrangement during the pyrolysis experiments

676 Figure 2 The yields of the three main components char, liquids, and gases at the different reactor
677 temperatures from the two biomasses (a) energy cane (b) Chinese Tallow wood

678 Figure 3 The water yield of the pyrolysis reaction and the remaining bio-oil remaining after the
679 water is removed from the liquid fraction as a percentage of total liquid yields from the two
680 biomasses (a) energy cane (b) Chinese Tallow wood. Standard deviations excluded for clarity

681

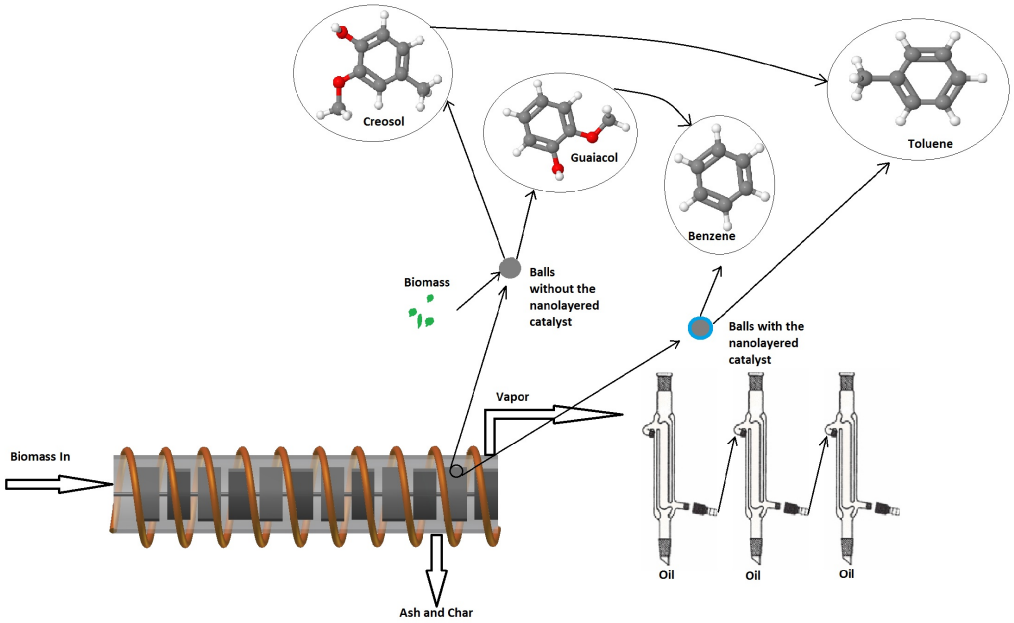
682 **Tables**

683 Table 1 The percentages of carbon, hydrogen, nitrogen, and assumed oxygen present in the
684 unburned biomass and the char and liquid products from each pyrolysis temperature

685 Table 2 The relative concentration of compound grounds identified in the GC-MS of the liquid
686 fraction.

687 Table 3 Energy balance of the induction pyrolysis of energy cane and Chinese Tallow wood
688 biomasses

Graphic Abstract for Manuscript



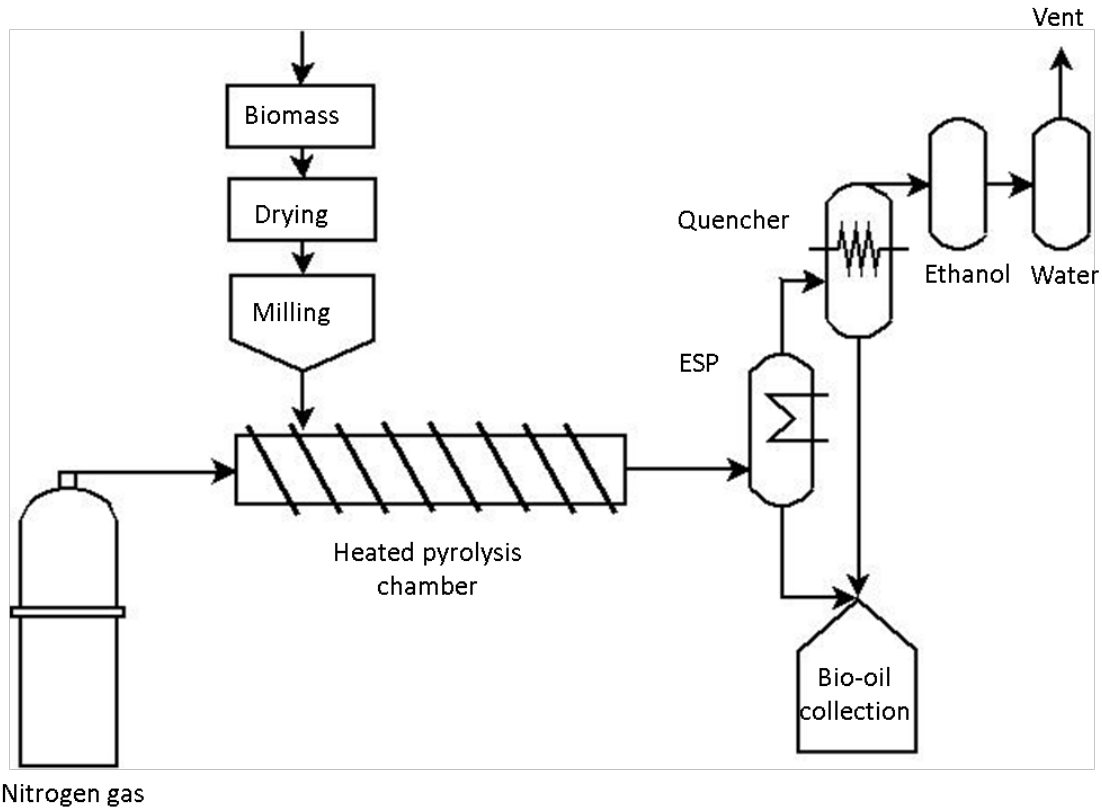
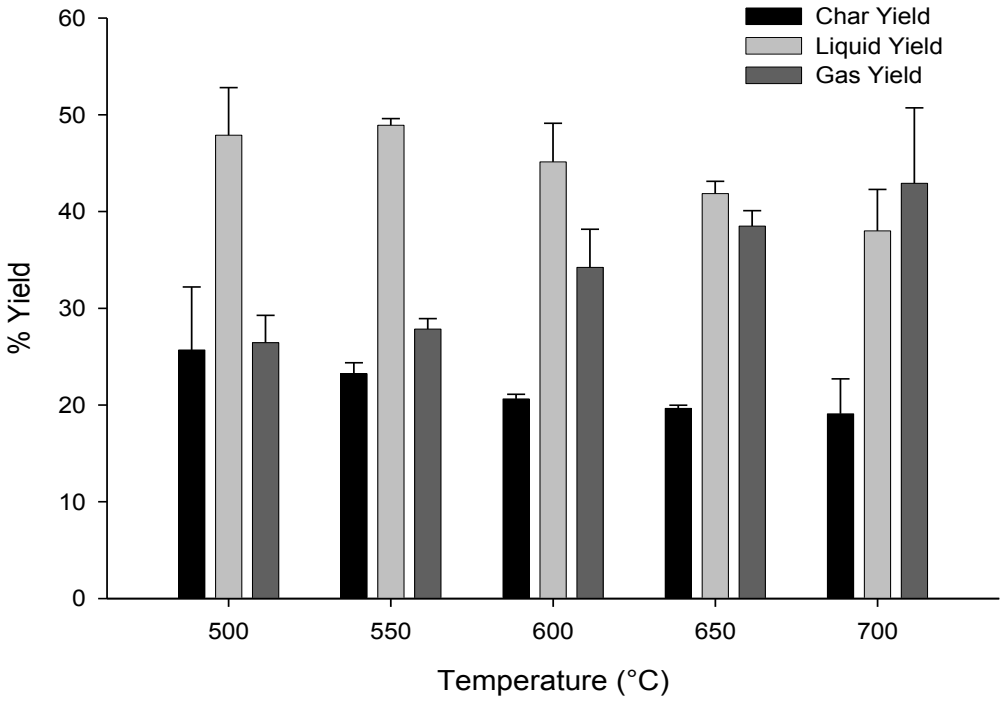


Figure 1. The process flowchart showing the main components of the pyrolysis system and their arrangement during the pyrolysis experiments

(a)



(b)

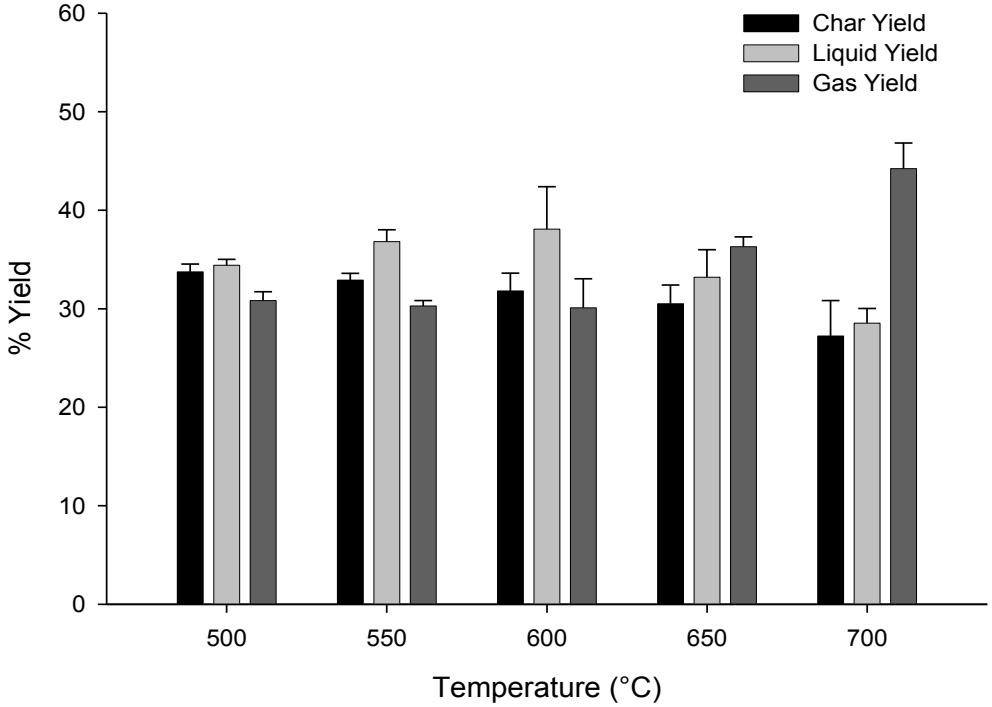
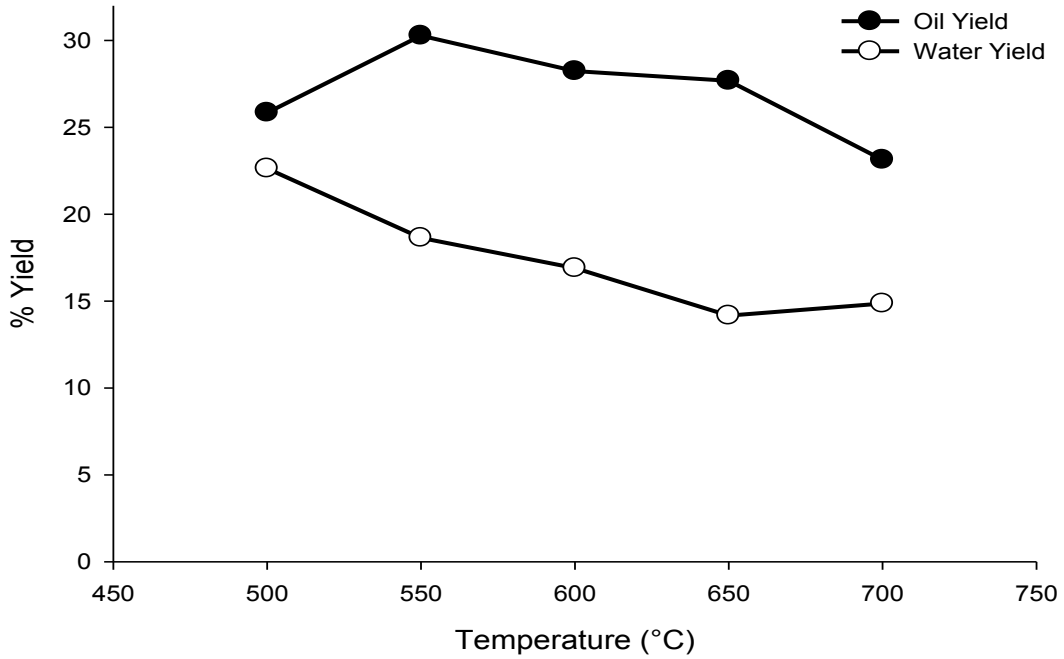


Figure 2. The yields of the three main components char, liquids, and gases at the different reactor temperatures from the two biomasses (a) energy cane (b) Chinese Tallow wood

707 (a)



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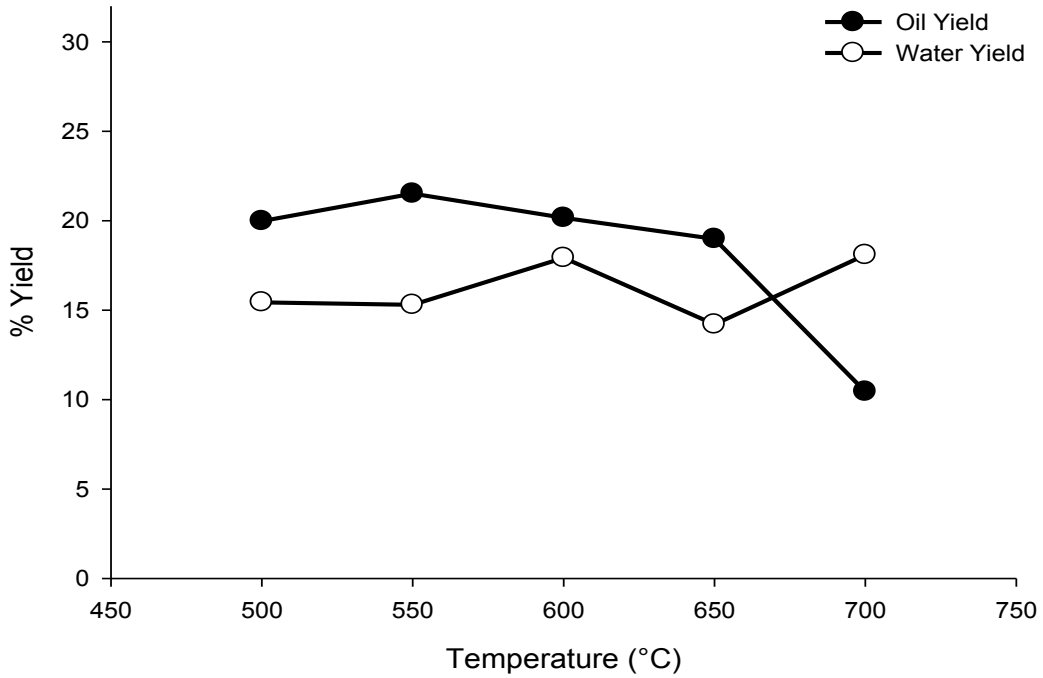
709 (b)



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711 Figure 3. The water yield of the pyrolysis reaction and the remaining bio-oil remaining after the
712 water is removed from the liquid fraction as a percentage of total liquid yields from the two
713 biomasses (a) energy cane (b) Chinese Tallow wood. Standard deviations excluded for clarity

Table 1. The percentages of carbon, hydrogen, nitrogen, and assumed oxygen present in the unburned biomass and the char and liquid products from each pyrolysis temperature

		Temperature (°C)	% Carbon	% Hydrogen	% Nitrogen	% Oxygen*
Energy Cane		Unburned	46.68	6.71	0.89	45.73
	Char Product	500	71.91	2.95	1.33	23.81
		550	73.99	3.47	0.8	21.74
		600	80.31	2.27	0.79	16.63
		650	81.74	1.75	0.75	15.77
		700	80.76	1.45	0.72	17.07
	Liquid Product	500	62.58	12.34	0.69	24.4
		550	55.12	9.97	0.6	34.31
		600	57.09	11.14	0.62	31.15
		650	48.64	8.59	0.57	42.21
		700	59.44	9.6	0.64	30.31
Chinese Tallow Tree		Unburned	48.68	6.17	1.46	43.69
	Char Product	500	70.08	2.72	2.06	25.14
		550	72.61	2.33	1.68	23.39
		600	70.968	1.92	1.24	25.87
		650	73.76	1.52	1.27	23.45
		700	72.52	1.31	1.29	24.88
	Liquid Product	500	48.9	10.42	1.34	39.34
		550	32.69	7.4	1.06	58.85
		600	35.94	8.26	1.36	54.44
		650	32.56	9.26	2.01	56.17
		700	52.03	13.18	3.67	31.11

* determined by difference

719 Table 2. The relative concentration of compound grounds identified in the GC-MS of the liquid
720 fraction.

		% Yield				
	Compound Type	**500 °C**	**550 °C**	**600 °C**	**650 °C**	**700 °C**
Energy Cane	Furans	1.34	2.33	9.85	4.60	22.49
	Ketones	12.60	2.33	6.88	9.74	5.73
	Aldehydes	2.00	2.37	3.20	5.01	5.96
	Alcohols	0.00	0.62	0.00	1.46	1.35
	Acids	4.15	15.01	3.83	0.00	1.45
	Phenols	71.73	70.50	67.60	71.32	52.23
	Other	8.19	4.59	8.64	7.87	10.79
	Polyaromatic Hydrocarbons	0.00	0.66	0.00	0.00	0.00
	Fatty Alcohols	0.00	0.00	0.0	0.00	0.00
Chinese Tallow wood	Furans	5.64	4.95	10.54	4.11	2.33
	Ketones	3.08	0.00	15.96	13.32	1.07
	Aldehydes	6.27	1.91	3.14	2.01	0.00
	Alcohols	10.36	0.00	11.18	10.08	2.64
	Acids	4.07	0.00	8.75	8.01	0.00
	Phenols	59.51	79.47	38.18	51.10	79.60
	Other	6.15	8.96	0.00	0.00	0.00
	Polyaromatic Hydrocarbons	0.00	0.00	0.00	0.00	3.75
	Fatty Alcohols	4.91	4.72	12.24	11.36	4.35

721 Table 3. Energy balance of the induction pyrolysis of energy cane and Chinese Tallow wood
722 biomasses
723

Biomass Type	Temperature (°C)	Biomass energy content (MJ/kg)	Energy Outputs (MJ/kg)	
			Liquid	Char
Energy Cane (per 15 g)	500	17.221	34.568	24.282
	550		26.838	26.109
	600		29.763	27.437
	650		21.231	27.325
	700		28.487	26.327
Chinese Tallow (per 30 g)	500	17.486	24.477	23.091
	550		11.119	23.700
	600		14.254	22.106
	650		14.242	22.909
	700		31.002	21.929

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