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Corncob dry matter loss in storage as affected by temperature and moisture content

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Corn cob dry matter loss in storage as affected by temperature and moisture content

by

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A thesis submitted to the graduate faculty

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Ames, Iowa

2010

To my family and friends

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CHAPTER 1: GENERAL INTRODUCTION

Rationale and Overview

The petroleum-based economy has been playing a key role in the development of countries. Since the Industrial Revolution, fossil fuels have leveraged the growth and progress of nations, reaching a vital function in our energy-dependent society. Nevertheless, the uses of fossil fuels have several disadvantages that have become strongly evident in the present. Global warming, pollution, glacial melting, petroleum spills and gas leaks, contamination and health problems are just few of the countless problems associated with burning petroleum, natural gas and coal. Conversely, a promising area getting stronger is developing fuels, chemicals and materials in a bio-sustainable way. The bioeconomy, a bio-based platform economy, is enlightening the challenge but has a long way to go through before achieving its final goal of replacing petroleum products and non-renewable energy sources.

Biomass has the potential to strongly contribute to the bioeconomy, supplying a myriad of ingredients and energy alternatives, yet to be discovered. Biomass is abundant and can be produced and harvested from crops, forest, animal wastes, etc. around the globe.

Biomass, as defined by Perlack et al. (2005) is “Any organic matter that is available on a renewable or recurring basis, including agricultural crops and trees, wood and wood residues, plants (including aquatic plants), grasses, animal manure, municipal residues, and other residue materials.” And it is generally “produced in a sustainable manner from water and carbon dioxide by photosynthesis.”

The challenge of biomass is to find an economically feasible assembly of every link in the production process and to cost-effectively compete with petro-base products. The Achilles' heel of this bio-based platform would be the association between the current enormous usage of resources and the potentially available biomass, harvested using environmentally friendly methods. Although lignocellulosic materials are very promising, the amounts needed, the means to harvest and handle, the storage facilities, the low energy density, the water content, the embedded lignin guard for fermentation, the recycling of nutrients back to the crop lands, together with the competition for land and input for food crops and the environmental considerations, all pose great challenges to the bioeconomy growth and development.

McKibben (2007) emphasized that environmental stewardship as well as economic prosperity should be faced urgently. The author contends that climate change and global warming are the biggest challenge that human beings are yet to face. Needless to say, the anthropocentric increase of carbon dioxide is the main contributor to the problem, increasing at a pace of 2 ppm per year. Before the industrial revolution, the Earth's atmosphere retained 280 ppm and with the burning of fossil fuels in 1950 ramped up 35 ppm more, reaching 315 ppm and currently being at 380 ppm, 100 ppm more from previous fossil fuel extended usage. In fact, with the present adoption of technologies and lifestyle changes, the world could build to 450 ppm of CO₂ in the atmosphere by 2050, set as the threshold of irreversible damage to ecosystem and environment (McKibben, 2007). As a whole, humankind will witness the melting of glaciers and perennial ice regions, changes in seasonal patterns', pronounced droughts and floods, rising sea levels, just to mention a few. The scale of the problem will need several strategies, like

substitution of fossil fuels, in order to reduce current emissions, to strongly embrace conservation and to achieve carbon negative technologies. Such technologies, like biochar or CO₂ sequestration would entail CO₂ burial in forms of solid or gas deposits that would prevent it from returning back to the atmosphere.

Dissertation Organization

This dissertation contains a general introduction, literature review, followed by a paper. The paper is presented in the required format for publishing in Transaction of the American Society of Agricultural and Biological Engineers.

Objective

During storage, biomass feedstock encounters considerable material losses due to microbial respiration. Therefore, studies should be directed to understand the causes of deterioration to appropriately handle roughage biomasses on storage. The objective of the study was to quantify corn cobs' decay exposed to different storage conditions 10, 20 and 30°C and cobs moistures of 15, 25 and 35% w.b., by measuring the evolution of carbon dioxide over 21 days.

The hypothesis underlined was that the higher storage temperatures and moisture contents increases the dry matter losses of biomass.

CHAPTER 2: LITERATURE REVIEW

Biomass, Cellulosic Potential

Only after times of scarcity and energy independence constraints, such as OPEC's embargo in 1967, the oil crisis in 1973, the rise in oil price in 2008, etc, is when we realize how brittle and reliant on petroleum our society is, with the resulting interest in finding and exploring alternative energy avenues. Many countries have taken the initiative to walk the path of substitutes, and breaking the scheme of fossil energy's monopoly. Bourne (2007) emphasized that current replacement of conventional fuels by alternatives are small but highly promising. He claims that at most 12 % of gasoline and 6 % of the diesel demand (as to that particular year) could be supplied if all the corn and soybean cropped in the US was to be processed into biofuels. However, the information only referred to conventional food crops that are now being routed towards liquid fuels. But prospective technology breakthroughs could increase by many fold the current biofuel production threshold. In this respect, biomass has been a leading candidate as a substitute for liquid fuel transportation.

The National Renewable Laboratories in Golden, Colorado, estimate a maximum conversion rate of corn crop residues of 113 gallons of ethanol per dry metric ton (NREL, 2007); however, Reeder and Li (2010) estimate that feasible carbohydrate fermentation will yield around 73 gal/dry ton. The Billion Ton Study presented by the U.S. Department of Agriculture showed that the U.S could produce 1.3 billion tons of feedstock for bioethanol conversion, reaching approximately 90 billion gallons of ethanol (Perlack et al., 2005). Thermochemical

processes could greatly overcome fermentation yields, but still, biomass conventional processed could replace more than half of the transportation fuel currently burned each year.

Corn Cob Commercial Utilization

Corn cobs are an abundant source of thermal energy for producing heat, power, fuels and many chemicals too (Kaliyan & Vance, 2008). Historically, corn cobs have been used for whole array of different products, from small modifications of its original physical and chemical properties to highly industrialized goods. For instance, The Andersons Inc. located in Indiana has long processed cobs for many agrichemical and commercial applications such as abrasives, absorbents, activated carbon, asphalt shingle and roofing, chemical waste absorbent, concrete additive, feedstock for petrochemical industry (xylitol, furfural, oxalic acid), fermentation substrates, fertilizer diluents, food fiber source, carriers for chemicals such as herbicide, insecticide and pesticides, insulating materials, plastic extenders, and many more products (Anderson Inc). Recently, studies are exploring the use of corn cob for its energy content mainly for ethanol fermentation, co-firing and as a feedstock in thermochemical conversion technologies, thus potentially broadening the demand and importance of this so called “farm residue”.

Further work to refine specific systems of utilizing corn cobs would be of great benefit to agriculture, finding markets and alternative uses of material for farmers’ profits. Economic comparison between storage options and deterioration during storage will influence cobs value and cost of storage. In energy systems, cob costs need to include dry matter loss and changes of moisture content, whereas if the cobs are being stored for chemical production then mass loss but

even more important, compositional changes will be a factor determining cob storing and handling.

Ethanol sector has rapidly grown in the last decade, reaching close to 11 billion gallons in 2009 (Renewable Fuel Association). Private and public sector are strongly supporting the development of this renewable fuel as it has a number of advantages in terms of social, economic and environmental aspects. Currently, ethanol is mainly produced from the corn kernel, but it is envisioned to be also produced from lignocellulosic, such as corn stover, switchgrass, woody biomass, etc. The new regulations proposed by Environmental Protection Agency establishes the production of 36 billion gallon of renewable fuels, in which 16 billion gallons will come from cellulosic biofuels, in which the cellulose fermentation pathway would be one of the major contributors (EPA, 2009).

Decades ago, corn cobs have been used for drying seed and more recently as an energy source. The seed industry and farmers tried to benefit from cobs barely used before and find a new use for the material that could let them save money on drying operations (Dahlberg R. 1977). In the past, many cob burners and gasifiers were proposed to be used. The energy content of corn cobs is around 18.4 MJ/kg (high heating value), comparable to other cellulosic materials such as wood, and even cobs have 6% more energy than shelled corn and 11% more than cornstalks (Dahlberg, 1977). He also claimed that from kernel with 35% moisture and 66% efficient drier, there is enough energy in the cob to dry the corresponding kernels under average corn-belt drying conditions. Many seed plants had implemented different types of burners, and

have successfully decreased drying expenses; however, problems in cob handling and burners prevented the technology from being extensively adopted.

Main problems were focused on material handling, particulate matter emission (very fine ash). Also, corrosion caused by water vapor in combination with sulfur and chlorides producing acids, difficulties for temperature control, greater maintenance required than conventional natural gas burners, and slag formation at high temperature (950°C) where minerals components melt and solidify as green glass-like substance. These problems highlighted by Dahlberg (1977) which prevented cobs from replacing natural gas for seed companies in drier facilities. Furthermore, natural gas could be easily hooked on and it is a relatively cheap source of energy.

Other problems associated with this types of seed dryers were tar material condensation at low temperature (below 300°C), which would plug pipes, fans, burners and valves. Approaches to solving tar condensation were to burn the producer gas at high temperature before it condense, use down-draft gasifiers in order to oxidize and burn tars, or cool down the gas to condense the tar and burn the gas once it has been cleaned.

A latter more sophisticated approach to solve many of the problems with cobs burners was the use of gasifiers or pyrolysis units to produce low energy gas (in comparison to methane). If utilized within short distances, low BTU values for the gas wouldn't be detrimental; but it is still a problem that adds to the cost (heat content of 150 BTU/cu. ft vs. natural gas 1000 BTU/cu. ft).

Morey et al. (1984) proposed that a farmer with 200 ha requires approximately 50 tons of cobs to dry his corn with average yielding. Cob piles in farm drying operations are a feasible

alternative system to be used in the same season or, depending on the conditions, dried and stored for later use.

Cobs: harvesting, transportation and processing

Although corn cobs are a potential feedstock for producing heat, power, fuels and chemicals, pitfalls on harvesting, transporting and processing have to be thought for establishing profitable commercial channels for its use (Kaliyan & Vance, 2008; Morey et al., 1984; Foley et al., 1978). Improvements for harvesting the residues have to be rapidly addressed so that the material could be more efficiently harvested with less passes, and by removing the least amounts of nutrients as to maintain soil long term productivity (Johnson et al., 2010). Densification of corn cobs into briquettes/pellets has being proposed for improving their bulk density and its viability for handling, transportation, and storage (Kaliyan & Vance Morey, 2008).

With the existing commercial harvesters, only kernels are saved while stover and cobs are left on the field. Several modifications to existing corn harvesting systems have been suggested to collect either cobs or stover and cobs in a single pass concurrent to the grain harvest. Smith et al. (1985) emphasize that corn cobs are the densest fraction of corn's residues, are also harvested with the kernels making them easier to collect and redirect, so less modifications need be implemented into the harvesters.

In terms of availability, nearly 15-20% (d.b.) of above ground corn residues (non-grain) are corn cobs (Pordecimo et al., 2005; Kaliyan & Vance, 2008). Although, at harvest, the driest fraction of the corn's residue is the cobs, the moisture content may range from 20 to 55% (w.b.) depending on the grain moisture content at the time of harvest (Morey and Thimsen, 1980). The

harvest window for the Midwest is generally limited from October to November. Therefore, gathering locations, centralized or distributed, will be needed to store cobs if they are to be processed year-around (Smith et al., 1985). From a broader perspective, current sizes of commercial cobs' piles are around 1,000 to 50,000 Mg (Anderson Inc.). Still, if cellulosic ethanol plants utilizing corn cobs are to be scaled up to 2,000 Mg/day (330 days operation x 2,000 Mg/day) that would imply provisioning of 660,000 Mg. Theoretically, this is equivalent to a 50 million gallons per year ethanol plant that is roughly half the size of a current typical dry grind ethanol facility. Considering that this material has a low density of 0.16-0.21 g/cm³ (Dunning et al., 1948), it will demand 4.0×10^6 m³ to contain such an amount, equivalent to a prism of one hectare base and 400m high. It seems appropriate to think that outside storage, or with little cover, is likely to happen at first.

If driven by economies of scale, biorefineries will need to economically compete with petrochemical distilleries. Each refinery will need to have at least 4.7 to 7.8 million Mg of biomass capacity annually (Wright and Brown, 2007). This will undoubtedly challenge the whole production chain from handling, transportation and storage operations. Problems related to handling, dry matter and quality loss due to weathering and microbial deterioration are likely to grow if they are not correctly addressed. In addition, since corn stover is only harvested for a short period each year, long-term storage is required to provide supplies year-round to the biorefineries distributed in one or multiple locations but reasonably close to the facility.

Biomass long-term storage

According the Billion Ton study (Perlack et al., 2005), agricultural land would be able to supply almost one billion tons of dry biomass, where the greater portion of readily available biomass (450 million tons) would come from crop residues, such as corn cobs and stover, wheat, soybean and small grain straw. Needless to say, it is not just a matter of producing the biomass but harvesting, collecting, transporting and effectively storing it. The last aspect is explored in this study, researching decomposition under aerobic respiration of corn cobs.

Several studies indicate that numerous roughages under certain conditions encounter large amounts of decomposition, aggravated over long periods of stacking. In addition, quality and physical property changes are likely to occur and limit the final utilization of the biomass. Blunk et al. (2003) claimed that annual crop harvests pose important challenges on long-term storage if the material is to be available throughout the year. Studying deterioration in rice straw during long-term storage, they found that the material's final quality was strongly dependent on the storage conditions and length of storage. Major factors influencing the storage quality of baled rice straw were related to weathering and biochemical degradation. Therefore, tarps, permanent covers and protected storage would greatly impact the final product over 12 months of sheltering. Water gain, leaching, ultraviolet degradation, material erosion and microbial degradation have profound impact on the amount and final characteristic of stored straw rice bales. Bales exposed at the top of uncovered stacks suffered large losses of organic matter, substantial reduction in heating value, volatile matter, fixed carbon, and related properties. Losses in lower bales were not that important, neither side bales, but still there will be different

grades of decay within regions. Different regions of a stack encounters different property changes but exposed surfaces to weathering resulted in high organic matter losses of 40% or more (Blunk et al., 2003).

Lignocellulosic materials were found to have comparable relation with high moisture and dry matter loss. Nelson et al. (1983) found that baled ryegrass initially stored at 18% moisture (w.b.) lost 27.6% of dry matter (DM) through decomposition and 15% due to handling losses after 7 months, while losing 39.8% and 12.4% respectively after 12 months study. Also, plastic covers and racks stands with covers around the bales reduced dramatically the moisture and the DM losses. What seems to be clear is that moisture contents within piled material strongly influences microbial rates of degradation. White et al. (1983) reported 84%, 108% and 190% increase in average moisture content of chips, bark and sawdust piles, respectively after one year.

Similar conclusions on deterioration gradients were drawn from Smith et al. (1985) as well as important information provided on different initial material moisture contents and the progressive decay on corn cobs, from small farm scale and commercial piles. In this study, microbial respiration and auto-oxidation were identified as the main sources of degradation.

Outside piles of corn cobs in the Midwest showed a rise in moisture content during storage (Dunning et al. 1948; Smith et al., 1985). The latter author reported different moisture increases over different pile zones. In surrounding layer of about 0.9 m, moisture increased from 12-18% to 40-80%, whereas the interior reached 33% after 24 months time frame. It appears to

be clear that not only the materials initial moisture but also the weathering and deterioration processes are responsible for pile's moisture increase.

Moisture also has been cited to have a direct relationship with temperature increase. Self heating was observed on rice straw stacks with more than 20% moisture content, and those with 40-50% moisture had maximum temperatures of approximately 65°C within 4 days (Dobie and Haq, 1980). Likewise, Blunk et al. (2003) observed self heating over the first few weeks of storage of rice straw where moisture higher than 12% exhibited increases of 10 to 40°C over ambient air, plus additional heating following rains. Nonetheless, indoor bales initially experienced some heating, but later followed the ambient temperature. Increases of water from rainfall also result in rising temperatures and losses bales in storage on quantity and quality, influencing overall utilization (Blunk et al., 2003).

Another less important moisture gain was the upward migration from the ground and condensation under surface cover. The potential decay of some materials under favorable conditions is clearly visible. Hence, it would be essential to have an overall understanding of the process of deterioration, taking into account the changes produced throughout the storage, which parameters are important to track, on what range they have significant effect and how.

Small stack storage experiments suggest that open stacks, pole barns, and fully enclosed metal barns should cost between \$4- 7 /ton (Blunk et al. 2003). On the other hand, open stacks will incur higher overall quality losses that could significantly impact the posterior usage and

later costs of processing. In addition to the higher chances of spontaneous combustion that could occur from the combination of moisture and self-heating of the material.

Corn Cob Characterization

Chemical composition

Cobs are classified as a lignocellulosic material, mainly composed of cellulose, hemicellulose and lignin. Lignin is the most stable component of biomass, followed by cellulose and hemicellulose (Dunning et al., 1948; Smith et al., 1985). The carbohydrates (cellulose and hemicellulose) are tightly bound to the lignin fraction posing important challenges for ethanol fermentation and possibly for deterioration too.

The cellulose is an organic compound consisting of several hundred of glucose units with β (1-4) linkage. Unlike cellulose, hemicellulose consists on several hundred of different monomers, not just glucose, with different linkage too. Lignin is a complex chemical and is an integral part of secondary cell walls, filling spaces of the fibers conferring mechanical strength to the plant.

Foley et al. (1978) reported contents of 45.6% cellulose, 39.8% hemicelluloses and 6.7% lignin (on a dry base), whereas the pentosan comprises 38% of the hemicelluloses, and xylan 87% of the pentosan fraction. Clark and Lathrop (1953) found mean values of 32.3% cellulose, 41.3% pentosan and 13.9% lignin, on average for 31 hybrids of corn.

Ultimate analysis

Ultimate analysis performed by Clark and Lathrop (1953) showed carbon content of 48.4%, hydrogen 5.6%, nitrogen 0.3%, ash 1.4% and oxygen (calculated by difference) 44.3%, on a moisture free basis. Similar values were reported by Brown (2003), where the elemental composition was: carbon 46.58%, hydrogen 5.87 %, oxygen 45.46%, nitrogen 0.47% and 1.4% ash.

Energy content and available energy

Several parameters have being established to define the biomass energy content's depending on its application. The most common are:

- **GHC** (gross heat of combustion) is the energy released by heat when a material is combusted in presence of oxygen under standard conditions. Also accounting for the energy released as the water vapors condense.
- **NHC** (net heat of combustion) is the energy released by heat when a material is combusted in presence of oxygen without condensing the water vapors, therefore, not accounting for the energy present in the water vapor phase.
- **EA** (energy available) is the energy released by heat when a material is combusted in the presence of oxygen, not accounting for the energy present in form of water vapor neither the energy needed to evaporate the water already present in the biomass (previous parameters refers to dry biomass).

The gross heat of combustion (GHC) was reported to be 18.25 and 19.18 MJ/kg (Clark and Lathrop, 1953). Foley (1978) reported values of 18.52-18.78 MJ/kg and corn residues 18.72 MJ/kg Net heat of combustion (NHC). Smith et al. (1985) stated:

$$\text{NHC} = \text{GHC} - L (H \times 0.09)$$

Where the L is the latent heat of vaporization of water and H is the percentage of total hydrogen (ASTM 1979). In general, corn cobs will contain about 6% of hydrogen, reported $\text{NHC} = 0.93 \times \text{GHC}$ resulting in NHC for dry cobs around 17.34 MJ/Kg.

Although it is important to establish the energy that could be harvested from the complete combustion with air of cobs, the energy available (EA) could be on practice more important. The moisture content (water contained in the biomass) would play an important role in determining the energy that could be effectively used as part of it is used to evaporate the free water in the biomass, hence the importance to handle dry materials.

Smith et al. (1985) also calculated EA as:

$$\text{EA} = (\text{NHC} \times B) - (L \times M)$$

Where Energy Available (in MJ) is the result of the NHC (in MJ/dry kg), B is the total dry mass of material in the zone, L is the latent heat of vaporization of free water (MJ/kg) and M the total mass of moisture within the material B (in kg).

The gross heat of combustion is determined with Parr Adiabatic Calorimeter, ASTM 1979 standard procedures. A calorimeter consists of a metal container filed with water with a thermometer attached to measure the heat capacity of a substance after combustion.

Knowing the composition (chemical fraction) of the cobs could give a close approximation of the GHC. The hemicellulose and cellulose fraction contains around 17.5 MJ/kg and the lignin 26.7 MJ/kg (Shafizadeh & Degroot 1976). Therefore, knowing the constituents can be used to approximately determine the GHC. What can be easily seen is whether carbohydrates increase in proportion to lignin, or ash increase in proportion to other fractions, it will lessen the energy content of cobs. That was the reason stated by Smith et al. (1985), in which the gross heat of combustion slightly increased for deteriorated layers of cobs in contrast to the original energy content of the material, as the ratio of lignin increased over carbohydrates. Similarly, the gross heat of combustion per dry kg increased in the wet and surface layers, in commercial and farm piles. But if the GHC is based on the original mass of cobs, the outside storage of high moisture corn cobs could result in significant losses of the energy available as the material is consumed (primarily the carbohydrate fraction) and water is also gained. Smith et al. (1985) reported drops of up to 33% of the energy available in cobs under severely weathered piles. The energy loss on outside storage with partially drying with ambient air, (the pile still being weathered) was reduced to about 20%, yet a considerable loss.

As it has been mentioned above, the use of decentralized outdoor storage facilities would be challenging; because reducing the size of the pile would increase the proportion to potentially decay from weathering effects. In this regards, Smith et al. (1985) suggested that outside stored

small piles are not practical in the Midwest without losing a large proportion of the energy available.

Cob Storage and Deterioration

Pile regions and deterioration

Several researchers have shown marked differences between regions with cob piles, with regard to the final chemical composition and deterioration. Mainly, two layers have been classified, the exterior layer and the inside of a pile (Blunk et al. 2003). Sometimes a third layer is defined as the outside crust of the surface layer of the wet exterior. For a large pile study, Smith et al. (1985) identified three zones. The surface layer wet zone (up to 0.2 m from the surface) with 50 to 80% moisture w.b, an intermediate zone from 0.3 to 0.9 m and an interior established more than 1.5m depth, identified by visual observation. The surface layer suffers from externalities such as rain, snow, sunlight, wind, etc., resulting in higher moisture content and greater degradation. The intermediate zone will be a transition and will have in-between conditions. The interior of the pile will have properties that will better match the original conditions of the biomass, influenced somewhat by degradation, but clearly not experiencing as much weathering effects. Therefore, on large piles most of the material will be on the interior and will greatly respond to conditions of initial storage, whereas in small piles the outside layer will comprise a greater portion and, consequently, the weathering effects on the pile. Tracking the layers' conditions will become important to predict precise deterioration on large piles.

Large piles studies

Most deterioration studies of biological materials are done in vitro or with small piles of material (Chitrakar et al., 2006; Bern et al., 2002; White, 2007; Moog et al., 2008). However, some researchers have been implementing larger storage of biomass (Smith et al., 1985; Blunk et al., 2003; Buggelnl and Rynk, 2002; Collins et al., 1997; Hogland et al., 1996). For example, Smith et al. (1985) used nylon mash bags with cobs placed in a large commercial pile as it was being formed. In 18 months of storage, the author indicated similar layer structure to the analogous study on a farm pile, but the interior portion compromised the largest share of the total mass. Originally, the moisture was 9-12% w.b. but increased to 12-17%. The dry matter loss from the interior zones of the large piles through direct measure of mash bags dry matter loss was not significant. On the other hand, the wet surface layer and the middle layer were similar in structure to the small piles with moisture contents of 70 % and 31%, respectively. For the two wetter regions, the dry mass loss (determined from bulk density test) had an average of 28% in the wet layer and 21% in the subsequent layer. The wet and surface layers comprised about 26% of the total mass of the large commercial piles as opposed to 45% farm scale piles on the parallel study. Further losses also occur along the base of the biomass piles directly on the ground. The dry matter loss losses due to degradation within the base of the pile in contact to the ground will be similar to the losses in the wet and surface layers (Blunk et al., 2003). Nonetheless, the major ground losses occur in handling the cobs, when mixing with soil can cause unwanted contamination and complication on further processing. Therefore, it is inevitable to have substantial leftovers, i.e. cobs that cannot be utilized.

The greatest losses of energy content occurred within the wet layer, which are between the surface and 0.9m depth in the small piles. The wet layer is increasingly important in small piles, therefore, piling up the cobs as high as possible will decrease the portion of this layer compared to the total amount stored, thus reducing the great losses that occurs within this zone. Safety considerations should be taken when piling up too high large amounts as it can collapse or slide down when removing material from the base.

On the whole, in outside storage, important quantity and quality losses occurred when moisture contents were above 20%. The moisture resulted from the materials initial moist plus the water gained throughout storing time. As a matter of fact, dry matter loss and composition changes resulted in losses of 43% of the available pentosan (used for chemicals and product synthesis) from the wet layers after 18 months of storage (Smith et al., 1985). But the interior layer cobs did not deteriorate significantly if they were dried below 12% before storage.

Focusing on energy production for drying seeds, Smith et al. (1985), states that small piles outside are not practical for the Midwest due to remaining energy available and dry matter losses. Other concern is the health hazard associated with handling the moldy material and potential produced mycotoxins through spoiled material.

Corn cobs are a rich source of energy and chemical feedstock, yet economic evaluation between storage costs and handling opportunities (drying, covering, etc) as well as deterioration during storage, will be necessary to determine whether or not is practical and economically feasible to store cobs and use them for energy and products. In energy platforms

(thermochemical or biological fermentation) might not be as stringent as chemical platform especially to those associated with the hemicelluloses and cellulose transformation which have shown to be highly degradable. For farm use of burners and gasification technologies, tracking dry matter loss is as important as moisture gains and losses of available energy.

Cob harvest moisture variation

Two main corn cob streams are commercially found today differing in origins and management. One comes from the collection of corn ears for the production of hybrid seeds, where parental lines are crossed for the production of corn hybrid seed. The second, and increasingly important, is the collection of cobs from commercial corn production. The two types of cobs differ mainly in that for seed production, the ears are harvested at high moisture but are taken to the facility for post-harvest drying, thus thoroughly drying the kernel and cobs.

On the other hand, in the collection of cobs from the commercial corn production, besides including different genotypes that may vary in composition, the main difference is a wide range of water content depending on the time in which they are harvested. The harvest time is mainly driven by kernel moisture, which is typically harvested below 30% moisture for the Corn Belt (Pordesimo et al., 2005). In other words, if cobs are collected from corn lines for the production of hybrid seed, the moisture is typically 10-12% moisture (cobs and kernel dried together in the facility and later shelled). However, when the cobs are coming from commercial crops, the moisture can be determined by the harvesting time of the kernel, in which its moisture will be related to the moisture of the kernels. Indeed, large collection of cobs from commercial grain

fields will imply higher moistures in comparison to cobs from lines ranging from 20 to 55% w.b. (Kaliyan & Vance, 2008).

The moisture correlation between the cob and the kernel has being addressed by many authors (e.g., Pordesimo et al., 2005). Therefore, wetter kernel harvest due to environmental conditions or farmer decision will entail higher cobs' moisture. Thus it will encourage microbe's growth and material degradation if it is not handled correctly.

Moisture increase with storage

Besides the original moisture in which cobs are stored there is strong evidence indicating that moisture content inside and outside located piles in the Midwest were found to increase during storage e.g. 36 months of storage study carried on by Dunning et al. (1948). Also, after one year storage, sawdust piles slightly increased the interior moisture but more prominent the surface of the pile became highly saturated (White et al., 1983). Also Smith et al. (1985) noted that moisture increased differently depending on the layer of the pile as initially stored at 12-18%. After 24 months, in large piles the outer 0.9m was 40 to 80% while interior reached 33%. Besides weathering factors such as rainfall, snow, high relative humidity days, etc., the water produced during respiration process would result into raise of water within the material. From an hypothetical degradation of 10g of cellobiose per 100g of original DM (approximately 10% degradation), would result in 5.56g of additional water to the material having double effect on moisture content, firstly increasing the water content on the material and also reducing the proportion of dry matter. It should also be important to highlight the potential positive feedback

that greater moisture could generate greater deterioration and, consequently, this deterioration will potentially increase the moisture too. It has being cited that moisture gains also promotes increases in temperature as a result of oxidation or fermentation (depending if the conditions are aerobic or anaerobic) also leveraging microbial respiration between certain temperature range. This heat produced could eventually be accumulated to the point of reaching uncontrollable temperatures were spontaneous combustion could occur.

Pile temperature

Temperature in the stored material is another important factor to be considered for a safe and durable storage. Blunk et al. (2003) study over rice straw observed self heating over the first few weeks of storage with moistures higher than 12%. Self heating exhibited increases of 10 to 40°C over ambient air closely related with initial moisture. Nevertheless, the main rise in temperature was observed right after the material was stored, but secondly important determining the temperature rise, were rainfall events. Obviously, indoor storage of straw observed temperature increase only during the first days of storage. Overall, temperature is an important factor in determining chemical reaction and microbial growth rates. Therefore, it should be considered and safely managed for good preservation.

On the other hand, temperature rise pose a potential benefit for self drying, as manifested by Smith et al. (1985). Where a fan coupled with a thermostat automatically switched on when the temperature exceeded 24°C and turned off when reached 19°C, finding the internal heat of the pile useful to assist in drying. Another experiment was performed with a pile of approximately

18 tons where a fan blew for 6.5 h/day and the pile temperatures followed the average ambient air warmth closely. Still, there are some challenges identified in this experiment where unventilated zones near the base of the pile isolated by layers of husk material were heavily molded. Also, the initial and final moisture of this base portion of the pile was almost the same, not having a relevant drying.

Spontaneous combustion

Spontaneous combustion (SP) is defined as sudden firing of the material in the absence of "forced ignition", such as spark or flame. It is defined as a series of chemical and physical events that initiate heat producing reaction via biotic and abiotic processes involving oxygen and some water. (Hogland et al.,1996).

Each year spontaneous combustion causes great losses of material and safety hazards in Virginia and throughout US (Cundiff & Marsh, 1996). Organic material such as corn stover, hay stacks, baled straws, nuts, hulls, linseed, etc., with adequate conditions is prone to self combust (Pordesimo et al., 2005; Blunk et al., 2003).

Not only corn stover but also cobs themselves can self ignite. On 27th of December 2008 in Anderson's grain facility (near Delphi, Indiana) a corn cob pile of 17,000 tons suddenly caught fire. It started deep in the pile and the fire traveled upward through the pile. Also in 1989 the company had another fire with a 35,000 tons pile where again instantaneous combustion was responsible (in press December 27th 2008, www.Pharoatribune.com)

Buggelnl and Rynk (2002) described the complex reactions and steps that follow spontaneous combustion on a yard trimming wastes, as a combination of biotic and abiotic factors that triggers the ignition. Biological processes such as fermentation and respiration are primary responsible for the heat of composting. Chemical oxidation might also contribute, but the activation energy required to start up the reaction would challenge this path to initially happen. These biological processes are described as initiators, but the temperature keeps building up above microorganism temperature zone killing them and also evaporating part of the water. Below 80°C heat is generated in the pile by aerobic respiration from living plant cells and microbes as they consume plants and residues in the pile. Heat released by the respiration-oxidation of the material also release chemicals that could react with oxygen in the air following abiotic reactions. This heat serves primarily to feedback the abiotic reactions initially not being significant. Although some heat is distributed and maintained, some is utilized to evaporate water and is carried out in the form of vapor. As the mound heats up to 70-90°C two important changes occur, the pile had evaporated most of the free water and also raised the temperature enough to kill the microbes. The accumulation of heat also depends on the rate of heat lost and production, when the former is lower than the latter a critical internal temperature may be reached (Buggelnl and Rynk, 2002). At this point the biotic reaction contributing heat cease but abiotic and most aggressive reactions take rapidly over. Depending on material characteristics and how compacted is, the air will flow into the pile and oxygen would keep reacting with plant's chemicals. With increased temperatures and accelerating rates the chemical reaction occurs having a positive response on the whole process. At this point, much depends on air

movement and oxygen concentrations (consumed by the oxidation but supplied by the incoming airstream) but if the temperature keeps increasing eventually will catch fire, thus spontaneously combust. The activation energy required for direct chemical oxidation of glucose in air is much higher than undergoing biochemical oxidation by microbial enzymatic reactions but when the chemical reaction happens the rate of reaction accelerate much faster.

Different materials vary in compositions that could facilitate abiotic oxidation like, oils and resins, within the lower temperature regime, for example coniferous materials will contain more resin and linseed more oil. Availability of oxygen can determine where the process eventually goes, and carbon dioxide produced dissolved in water will form weak acids that can further accelerate the decomposition of complex molecules into more reactive acidic organic compounds (Buggelnl & Rynk, 2002).

Woodward (2004) stated that wet hay is more likely to lead to a spontaneous combustion than dry hay does if it gets higher than 22 percent moisture. Also, hay helps to insulate, so the larger the haystack the less chances to cool the pile and offset the heat. Internal temperature of 55°C leads to chemical reactions producing flammable gases that can potentially ignite if the temperature goes high enough. Temperature will rise within a stack and then declines to a safe level in 15 to 60 days, depending on bale, density, ambient temperature, humidity, and rainfall. However, when spontaneous combustion occurs, it does not originate in the center of the round bale, but nearer the outside, because oxygen levels in the middle of the bale are usually too low for combustion to occur (Collins et al., 1997). On waste management piles, Hogland, et al., (1996) also claimed that oxygen content decreases to almost zero in the lower parts of the storage

pile but after several months of high but stable temperature conditions, self-ignition occurred in stored piles. Nevertheless, waste management materials have a very different chemical composition and prevailing reactions.

Changes in chemical composition

During storage, Dunning et al. (1948) quoted that on a 24 months outside storage, cellulose and hemicellulose were the ones that mostly decreased. In depth of 0.6m, it decreased from 38.6 to 30% cellulose and Pentosan from 33.9 to 24.7%. However, these components did not change when cobs were air dried and stored inside. Pentosan content decreased more than cellulose content during storage, Smith et al., (1985) showing the highest loss of 21% from wet layer samples of large piles after 18 months storage, while cellulose decrease were 11% lower than control. Decrease in cellulose and pentosan content resulted in higher proportion of lignin (mostly) and ashes, hence resulted in an increase of heat of combustion (on a dry base).

These carbohydrates were particularly reduced in the wet layers where weathering and microbes could have greater chances to grow. Important considerations must be taken in regards to quantity and quality during outside storage when moisture contents are above 20% (Smith et al. 1985). The combined effects of mass loss and composition change resulted in losses of 43% of the available Pentosan (main component of the hemicelluloses fraction) while cellulose had 11% less than the control in the wet layers after 18 months of storage. The interior layer of cobs was dried below 12% before stored, not being significantly deteriorated. All studies point out the importance of moisture associated with deterioration, whether is weathering the cause of water gain or high initial moisture content. If the material is being stored for chemical production or to

be fermented, where it is specifically interested in these carbohydrates, outside storage for long periods of time might not be the best solution. On the other hand, if the material is to be burned or pyrolyzed might not be such a detrimental problem besides the loss of material and energy. Certainly, gains of moisture will consume greater fraction of the heat released thus having less energy available as a whole. Nevertheless, the gross heat of combustion increases with deterioration of cobs, on a dry basis, due to increased proportion of lignin that has less oxygen content and more energy density for thermochemical processes than the carbohydrates. Outside storage for farm scale piles (Smith et al., 1985) resulted in losses of up to 33% of the available energy in high material moisture due to dry matter loss and water gains within the pile. In contrast, the energy loss was reduced to about 20% for the interior of the pile when it was dried with ambient air.

Shelled Corn Storage Time and Previous Respirometer Studies

Direct measurement of dry matter loss

The development of objective methods to precisely quantify dry matter loss will have a key role for understanding deteriorations, favorable conditions and tools to remediate/diminish losses. Directly quantifying material losses poses great challenges, such as measuring weight losses in which moisture variation within the materials and the methods used to quantify may have substantial disparity when trying to account small percentage of weight changes. Also, the need to oven dry and destroy the sample so as to directly measure moisture content and dry matter have an obvious impediment for consecutive measurement of the sample over time. The

overall sample requirements to overcome variability of the measuring procedures make direct measures of DM loss difficult to achieve.

Indirect measurement

Indirect measures of dry matter are found to be useful in most cases. CO₂ evolution has been used in many agricultural and environmental studies due to its biological role in living organism. For instance, tracking CO₂ emissions from the material being stored has been proposed as a correlation method to estimate material losses during storage (Wilcke et al., 2001; Chitrakar et al., 2006; Friday et al., 1989; Bern et al., 2002; White S., 2007) . Therefore, equations have been established to predict CO₂ production from the respiration of corn samples with varying moisture, temperature, and mechanical damage (Bern et al., 2002) with the aim of establishing storage time remaining before deterioration becomes significant (reducing by one USDA grade) . The assumption underlined is that dry matter loss of 1% will represent 14.66g of CO₂ released, so by tracking carbon dioxide emitted, the dry matter consumed by microbes, respired by the seed and chemically oxidized could be back calculated.

Various techniques have been used to measure carbon dioxide release. Frequently, reacting the CO₂ from the air and sequestering it into hydroxides (such as NaOH or KOH), or measuring the CO₂ in the air by analytical methods (such as gas chromatography and infra-red analysis). Alternatively, another indirect method has been successfully implemented for rapidly measuring this gas, Solvita gel, which is used to evaluate CO₂ respiration, from soil, compost or grain in an efficient and cost-effective manner (Haney et al., 2008; Chitrakar et al., 2006).

Solvita gel technology is different from alkali traps in the sense that it does not absorb all the CO₂ but a portion of it. This pH-sensitive gel (paddle) changes color as it absorbs CO₂ and after certain time allotted the paddle is removed from the incubation chamber to be analyzed with a digital color reader. Haney et al. (2008) compared solvita gel with chemical titration and Infra-red gas analyzer for measuring soil respiration, and found that Solvita number had good correlation with the other two traditional methods. However, it could have small interference from volatile fatty acids which form a positive response with CO₂ gel, also has to be prior calibrated and it is influenced by the chamber volume. Another big disadvantage is that the paddles have better response at room temperatures between 20°C and 25°C (Woods End Research, 2002) thus limiting the range of its uses.

Another indirect measure that doesn't involve carbon dioxide would be the correlate decomposition of the biomass with acid- insoluble ash. This fraction should remain relatively constant, on a weight basis, before and after storage. Therefore, the changes in the proportion of the rest of the fractions in comparison to the acid insoluble ashes could be associated with the decomposition. Still, Blunk et al. (2003) found high level of uncertainty in samples with the acid insoluble ashes (big variation and inconsistent results) and bias in the overall deterioration.

CHAPTER 3: CORNCOB DRY MATTER LOSS IN STORAGE AS AFFECTED BY TEMPERATURE AND MOISTURE CONTENT.

A paper to be submitted to the *Transactions of the ASABE*

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Abstract. *Agricultural residues, like corn cobs, are one of the first promising cellulosic materials to be fermented and thermochemically processed into fuel in the emerging bio-based economy. Few studies have been conducted on the deterioration of cellulosic feedstock in storage. This study measured the loss of corn cob dry matter, as measured by carbon dioxide evolution, under various storage conditions (temperature and moisture content) for 21 days. High moisture content and temperature conditions (35% w.b. and 30°C) resulted in almost 3 % dry matter loss in 21 days, as opposed to negligible losses at drier conditions (15% w.b.). There was a significant interaction between the effects of moisture content and temperature on dry matter loss. These data provide a first approach on understanding the material loss due to microbial activity, thus helping to identify storage strategies to maximize the conservation of cellulosic feedstock.*

Keywords: *Corn cobs, deterioration, cellulosic feedstock.*

The second generation of biofuels will be derived from residues generated mainly by agricultural and forestry endeavors (Arvelakis and Koukios, 2002; Blunk et al., 2003; Johnson et al., 2010; Perlack et al., 2005). Agro-residues have the advantage of being renewable and with the potential of being converted into heat, power and fuels on a decentralized platform (Arvelakis and Koukios, 2002; Kaliyan et al., 2008; Latif and Rajoka, 2001; Ioannidou et al., 2009; Shinnars et al., 2003). Corn cobs and corn stover are some of the first lignocellulosic agricultural materials to be fermented into alcohols and thermochemically transformed. While many studies target the improvement in production, transportation, densification and utilization of this type of biomass (e.g., Shinnars et al. 2003; Kaliyan and Vance, 2008; Wilcke et al., 2001), few articles have been published on what happens during storage of these materials between harvest and processing.

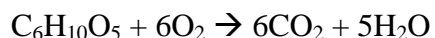
Smith et al. (1985) reported a decrease in corn cob's cellulose and hemicellulose during outside storage increasing the concentration of the lignin fraction over time. As a result of deterioration, intermediate organic compounds were produced and little is known regarding their quantity and impact on the overall fermentation process. Olsson and Hahn-Hagerdal (1996) published compelling information regarding inhibitors that could be co-produced, their influence on microorganisms, and their effect on ethanol fermentation.

Many authors (Chitrakar et al., 2006; Bern et al., 2002; White 2007; Wilcke et al., 2001; Moog et al., 2008) quantified corn kernel deterioration due to fungal growth with different conditions of moisture, temperature, mechanical damage, genetic hybrid resistance, ozone

treatments and fungicide treatments. Nevertheless, little is known about handling and appropriately storing cellulosic biomass for biofuels production.

Considerable dry matter loss in biomass feedstock during storage is possible due to microbial activity (Blunk et al., 2003; Smith et al., 1985; Hogland et al., 1996; Huhnke, 2003; Collins et al., 1997). Objective data on dry matter loss in such feedstock are necessary to develop storage recommendations and practices. However, quantifying losses directly is difficult due to such things as difficulties measuring small changes in weight losses and moisture, the need to destroy the samples to directly measure dry matter, the difficulty of consecutive measurements over time, and the sample quantity requirements to overcome variability of the measuring procedures.

The deterioration of corn kernel dry matter has been modeled by Saul and Steele (1966) as the complete oxidation of glucose under aerobic conditions. In corn cobs, the sugars oxidized would come from the cellulosic and hemicellulosic portion of the biomass containing glucose and pentose. Oxidation of glucose with β 1-4 linkages in large chains of cellulose would be as follows (Haug, 1993):



The objective of this study was to quantify the loss of corn cob dry matter (as measured by carbon dioxide evolution) in storage under different temperatures and moisture contents. For this study, 21 days was chosen based on previous trials where significant dry matter loss was achieved with high moisture cobs, exceeding the apparatus scale.

Materials and Methods

Sample Material

Corn cobs were harvested from an 111 day hybrid on October 26th 2009 from a field near Ames, Iowa. A modified John Deere 9860 combine separated cobs from the grain and stover. The cobs were harvested at approximately 26% moisture w.b. and stored in polyethylene plastic bags (three bags to prevent moisture exchange with the environment) in a cold room at 4°C until needed for the experiment. Foreign material and remaining stover were removed from the samples by hand separation once the cobs were taken from storage.

Prior to testing all cob moistures were determined using a hot air oven for 24 hours and 103°C (ASABE Standards, 2003).

The moisture content of the corn cobs were adjusted, as necessary, to obtain desired levels for the experiment (15, 25 and 35% w.b.). If the moisture level had to be increased, the samples were sprayed with a calculated amount of distilled water necessary to reach the desired MC and then stored at 4°C for 48 hours to allow the moisture to equilibrate within the material. If samples needed to be dried, they were left in open air at ambient conditions, occasionally weighed until the desired MC (weight) was achieved, usually few hours. Immediately before the experiment was performed, sample MC was re-determined.

Experimental Apparatus

Three temperature-controlled chambers were used (model I-35LLVL Incubator, Percival Scientific, Inc., Boone, Iowa) and set to one of the treatment temperatures (10, 20 and 30°C),

according to the treatment randomization. Each chamber contained one sample of each of the three MC corn cobs used (15, 25 and 35 % w.b.). The individual sample size varied depending on degradation rates from pre-experimental tests for the different temperatures and MCs. Large samples with favorable microbial conditions had high rates of CO₂ evolution and exceeded the full-scale capacity of the CO₂ measurement device, hence smaller sample sizes were needed for these conditions. For this reason, sample size varied from 200 to 500 g of dry matter.

Within a chamber, individual samples were placed in a 15.2 cm O.D acrylic tubes approximately 60 cm in height, capped with 15.2 cm flexible cap (Figure 1). At both ends, a 0.625 cm plastic hose coupler connected with tygon R-3603 tubing (Saint-Gobain Performance Plastics Corporation, Akron, Ohio) through which air was provided to maintain aerobic conditions and to carry away carbon dioxide produced by microbial activity. Three diaphragm pumps (model MOA-P122-AA, Gast Manufacturing, Benton Harbor, MI) were used to pump air through the system.



Figure 1: Containers used to hold corn cob samples for the experiment.

Depending on the moisture content of the samples, air could be bubbled through a 0.5 m distilled water column before entering the samples in order to gain moisture or be mixed with ambient air to approximate to the relative humidity that would enable to get the desired equilibrium moisture content of the samples, as determined by ASAE Standard D245.5 (ASAE, 2001). Porcelain filters were placed at the entrance to these water columns to decrease bubble size, increasing the rate of water transfer to the air. A 250 mL flask was placed outside of each of the 20 and 30°C chambers downstream from the samples to collect condensing water that might interfere with the CO₂ measurement system.

One empty sample tube was used in each chamber to determine the ambient CO₂ concentration. In pre-experiment tests, ambient CO₂ concentration varied widely, depending on human activities within the laboratory, which was connected to a teaching laboratory. For this reason, an approximately 150 L plastic bag enclosure was used as an air reservoir before the air pumps, buffering changes in the CO₂ concentration of incoming air to the system.

Data collection

Temperature within the chambers was monitored using an LM 35 integrated-circuit temperature sensor (National Semiconductor Corporation, USA). Relative humidity of the air leaving the bubbling columns was monitored with an HIH- 4000-001 (Honeywell International Inc) relative humidity sensor.

Air leaving each of the sample tubes entered a gas multiplexer, a device that has the capacity to divert airflow from one of 24 ports for analysis (Figure 2). This apparatus consisted

of 24 0-5VDC solenoids operated through a SSR24 relay board (Measurement Computing Corp, Norton, MA). This relay board had 24 selectable terminals which, when directed by a computer program would select the specific port and the time to be opened to direct the airflow for CO₂ concentration measurement. The airflow rate into the CO₂ measurement device was determined by a TSI Thermal Mass Flowmeter Model 4140 (TSI Incorporated, Shoreview, MN). This sensor has a linear response to airflow from 0 to 10 volts corresponding to 0 to 20 Standard L/min (2 Standard L/min per Vdc).



Figure 2: 24 port manifold, regulator valves and air gauges controlling individual sample's air flow.

CO₂ concentration (ppm) was measured with a Rosemount Analytical Model 880A Non-Dispersive Infrared Analyzer (Emerson Process Management, Orrville, Ohio). The analyzer was calibrated at the beginning of each replicate and weekly thereafter according to the

manufacturer's specifications using a gas containing 1200 ppm of CO₂. The accuracy as stated by the manufacturer is $\pm 1\%$ full scale.

A laptop computer was used to record the data from the sensors and also to operate the solenoids, relay boards and microcontroller. The device used for analog to digital conversion (microcontroller) was a PMD 1408 LS (Measurement Computing Corp, Norton, MA), which is a USB bus-powered module with eight 14-bit analog inputs, two analog 12-bit analog outputs, and 16 digital I/O lines. The codes were written in Visual Basic Application for Microsoft Office Access 2007.

The air being analyzed (when the solenoid valve was opened) would pass through the airflow meter to the CO₂ sensor transducer. Measures were taken from 12 a.m. to 8 a.m. in order to minimize the effect of the carbon dioxide variation in the laboratory. Every three minutes the gas multiplexer switched to the next sample and recorded the measurement. For every on each sample, the average of all the measurements collected on the 8 hour period was recorded for later analysis.

Calculation of dry matter loss

From the measured CO₂ concentration and the airflow rate, the amount of CO₂ produced (difference between atmospheric and the sample measurement) was calculated by:

$$\text{CO}_2 = (C/1000) \times (A) \times 1440$$

Where: CO₂ = standard L of CO₂ produced per day

C = measured CO_2 concentration (ppm) averaged over 8 hour collection period

A = airflow rate (standard L/min)

1440 = 1440 minutes per day

Applying the Ideal Gas Law:

$$N = (P \times \text{CO}_2) / (R \times T)$$

Where : N = moles of CO_2 produced per day

CO_2 = standard L of CO_2 produced per day

P = standard pressure = 1 atm

R = constant = $0.082056 \text{ L} \cdot \text{atm} / (\text{°K} \cdot \text{mol})$

T = standard temperature = 294 °K

One mole of $\text{C}_6\text{H}_{10}\text{O}_5$ (monomer constitute of the cellulose chain) with a molecular weight of 162 g/mol, when oxidized, results in six moles of carbon dioxide with a molecular weight of 44 g/mol. Multiplying the number of moles CO_2 , produced per day by $162/(44 \times 6)/162$ or 0.6136 resulted in the amount of glucose (dry-matter) consumed per day in grams. Dividing by the initial amount of dry-matter gave the % dry matter loss.

Statistical Analysis

Nine treatments (experimental units) were formulated from the combination of three MC levels (15, 25 and 35 % w.b.) and three temperatures (10, 20 and 30°C), performed in triplicate (three runs), corresponding to a 3×3 complete factorial design. Temperature treatments were randomly allocated to a chamber and moisture treatments were randomly allocated to certain

order within each chamber. For every replication (run) there would be a chamber randomly assigned to one of the three temperatures and successively randomized on the later runs. Statistical Analysis System (SAS Institute Inc) was used to analyze the data, with ANOVA (analysis of variance). Differences in means were determine using Tukey-Kramer method with $\alpha \leq 0.05$.

Results and Discussion

Table 1 gives the amount of dry matter loss, as estimated by CO₂ evolution for each of the treatments after 21 days of incubation. In general, treatments with 15% moisture content and 10°C had nearly no dry matter loss (average of 0.1 percent), while higher moisture (35% moisture content) and higher temperature (30°C) had on average 2.75 % loss. Similar rates of degradation were observed under 35% moisture and 20°C averaging 2.4% DM loss.

Results drawn from the ANOVA indicates that temperature, moisture and the interaction within both are highly significant (p values = 0.00032, <0.0001 and 0.0017 respectively), whereas the replication was not significant.

Table 1: Average dry matter loss (%) for every combination between 15, 25 and 35% moisture and 10, 20 and 30°C.

Moisture	15%	25%	35%	
Temp.	DM Loss	DM Loss	DM Loss	Average
10 °C	0.01 (Aa)	0.24(Ab)	1.09 (Ac)	0.45
20 °C	0.07 (Ba)	0.62 (Bb)	2.40 (Bc)	1.03
30 °C	0.17 (Ca)	1.66 (Cb)	2.75 (Cc)	1.53
Average	0.08	0.84	2.08	

Note: Tukey's standardized range is symbolized with capital letters for temperature difference (between rows) and lower case letters for difference between moisture contents (within columns). Significantly different means was tested with $\alpha < 0.05$.

A T test (LSD) was performed with alpha 0.05 for the treatments identifying differences among moistures and another test performed for the differences in temperatures. The least significant difference among temperature means was found to be 0.22% DM, whereas the least significant difference among moisture was 0.34% DM loss. The greatest deterioration was achieved with 35% moisture significantly different from the 25 and 15%. Likewise, lower temperature of 10C was statistically different 20 and 30C. As a whole, every moisture and temperature was statistically different from each other. The resulting combination of both factors high temperature and moisture resulted in 2.73 % $\pm 0.40\%$ of dry matter loss, whereas negligible dry matter loss was observed with 10C and 15% moisture. On average, for every increase of one percent of moisture, the dry matter loss increased 0.1 percentage point versus 0.05 percentage point for every Celsius degree over 21 days. Thus moisture content should be carefully kept in mind while storing this kind of biomass.

The interaction makes the analysis and interpretation more complicated, in the sense that not only moisture and temperature had additive effects on the deterioration model but also an interaction effect which was highly significant. Therefore, it is not appropriate to just consider each variable separately; both have to be considered for calculation of the resulting dry matter loss.

The deterioration trend lines (Figure 3) are intended to predict what would happen to materials with different moisture content after being stored for 21 days. Although the experiment was performed in vitro, it was intended to be useful in some extent for commercial cobs piles. Knowing the moisture content and tracking the temperature within the pile, equations 1 would give a useful approximate to predict deterioration rate after 21 days.

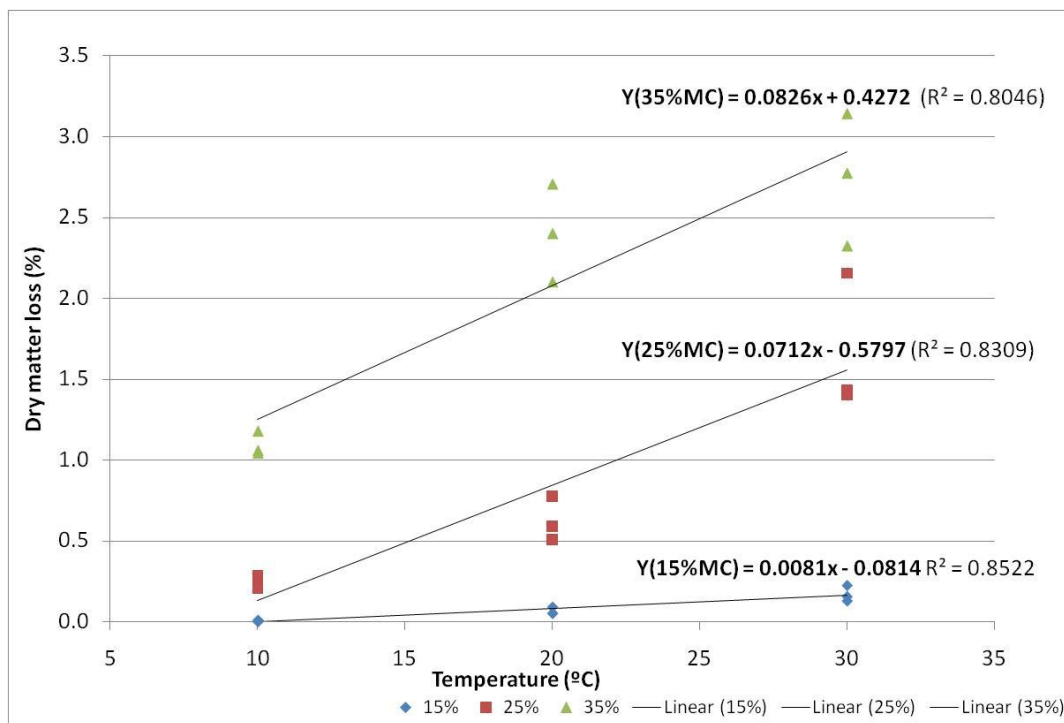


Figure 3: Deterioration trend lines in DM loss (%) for 21 days

Linear regression of the deterioration for the three moisture contents

$$\text{Dry matter loss (15\%MC)} = 0.0081(\text{Temp } ^\circ\text{C}) - 0.0814 \quad (R^2 = 0.85)$$

$$\text{Dry matter loss (25\%MC)} = 0.0712(\text{Temp } ^\circ\text{C}) - 0.5797 \quad (R^2 = 0.83)$$

$$\text{Dry matter loss (35\%MC)} = 0.0826(\text{Temp } ^\circ\text{C}) + 0.4272 \quad (R^2 = 0.80)$$

Although there are 9 points for every model to define the trend lines, all of them have a coefficient of determination greater than 0.80, fitting quite well the data collected. The interaction between temperature and moisture can also be seen by the different slopes presented in each equation.

Table 2 combines information from the estimated dry matter loss of corn kernels presented by Bern et al. (2002) with the deterioration rates resulted from this research, in order to roughly evaluate kernels and cobs DM loss with similar storage conditions. Kernels were assumed to have 30% damage and no fungicide and a generic hybrid was used. The shelled corn and cobs storage time for 0.5% DM loss in days would approximately be as follow:

Table 2: Estimated 0.5 % DM loss of cobs and kernels in days.

Moisture	15%		25%		35%	
Temp.	Kernel	Cobs	Kernel	Cobs	Kernel	Cobs
10 °C	629	1480	22	44	9	10
20 °C	175	160	7	17	3	5
30 °C	63	63	3	6	1	4

For this table, it was assumed that the cob deterioration linear trend appropriately fit prolonged periods of time, greater than 21 days. More studies are necessary to verify this assumption. Overall, corn kernels with 15% moisture showed less deterioration than cobs (besides 30 °C) whereas other conditions clearly favored.

The rate of dry matter loss (Figure 4) presented a linear trend for all the treatments as opposed to the equivalent conditions for kernels, in which after a short lag phase an exponential curve was observed (Moog et al. 2008; Wilcke et al. 2001; Friday et al. 1989).

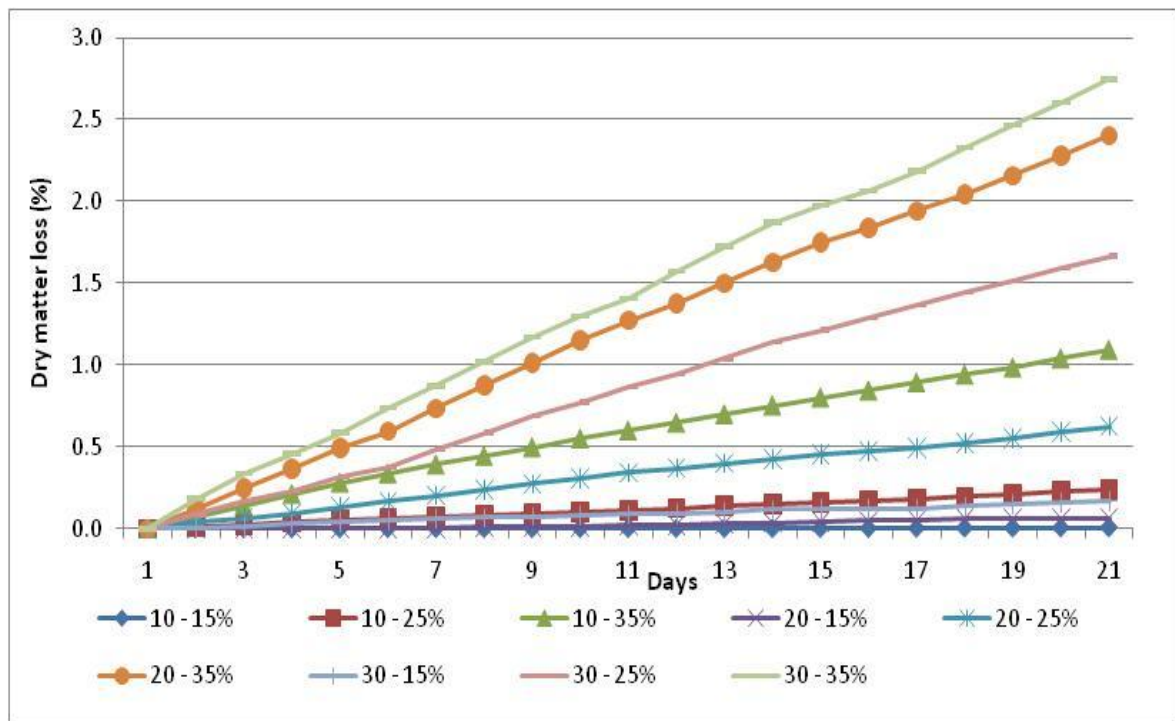


Figure 4: DM loss for each treatment as a function of time.

Following the regression model observed in this study, important losses would be reached (almost 25% over 6 months) if the deterioration rate for 6 months fits the one observed in this study (Table 3), hence the importance of extend the study for prolonged times.

Table 3: Predicted cob DM loss (%) over 6 months storage

Temp/Moisture	15%	25%	35%
10 °C	0.05	2.1	9.5
20 °C	0.6	5.5	20.8
30 °C	1.5	14.5	23.8

Conclusions

Important deterioration can occur with aerobic conditions while storing cobs. Moisture content and temperature are important variables that strongly influence the rate of dry matter loss. Overall, corn cobs at 15% MC had low rates of dry matter loss, regardless temperature. Higher moisture contents had correspondingly greater rates of dry-matter loss achieving nearly 3% for 30°C and 35% MC, closely followed by 20°C and 35% MC for only 21 days of storing. For similar temperatures, 35% MC had significantly higher dry matter loss than 15 and 25% MC.

Drying of corn cobs could significantly reduce the amount of dry matter loss over time, while managing the temperature could be initially of greater challenge and practically unfeasible. Nevertheless, accurately assessing deterioration, price of biomass and handling practices cost could be used to broadly estimate handling avenues.

The deterioration rates showed by cob clearly differ to those shown by kernel. While kernel has being extensively shown to be exponential, a linear trend seems to better match cob DM decay. This trend could be related to the different types of carbohydrates present in both materials, as to the germination and respiration process that could take place by the seed, or as a result of the lignin fraction on cobs that serves as a barrier to microorganism growth. Yet, larger periods should be considered in order to have a better response over longer periods of time.

Future studies should be carried out to determine dry matter loss for time periods longer than 21 days. Also, the dry matter losses under aerobic conditions in this study should be compared to that under actual storage conditions, where a combination of aerobic and anaerobic condition might prevail. Furthermore, the impact of cob size, contaminants such as chaff, stover and dirt may carry inoculums increasing the rates of microbial activity. Also, other situations that will likely occur in storage should be examined, not only greater ranges of temperatures and moistures but variation on both parameters throughout storage.

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CHAPTER 4: GENERAL CONCLUSIONS

Biomass may encounter considerable dry matter losses due to microbial activity, depending on the material, the storage conditions and prevention practices. The next generation of biofuels and the intended bioeconomy will need large amounts of feedstock for producing food, fuel and fibers in a renewable fashion. Thus it is necessary to understand and quantify the losses and quality changes that varied feedstock could encounter before being processed.

Although it is important to quantify this parameters, the difficulties associated with measuring deterioration directly, the technical challenges for relatively small amounts over long periods and the associated measuring errors poses important challenges for collecting adequate data.

What appears to be clear is that the amount of dry matter loss can be quite significant. The microbes' respiration is directly related to the conditions for their development, i.e., whether the type material and the environment of storage is supporting their growth. Different types of cellulosic microorganisms have being identified, with different optimum ranges of moistures, temperatures, PH, salinity, oxygen levels (aerobic and anaerobic), etc., that directly support their growth rate. Thereby, the importance of identifying the type of microorganism and the conditions that prevent their development to consequently improve handling strategies can help maximize material's quantity and quality. Needless to say that feedstock, such as agricultural residues, might need to be stored for prolonged times such as a year or more. Not only biological decomposition but chemical oxidation will be a concern too. In this sense, extreme conditions

(biological activity could serve as a starter) could lead to spontaneous combustion and large number of consequences associated with it.

Corn cobs have been shown to degrade while in storage. Although it is a lignocellulosic material, in which many cases is claimed to be extremely resilient, with sugars attached with beta linkage and lignin protecting the fibers, we experience considerable losses in short periods of time. For the greatest treatment reaching almost 3% in 21 days, and those conditions are yet likely to be seen in accumulation areas. Although temperature is an important factor, higher moisture content appeared to be more detrimental, resulting in greater difference of decay for every percentage in increase (for the range of conditions in this study). Moreover, current storage practices will likely increase decaying conditions with higher moistures, higher pile temperature's, with more degradable materials (chaffs and stover), smaller particle size or with greater amount of inoculum (for example with soil contamination) that might ramp up the rates of deterioration. Further studies with other materials, and conditions listed above should follow this preliminary study to correctly assess storage conditions and consequently improve handling strategies.

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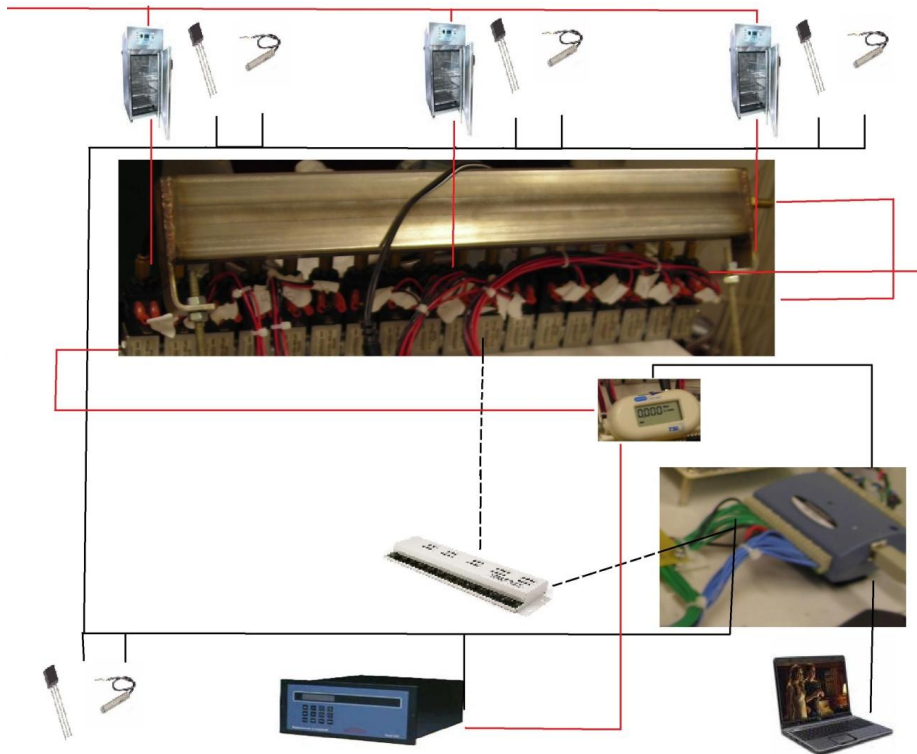
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APPENDIX A. DIAGRAM AND CODING

Diagram for the Electrical Components and Experimental set up



List of Materials and Datasheets

Vendor	Qty	Vendor Part Number	Description
			SSR 24
DigiKey	18	67-1068-nd	
DigiKey	18	470h-nd	
DigiKey	6	HE-100-nd	
reused	12	Rlyfma105c	
DigiKey	1	Mm74hc4514n-nd	
DigiKey	1		Relative humidity sensor
DigiKey	1		Temperature Transducer
Radio Shack	1		Relays
DigiKey	1		PGA 204

DigiKey	2	Wm4648-nd	Breadboard
DigiKey	3	Wm4650-nd	
DigiKey	2	Wm2104-nd	
DigiKey	2	Wm2108-nd	
DigiKey	3	Wm2110-nd	
DigiKey	58	Wm2300-nd	
reused	1	LPS22(-T)	Astec / Emerson Power Supply 5 volts – 2 amps
Measurement Computing	1	PMD-1208-LS	Personal Measurement Device
Lowes	36	na	

Pneumatic valves manufactured by ARS Ingersoll-Rand –inserts from the ARS sales catalog are included.

Digikey – <http://www.digikey.com>

Measurement Computing - <http://www.measurementcomputing.com/>

Codes for the Interface:

Option Explicit ' **Force explicit variable declaration**

'Graphic User Interface Define Dependent Constants

Const colPort As String = "A" 'Column used for port number

Const colPortName As String = "B" 'Column used for port name

Const colCO2 As String = "C" 'Column used for CO2

Const colAirF As String = "D" 'Column used for Air Flow

Const colTemp As String = "E" 'Column used for Temperature

Const colRH As String = "F" 'Column used for Relative Humidity

Const colDryMat As String = "G" 'Column used for the % of Dry Matter Loss

Const colControlCO2 As String = "H" 'Column used for the TimeStamp

Const colTime As String = "I" 'Column used for the TimeStamp

Const startingRow As Long = 3 'Address of the row where the data starts to be stored

Const sheetName As String = "Interface"

'Device Dependent Constants

```

Const BoardNum = 0           'PMD 1208
Const PMDBoard = 0
Const RelayBoard = 1
Const RelayOn = 1: Const RelayOff = 0

```

'Global variables Dim: Declares variables and allocates storage space

```

Dim startingTime As Date
Dim stopRunning As Boolean 'but they can only be True or False
Dim thisBook As Workbook

```

The idea was to set different channels and displayed in the interface for fast trouble shooting

```

Dim chTempertature As Integer   'Temperature Channel
Dim chCO2 As Integer           'CO2 Channel
Dim chRH As Integer            'Relative Humidity Channel
Dim chAirFlow As Integer       'Air Flow Channel

```

```

Dim portNames()                'Array of port Names
Dim portWeight()               'Array of port Samples Weight
Dim portLastCO2()              'Array of port Last CO2 Sample
Dim portlastAirf()             'Array of port Last Airf Sample
Dim portControl()              'Array of port Control (that is which port is witness)

```

```

'#####      Graphic      User      Interface      EVENTS      HANDLING
'#####

```

```

'+-----BtnReset_Click-----
'| Fired when Reset button is pressed. Asks for confirmation
'| Clears the content (not the format) of the data range => from "startingRow" to 1048576 row
'+-----
Private Sub BtnReset_Click()
    If MsgBox("Are you sure you want to reset data? All data will be lost.", vbYesNoCancel,
    "Attention!") = vbYes Then 'Clears all content in data range
        Worksheets(sheetName).Range(colPort & startingRow & ":" & colTime &
    1048576).ClearContents
    End If
End Sub

```

```

'+-----BtnStop_Click-----

```

```

'| Fired when Stop button is pressed. Asks for confirmation
'| Changes the "stopRunnig" Flag checked on main loop
'+-----
Private Sub BtnStop_Click()
    If MsgBox("Are you sure you want to STOP?", vbYesNoCancel, "Warning!") = vbYes Then
        stopRunning = True
    End If
End Sub

'+-----BtnStart_Click -----
'| Fired when Start button is pressed.
'| Main procedure:
'| 1) Call init proc (checks if environment settings are correct) and global vars are settled
'| 2) Configures PMD
'| 3) Loop until Stop button is pressed
'|     3.1) Open current Relay
'|     3.2) Save file if it has to DEPENDING ON THE SETTINGS!
'|     3.3) Wait for the Sampling time interval (less the time used for saving the book)
'|     3.4) Read data measurement from the PMD device take CO2, Airflow, Temperature,
RH Data
'|     3.5) Store Data on a row and print results
'|     3.6) Close current relay and move to the next
'| 4) Close all relays, SAFE FAIL
'+-----

Private Sub BtnStart_Click()
    Dim co2 As Single, Airf As Single, temp As Single, RH As Single, portName As Variant
    Dim row As Long, currentPort As Integer, portCount As Integer , i As Integer
    Dim lastTimeStamp, initialTimeStamp, savingTime
    Dim SamplingInterval As Long, savePeriod As Integer , saveCounter As Integer

    '1) Global vars are settled and inic proc is called
    Set thisBook = ActiveWorkbook 'ActiveBook is stored on auxiliary var because may fail if
    user changes focus on a different book
    'Calculate the sampling interval in seconds
    SamplingInterval = 3600 * ReadRange("IntervalHour") + 60 * ReadRange("IntervalMin") +
    ReadRange("IntervalSec")
    'init proc is called, checks if all settings are correct, exits if not
    If Not init() Then Exit Sub

    'vars initialization
    row = getLastRow() 'Find in which row to start writing data

```

```

currentPort = 0
portCount = ReadRange("PortsUsed")
savePeriod = ReadRange("SaveFilePeriod")
saveCounter = 0

```

'Save the current book with the name prefix followed by date time in format "YYYY-mm-dd HH nn ss"

```

If (savePeriod) Then
    Call saveBook(ReadRange("FilenamePrefix") & " " & Year(Now) & "-" & Month(Now) &
    "-" & Day(Now) & " " & Hour(Now) & " " & Minute(Now) & " " & Second(Now))
End If

```

'2) Configure PMD 1208

```

Call configurePMD1208(portCount)

```

```

initialTimeStamp = Timer    'Used to print Elapsed Time, initial value
stopRunning = False        'Flag used to determinate when to stop

```

```

Call writeOnRange("StartingTimeStamp", Now) 'Print Date-Time Started

```

'3) Loop until Stop button is pressed

```

While Not stopRunning 'while Stop button it's not been pressed

```

'3.1) Open current Relay

```

Call setRelayState(currentPort, RelayOn)
Call writeOnRange("SamplingPort", currentPort + 1) 'Print Active Sampling Port

```

'Wait for the interval specified

```

savingTime = 0
lastTimeStamp = Timer

```

'3.2) Save file if it has to

'Good time for saving if needed

```

If savePeriod > 0 Then 'If savePeriod >0
    saveCounter = (saveCounter + 1) Mod savePeriod
    If saveCounter = 0 Then savingTime = saveBook()
End If

```

'3.3) Wait for the Sampling time interval (less the time used for saving the book)

```

Do While Timer < lastTimeStamp + SamplingInterval - savingTime
    DoEvents ' Change to other events.

```

```

Sleep (500) ' idle for half second to make stop button response better
If stopRunning Then Exit Do
Call writeOnRange("ElapsedTime", Format(Timer - initialTimeStamp, "Standard"))
Call writeOnRange("RemainingTime", Format(lastTimeStamp + SamplingInterval -
Timer, "Standard"))
Loop

```

'3.4) Read data measurement from the PMD device take CO2, Airflow, Temperature, RH Data

'Start Measuring time 0.5 second before switching to different Valve

```
Call MeasureData(co2, Airf, temp, RH)
```

'3.5) Store Data and print results

```
Call WriteData(row, currentPort, co2, Airf, temp, RH)
```

```
Call writeOnRange("LastPort", currentPort)
```

```
Call writeOnRange("LastCO2", co2)
```

```
Call writeOnRange("LastAirFlow", Airf)
```

```
Call writeOnRange("LastTemperature", temp)
```

```
Call writeOnRange("LastRelHum", RH)
```

'3.6) Close current relay and move to the next

```
Call setRelayState(currentPort, RelayOff)
```

```
currentPort = (currentPort + 1) Mod (portCount) 'Modular arithmetic XE: 4 mod 3 = 1 (rest)
```

```
row = row + 1
```

Wend **'Loop until press Stop Button**

'4) Close all relays

'Before exit close all relays

For i = 0 To portCount - 1 **'Close all in case something goes wrong**

```
Call setRelayState(i, RelayOff)
```

Next

End Sub

```

#####                                PMD                                Functions
#####

```

```
'+----- configurePMD1208 -----
```

```
'| Configures PMD1208 device. First set environment configs
```

```
'| Then closes all relays to be used
```

```
'+-----
```

Private Sub configurePMD1208(portCount **As Integer**)

Dim i As Integer , ulstat

'-----

'First configure the PMD

'-----

ulstat = cbDeclareRevision(CURRENTREVNUM)

ulstat = cbErrHandling(PRINTALL, DONTSTOP)

If ulstat <> 0 **Then Stop**

'for setting the PGA204 gain x10 for the Temp sensor

ulstat = cbDConfigPort(BoardNum, FIRSTPORTA, DIGITALOUT)

ulstat = cbDOut(BoardNum, FIRSTPORTA, 0) **' to set gain x10 pin 16=0**

ulstat = cbDOut(BoardNum, FIRSTPORTA, 1) **' to set gain x 10 pin 15 = 1**

'Close all Relays to be used

For i = 0 To portCount - 1

 Call setRelayState(i, RelayOff)

Next

End Sub

'+-----MeasureData -----

'| Reads data from the device (CO2, air flow, temperature and Relative Humidity)

'| Returns data in ByRef variables

'+-----

Private Sub MeasureData(**ByRef** co2 **As Single**, **ByRef** airflow **As Single**, **ByRef** temperature **As Single**, **ByRef** RH **As Single**)

Dim Ch0Binary, Ch1Binary, Ch2Binary, Ch3Binary, Ch4Binary, ulstat

 ulstat = cbAIn(BoardNum, chCO2, BIP10VOLTS, Ch0Binary) **'Carbon Dioxide (Potentiometer instead)**

 co2 = (((Ch0Binary / 4096) * 20 - 10) * (1500 / 4.995))

 ulstat = cbAIn(BoardNum, chAirFlow, BIP10VOLTS, Ch1Binary) **'AirFlow**

 airflow = (((Ch1Binary / 4096) * 20 - 10) * (20 / 10))

 ulstat = cbAIn(BoardNum, chTemperture, BIP10VOLTS, Ch4Binary) **'Temperature**

 temperature = (((Ch4Binary / 4096) * 20 - 10) * 10)

 ulstat = cbAIn(BoardNum, chRH, BIP10VOLTS, Ch2Binary) **'Relative Humidity**

 RH = (((Ch2Binary / 4096) * 20 - 10) * 1000) * 0.0391 - 42.5 **' From Dr Tong**

End Sub

'+----- setRelayState -----

'| Turns On/Off a specified Relay defined on port number.

'| 0:RelayOff, 1:RelayOn

'-----

Private Sub setRelayState(port **As Integer** , state **As Integer**)

Dim ulstat

 ulstat = cbDBitOut(RelayBoard, FIRSTPORTA, port, state)

End Sub

#####

AUXILIARY

FUNCTIONS

#####

'-----WriteData -----

'| Stores the measures read on the row specified

'| Calculates CO2 index, it's a measure for us to have a deterioration index

'-----

Private Sub WriteData(row **As Long**, port **As Integer** , co2 **As Single**, airflow **As Single**,
temperature **As Single**, RH **As Single**)

Dim sheet **As** Worksheet, control **As Integer**

 Set sheet = thisBook.Worksheets(sheetName)

 portLastCO2(port) = co2

 portlastAirf(port) = airflow

 control = portControl(port) - 1

 sheet.Range(colPort & row) = port + 1

 sheet.Range(colPortName & row) = portNames(port)

 sheet.Range(colCO2 & row) = co2

 sheet.Range(colAirF & row) = airflow

 sheet.Range(colTemp & row) = temperature

 sheet.Range(colRH & row) = RH

 sheet.Range(colDryMat & row) = dryMatterLoss(co2, airflow, portWeight(port),
portLastCO2(control), portlastAirf(control))

 sheet.Range(colControlCO2 & row) = portLastCO2(control)

 sheet.Range(colTime & row) = Now()

 Set sheet = Nothing

End Sub

'-----dryMatterLoss -----

'| Calculates the % CO2 index (simplified dry matter loss)

'| Returns null if sample is null or sample equals 0

'-----

```
Public Function dryMatterLoss(co2 As Single, airflow As Single, weight As Variant, ByVal controlCO2 As Single, ByVal ControlAirf As Single) As Variant
```

```
    dryMatterLoss = Null
```

```
    If IsNumeric(weight) Then
```

```
        If weight <> 0 Then dryMatterLoss = (co2 * airflow - controlCO2 * ControlAirf) / weight
```

```
    End If
```

```
End Function
```

```
'+----- init -----
```

```
'| Configures environment settings
```

```
'| Checks the preconditions to detect everything if it is fine before start
```

```
'| Resets some values
```

```
'+-----
```

```
Private Function init() As Boolean
```

```
    Dim OK As Boolean, description As String, sheet As Worksheet
```

```
    Set sheet = thisBook.Worksheets(sheetName)
```

```
    OK = checkNames() 'Check If the application has all variables defined
```

```
    Call loadPortsData
```

```
    If OK Then
```

```
        'Failsafe #1 First Check that the Ports to be used is valid (between 1 and 24)
```

```
        If Not isBetween(1, 24, sheet.Range("PortsUsed")) Then 'Check a numerical value
```

```
            OK = False
```

```
            description = "Number of port used must between 1-24"
```

```
        End If
```

```
        'Failsafe #2 First Check that the Sampling Interval is valid
```

```
        '2.1 Check Hours are correct, between 0-23
```

```
        If Not isBetween(0, 23, sheet.Range("IntervalHour")) Then
```

```
            OK = False
```

```
            description = description & vbNewLine & "Sample Interval hours must be between 0-23"
```

```
        End If
```

```
        '2.2 Check Minutes are correct, between 0-59
```

```
        If Not isBetween(0, 59, sheet.Range("IntervalMin")) Then
```

```
            OK = False
```

```
            description = description & vbNewLine & "Sample Interval minutes must be between 0-59"
```

End If

'2.3 Check Minutes are correct, between 0-59

If Not IsBetween(0, 59, sheet.Range("IntervalSec")) Then
 OK = False
 description = description & vbNewLine & "Sample Interval seconds must be between
 0-59"

End If

'#3 First Check that the Temperature Channel

If Not IsNumeric(ReadRange("ChannelTemperature")) Then 'Check a numerical value
 OK = False
 description = description & vbNewLine & "Temperature Channel must be numeric. See
 'Settings' sheet."

End If

'#4 First Check that the CO2 Channel

If Not IsNumeric(ReadRange("ChannelCO2")) Then 'Check a numerical value
 OK = False
 description = description & vbNewLine & "CO2 Channel must be numeric. See 'Settings'
 sheet."

End If

'#5 First Check that the Air Flow Channel

If Not IsNumeric(ReadRange("ChannelAirFlow")) Then 'Check a numerical value
 OK = False
 description = description & vbNewLine & "Air Flow Channel must be numeric. See
 'Settings' sheet."

End If

'#6 First Check that the Rel Humidity Channel

If Not IsNumeric(ReadRange("ChannelRH")) Then 'Check a numerical value
 OK = False
 description = description & vbNewLine & "Relative Humidity Channel must be numeric.
 See 'Settings' sheet."

End If

If Not OK Then MsgBox description, vbCritical, "Error: Invalid settings!"

Call writeOnRange("LastSaved", "Never")

Call writeOnRange("LastSavedTime", "Never")

End If

If OK Then

chTemperature = ReadRange("ChannelTemperature")

chCO2 = ReadRange("ChannelCO2")

chAirFlow = ReadRange("ChannelAirFlow")

chRH = ReadRange("ChannelRH")

End If

init = OK

End Function

```
'+----- getLastRow -----
'| Finds the first empty data row. Starting from "startingRow" and seeking in the port
column for the
'| first empty cell.
'+-----
```

Private Function getLastRow()

Dim ready **As** Boolean, sheet **As** Worksheet, row **As** Long

Set sheet = Worksheets(sheetName)

row = startingRow

While Not ready

If IsEmpty(sheet.Range(colPort & row)) Then

ready = True

Else

row = row + 1

End If

Wend

getLastRow = row

End Function

```
'+----- CheckNameExists -----
'| Checks if a Name on the book exists, if not exists write an error message on
"errorDescription" var
'+-----
```

Private Function CheckNameExists(rangeName **As** String, **ByRef** errorDescription **As** String)

As Boolean

Dim temp

CheckNameExists = True

On Error GoTo NotExists

temp = thisBook.Names(rangeName)

```

Exit Function
NotExists:
    errorDescription = errorDescription & vbNewLine & "A cell with the name '" & rangeName
    & "' is needed."
    CheckNameExists = False
End Function

```

```

'+----- checkNames -----
'| Checks if all names used here are defined on the book
'+-----

```

```
Private Function checkNames() As Boolean
```

```
    Dim description As String
```

```
    Call CheckNameExists("StartingTimeStamp", description)
```

```
    Call CheckNameExists("ElapsedTime", description)
```

```
    Call CheckNameExists("LastPort", description)
```

```
    Call CheckNameExists("LastCO2", description)
```

```
    Call CheckNameExists("LastAirFlow", description)
```

```
    Call CheckNameExists("LastTemperature", description)
```

```
    Call CheckNameExists("LastRelHum", description)
```

```
    Call CheckNameExists("PortsUsed", description)
```

```
    Call CheckNameExists("LastSaved", description)
```

```
    Call CheckNameExists("LastSavedTime", description)
```

```
    Call CheckNameExists("RemainingTime", description)
```

```
    Call CheckNameExists("IntervalHour", description)
```

```
    Call CheckNameExists("IntervalMin", description)
```

```
    Call CheckNameExists("IntervalSec", description)
```

```
    Call CheckNameExists("FilenamePrefix", description)
```

```
    Call CheckNameExists("ChannelCO2", description)
```

```
    Call CheckNameExists("ChannelTemperature", description)
```

```
    Call CheckNameExists("ChannelAirFlow", description)
```

```
    Call CheckNameExists("ChannelRH", description)
```

```

    If Len(description) > 0 Then MsgBox description & vbNewLine & "These named cells are
    used for reading or writing data", vbCritical, "Error: Invalid Environment settings!"

```

```
    checkNames = (Len(description) = 0)
```

```
End Function
```

```

'+----- isBetween -----
'| Simple function to check that a value it is in the range between iniValue and endValue
'+-----

```

```
Private Function isBetween(iniValue, endValue, value) As Boolean
```

```
isBetween = True
```

```
If Not IsNumeric(value) Then 'Check a numerical value
```

```
    isBetween = False
```

```
Else
```

```
    If value < CInt(iniValue) Or value > CInt(endValue) Then isBetween = False
```

```
    End If
```

```
End Function
```

```
'+----- ReadRange -----
```

```
'| reads and returns data from a range
```

```
'+-----
```

```
Private Function ReadRange(rangeName As String) As Variant
```

```
    ReadRange = thisBook.Names(rangeName).RefersToRange
```

```
End Function
```

```
'+----- writeOnRange -----
```

```
'| write data on a range name or range address
```

```
'+-----
```

```
Private Sub writeOnRange(rangeName As String, value As Variant)
```

```
    thisBook.Sheets(sheetName).Range(rangeName) = value
```

```
End Sub
```

```
'+----- saveBook -----
```

```
'| Saves the book if not name is defined, or do a "Save as" command if name is given
```

```
'| Print the time when was Saved and how Long it took
```

```
'+-----
```

```
Private Function saveBook(Optional bookName As String = "") As Long
```

```
    Dim timestamp
```

```
    timestamp = Timer
```

```
    If Len(bookName) > 0 Then
```

```
        thisBook.Saveas bookName
```

```
    Else
```

```
        thisBook.Save
```

```
    End If
```

```
    Call writeOnRange("LastSaved", Now)
```

```
    Call writeOnRange("LastSavedTime", Format((Timer - timestamp), "Standard") & " sec")
```

```
    saveBook = Timer - timestamp
```

```
End Function
```

```
'+----- loadPortsData -----
```

```

'| Loads ports data:
'| Ports names on global portNames array defined
'| Ports samples on global portSamples array defined
'+-----
Private Function loadPortsData()
    Dim portNum As Integer , port As Integer , table As Range, portCount As Integer
    Set table = thisBook.Worksheets("Settings").ListObjects("Ports").Range

    portCount = ReadRange("PortsUsed")
    ReDim portNames(portCount)
    ReDim portWeight(portCount)
    ReDim portLastCO2(portCount)
    ReDim portControl(portCount)
    ReDim portlastAirf(portCount)

    On Error GoTo NotValid
    For port = 0 To portCount - 1

        portLastCO2(port) = Null
        portlastAirf(port) = Null
        portNum = table.Cells((port + 2), 1)      'Column 1 port number
        If (port + 1 <> portNum) Then GoTo NotValid    'Check If the row equals the port
number
        portNames(port) = table.Cells((port + 2), 2)  'Column 2 port name
        portControl(port) = table.Cells((port + 2), 3) 'Column 3 control port number
        portWeight(port) = table.Cells((port + 2), 4) 'Column 4 port sample weight
        GoTo Continue
    NotValid:
        portNames(port) = "Unknown"
        portControl(port) = 1      'Default uses 1
    Continue:
    Next

End Function

```


APPENDIX B. STATISTICAL RESULTS

Codes

DATA COBS;

INPUT REP CHAMBER \$ TEMP MOISTURE \$ DM;

CARDS;

1	A	10	15%	0
1	A	10	25%	0.3
1	A	10	35%	1.1
3	A	20	15%	0.1
3	A	20	25%	0.5
3	A	20	35%	2.1
2	A	30	15%	0.2
2	A	30	25%	1.4
2	A	30	35%	2.8
2	B	10	15%	0
2	B	10	25%	0.2
2	B	10	35%	1.2
1	B	20	15%	0.1
1	B	20	25%	0.8
1	B	20	35%	2.4
3	B	30	15%	0.2
3	B	30	25%	1.4
3	B	30	35%	3.1
3	C	10	15%	0
3	C	10	25%	0.2
3	C	10	35%	1
2	C	20	15%	0.1
2	C	20	25%	0.6
2	C	20	35%	2.7
1	C	30	15%	0.1
1	C	30	25%	2.2
1	C	30	35%	2.3

;

PROC GLM;

CLASS REP CHAMBER TEMP MOISTURE;

MODEL DM = CHAMBER CHAMBER*TEMP TEMP MOISTURE TEMP*MOISTURE/**SS3**;

TEST H= CHAMBER TEMP **E=**CHAMBER*TEMP;

MEANS TEMP/**TUKEY E=**CHAMBER*TEMP;

MEANS MOISTURE TEMP*MOISTURE/**TUKEY**;

RUN;

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The GLM Procedure

Class Level Information

Class	Levels	Values
REP	3	1 2 3

CHAMBER	3	A B C
TEMP	3	10 20 30
MOISTURE	3	15% 25% 35%

Number of Observations Read	27
Number of Observations Used	27

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The GLM Procedure

Dependent Variable: DM

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	14	26.05629630	1.86116402	25.00	<.0001
Error	12	0.89333333	0.07444444		
Corrected Total	26	26.94962963			

R-Square	Coeff Var	Root MSE	DM Mean
0.966852	27.18383	0.272845	1.003704

Source	DF	Type III SS	Mean Square	F Value	Pr > F
CHAMBER	2	0.04962963	0.02481481	0.33	0.7230
CHAMBER*TEMP	4	0.07037037	0.01759259	0.24	0.9125
TEMP	2	5.24962963	2.62481481	35.26	<.0001
MOISTURE	2	18.14296296	9.07148148	121.86	<.0001
TEMP*MOISTURE	4	2.54370370	0.63592593	8.54	0.0017

Tests of Hypotheses Using the Type III MS for CHAMBER*TEMP as an Error Term

Source	DF	Type III SS	Mean Square	F Value	Pr > F
CHAMBER	2	0.04962963	0.02481481	1.41	0.3439
TEMP	2	5.24962963	2.62481481	149.20	0.0002

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The GLM Procedure

Tukey's Studentized Range (HSD) Test for DM

NOTE: This test controls the Type I experimentwise error rate, but it generally has a higher Type II error rate than REGWQ.

Alpha	0.05
Error Degrees of Freedom	4
Error Mean Square	0.017593
Critical Value of Studentized Range	5.04024

Minimum Significant Difference 0.2228

Means with the same letter are not significantly different.

Tukey Grouping	Mean	N	TEMP
A	1.52222	9	30
B	1.04444	9	20
C	0.44444	9	10

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The GLM Procedure

Tukey's Studentized Range (HSD) Test for DM

NOTE: This test controls the Type I experimentwise error rate, but it generally has a higher Type II error rate than REGWQ.

Alpha 0.05
 Error Degrees of Freedom 12
 Error Mean Square 0.074444
 Critical Value of Studentized Range 3.77293
 Minimum Significant Difference 0.3431

Means with the same letter are not significantly different.

Tukey Grouping	Mean	N	MOISTURE
A	2.0778	9	35%
B	0.8444	9	25%
C	0.0889	9	15%

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The GLM Procedure

Level of TEMP	Level of MOISTURE	N	-----DM----- Mean	Std Dev
10	15%	3	0.00000000	0.00000000
10	25%	3	0.23333333	0.05773503
10	35%	3	1.10000000	0.10000000
20	15%	3	0.10000000	0.00000000
20	25%	3	0.63333333	0.15275252
20	35%	3	2.40000000	0.30000000
30	15%	3	0.16666667	0.05773503
30	25%	3	1.66666667	0.46188022
30	35%	3	2.73333333	0.40414519

```
DM 'Clear Log; Clear output;';
```

```
PROC IMPORT OUT= WORK.CORN
    DATAFILE= "C:\Documents and Settings\bernidc\My Documents\Datos
para correr en SAS COBS EXPERIMENT.csv"
    DBMS=CSV REPLACE;
    GETNAMES=YES;
    DATAROW=2;
RUN;
```

```
Data Corn2;
Set Corn;
If (Temp = 10) And (Run = 1) Then Chamber = 'A';
If (Temp = 20) And (Run = 1) Then Chamber = 'B';
If (Temp = 30) And (Run = 1) Then Chamber = 'C';
If (Temp = 10) And (Run = 2) Then Chamber = 'B';
If (Temp = 20) And (Run = 2) Then Chamber = 'C';
If (Temp = 30) And (Run = 2) Then Chamber = 'A';
If (Temp = 10) And (Run = 3) Then Chamber = 'C';
If (Temp = 20) And (Run = 3) Then Chamber = 'A';
If (Temp = 30) And (Run = 3) Then Chamber = 'B';
```

```
Proc Print Data= Corn2;
Proc Mixed Data = Corn2 Method = Type3;
Class Run Temp Material Moisture Chamber;
Model DM = Chamber Temp Moisture Temp*Moisture/ DDFM = Satterthwaite;;
Random Chamber*Temp;
LSMeans Temp Moisture / Adjust = Tukey;
LSMeans Temp*Moisture / diff;
Where Day = 21 And Material = 'Cobs';
Run;
Quit;
```

```
-----
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```

```
The Mixed Procedure
```

Model Information

Data Set	WORK.CORN2
Dependent Variable	DM
Covariance Structure	Variance Components
Estimation Method	Type 3
Residual Variance Method	Factor
Fixed Effects SE Method	Model-Based
Degrees of Freedom Method	Satterthwaite

Class Level Information

Class	Levels	Values
-------	--------	--------

Run	3	1 2 3
Temp	3	10 20 30
Material	1	Cobs
Moisture	3	15% 25% 35%
Chamber	3	A B C

Dimensions

Covariance Parameters	2
Columns in X	19
Columns in Z	9
Subjects	1
Max Obs Per Subject	27

Number of Observations

Number of Observations Read	27
Number of Observations Used	27
Number of Observations Not Used	0

Type 3 Analysis of Variance

Source	DF	Sum of Squares	Mean Square
Chamber	2	0.049630	0.024815
Temp	2	5.249630	2.624815
Moisture	2	18.142963	9.071481
Temp*Moisture	4	2.543704	0.635926
Temp*Chamber	4	0.070370	0.017593
Residual	12	0.893333	0.074444

Type 3 Analysis of Variance

Source	Expected Mean Square
Chamber	$\text{Var}(\text{Residual}) + 3 \text{ Var}(\text{Temp*Chamber}) + Q(\text{Chamber})$
Temp	$\text{Var}(\text{Residual}) + 3 \text{ Var}(\text{Temp*Chamber}) + Q(\text{Temp}, \text{Temp*Moisture})$
Moisture	$\text{Var}(\text{Residual}) + Q(\text{Moisture}, \text{Temp*Moisture})$
Temp*Moisture	$\text{Var}(\text{Residual}) + Q(\text{Temp*Moisture})$
Temp*Chamber	$\text{Var}(\text{Residual}) + 3 \text{ Var}(\text{Temp*Chamber})$
Residual	$\text{Var}(\text{Residual})$

Type 3 Analysis of Variance

Source	Error Term	Error DF	F Value	Pr > F
Chamber	MS(Temp*Chamber)	4	1.41	0.3439
Temp	MS(Temp*Chamber)	4	149.20	0.0002
Moisture	MS(Residual)	12	121.86	<.0001
Temp*Moisture	MS(Residual)	12	8.54	0.0017
Temp*Chamber	MS(Residual)	12	0.24	0.9125
Residual

Covariance Parameter
Estimates

Cov Parm	Estimate
Temp*Chamber	-0.01895
Residual	0.07444

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The Mixed Procedure

Fit Statistics

-2 Res Log Likelihood	11.3
AIC (smaller is better)	15.3
AICC (smaller is better)	16.2
BIC (smaller is better)	15.7

Type 3 Tests of Fixed Effects

Effect	Num DF	Den DF	F Value	Pr > F
Chamber	2	4	1.41	0.3439
Temp	2	4	149.20	0.0002
Moisture	2	12	121.86	<.0001
Temp*Moisture	4	12	8.54	0.0017

Least Squares Means

Effect	Temp	Moisture	Estimate	Standard Error	DF
Temp	10		0.4444	0.04421	4
Temp	20		1.0444	0.04421	4
Temp	30		1.5222	0.04421	4
Moisture		15%	0.08889	0.07852	14.4
Moisture		25%	0.8444	0.07852	14.4
Moisture		35%	2.0778	0.07852	14.4
Temp*Moisture	10	15%	-444E-18	0.1360	14.4
Temp*Moisture	10	25%	0.2333	0.1360	14.4
Temp*Moisture	10	35%	1.1000	0.1360	14.4
Temp*Moisture	20	15%	0.1000	0.1360	14.4
Temp*Moisture	20	25%	0.6333	0.1360	14.4
Temp*Moisture	20	35%	2.4000	0.1360	14.4
Temp*Moisture	30	15%	0.1667	0.1360	14.4
Temp*Moisture	30	25%	1.6667	0.1360	14.4
Temp*Moisture	30	35%	2.7333	0.1360	14.4

Least Squares Means

Effect	Temp	Moisture	t Value	Pr > t
Temp	10		10.05	0.0006
Temp	20		23.62	<.0001
Temp	30		34.43	<.0001
Moisture		15%	1.13	0.2761
Moisture		25%	10.75	<.0001
Moisture		35%	26.46	<.0001
Temp*Moisture	10	15%	-0.00	1.0000

Temp*Moisture	10	25%	1.72	0.1077
Temp*Moisture	10	35%	8.09	<.0001
Temp*Moisture	20	15%	0.74	0.4740
Temp*Moisture	20	25%	4.66	0.0003
Temp*Moisture	20	35%	17.65	<.0001
Temp*Moisture	30	15%	1.23	0.2401
Temp*Moisture	30	25%	12.25	<.0001
Temp*Moisture	30	35%	20.10	<.0001

Differences of Least Squares Means

Effect	Temp	Moisture	_Temp	_Moisture
Temp	10		20	
Temp	10		30	
Temp	20		30	
Moisture		15%		25%
Moisture		15%		35%
Moisture		25%		35%
Temp*Moisture	10	15%	10	25%
Temp*Moisture	10	15%	10	35%
Temp*Moisture	10	15%	20	15%
Temp*Moisture	10	15%	20	25%
Temp*Moisture	10	15%	20	35%
Temp*Moisture	10	15%	30	15%
Temp*Moisture	10	15%	30	25%
Temp*Moisture	10	15%	30	35%
Temp*Moisture	10	25%	10	35%
Temp*Moisture	10	25%	20	15%
Temp*Moisture	10	25%	20	25%
Temp*Moisture	10	25%	20	35%
Temp*Moisture	10	25%	30	15%
Temp*Moisture	10	25%	30	25%
Temp*Moisture	10	25%	30	35%
Temp*Moisture	10	35%	20	15%
Temp*Moisture	10	35%	20	25%
Temp*Moisture	10	35%	20	35%
Temp*Moisture	10	35%	30	15%
Temp*Moisture	10	35%	30	25%
Temp*Moisture	10	35%	30	35%
Temp*Moisture	20	15%	20	25%
Temp*Moisture	20	15%	20	35%
Temp*Moisture	20	15%	30	15%
Temp*Moisture	20	15%	30	25%
Temp*Moisture	20	15%	30	35%
Temp*Moisture	20	25%	20	35%
Temp*Moisture	20	25%	30	15%
Temp*Moisture	20	25%	30	25%
Temp*Moisture	20	25%	30	35%
Temp*Moisture	20	35%	30	15%
Temp*Moisture	20	35%	30	25%
Temp*Moisture	20	35%	30	35%
Temp*Moisture	30	15%	30	25%
Temp*Moisture	30	15%	30	35%
Temp*Moisture	30	25%	30	35%

Differences of Least Squares Means

Effect	Temp	Moisture	Estimate	Standard Error	DF
Temp	10		-0.6000	0.06253	4

Temp	10		-1.0778	0.06253	4
Temp	20		-0.4778	0.06253	4
Moisture		15%	-0.7556	0.1286	12
Moisture		15%	-1.9889	0.1286	12
Moisture		25%	-1.2333	0.1286	12
Temp*Moisture	10	15%	-0.2333	0.2228	12
Temp*Moisture	10	15%	-1.1000	0.2228	12
Temp*Moisture	10	15%	-0.1000	0.1923	14.4
Temp*Moisture	10	15%	-0.6333	0.1923	14.4
Temp*Moisture	10	15%	-2.4000	0.1923	14.4
Temp*Moisture	10	15%	-0.1667	0.1923	14.4
Temp*Moisture	10	15%	-1.6667	0.1923	14.4
Temp*Moisture	10	15%	-2.7333	0.1923	14.4
Temp*Moisture	10	25%	-0.8667	0.2228	12
Temp*Moisture	10	25%	0.1333	0.1923	14.4
Temp*Moisture	10	25%	-0.4000	0.1923	14.4
Temp*Moisture	10	25%	-2.1667	0.1923	14.4
Temp*Moisture	10	25%	0.0667	0.1923	14.4
Temp*Moisture	10	25%	-1.4333	0.1923	14.4
Temp*Moisture	10	25%	-2.5000	0.1923	14.4
Temp*Moisture	10	35%	1.0000	0.1923	14.4
Temp*Moisture	10	35%	0.4667	0.1923	14.4
Temp*Moisture	10	35%	-1.3000	0.1923	14.4
Temp*Moisture	10	35%	0.9333	0.1923	14.4
Temp*Moisture	10	35%	-0.5667	0.1923	14.4
Temp*Moisture	10	35%	-1.6333	0.1923	14.4
Temp*Moisture	20	15%	-0.5333	0.2228	12
Temp*Moisture	20	15%	-2.3000	0.2228	12
Temp*Moisture	20	15%	-0.0667	0.1923	14.4
Temp*Moisture	20	15%	-1.5667	0.1923	14.4
Temp*Moisture	20	15%	-2.6333	0.1923	14.4
Temp*Moisture	20	25%	-1.7667	0.2228	12
Temp*Moisture	20	25%	0.4667	0.1923	14.4
Temp*Moisture	20	25%	-1.0333	0.1923	14.4
Temp*Moisture	20	25%	-2.1000	0.1923	14.4
Temp*Moisture	20	35%	2.2333	0.1923	14.4
Temp*Moisture	20	35%	0.7333	0.1923	14.4
Temp*Moisture	20	35%	-0.3333	0.1923	14.4
Temp*Moisture	30	15%	-1.5000	0.2228	12
Temp*Moisture	30	15%	-2.5667	0.2228	12
Temp*Moisture	30	25%	-1.0667	0.2228	12

Differences of Least Squares Means

Effect	Temp	Moisture	t Value	Pr > t
Temp	10		-9.60	0.0007
Temp	10		-17.24	<.0001
Temp	20		-7.64	0.0016
Moisture		15%	-5.87	<.0001
Moisture		15%	-15.46	<.0001
Moisture		25%	-9.59	<.0001
Temp*Moisture	10	15%	-1.05	0.3156
Temp*Moisture	10	15%	-4.94	0.0003
Temp*Moisture	10	15%	-0.52	0.6110
Temp*Moisture	10	15%	-3.29	0.0052
Temp*Moisture	10	15%	-12.48	<.0001
Temp*Moisture	10	15%	-0.87	0.4004
Temp*Moisture	10	15%	-8.67	<.0001
Temp*Moisture	10	15%	-14.21	<.0001
Temp*Moisture	10	25%	-3.89	0.0021
Temp*Moisture	10	25%	0.69	0.4992
Temp*Moisture	10	25%	-2.08	0.0559

Temp*Moisture	10	25%	-11.26	<.0001
Temp*Moisture	10	25%	0.35	0.7339
Temp*Moisture	10	25%	-7.45	<.0001
Temp*Moisture	10	25%	-13.00	<.0001
Temp*Moisture	10	35%	5.20	0.0001
Temp*Moisture	10	35%	2.43	0.0289
Temp*Moisture	10	35%	-6.76	<.0001
Temp*Moisture	10	35%	4.85	0.0002
Temp*Moisture	10	35%	-2.95	0.0104
Temp*Moisture	10	35%	-8.49	<.0001
Temp*Moisture	20	15%	-2.39	0.0339
Temp*Moisture	20	15%	-10.32	<.0001
Temp*Moisture	20	15%	-0.35	0.7339
Temp*Moisture	20	15%	-8.15	<.0001
Temp*Moisture	20	15%	-13.69	<.0001
Temp*Moisture	20	25%	-7.93	<.0001
Temp*Moisture	20	25%	2.43	0.0289
Temp*Moisture	20	25%	-5.37	<.0001
Temp*Moisture	20	25%	-10.92	<.0001
Temp*Moisture	20	35%	11.61	<.0001
Temp*Moisture	20	35%	3.81	0.0018
Temp*Moisture	20	35%	-1.73	0.1044
Temp*Moisture	30	15%	-6.73	<.0001
Temp*Moisture	30	15%	-11.52	<.0001
Temp*Moisture	30	25%	-4.79	0.0004

Differences of Least Squares Means

Effect	Temp	Moisture	Adjustment	Adj P
Temp	10		Tukey	0.0015
Temp	10		Tukey	0.0001
Temp	20		Tukey	0.0035
Moisture		15%	Tukey-Kramer	0.0002
Moisture		15%	Tukey-Kramer	<.0001
Moisture		25%	Tukey-Kramer	<.0001
Temp*Moisture	10	15%		.
Temp*Moisture	10	15%		.
Temp*Moisture	10	15%		.
Temp*Moisture	10	15%		.
Temp*Moisture	10	15%		.
Temp*Moisture	10	15%		.
Temp*Moisture	10	15%		.
Temp*Moisture	10	15%		.
Temp*Moisture	10	25%		.
Temp*Moisture	10	25%		.
Temp*Moisture	10	25%		.
Temp*Moisture	10	25%		.
Temp*Moisture	10	25%		.
Temp*Moisture	10	25%		.
Temp*Moisture	10	25%		.
Temp*Moisture	10	35%		.
Temp*Moisture	10	35%		.
Temp*Moisture	10	35%		.
Temp*Moisture	10	35%		.
Temp*Moisture	10	35%		.
Temp*Moisture	20	15%		.
Temp*Moisture	20	15%		.
Temp*Moisture	20	15%		.
Temp*Moisture	20	15%		.
Temp*Moisture	20	25%		.

Temp*Moisture	20	25%	.
Temp*Moisture	20	25%	.
Temp*Moisture	20	25%	.
Temp*Moisture	20	35%	.
Temp*Moisture	20	35%	.
Temp*Moisture	20	35%	.
Temp*Moisture	30	15%	.
Temp*Moisture	30	15%	.
Temp*Moisture	30	25%	.

```

PROC GLM;
CLASS REP CHAMBER TEMP MOISTURE;
MODEL DM = CHAMBER CHAMBER*TEMP TEMP MOISTURE TEMP*MOISTURE/SS3;
TEST H= CHAMBER TEMP E=CHAMBER*TEMP;
MEANS TEMP/TUKEY E=CHAMBER*TEMP;
MEANS MOISTURE TEMP*MOISTURE/TUKEY;
RUN;

```

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The GLM Procedure

Class Level Information

Class	Levels	Values
REP	3	1 2 3
CHAMBER	3	A B C
TEMP	3	10 20 30
MOISTURE	3	15% 25% 35%

Number of Observations Read	27
Number of Observations Used	27

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The GLM Procedure

Dependent Variable: DM

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	14	26.05629630	1.86116402	25.00	<.0001
Error	12	0.89333333	0.07444444		
Corrected Total	26	26.94962963			

R-Square	Coeff Var	Root MSE	DM Mean
----------	-----------	----------	---------

0.966852 27.18383 0.272845 1.003704

Source	DF	Type III SS	Mean Square	F Value	Pr > F
CHAMBER	2	0.04962963	0.02481481	0.33	0.7230
CHAMBER*TEMP	4	0.07037037	0.01759259	0.24	0.9125
TEMP	2	5.24962963	2.62481481	35.26	<.0001
MOISTURE	2	18.14296296	9.07148148	121.86	<.0001
TEMP*MOISTURE	4	2.54370370	0.63592593	8.54	0.0017

Tests of Hypotheses Using the Type III MS for CHAMBER*TEMP as an Error Term

Source	DF	Type III SS	Mean Square	F Value	Pr > F
CHAMBER	2	0.04962963	0.02481481	1.41	0.3439
TEMP	2	5.24962963	2.62481481	149.20	0.0002

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The GLM Procedure

Tukey's Studentized Range (HSD) Test for DM

NOTE: This test controls the Type I experimentwise error rate, but it generally has a higher Type II error rate than REGWQ.

Alpha	0.05
Error Degrees of Freedom	4
Error Mean Square	0.017593
Critical Value of Studentized Range	5.04024
Minimum Significant Difference	0.2228

Means with the same letter are not significantly different.

Tukey Grouping	Mean	N	TEMP
A	1.52222	9	30
B	1.04444	9	20
C	0.44444	9	10

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The GLM Procedure

Tukey's Studentized Range (HSD) Test for DM

NOTE: This test controls the Type I experimentwise error rate, but it generally has a higher Type II error rate than REGWQ.

Alpha	0.05
Error Degrees of Freedom	12
Error Mean Square	0.074444
Critical Value of Studentized Range	3.77293
Minimum Significant Difference	0.3431

Means with the same letter are not significantly different.

Tukey Grouping	Mean	N	MOISTURE
A	2.0778	9	35%
B	0.8444	9	25%
C	0.0889	9	15%

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The GLM Procedure

Level of TEMP	Level of MOISTURE	N	-----DM----- Mean	Std Dev
10	15%	3	0.00000000	0.00000000
10	25%	3	0.23333333	0.05773503
10	35%	3	1.10000000	0.10000000
20	15%	3	0.10000000	0.00000000
20	25%	3	0.63333333	0.15275252
20	35%	3	2.40000000	0.30000000
30	15%	3	0.16666667	0.05773503
30	25%	3	1.66666667	0.46188022
30	35%	3	2.73333333	0.40414519

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