BIOMASS AND BIOENERGY 34 (2010) 1961–1967

Available at www.sciencedirect.com

ScienceDirect

http://www.elsevier.com/locate/biombioe

# Utilization of summer legumes as bioenergy feedstocks

*Keri B. Cantrell**, *Philip J. Bauer*, *Kyoung S. Ro*

*United States Department of Agriculture, ARS, Coastal Plains Soil, Water, and Plant Research Center, 2611 W. Lucas St. Florence, SC 29501, USA*

ARTICLE INFO

*Article history:*
Received 11 June 2010
Received in revised form
19 July 2010
Accepted 2 August 2010
Available online 9 September 2010

*Keywords:*
Energy conversion
Thermogravimetric analysis
Thermal analysis
Crop production
Pyrolysis

ABSTRACT

Sunn hemp (*Crotolaria juncea*), is a fast growing, high biomass yielding tropical legume that may be a possible southeastern bioenergy crop. When comparing this legume to a commonly grown summer legume – cowpeas (*Vigna unguiculata*), sunn hemp was superior in biomass yield (kg $ha^{-1}$) and subsequent energy yield (GJ $ha^{-1}$). In one year of the study after 12 weeks of growth, sunn hemp had 10.7 Mg $ha^{-1}$ of biomass with an energy content of 19.0 Mg $ha^{-1}$. This resulted in an energy yield of 204 GJ $ha^{-1}$. The energy content was 6% greater than that of cowpeas. Eventhough sunn hemp had a greater amount of ash, plant mineral concentrations were lower in some cases of minerals (K, Ca, Mg, S) known to reduce thermochemical conversion process efficiency. Pyrolytic degradation of both legumes revealed that sunn hemp began to degrade at higher temperatures as well as release greater amounts of volatile matter at a faster rate.

Published by Elsevier Ltd.

## 1. Introduction

Increasing demands have developed globally for renewable bioenergy feedstocks. This in turn has led to a worldwide focus on biofuel production. Prominent bioenergy feedstocks include corn, sugarcane, and soybean. In addition, wood, crop residues and perennial forage crops are the second generation biomass feedstocks that have been the focus of recent research [1]. Alongside this increase in acceptable bioenergy feedstocks are increased concerns over sustainable use of current land and water resources as well as the dilemma of diverting arable land from food production to bioenergy production [2,3]. This is especially true considering the increased food and fuel demands currently placed on traditional agriculture.

One way to help ease the strain from the "food vs. fuel" debate is to establish bioenergy crops during fallow periods between major cash crops. Planting a fast growing bioenergy crop during fallow periods could have many of the environmental benefits that are obtained from cover crops such as the following: reduction in soil erosion; suppression of weeds and insects; and increase in soil organic carbon [4,5]. Suitable bioenergy crop candidates should have the following: high dry matter and energy yields; reduced agricultural input requirements, and low-contaminant compositions [6–8]. Keeping these in mind, legumes grown during late summer in the Southeast region are a high biomass yielding option with no N-fertilizer requirements.

One such summer legume, sunn hemp (*Crotolaria juncea*), is a fast growing legume capable of accumulating large amounts of biomass in a short time frame. During a three-year study in Alabama, sunn hemp biomass accumulation within a 9 to 12 week growing period averaged 5.9 Mg $ha^{-1}$ [9]. When tested as a cover crop for corn in Alabama, sunn hemp at approximately 14 weeks had a reported biomass yield of 7.6 Mg $ha^{-1}$ [10]. Greater biomass yields were reported for sunn hemp grown in Florida as a green manure source – ≤12.2 Mg $ha^{-1}$ [11].

* *Corresponding author*. Tel.: +1 843 669 5203x113; fax: +1 843 669 6970.
E-mail address: keri.cantrell@ars.usda.gov (K.B. Cantrell).
0961-9534/$ – see front matter Published by Elsevier Ltd.
doi:10.1016/j.biombioe.2010.08.005

In addition to quantity, the quality of a bioenergy feedstock for thermochemical conversion affects the net energy yield and conversion process efficiency. This quality can be variable due to environmental influences as well as plant physiology. Increased ash content is known to negatively affect the heating value, thus lowering the net energy yield [6,12]. The ash portion is comprised of plant minerals that exert both adverse and beneficial influences on bioenergy thermal conversion unit operations. The common inorganic minerals, Si, K, and Ca, contribute to slagging and fouling in combustion processes [13]; whereas, some inorganic components, such as Zn, can behave as catalysts during pyrolysis leading to both char yield reductions and greater combustible gas formation [14,15].

The objective of this investigation was to assess differences in two legumes sunn hemp and cowpeas, a commonly grown legume, with regards to biomass quality as a bioenergy feedstock and bioenergy production. Specifically, this was accomplished by evaluating: (1) biomass yield; (2) energy content; (3) energy yield; (4) plant mineral concentrations; and (5) pyrolytic degradation characteristics.

## 2. Methods

### 2.1. Plant materials and energy production

Sunn hemp and cowpeas (Fig. 1) were grown near Florence, SC in a randomized complete block design with four replicate plots in 2004 and 2006 (see details in [16]). In 2004, the legumes were grown in 48 m × 15 m plots on Nobocco loamy sand. In 2006, the legumes were grown in 16 m × 15 m plots on Bonneau sand. The legume plots were established in late July each year. An experiment was established in 2005–2006, but dry soil conditions following summer legume planting resulted in poor stands. No pest control measures were used in growing the legumes.

Legume biomass was harvested three times in both 2004 (26 August, 1 October, and 5 November) and 2006 (30 August, 29 September, and 25 October). The last biomass collection of each season was made right after the first killing freeze of the fall. For cowpeas however, there were not many plants remaining at the last sampling time in 2004; so, these were not sampled. Legume biomass yields within each plot were determined by collecting 0.57 $m^2$ areas. After collection, samples were placed in a 65 °C oven until dry and then weighed. A portion of dried legume samples were ball milled and analyzed for energy content or higher heating value (HHV) using a LECO AC500 Isoperibol Calorimeter (Leco Corp., St. Joseph, MI) following ASTM Standard D5865 [17]. Subsequent legume energy yields ($E_{ha}$) were calculated as the product of the energy content and biomass yield.

**Fig. 1 – Sunn hemp (left) and cowpeas (right) about 6 weeks after planting.**

### 2.2. Plant tissue characterization

Dried and milled grass samples were analyzed for the following minerals: phosphorous (P); potassium (K); calcium (Ca); magnesium (Mg); sulfur (S); zinc (Zn); copper (Cu); manganese (Mn); iron (Fe); and sodium (Na). Plant mineral analyses by inductive coupled plasma (ICP) were provided by the Agricultural Service Laboratory at Clemson University and conducted following general procedures outlined elsewhere [18]. Samples were also subjected to a proximate analysis that yielded a biomass sample's ash, volatile matter and fixed carbon contents. These components were determined using a thermogravimetric analyzer (TGA; Model TGA/DSC1, Mettler Toledo International Inc., Columbus, OH) following the same temperature programs referenced in ASTM D3172 [17].

### 2.3. Thermal analysis

Pyrolytic experiments were conducted on each harvested sample ($n = 4$) using the TGA where the mass loss (thermogravimetry, TG) and temperature changes (differential thermal analysis, DTA) are recorded simultaneously. The derivative of the mass loss, or rate of loss, (DTG) was determined using the TGA software (STARe software v9.10 software (Mettler Toledo International Inc., Columbus, OH)). This unit operated under a three-point calibration using indium, aluminum, and gold. All samples were placed in an $AlO_3$ 70 μl crucible and pyrolyzed in UHP $N_2$ atmosphere at a flow rate of 60 ml $min^{-1}$ at a constant heating rate of 20 °C $min^{-1}$ within the temperature range of 40–800 °C.

### 2.4. Statistical analysis

Data were analyzed by Proc GLM (General Linear Model) and LSD (least significant difference) with Version 9.2 of Statistical Analysis System (SAS Institute Inc., Cary, NC). Significant differences between legumes were based on F-test ($P < 0.05$).

## 3. Results and discussion

### 3.1. Energy production and plant tissue characterization

Sunn hemp and cowpea energy content (MJ $kg^{-1}$) and energy yields (MJ $ha^{-1}$) on a dry-basis were analyzed for statistical differences by year (i.e., within each harvest within a year) due to differences in type of soil as well as rainfall. Rainfall accumulation totaled 56 cm in 2004 and 22 cm in 2006 [16]. The ample rainfall in 2004 benefited sunn hemp growth resulting in a 3 month biomass yield of almost 11 $Mg\,ha^{-1}$. This was almost twice the biomass accumulated by that reported by Mansoer et al. [9] as 5.9 $Mg\,ha^{-1}$; however, this yield was close to that reported by Cherr [11]. With this large amount of biomass, sunn hemp would be within the spectrum of other second generation bioenergy crops with biomass yields ranging from 4.2 to 19.9 $Mg\,ha^{-1}$ [1,7]. The limited rainfall for 2006 and plant growth on a more droughty soil resulted in lower total biomass [16]. During this time, there was no significant difference in biomass yield for the two species at any sampling time.

For both years, sunn hemp at 2 months after planting was more energy dense than the cowpeas ($p$-value $< 0.05$) with an HHV 4–5% greater (Table 1). Over the entire study, cowpea HHV ranged from 17.77 to 18.10 $MJ\,kg^{-1}$ while sunn hemp HHV ranged from 17.82 to 19.19 $MJ\,kg^{-1}$. For the case of sunn hemp, the maximum HHV's were greater than the HHV reported for switchgrass (18.57 $MJ\,kg^{-1}$ [19]), bermudagrass (18.78 $MJ\,kg^{-1}$ [6]), reed canarygrass (17.7 $MJ\,kg^{-1}$ [20]) and alfalfa (18.74 $MJ\,kg^{-1}$ [21]). For the case of sunn hemp grown on Nobocco sand with ample rainfall in 2004, the HHV increased with biomass production. However, for sunn hemp harvested on Bonneau sand in 2006 under limited rainfall, the sunn hemp HHV decreased with plant age in accordance to increases with the ash component (Table 2). These phenomena may be attributed to physiological adaptations of these annual plants – during water-deficit stress conditions, plants shed leaves leaving behind the stalk or stem that has greater ash content than leaves. This explanation is supported by the sunn hemp exhibiting little biomass accumulation during their third month of growth. It was interesting to note a significant decrease for both years in ash content for the cowpeas after one month suggesting a different physiological change with maturity than sunn hemp. Eventhough for most instances, the ash content was considered similar for both legumes, differences were noted in 2006 after the second month with cowpeas having a lesser ash content (Table 2). While both legumes' ash content were greater than that known for wood varieties, the cowpea ash content was within the range reported for alfalfa, reed canarygrass, and switchgrass [20].

**Table 2 – Volatile matter (VM), fixed carbon (FC), and ash compositions at various months after planting (MAP) of sunn hemp (SH) and cowpeas (CP).**

| Year | Legume | MAP | VM $wt\%_{db}$ | FC[a] $wt\%_{db}$ | Ash $wt\%_{db}$ |
|---|---|---|---|---|---|
| 2004 | CP | 1 | 67.92 (1.60)[b] | 15.82 (2.82) | 15.08 (4.16) |
| | | 2 | 70.10 (1.73) | 19.88 (3.74) | 9.59 (2.62) |
| | SH | 1 | 64.76 (1.69) | 25.91 (5.49) | 9.45 (3.17) |
| | | 2 | 65.31 (2.93) | 21.89 (4.89) | 12.84 (2.43) |
| | | 3 | 72.07 (3.58) | 14.22 (4.71) | 14.82 (4.23) |
| 2006 | CP | 1 | 70.31 (1.88) | 18.19 (0.67) | 11.49 (1.72) |
| | | 2 | 72.96 (2.44) | 22.25 (2.83) | 4.79 (2.66)** |
| | | 3 | 69.09 (0.19)** | 22.70 (0.66) | 8.21 (0.81)** |
| | SH | 1 | 72.66 (4.32) | 16.01 (3.34) | 11.94 (1.47) |
| | | 2 | 69.81 (0.78) | 15.86 (3.38) | 13.61 (2.60) |
| | | 3 | 64.98 (1.92) | 22.44 (1.66) | 13.51 (1.63) |

**Statistically different from SH counterpart.
a Fixed carbon calculated as 100 − VM − Ash.
b Values in parentheses are standard deviations.

In addition to a greater HHV, the sunn hemp at 2 months after planting had a statistically significant greater energy yield ranging from 148 to 204 $GJ\,ha^{-1}$ ($p$-value $< 0.002$). Despite sunn hemp yielding significantly greater HHV than cowpeas in 2006, the overall energy yields were not considered different ($p$-value $< 0.28$, 0.057, and 0.12, month after planting, respectively). However, for 2004 the significant sunn hemp growth after 2 months along with greater HHV resulted in significantly greater energy yields – almost 2.5 times.

Among the measured plant minerals (Tables 3 and 4), K was the most significant mineral present with concentrations upwards of 3.13 $wt\%_{db}$ for cowpeas and 2.92 $wt\%_{db}$ for sunn hemp. Plant Ca, Mg, and P were also present in relatively large quantities. Plant Cu concentrations were the lowest of measured nutrients ranging from 6.00 to 17.8 ppm. All above-ground plant nutrient concentrations decreased as plant biomass matured. Few nutrient concentration differences ($\alpha = 0.05$) were noted between cowpeas and sunn hemp. When differences were noted, cowpeas consistently had greater concentrations of those nutrients. The one exception was for Na. Plant nutrient concentrations at time of harvest were

**Table 1 – Biomass yield, energy content (HHV), and energy yield at various months after planting (MAP) for sunn hemp (SH) and cowpeas (CP).**

| Year | Legume | Biomass[a] $kg_{db}\,ha^{-1}$ | | | HHV $MJ\,kg_{db}^{-1}$ | | | Energy yield $GJ\,ha^{-1}$ | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | MAP | | | MAP | | | MAP | | |
| | | 1 | 2 | 3 | 1 | 2 | 3 | 1 | 2 | 3 |
| 2004 | SH | 2070 | 7891 | 10718 | 17.82 | 18.67 | 18.94 | 37.0 | 147.8 | 203.6 |
| | CP | 1628 | 3222 | – | 18.10 | 17.80 | – | 29.6 | 57.4 | – |
| | P-value | 0.15 | 0.01 | – | 0.055 | 0.000 | – | 0.176 | 0.002 | – |
| 2006 | SH | 1264 | 6973 | 7253 | 19.19 | 18.75 | 18.83 | 24.3 | 131.1 | 137.0 |
| | CP | 1683 | 5507 | 5909 | 18.06 | 17.81 | 17.77 | 30.5 | 98.3 | 105.2 |
| | P-value | 0.19 | 0.11 | 0.20 | 0.000 | 0.000 | 0.000 | 0.28 | 0.057 | 0.12 |

a Biomass yields previously published in [16].

**Table 3 – Major plant mineral concentrations (with standard deviations) at various months after planting (MAP) of sunn hemp (SH) and cowpeas (CP).**

| Year | Legume | MAP | P wt%$_{db}$ | K wt%$_{db}$ | Ca wt%$_{db}$ | Mg wt%$_{db}$ | S wt%$_{db}$ |
|---|---|---|---|---|---|---|---|
| 2004 | CP | 1 | 0.38 (0.01)** | 3.13 (0.68) | 1.18 (0.10)** | 0.47 (0.03) | 0.22 (0.05) |
| | | 2 | 0.23 (0.02) | 2.23 (0.34)** | 0.49 (0.13) | 0.29 (0.02) | 0.19 (0.03)** |
| | SH | 1 | 0.31 (0.05) | 2.92 (0.46) | 0.73 (0.17) | 0.38 (0.09) | 0.20 (0.04) |
| | | 2 | 0.25 (0.03) | 1.54 (0.24) | 0.78 (0.27) | 0.38 (0.09) | 0.14 (0.01) |
| | | 3 | 0.24 (0.04) | 1.33 (0.23) | 0.62 (0.20) | 0.33 (0.07) | 0.13 (0.03) |
| 2006 | CP | 1 | 0.32 (0.05) | 2.92 (0.46) | 1.15 (0.15)** | 0.58 (0.09) | 0.24 (0.02) |
| | | 2 | 0.18 (0.05) | 1.22 (0.14) | 0.81 (0.33) | 0.39 (0.01) | 0.13 (0.02) |
| | | 3 | 0.16 (0.03) | 1.25 (0.17)** | 0.57 (0.12) | 0.44 (0.03)** | 0.15 (0.01)** |
| | SH | 1 | 0.35 (0.08) | 2.52 (0.13) | 0.78 (0.20) | 0.49 (0.09) | 0.21 (0.03) |
| | | 2 | 0.19 (0.01) | 1.25 (0.06) | 0.58 (0.04) | 0.37 (0.04) | 0.11 (0.02) |
| | | 3 | 0.14 (0.02) | 0.88 (0.15) | 0.45 (0.11) | 0.33 (0.08) | 0.09 (0.02) |

**Statistically different from SH counterpart.

greater in cowpeas than sunn hemp for K, Mg, S, and Zn. This results in 3–28% more mass (kg ha$^{-1}$) of these nutrients being removed and potentially residing in the residual combustion ash portion. In addition, the exact role of these minerals is unknown during thermochemical conversion.

During pyrolysis and gasification, the inorganic components K, Ca, and Na are thought to act as catalysts improving the rate of degradation and conversion efficiency. Inorganic salts have been shown to reduce the onset temperature for degradation as well as increase gaseous volatiles [15,22]. Additionally, both K and Na have been identified to promote the secondary char gasification reactions with $CO_2$ and $H_2O$ that generate the combustible gases of CO and $H_2$ [23]. These components (CO and $H_2$) positively influence the caloric value of the gas. However, the removal of precipitating minerals like Ca, Mg, and P as well as S may be necessary as these have been identified as poisoning metal catalysts used in catalytic driven gasification processes [24]. Thus, developing a quality bioenergy feedstock for gasification or pyrolysis where a combustible gas or oil is desired will require a balance among minerals. This balance may be achieved with pretreatments to decrease salt content or potentially through manipulation of soil nutrient levels.

### 3.2. *Thermal analysis*

The weight loss (TG) and derivative of weight loss (DTG) curves of the plants (Fig. 2) exhibited typical pyrolytic degradation profiles of other plant materials [25,26]. After water evaporation, samples underwent a primary devolatilization stage. The onset temperature of this stage was determined to be the temperature corresponding to 5% of the weight loss with respect to the final dry-basis weight loss. Once the bulk of biomass was removed, the next stage was a slow and continuous weight loss. This weight loss has been attributed to the degradation of heavier chemical structures in the plant matrix [25]. Some of these materials may be native to the plant structure or produced during the primary pyrolysis stage, sometimes referred to as "secondary thermolysis" [27]. A final temperature of primary devolatilization was defined on the DTG curve as the temperature corresponding to the intersection of

**Table 4 – Minor plant mineral concentrations (with standard deviations) at various months after planting (MAP) of sunn hemp (SH) and cowpeas (CP).**

| Year | Legume | MAP | Zn ppm | Cu ppm | Mn ppm | Fe ppm | Na ppm |
|---|---|---|---|---|---|---|---|
| 2004 | CP | 1 | 50.3 (7.63)** | 8.25 (1.71) | 95.5 (18.1)** | 104.8 (8.22)** | 40.8 (5.44) |
| | | 2 | 42.0 (3.74)** | 6.50 (0.58) | 72.5 (9.68) | 66.8 (20.7) | 60.8 (6.55) |
| | SH | 1 | 38.3 (3.77) | 6.00 (0.82) | 44.5 (11.2) | 72.8 (20.6) | 43.0 (10.8) |
| | | 2 | 32.3 (0.96) | 9.25 (4.57) | 56.0 (9.56) | 56.0 (7.39) | 45.8 (12.0) |
| | | 3 | 32.5 (5.20) | 6.50 (1.00) | 38.8 (10.3) | 47.0 (13.7) | 21.5 (5.20) |
| 2006 | CP | 1 | 47.3 (6.55) | 17.8 (7.80) | 64.8 (10.3)** | 174.0 (58.1) | 33.0 (6.38) |
| | | 2 | 42.8 (13.1) | 6.00 (2.45) | 52.0 (31.9) | 65.0 (26.7) | 19.0 (2.83)** |
| | | 3 | 51.0 (7.87)** | 5.50 (1.29) | 38.3 (7.50) | 49.3 (9.91) | 32.8 (8.42) |
| | SH | 1 | 36.3 (7.85) | 13.3 (2.63) | 43.0 (9.31) | 101.3 (14.4) | 35.3 (10.2) |
| | | 2 | 30.3 (8.14) | 7.50 (2.52) | 36.5 (6.03) | 50.5 (10.8) | 29.8 (8.06) |
| | | 3 | 29.8 (10.6) | 6.75 (0.50) | 29.0 (7.39) | 42.0 (19.1) | 23.0 (8.91) |

**Statistically different from SH counterpart.

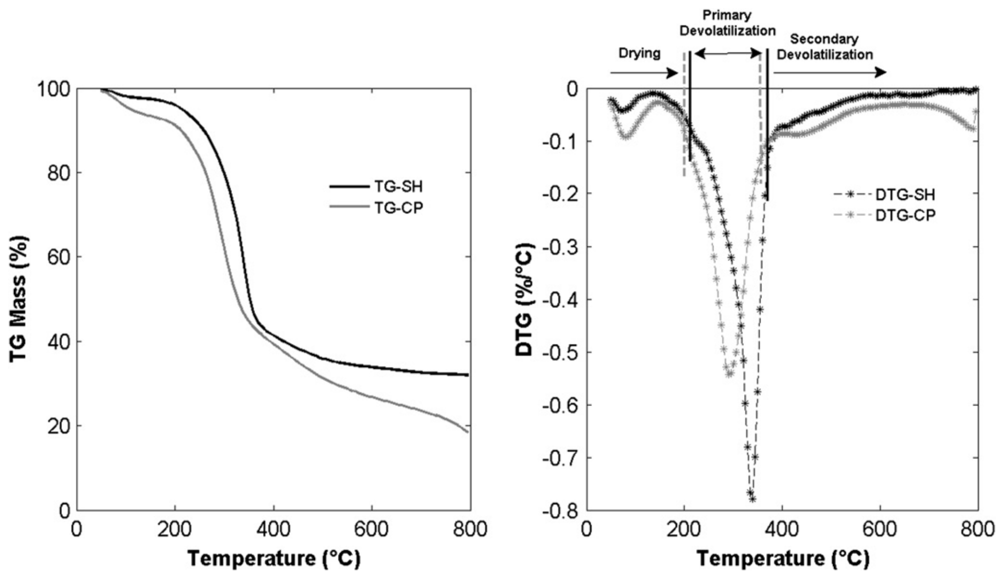


**Fig. 2 – Mass (TG) and derivative mass curves (DTG) (*n* = 4) of the pyrolysis of sunn hemp (SH) and cowpeas (CP) three months after planting. (TGA Method: 40–800 °C; 20 °C min$^{-1}$; $N_2$ atmosphere).**

tangent lines in both devolatilization stages. Comparing the two stages, the primary devolatilization stage released more volatile matter that can be used in combustion systems for combined heating and power production or converted into higher-value fuels via catalytic thermochemical conversion processes (Table 5) [21]. In addition, the maximum rate of weight loss ($DTG_{max}$) was in all cases greater for sunn hemp. At full maturity, sunn hemp $DTG_{max}$-value averaged 0.74%/°C. This was similar to rice husks pyrolyzed at 20 °C min$^{-1}$ by Biagini [28] at 0.79%/°C. The rate of maximum weight loss for cowpeas was consistently closer to that of cotton stalks and sugarcane bagasse at 0.51–0.57%/°C, respectively [29].

For this current study, the temperature for the onset of devolatilization ($T_{on}$) was higher for sunn hemp than for cowpeas and ranged between 200 and 229 °C (Table 5; Fig. 2). Additionally, $T_{on}$ was observed to increase with the age and physiological changes of the plant. The same was true for the end temperature of the primary devolatilization stage – $T_p$ (Table 5; Fig. 3). However, the temperature range for primary devolatilization among the two plant species was comparable to one another. Temperature at maximum devolatilization, $T_{max}$, for these two legumes ranged between 295 and 343 °C. This range was lower than those values for pine wood at 371 °C [25], rice husk at 357 °C [28], and corn stover near 360 °C [26].

**Table 5 – Devolatilization characteristics at various months after planting (MAP) of sunn hemp (SH) and cowpeas (CP).**

| Year | Legume | MAP | $T_{on}$[a] (°C) | $T_{max}$[b] (°C) | $T_p$[c] (°C) | $DTG_{max}$[d] (%/°C) | $VM_p$[e] ($wt\%_{db}$) | $VM_s$[f] ($wt\%_{db}$) |
|---|---|---|---|---|---|---|---|---|
| 2004 | CP | 1 | 200 | 316 | 359 | 0.50 | 44.4 | 8.8 |
| | | 2 | 219 | 323 | 360 | 0.58 | 49.3 | 20.1 |
| | SH | 1 | 211 | 328 | 356 | 0.56 | 41.3 | 10.0 |
| | | 2 | 229 | 332 | 358 | 0.70 | 47.0 | 12.9 |
| | | 3 | 223 | 335 | 361 | 0.75 | 54.5 | 29.5 |
| 2006 | CP | 1 | 206 | 310 | 350 | 0.52 | 43.7 | 11.6 |
| | | 2 | 208 | 296 | 352 | 0.49 | 45.6 | 21.1 |
| | | 3 | 205 | 295 | 356 | 0.55 | 49.0 | 26.3 |
| | SH | 1 | 211 | 323 | 359 | 0.56 | 48.1 | 13.9 |
| | | 2 | 213 | 338 | 360 | 0.80 | 52.1 | 21.2 |
| | | 3 | 221 | 343 | 365 | 0.72 | 50.7 | 17.9 |

a Onset temperature corresponded to a weight loss of 5%db of the final weight loss.
b Temperature at maximum devolatilization.
c Temperature at end of primary devolatilization stage.
d Maximum rate of weight loss.
e Volatile matter removed during primary devolatilization stage.
f Volatile matter removed during secondary devolatilization stage.

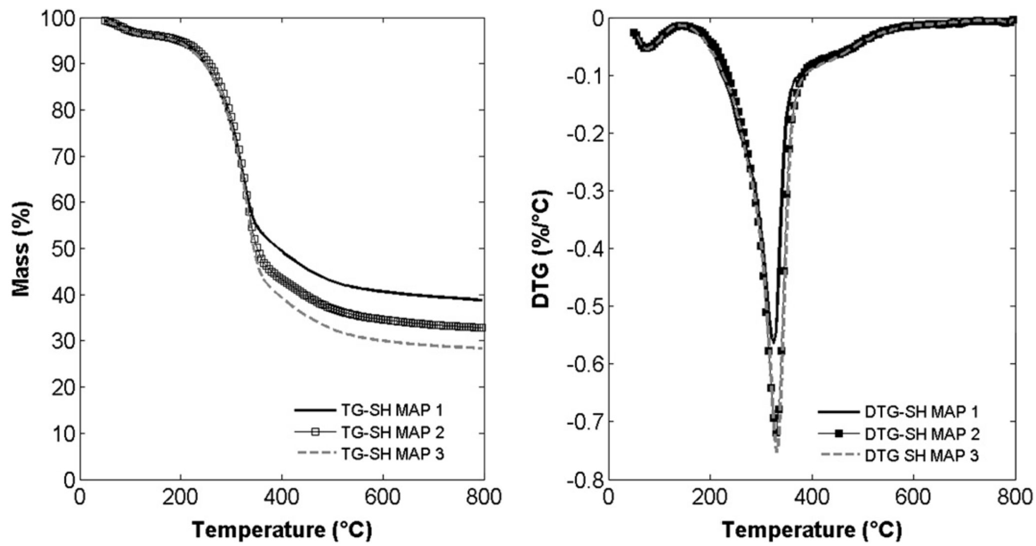


**Fig. 3 – Mass (TG) and derivative mass curves (DTG) (*n* = 4) of the pyrolysis of sunn hemp (SH) at various months after planting (MAP). (TGA method: 40–800 °C; 20 °C $min^{-1}$; $N_2$ atmosphere).**

## 4. Conclusion

Sunn hemp (*Crotolaria juncea*) is a fast growing, high biomass yielding, tropical legume that can be grown during fallow periods of cash crops lending itself to become a suitable southeastern bioenergy crop. When comparing this legume to another commonly grown summer legume – cowpea, sunn hemp was superior in biomass yield (kg $ha^{-1}$) and subsequent energy yield (GJ $ha^{-1}$). Interlinked with energy yield, the sunn hemp energy content (MJ $kg^{-1}$) at the greatest maturity sampled was 18.94 MJ $kg^{-1}$. This was 6% greater than that of cowpeas. Despite sunn hemp having a greater amount of ash, sunn hemp concentration of nutrients was lower in some cases of minerals (K, Ca, Mg, S) known to influence thermochemical conversion process. Pyrolytic degradation of both legumes revealed that sunn hemp began to degrade at higher temperatures as well as released more volatile matter.

## Acknowledgements

The authors are grateful to Cody Alexander, Ashley Kelly, Jerry Martin II, Ernie Strickland, and Don Watts for help with sample collection, preparation, and analyses.

Mention of trade names or commercial products in this publication is solely for the purpose of providing specific information and does not imply recommendation or endorsement by the U.S. Department of Agriculture.

## REFERENCES

[1] Sanderson MA, Adler PR. Perennial forages as second generation bioenergy crops. Int J Mol Sci 2008;9:768.

[2] Stone KC, Hunt PG, Cantrell KB, Ro KS. The potential impacts of biomass feedstock production on water resource availability. Bioresour Technol 2010;101:2014.

[3] Pimentel D, Marklein A, Toth MA, Karpoff MN, Paul GS, McCormack R, et al. Food versus biofuels: environmental and economic costs. Human Ecology 2009;37:1.

[4] Franzluebbers AJ. Integrated crop-livestock systems in the southeastern USA. Agronomy Journal 2007;99:361.

[5] Rao SC, Northup BK. Capabilities of four novel warm-season legumes in the Southern Great Plains: biomass and forage quality. Crop Sci 2009;49:1096.

[6] Cantrell KB, Stone KC, Hunt PG, Ro KS, Vanotti MB, Burns JC. Bioenergy from coastal Bermudagrass receiving subsurface drip irrigation with advance-treated swine wastewater. Bioresour Technol 2009;100:3285.

[7] Adler PR, Sanderson MA, Boateng AA, Weimer PJ, Jung HJG. Biomass yield and biofuel quality of switchgrass harvested in fall or spring. Agron J 2006;98:1518.

[8] McKendry P. Energy production from biomass (part 1): overview of biomass. Bioresour Technol 2002;83:37.

[9] Mansoer Z, Reeves DW, Wood CW. Suitability of sunn hemp as an alternative late-summer legume cover crop. Soil Sci Soc Am J 1997;61:246.

[10] Balkcom KS, Reeves DW. Sunn-hemp utilized as a legume cover crop for corn production. Agron J 2005;97:26.

[11] Cherr CM, Scholberg JMS, McSorley R, Mbuya OS. Growth and yield of sweet corn following green manure in a warm temperate environment on sandy soil. J Agron Crop Sci 2007;193:1.

[12] Monti A, Di Virgilio N, Venturi G. Mineral composition and ash content of six major energy crops. Biomass Bioenergy 2008;32:216.

[13] Ohman M, Nordin A, Skrifvars BJ, Backman R, Hupa M. Bed agglomeration characteristics during fluidized bed combustion of biomass fuels. Energy Fuels 2000;14:169.

[14] Priyadarsan S, Annamalai K, Sweeten JM, Mukhtar S, Holtzapple MT. Fixed-bed gasification of feedlot manure and poultry litter biomass. Trans ASAE 2004;47:1689.

[15] Raveendran K, Ganesh A, Khilar KC. Influence of mineral matter on biomass pyrolysis characteristics. Fuel 1995;74:1812.

[16] Bauer PJ, Park DM, Campbell BT. Cotton production in rotation with summer legumes. J Cotton Sci 2009;13:183.

[17] ASTM. Petroleum products, lubricants, and fossil fuels: gaseous fuels; coal and coke. West Conshohocken, PA: ASTM International; 2006.
[18] Jones Jr JB, Wolf B, Mills HA. Plant Analysis Handbook. Athens, GA: Micro-Macro Publishers; 1991.
[19] Boateng AA, Daugaard DE, Goldberg NM, Hicks KB. Bench-scale fluidized-bed pyrolysis of switchgrass for bio-oil production. Ind Eng Chem Res 2007;46:1891.
[20] Dien BS, Jung H-JG, Vogel KP, Casler MD, Lamb JFS, Iten L, et al. Chemical composition and response to dilute-acid pretreatment and enzymatic saccharification of alfalfa, reed canarygrass, and switchgrass. Biomass Bioenergy 2006;30:880.
[21] Boateng AA, Jung HG, Adler PR. Pyrolysis of energy crops including alfalfa stems, reed canarygrass, and eastern gamagrass. Fuel 2006;85:2450.
[22] Williams PT, Horne PA. The role of metal salts in the pyrolysis of biomass. Renew Energy 1994;4:1.
[23] Raveendran K, Ganesh A. Heating value of biomass and biomass pyrolysis products. Fuel 1996;75:1715.
[24] Ro KS, Cantrell K, Elliott D, Hunt PG. Catalytic wet gasification of municipal and animal wastes. Ind Eng Chem Res 2007;46:8839.
[25] Biagini E, Barontini F, Tognotti L. Devolatilization of biomass fuels and biomass components studied by TG/FTIR technique. Ind Eng Chem Res 2006;45:4486.
[26] Kumar A, Wang L, Dzenis YA, Jones DD, Hanna MA. Thermogravimetric characterization of corn stover as gasification and pyrolysis feedstock. Biomass Bioenergy 2008;32:460.
[27] Fisher T, Hajaligol M, Waymack B, Kellogg D. Pyrolysis behavior and kinetics of biomass derived materials. J Anal Appl Pyrolysis 2002;62:331.
[28] Biagini E, Fantei A, Tognotti L. Effect of the heating rate on the devolatilization of biomass residues. Thermochim Acta 2008;472:55.
[29] Munir S, Daood SS, Nimmo W, Cunliffe AM, Gibbs BM. Thermal analysis and devolatilization kinetics of cotton stalk, sugarcane bagasse and shea meal under nitrogen and air atmospheres. Bioresour Technol 2009;100:1413.