

## STORAGE AND CHARACTERIZATION OF COTTON GIN WASTE FOR BIOETHANOL PRODUCTION

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### Abstract

The disposal of cotton gin waste (CGW) is a significant problem in the cotton ginning industry, but CGW could be potentially used as feedstock for bioethanol. Freshly discharged CGW and stored CGW were characterized for storage stability and potential for ethanol production by determining their summative compositions. The bulk densities of the fresh wet and dry CGW were  $210.2 \pm 59.9 \text{ kgm}^{-3}$  and  $183.3 \pm 52.2 \text{ kgm}^{-3}$ , respectively. After six-months of storage the volume of piles A, B, and C decreased by 38.7%, 41.5%, and 33.3%, respectively relative to the volume of the pile at the start of the storage. The ash content of the CGW was very high ranging from 10% to 21% and the acid insoluble fraction was high (21% to 24%). The total carbohydrate content was very low and ranged from 34% to 49%. After three months storage, the loss of total carbohydrates was minimal but after six months the losses were as high as 25%. This loss of carbohydrates suggests that under open storage conditions, the feedstock must be processed within three months to reduce ethanol yield losses.

### Introduction

Waste management is a significant problem facing the cotton ginning industry. The ginning of one lint bale (227 kg) of spindle harvested seed cotton generates between 37-147 kg of waste (Thomasson, 1990). In 2002, about 17.1 million bales of cotton were ginned in the United States (Adams et al., 2003) and the estimated cotton gin waste was  $2.25 \times 10^9$  kg. Cotton gin waste (CGW) consists of sticks, leaves, burs, soil particles, mote, cotton lint, and other plant materials (Schacht et al., 1978). Slight differences in the proportions of the components are usually found between varying mechanical harvest methods (Thomasson, 1990).

The traditional methods of CGW disposal include incineration, landfilling, and incorporation into the soil (Thomasson, 1990). Until the enactment of the Clean Air Act in 1970, incineration was an acceptable and convenient choice. The most recent amendment of the act, (July 1997) further restricts particulate matter discharge into the atmosphere, thus eliminating incineration as an option for small cotton gins (Fuller et al., 1997). Furthermore, because of the high ash content of the feedstock, there could be potential slagging problems associated with large-scale incineration.

Landfilling is not a viable option because tipping fees are very high. The current method of choice is the incorporation of the waste into the soil, an option that is unsuitable for the climatic conditions of some states such as Virginia. There is much concern over the presence of weed seeds, insect infestations, diseases, and excess chemicals in the waste that may degrade the receiving land. However, if the cotton gin waste is composted at 55% moisture, the infestation and weed problems can be minimized (Anthony, 2001).

The conversion of CGW to value-added products has not been extensively studied. Brink (1981) and Beck and Clements (1982) studied the conversion of CGW to ethanol and concluded that 142.8 L (37.8 gal) ethanol per ton could be produced from this feedstock. Griffin (1974), Schacht and Lepori (1978) analyzed cotton gin waste to assess its fuel value for combustion. These researchers proposed using the feedstock for the production of char, hydrogen, protein, and pyrolysis gases. Parnell *et al.* (1991) investigated the gasification of cotton gin waste in a fluidized bed reactor. The gas produced had a low heating value and the projected net revenue from the process was very low. However, activated carbon produced from the gasification of the feedstock was found to be cheaper, but less effective than those produced from conventional carbon sources (Capareda et al., 1989).

Our studies (Agblevor et al., 2001) on CGW using steam explosion/enzyme hydrolysis and fermentation showed that ethanol yield was dependent on the source of feedstock. The ethanol yields ranged from 113 L/ton to 190 L/ton CGW. The differences stemmed from the cotton lint and hull content of the CGW. Where the lint content was high the ethanol yield was subsequently high and vice versa. We observed that because of the high cotton lint content of the raw material and the method of processing at the various gins in Southeast Virginia, the material was easily

degraded by microorganisms. For a year-round production of ethanol from this feedstock, effective storage will be essential. Our literature survey did not reveal any published data on the stability of CGW during storage. Thus, the need to characterize both fresh and stored CGW is warranted. In this paper we report the influence of storage on the composition and potential ethanol yield from CGW.

## **Experimental Methods**

### **Sampling of freshly discharged cotton gin waste**

Cotton gin waste (CGW) samples were collected from five cotton gins (Mid Atlantic Cotton Gin, Emporia, VA; Commonwealth Cotton Gin, Franklin, VA; Commonwealth Cotton Gin, Windsor VA; Suffolk Cotton Gin, Suffolk, VA; and Wakefield Cotton Growers Gin, Wakefield, VA) in southeastern Virginia. During the ginning season, CGW samples were collected three times. The sampling was at the beginning of the ginning season; mid-season and at the end of the season. During each sampling period, about 5 kg samples were collected from freshly discharged CGW from each gin. Grab samples were collected from the perimeter of the heaps of material as they were being discharged onto the dumpsite. The samples were collected in polyethylene bags and sent by truck to Virginia Tech, Blacksburg, VA on the same day. The samples were air-dried at ambient conditions to equilibrium moisture content and then stored at room temperature until the time of analysis.

### **Preparation and sampling of cotton gin waste storage piles**

Three piles were prepared from freshly discharged CGW material and a front-end loader was used to transport the CGW from the waste dumpsite to the storage area. The materials were dumped into conical piles with a 5 m base diameter and a maximum height of 2 m. Three thermocouples were inserted into each pile to a depth corresponding to the middle of the weathered, transition, and core layers. The weathered layer was defined as a layer of material from the outer surface to a depth of 10 cm. The transition layer was a layer between 10-30 cm thick and the core was defined as any material which was greater than 30 cm from the surface of the pile. The thermocouple probes were connected to a data-logger at a data collection station at the storage site. The temperatures were recorded hourly and daily averages were calculated. At defined periods (1 month, 3 months, and 6 months) the data were downloaded into a lap top computer for analysis.

The ambient temperature and precipitation events and amounts were obtained from the Virginia Tech Tidewater Agricultural Research and Extension Center, Suffolk, VA. The station was located about 35 miles east of the storage location.

The three storage piles A, B, and C were each sampled four times during the storage period at the beginning of storage (time zero), one month after storage, three months after storage and six months after storage. For time zero samples, about 1 kg grab materials were collected from the perimeter of each pile. Samples for one, three, and six months storage were taken at three equidistant positions around the perimeter of the pile using a 25-cm diameter aluminum sampling tube with sharpened front edge. The tube was sawed into the pile to a depth of 10 cm and the weathered layer was removed by hand and collected into a sampling bag. The tube was further sawed into the pile to a depth of 30 cm and the transition layer was removed by hand and deposited into a sampling bag. The core layer was obtained by further sawing of the pile. The samples taken from the three locations around the perimeter of the pile were combined as composite material for each layer. Nine composite samples (3 layers x 3 piles) were obtained from the storage piles during each sampling period. The storage samples were transported the same to Virginia Tech, where they were air-dried at ambient laboratory conditions to equilibrium moisture content and then stored at room temperature until the time of analysis.

### **Fractionation of cotton gin waste**

About 1 kg dry CGW samples from each of the five gins were shipped to the USDA Cotton Ginning Laboratory, (Stoneville, MS) where they were fractionated into eight fractions consisting of clean lint, hulls, sticks and stems, grass, seeds, small leaf, and pin trash. About 150 g of each sample was fractionated manually according to the method of Shepherd (1972).

### **Chemical analysis of cotton gin waste**

All samples for compositional analysis were first hammer-milled and then ground in a Wiley mill until all the samples passed through a 20-mesh sieve. The milled CGW samples were analyzed for moisture, ash, 95% ethanol extractives, acid insoluble material, and carbohydrates. All samples were analyzed using American Society of Materials and Testing (ASTM) standard testing methodologies. The description of each analysis follows.

### **Determination of moisture content (ASTM E 1756-01, 2001)**

The oven dry method was used to determine the moisture content of the CGW. Thus, 0.5 g of ground CGW (-20-mesh) was weighed into a pre-dried aluminum-weighing pan. The pan and its contents were dried in a gravity oven

at 105 °C for 3 hours. The samples were cooled to room temperature in a desiccator and weighed. The process was repeated until a constant mass was recorded. The moisture content was calculated from the difference between the original mass and that obtained after drying to a constant mass.

#### **Determination of ash (ASTM E 1755-01, 2001)**

About 1.0 g of ground CGW (-20-mesh) was weighed into ceramic crucibles that had been preheated and ignited at 575 °C in a muffle furnace. The crucibles and biomass were held at 575 °C for 3 hours and then cooled to room temperature in a desiccator and weighed. The process was repeated until a constant weight was achieved. The ash content was calculated on moisture free basis for triplicate samples.

#### **Determination of extractives (ASTM E 1690-01, 2001)**

About 10 g of ground CGW (-20-mesh) samples were weighed into dry cellulose extraction thimbles and placed in a Soxhlet extraction apparatus. About 350 mL 95% ethanol was added to a 500-mL round bottom flask containing boiling chips. The samples were refluxed for eight hours at a solvent exchange rate of six per hour.

After the extraction, the flasks were cooled to room temperature and the residual solids were vacuum filtered in a Buchner funnel. The solid residues were washed several times with 95% ethanol until the filtrate was clear. The filtrate was added to the ethanol extract and vacuum evaporated to dryness using a Buchii rotary evaporator at 40 °C and 84 kPa. The final product was dried overnight in a vacuum oven at 40 °C and weighed. The ethanol extractives content was calculated from the residue on a moisture-free basis.

The filtered and washed solids were air-dried overnight at ambient laboratory conditions in aluminum boats. These samples were labeled extractives-free solids and were used for the acid-insoluble material and carbohydrates analyses. The samples were stored at room temperature until the time of each analysis.

#### **Determination of acid-insoluble residue (ASTM 1721-01, 2001)**

About 0.3 g extractives-free CGW samples were weighed into test tubes. Sulfuric acid (3 mL, 72%) was added to each sample and stirred until thoroughly mixed and hydrolyzed at 30 °C for 2 h while stirring at 15 min intervals. The samples were transferred to glass serum bottles and diluted with deionized water to 4% sulfuric acid. The samples were then autoclaved using a liquid vent cycle at 121 °C for 1 h and then allowed to cool to room temperature. The samples were then filtered under vacuum with previously ignited ceramic filtering crucibles. Some of the filtrate from each sample was saved and stored in a refrigerator and later used for carbohydrate analysis. The solid residues were initially dried to constant mass at 105 °C as per the ASTM E 1756-01 (2001). The crucibles and oven-dried samples were heated in a muffle furnace at 575 °C for 3 hours and then cooled to room temperature in a desiccator and weighed. The process was repeated until a constant weight was achieved. The ash content was calculated on moisture free basis for triplicate samples. The ash-free acid insoluble material was then calculated on oven-dry biomass basis.

#### **Determination of carbohydrate by gas chromatography (ASTM E 1821-01, 2001)**

The carbohydrates content of the CGW samples were determined as alditol acetates using a gas chromatograph. The acid hydrolyzed samples saved from the acid insoluble material analysis procedure were used for these analyses. The analytes were prepared according to ASTM standard method E 1821-01 (2001). This method describes the procedure for converting sugars to alditol acetates.

The derivatized hydrolysate samples were analyzed by gas chromatograph (Shimadzu GC 14A) using DB-225 capillary column (15 m, 0.25 µm ID, 0.2 µm film thickness). The following conditions were used for the gas chromatographic analysis:

Carrier gas: helium; total gas flow rate: 64 mL/min; column gas flow rate: 0.6 mL/min; column temperature was programmed: initial temperature: 190 °C for 5 min.; heating rate 10 °C/min.; final oven temperature: 210 °C; total run time was 25 min. Injection port temperature: 240 °C; detector: flame ionization (FID) at 220 °C; sample size: 2 µL; split ratio: 33:1. The samples were analyzed for glucan, xylan, arabinan, mannan, and galactan. All samples were run in triplicates.

## **Results and Discussion**

### **Storage pile characteristics**

The bulk densities of the fresh wet and dry CGW were  $210.2 \pm 59.9 \text{ kg m}^{-3}$  and  $183.3 \pm 52.2 \text{ kg m}^{-3}$ , respectively. After six-months of storage the volume of piles A, B, and C decreased by 38.7%, 41.5%, and 33.3%, respectively relative to the volume of the pile at the start of the storage. When the piles were opened after six months, the cores were very warm and felt very uncomfortable when touched with bare hands.

The temperature variation in the cores of the three piles was more pronounced than those for the weathered and transition layers during the initial storage period, but the differences were minimal as the piles stabilized. There was a very rapid rise in the core temperatures within the first five days of storage followed by a rapid decrease. The highest daily average core temperature ( $62.9^\circ\text{C}$ ) was recorded for Pile C on the fourth day of storage. The highest core temperatures for Piles A and B were  $59^\circ\text{C}$  and  $60^\circ\text{C}$ , respectively, but these occurred after 60 days of storage. After forty days of storage, it appeared that all piles had stabilized, thus temperature spikes for all three piles were similar until the end of the storage period.

Temperature spikes occurred shortly after any precipitation event. This suggests that the rise in temperature of the piles was mostly due to microbial activities. It appeared that as the moisture content of the pile decreased, the piles cooled gradually because there was not enough moisture to support rapid microbial growth. However, after any precipitation event the moisture content of the pile increased and this tended to support more microbial activity and therefore there was a corresponding rise in the temperature of the piles. As the pile moisture content decreased, the microbial activity also decreased resulting in a decrease in the temperature of the pile. The increase in CGW piles temperatures were similar to those reported for other pile studies. However, in some of those reports the piles eventually underwent spontaneous combustion (Kubler, 1978).

### **Fractionation of cotton gin waste**

Cotton gin waste is a heterogeneous material composed of clean lint, seeds, hulls, leaves, sticks, and dirt which makes chemical analysis very time consuming. The interpretation of the data is sometimes difficult because of the heterogeneity. To improve interpretation and understanding of the cotton gin waste data, we fractionated the cotton gin waste into various components using the methodology of the U.S. Cotton Ginning Laboratory, Stoneville, Mississippi (Shepherd, 1972).

The fractional composition of the cotton gin waste is shown in Table 1. The data consist of samples collected during the 2000 and 2001 ginning seasons and it varied between seasons and between gins. The cottonseed had the largest variation, which ranged from 0% to 24%. The stick/stems and grass fractions did not vary much.

The small leaf fraction showed a large variation ranging from 14% to 35%. Leafy materials normally do not contain high levels of structural biopolymers such as cellulose, hemicellulose, and lignins. Thus, their contribution to the overall ethanol yield was expected to be low. The small leaf content correlated positively with the theoretical ethanol yield, but leveled off at higher leaf content (Agblevor et al., 2003b). These data suggest that high levels of small leaf in the feedstock could be deleterious to ethanol yield. The hull content of the samples varied strongly between gins (16% to 48%) and correlated negatively with the theoretical ethanol yield (Agblevor et al., 2003b).

The clean lint, which has a considerable influence on the overall cellulose content of the feedstock, showed a considerable variation between gins and ranged from 5% to 15%. If it is assumed that the chemical composition of the hulls and small leaf fractions were similar for all gins, then the most important variable that will influence the total sugar content will be the cotton fiber. Thus, ethanol yields could be strongly dependent on the clean lint and mote contents of the CGW. The above explanation was borne out by the ethanol yield from our studies (Agblevor et al., 2001). There was a quadratic correlation between the clean lint and the ethanol yield with an  $R^2$  value of 0.98.

The fractional composition also appears to vary with the ginning season. Although the data collected was for only two ginning seasons, there were differences in the fractional composition. During the 2000 ginning season, the Suffolk sample had the highest clean lint content (12.5%), but during the 2001 ginning season, the highest clean lint content was detected in the sample from Windsor (15%). The hull content varied with the ginning season except for the Franklin gin where hull content was almost constant. The hull, seed, motes, and clean lint contents of the CGW reflect the ginning practice. Because these fractions showed considerable variation between gins and during the two seasons, this implies that ginning practices were not uniform across gins.



The influence of harvesting practices in the variation in the CGW composition could be reflected in the sum of the pin trash, small leaf, grass, and stick/stem fractions of the samples. However, this composite fraction showed random variation. The average for four gins in the 2000 and 2001 were  $34.5 \pm 8.1\%$  and  $37.9 \pm 8.2\%$  respectively, which implies that extraneous material introduced during the harvesting was similar during both ginning seasons. It can be concluded that the harvesting practice was more uniform than the ginning practice.

#### **Summative composition of fresh discharged cotton gin waste**

The summative compositions of the samples are shown in Tables 2 and 3. There appeared to be no trend in the variation of the ash content (10.8% to 21.9%) of samples taken from the five gins during the three sampling periods. For each site, the variation appeared to be random. In comparison to woody biomass ash (<1% for softwoods and 1% to 3% for hardwoods (Fengel and Wegener, 1989) the ash contents of the CGW from all gins were extremely high, but they were typical for agro-industrial residues. Ash contents for sugarcane bagasse, wheat straw, and corn stover have been reported to range from 5% to 10 wt% (Milne et al., 1992, Agblevor et al., 1996).

The 95% ethanol extractives of CGW had a greenish coloration similar to dried leaves extractives probably because of the small leaf content. The ethanol extractives content ranged from 7.7% to 11.7% and did not vary much between gins and within gins (Tables 2 and 3). The ethanol extractives content of the CGW was relatively low in spite of the leaves, motes, twigs, burs, and other plant components of this feedstock. However, this was comparable to those for other agro-industrial residues such as wheat straw and sugarcane bagasse (Milne et al., 1992).

The fraction of CGW that was insoluble in 72% sulfuric acid (19.6% to 24%) was comparable to those found in woody biomass (Table 2 and 3). This is unusual for a shrubby biomass, which has a hardwood type of lignin (G-S lignin). For hardwoods, the acid insoluble material (Klason lignin) is typically 18% to 25% (Fengel and Wegener, 1989) on an extractives-free wood basis and for softwoods 25% to 30% (Fengel and Wegener, 1989). The acid-insoluble material from woody biomass is normally classified as lignin. However, it would be erroneous to classify the material from the CGW as lignin. Since CGW is a complex mixture of organic and inorganic materials, there could be other acid-insoluble material apart from lignin, which contributed to the high values. Probable sources of non-lignin acid-insoluble material are the cottonseed, small leaf, and the hulls.

A typical ginned cottonseed is composed of 32% hull, 23% protein, 12% fibers, 20% oil, and 14% carbohydrates (Hui, 1996). It is known (Agblevor et al, 1994) that proteins condense and become insoluble in concentrated sulfuric acid. Lipids are also known to condense with lignin and with carbohydrates (Moser, 1980). Thus, one could attribute the high acid-insoluble material content to a combination of lignin, condensed proteins, and lipids from the cottonseed, and small leaf fraction of the CGW.

The carbohydrate contents of the CGW are shown in Tables 2 and 3. It is clear from these data that variation in carbohydrate composition was more pronounced than the non-carbohydrate fraction discussed above. The total carbohydrate content varied within and between gins. The samples from the Commonwealth Gin, Windsor, VA had the highest concentration of carbohydrates (44% to 49%) and those from the Wakefield Cotton Growers Gin had the lowest carbohydrates content (34% to 36%). The total carbohydrates contents ranged from 34% to 49%, and these were relatively low compared to woody or herbaceous biomass. For woody biomass, the total carbohydrate content ranges from 67% to 82% for softwoods and 49% to 85% for temperate zone hardwoods (Fengel and Wegener, 1989).

The mannan, arabinan and galactan contents were very low as expected from an agro-industrial residue. Within any gin, these sugars did not vary much and neither was there much variation between gins. Because of their relatively low concentrations, their potential influence on ethanol yield is expected to be minimal.

The glucan and xylan constituted 80% to 90% of the total carbohydrates. Our results for the xylan content agree with Jeoh and Agblevor (2001) and Agblevor *et al.* (2003a). The xylan content was lower than that reported for most agro-industrial residues and hardwoods (15% - 35%). Such low xylan contents are typical of softwoods. The xylan content also varied widely between gins (3% - 8%) while within gins variation was low (Tables 2 and 3).

The glucan content varied widely between gins (23% - 32%) (Tables 2 and 3). The glucan variation between gins could be attributed to the ginning methods. The Suffolk, Franklin, and Emporia gins had similar but relatively low clean lint fraction (Table 2), which resulted in the low glucan yield. On the other hand, the Windsor gin had relatively high clean lint fraction and consequently the glucan content was the highest.

The overall glucan content of the CGW from all the gins was low compared to other lignocellulosics such as herbaceous and woody biomass. Although visual inspection of the feedstock showed an apparent high fraction of cotton fiber, fractionation of the CGW showed only 8.5% clean lint and 20.5% motes. The clean lint contains 95% cellulose (Kirk-Othmer, 1996) but the motes contain both immature fiber and undeveloped seed pod. Thus, the total cotton fiber content of the CGW was less than 30%.

The low glucan content was attributed to the following factors: the hulls, small leaf, high ash, and seed contents. The hulls fraction was very high and together with the small leaf fraction constituted about 48% of the CGW. The hulls fraction correlated negatively with ethanol yield and while the small leaf fraction correlated positively with the ethanol yield (Aglevor et al., 2003b).

The second reason for the low glucan content was probably because the feedstock had high ash content due to the incorporation of inorganic materials and the intrinsic ash in the hulls and seed. Thirdly, cottonseed is typically about 1.7 times heavier than the cotton fiber (Hui, 1996), but its sugar content is less than 3%. Although the cottonseed content was relatively low, it also could have potentially contributed to the low glucan yield. The combination of the above factors will tend to dilute the glucan content of the feedstock on a moisture-free whole-biomass basis.

#### **Mass balance**

The total mass balance for samples collected ranged from 80% to 96% (Tables 2 and 3) as compared to 69% to 98%. The large variation in mass closure could be attributed to the heterogeneity of the feedstocks, the ginning method, and perhaps the sampling method as well.

The objective of this analysis was to determine the carbohydrate content of the feedstock and thus assess theoretical and practical ethanol yields. The analytical method was therefore optimized for the carbohydrate fraction at the expense of other fractions such as lipids, which could constitute an appreciable fraction of the feedstock especially when it contains cottonseed. The feedstock may also contain residual pesticide and herbicides, uronic residues, acetyl groups, and other extraneous materials, which were not amenable to the method of analysis. Thus, samples that contained large fractions of other materials could have low mass closure because those components were not determined and vice versa.

#### **Summative composition of stored cotton gin waste piles**

The data for the summative analyses of the stored piles are shown in Tables 4-6. The results are reported for the weathered, transition, and the core layers. The 95% ethanol extractives (extractives) had greenish color similar to those observed for the fresh material and ranged from 4% to 10%. This coloration suggests that after six months storage the small leaves were still present in the piles. The extractives content decreased considerably during storage for all piles and all layers. The loss of extractives ranged from 38% to 60% and was pile dependent. The highest pile loss ( $53.0 \pm 7.5\%$ ) occurred in Pile A, while in Piles B and C, the losses were  $42 \pm 4.0\%$  and  $50.3 \pm 9.8\%$ , respectively. The losses were highest in the core layers. The highest layer loss (60%) occurred in the core layer of Pile A while the least loss occurred in the transition layer of Pile B and the weathered layer of Pile C.

The loss of extractives could be attributed to leaching and evaporation. Since the highest extractives losses occurred in the core layers, which also had the highest pile temperatures, it could be inferred that evaporation was a major contributory factor. This was corroborated by the core layer of Pile A, which had the highest temperature ( $69^{\circ}\text{C}$ ) and the highest loss of extractives (60%). Leaching could also play some role in the loss of extractives, but leachates were not collected.

The ash contents of all the stored piles were high and ranged from 11% to 18%. This range was slightly smaller than those for the fresh samples collected from the five cotton gins (11% to 22%). Although there was some variation in the ash content with respect to layers and storage time, these variations appeared to be random. These suggest that perhaps the variation in ash content was due to the heterogeneity of the piles rather than the storage effect. The sample heterogeneity appeared to have confounded the storage effect.

The acid-insoluble materials (AIM) content were very high for most samples and ranged from 21% to 27% compared to 20% to 25% for the fresh material. Thus, there appeared to be some increase in the AIM content for most piles. The highest increase in the AIM content (23%) occurred in the core layer of Pile A. This apparent increase in the AIM content is consistent with the decrease in the extractives content. With the loss of the extractives, the relative amounts of the other CGW components were expected to increase. The slight increases in AIM content are consistent with those observed for stored sugarcane bagasse and other biomass feedstocks (Agblevor et al., 1996). However, unlike the bagasse, switchgrass, and hybrid poplar chip piles where most of the changes occurred in the weathered layer, the CGW changes occurred randomly with respect to the layers. This difference could be due to the relatively loose packing of CGW.

The stability of the carbohydrate component during storage was the thrust of the current studies because appreciable loss of this component during storage could result in the reduction in the yield of ethanol. Although there were reductions in the glucan and xylan contents of the piles, these were also partly confounded by the heterogeneity of the material. The decrease in total carbohydrate ranged from 12% to 25% and the highest loss ( $25.5 \pm 6.0\%$ ) occurred in Pile B while losses in Pile A and Pile C were  $12.2 \pm 1.6\%$  and  $16.0 \pm 3.5\%$ , respectively.

The arabinose, galactose, and mannose contents of the samples were very low before and after storage. Because of the sample heterogeneity, it was difficult to assess the storage impact on these minor components. Further, because all three sugars constitute less than 5% of the feedstock they are not expected to strongly influence the yield of ethanol from CGW. Thus, the following discussion will focus on the impact of the storage on xylan and glucan.

The xylan and glucan contents of the CGW decreased with storage time. The loss of xylan ranged from 18% to 40% for all three piles. The highest overall decrease in the xylan content ( $34.0 \pm 5.3\%$ ) occurred in Pile A, while Piles B and C decreased by  $22.0 \pm 6.3\%$  and  $26.3 \pm 4.7\%$ , respectively. Within Pile A, the highest xylan loss occurred in the transition layer (40%) and the least occurred in the core layer. For Pile B, the highest xylan loss (27%) occurred in the core layer and the least in the transition layer (18%). In the case of Pile C, the highest loss (30%) occurred in the core layer and the least in the transition layer. Thus, xylan losses in the pile layers were random and could be attributed to the loose packing of the material because the piles did not develop any distinct surface layer. The loose packing is in contrast to sugar cane bagasse piles, which normally packed very tightly and formed thick layers on the surface that protected the inner core of the piles. Thus, in sugar cane bagasse piles, the losses were mostly confined to the weathered layer with minimal loss in the core layer (Agblevor et al., 1996).

The glucan losses varied widely among the three piles and ranged from 8% to 42%. The highest overall glucan loss occurred in Pile B ( $32.6 \pm 8.6\%$ ) while Pile A and C lost  $10.6 \pm 4.6\%$ , and  $13.8 \pm 6.2\%$ , respectively. Glucan losses varied by layers and by piles and did not follow any defined trend. The highest glucan loss (16%) in Pile A occurred in the transition layer while the losses in the core (8%) and weathered (8%) layers were similar.

In Pile B, the highest glucan loss was 42%, this occurred in the transition layer while in the weathered, and core layers, the losses were 31% and 25%, respectively. In Pile C, the highest glucan loss (21%) occurred in the core layer and the losses in the weathered and transition layers were 10.5% and 10%, respectively.

The losses of glucan and xylan during storage can be attributed to microbial degradation of the biopolymers. Although, the samples were not analyzed for microbial content and neither was any microbial species identified, the consistent rise in pile temperature after precipitation events suggested that there was microbial activity, which generated metabolic heat.

The glucan losses can also be attributed to the high clean lint and mote content (30-35%) of the CGW. These CGW fractions, unlike lignocellulosics are bare cellulose fibers that could be easily attacked by microorganisms. Further, during discharge the CGW is usually sprayed with water to reduce particulate emissions into the atmosphere. With the addition of moisture, the lint is ideal for microbial attack.

The variation in the pile temperatures and the randomness of the carbohydrate losses, it could be inferred that if the feedstock were stored under dry conditions, the losses could be considerably reduced. The losses after three months of storage were minimal for most piles. However the total carbohydrate losses in six months (25%) were considerable so one would expect a corresponding decrease in the yield of ethanol.



### **Conclusions**

We characterized fresh cotton gin waste from five cotton gins in Southeastern Virginia and showed the effect of storage on the chemical composition of the feedstocks. Fractionation of cotton gin waste from the five cotton gins showed that the incorporation of sticks/stems, grass, and pin trash were similar for both the 2000 and 2001-ginning seasons. This implied that variation in feedstock composition due to the harvesting practice was minimal. However, other fractions such as clean lint, seeds, hulls, and small leaf varied considerably with the ginning season and the cotton gin. Thus, it appeared the ginning protocol had a considerable influence on the composition of the CGW.

The summative composition of the feedstock varied between gins. Although the ash content of CGW was high, it was within the range for other agro-industrial residues such as wheat straw and corn stover. The acid-insoluble materials content was very high probably because of condensation of lipids and proteins on the lignin during the acid hydrolysis. The total carbohydrate content was relatively low compared to woody and herbaceous biomass feedstocks.

Storage of CGW for six months had a considerable influence on the composition of the feedstock. Both extractives and total carbohydrates were lost because of the storage in the open atmosphere. The ash and acid-insoluble material increased slightly during storage. However, chemical compositional changes were minimal for storage periods of three months or less. The temperature in the piles increased considerable to as high as 69 °C. Temperature spikes were observed shortly after precipitation events, which suggested that the increase in temperature was probably due to the metabolic activity of microorganisms. The considerable loss in the total carbohydrate content of the feedstock during the storage implies that ethanol yields will decrease correspondingly.

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Table 1. Fractional composition of cotton gin waste samples collected during two ginning seasons.

<b>Gin Name</b>	<b>Clean (%)</b>	<b>lint</b>	<b>Hulls (%)</b>	<b>Stick/stems (%)</b>	<b>Grass (%)</b>	<b>Seed (%)</b>	<b>Motes (%)</b>	<b>Small (%)</b>	<b>leaf</b>	<b>Pin (%)</b>	<b>trash</b>	<b>Total (%)</b>
2001 Ginning Season												
Emporia	9.8		24.7	5.9	0.3	2.9	21.6	28.8		5.0		99.0
Franklin	8.0		18.5	5.6	1.1	0	21.1	34.9		6.7		95.9
Suffolk	8.9		29.6	5.2	0.1	1.6	20.4	26.8		2.4		94.7
Windsor	15.0		32.9	6.7	0.4	0	20.9	19.4		2.4		97.6
2000 Ginning Season												
Emporia	5.3		35.6	7.1	0.4	12.7	16.1	21.3		0.6		99.1
Franklin	10.4		19.7	7.1	0.4	5.6	19.5	30.3		5.0		98
Suffolk	12.5		15.9	5.4	0.3	24.0	18.6	18.5		2.2		97.4
Windsor	9.0		16.8	3.6	0.2	6.9	23.9	34.6		1.6		96.6
Wakefield	7.1		48.1	6.1	0.4	7.7	15.6	13.9		0.6		99.5

Table 2. Summative composition of three fresh discharged cotton gin waste samples collected during the ginning season (10-15-01= sample collected at the beginning of the season; 11-15-01= sample collected at the middle of season; 12-17-01= sample collected at the end of the season).

	<b>10-15-01</b>	<b>11-15-01</b>	<b>12-17-01</b>
<b>Emporia Gin</b>			
Ash	11.2±0.78	21.9±0.56	10.0±0.6
Ethanol extractives	10.7±0.13	9.6±0.23	10.5±0.2
Acid-insoluble material (AIM)	21.7±1.05	23.7±0.21	24.9±1.3
Arabinose	1.45±0.17	1.74±0.06	1.37±0.05
Xylose	6.41±0.12	5.56±0.08	5.69±0.08
Mannose	1.30±0.04	0.74±0.00	0.96±0.00
Galactose	1.38±0.14	1.65±0.09	2.14±0.12
Glucose	26.52±0.34	25.73±0.36	28.17±0.39
<b>Total carbohydrates</b>	<b>37.06</b>	<b>35.42</b>	<b>42.55</b>
<b>Mass balance</b>	<b>80.66</b>	<b>90.62</b>	<b>87.95</b>
<b>Franklin Gin</b>			
	<b>10-15-01</b>	<b>11-15-01</b>	<b>01-24-02</b>
Ash	17.1±0.47	14.1±0.19	20.4±0.77
Ethanol extractives	8.4±0.38	11.7±0.16	9.0±0.10
Acid-insoluble material (AIM)	21.9±0.31	24.7±0.54	24.9±1.20
Arabinose	1.18±0.13	3.41±0.50	1.26±0.15
Xylose	4.55±0.08	5.84±0.06	3.40±0.04
Mannose	2.04±0.05	1.08±0.06	0.64±0.02
Galactose	2.70±0.26	1.77±0.22	1.92±0.19
Glucose	30.23±0.38	26.68±1.10	25.70±0.46
<b>Total carbohydrates</b>	<b>40.7</b>	<b>38.78</b>	<b>32.92</b>
<b>Mass balance</b>	<b>88.10</b>	<b>89.28</b>	<b>87.22</b>
<b>Suffolk Gin</b>			
	<b>10-15-01</b>	<b>11-15-01</b>	<b>01-24-02</b>
Ash	13.1±0.11	17.8±0.02	10.8±0.02
Ethanol extractives	10.6±0.34	10.2±0.13	11.6±0.15
Acid-insoluble material (AIM)	24.2±0.95	23.3±0.30	19.6±0.32
Arabinose	2.04±0.04	1.40±0.02	1.56±0.04
Xylose	8.01±0.16	5.84±0.13	5.83±0.07
Mannose	0.94±0.08	0.99±0.09	1.03±0.08
Galactose	1.62±0.02	2.49±0.02	2.04±0.04
Glucose	24.94±0.33	25.47±0.27	27.13±0.58
<b>Total carbohydrates</b>	<b>37.55</b>	<b>36.19</b>	<b>37.59</b>
<b>Mass balance</b>	<b>85.45</b>	<b>87.49</b>	<b>79.59</b>

Table 3. Summative composition of three fresh discharged cotton gin waste samples collected during the ginning season (10-15-01= sample collected at the beginning of the season; 11-15-01= sample collected at the middle of season; 12-17-01= sample collected at the end of the season).

	<b>10-15-01</b>	<b>11-15-01</b>	<b>12-17-01</b>
<b>Wakefield Gin</b>			
Ash	ns*	13.8±0.16	13.5±0.19
Ethanol extractives	ns	8.5±0.28	10.6±0.07
Acid-insoluble material (AIM)	ns	23.4±0.03	23.2±1.06
Arabinose	ns*	3.11±0.36	2.11±0.30
Xylose	ns	5.39±0.09	5.65±0.06
Mannose	ns	0.72±0.01	1.11±0.06
Galactose	ns*	1.48±0.14	1.58±0.20
Glucose	ns	23.39±0.29	25.82±1.07
<b>Total carbohydrates</b>	ns	<b>34.09</b>	<b>36.27</b>
<b>Mass balance</b>	ns*	<b>79.79</b>	<b>83.57</b>
<b>Windsor Gin</b>			
	<b>10-15-01</b>	<b>11-15-01</b>	<b>12-17-01</b>
Ash	12.5±0.41	11.3±0.16	21.4±0.76
Ethanol extractives	8.2±0.21	9.0±0.56	7.7±0.22
Acid-insoluble material (AIM)	21.6±0.71	23.2±1.48	22.7±0.47
Arabinose	1.84±0.04	2.53±0.07	1.60±0.02
Xylose	6.59±0.13	10.52±0.14	8.64±0.21
Mannose	1.39±0.12	1.37±0.11	0.72±0.07
Galactose	1.23±0.01	1.87±0.03	1.49±0.01
Glucose	32.75±0.44	32.71±0.65	32.49±0.30
<b>Total carbohydrates</b>	<b>43.80</b>	<b>49.00</b>	<b>44.94</b>
<b>Mass balance</b>	<b>86.10</b>	<b>92.50</b>	<b>96.74</b>



Table 4. Summative composition of various layers of stored cotton gin waste Pile A (10-15-01= time zero; 11-15-01= 1 month storage; 10-24-02 = 3 months storage; 05-07-02 = 6 months storage).

	<b>10-15-01</b>	<b>11-15-01</b>	<b>01-24-02</b>	<b>05-07-02</b>
<b>Weathered layer</b>				
Ash	11.2±0.78	11.6±0.15	13.7±0.18	13.3±0.2
Ethanol extractives	10.7±0.13	11.7±0.23	8.4±0.07	5.9±0.6
Acid-insoluble material (AIM)	21.7±1.05	24.4±0.72	25.5±0.42	24.3±0.7
Arabinose	1.61±0.24	1.71±0.18	1.33±0.14	1.46±0.17
Xylose	6.35±0.30	5.42±0.24	5.61±0.25	4.30±0.10
Mannose	1.30±0.14	0.81±0.08	1.04±0.11	1.05±0.08
Galactose	1.67±0.21	1.67±0.17	2.46±0.27	1.24±0.09
Glucose	29.35±0.24	27.35±0.24	27.12±0.25	27.07±0.27
<b>Total carbohydrates</b>	<b>40.28</b>	<b>36.96</b>	<b>37.56</b>	<b>35.12</b>
<b>Mass balance</b>	<b>83.88</b>	<b>84.66</b>	<b>85.16</b>	<b>78.62</b>
	<b>10-15-01</b>	<b>11-15-01</b>	<b>01-24-02</b>	<b>05-07-02</b>
<b>Transition layer</b>				
Ash	11.2±0.78	13.5±0.47	12.9±0.25	11.2±0.1
Ethanol extractives	10.7±0.13	10.2±0.29	7.2±0.06	4.9±0.2
Acid-insoluble material (AIM)	21.7±1.05	26.9±0.30	23.4±0.29	25.4±0.1
Arabinose	1.61±0.24	1.07±0.04	1.19±0.04	1.61±0.18
Xylose	6.35±0.30	3.78±0.06	4.74±0.07	5.77±0.14
Mannose	1.30±0.14	1.04±0.00	1.11±0.00	1.10±0.08
Galactose	1.67±0.21	2.15±0.12	1.54±0.08	1.56±0.12
Glucose	29.35±0.24	27.56±0.38	32.76±0.46	24.57±0.25
<b>Total carbohydrates</b>	<b>40.28</b>	<b>35.62</b>	<b>41.34</b>	<b>34.61</b>
<b>Mass balance</b>	<b>83.88</b>	<b>86.22</b>	<b>84.84</b>	<b>76.11</b>
	<b>10-15-01</b>	<b>11-15-01</b>	<b>01-24-02</b>	<b>05-07-02</b>
<b>Core layer</b>				
Ash	11.2±0.78	15.6±0.33	11.7±0.14	11.99±0.4
Ethanol extractives	10.7±0.13	11.2±0.19	6.9±0.39	4.2±0.1
Acid-insoluble material (AIM)	21.7±1.05	24.5±0.29	25.6±0.19	26.9±0.5
Arabinose	1.61±0.24	1.17±0.13	1.21±0.13	1.88±0.21
Xylose	6.35±0.30	4.41±0.22	5.62±0.28	4.59±0.11
Mannose	1.30±0.14	0.91±0.07	0.95±0.08	1.00±0.07
Galactose	1.67±0.21	2.28±0.24	1.64±0.17	1.12±0.08
Glucose	29.35±0.24	26.94±0.25	30.15±0.29	26.89±0.27
<b>Total carbohydrates</b>	<b>40.28</b>	<b>35.71</b>	<b>39.57</b>	<b>35.48</b>
<b>Mass balance</b>	<b>83.88</b>	<b>87.01</b>	<b>83.77</b>	<b>78.57</b>

Table 5. Summative composition of various layers of stored cotton gin waste Pile B (10-15-01= time zero; 11-15-01= 1 month storage; 10-24-02 = 3 months storage; 05-07-02 = 6 months storage).

	<b>10-15-01</b>	<b>11-15-01</b>	<b>01-24-02</b>	<b>05-07-02</b>
<b>Weathered layer</b>				
Ash	13.3±0.43	14.1±0.15	15.0±0.60	18.1±1.2
Ethanol extractives	10.6±0.52	11.7±0.83	9.6±0.39	5.8±0.14
Acid-insoluble material	21.9±0.25	27.2±0.58	26.4±0.60	24.3±0.3
Arabinose	1.38±0.11	1.49±0.18	1.37±0.19	1.85±0.21
Xylose	4.21±0.02	3.79±0.21	5.69±0.37	5.27±0.13
Mannose	1.11±0.05	0.55±0.05	0.93±0.07	0.77±0.06
Galactose	1.23±0.12	1.47±0.15	1.40±0.1	1.49±0.87
Glucose	37.76±0.78	25.90±0.22	30.89±0.63	26.04±0.26
<b>Total carbohydrates</b>	<b>45.69</b>	<b>33.2</b>	<b>40.28</b>	<b>35.42</b>
<b>Mass balance</b>	<b>91.49</b>	<b>86.2</b>	<b>91.28</b>	<b>83.62</b>
	<b>10-15-01</b>	<b>11-15-01</b>	<b>01-24-02</b>	<b>05-07-02</b>
<b>Transition layer</b>				
Ash	13.3±0.43	15.4±0.75	15.7±0.35	16.0±0.2
Ethanol extractives	10.6±0.52	12.8±0.56	8.2±0.24	6.6±0.43
Acid-insoluble material	21.9±0.25	24.8±0.10	27.2±0.74	26.8±0.4
Arabinose	1.38±0.11	1.65±0.013	1.54±0.13	1.59±0.18
Xylose	4.21±0.02	3.79±0.02	4.49±0.02	3.42±0.08
Mannose	1.11±0.05	0.97±0.05	0.99±0.05	1.79±0.10
Galactose	1.23±0.12	1.82±0.17	1.71±0.16	2.40±0.18
Glucose	37.76±0.78	27.58±0.57	28.08±0.58	21.63±0.22
<b>Total carbohydrates</b>	<b>45.69</b>	<b>35.81</b>	<b>36.81</b>	<b>30.83</b>
<b>Mass balance</b>	<b>91.49</b>	<b>88.81</b>	<b>87.91</b>	<b>80.23</b>
	<b>10-15-01</b>	<b>11-15-01</b>	<b>01-24-02</b>	<b>05-07-02</b>
<b>Core layer</b>				
Ash	13.3±0.43	22.2±0.59*	12.5±0.53	14.6±0.5
Ethanol extractives	10.6±0.52	13.5±0.18	7.1±0.25	5.86
Acid-insoluble material	21.9±0.25	24.1±1.20	26.8±1.20	25.2±1.6
Arabinose	1.38±0.11	1.36±0.11	1.60±0.09	1.01±0.11
Xylose	4.21±0.02	3.04±0.01	5.19±0.19	4.89±0.12
Mannose	1.11±0.05	0.84±0.04	1.08±0.08	0.68±0.05
Galactose	1.23±0.12	2.73±0.25	1.74±0.20	1.11±0.08
Glucose	37.76±0.78	20.72±0.43	33.94±0.14	27.9±0.28
<b>Total carbohydrates</b>	<b>45.69</b>	<b>28.69</b>	<b>43.55</b>	<b>35.59</b>
<b>Mass balance</b>	<b>91.49</b>	<b>88.49</b>	<b>89.95</b>	<b>81.25</b>

Table 6. Summative composition of various layers of stored cotton gin waste Pile C (10-15-01= time zero; 11-15-01= 1 month storage; 10-24-02 = 3 months storage; 05-07-02 = 6 months storage).

	<b>10-15-01</b>	<b>11-15-01</b>	<b>01-24-02</b>	<b>05-07-02</b>
<b>Weathered layer</b>				
Ash	10.7±0.34	17.6±0.61	17.2±0.79	15.5±0.38
Ethanol extractives	10.7±0.15	13.0±0.49	7.5±0.30	6.53±0.36
Acid-insoluble material	22.4±1.05	23.7±0.84	25.8±0.64	23.7±0.3
Arabinose	1.78±0.01	1.69±0.01	1.57±0.01	0.87±0.08
Xylose	5.57±0.12	4.09±0.09	4.35±0.09	4.00±0.01
Mannose	1.20±0.19	0.91±0.15	1.60±0.26	0.86±0.08
Galactose	1.64±0.07	1.89±0.08	1.56±0.07	1.07±0.04
Glucose	32.89±0.71	23.84±0.52	34.46±0.75	29.41±1.14
<b>Total carbohydrates</b>	<b>43.08</b>	<b>32.42</b>	<b>43.54</b>	<b>36.21</b>
<b>Mass balance</b>	<b>86.88</b>	<b>86.72</b>	<b>84.04</b>	<b>81.94</b>
	<b>10-15-01</b>	<b>11-15-01</b>	<b>01-24-02</b>	<b>05-07-02</b>
<b>Transition layer</b>				
Ash	10.7±0.34	18.1±0.69	13.6±0.34	14.3±0.32
Ethanol extractives	10.7±0.15	9.8±0.28	9.7±0.50	4.8±0.4
Acid-insoluble material	22.4±1.05	25.9±0.84	27.6±0.74	24.5±0.2
Arabinose	1.78±0.01	1.46±0.01	1.51±0.01	1.32±0.12
Xylose	5.57±0.12	3.44±0.07	4.62±0.10	4.37±0.01
Mannose	1.20±0.19	1.45±0.23	0.98±0.16	0.83±0.09
Galactose	1.64±0.07	3.89±0.16	2.23±0.09	1.28±0.07
Glucose	32.89±0.71	26.62±0.58	29.01±0.63	29.83±1.08
<b>Total carbohydrates</b>	<b>43.08</b>	<b>36.86</b>	<b>38.35</b>	<b>37.63</b>
<b>Mass balance</b>	<b>86.88</b>	<b>90.66</b>	<b>89.25</b>	<b>81.23</b>
	<b>10-15-01</b>	<b>11-15-01</b>	<b>01-24-02</b>	<b>05-07-02</b>
<b>Core layer</b>				
Ash	10.7±0.34	17.5±0.16	15.4±0.32	17.46±0.62
Ethanol extractives	10.7±0.15	10.6±0.07	11.5±0.21	4.6±0.1
Acid-insoluble material	22.4±1.05	24.1±0.31	26.8±1.42	24.5±0.2
Arabinose	1.78±0.01	0.88±0.01	1.70±0.07	1.31±0.11
Xylose	5.57±0.12	4.29±0.09	3.88±0.26	3.95±0.00
Mannose	1.20±0.19	0.66±0.11	1.06±0.24	0.85±0.08
Galactose	1.64±0.07	1.67±0.07	1.64±0.00	1.83±0.08
Glucose	32.89±0.71	25.73±0.56	26.33±0.70	30.36±1.00
<b>Total carbohydrates</b>	<b>43.08</b>	<b>33.23</b>	<b>34.61</b>	<b>38.30</b>
<b>Mass balance</b>	<b>86.88</b>	<b>85.43</b>	<b>88.31</b>	<b>84.86</b>