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Optimization of bio-oil pH with co-pyrolysis of cotton gin trash, animal manure and micro-algae

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Abstract

Lower pH increases corrosive nature of bio-oil and hence creates problem in its applications for a replacement of crude oil. We controlled pH of bio-oil by optimizing the temperature and feedstock composition in a fixed bed batch pyrolysis reactor. The feedstock used for pyrolysis of co-biomass included cotton gin trash (CGT), cow manure (CM), and algae (*Nanochloropsis oculata*). The bio-oil from co-pyrolysis process was also characterized for water content viscosity, pH, and acid number. The co-biomass in different ratios was processed to produce bio-oil at five operating temperatures (400, 450, 500, 550, and 600°C). The results obtained during the experiment showed a significant change in the product yields and characteristics. The pH of produced bio-oil ranged from 6.36 to 8.96. The ratios of feedstock compositions showed synergistic effect on the pH, acid number, and viscosity of bio-oil. The results indicated that operating temperature and composition of co-biomass are critical in improving the pH of the bio-oil.

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Introduction

In the time of rapid growth towards population, raising standards of living and improving quality of life by upgrading socio-economic conditions. This has increased energy demand, as it is often result of economic growth of that region (Ramachandra, Kamakshi, & Shruthi, 2004). The pattern of increase is dependent on industrial growth that heavily utilizes energy sources (fossil fuels). These fossil fuels are facing many issues; unsustainable, increased in prices on daily basis and degradation of environment which results in alarmingly increased rate of greenhouse gas emissions. This scenario of increased demand, depletion of fossil fuels reserves and, global warming prompted the trend of scientists to research sustainable alternate renewable sources.

The use of biomass as an energy source is under research and proven to be effective, as it serves as an alternative solution for the replacement of fossil fuels. The transformation of biomass into other forms of energy (Bio-Fuels) has been a subject of study in present energy demanding world. Biofuels are fuels obtained from biomass (renewable feedstock) in the form of solid, liquid or gaseous (Miao, Wu, & Yang, 2004). These biofuels are obtained from different conversion technologies (chemical, biological, thermal and hybrid). Among thermal conversion, pyrolysis technology is under exploration that produces biofuels in complete absence of oxygen. Pyrolysis (thermochemical conversion) process produces energy fuels with high fuel-to-feed ratio, and is easily adjustable to favor char, bio-oil or gas production according to need (Maguyon & Capareda, 2013).

The product yield of pyrolysis from agricultural biomass is comparable i.e. i) Liquid i.e. bio-oil to crude oil, having low nitrogen and sulfur contents. The bio-oil can be stored and transported under normal conditions. The bio-oil can be upgraded to liquid transport fuels and bio-chemicals (Grierson, Strezov, Ellem, Mcgregor, & Herbertson, 2009; Maguyon & Capareda, 2013) ii) Solid i.e. Bio-Char has high contents N, P and K and could potentially be used as fuel or fertilizer (Miao *et al.*, 2004) iii) Gaseous i.e. Syngas recovered has heating value possible to compensate the energy requirement of the pyrolysis (Grierson *et al.*, 2009). However, Biofuels are considered to be the only available sustainable energy source these days as the biomass-to-fuel cycle neutralizes CO_2 and report overcome greenhouse effect (Huber, Iborra, & Corma, 2006; Ji-lu, 2007).

The nature and characteristics of feedstock is important in designing thermo chemical conversion system. The main characteristics (ash content, density, and particle size) govern the applicability of various wastes in these conversions (Peng, Wu, Tu, & Zhao, 2001). This diverse nature of feedstock restricted researchers to go for using co-biomass in pyrolysis. All types of renewable feedstock i.e. rice husks, rice straw, bagasse, sawdust, wheat straw, rapeseed straw and stalk, corn residues, switch-grass, cotton gin trash, and others were tested during the last decade to produce biofuels. It is observed that very less work was done in using co-biomass to produce bio-fuels, which can alter the characteristics of biofuels.

In this paper three different biomass cotton gin trash, Cow Manure, and Algae are used to produce the biofuels at varied temperatures i.e. 400°C to 600 °C. We have hypothesized that when different feedstock are mixed and pyrolyzed the desired product's quality and quantity can be achieved. Bio-oil is an important product that needs to have properties near commercial hydrocarbon. The objective of study was to up-grade bio-oil in terms of pH by using multiple feedstock. The basic aim of the study is to produce bio-oil using co-biomass that has non corrosive nature.

Materials and methods

Characterization of Biomass

The Co-biomass used in this experiment was obtained from three different sources i) Cotton Gin Trash (CGT) from Varisco Cotton Gin near College Station, Brazos County, Texas ii) Cow dung from animal farm in Bryan, Texas and, iii) Dewatered Micro Algae from Texas Agri-Life Research Algae Pond, Pecos, Texas.

The co-biomass was dried in oven for 24 hrs at 105°C to reduce the moisture content lesser to 0.1 kg of H_2O / kg of dried mass. Each dried Co-biomass was grounded in Wiley Mill to obtain an average particle size of 2 mm. The uniform particle size of co-biomass was then fed into the pyrolyzer. The determination of moisture content and, proximate analysis was done according to standard methods (ASTM). Design expert 8.0 was used to attain different ratios of the Co-biomass. Algae was made constant by three variables including Cow Dung, Micro Algae and, Temperature (400 to 600 °C). To analyze the effect of Co-biomass on the yield of pyrolysis the co-biomass was mixed on the basis of different proportions as shown in Table 1. After preparation, the proportionate prepared Co-biomass was packed in sealed polythene bags to avoid any change in moisture content.

Co-Pyrolysis Setup

The co-pyrolysis of Co-biomass mixtures were carried out in a Series 4580 HP/HT, Parr Instrument Company, Moline, IL. The co-pyrolysis reactor equipment is fixed-bed batch type, Parr pressure, stainless steel with loading capacity of 1.5 L was used for pyrolysis in this experiment. This reactor is hosed to cylindrical ceramic fiber electrical heater with thermowell attached to the reactor controller. The inside temperature was measured by Type-J (iron-constantan) thermocouple. The pressure variation in the reactor was measured by pressure gauge (detection limit = 0–5000 psi) having T316 Stainless Steel Bourdon tube.

The reactor was loaded with 280 g of Co-biomass. Oxygen was eliminated from the system by purging nitrogen gas for 20 min at 10 psi. The reactor temperature increased in increments of 5.5°C/min until the desired temperature is attained. The desired mixing within the reactor was achieved by a stirrer attached to magnetic drive operated at 600 rpm. The reaction continued for a period of 30 min, after achieving the desired temperature in the reactor. The yield produced in this experiment was measured by measuring i) the volume of gas using a gas meter (METRIS 250, Iron, Owenton, KY with air/gas capacity of 250/195 CPH), ii) the liquid product and, iii) the char). The liquid and char were weighed by using an analytical balance.

Characterization of Bio-Oil

Bio-oils obtained from Co-biomass mixtures were analyzed to determine their pH values. The pH of the bio-oil was measured by using a digital pH meter (Fisher Scientific Accumet Mercury-free). The pH data were obtained after 10 min stabilization of the mechanically stirred oil. Viscosity of the bio-oils was measured in a water bath at 40°C using standard BS 188:1977 method. The acid number was measured using a Mettler Toledo G20 compact Titrator according to ASTM D664-07.

Results and discussion

Influence of temperature on product yields

Operating temperature during the process of pyrolysis is an important parameter and effects the products yield. The effects of temperature on the products yield of co-biomass are shown in the fig 1, 2 and 3 respectively. The pyrolysis runs were carried out at five operating temperatures 400, 450, 500, 550, and 600 °C with 30 min of reaction time at the desired temperature. The variation of temperature showed significant results on the products yield during the pyrolysis of co-biomass.

Liquid Product

The liquid product obtained contains two immiscible fractions i.e. (i) the pale yellowish aqueous fraction, and (ii) the blackish brown organic fraction or bio-oil. The products were separated immediately during their collection. Based on the Fig 1, the liquid product increased significantly with increase in operating temperature from 15.25 % (42.70 g) at 400 °C to 43.56% (121.97 g) at 550 °C operating temperature. The increased yield at 550°C can be attributed to the lipid products carried in the co-biomass specially Algae. The co-biomass contains 50% by weight algae which undergoes thermal decomposition at that is further divided to three temperatures as i) dehydration carried out at an operating temperature

< 180 °C ii) devolatilization between the operating temperatures of 180-540 °C and iii) Solid decomposition at temperatures > 540 °C. During the step 2 i.e. devotilizations, whole of the pyrolysis occurs(Li *et al.*, 2010; Maguyon & Capareda, 2013; Peng *et al.*, 2001). The liquid product intended to decrease from the operating temperature of 550 °C to 600 °C. This decrease at 600 °C could be due to the secondary cracking of oil vapors forming incondensable gaseous products (Pan *et al.*, 2010). Hence the decrease of this liquid product from 550 oC to 600 oC can be directly attributed to decrease in production of organic fraction within the liquid product. The results of this study show that the maximum yield of the liquid product was observed at the operating temperature of 550 °C with 43.56 % (121.97 g).

Table 1. Ratios of Co-biomass with operating temperatures for each reactor run.

Runs in Reactor	Operating Temperature (°C)	Co-Bio mass		
		CGT	Cow manure	Algae
		Sample (%)		
1	450	37.5	12.5	50
2	600	35	15	50
3	400	35	15	50
4	500	35	15	50
5	550	37.5	12.5	50
6	500	30	20	50
7	400	40	10	50
8	450	40	10	50
9	600	35	15	50
10	600	30	20	50
11	400	30	20	50
12	600	40	10	50
13	600	40	10	50
14	550	32.5	17.5	50
15	400	30	20	50
16	500	40	10	50
17	600	30	20	50
18	450	32.5	17.5	50
19	400	40	10	50

Solid Product

Bio-char as the solid product of pyrolysis is used for wide range of applications such as fuel, adsorbent and production of value added products. Fig 2. shows the effects of operating temperatures on bio-char yield. The bio-char produced in pyrolysis of co-biomass decreased significantly from the 400 °C to 600 °C with respective yields of 66.69 % (186.72 g) to 36.59 % (102.44 g). The decrease in bio-char yields with increase in operating temperature is due to a greater primary decomposition of cattle manure at high temperatures or through secondary decomposition of the solid residue (Heo *et al.*, 2010).

Gaseous Product

The gaseous products obtained at different pyrolysis operating temperatures are shown in Fig. 3. It was observed that the Gas yield significantly increased from 400°C (8.84%) to 600°C (21.92wt%). The combustible syngas produced is a mixture of H_2, CO, CH_4, C_2H_4 and C_2H_6. The concentration of hydrocarbons in the gaseous product intended to increase with further heating of the biomass, which can be due to cracking of the vapors forming incondensable gaseous compounds. The maximum production of gas was observed at 600 °C operating temperature on the co-biomass ratio of CGT: CM: Algae (30:20:50).

Mass Conversion Efficiencies

The mass conversion efficiencies were calculated using eq. 1 and 2. Mass balance around the reactor shown in Eq. (2) was then used to calculate the losses (wt %), and consequently, the mass conversion of the process.

Product yield (%wt) = (mass of product/mass of dry algae used) *100 ----- Eq. 1

%Char yield + %Liquid product yield + %Gas yield + %Losses = 100%----- Eq. 2The mass conversion efficiencies are estimated using equation no 2 at different operating temperatures and co-biomass ratios. The mass conversions efficiency of the process was mostly about 85% or more. Efforts were made to collect maximum bio-char from the reactor using best possible cleaning practices. The uncondensed liquid was re-trapped by introducing a second condensation unit before the gas meter. However, still some mass was adhered to the surface of the reactor and also was trapped within the filter attached to the gas meter. The conversion of biomass to solid product (bio-char) dominated at all temperatures and ratios of co-biomass.

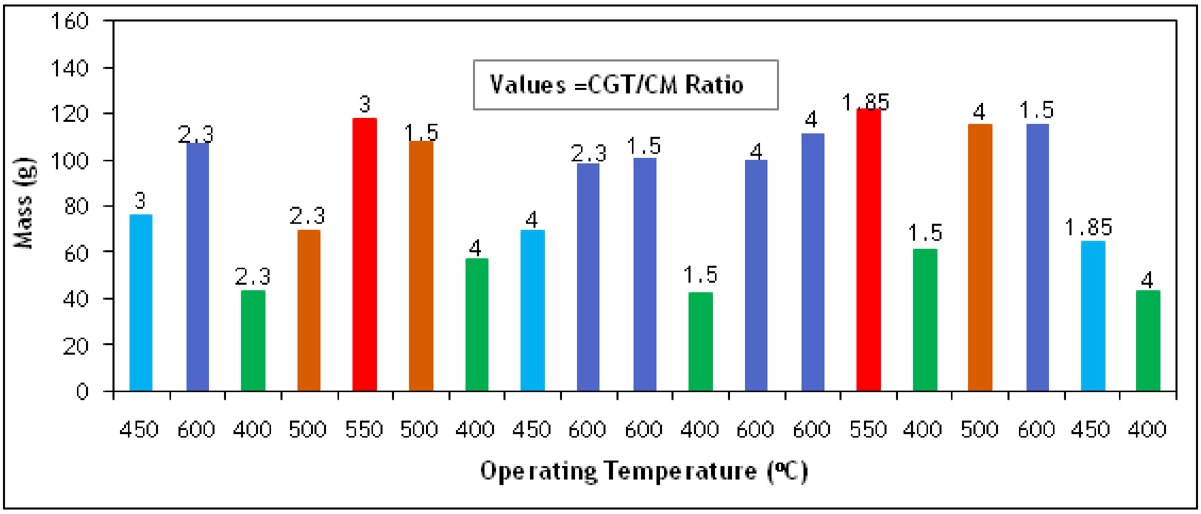

Fig. 1. Influence of operating temperatures on the yield of Liquid Product.

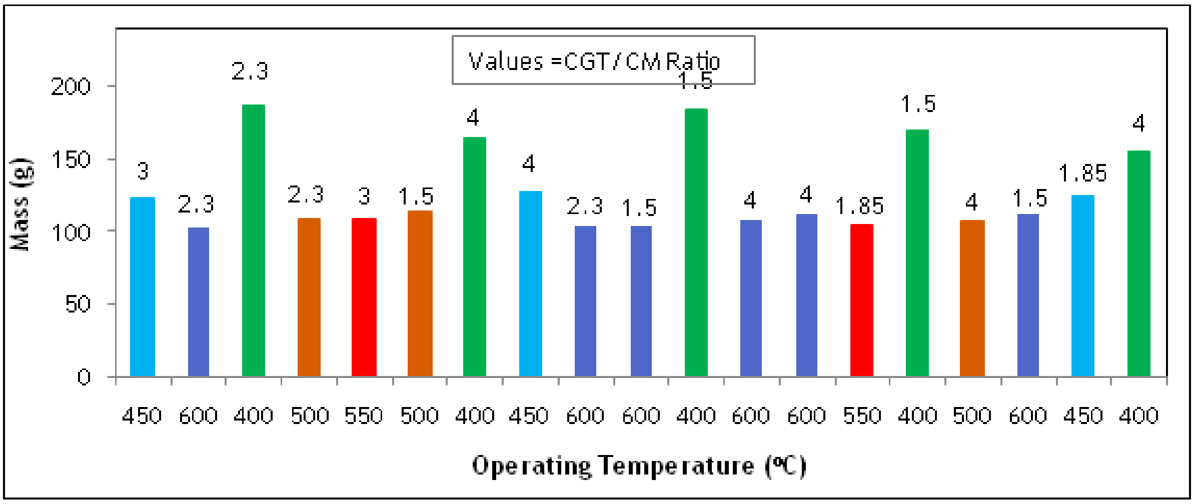

Fig. 2. Influence of operating temperature on the yield of solid product.

pH of Bio-oils

The pH values of bio-oils produced from different ratios of co-biomass of Cow Manure, Cotton Gin Trash and Algae at different operating temperatures are shown in Table II. The results of mixtures were compared with pure (100 wt%) algae pyrolysis results to understand the effect of CM and CGT on product quality. From this table, it was seen that the lowest pH value (6.96) of the bio-oil was observed at operating temperature of 400 °C and highest pH value (8.96) at 500°C. This pH value is very much different than pH of the bio-oil obtained from lignocellulosic materials with pH between 2-3 (Budarin *et al.*, 2011), these observations are consistent with the (Maguyon & Capareda, 2013). The alkaline pH shows the presence of weak bases such as pyrrole.

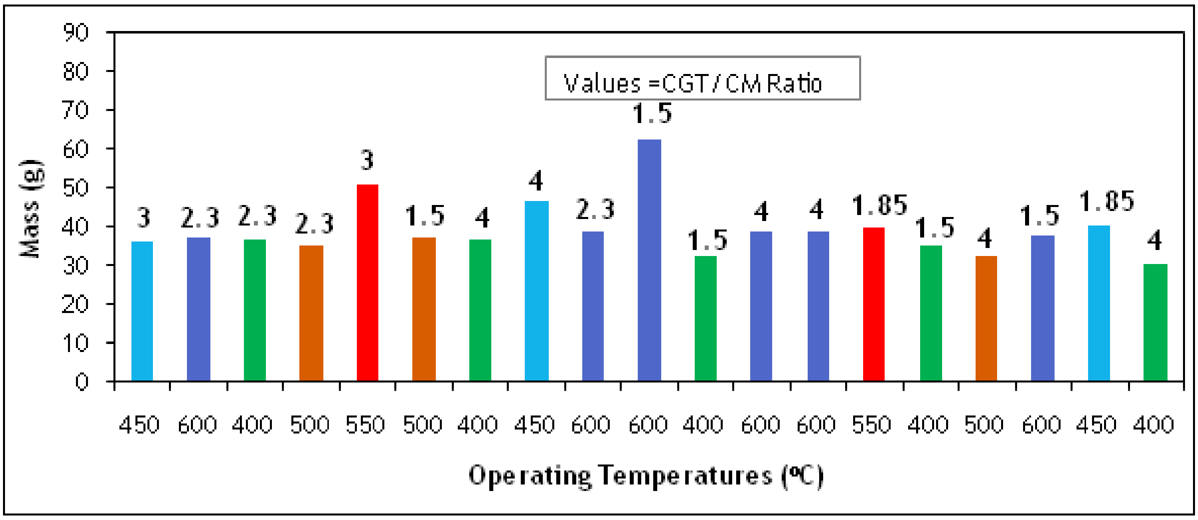

Fig. 3. Influence of operating temperature co-biomass ration on Gaseous product.

Conclusions

Pyrolysis of Co-biomass at five operating temperatures (400, 450, 500, 550, and 600°C) in a fixed-bed batch reactor showed that the process can be optimized to produce desired product among char, bio-oil and syngas. The bio-oil production increased with increase in temperature. While yield of bio-oil decreased from 550-600 °C of operating temperature. In addition, the pH of produced bio-oils remained at the alkaline while the lowest pH of 6.36 was obtained at 400 °C of operating temperature with co-biomass combination of 4:1 (CGT:CM).

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