DESIGN AND EVALUATION OF A GRAIN RESPIRATION MEASUREMENT SYSTEM FOR DRY MATTER LOSS OF SOYBEANS

BY

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THESIS

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ABSTRACT

A respiration measurement system was designed, fabricated and tested to estimate dry matter loss (*DML*) of soybeans through monitoring carbon dioxide (CO_2) from grain respiration by gravimetric analysis. The system consisted of three parts: conditioned air input, grain respiration column, and moisture and carbon dioxide absorption columns. The system was tested for maximum loading rates ($r^*_{CO_2}$), minimum residence times (*RT*), capacities (A_{H_2O}, A_{CO_2}) and efficiencies (η_{H_2O}, η_{CO_2}) of moisture and CO_2 absorption columns. A pair of preliminary tests with 14% moisture soybeans at 35°C was conducted to demonstrate how to estimate respiration rate (r_{CO_2}) and *DML* rate (r_{DML}). Results showed that moisture absorption columns had A_{H_2O} = 21 g, no minimum *RT* and overall η_{H_2O} = 0.96 ± 0.07 when flow rate, *Q* = 200 to 2000 ml/min. Similarly, the CO_2 absorption columns had A_{CO_2} = 12.6 g with $r^*_{CO_2}$ = 2.1 g/h, minimum *RT* of 5.4 s and overall η_{CO_2} = 0.99 ± 0.01 when $MC_{ad} \geq 11.27\%$. Results from a soybean respiration test showed a r_{CO_2} = 15.7 mg/(kg·h) and r_{DML} = 0.010%/d, which were comparable to rates reported by Rukunudin et al. (2004). Compositional analysis showed changes in soluble protein, FFA and mold counts may be significant even after 4-5 d of storing 14% moisture soybeans. These results showed the system may be used to evaluate a wide range of respiration and *DML* rates for various oilseeds, cereal grains, and other agricultural or food products.

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TABLE OF CONTENTS

CHAPTER 1. INTRODUCTION

The Food and Agriculture Organization (FAO) of United Nations predicts the global agricultural production needs to increase by 60% over the next 40 years (FAO, 2012). Food availability and accessibility can be enhanced by increasing production, improving distribution, and reducing postharvest losses (PHL). Since more than one third of the food produced by weight is lost or wasted (FAO, 2009), reduction of food losses during postharvest processing and consumption is a critical component of ensuring future global food security. Based on calorie content alone, cereals and oilseeds contribute to 61% of total 1.5 quadrillion kilocalories of food lost or wasted (FAO, 2011). This comprises the largest share of global food loss and waste when compared to other food groups such as fruits, vegetables, roots, tubers and meats. In developing countries, food losses occur predominantly after harvest due to poor handling, transportation, storage, and limited markets and equipment for value added processed products. Traditional storage practices of cereal grains, which typically involve solar or open drying of grains and storing in jute bags in warehouses, provide inadequate protection against major storage pests and pathogens and often lead to degraded quality of commodity. For cereals and oilseeds, annual losses of 4 to 10% due to improper storage are typical (FAO, 2011). By region, cereal postharvest handling and storage losses are estimated at 10% in industrialized Asia, 8% in Sub-Saharan Africa, 7% in Southeast Asia and 4% in Latin America (FAO, 2011).

Safe storage guidelines are needed for all cereal grains for a range of grain moisture content (MC) and storage temperature (T). These guidelines provide farmers and grain storage facility personnel information to schedule different postharvest treatments or provide adequate aeration to the stored grain before quality loss or deterioration occurs. The guidelines are often based on the rates of quality degradation. For cereal grains, feed and fiber, quality degradation is

quantified in terms of dry matter loss (*DML*). Current maximum allowable storage time guidelines for shelled corn over a wide range of storage temperature and *MC* are based on 0.5% *DML* (ASABE, 2005). As most *DML* studies have been conducted with corn based on work by Steel et al. (1969), there is a lack of *DML* data for other cereal grains and oilseeds such as soybeans. Therefore, corn *DML* rates are often the only available reference for storage guidelines for other grains. Additionally, there is limited data available for quality degradation during conditions such as high harvest temperature and *MC*. This is a significant roadblock in the overall goal to reduce PHL during storage in low latitude areas where such conditions are prevalent. In order to determine the time it takes for grain such as soybeans to reach 0.5% *DML* threshold over a wide range of *T* and *MC*, its respiration rate (r_{CO_2}) must be known. To monitor respiration, continuous measurement of carbohydrates content, oxygen (O_2) consumption, or carbon dioxide (CO_2) production is needed. Previous studies with cereal grains focused on monitoring CO_2 production. Measurement systems including the use of non-dispersive infrared (NDIR) sensors, pH sensitive color changing gels, gravimetric analysis or gas chromatography (GC) have been described in the literature. Each method has advantages and disadvantages but design criteria and equations to optimize system performance have not been well described.

Therefore, the objectives of this thesis were to design, fabricate and evaluate a grain respiration measurement system based on monitoring CO_2 production by gravimetric analysis. The system consisted of three parts: (a) conditioning input air, (b) grain respiration column, and (c) moisture and CO_2 absorption columns. A series of tests to determine the absorption capacities, maximum loading rates, minimum residence times, and efficiencies of moisture and CO_2 absorption were carried out. A pair of preliminary tests with 14% moisture soybeans at 35°C was conducted to demonstrate how to estimate respiration rate (r_{CO_2}) and *DML* rate (r_{DML}).

CHAPTER 2. LITERATURE REVIEW

Food loss is defined by the U.S. National Academy of Sciences (1978) as any change in availability, edibility, wholesomeness or quality of the food that prevents it from being consumed by people. Losses in terms of quantity (i.e., weight or volume) and quality (e.g., physical condition or characteristics) can occur at various stages of food value chain. The loss accounts for all the interconnected points since the harvest – from storage, grading, packaging, transporting, and marketing to retail processing. During storage, the primary cause of loss can be biological (e.g., respiration, ethylene production, compositional changes, early germination), mechanical (e.g., bruises, cracks), chemical (e.g., contamination), or pathological (e.g., breakdown from fungi, bacteria, and other pests) (Bartz and Brecht, 2002). Secondary causes of loss are conditions that encourage and accelerate primary causes. These include improper harvesting and handling skills, lack of proper storage conditions (temperature, climate, oxygen level), inadequate transportation facilities, poor drying equipment, and lack of storage and legal standards (Kader, 1988). Fluctuations in available quantities of food, feed and fiber in between seasons of planting, growing and harvesting impact commodity pricing and storage decisions (Sahn, 1989). Storage is therefore integral to the total resource allocation for farmers. The storage structures required per crop type depend on the specific need and suitability for particular application such as crop harvest, volume and delivery to market. Often, centralized bulk storage facilities can be utilized by both large producers and by smallholder farmers working in cooperatives. The benefits associated with bulk storage include automated temperature control, mechanized rapid handling, low spillage, low operating costs and higher resistance against pests and rodents as compared to smallholder storage methods. Besides structural barriers, other methods of produce safety can be deployed such as insecticide application using sprays and

fumigants, sanitation of storage structures in between refill and hermetic storage to arrest insect and mold development.

The lack of data for standardized storage and handling guidelines makes it challenging for local authorities and international partners to assess the extent of PHL, especially so during storage phase in developing countries. Bailey and Gurjar (1918) were the first to propose the practical application and importance of developed storage guidelines for wheat. They studied the respiration of wheat in terms of CO_2 produced per unit time and material. Observing the gradual and uniform rise of respiration with moisture content up to 14.5% and an accelerated rise thereafter, Bailey and Gurjar (1918) proposed wheat must be stored while clean and dry to avoid high respiration rates indicating damage. In general, the guidelines for storing grain at low *MC* have persisted and specific additions have been made to consider effects of temperature, damage and microbial resistance.

Since Bailey and Gurjar (1918) proposed guidelines based on relationship between r_{CO_2} and r_{DML}, a variety of grain respiration measurement systems have been developed and described in the literature using this relationship to form storage guidelines. Primarily, the guidelines have been developed using various respiration measurement methods for corn and have yet to be extensively studied for other commodities (Table 2.1).

Table 2.1. Different materials and methods used in previous respiration measurement studies.

Grain	Method	Reference
wheat	Gravimetric	Bailey and Gurjar (1918)
barley, oat, flaxseed	Gravimetric	Bailey (1940)
corn	Gravimetric	Steele et al. (1969)
wheat	Gas chromatography	White et al. (1982)
corn	Gravimetric	Fernandez et al. (1985)
corn	Gravimetric	Friday et al. (1989)
corn	Infrared sensor	Wilcke et al. (1993)
corn	Gravimetric	Al-Yahya et al. (1993)
corn	Gravimetric	Aljinovic et al. (1995)
corn	Gravimetric	Dugba et al. (1996)
corn	Gas chromatography	Ng et al. (1998)
soybean	Gravimetric	Rukunudin et al. (2004)
wet distiller grain	Infrared sensor	Nyedu (2011)
corn	Infrared sensor	Huang et al. (2013)
corn cob	Infrared sensor	Campo et al. (2014)

Since 1989, most studies above use methodologies described by Friday et al. (1989) and Al-Yahya et al. (1993); however, very few mention design criteria to assemble respiration measurement systems. Before important design criteria and equations to optimize respiration measurement system performance can be identified, it is essential to understand the relationships between r_{CO_2} and r_{DML}.

2.1. Rates of respiration and dry matter loss

Quality degradation of grains has been quantified in terms of *DML*. *DML* is the loss of available carbohydrates via aerobic respiration:

$$C_6H_{12}O_6 + 6\,O_2 \rightarrow 6\,CO_2 + 6\,H_2O + 2835\,kJ/mol \quad [2.1]$$

All food and agricultural products are composed of structural carbohydrates (cellulose and hemicellulose), lignin, fats and proteins. Of these components, structural carbohydrates tend to be combusted, or respired, at faster rates (Rees, 1982). Respiration rate (r_{CO_2}) can be described as the rate of CO_2 production per unit mass of food or agricultural product. The quality

degradation commonly quantified in terms of r_{CO_2} is directly related to r_{DML} and is dictated by initial *MC*, *T*, and rate of loss in crop moisture (Ulreich, 1967). Once either r_{CO_2} or r_{DML} is known, the amount of *DML* over a storage period of time can be estimated and used in evaluating safe storage practices and conditions for different foods (Bailey, 1921; Milner and Geddes, 1945; Friday et al., 1989; Dugba et al. 1996; Rukunudin et al., 2004), feed (Nyendu, 2011), fiber (Rotz, 2005) and lignocellulosic feedstocks (Sanderson et al., 1997; Shinners et al., 2009; Shah et al., 2011; Campo et al., 2014). After harvest, the internal physiology of the plant that affects respiration cannot be altered, therefore, PHL mitigation and retention of quality is aimed towards reducing r_{CO_2} by manipulating factors such as *MC* and *T*.

2.1.1. Effects of moisture content on respiration rate

During a typical plant cycle, r_{CO_2} is high during plant growth (Pizarro and James, 1972). As the plant matures, its moisture content decreases which causes r_{CO_2} to also decrease. During cutting and harvesting of crop, r_{CO_2} peaks again but ceases once plant moisture falls below 40% (Rotz and Muck, 1994). Harvested crops are 'living' organisms and continue to perform metabolic functions even after harvest. For example, Reed et al. (2007) measured the rates of O_2 consumption and CO_2 production of re-wetted corn at three different moisture contents over a 60-day period. They reported O_2 consumption rates of 0.5, 5 and 18 mg O_2/(kg·h) for 15.0, 16.6 and 18.0% moisture corn, respectively (Table 2.2). These also corresponded to 1.4, 13.7 and 49.5 mg CO_2/(kg·h), respectively. Even with small differences in moisture content, a wide and nonlinear range of O_2 consumption and CO_2 production were observed. Other researchers have reported similar trends. Bailey (1940) reported respiration rates of 0.08 to 4.7 mg CO_2/(kg·h) for re-wetted oats, 0.08 to 5.7 mg CO_2/(kg·h) for barley, and as variable as 1.0 to 66.3 mg CO_2/(kg·h) for flax, all corresponding to range of 11 to 17% moisture grain. In general, for all

grain types studied by Bailey (1940), the respiration rate ranged from 0.08 to 66.3 mg CO_2/(kg·h) for 11 to 17% *MC*. Dry corn (*MC* < 14%) exhibited r_{CO_2} values between 0.16 to 0.54 mg CO_2/(kg·h) (Huang et al., 2013) to as high as 0.62 mg CO_2/(kg·h) (Bailey, 1940). For freshly harvested corn at 22.2%, r_{CO_2}= 30 mg CO_2/(kg·h) at 20°C was observed (Huang et al., 2013); re-wetted corn at the same moisture content had a lower r_{CO_2} value of 5 mg CO_2/(kg·h) (Fernandez et al., 1985). Similarly, for freshly harvested soybeans at 22%, r_{CO_2}= 9.7 mg CO_2/(kg·h) at 26°C was observed and rewetted soybeans after 48 weeks of preservation at the same moisture content had lower r_{CO_2} value of 2.3 mg CO_2/(kg·h) (Rukunudin et al., 2004).

Table 2.2. Estimated respiration rates of grains in previous studies.

Grain	Moisture content *MC* (%)	Temperature *T* (°C)	Respiration rate r_{CO_2}(mg CO_2/(kg.h)	Reference
rice	11 – 25	20	0 – 8	Dillahunty et al. (2000)
		50	15 – 85	
barley	11 – 17	37.8	0.08 – 5.7	Bailey (1940)
flax			1 – 66.3	
oats			0.08 – 4.7	
corn	< 14		0.62	
corn	< 14		0.16 – 0.54	Huang et al. (2013)
	22.2	20	30	
corn	15 – 18	25	1.4 - 49.5	Reed et al. (2007)
corn (rewetted)	22.2	26	5	Fernandez et al. (1985)
soybean	22	26	9.7	Rukunudin et al. (2004)
soybean (rewetted)			2.3	
wheat	22	10 – 40	1 – 12	White et al. (1982)

2.1.2. Effects of temperature on respiration rate

Just as with *MC*, increases in *T* also enhance r_{CO_2}. Rehman et al. (2002) reported up to 20.4% decrease in soluble sugars, which can be interpreted as *DML*, in corn stored at 45°C over a six month period. While increases in *MC* results in ever increasing r_{CO_2}, increases in *T* cause increases in r_{CO_2} up to a certain point, after which the rates decline (Dillahunty et al., 2000). This

trend results from a reduction in microbial growth and lower metabolic activity at high *T*s. For example, Bengal rice at 11.6 to 25% moisture exhibited r_{CO_2} values 0 to 8 mg CO_2/(kg·h) when stored at 20°C and 15 to 85 mg CO_2/(kg·h) when stored at 50°C (Dillahunty et al., 2000). At *MC* = 25%, as *T* increased beyond 50°C and up to 80°C, r_{CO_2} declined from 85 to 15 mg CO_2/(kg·h). Huang et al. (2013) reported r_{CO_2} nearly doubled with each 10°C increase in *T* for corn at 14 to 22% moisture when stored at 10 to 30°C. Similarly for wheat at 22% moisture, White et al. (1982) reported respiration rates of 1 to 12 mg CO_2/(kg·h) as storage temperatures increased from 10 to 40°C.

High *MC* and *T* promote mold growth (Christensen and Kaufmnann, 1965) and seed germination (Ileleji et al., 2006). Molds can develop in a wide range of *MC* (13 to 33%) and *T* (10 to 40°C) so long as the environment has a high relative humidity (*RH* > 80%) (Montross et al., 1999; Garcia et al., 2008). As mold grows, they preferentially consume nonstructural sugars upon respiration, contributing to *DML* during storage (Rotz and Muck, 1994). It has been concluded that the fungi affecting the grain during storage does not initially cause enough damage to deteriorate quality (Sauer, 1992) but the process itself becomes self-sustaining as the evolved heat from respiration further promotes the microbial activity leading to eventual higher loss of carbon (Williams et al., 1997).

2.2. Application of dry matter loss rate to developing storage guidelines

Several researchers used r_{DML} data to develop the maximum allowable storage time guidelines recommendations. Kreyger (1972) investigated safe storage times for grains such as wheat, barley, oats and rye to be fit for animal feed so long as *DML* was below 2%, using visible mold appearance as best method for determination of safe storage time (Kreyger, 1972). Other studies have followed Kreyger's (1972) recommendation and adopted visible mold count as the

best criterion (Nellist, 1998; Fleurat-Lessard, 2002). However, this criterion is highly subjective and, overall, considered by many as a regressive approach. With this method, the grain likely has degraded in quality by the time mold is noticeable. Seib et al. (1980) suggested using a *DML* threshold instead in their study using rough rice stored in static, non-aerated containers at *T* (10 to 30°C) and *MC* (11 to 20%). They developed a model to determine *DML* of rough rice (also called paddy rice) as a function of *MC*, *T* and storage time to be used for rough rice storage guidelines with constant airflow being carried through a grain sample. In the experiment with airtight containers, available O_2 decreased over time, reducing r_{CO_2} and r_{DML}. Therefore, estimated *DML* values reported by Seib et al. (1980), were higher than measured *DML* values since the estimates were based on a constant supply of O_2. They reported that the amount of *DML* from respiration in rough rice stored at 15% and 18% moisture fell below U.S. Grade Nos. 1 and 2 when *DML* exceeded 0.75%. They also noted higher rates in quality changes in airtight containers as a result of respired heat building up in the container.

Steele et al. (1969) studied the effects of *MC*, *T* and mechanical damage on grain. They noted that combine harvested corn developed enough mold damage during storage to drop from U.S Grade No. 2 to No. 3 as early as when 0.5% *DML* occurred. The current maximum allowable storage guidelines for corn are based on this threshold (ASABE, 2005), which has been extensively used in designing grain storage and low temperature drying systems (Thompson, 1972; Stroshine and Yang, 1990). Other researchers have disputed this threshold, recommending it be made stricter. For example, Friday et al. (1989) observed corn quality dropped to at least U.S. Grade No. 4 when 0.5% *DML* has been reached. During the time required to observe 0.5% *DML*, the stored grain often develops molds. The mold itself impacts the quality of the grain and contributes towards the increased rate of respiration. For this reason,

Wilcke et al. (1993) stated that by the time U.S. Grade No. 1 or No. 2 reached 0.5% *DML*, it had enough mold damage to be graded as U.S. No. 4 or 5. It has been estimated that 25% moisture corn reaches 0.5% *DML* in seven days, sometimes without any noticeable molding but the corn could be unfit for use due to contamination by aflatoxins (Marin et al., 1999). Therefore, Marin et al. (1999) recommended that the safe storage *DML* should be well below 0.5% *DML*.

For wheat, Hall and Dean (1978) suggested 1% *DML* was acceptable for food use since commonly used high temperature dryers prior to storage help minimize quality changes. White et al. (1982), however, suggested stricter guidelines. Their data suggested that even 0.1% *DML* was unacceptable for premium grade wheat and proposed an absolute limit of 0.04% *DML* since visible molds occur long after quality has deteriorated. They also argued that *DML* is often not fully quantified by using respired CO_2 as the only indicator.

While it is generally accepted that different types of grain warrant different *DML* thresholds for maximum allowable storage guidelines, for practical purposes, strict or overly low thresholds are rejected as they lead to high volumes of rejected grains and can have significant economic impacts. Additionally, there appears to be no consensus on the acceptable limit for *DML* and what other quality parameters should be used in these guidelines. The quality parameters can vary depending on the consumer's use of product and food manufacturer's end product. For example, grain deterioration is accompanied by deteriorative changes in oils due to oxidative reactions that can result in rancid flavors, odors and increased levels of free fatty acids (FFA) in wheat (Fellers and Bean, 1977) and soybeans (Erickson, 1993). Although FFA levels are currently not a grade-determining factor, high levels of FFA impact the taste of the end product and oil quality (Orthoefer, 1978). Frankel et al. (1987) reported an increase in FFA from 0.2 to 1.25% for soybeans stored at 13% *MC* for 49 days, which exceed allowable oil FFA

content limits of 0.75% in the U.S and 1% FFA in Brazil as set by National Oilseed Processors Association (NOPA, 2014). For soybean buyers, high oil FFA content indicates increased refining and processing costs and higher refining losses to ensure the oil is not bitter. Similarly, quality of corn used for wet milling can be dependent on the amount of residual thermo-sensitive proteins present in the grains post storage (Courtois, 1995).

2.3. Measurement of respiration rate

The r_{CO_2} can be measured statically or dynamically. In a static system, the grain sample is placed in a sealed container with fixed volume and accumulation of CO_2 within the container is measured over time. Static systems have been used for small sample sizes and short test durations (Bailey and Gurjar, 1918; Milner and Geddes, 1945). Longer experiments can be performed using a dynamic system, where the grain sample is placed in a container with continuous ventilation at a known flow rate (Q) and r_{CO_2} is determined by sampling the gas at inlet or outlet and testing for CO_2 using gas analyzers (Al-Yahya et al., 1993; Rukunudin et al., 2004; Campo et al., 2014). A dynamic system consists of three components: (a) air conditioning and flow management, (b) grain column, and (c) moisture removal and CO_2 measurement (Figure 1). CO_2 levels are often determined gravimetrically or by using a non-dispersive infrared (NDIR) sensor or gas analyzer. In the gravimetric method, the respired CO_2 passes through an adsorbent material and the increased mass of the adsorbent material is monitored over time. Often, the mass change is directly related to the amount of respired CO_2, and interpreted as the *DML* by the grain (Milner and Geddes, 1945; Fawole, 1969). Dynamic systems with gravimetric CO_2 measurements have been used extensively for determining r_{CO_2} of corn (Steele et al., 1969; Fernandez et al., 1985; Friday et al., 1989; Wilcke et al., 1993; Al-Yahya et al., 1993; Dugba et al., 1996; Ng et al. 1998; White et al., 2010), soybeans (Rukunudin et al., 2004), wet distillers

(Nyendu, 2011) and corn cobs (Campo et al., 2014). In these studies, respiration tests were conducted over at least a 96-h period and the mold growth in the grain column contributed CO_2 to the respired airstream.

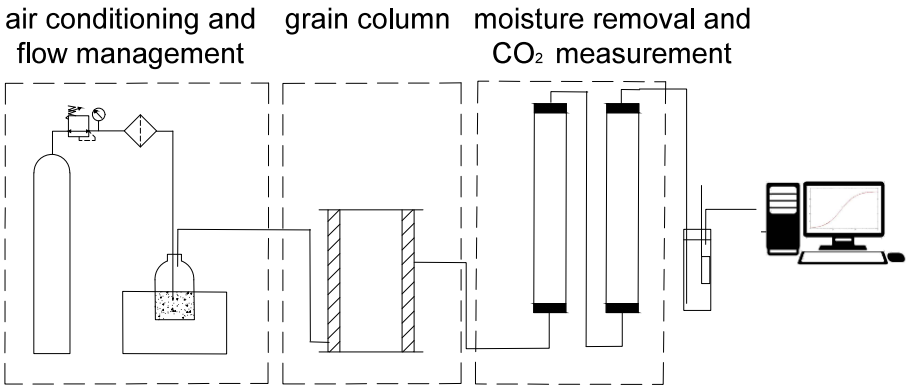

Figure 2.1. A dynamic grain respiration measurement system consists of (a) air conditioning and flow management, (b) grain column, and (c) moisture removal and CO_2 measurement. CO_2 is often absorbed into a material whose mass is periodically measured, and an increase in adsorbent mass is directly related to amount of respired CO_2. CO_2 may also be measured using GC/NDIR sensors.

Grain is often held in cylindrical columns or enclosed glass jars that are thermally insulated and placed in temperature-controlled incubators to minimize *T* fluctuations during the respiration test. To maintain the equilibrium moisture content (*EMC*) of the grain during testing, air must be supplied at the appropriate *T* and *ERH* (ASABE, 2007). This may be achieved by passing the input air through a temperature-controlled humidifier filled with a saturated salt solution or a glycerol-water solution. Saturated salt solutions have been long used as the standard method for humidification for closed systems in operating range of 0 to 50°C (Greenspan, 1977; ASTM, 2012). For example, in order to maintain soybean *MC* = 14% stored at 35°C during testing, air must be conditioned to 35°C and *RH* = 78% (Figure 2.2). To achieve this, a saturated solution of potassium chloride or sodium chloride may be used. Drawbacks to this method include (1) lengthy periods to achieve equilibrium; (2) difficulty in maintaining saturated salt conditions over long respiration tests; (3) some salts are expensive and are corrosive; and (4)

tendency of salts to crystallize at the bubbler and tubing surfaces which blocks air flow over time (Levoguer and Williams, 1997). Grain samples tend to get contaminated with mold or salt deposits over time. Despite these drawbacks, saturated salt solutions have been extensively used as the humidification method in several grain respiration studies (Fernandez et al., 1985; Friday et al., 1989; Aljinovic, 1995; Dugba, 1996; Al-Yahya et al., 1993; Rukunudin et al., 2004; Huang et al., 2013).

An alternative is the use of glycerol-water solutions described by Forney and Brandl (1992) and described as a standard practice (ASTM, 2003). Different volumetric concentrations of glycerol-water solutions can be used in the same manner as saturated salt solutions to achieve *RH* conditions between 30 to 98% at 0 to 70°C. As the volumetric fraction of glycerol increases in the solution, resulting *RH* decreases. Using the previous example of soybean *MC* = 14% stored at 35°C, a glycerol-water solution with specific gravity (*SG*) of 1.18 may be used (Figure 2.2). These solutions offer the following advantages over saturated salt solutions: glycerol is generally less expensive than most reagent-grade salts; it is non-corrosive; and it does not readily precipitate or form deposits when the solution is constantly agitated with air bubbles. There are some drawbacks with this method: (1) compared to saturated salt solutions, the resulting *RH* from glycerol-water solutions is not highly sensitive to temperature (Forney and Brandl, 1992), therefore if grain *T* and *ERH* change, glycerol-water solutions need to be maintained at different T for desired EMC; (2) over time, water may need to be added to the glycerol-water solution to maintain proper concentration; and (3) since glycerol is a biological nutrient, the potential for mold growth inside the humidification reservoir is higher than with saturated salt solutions.

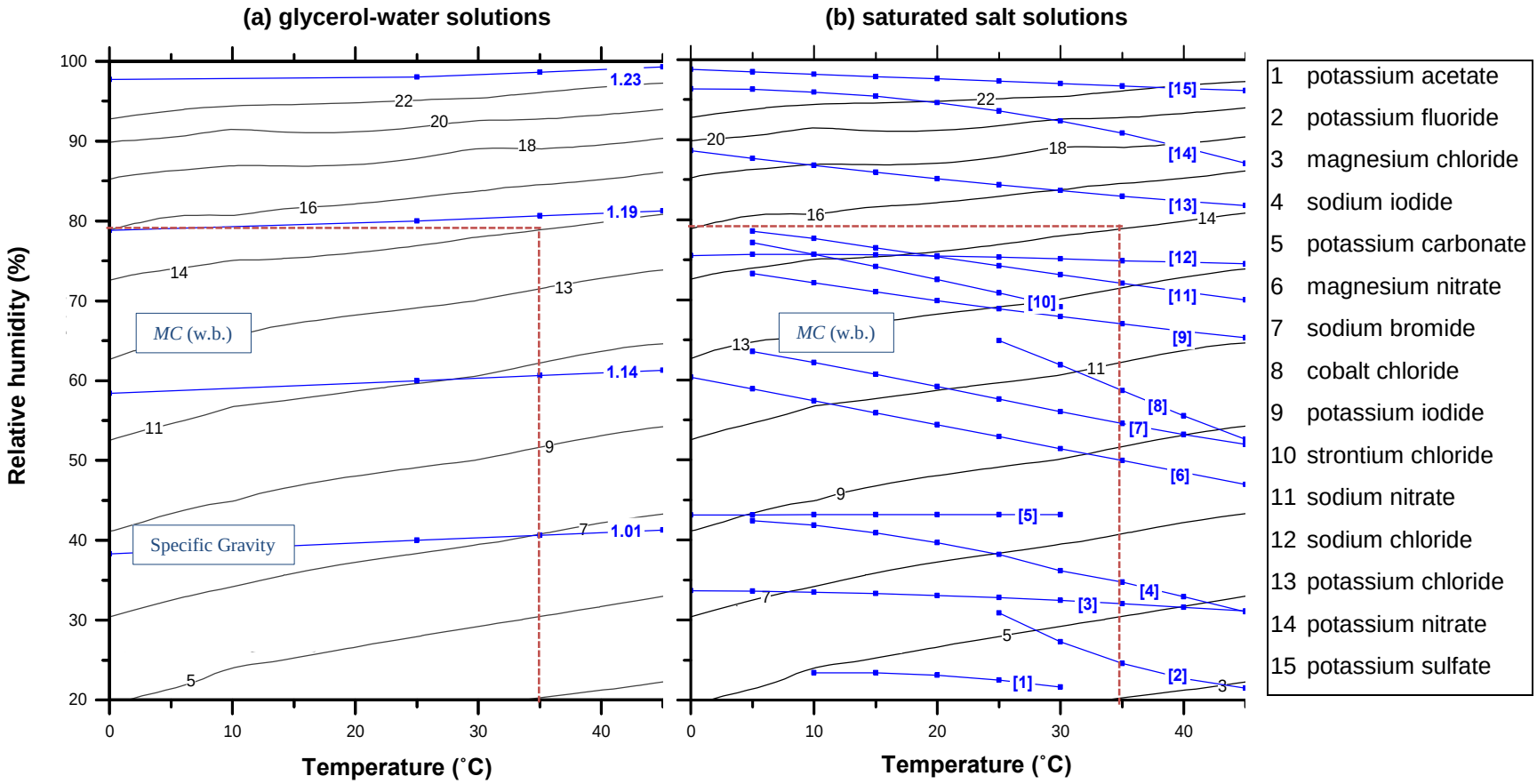

Figure 2.2. Moisture sorption isotherms of 5 to 22% moisture soybeans at 0 to 45˚C (ASABE, 2007). The equilibrium relative humidity (*ERH*) of soybeans at a particular moisture-temperature combination can be achieved by either using (a) a glycerol-water solution or (b) a saturated salt solution. The dotted lines show the intersection of 35˚C and 78% *ERH* to maintain an *EMC* = 14%.

Nevertheless, glycerol-water solutions were used by Wilcke et al. (1993) and Ng et al. (1998) in their grain respiration studies.

The conditioned air is passed through the grain column that is maintained at the same temperature as the air. When the air exits the grain column, it carries with it moisture from humidification and all products of respiration – moisture, CO_2, and heat. All moisture must first be stripped from the respired airstream using a desiccant. Afterwards, the dry airstream can be passed through a CO_2 adsorbent. A system developed by Al-Yahya (1993) to study the fungicide effect on high *MC* corn demonstrated the use of a mixture of vermiculite and potassium hydroxide (KOH) to absorb the evolved CO_2. The key principle is to sequester the CO_2 into a hydroxide as described by Friday et al. (1989):

$$2\,\mathrm{KOH} + \mathrm{CO_2} \rightarrow \mathrm{K_2CO_3} + \mathrm{H_2O} \qquad [2.2]$$

Al Yahya (1991) developed a procedure for embedding KOH in vermiculite granules. He tested the overall performance of the KOH-vermiculite mixture against ascarite by monitoring CO_2 accumulation in the column, every 24 h for 168 h. Results of the simple evaluation showed that the rate of accumulation of CO_2 in both adsorbent materials were not significantly different. He also demonstrated that the accumulation was linearly related to *Q*.

Al-Yahya et al. (1993) assumed that all the respired CO_2 was captured in the KOH-vermiculite mixture and, hence, the column's change in mass over time was directly related to r_{CO_2}. This assumption holds true when all the products of the reaction (Equation 2.1) are retained in the column. For every 1 mole of glucose consumed, 6 moles of CO_2 are produced. Using molecular weight of glucose, $M_{C_6H_{12}O_6}$ = 180 g/mol and molecular weight of CO_2, M_{CO_2} = 44 g/mol, we can determine the mass of respired CO_2 due to mass of glucose ($m_{C_6H_{12}O_6}$) consumed:

$$m_{CO_2} = \frac{DML \cdot M_{CO_2}}{M_{C_6H_{12}O_6}} \qquad [2.3]$$

Based on maximum allowable storage time guidelines for shelled corn (ASABE, 2005), for 0.5% *DML* or 5 g of glucose consumed per kg dry matter, Equation 2.3 gives:

$$m_{\mathrm{CO_2}} = \frac{5\ g\ \cdot \frac{44\ g}{1\ mol\ CO_2}}{\frac{180\ g}{1\ mol\ C_6H_{12}O_6}} \cdot \frac{6\ mol\ CO_2}{1\ mol\ C_6H_{12}O_6} = 7.33\ g\ CO_2. \quad [2.4]$$

It is worth noting that, by Equation 2.3, only glucose is assumed to contribute to the dry matter loss of the grain. A *DML* = 0.5% corresponds to 7.33 g respired CO_2 per kg of dry matter.

As respired air enters a column over a period of time t_s, CO_2 reacts with KOH to produce a carbonate (CO_3^{2-}) and water (H_2O). The products of the reaction accumulates in the column. Provided that all CO_2 reacts with KOH, the mass of accumulated CO_2 ($\sum m_{\mathrm{CO_2}}$) over t_s is the sum of the mass of the products minus the amount of hydroxide used in the chemical reaction:

$$\Sigma\, m_{\mathrm{CO_2}} = \Sigma(\, m_{\mathrm{CO_3^{-2}}} + m_{\mathrm{H_2O}} - 2m_{\mathrm{OH^-}}) \quad [2.5]$$

The accumulated mass of CO_2 can be converted to the amount of DML for any grain at given *MC* (%):

$$DML = \frac{\sum m_{\mathrm{CO_2}} \cdot M_{\mathrm{C_6H_{12}O_6}}}{M_{\mathrm{CO_2}} \frac{(100-MC)}{100}} \quad [2.6]$$

For example, suppose a 1 kg grain sample at 14% *MC* respired $\sum m_{\mathrm{CO_2}}$= 10 g CO_2 all of which was absorbed in the KOH-vermiculite mixture. The corresponding *DML* is

$$DML = \frac{10\ g\ CO_2 \cdot \frac{180\ g}{mol\ glucose}}{\frac{44\ g\ CO2}{mol\ CO_2} \frac{(100-14)}{100} kg\ dry\ matter} \cdot \frac{1\ mol\ glucose}{6\ mol\ CO_2} = 7.9\ \frac{g\ glucose}{kg\ dry\ matter} = 0.79\%. \quad [2.7]$$

The advantages of the gravimetric method include the use of inexpensive raw materials, low instrumentation errors, high accuracy and resolution based on weighing scale and the visibility of the CO_2 absorption process since most adsorbents exhibit color changes as CO_2 is absorbed. The disadvantages of this method include measurements at discrete time points (i.e., enough time must pass in order to noticeably measure mass change and, therefore, this is not a

continuous monitoring or respiration); human error and low resolution of scale can cause a significant impact on estimated respiration rates; and, most significantly, since the chemical reaction (Equation 2.2) requires a minimum *MC* of the adsorbent material (Nuckols et al., 1983), the absorption rate tends to decrease over time as continuous airflow dries out the adsorbent material. When the adsorbent *MC* falls below a threshold value, CO_2 is not absorbed and leads to an underestimation of r_{CO_2}.

Continuous CO_2 monitoring can be achieved by using CO_2 gas sensors or samplers. These may include gas chromatographs and NDIR sensors, which have been used by Steele (1967), White et al. (2010), Nyendu (2011) and Campo et al. (2014). The advantages of this approach are high sampling rates, small sample requirement (μl or μg), high sensitivity (ppm to ppb), and high accuracy. Key disadvantages include variations in measurements due to thermal drift, unsteady illumination source, light scattering from particles and change in level of infrared energy in the overall system (Kinkade, 2000). For many sensors, regular calibration against an inert zero gas (e.g., N_2 gas) is essential and, in some cases, a secure enclosure for the sensor during sampling is required to protect it against water vapor interference. While a GC provides an accurate measure of CO_2 concentration it requires periodic calibration, requiring mass spectroscopy for peak identification often with long time durations to complete an analysis. Additionally, a qualitative match purity of 75% is needed for accurate identification of compounds (CTEH, 2007). Since CO_2 absorbs infrared radiation in the wavelength range 2.7 to 15 μm (Skoog, 1985), NDIR sensors offers advantages such as quick response times and a variety of commercially available specifications for required detection ranges. However, NDIR sensors are expensive and readings are influenced by flow rate as well as variations in thermal drift, water vapor and carbon monoxide levels within the sensing chamber.

Other CO_2 measurement methods include the use of pH-sensitive, color-changing Solvita® gel kits to measure CO_2 levels via absorption (Chitrakar et al., 2006; Moog et al., 2008; Haney et al., 2008). Although the technology is inexpensive, interference from volatile fatty acids can result in false positive reactions for CO_2 concentrations. The kits are highly sensitive to temperature so use is restricted to 20 to 25°C and also sensitive to container size.

2.4. Critical residence times and breakthrough time through system components

Even though many researchers have described the grain respiration measurement systems they used, few discuss system design equations to optimize each component's performance. For example, for adequate humidification of the stored grain, input air must pass through a saturated salt or glycerol-water solution and be allowed to reach *ERH* conditions. To understand the proper humidification of air required for dynamic systems, the literature available is scarce. Forney and Brandl (1992) specified the ideal height ratio of glycerol-water solution to diffuser was 2.4:1 to provide the minimum residence time (*RT*) through the solution when Q = 100 ml/min but provided no other guidance for other values of Q or additional information on diffuser size, shape, and porosity. As diffuser porosity increases, moisture increases into the air, achieving *ERH* conditions faster. However, fine pore diffusers are susceptible to fouling, which require regular cleaning. Fine pore diffusers are especially problematic when used with saturated salt solutions since salt crystals tend to accumulate in the pores over time, decreasing diffuser efficiency.

Since *T* and *RH* of the air passing through the grain column are in equilibrium with the grain *MC*, *RT* through the grain column is not critical. Previous respiration studies reported airflow rates and dimensions of grain columns for which empty bed residence times (*EBRT*s) and residence times (*RT*s) may be estimated (Table 2.3).

Table 2.3. Estimated empty bed residence time and residence time of airstreams used in previous grain respiration measurement studies.

Grain	Moisture content	Length of 0.05 m dia. grain column	Porosity[a]	Flow rate	Residence times		Reference
	MC	L_c	ϕ_g	Q	Empty bed ($EBRT$)	(RT) [a]	
	(%)	(m)	(decimal)	(ml/min)	(s)	(s)	
soybeans	11.5	1.0	0.39	200	607	235	Rukunudin (2004)
	17.4	1.0	0.38	200	607	228	
corn	15.3	0.9	0.50	200	555	277	Dugba et al. (1996)
	18.0	1.0	0.51	200	607	312	Al-Yahya (1993)
	18.0	1.0	0.52	940	112	57.6	White et al. (2010)

[a]The porosity of the grain was estimated using the following relationship: $\phi_g = a + b\left(\frac{MC}{100-MC}\right)$, where a = 0.405 and b = -0.136 for soybeans at 8 to 28% moisture (Deshpande, 1993) and a = 0.420 and b = 0.441 for corn at 4.7 to 22% moisture (Seifi, 2010).

However, proper *RTs* through the rest of the respiration measurement system are critical to ensure all moisture is removed and all CO_2 is absorbed in their respective columns. A low *RT* through the desiccant may lead to residual water in the exit stream. As this residual moisture passes through the CO_2 absorption column, it will likely be absorbed by the CO_2 adsorbent material and lead to overestimation of r_{CO_2}. A low *RT* through the CO_2 absorption column may not allow for all CO_2 to be absorbed leading to an underestimation of r_{CO_2}.

The *RT* through each system component is affected by the material porosity (ϕ_{ad}), column volume (V_c) and Q:

$$RT = EBRT\,\phi_{ad} \quad [2.8]$$

where *EBRT* is defined as:

$$EBRT = \frac{V_c}{Q} \quad [2.9]$$

For a column filled with CO_2 adsorbent material, the amount of time it takes to exhaust the entire column, known as its breakthrough time t_B, can be defined as a function of the properties of the air sample and adsorbent material, volumetric concentrations of CO_2 (C_{CO_2}) and

moisture (C_{H_2O}) in the air, properties of the adsorbent container, and rate of the chemical reaction or formation of carbonates ($r_{CO_3^{2-}}$). The air properties are velocity (u), temperature (T), dynamic viscosity (μ), and diffusivity through the adsorbent (D_{air}). Adsorbent properties include bulk density ($\rho_{b,ad}$), moisture content (MC_{ad}), mass (m), equivalent diameter of particle size (d_e), and absorption capacity (A_{ad}). The physical dimensions – length (L_c) and diameter (D_c) are of the CO_2 absorption column are needed. Thus,

$$t_B = f\,(u, T, \rho_{b,ad}, \mu,\ D_{air,} C_{CO_2}, C_{H_2O}, MC_{ad}, m,\ d_e, A_{ad}, L_c, D_c, r_{CO_3^{2-}}) \qquad [2.10]$$

Some of these parameters are known or can be estimated while others may be difficult to determine or control. If these parameters can be held constant for a narrow range of test conditions, Equation 2.10 can be simplified and solved through dimensional analysis (Appendix A.3).

Nuckols et al. (1983) demonstrated that t_B of CO_2 scrubbers deduced the following functional relationship:

$$\frac{t_B u}{D_c} = f\left(N_{Re}, T, C_{CO_2}, C_{H_2O}, \frac{m}{\rho_{b,ad} D_c^3}, \frac{d_e}{D_c}, \frac{L_c}{D_c}\right) \qquad [2.11]$$

where N_{Re} is the Reynolds number. Theoretically, one may determine the time it takes to consume all the hydroxides in the CO_2 absorption column by taking the ratio of A_{ad} to the rate at which CO_2 is delivered into the column (Nuckols et al., 1983):

$$t_B^* = \frac{A_{ad} m}{\frac{\pi}{4} D_c^2 u C_{CO_2} \rho_{b,ad}} \qquad [2.12]$$

where the asterisk (*) denotes theoretical breakthrough time. The efficiency of CO_2 scrubbers is, therefore, described as the ratio

$$\eta_t = \frac{t_B}{t_B^*} \qquad [2.13]$$

Since the CO_2 scrubbers were used in diving masks, a decrease in efficiency of CO_2 absorption for a given column over time directly impacts the time duration for the dive and consequently the well-being of the diver. Nuckols et al. (1983) conducted a series of experiments to evaluate the relationships described in Equations 2.12 and 2.13. In their tests, a saturated airstream at 21.1°C containing 10,000 ppm CO_2 was passed through a scrubber with L_c/D_c ranging from 6.5 to 7.0 and D_c/d_e = 2.75. They reported, in general, η_t increased as L_c/D_c increased for $N_{Re} < 1$. When $N_{Re} = 1$, the L_c/D_c ranged from 1.7 to 7 and the η_t was in the range of 0.15 to 0.95, respectively. As N_{Re} approached 10, the η_t stabilized at 0.1 for all the curves in the L_c/D_c range (1.7 to 7). The η_t decreased from 1 to 0.2 as N_{Re} increased from 0.1 to 10 owing to decreasing laminar conditions and mass transfer rates and inadequate *RT*. Additionally, replacing the saturated airstream with a drier airstream (*RH* < 50%) caused η_t to decrease much faster, from 0.7 to 0.15, as N_{Re} increased from1 to 10. Since KOH and NaOH react with CO_2 in the presence of H_2O, decreased *RH* in the incoming stream strips the CO_2 scrubber of required moisture, hence reducing the rate of reaction with CO_2. When C_{CO_2} was increased to 40,000 ppm, η_t = 0.90 was achieved at $N_{Re} < 0.1$; at $N_{Re} > 0.1$, η_t decreased likely due to inadequate *RT*.

Nuckols et al. (1983) used Sodasorb®, a commercially available CO_2 adsorbent of 4 to 8 mesh particle size that has A_{CO_2} = 0.41 kg CO_2/kg when maintained at 12 to 14% moisture. The adsorbent contains an ethyl violet color indicator which turns the active white granules to purple upon exhaustion. The three-step reaction involved in the absorption of CO_2 by Sodasorb® is as follows:

$$CO_2 + H_2O \rightarrow H_2CO_3 \quad [2.14]$$

$$2\ H_2CO_3 + 2\ NaOH + 2\ KOH \rightarrow Na_2CO_3 + 4\ H_2O + K_2CO_3 \quad [2.15]$$

$$2\ Ca(OH)_2 + Na_2CO_3 + K_2CO_3 \rightarrow 2\ CaCO_3 + 2\ NaOH + 2\ KOH \quad [2.16]$$

Similar to the KOH-vermiculite mixture, moisture is necessary to initiate the CO_2 absorption (Equation 2.14). Moisture is a byproduct of the absorption process (Equation 2.15). MC_{ad} plays a key role in the absorption efficiency of Sodasorb®. If it's too wet, moisture coats the outside surfaces and pores of the adsorbent impeding CO_2 absorption. If it's too dry, the first reaction is inhibited. The US Navy Diving Manual recommends moisture levels of the incoming gas stream should be maintained between 30 and 80% *RH* (US Navy, 2008) for proper CO_2 scrubber performance.

From Nuckols et al. (1983)'s work, it is evident that system parameters, such as Q, N_{Re}, and RT, play a vital role in designing a robust grain respiration measurement system based on gravimetric measurement of respired CO_2. Their analyses form the basis for optimizing the performance of the system components and guide the design and testing of the respiration system developed in this study.

CHAPTER 3. MATERIALS AND METHODS

3.1. Grain respiration measurement system

A grain respiration measurement system (Figure 3.1) was developed based on principles described by Al-Yahya et al. (1993). The system is divided into three parts: (a) air conditioning and flow management, (b) grain column, and (c) moisture removal and CO_2 measurement.

3.1.1. Air conditioning and flow management

A mixture of compressed air (80% N_2, 20% O_2, and < 50 ppm CO_2) was regulated, filtered (Model No. 33001, WIX Filters, Gastonia, NC , USA), and supplied at 500 ml/min using a mass flow controller (Model No. GFC17A, Aalborg, Orangeburg, NY) (Figure 3.1). The low CO_2 concentration of the airstream was confirmed using an NDIR sensor (Model No. GMP222, Vaisala, Boulder, CO, USA) for each compressed air tank used (Appendix B).

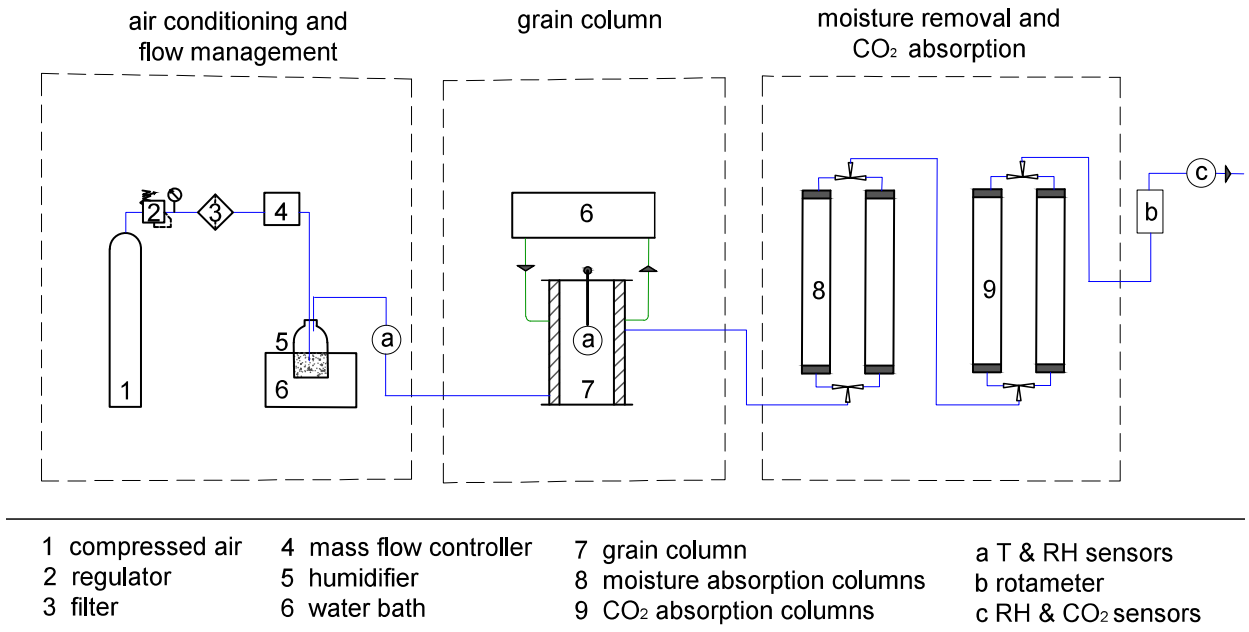

Figure 3.1. Schematic of the grain respiration measurement system used in this study.

T and *RH* of the air were controlled by passing the airstream through a bubbler (Part No. 50033, Red Sea, Houston, TX, USA) placed in a water bath (Model RTE7, NESLAB, Thermo

Electron Corporation, Newington, NH, USA). The bubbler contained a glycerol-water solution that would deliver humidified air in equilibrium to the *MC* of the soybeans (Figure 2.2b). Glycerol-water solutions were prepared using analytical grade glycerol (Product No. G33500, Fisher Scientific, Hampton, NH, USA) in 3500 ml of deionized water and mixed for 30 min at 50°C (Table 3.1). Preliminary tests showed that desired *RH* in the airstream was achieved after 30 min of bubbling (Appendix B, Section B.4).

Table 3.1. Required glycerol-water solutions when testing 12 to 14% moisture soybeans at 25 to 45°C.

Moisture content *MC* (%)	Temperature *T* (°C)	Equilibrium relative humidity, *ERH* (%)	Glycerol-water solution	
			Specific gravity, *SG*	Concentration (% w/w)
12	25	65	1.16	68.1
	35	68	1.17	65.3
	45	70	1.17	63.3
14	25	78	1.17	54.1
	35	80	1.18	51.5
	45	82	1.19	48.6
18	25	85	1.21	43.8
	35	88	1.21	38.4
	45	90	1.21	34.9

3.1.2. Grain respiration column

The grain respiration column was made of a sealed acrylic cylindrical unit, which can hold 1850 g of soybeans for each test (Figure 3.2). The temperature of the chamber was maintained with a water jacket made of Tygon® tubing (Part No. AJK00017, Saint-Gobain, Akron, OH, USA) wrapped around the column. Water was recirculated through the jacket using a water bath (Model 9102A11B, PolyScience, Niles, IL, USA). Grain *T* was visually monitored using a digital thermometer (Model No. 11050, DeltaTRAK, Pleasanton, CA, USA) located at the top of the column and inserted 7.5 cm deep into the grain bed. A photograph of Figure 3.2 is available in Appendix C, Figure C.2.

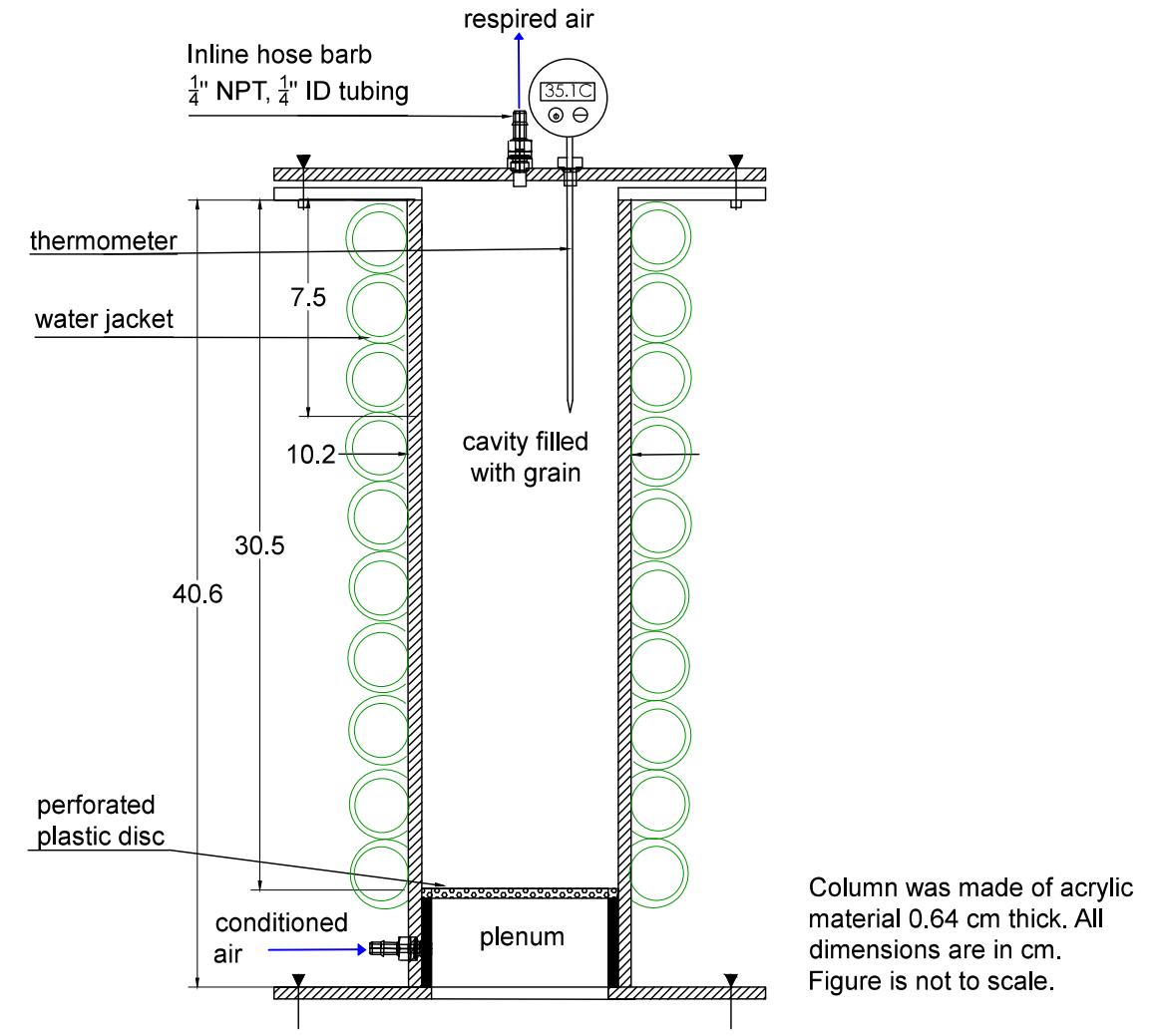

Figure 3.2. A grain respiration column was fabricated out of acrylic and designed to hold 1850 g of soybeans. Tygon® tubing was wrapped around the column (33 turns) and used as a water-jacket.

3.1.3. Moisture removal and CO_2 measurement

Air exiting the grain column was passed through a gas-drying unit (Model No. 26800, W. A. Hammond Drierite Co., Xenia, OH, USA) to remove moisture from both humidification and grain respiration (Figure 3.3). The unit was filled with a 550 g mixture of 4-mesh desiccant (Part No. 11001, W. A. Hammond Drierite Co. Ltd, Xenia, OH) and 4-mesh desiccant with an indicator (Part No. 21001, W. A. Hammond Drierite Co. Ltd, Xenia, OH) to allow visual monitoring of the moisture removal process. The absorption capacity of the Drierite is 0.06 kg water/kg desiccant. A photograph of Figure 3.3 is available in Appendix C, Figure C.3.

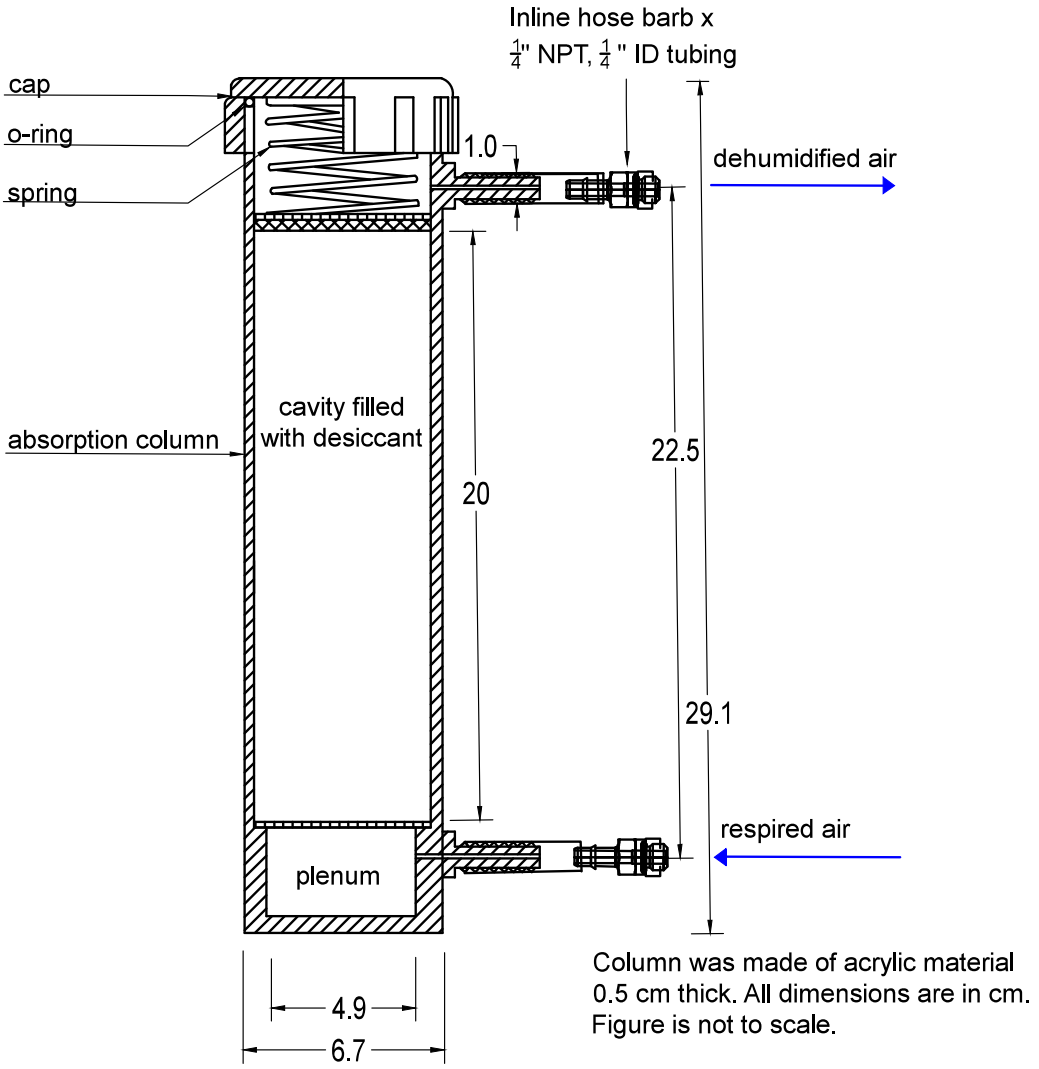

Figure 3.3. Gas drying units filled with 4 mesh indicating Drierite were used for moisture removal. Each unit held 550 g of desiccant.

After dehumidification, the air was passed through a CO_2 absorption column made of a gas-drying unit filled with 150 g of Sodasorb® and topped with 300 g of the desiccant mixture (Figure 3.4). The absorption capacity of Sodasorb® is 0.41 kg CO_2/kg adsorbent. The two layers were separated using a small plastic cylinder (2.5 cm ID x 1.5 cm height) with perforated disks at each end (40% open, 0.3 cm dia. holes). The purpose of this separator was to mitigate diffusion of moisture from the Sodasorb® to the desiccant prior to testing. A photograph of Figure 3.4 is available in Appendix C, Figure C.4. As dry air passed through the Sodasorb® layer, CO_2 was

absorbed following the chemical reactions described in Equations 2.14 to 2.16. The amount of moisture produced as a byproduct of the reactions need to be captured, as well, and was absorbed in the desiccant layer.

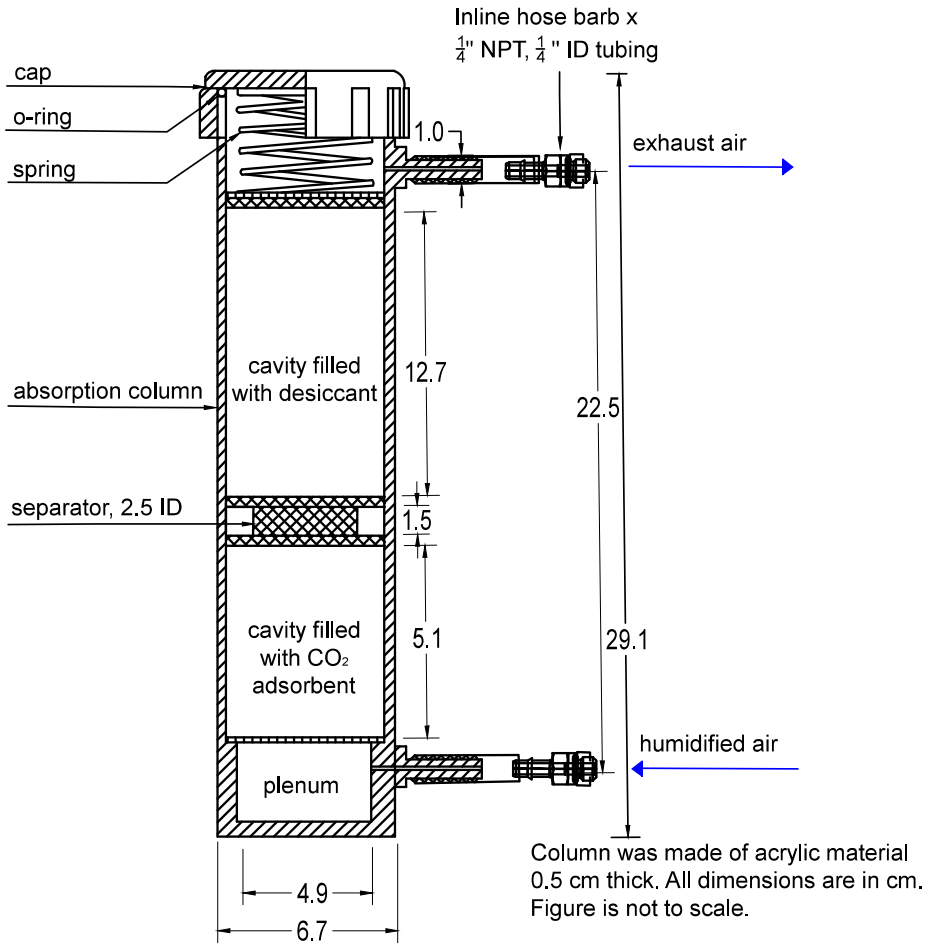

Figure 3.4. Gas drying units were used for CO_2 absorption. Each unit held 300 g of Drierite and 150 g of Sodasorb®.

The system was equipped with two moisture absorption columns and two CO_2 absorption columns. The first column in each set was designated the primary column through which air was passed through during testing. Since the primary moisture absorption column was expected to remove a large amount of moisture as a result of humidification and respiration, a secondary column was placed in parallel to the primary column (Figure 3.1). Airflow was easily diverted between columns using valve pairs upstream and downstream of the columns, providing access

to the secondary column once the desiccant in the primary column was exhausted. Likewise, a secondary CO_2 absorption column was placed in parallel to the primary column (Figure 3.1) so that airflow could be diverted to the secondary column on a periodic basis such as when the primary column was weighed to obtain the mass of absorbed CO_2.

3.1.4. Auxiliary sensors

A series of *T*, *RH*, and CO_2 sensors were placed at key locations to monitor the system performance (Figure 3.1). The *T* and *RH* of the conditioned air was monitored continuously using an SHT15 sensor package (Sensirion AG, Stäfa, Switzerland). The SHT15 sensor was mounted on a breakout board (Part No. SEN-08257, Sparkfun Electronics, Niwot, CO, USA). The *RH* and CO_2 concentration in the exhaust airstream were also monitored using a second SHT15 sensor and an NDIR sensor, respectively. The NDIR sensor probe (Model No. GMP222, Vaisala, Boulder, CO, USA) was connected to a transmitter (Model No. GMP222G0N0, Vaisala, Boulder, CO, USA). All measurements were logged every 2 min onto a micro SD memory card using a microcontroller board based on the ATmega2560 (Mega 2560, Arduino, Ivrea, Italy) and a wireless SD shield (Arduino, Ivrea, Italy) (Figure 3.5). The same program written in IDE (Version 1.5.5r2, Arduino, Ivrea, Italy) described by Olsen et al. (2013) was used for data acquisition. Finally, while *Q* was controlled using a mass flow controller, a rotameter (Model No. MMA-4, Dwyer Instruments, Michigan City, IN, USA) was placed in the exhaust airstream to confirm *Q*.

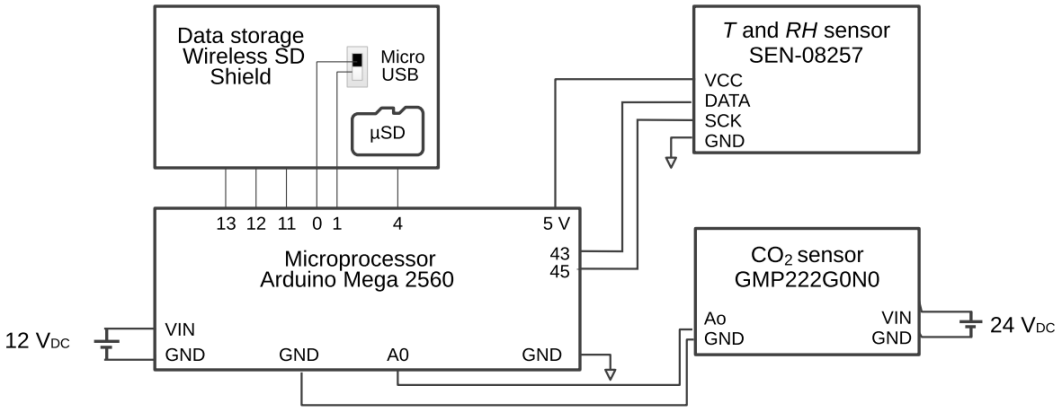

Figure 3.5. Data acquisition system used to monitor temperature, relative humidity, and CO_2 levels in the humidified and exhaust air streams.

3.2. Minimum residence times and capacity

3.2.1. Moisture absorption column

Since *Q* and subsequent *RT* were critical for complete moisture removal, the capacity of a moisture absorption column was tested with 89.6 ± 1 % *RH* air at 40.6 ± 0.5°C and 200 to 2000 ml (Figure 3.6, Table 3.2). Under these conditions, the humidity ratio, *W* = 45.1±1.3 g water/kg air. With this information and known *Q*, the amount of moisture passed through the column over a given period of time:

$$m^*_{\mathrm{H_2O}} = W \rho_{\mathrm{air}} Q t_{\mathrm{s}} \quad [3.1]$$

where $m^*_{\mathrm{H_2O}}$ was the theoretical amount of moisture absorbed, ρ_{air} is the density of the humidified air, and t_{s} is the elapsed time of testing.

Further, the efficiency of the moisture absorption column was defined as the ratio of moisture accumulated in the column, $\sum m_{\mathrm{H_2O}}$, to the moisture passed through the column over t_{s} as follows:

$$\eta_{\mathrm{H_2O}} = \frac{\sum m_{\mathrm{H_2O}}}{W\, Q\, \rho_{\mathrm{air}}\, t_{\mathrm{s}}} = \frac{\sum m_{\mathrm{H_2O}}}{\sum m^*_{\mathrm{H_2O}}} \quad [3.2]$$

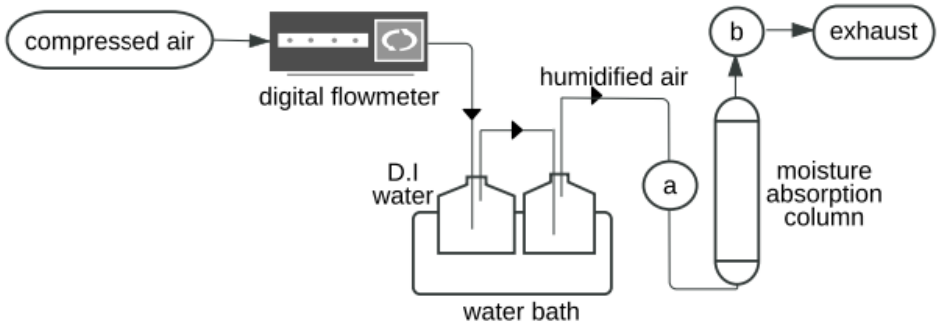

Figure 3.6. Setup for testing the capacity of a moisture absorption column and minimum residence time for efficient moisture removal. The digital flowmeter used was Environics Model No. 4040 (Tolland, CT, USA). *T* and *RH* sensors were placed at locations *a* and *b*.

Table 3.2. Flow rates and residence times used in determining capacity of and minimum residence time through a moisture absorption column.

Test No.	Flow rate	Residence time		No. of replications
	Q (ml/min)	Empty bed, *EBRT* (s)	*RT*[a] (s)	
1	200	234.2	175.6	3
2	400	117.2	87.9	3
3	1000	46.9	35.2	3
4	2000	23.4	17.6	3

[a]*RT* was calculated using Equation 2.8 and ϕ_{ad} = 0.75.

Prior to testing, compressed air was passed through deionized water. The *RH* of the humidified air was monitored using a SHT15 sensor until it reached saturated conditions. In the mean time, a moisture absorption column filled with desiccant was weighed (Model P3000, Denver Instrument, Bohemia, NY, USA). The scale, which has a manufacturer stated limit of 3000 g and resolution of 0.1 g, was used for all mass measurements in this study. Once the air was saturated, it was passed through the column for 30 min, weighed, and the mass was corrected by subtracting the initial mass of the column to determine the actual mass of moisture absorbed (m_{H_2O}). The test was repeated for an additional 3 h, with weight measurements conducted every 30 min, or until the *RH* of the exhaust airstream was greater than 1%. The data processing for comparison of m_{H_2O} values to $m^*_{H_2O}$ at each *RT* is presented in Section 3.4.

3.2.2. CO_2 absorption column

As with the moisture absorption column, the minimum *RT* for and capacity of the CO_2 absorption column needed to be determined. Tests were conducted by supplying 100% CO_2 (Catalog No. UC3138, AirGas, Inc., Danville, IL, USA) and 1% CO_2 (Catalog No. X02N199C3009430, AirGas, Inc., Danville, IL, USA) at 10 to 2000 ml/min (Figure 3.7, Table 3.3). To remove interstitial air, the CO_2 absorption column was first purged with 100% CO_2 gas. Air at 100 ml/min was supplied until exhaust air contained CO_2 < 400 ppm. Afterwards, the column was weighed and the mass was used as the initial mass of column for testing. The test was conducted for 8 to 12 h, with weight measurements conducted every 1 h, or until the CO_2 concentration of the exhaust airstream exceeded 50 ppm.

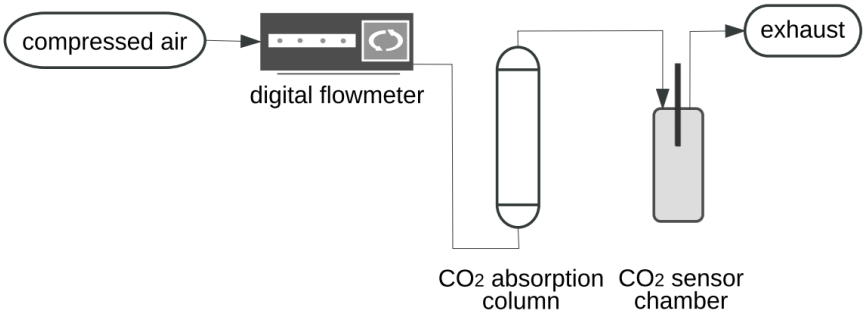

Figure 3.7. Setup for testing the capacity of a CO_2 absorption column and minimum residence time for efficient CO_2 removal.

Table 3.3. Flow rates, loading rates and residence times used in determining capacity of and minimum residence time through a CO_2 absorption column.

Test No.	Flow rate, *Q* (ml/min)	Loading rate[a], $r^*_{CO_2}$ (g CO_2/h)	Residence time		No. of replications
			Empty bed, *EBRT* (s)	*RT*[b] (s)	
1	10	1.2	2048.5	979.7	1
2	20	2.4	1042.2	489.8	1
3	500	0.6	41.7	19.6	2
4	1000	1.2	20.8	9.8	2
5	1500	1.8	13.9	6.5	2
6	1800	2.1	11.5	5.4	2
7	2000	2.4	10.4	4.9	2

[a] The loading rate, $r^*_{CO_2} = \frac{m^*_{CO_2}}{t}$.

[b] *RT* was calculated using Equation 2.8 and ϕ_{ad} = 0.47.

The theoretical accumulated mass, $\sum m^*_{CO_2}$ was calculated as

$$\sum m^*_{CO_2} = C_{CO_2} \rho_{CO_2} Q t_s \quad [3.3]$$

For the purpose of this study, the primary goal was to capture all the respired products at all times; therefore a mass-based efficiency can be defined as another way of defining the efficiency of CO_2 absorption to ensure no loss of mass would occur. The efficiency (η_{CO_2}) is equal to the ratio of CO_2 accumulated in the column, $\sum m_{CO_2}$ to the mass of CO_2 passed through the column over t_s :

$$\eta_{CO_2} = \frac{\sum m_{CO_2}}{Q\, C_{CO_2}\, \rho_{CO_2} t_s} = \frac{\sum m_{CO_2}}{\sum m^*_{CO_2}} \quad [3.4]$$

Note the η_{CO_2} can be determined from taking the slope of the measured vs. theoretical accumulated mass of CO_2 curve.

A test was also conducted to determine the minimum MC_{ad} that was needed for the CO_2 absorption column. To identify the minimum MC_{ad}, 150 g Sodasorb® was dried for 24, 48, 72 and 96 h each in desiccators containing 300 g of desiccant to obtain MC_{ad} of 11.27, 9.20, 8.07 and 6.84%, respectively. MC_{ad} was determined at 105°C for 24 h. After the specified drying time, the Sodasorb® samples were tested using the set up in Figure 3.7 with 2500 ppm CO_2 at 1500 ml/min. Each MC_{ad} was tested only once. The data processing for comparison of m_{CO_2} values to $m^*_{CO_2}$ at each *RT* is presented in Section 3.4.

3.3. Determining the respiration rate and dry matter loss rate of soybeans

3.3.1. Soybean samples and sample preparation

Soybeans (Pioneer 93Y15) at 12 to 14% moisture content were harvested from the Agricultural Engineering Farm at the University of Illinois in Urbana, IL on 29 September and 23 October in 2014. Immediately after harvest, all soybeans were placed in sealed buckets (19 l)

and stored at -17.4°C. Prior to testing, beans were manually mixed in the bucket. A 3 kg sample was removed from storage and manually cleaned of foreign materials (e.g., leaves, soil, sand). Split and broken seeds, as defined by the USDA Grain Inspection Handbook (USDA, 2013) were also separated using aluminum grain sieves (AGDS Sieve I, Hoffman Manufacturing Inc., Jefferson, OR, USA). The sieves were 33 cm ID with slotted screens of 0.39 cm x 1.9 cm for the foreign materials and round slotted screen of 0.32 cm for the splits removal. The sample was cleaned in small batches to ensure all unknown materials were removed. Three subsamples (20 g each) of clean beans were used to estimate *MC* using a handheld moisture meter (SW16060, John Deere, Moline, IL, USA). Afterwards, the subsamples were placed in a convection oven set at 103°C for 72 h to determine *MC* according to ASABE Standard S352.2 (2012). Another set of subsamples (6 x 100 g) was sent to two laboratories for mold count, crude protein and starch content measurement (Analab, Fulton, IL, USA) and FFA content determination (Midwest Laboratories, Omaha, NE, USA).

3.3.2. Preparation of grain respiration measurement system

Using the estimated *MC* of soybeans, a fresh batch of glycerol-water solution was prepared that would deliver an *RH* (72 to 87%) in equilibrium with the soybean *MC* at 35°C. Compressed air was passed through the solution at 500 ml/min for 30 min to allow the airstream to reach desired *RH*. In the mean time, two moisture absorption columns were prepared with fresh desiccant (550 g each) and two CO_2 absorption columns were filled, each with 150 g each of Sodasorb® and 300 g of desiccant. Each moisture or CO_2 absorption column was weighed and initial mass recorded. The columns were put in place using quick disconnect connectors (Catalog Nos. 60719 and 60721, US Plastics, Lima, OH, USA) and three-way valves (Catalog No. 22259, US Plastics, Lima, OH, USA). A sample (1850 g) of clean beans was transferred to a grain

column and acclimatized to room temperature during 2 h time period required for sample cleaning and system set up. The humidifier, full grain column and primary moisture and CO_2 absorption columns were connected using quick disconnect connectors. A final check that all tubing connections were secure was made and that all sensor readings were within an acceptable range: T = 35 ± 1°C; RH = 78 ± 5%; and C_{CO_2} < 50 ppm. When readings failed to meet T and RH conditions, adjustments to the water bath temperature or glycerol-water solution concentration were made accordingly. If C_{CO_2} > 50 ppm was observed, initial CO_2 levels were recorded or the absorption column was replaced with a fresh column. During the first 10 min of operation, it was assumed that exhaust airstream did not contain any respiration products and was merely the volume of air initially trapped in the piping and void spaces of the grain and absorption columns.

3.3.3. Respiration rate measurement

Periodically, m_{CO_2} in the primary CO_2 absorption column was measured. To do this, airflow was diverted to the secondary column before detaching the primary column and placing it on a scale. Three measurements of m_{CO_2} were taken with each measurement taken after the column was rotated 120° on the scale. These measurements were averaged and a mean m_{CO_2} was recorded. The primary column was placed back in the system and airflow diverted back to it. This process was repeated for 79 h for the first test and 153 h for the second, with m_{CO_2} measurements taken twice a day at every 6 to 12 h intervals. At the end of the test, both primary and secondary CO_2 absorption columns were weighed. Next, all the accumulated mass from columns used during the entire test was summed and the initial column masses were subtracted to obtain $\sum m_{\mathrm{CO}_2}$. The respiration rate calculated as

$$r_{\mathrm{CO}_2} = \frac{\sum m_{\mathrm{CO}_2}}{t_s} \qquad [3.5]$$

Occasionally, when the primary column had reached 70% of m_{CO_2}, airflow was diverted

to the secondary column for the duration of the test. The mass and time of removal of the primary column were noted. Likewise, when the primary moisture absorption column has reached 70% of $m^*_{H_2O}$, airflow was diverted to the secondary moisture absorption column.

All tests were planned to last 72 to 150 h or stopped when either of the following conditions was reached:

1. $\sum m_{CO_2}$ > 7.33 g, which indicated 0.5% DML had been reached based on Equation 2.1.
2. C_{CO_2} > 50 ppm in the exhaust air, indicating the absorption column had failed to capture all respired CO_2. In this case, the last $\sum m_{CO_2}$ measurements and corresponding t_s will be used to estimate r_{CO_2}.

3.3.4. Final sampling and system shutdown

At the end of each respiration test, the mass of the soybeans was recorded. Triplicate samples (20 g each) were tested for moisture content (ASABE, 2012). Another set of subsamples (6 x 100 g) was sent to two laboratories for mold count, crude protein and starch content measurement (Analab, Fulton, IL) and FFA content determination (Midwest Laboratories, Omaha, NE). Remaining beans were bagged and stored at -17.4^o C temporarily until quality measures were obtained from the labs. The grain respiration column and all moisture absorption and CO_2 absorption columns were emptied and cleaned using hot, soapy water followed by a cold deionized water rinse and air drying. The desiccant were regenerated at 210°C for 1 h in a convection oven, while used Sodasorb® was disposed of following guidelines by the University of Illinois Division of Research Safety (www.drs.illinois.edu).

3.4. Data processing and statistical analyses

All recorded sensor readings and mass measurements were transferred into a spreadsheet (MS Excel 2011) and analyzed using statistical package StatPlus (v5.9.20, AnalystSoft Inc,

2015). For the moisture absorption column tests, resulting m_{H_2O} values were compared to $m^*_{H_2O}$ at each *RT* by testing whether a 1:1 relationship existed between these values using two sample Student's *t*-test for means at $\alpha = 0.05$. Regression results were also used to determine the mass at which the slope deviated from unity at $\alpha = 0.05$; this point represented the capacity of the moisture absorption column. The minimum *RT* was determined by observing the maximum *Q* above which the *RH* > 1%. Similarly, measurements of absorbed CO_2 (m_{CO_2}) were compared to theoretical values, $m^*_{CO_2}$, at each *RT*. The minimum *RT* was determined by observing the maximum *Q* above which the CO_2 readout by the sensor was > 50 ppm or for which the efficiency, η_{CO_2} dropped below desired threshold. The point at which the slope deviated from unity represented the capacity of the CO_2 absorption column. Finally, for the grain respiration tests, means and standard deviations of *T*, *RH*, and CO_2 levels during the test were reported along with initial and final moisture, mold count, crude protein, starch, and free fatty acids contents for each test. The respiration rate, r_{CO_2} and *DML* rate, r_{DML} were also calculated for each grain respiration test using Equations 3.5 and 2.6 respectively.

CHAPTER 4. RESULTS AND DISCUSSION

4.1. Minimum residence time, loading rate, absorption capacity and efficiency

4.1.1. Moisture absorption column

The mass of moisture absorbed, m_{H_2O} were similar across *Q* of 200 and 2000 ml/min but deviated from $m^*_{\mathrm{H_2O}}$ at *Q* of 400 and 1000 ml/min (Figure 4.1). The discrepancy was due to the difficulty in estimating $m^*_{\mathrm{H_2O}}$, which was estimated using humidity ratio *W* (Equation 3.1). The *W* values were estimated using a psychrometric calculator (www.sugartech.co.za/psychro) and were highly dependent on the measured *RH* (89.6 ± 1%) and *T* (40.6 ± 0.5°C) values. Because of the low manufacturer's stated accuracy (± 5% *RH*), it was possible to have uncertainties of 0 to 8.6 g/kg in *W* in the calculation (Gates, 1994). When a *W* in range of 43.9 to 47.1 g/kg were used, all m_{H_2O} measurements fell within the range of $m^*_{\mathrm{H_2O}}$ except for a few data points for a replicate tested at *Q* = 1000 ml/min. Hence, for practical purposes, there were no differences between $m_{\mathrm{H_2O}}$ and $m^*_{\mathrm{H_2O}}$ at 200 to 2000 ml/min. Given these results and since *RH* measurements in the exhaust air stream never exceed 1%, no minimum *RT* was found with the moisture absorption column.

Since $m_{\mathrm{H_2O}}$: $m^*_{\mathrm{H_2O}}$ = 1: 1, $A_{\mathrm{H_2O}} = \sum m^*_{\mathrm{H_2O}}$ = 21 g. For prolonged grain respiration measurement tests, however, it is advisable that all absorption columns be replenished often. Al-Yahya et al. (1993) recommend the columns be weighed every 24 h and replenished solely based on color change. Therefore, in this study, moisture absorption columns were replenished at 70% of $A_{\mathrm{H_2O}}$, of 14.7 g. The average efficiency of the moisture absorption column was $\eta_{\mathrm{H_2O}}$ = 0.96 ± 0.07 (Table 4.1) over a range of *Q* of 200 to 2000 ml/min with *W* = 45.09 ± 1.3 g water/kg air. Data from these tests are available in Appendix D, Table D.1.

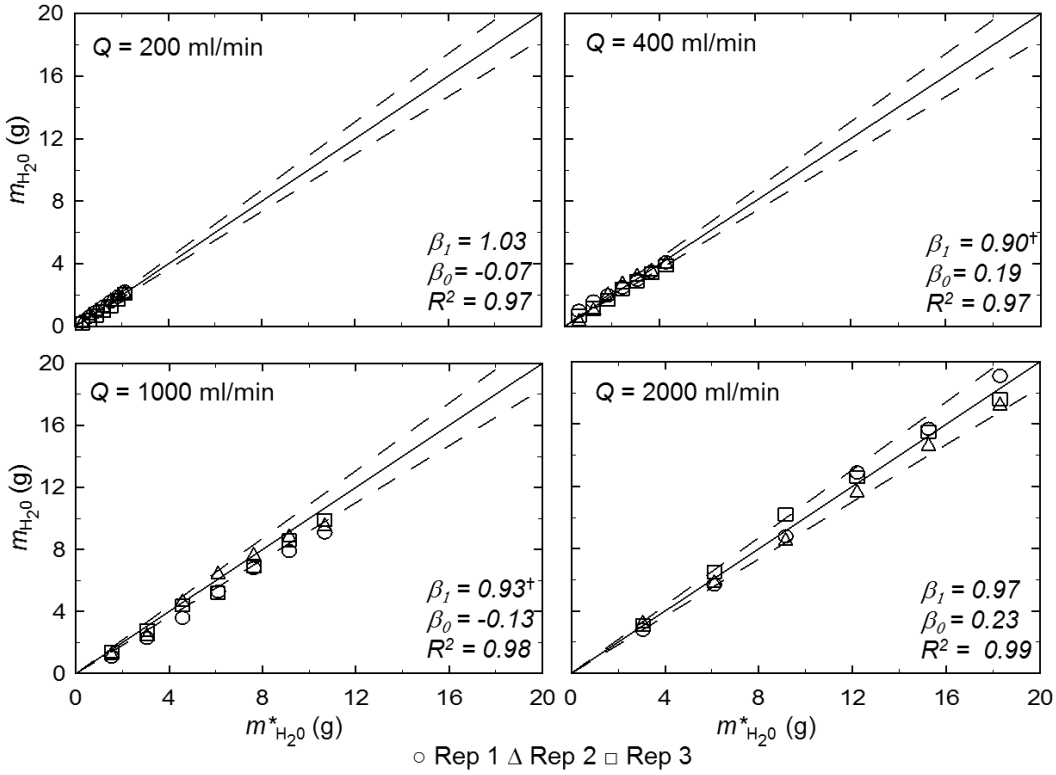

Figure 4.1. Comparison of measured to theoretical mass of moisture absorbed at 200, 400, 1000, and 2000 ml/min. The '†' indicates slope (β_1) and intercept (β_0) were different from unity and zero, respectively (p < 0.05).

Table 4.1 Efficiency of a moisture absorption column at different flow rates.

Test No.	Flow rate, Q (ml/min)	Column RT^a (s)	Loading Rate, $m^*_{H_2O}/t$ (g H_2O/h)	Mean absorption efficiency $\eta_{H_2O}{}^b$
1	200	175.6	0.30 ± 0.01	1.00 ± 0.09
2	400	87.9	0.61 ± 0.02	0.90 ± 0.04
3	1000	35.2	1.52 ± 0.06	0.94 ± 0.02
4	2000	17.6	3.05 ± 0.13	1.02 ± 0.05
				Mean = 0.96 ± 0.07

[a] RT was calculated using Equation 2.8 and ϕ_{ad} = 0.75.
[b] η_{H_2O} was calculated using Equation 3.2.

4.1.2. CO_2 absorption column

The mass of absorbed CO_2, m_{CO_2} and $m^*_{CO_2}$ were similar across tested Q from 500 to 2000 ml/min with C_{CO_2} = 10,000 ppm resulting in $r^*_{CO_2}$ range of 0.6 to 2.4 g CO_2/h. However, m_{CO_2} deviated from $m^*_{CO_2}$ when tested at Q of 10 and 20 ml/min with C_{CO_2} = 10^6 ppm resulting

in $r^*_{CO_2}$ =1.2 and 2.4 g CO_2/h (Figure 4.2). It is worth noting, at $r^*_{CO_2}$ = 1.2 and 2.4 g CO_2/h , the column performance varied based on Q and C_{CO_2}. Additionally, a sensor reading of C_{CO_2} > 50 ppm was observed in the exhaust air stream, therefore t_B = 6 h for both $r^*_{CO_2}$ = 2.1 and 2.4 g CO_2/h. Thus, the minimum *RT* through the CO_2 absorption column was determined to be 5.4 s based on the lower $r^*_{CO_2}$, i.e. 2.1 g CO_2/h at which column breakthrough was observed.

For the other loading rates, m_{CO_2}: $m^*_{CO_2}$ = 1:1,therefore, $A_{CO_2} = \sum m^*_{CO_2}$= 12.6 g. Similar to moisture absorption columns, it is advisable to replenish the CO_2 absorption column often during prolonged respiration tests. As with the moisture adsorption column, CO_2 adsorption columns need to be replaced often with weight gains recorded every 24 h or shortly before the entire column was depleted (Dugba et al., 1996). For the Sodasorb®-based column used in this study, a maximum $r^*_{CO_2}$ of 2.1 g CO_2/h is recommended based on observed column breakthrough. During soybean respiration tests, the columns were replenished at 70% of A_{CO_2} of 8.8 g. The average efficiency of the CO_2 absorption column was η_{CO_2} = 0.99 ± 0.01 (Table 4.2) over the range of Q of 500 to 2000 ml/min with constant C_{CO_2} = 10,000 ppm and ρ_{CO_2}= 1.977 x 10^{-3} g/ml. However, η_{CO_2} = 0.95 ± 0.03 for Q of 10 to 20 ml/min and constant C_{CO_2} = 10^6 ppm. Across the loading rates tested, η_{CO_2} was not affected below t_B (Appendix C) and were higher than efficiencies reported by Al-Yahya (1991) for KOH-vermiculite columns (η_{CO_2} = 0.75 ± 0.04) and ascarite columns (η_{CO_2} = 0.76 ± 0.48). Overall, Sodasorb® was determined to be more efficient, inexpensive, readily available, easier to handle, dispose and to pack in columns compared to KOH-vermiculite mixtures, which were sloppy to handle and resulted in uneven MC_{ad} regions.

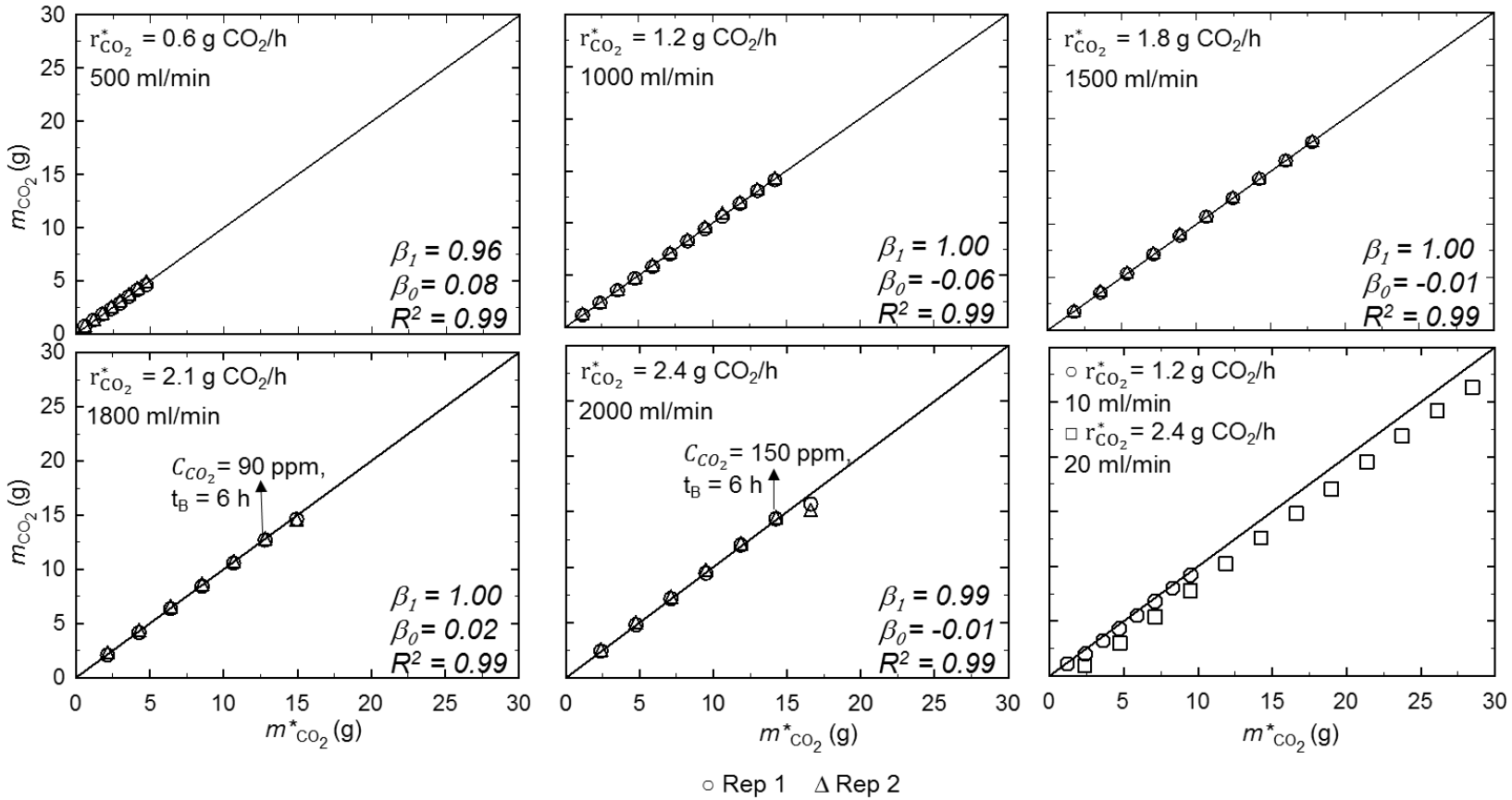

Figure 4.2. Comparison of measured to theoretical mass of CO_2 absorbed at 0.6 to 2.4 CO_2/h loading rates.

Table 4.2 Efficiency of CO_2 absorption column at different loading rates.

Test No.	Concentration C_{CO_2}(ppm)	Flow rate, Q (ml/min)	Loading Rate, $r^*_{CO_2}$ (g CO2/h)	Residence time RT^a (s)	Absorption efficiency $\eta_{CO_2}{}^b$
1	106	10	1.2	979.7	0.96
2	106	20	2.4	489.8	0.92
3	10,000	500	0.6	19.6	0.97 ± 0.00
4	10,000	1000	1.2	9.8	0.99 ± 0.00
5	10,000	1500	1.8	6.5	0.99 ± 0.00
6	10,000	1800	2.1	5.4	0.99 ± 0.00
7	10,000	2000	2.4	4.9	1.00 ± 0.00
					Mean = 0.99 ± 0.01

[a]*RT* was calculated using Equation 2.8 and ϕ_{ad} = 0.47.
[b]$\eta_{CO_2}$was calculated using Equation 3.4

4.1.3. Effects of adsorbent moisture content on CO_2 absorption

During grain respiration measurement tests, the respired air is dehumidified prior to entering the CO_2 absorption column. Over time, this dry respired air could dehydrate the Sodasorb® layer in the CO_2 absorption column and the moisture produced by the second chemical reaction (Equation 2.15) is not sufficient to keep the layer hydrated to initiate the first chemical reaction (Equation 2.14). Indeed, in adsorbent moisture content tests, m_{CO_2} were similar for MC_{ad} = 11.3 ± 0.93%, but deviated from $m^*_{CO_2}$ when MC_{ad} decreased between 9.20 ± 0.67 to 6.8 ± 0.71% (Figure 4.3). It is expected, therefore, for $MC_{ad} \leq 11.3 \pm 0.93\%$, CO_2 absorption column will not capture all the supplied CO_2 even at a reduced loading rate of 0.4 g CO_2/h. It is worth noting that this $r^*_{CO_2}$ used in this test was lower than those used in testing the CO_2 absorption column characteristics (Section 4.1.2). Hence, observations from this limited test of adsorbent moisture (i.e., only one replication was completed at each moisture content) may not be directly comparable to observations made in Section 4.1.2. Additionally, *Q* for these tests was controlled using a different digital flow meter (Model No. 4040, Environics, Tolland, CT, USA) which was found to be "off-calibration" after testing. The flow rates tended to be 87%

lower than what the meter displayed when tested at Q of 2000 ml/min with C_{CO_2} = 10,000 ppm, compared to the gas flow controller (Model No. GFC17A, Aalborg, Orangeburg, NY) used for the moisture and CO_2 absorption columns. Therefore, the recommendation of maintaining MC_{ad} above11.3 ± 0.93% should be used with caution and needs further testing.

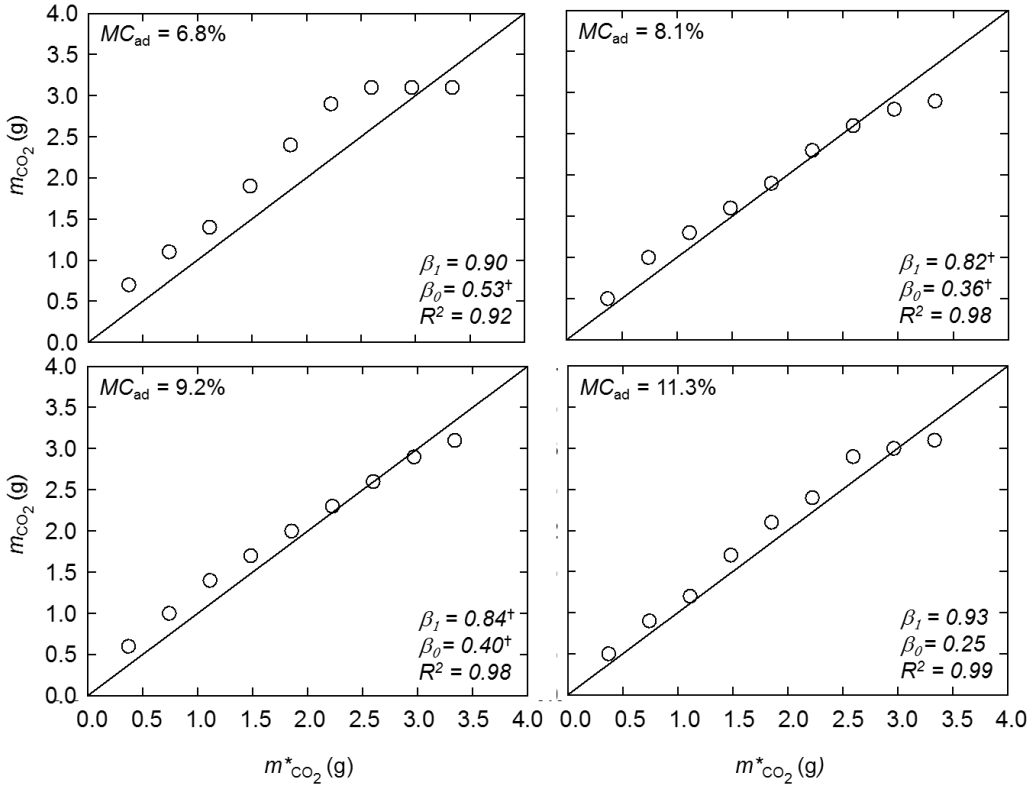

Figure 4.3. Effects of moisture content of Sodasorb® on CO_2 absorption at a loading rate of 0.4 g CO_2/h. The '†' indicates slope (β_1) and intercept (β_0) were different from unity and zero, respectively ($p < 0.05$).

4.2. Soybean respiration measurement test

4.2.1. Respired CO_2

A pair of soybean respiration tests was conducted, each with 1850 g of 14% moisture soybeans at 35°C. The first test was conducted for 79 h, where an initial 24 h lag period was observed. CO_2 production increased from t = 21 to 48 h but stopped afterwards (Figure 4.4). A similar short initial lag period prior to respiration activity has been previously reported for a wide range of stored grains such as soybean, canola, wheat and corn (Fernandez et al, 1985; Al-

Yahya, 1991; Lacey et., 1994, Dugba et al., 1996; Jian et al., 2014). The lag can be due to time required by the grain to acclimatize at given set of storage conditions. However, the second lag period and lack of respiration activity observed after *t* = 48h could not be explained and can likely be attributed to physiological variation in grain samples. Similar lag has been observed in replicates for corn respiration measurement testing by Al-Yahya (1991), after which the respiration of corn samples continued to increase. Based on these observations, a longer storage test time was deemed necessary to obtain an appreciable amount of accumulated CO_2 and measure corresponding r_{CO_2} and r_{DML}. A second respiration test was conducted for a longer duration; however, to obtain r_{CO_2} based on grain respiration without effect from increased mold count, presence of any visible molding was used as an indicator to terminate the test run.

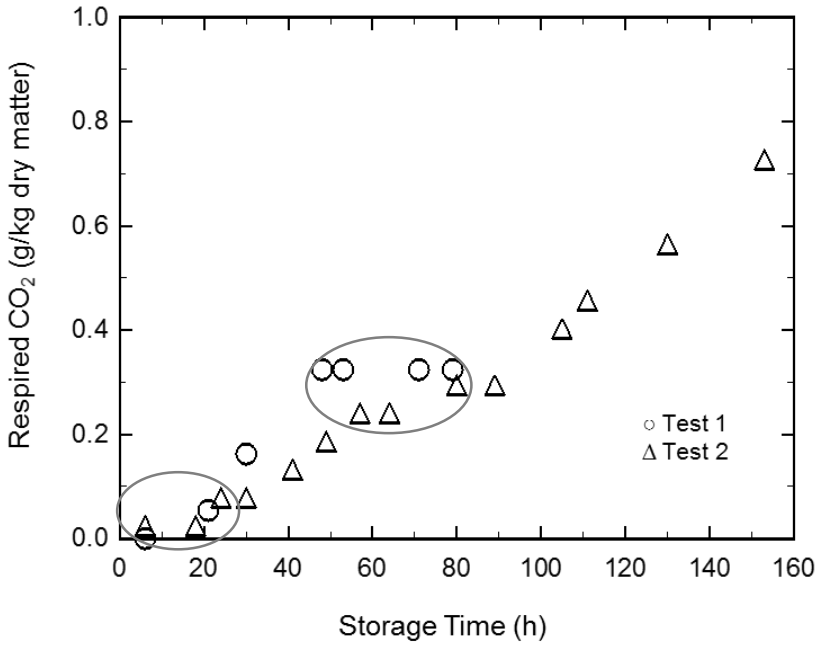

Figure 4.4. Respired CO_2 by 14 % moisture soybeans at 35°C. Noted regions indicate periods of lag during respiration.

For the second soybean respiration test, an initial 24 h lag period was also observed. The CO_2 production occurred from *t* = 24 to 153 h (Figure 4.4). CO_2 production slowed from *t* = 57

to 85 h but did not halt as it did with the first test. Using Equation 3.5, r_{CO_2} was determined to be 15.7 mg CO_2/(kg·h). The corresponding *DML* was determined as follows:

$$DML = \frac{1.3\ g\ CO_2 \cdot \frac{180\ g}{mol\ glucose}}{\frac{44\ g\ CO2}{mol\ CO_2}\frac{(100-14.9)}{100}\ 1.85\ kg\ dry\ matter} \cdot \frac{1\ mol\ glucose}{6\ mol\ CO_2} \quad [4.1]$$

$$DML = 0.56\ \frac{g\ glucose}{kg\ dry\ matter} = 0.056\% \quad [4.2]$$

Hence, r_{DML} was

$$r_{DML} = \frac{0.056\%}{129\ h} \cdot \frac{24\ \text{h}}{1\ \text{day}} = 0.010\%. \quad [4.3]$$

Rukunudin et al. (2004) reported soybeans stored for 0 and 48 weeks at 21% MC and 26°C reached 0.5% *DML* in 22.5 and 12.4 days respectively. This implies that mean daily r_{DML} was determined to be 0.02 and 0.04%/day, respectively. These values were comparable to the 0.01%/day found with 14% moisture soybeans at 35°C tested in this study.

4.2.2. Compositional changes and other observations

For the first grain respiration test, initial *MC* of 14.9 ± 0.01% increased to 15.2 ± 0.1%. *MC*, however, was not uniform throughout the grain column as soybeans in the top layer were more swollen in appearance, likely due to condensation. There were no differences in starch, oil and crude protein content (Table 4.3). However, some noticeable differences were observed between soluble protein (%), FFA (%) and mold count (cfu/g). Soluble protein (%) decreased from initial 96.7 ± 1.0 to 87.0 ± 2.6, initial FFA (%) of 0.69% decreased to 0.46% and mold count decreased from 636 ± 403 to 63 ± 20 cfu/g.

Table 4.3 Compositional analysis of 14% moisture soybeans stored at 35°C for 79 and 153 h.

Component	(Mean ± S.D.[a])		
	Initial	After the first test	After the second test
MC (%)	14.9 ± 0.0	15.2 ± 0.1	14.1 ± 1.1
Starch (%)[b]	1.08 ± 0.5	1.03 ± 0.1	1.08 ± 0.0
Oil (%)[b]	21.1 ± 0.2	21.1 ± 0.1	21.3 ± 0.0
FFA (%)[b]	0.69 ± 0.1	0.46 ± 0.1	0.82 ± 0.0
Crude Protein (%)	32.6 ± 0.6	34.6 ± 0.6	34.87 ± 0.8
Protein Soluble (%)	96.7 ± 1.0	87.0 ± 2.6	88.0 ± 2.0
Mold Count (cfu/g)	636 ± 403	63 ± 20	996 ± 204

[a]S.D. = Standard deviation.
[b]Values are presented in % d.b.

During the second test, initial *MC* decreased to 14.1 ± 1.1%. Similar to first test, there were no differences in starch, oil and crude protein content but noticeable differences were observed between soluble protein, FFA, and mold count. Soluble protein decreased to 88.0% ± 2.0%. Previous studies have reported increase in soluble proteins due to decrease in sample dry matter over time (Milner and Geddes, 1946; Wilson, 1995). The FFA increased to 0.82%. An increase in FFA content has been observed with increased DML in mechanically-damaged soybeans by Urbanski et al. (1980) and Bern et al. (1998). Note that the FFA assay was based on AOCS Ca method 5a-40 (2012), which was designed for oil or fat matrix samples. The uncertainties, therefore, in the FFA values reported here may be high since soybean samples were sent to the lab, not oil samples.

Mold counts increased to 996 ± 204 cfu/g over a period of 6 days along with visible molding in the top layer of the stored grain column. A similar increase in mold was observed by Surour et al. (2004) for stored soybeans at 20 to 30°C and 18% MC from 166 to 1433 cfu/g over a 10 day period.

Keeping in mind that CO_2 production slowed down after t = 50 h for both tests and that visible molding was observed at the end of the second test, it is recommended that future grain

respiration tests conducted at higher *T* such as 35°C be completed within 100 h, or 4 days. It is expected that any respiration test after the fourth day would include the amount of CO_2 respired by mold. Other researchers noted molding during their grain respiration studies after the first week of storage at above 25°C (Milner and Geddes, 1946; Aljinovic et al., 1994; Dugba et al., 1996; Reed et al., 2007; Surour et al., 2004). Further, Alijonic et al. (1994) studied the effectiveness of fungicide use on storability of corn and time required to read 0.5% DML. Corn samples treated with fungicide required significantly longer times to reach 0.5% DML than those for untreated corn (Aljinovic et al., 1994), implying molding affects the rate of respiration and DML. Therefore, to accurately determine the r_{CO_2} and r_{DML}, test duration should be kept to a minimum duration to prevent formation of molds.

It is recommended that adequate insulating material should be used to cover the grain column and surrounding Tygon® tubing to minimize condensation. Overall, to conduct a grain respiration test for a duration of t = 100 h, the following guidelines should be followed:

1. The humidification system should be replenished by adding 19 ml of deionized water to the glycerol-water solution for every two days of testing.
2. The moisture absorption columns should be replaced after accumulating 14.7 g H_2O.
3. The CO_2 absorption columns containing Sodasorb® should be replenished every two days of testing due to saturation of the desiccant (Drierite) layer.

CHAPTER 5. CONCLUSIONS AND FUTURE WORK

A grain respiration measurement system was designed, fabricated, tested and demonstrated with soybeans at 14% moisture at 35°C. The moisture absorption columns had A_{H_2O} = 21 g and overall η_{H_2O} = 0.96 ± 0.07 but no minimum *RT* when *Q* = 200 to 2000 ml/min. Similarly, the CO_2 absorption columns had A_{CO_2} = 12.6 g, a maximum loading rate of 2.1 g CO_2/h, overall η_{CO_2} = 0.99 ± 0.01 and a minimum *RT* of 5.4 s. These characteristics held true when $MC_{ad} \geq 11.3\%$. Results from a soybean respiration test showed a r_{CO_2} = 15.7 mg CO_2/(kg·h) and r_{DML} = 0.010%/d, which were comparable to rates reported by Rukunudin et al. (2004). Compositional analysis showed changes in soluble protein, FFA and mold counts may be significant even after 4-5 d of storing 14% moisture soybeans. From these results, it is recommended that future soybean respiration tests be conducted within 100 h. Additional recommendations on how to properly operate the grain respiration system are listed in the standard operating procedures (SOPs) detailed in Appendix C.

Because r_{CO_2} and r_{DML} data are lacking for soybeans stored at 12 to 18 % moisture, with varying levels of splits content (%), and at temperatures 25 to 45°C for developing maximum allowable storage guidelines for low latitude regions, the following experiment is recommended for future work. A minimum of nine treatments should be formulated with three moisture content levels (12, 15 and 18% w.b.) and three temperatures (25, 35 and 45°C) performed in triplicate. This corresponds to a 3x3 completely randomized design. A two-way factorial ANOVA can be used to determine the significance of moisture and temperature main effects on *DML*. Additionally, Tukey-Kramer method is recommended for conducting pair-wise comparisons for differences among means with $\alpha \leq 0.05$. For each treatment, FFA and mold count should be determined at the beginning and termination of test and analyzed for differences using Student's

t-test. As a starting reference point, *DML* can be described as by Bern et al. (2002) to allow use of multipliers specific to soybeans, such as effect of moisture content (M_{MC}), temperature (M_T), FFA deterioration (M_{FFA}), mold resistance (M_F) and splits ratio (M_S). At reference conditions as determined by Bern et al. (2002), the grain is stored at 15.6°C with 25% *MC* and 30% mechanical damage, DML can be defined as follows:

$$DML = a\,(e^{b*t_s} - 1) + \; c\,t_s \qquad [5.1]$$

where, t_s is the time in h to reach 0.5% DML and, a, b and c are constants. For non-standard conditions, storage time t_n can be defined as,

$$t_n = t_s\,M_{MC}\,M_T\,M_{FFA}\,M_F\,M_S \qquad [5.2]$$

Note, for reference or "control" conditions, $M_{MC} = M_T = M_{FFA} = M_F = M_S = 1$.

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APPENDIX A. ABBREVIATIONS, SYMBOLS AND DIMENSIONAL ANALYSIS

A.1. List of abbreviations

AGDS……..	Aluminum Grain Dockage Sieves
ANOVA……..	Analysis of Variance
AOCS……..	American Oil Chemists' Society
ASABE……..	American Society of Agricultural and Biological Engineers
ASTM…….	American Society for Testing and Materials
cfu……...	Colony forming unit
$C_6H_{12}O_6$……..	Glucose
$CaCO_3$…….....	Calcium carbonate
$Ca(OH)_2$	Calcium hydroxide
CO_2…….	Carbon dioxide
CO_3^{2-}……..	Carbonate
COM……..…	Communication port
CTEH…….	Center for Toxicology and Environmental Health
FAO……	Food and Agriculture Organization
GC……..	Gas chromatography
H_0……	Null hypothesis
H_A……...…	Alternate hypothesis
H_2CO_3…….....	Carbonic acid
H_2O……..……	Water or moisture
K_2CO_3…….	Potassium carbonate
KOH……...	Potassium hydroxide
N_2…..……...	Nitrogen
Na_2CO_3……...	Sodium carbonate
NaOH…….	Sodium hydroxide
NDIR……..	Nondispersive infrared
NOPA…….	National Oilseed Processors Association
NPT…….	National Pipe Thread
O_2…..……...	Oxygen
OH^-…..……...	Hydroxide
PC……	Personal computer (generic)
PHL…….	Postharvest loss
Rep……..	Replication
SD……	Secure Digital (type of memory card)
SOP…….	Standard Operating Procedure
US…..…….....	United States
USDA……..	United States Department of Agriculture

A.2. List of symbols

Symbol	Explanation	Units used
A_{ad}……..	Absorption capacity of adsorbent	g/kg
A_{CO_2}……...	Absorption capacity of carbon dioxide absorption column	g/kg
A_{H_2O}……..	Absorption capacity of moisture absorption column	g/kg
b…….	Exponents of basic dimensions in dimensional analysis	---
$C_{C_3H_8O_3}$…..……	Concentration of glycerol	% or g/g
C_{CO_2}……	Concentration of carbon dioxide	ppm
C_{H_2O}……...	Concentration of water vapor	m^3/m^3
D_{air}……..	Diffusivity of air through adsorbent	m^2/s
D_c……...	Column diameter	m
d_e……	Equivalent particle diameter	m
df……	Degrees of freedom	---
DML……..	Dry matter loss	%
EBRT……..	Empty bed residence time	s
EMC……...	Equilibrium moisture content of grain, wet-basis	%
ERH……...	Equilibrium relative humidity	%
FFA……	Free fatty acids, expressed in per unit mass of crude fat	%
ID……...	Nominal inside diameter used for tubing, fittings or separator	in
L…….	Length	m
L_c…….....	Length of column	m
m…….….	Mass	g
m_{ad}……	Mass of desiccant or adsorbent	g
$M_{C_6H_{12}O_6}$.....	Molar mass of glucose	g/mol
$m_{C_6H_{12}O_6}$…….	Mass of glucose	g
M_{CO_2}.....	Molar mass of carbon dioxide	g/mol
m_{CO_2}……..	Mass of carbon dioxide that is respired by grain or absorbed in an adsorbent at any given time *t*	g
$m^*_{CO_2}$……...	Theoretical mass of carbon dioxide that is respired by grain or absorbed in an adsorbent at any given time *t*	g
$m_{CO_3^{-2}}$…..…...	Mass of carbonate that is produced in an adsorbent at any given time *t*	g
M_F……	Multiplier to account for fungal or mold effects	decimal
M_{FFA}……	Multiplier to account for free fatty acids effects	decimal
m_{H_2O}……....	Mass of moisture that is absorbed in desiccant or absorbent at any given time *t*	g
$m^*_{H_2O}$……...	Theoretical mass of moisture that is absorbed in desiccant at any given time *t*	g
m_{in}……..	Mass of input reactant into a system at any given time *t*	g
m_{OH^-}……...	Mass of hydroxide that is consumed in an adsorbent at any given	g

	time *t*	
m_{out}……..	Mass of output product from a system at any given time *t*	g
M_{MC}……	Multiplier to account for moisture content effects	decimal
M_{S}……...	Multiplier to account for splits content effects	decimal
M_{T}……..	Multiplier to account for temperature effects	decimal
MC…….	Moisture content of grain, wet-basis	%
MC_{ad}……..…	Moisture content of adsorbent, wet-basis	%
N_{Re}……..	Reynolds number	---
N_{Sc}……..…...	Schmidt number	---
p-level……	Probability level	decimal
Q……	Volumetric flow rate	ml/min
R^2……...…	Correlation coefficient	decimal
r_{CO_2}……...	Rate of carbon dioxide production or respiration rate, may be expressed on per unit mass of grain or dry matter	mg/h or mg/(kg·h)
$r^*_{\text{CO}_2}$…….....	Theoretical rate of carbon dioxide production or loading rate	g/h
$r_{\text{CO}_3^{2-}}$……..	Rate of carbonate formation as carbon dioxide reacted with a hydroxide	g/h
r_{DML}……...	Rate of dry matter loss	%/d
RH……..	Relative humidity	%
RT……..	Residence time	s or min
SD……..	Standard deviation	variable
SE……..	Standard error	variable
SG……..…...	Specific gravity	decimal
T…….	Temperature of grain, conditioned air or storage	°C
t……..	Time	s or min
t_{B}…….	Breakthrough time	h
t^*_{B}……	Theoretical breakthrough time or bedlife of column filled with adsorbent	h
t_{n}…….	Allowable storage time	d
t_{s}…….	Time in storage	d
u……..	Velocity	m/s
V_{c}…….	Column volume	m^3
W…….	Humidity ratio	g/kg
*W**……..	Theoretical humidity ratio	g/kg
α.....	Confidence level in statistical tests	decimal
β.....	Regression coefficients	---
Δt…….	Elapsed time	h or d
η_{CO_2}……	Efficiency of carbon dioxide absorption column	decimal
$\eta_{\text{H}_2\text{O}}$……...	Efficiency of moisture absorption column	decimal

η_t……	Efficiency of carbon dioxide scrubbers used in diving equipment	decimal
μ…….	Dynamic viscosity of a fluid	kg/(m·s)
ν…….	Kinematic viscosity of a fluid	m^2/s
ρ_{air}.....	Density of air	kg/m^3
ρ_b……	Bulk density of grain	kg/m^3
$\rho_{b,ad}$……	Bulk density of adsorbent	kg/m^3
ρ_{CO_2}.....	Density of carbon dioxide	kg/m^3
$\sum m_{CO_2}$….....	Accumulated mass of carbon dioxide in an absorption column after a period of time Δt	g
$\sum m^*_{CO_2}$….....	Theoretical accumulated mass of carbon dioxide in an absorption column after a period of time Δt	g
$\sum m_{H_2O}$….....	Accumulated mass of moisture in an absorption column after a period of time Δt	g
$\sum m^*_{H_2O}$….....	Theoretical accumulated mass of moisture in an absorption column after a period of time Δt	g
$\sum m^*_{H_2O}$….....	Theoretical accumulated mass of moisture in an absorption column after a period of time Δt	g
Σm_{sys}…..…...	Accumulated mass in the system after a period of time Δt	g
ϕ_g…….	Porosity of the grain	decimal
ϕ_{ad}…….....	Porosity of the adsorbent	decimal

A.3. Dimensional analysis of breakthrough time

Nuckols et al. (1983) demonstrated the use of Buckingham Pi dimensional analysis to form dimensionless groups that can be used to describe the functional relationship. Disregarding MC_{ad}, A_{ad}, and $r_{CO_3^{2-}}$ in Equation 2.10 while substituting basic dimensions (time, *t*; length, *L*; temperature, *T*; and mass, *m*) of the remaining parameters, the following was obtained:

$$\mathrm{t} = \left[\frac{\mathrm{L}}{\mathrm{t}}\right]^{b_1} [\mathrm{T}]^{b_2} \left[\frac{\mathrm{m}}{\mathrm{L}^3}\right]^{b_3} \left[\frac{\mathrm{m}}{\mathrm{Lt}}\right]^{b_4} \left[\frac{\mathrm{L}^2}{\mathrm{t}}\right]^{b_5} \left[\frac{\mathrm{L}^3}{\mathrm{L}^3}\right]^{b_6} \left[\frac{\mathrm{L}^3}{\mathrm{L}^3}\right]^{b_7} [\mathrm{m}]^{b_8} [\mathrm{L}]^{b_9} [\mathrm{L}]^{b_{10}} [\mathrm{L}]^{b_{11}} \qquad [A.1]$$

where *b*'s are the exponents of the basic dimensions. Based on the law of dimensional homogeneity, the exponents of the basic dimensions on both sides of the equation were equated to determine the following four parameters:

$$b_2 = 0 \qquad [A.2]$$

$$b_3 = b_1 + b_5 + 1 - b_8 \qquad [A.3]$$

$$b_4 = - b_1 - b_5 - 1 \quad [A.4]$$

$$b_{11} = b_1 + 2 - 3\, b_8 - b_9 - b_{10} \quad [A.5]$$

Substituting these parameters back into Equation 2.10:

$$t_B = (u)^{b_1}(T)^0\left(\rho_{b,\mathrm{ad}}\right)^{b_1+b_5+1-b_8}(\mu)^{-b_1-b_5-1}(D_{\mathrm{air}})^{b_5}\left(C_{CO_2}\right)^{b_6}\left(C_{H_2O}\right)^{b_7}(m)^{b_8}(d_e)^{b_9}(L_c)^{b_{10}}(D_c)^{b_1+2-3b_8-b_9-b_{10}} \quad [A.6]$$

When variables are regrouped based on similar exponents, the following was obtained:

$$\frac{t_B\mu}{\rho_{b,\mathrm{ad}}D_c^2} = \left[\frac{\rho_{b,\mathrm{ad}}uD_c}{\mu}\right]^{b_1}[T]^0\left[\frac{\rho_{b,\mathrm{ad}}D_{air}}{\mu}\right]^{b_5}\left[C_{CO_2}\right]^{b_6}\left[C_{H_2O}\right]^{b_7}\left[\frac{m}{\rho_{b,\mathrm{ad}}D_c^3}\right]^{b_8}\left[\frac{d_e}{D_c}\right]^{b_9}\left[\frac{L_c}{D_c}\right]^{b_{10}} \quad [A.7]$$

where the term on the left hand side of the equation can be further simplified to $(t_B u)/D_c$ and the first and third terms on the right hand side of the equation are the Reynolds (N_{Re}) and Schmidt numbers (N_{Sc}). In CO_2 scrubbing systems used for diving, where operational pressure range is narrow, D_{air} does not fluctuate much. Therefore, N_{Sc} can be omitted from the analysis and Equation A.7 becomes

$$\frac{t_B u}{D_c} = f\left(N_{Re}, T, C_{CO_2}, C_{H_2O}, \frac{m}{\rho_{b,\mathrm{ad}}D_c^3}, \frac{d_e}{D_c}, \frac{L_c}{D_c}\right) \quad [A.8]$$

APPENDIX B. INSTRUMENTATION SETUP AND SYSTEM TESTS

B.1 Calibration of CO_2 sensor

B.1.1. Purpose

Calibrate carbon dioxide probe GMP222 with two-point calibration method with zero-gas N_2 and span gas CO_2.

B.1.2. Equipment required

Gas flow controller (Aalborg GFC 17), PC and terminal software (Windows® Hyper Terminal), power supply, 24 VDC/1A, pressure regulator (1000 hPa or 1 bar pressure), traceable reference gases with 1% or better accuracy – N_2, 1% CO_2, teflon tubing (1/4" ID), wrench for gas cylinder, serial cable (calibrator to PC), screw driver (1/8"), Vaisala carbon dioxide probe GMP222, Vaisala GMK220 Calibrator.

B.1.3. PC set up and connections

1. Download Hyper Terminal software (https://www.hilgraeve.com/hyperterminal-trial/)
2. Obtain values of ambient temperature (± 0.5°C) and barometric pressure (± 1 hPa) for input data during calibration.
3. Connect PC to GMK220 calibrator using a serial cable (Figure B.1).
4. Connect 24 V_{DC} supply power to the connectors on GMK220 calibrator and let calibrator settle for 10 min.
5. Insert and connect the probe to be calibrated into the chamber of the GMK220 calibrator.
6. Connect selected reference gas to the gas inlet port.

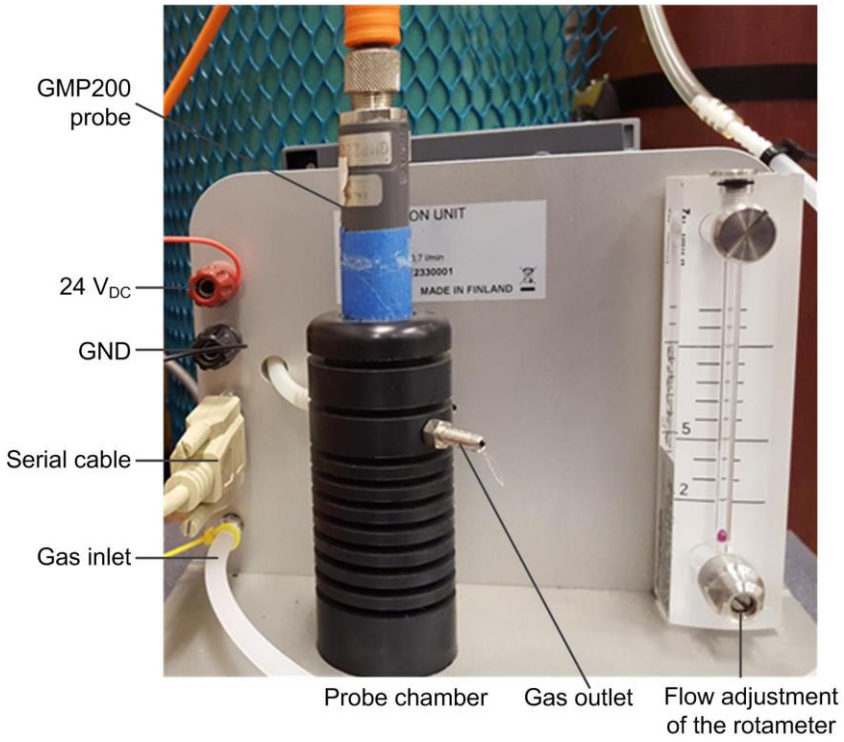

Figure B.1. GMP222 CO_2 sensor probe calibrator components.

B.1.4. Using the Hyper Terminal Calibration program

1. Open Hyper Terminal and a "New connection" window will appear.
2. Enter any name (eg. CO_2 Calibrator) and chose any icon.
3. In "Connect to" window, select the appropriate COM for connection according to the Serial cable connection to the PC (eg. COM1).
4. The communication parameters necessary for the monitor to communicate with the software are as shown below:

Bits per second	9600
Data bits	8
Parity	None
Stop bits	1
Flow control	None

1. If a successful connection is made between the PC and the software, following text appears on terminal window:

GMT220A - Version: STD 4.27
Copyright: Vaisala Oyj,1997-2013

2. Let the calibrator settle for 10 minutes. The calibrator is now ready.

B.1.5. Two-point calibration

This method is used for recalibration purpose and requires two sources of reference gas.

1. Connect the low end gas (N_2) to the calibrator and open the gas regulator valve until the pressure gauge indicates a value of 1000 hPa.
2. Using a screwdriver, adjust the flow rate of the gas calibrator using a screwdriver for the flow adjustment screw until the flow meter indicates 0.5 l/min.
3. Let the gas pass through system for a few minutes.
4. On the terminal window, enter password: PASSWORD 5120.
5. Hit enter and the following prompt should appear: >PASSWORD 1520.
6. Next, provide input data for calibration:

CALICALI L <sample quantity> <CO_2 concentration> <$P_{ambient}$> <$T_{ambient}$><cr>

NOTE: above command is case sensitive. CO_2 concentration (ppm); $P_{ambient}$ is pressure (hPa); and $T_{ambient}$ is temperature (°C). Sample quantity is the number of measurements for average to be calculated with a recommended minimum value of 200.

1. Example of prompt on terminal window: >CALICALI L 1500 0 1013 23<cr>.
2. The calibration should automatically begin and the end of calibration is indicated by the prompt: >Low gas (0 ppm) measurement done. Start high gas.
7. Disconnect the low-end gas from the calibrator and connect the high-end gas (e.g., 1% CO_2) to the calibrator.

8. Adjust the pressure on the gas regulator to 1000 hPa or 14 psi.
9. Using a screwdriver, adjust flow rate of gas calibrator until flow meter indicates 0.5 l/min.
10. Let the gas pass through system for a few minutes.
11. Provide input data for high-end calibration as done before with low-end calibration. Notice the change in command:

    CALICALI H<sample quantity><CO_2 concentration><$P_{ambient}$><$T_{ambient}$><cr>

    a. Example of prompt on terminal window: >CALICALI H 1500 10000 1013 23<cr>.
    b. The calibration should automatically begin and the end of calibration is indicated by the prompt: >High gas (10000 ppm) ready. Two point calibration completed.
12. Calibration is completed and can be saved on the non-volatile memory on the probe using the command: PROBE_SAVE<cr>.
13. The appearance of the following prompt indicates new calibration data is saved in probe: >PROBE_SAVE.
14. Using a screwdriver, adjust the gas flow to 0 l/min before disconnecting the gas flow and serial cable from the PC.

B.2. Instrumentation

B.2.1. Purpose

Set up data acquisition from *T*, *RH* and CO_2 sensors using Arduino Mega 2650 microprocessor.

B.2.2. Equipment required

Arduino Mega 2650, Colored connecting wires, PC and Arduino IDE software, power supply 12 VDC, 24 VDC/1A, pressure regulator (1000 hPa or 1 bar pressure), teflon tubing (1/4" ID), wrench for gas cylinder, SHT15 sensor package, USB cable and Vaisala carbon dioxide probe GMP222, Vaisala GMP222G0N0 transmitter.

B.2.3. Connections

1. Connect SHT15 sensor package (Sensirion AG) to the Arduino Mega 2560 using colored wires (e.g., red, black, yellow and blue wires to be used for power, ground, data and clock connections respectively) following Figure 3.5 and Figure B.2.
2. Connect Arduino Mega 2560 to the PC via USB cable and supply it with 12 V_{DC}.
3. Connect GMP222 probe to be connected to the transmitter.
4. Supply the GMP222G0N0 transmitter with 24 V_{DC}.
5. Supply the gas flow controller with 12 V_{DC}.

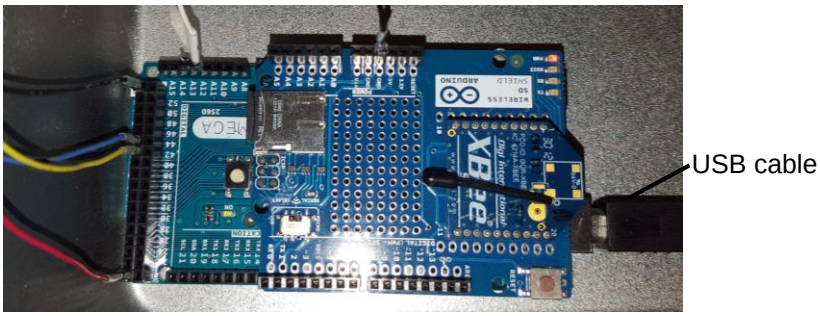

Figure B.2. Arduino Mega 2650 board is connected to the *T*, *RH* and CO_2 sensors using color-coded wiring and to the PC using USB cable.

B.3. Confirmation of low CO_2 concentration in compressed air source

B.3.1. Purpose

Confirm low CO_2 (>50 ppm) in supply air for grain respiration measurement system.

B.3.2. Equipment required

Arduino Mega 2650, gas flow controller (Aalborg GFC 17), compressed air source (80 % N_2, 20% O_2, and < 50 ppm CO_2), N_2 gas (1%), PC with Arduino IDE software, power supply 12 VDC, 24 VDC/1A, pressure regulator (1000 hPa or 1 bar pressure), teflon tubing (1/4" ID), USB cable, wrench for gas cylinder, and Vaisala carbon dioxide probe GMP222, Vaisala GMP222G0N0 transmitter.

B.3.3. Procedures

The CO_2 sensor was pre-calibrated against high purity, bottled N_2 gas for zero value of the probe and with known CO_2 gas concentrations (Figure B.3). Operating range of the GMP222 probe (Vaisala, Boulder, CO, USA) was from 0 to 10,000 ppm detection range. Permissible differences of CO_2 ppm of ± 150 ppm at lower range of 0°C and ± 350 ppm was noted for temperature of 22.6°C and pressure of 1006.3 hPa. Prior to testing, certified pure N_2 was passed through a sealed chamber containing the CO_2 sensor. Sensor readings were logged every 2 min and averaged over a 2 h period. The test was repeated two more times to yield three replications. The mean of the averages was taken as the offset value of the CO_2 sensor. Next, the same test was conducted with compressed air source (80 % N_2, 20% O_2, and < 50 ppm CO_2) three times. The mean of the averages was taken as the baseline CO_2 level in the airstream used in soybean respiration tests.

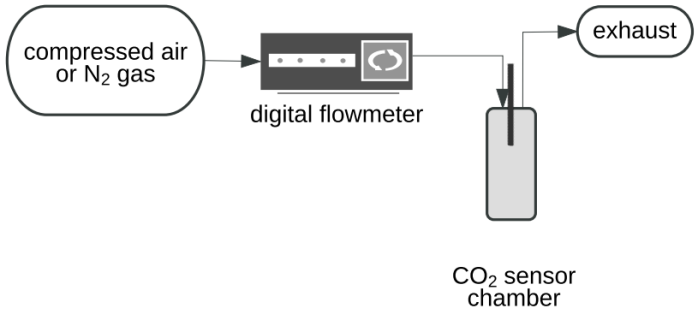

Figure B.3. Set up for confirming CO_2 levels in the compressed air source and the CO_2 sensor offset value.

B.3.4. Results

Results showed that the mean sensor readings (Table B.1) with compressed air were not different from those with N_2 gas (p = 0.22) (Table A.1). With a baseline value of 22.7 ± 4.8 ppm CO_2, a threshold value of 50 ppm CO_2 in the exhaust air of the soybean respiration measurement system was defined.

Table B.1. Mean sensor readings for CO_2 levels in N_2 and compressed air.

Replication	CO_2 measurements (Mean ± S.D. ppm)	
	N_2	Compressed air
1	23.6 ± 5.4	24.7 ± 5.0
2	23.3 ± 7.0	22.2 ± 4.5
3	22.0 ± 4.0	21.1 ± 4.3
Overall Mean ± S.D. (ppm)	23.0 ± 5.6	22.7 ± 4.8

B.4. Confirmation of *RH* in humidified air

B.4.1. Purpose

Determine steady input *W* based on measured *RH* generated using glycerol-water solutions to be used for maintaining grain *EMC* during experimentation.

B.4.2. Equipment required

PC with Arduino IDE software, power supply 12 VDC, 24 VDC/1A, pressure regulator (1000 hPa or 1 bar pressure), USB cable compressed air source (80 % N_2, 20% O_2, and < 50 ppm CO_2), digital flow meter (Environics 4040), teflon tubing (1/4" ID), water bath, wrench for gas cylinder SHT15 sensor package (Sensirion).

B.4.3. Procedures

A humidification system (Figure B.4) was designed and tested for a range of glycerol-water solutions at fixed temperatures to ensure a steady supply of conditioned air for experimentation. Compressed air (80 % N_2, 20% O_2, and < 50 ppm CO_2) was supplied at flow rate *Q*, controlled using a digital flow meter (Model No. 4040, Environics, Tolland, CT, USA) at 200 ml/min. The controlled airflow was bubbled through a series of required glycerol solutions placed in water bath (Model R134A, NESLAB, Thermo Electron Corporation, Newington, NH, USA) at temperature, *T*, to generate humidity, *RH* for a period of 24 h. The humidified air *RH* % was determined using *RH* and *T* sensor (Model SHT15, Sensirion, Zurich, Switzerland) placed in

a sealed chamber. Data were logged every 1 min. Mean RH readings were used to determine measured humidity ratio *W* (g/kg) of the air and compared to the theoretical values, *W** using a Student's *t*-test at $\alpha = 0.1$. The higher α level was selected due to the limitations in *RH* sensor accuracy (± 5 %).

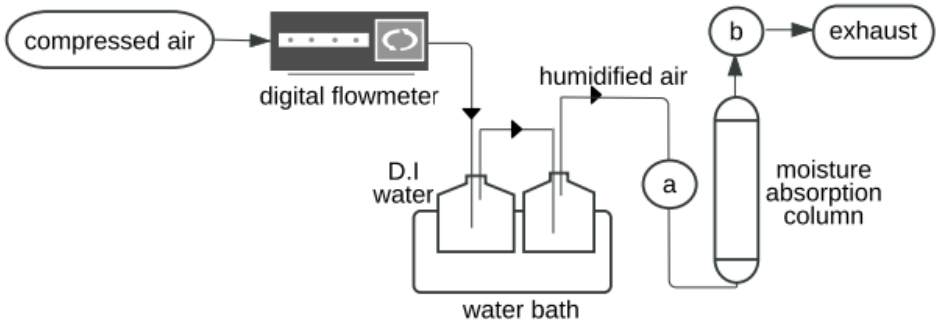

Figure B.4. Set up for testing temperature and relative humidity of compressed air stream. Sensors were located at *a* and *b*.

B.4.4. Results

Estimated mean *W* values (Table B.2), derived from *T* and *RH* measurements, were different from *W** ($p = 0.044$). The discrepancy results from difficulties with getting an accurate measure of *RH* with a low-cost SHT15 sensor.

Table B.2. Mean sensor readings and corresponding humidity ratios when using glycerol-water solutions to control relative humidity.

T (˚C)	Glycerol-water solution		Measured	Measured *T*	*W** (g/kg)	*W* (g/kg)
	SG	$C_{C_3H_8O_3}$ (%, w/w)	*RH* (%)	(°C)		
25	1.18	68.1	59.8	24.7	12.9	11.7
35	1.17	65.3	69.2	35.5	24.4	25.6
25	1.14	54.1	74.3	24.3	15.6	14.2
35	1.13	51.5	76.2	34.7	28.9	27.0
25	1.11	43.8	77.6	24.3	17.0	14.8
35	1.10	38.4	85.2	35.2	32.0	31.2

B.5. Confirmation that the soybean respiration measurement system is free of leaks

B.5.1. Purpose

Eliminate leaks to ensure all respired grain respiration products are captured in grain respiration system.

B.5.2. Equipment required

Compressed air source (80 % N_2, 20% O_2, and < 50 ppm CO_2), gas flow meter (Aalborg), pressure gauge, pressure regulator (1000 hPa or 1 bar pressure), teflon tubing (1/4" ID), wrench for gas cylinder

B.5.3. Procedures

A test for leakage of the assembled grain respiration system was conducted (Figure B.5). This was a crucial precaution to ensure the carrier gas containing the respired products from grain respiration stayed within the system and subsequently got absorbed by the moisture and CO_2 absorption columns. A pressure gauge (Part No. 4FLC2, W.W. Grainger, Lake Forest, IL) with a 0 to 2068 hPa (0 to 30 psi) range was mounted on a flat surface and placed in series with each column individually and the downstream outlet was blocked. The closed system was then pressurized to 689.5 hPa (10 psi) using compressed air (80 % N_2, 20% O_2, and < 50 ppm CO_2) and monitored for any change in pressure over time duration of 6 h. If a pressure drop >137.9 hPa (2 psi) was observed, the column joint seals were inspected and o-rings, vacuum grease, Teflon tape or hose clamps were used as needed. Afterwards, the process was repeated until each column had a less than 137.9 hPa change in pressure after 6 h.

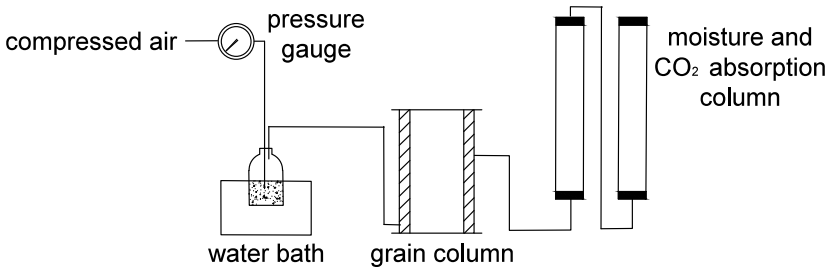

Figure B.5. Set up for testing leaks in the entire grain respiration measurement system.

APPENDIX C. SOYBEAN RESPIRATION TEST PROCEDURES

C.1. Soybean respiration measurement

C.1.1. Purpose

Measure CO_2 produced from soybean respiration.

C.1.2. Equipment required

Grain respiration measurement system (Figure 3.1), data acquisition system and sensors (Figure 3.5), compressed air (80% N_2, 20% O_2, < 50 pm CO_2), analytical grade glycerol with anti-foaming agent, deionized water, Drierite (4 mesh, indicating; 4 mesh, non-indicating), Sodasorb® (4 mesh, 12% moisture), soybeans, handheld grain moisture meter, sieves (8/64" round-hole sieve), scale (with 0.01 g resolution), hot plate, tools (screw drivers, wrenches, Teflon tape, etc.), and insulation fabric. Safety apparel (coat, goggles, mask and gloves) must be worn when handling Sodasorb®.

C.1.3. Pre-test checks

1. Make sure the system is leak-free (Appendix A.4).
2. Check compressed air levels on the gas regulator. If levels are below 34,000 hPa or 500 psi, replace with a new compressed air tank and confirm CO_2 levels in the compressed air (Appendix A.2).
3. Check if air filter is clogged. Replace if necessary.
4. Check water levels in all water baths and make sure they are set at the test temperature. Fill water baths with deionized water if necessary.
5. Turn "ON" Arduino IDE software.

C.1.4. Soybean sample preparation

1. Obtain 3000 g of soybeans and, using sieves, clean to remove splits, broken seeds, leaves, pods and debris (Figure C.1).

Figure C.1. Cleaned soybeans, foreign materials and moisture meter.

2. Estimate the moisture content of the clean soybeans using a handheld moisture meter (Figure C.1).
    a. Fill the chamber with clean soybeans. Ensure the soybeans are tightly packed.
    b. Close the chamber and lay the moisture meter on a flat surface. Switch it "ON", select "soybeans" from the available list of grains and press "Test". The estimated moisture content will be displayed on the screen in 30 s.
    c. Repeat Step 2b above three times and calculate average moisture content.
3. Use the average moisture content to prepare glycerol-water solution.
4. Obtain six 100-g subsamples from mixed clean beans. These samples will be sent to Analab (Fulton, IL) and Midwest Labs (Omaha, NE) for compositional and mold analyses.

C.1.5. Glycerol-water solution preparation

1. Place the glycerol-water solution over a hot plate (set at 50°C) and stir continuously for 30 min to ensure adequate mixing.
2. Store glycerol-water solutions in clean, plastic containers (3 l capacity).

3. Use silicone and tape to seal the caps of the containers filled with glycerol-water solutions.

C.1.6. Grain column preparation

1. Take a clean, dry grain column and re-place a perforated plastic disk at the bottom of the column to create the plenum.
2. Gently pour 1850 g of soybeans into the column.
3. Apply vacuum grease on the o-ring in the top flange prior to covering the column with the lid. Tighten wing nuts until the lid is securely in place (Figure C.2).
4. Wrap the column with insulation fabric (Figure C.2).

Figure C.2. Soybean-filled grain column before and after being wrapped with insulation.

C.1.7. Moisture absorption column preparation

1. Weigh two clean and empty gas-drying units.
2. Place a perforated steel disk in each column to create a plenum.

3. Gently pour 100 g of Drierite mixture (premixed with 50 g indicating and 50 g non-indicating) into each column and gently shake the column to allow the materials to pack tightly. Repeat until 550 g of Drierite mixture is in the column.
4. Place a second perforated steel disk on top of the desiccant, followed by a spring.
5. Apply vacuum grease to the O-ring in the cap and securely seal both columns using a plastic wrench (Figure C.3).
6. Weigh the freshly filled columns.

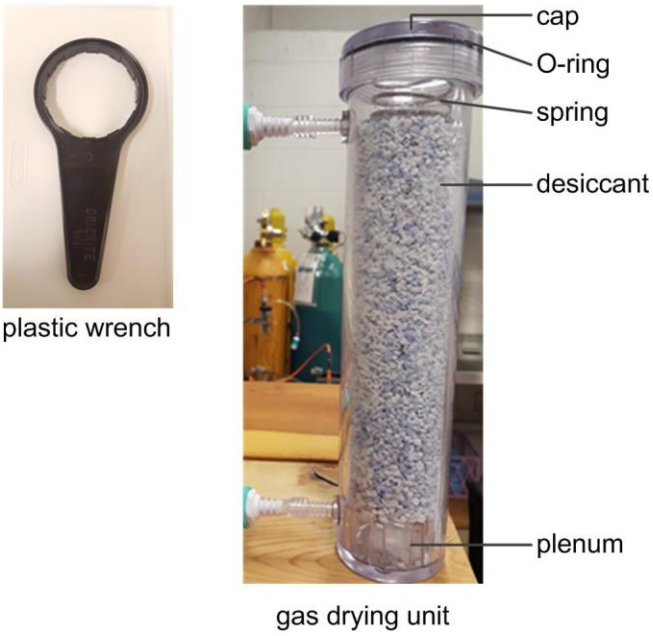

Figure C.3. Moisture absorption column was filled with desiccant and sealed tightly using a plastic wrench.

C.1.8. CO_2 absorption column preparation

1. Weigh two clean and empty gas-drying units.
2. Place a perforated steel disk in each column to create a plenum.
3. Gently pour 150 g Sodasorb®.
4. Place two perforated plastic disks separated by a plastic separator (Figure C.4).
5. Gently pour 300 g of Drierite mixture (Figure C.4).

6. Place a perforated steel disk on top of the desiccant, followed by a spring.
7. Apply vacuum grease to the O-ring in the cap and securely seal both columns using a plastic wrench.
8. Weigh the freshly filled columns.

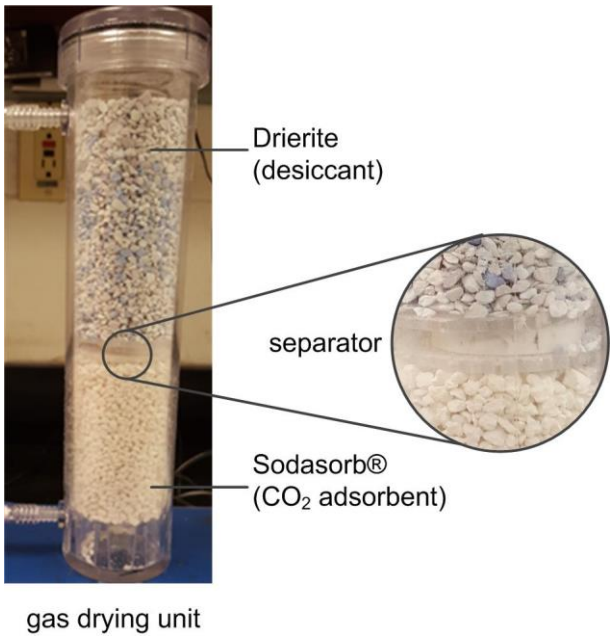

Figure C.4. A CO_2 absorption column was filled with CO_2 adsorbent and desiccant, separated by a separator.

C.1.9. System connections

1. Connect all components of the grain respiration measurement system using Tygon® tubing (1/4 in or 0.635 cm ID), keeping each connection as short as possible.
2. Use hose clamps whenever possible to secure connections.
3. Use Teflon tape when connecting gas regulators and mass flow controller connections with Swagelok® fittings to minimize leaks.
4. Install SHT15 and CO_2 sensors to monitor the temperature, relative humidity, and CO_2 levels of the exhaust air (Figures 3.5 and C.5).

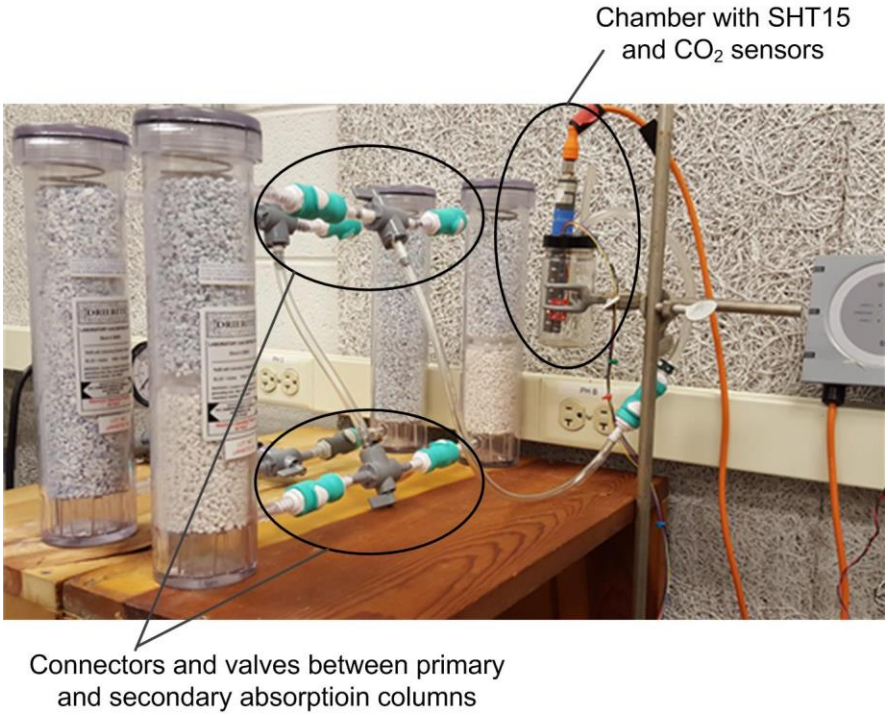

Figure C.5. A set of sensors was used to monitor temperature, relative humidity and CO_2 levels in the exhaust air of the grain respiration measurement system.

C.1.10. Grain respiration test

C.1.10.1. Managing and humidifying compressed air stream

1. Connect the wall power supply of the gas flow controller (PS-GFC-110NA-2, Aalborg, Orangeburg, NY) and allow the controller to warm up for 15 min and the transducer to return to "0" reading for an additional 5 min.
2. Ensure the regulator valves is in fully open position, i.e., the pressure regulator's Gauge 2 reading is 0 hPa (Figure C.6).

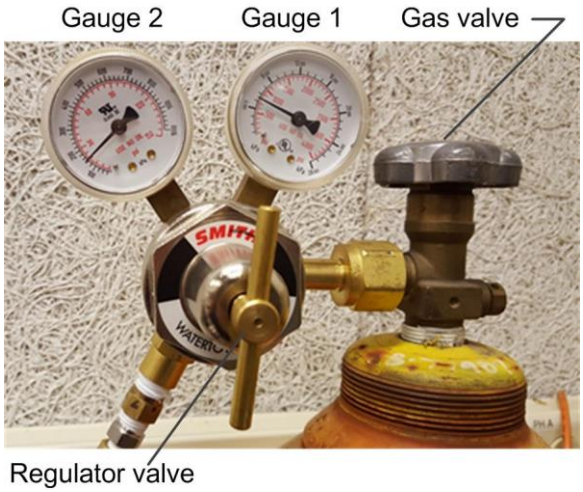

Figure C.6. Gas regulator on a compressed air source.

3. Open the compressed air tank valve and watch the needle on Gauge 1 indicate the pressure inside the tank. Gauge 2 should continue to read "0".
4. Supply the controller with an initial pressure of 689 to 1378 hPa (10 to 20 psi) prior to slowly turning the regulator valve to achieve the desired pressure, indicated on Gauge 2.
5. Using a screwdriver, slowly turn the potentiometer on the controller to the desired flow rate (Figure C.7). Once flow has stabilized, the flow rate will be indicated on the LCD display. The controller will also produce mechanical clicking sounds when the minimum or maximum flow rates (0 or 2 l) are reached.

Figure C.7. Connections and adjustment of the gas flow controller.

6. Let the compressed air flow through the entire system (with humidification) for approximately 10 min to push any air trapped in the crevices and tubing of the grain respiration measurement system.
7. After 10 min, turn “ON” the serial monitor on the Arduino software to start recording temperature, relative humidity, and CO_2 level data (Figure C.8). The prompt “Card Ready” indicates successful connection and marks the start of a grain respiration test.

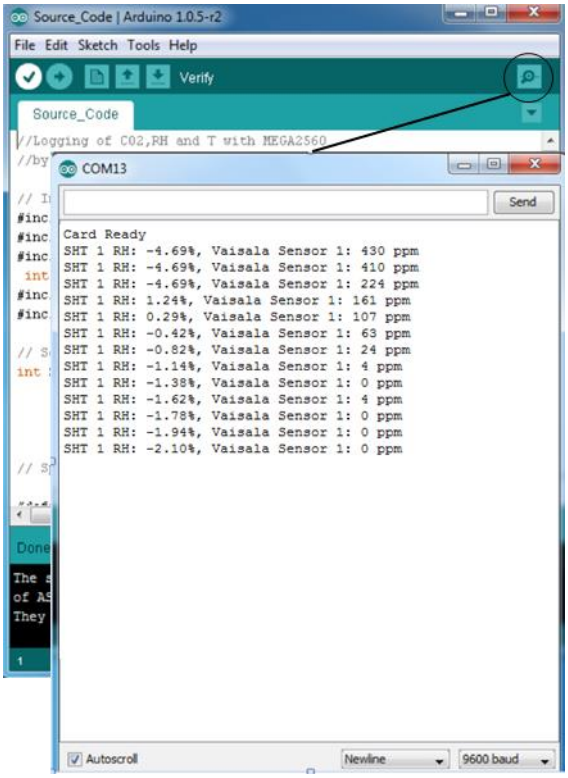

Figure C.8. Initiation of data acquisition on the serial monitor of the Arduino software.

8. Maintain glycerol-water ratio by adding 19 ml of water to the solution every two days.
9. The glycerol-water solution needs to be replenished after every two experimental runs of five days each.

C.1.10.2. Monitoring moisture and CO_2 absorption

1. Every 6 to 12 h, divert the flow of the airstream from the primary moisture and CO_2 absorption columns to the secondary absorption columns. Flow is diverted by turning the three-way valves 180° (Figure C.5).
2. Carefully remove the primary columns from the system using the quick-disconnect connectors (Figure C.5).
3. Get an average weight of the primary moisture absorption column by placing it on a scale, rotating it three times, and recording the weight between each rotation (Figure C.9).

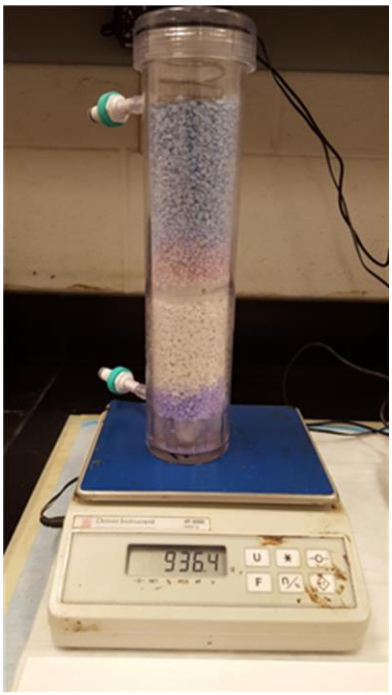

Figure C.9. Weighing an absorption column on a scale with 0.01 g resolution.

4. Repeat Step 3 above with the primary CO_2 absorption column.
5. Re-attach the primary columns in the system and divert the flow back to the primary columns by rotating the three-way valves 180°.
6. Manually record the grain temperature from the digital thermometer display.

7. When the weight of the primary moisture absorption column has reached 14.7 g, replace it with a freshly prepared column (Appendix C.1.6). Likewise, when the weight of the of primary CO_2 absorption column has reached 8.8 g or it has been used for two days of testing, replace it with a freshly prepared column (Appendix C.1.7).
8. When one of the following conditions has been reached, terminate the respiration test:
    a. $\sum m_{CO_2}$ > 7.33 g, which indicated 0.5% DML had been reached based on Equation 2.1.
    b. C_{CO_2} > 50 ppm in the exhaust air, indicating the absorption column had failed to capture all respired CO_2.

C.1.10.3. Ending a respiration test

1. Record the time that the respiration test is stopped.
2. Release any pressure on Gauge 2 of the regulator by rotating regulator valve (Figure B.6) until the pressure reads "0".
3. Using a screwdriver, rotate the potentiometer of the controller counterclockwise until the LCD display reads "0" and a mechanical clicking sound is heard.
4. Download data by importing while from micro SD memory card (Figure 3.5) or by copying text from the Serial Monitor (Figure C.8) and save all the sensor data locally and manually record the final grain temperature.
5. Record average weights of the primary and secondary moisture and CO_2 absorption columns.
6. Disassemble the grain respiration measurement system by slowly removing the components:
    a. Glycerol-water solution containers emptied and safely drained.
    b. Detach the grain column from the system.
    c. Remove insulation fabric.

d. Detach the moisture absorption columns. Empty the columns and clean using warm soapy water followed by deionized water rinse. Desiccant may be regenerated by being spread in an aluminum tray and heated at 210°C for 1 h in a convection oven.

e. Detach the CO_2 absorption columns. Empty the columns and clean same as 6c. The used Sodasorb® should be disposed of by pouring into sealed container for pick up by University of Illinois Division of Research Safety.

7. Slowly open the grain column and note appearance of the stored soybeans (e.g., molding, swelling, pockets of moisture in the grain column).
8. Obtain eight 20-g samples from the column – two from the top 1/3 layer; two from the middle 1/3 layer; two from the bottom 1/3 layer; and two subsamples from a mixed sample representing the entire column. These samples will be used to determine moisture content of the soybeans after testing, following ASABE Standard S352.2 (2012).
9. Obtain six additional 100-g subsamples from a mixed sample representing the entire column. These samples will be sent to Analab (Fulton, IL) and Midwest Labs (Omaha, NE) for compositional and mold analyses.
10. Place all remaining soybeans in a sealed container and store at -17.6°C until the study has ended.
11. Wash the empty the grain column with warm, soapy water and follow with a deionized water rinse.
12. Recondition SHT15 sensor by baking at 100 °C and < 5% *RH* for 10 h, shortly followed by re-hydration at 25°C and ~ 75% RH using saturated NaCl salt solution for 12 h.

APPENDIX D. DATA, REGRESSION AND COMPARISON OF MEANS

D.1. Moisture absorption column tests

Table D.1. Data from tests using 40.6°C and 89.1% RH airstream.

Test No.	Q (ml/min)	t (h)	$\sum m^*_{H_2O}$ (g)	$\sum m_{H_2O}$ (g)			η_{H_2O}		
				Rep 1	Rep 2	Rep 3	Rep 1	Rep 2	Rep 3
1	200	0.5	0.3	0.4	0.2	0.2	1.31	0.66	0.66
		1.0	0.6	0.7	0.7	0.4	1.15	1.15	0.66
		1.5	0.9	0.9	1.0	0.7	0.98	1.09	0.77
		2.0	1.2	1.3	1.2	1.0	1.07	0.98	0.82
		2.5	1.5	1.6	1.6	1.3	1.05	1.05	0.85
		3.0	1.8	2.0	1.9	1.7	1.09	1.04	0.93
		3.5	2.1	2.3	2.1	2.1	1.08	0.98	0.98
2	400	0.5	0.6	1.0	0.3	0.7	1.64	0.49	1.15
		1.0	1.2	1.6	1.0	1.2	1.31	0.82	0.98
		1.5	1.8	2.0	2.0	1.7	1.09	1.09	0.93
		2.0	2.4	2.5	2.7	2.4	1.03	1.11	0.98
		2.5	3.1	3.0	3.2	2.9	0.98	1.05	0.95
		3.0	3.7	3.5	3.5	3.4	0.96	0.96	0.93
		3.5	4.3	4.1	4.0	3.9	0.96	0.94	0.91
3	1000	0.5	1.5	1.1	1.2	1.4	0.72	0.79	0.92
		1.0	3.1	2.3	2.4	2.8	0.75	0.79	0.92
		1.5	4.6	3.6	4.6	4.4	0.79	1.01	0.96
		2.0	6.1	5.3	6.4	5.2	0.87	1.05	0.85
		2.5	7.6	6.8	7.6	6.9	0.89	1.00	0.91
		3.0	9.1	7.9	8.8	8.6	0.86	0.96	0.94
		3.5	10.7	9.1	9.5	9.9	0.85	0.89	0.93
4	2000	0.5	3.1	2.8	3.2	3.1	0.92	1.05	1.02
		1.0	6.1	5.7	5.8	6.5	0.94	0.95	1.07
		1.5	9.1	8.8	8.5	10.2	0.96	0.93	1.12
		2.0	12.2	12.9	11.6	12.6	1.06	0.95	1.03
		2.5	15.2	15.7	14.6	15.5	1.03	0.96	1.02
		3.0	18.3	19.1	17.2	17.6	1.04	0.94	0.96
		3.5	21.3	23.4	20.0	20.9	1.10	0.94	0.98

Table D.2. Linear regression results of moisture absorption column tests.

	Test No. 1 200 ml/min	Test No. 2 400 ml/min	Test No. 3 1000 ml/min	Test No. 4 2000 ml/min
Regression Statistics				
R	0.99	0.99	0.99	0.99
R^2	0.97	0.97	0.98	0.99
Adjusted R^2	0.97	0.97	0.98	0.99
Standard error	0.12	0.20	0.42	0.63
No. of observations	21	21	21	20
Analysis of Variance				
Degrees of freedom				
Regression	1	1	1	1
Residual	19	19	19	18
Total	20	20	20	19
Sums of Squares				
Regression	8.37	25.85	167.73	651.25
Residual	0.25	0.73	3.28	7.24
Total	8.62	26.58	171.01	658.49
Mean Square				
Regression	8.37	25.85	167.73	651.25
Residual	0.01	0.04	0.17	0.40
Total				
F-statistic	625	676	973	1620
p-level	5.4 E-16	2.6 E-16	8.8 E-18	4.4 E-19
Regression Estimates				
Intercept, β_0 (Value ± *S.E.*[a])	-0.07	0.19	-0.14	0.24
t-Statistic (H_0: $\beta_0 = 0$; H_A: $\beta_0 \neq 0$)	-1.21	2.00	-0.67	0.74
p-level	0.24	0.06	0.51	0.47
Slope, β_1 (Value ± *S.E.*[a])	1.03	0.91	0.93	0.97
t-Statistic (H_0: $\beta_1 = 1$; H_A: $\beta_1 \neq 1$)	0.84	-2.59	-2.45	-1.26
p-level	0.41	0.02	0.02	0.22

[a]*S.E.* = standard error

Table D.3. Comparison of means results from moisture absorption column tests.

Test No.	Q (ml/min)	Mean		Variance		*df*	Summary (H₀: $\overline{\sum m_{H_2O}} - \overline{\sum m^*_{H_2O}} = 0$)		
		$\sum m_{\mathrm{H_2O}}$ (g)	$\sum m^*_{H_2O}$ (g)	$\sum m_{\mathrm{H_2O}}$ (g)	$\sum m^*_{H_2O}$ (g)		*t-Statistic*	*t-Critical*[a]	*p-value*
1	200	1.23	1.26	0.41	0.36	38	0.15	2.02	0.87
2	400	2.48	2.52	1.28	1.45	38	0.13	2.02	0.89
3	1000	5.73	6.32	7.92	9.11	38	0.64	2.02	0.52
4	2000	12.08	12.19	32.04	34.07	36	0.06	2.03	0.95

[a]Two-tailed, 5%.

D.2. CO_2 absorption column tests

Table D.4. Data from tests using various loading rates.

Test No.	Test Conditions	*t* (h)	$\sum m^*_{CO_2}$ (g)	$\sum m_{\mathrm{CO_2}}$ (g)		r_{CO_2} (g/h)		$\eta_{\mathrm{CO_2}}$	
				Rep 1	Rep 2	Rep 1	Rep 2	Rep 1	Rep 2
1	C_{CO_2} = 10^6 ppm	1	1.2	1.0		1.0		0.87	
	Q = 10 ml/min	2	2.4	2.0		0.9		0.83	
	$r^*_{CO_2}$ = 1.2 g/h	3	3.6	3.2		1.2		0.89	
		4	4.7	4.3		1.1		0.91	
		5	5.9	5.5		1.2		0.92	
		6	7.1	6.8		1.3		0.96	
		7	8.3	8.0		1.2		0.96	
		8	9.5	9.2		1.2		0.97	
2	C_{CO_2} = 10^6 ppm	1	2.4	0.9		0.9		0.39	
	Q = 20 ml/min	2	4.7	3.0		2.1		0.63	
	$r^*_{CO_2}$ = 2.4 g/h	3	7.1	5.4		2.4		0.76	
		4	9.5	7.8		2.4		0.82	
		5	11.9	10.2		2.5		0.86	
		6	14.2	12.6		2.4		0.89	
		7	16.6	14.8		2.2		0.89	
		8	19.0	17.1		2.2		0.90	
		9	21.4	19.5		2.5		0.91	
		10	23.7	21.9		2.4		0.92	
		11	26.1	24.2		2.3		0.93	
		12	28.5	26.3		2.1		0.92	
3	C_{CO_2} = 10^4 ppm	1	0.6	0.7	0.6	0.7	0.6	1.24	0.96
	Q = 500 ml/min	2	1.2	1.3	1.2	0.6	0.6	1.10	1.01
	$r^*_{CO_2}$ = 0.6 g/h	3	1.8	1.8	1.8	0.5	0.6	1.03	1.03
		4	2.4	2.3	2.3	0.5	0.5	0.98	0.98
		5	3.0	2.9	2.9	0.5	0.6	0.97	0.98
		6	3.6	3.5	3.6	0.6	0.6	0.98	1.00
		7	4.2	4.1	4.2	0.6	0.6	1.00	1.00
		8	4.7	4.6	4.6	0.5	0.5	0.97	0.98

Table D.4. Continued

4	C_{CO_2} = 10^4 ppm	1	1.2	1.2	1.2	1.2	1.2	1.01	0.98
	Q = 1000 ml/min	2	2.4	2.4	2.3	1.2	1.1	1.00	0.96
	$r^*_{CO_2}$ = 1.2 g/h	3	3.6	3.6	3.5	1.2	1.2	1.00	0.98
		4	4.7	4.7	4.6	1.2	1.1	0.99	0.97
		5	5.9	5.8	5.8	1.1	1.2	0.98	0.98
		6	7.1	7.0	7.0	1.2	1.2	0.99	0.99
		7	8.3	8.3	8.3	1.3	1.2	1.00	1.00
		8	9.5	9.4	9.5	1.2	1.2	0.99	1.00
		9	10.7	10.6	10.8	1.2	1.3	0.99	1.01
		10	11.9	11.9	11.9	1.3	1.1	1.00	1.00
		11	13.0	13.1	13.1	1.2	1.2	1.00	1.00
		12	14.2	14.1	14.2	1.0	1.1	0.99	1.00
5	C_{CO_2} = 10^4 ppm	1	1.8	1.7	1.7	1.7	1.7	0.97	0.96
	Q = 1500 ml/min	2	3.6	3.5	3.6	1.8	1.9	0.99	1.00
	$r^*_{CO_2}$ = 1.8 g/h	3	5.3	5.3	5.3	1.8	1.8	1.00	1.00
		4	7.1	7.2	7.2	1.8	1.8	1.01	1.01
		5	8.9	8.9	9.0	1.8	1.8	1.00	1.01
		6	10.7	10.7	10.6	1.8	1.7	1.01	1.00
		7	12.5	12.5	12.4	1.7	1.8	1.00	1.00
		8	14.2	14.3	14.2	1.8	1.8	1.00	1.00
		9	16.0	16.0	16.0	1.7	1.7	1.00	1.00
		10	17.8	17.8	17.7	1.7	1.8	1.00	1.00
6	C_{CO_2} = 10^4 ppm	1	2.1	2.1	2.1	2.1	2.1	0.98	1.00
	Q = 1800 ml/min	2	4.3	4.2	4.2	2.1	2.1	0.98	0.98
	$r^*_{CO_2}$ = 2.1 g/h	3	6.4	6.4	6.4	2.2	2.2	0.99	1.00
		4	8.5	8.4	8.5	2.1	2.1	0.99	0.99
		5	10.7	10.6	10.6	2.1	2.1	0.99	0.99
		6	12.8	12.7	12.7	2.1	2.1	0.99	0.99
		7	14.9	14.6	14.4	1.9	1.7	0.98	0.96
7	C_{CO_2} = 10^4 ppm	1	2.4	2.4	2.4	2.4	2.4	1.03	1.00
	Q = 2000 ml/min	2	4.7	4.8	4.8	2.4	2.5	1.01	1.02
	$r^*_{CO_2}$ = 2.4 g/h	3	7.1	7.2	7.1	2.4	2.3	1.01	1.00
		4	9.5	9.5	9.6	2.3	2.4	1.00	1.01
		5	11.9	12.0	12.0	2.5	2.4	1.01	1.01
		6	14.2	14.4	14.3	2.4	2.3	1.01	1.00
		7	16.6	15.7	15.0	1.3	0.7	0.95	0.90

Table D.5. Linear regression results of CO_2 absorption column tests[a].

	Test No. 3 0.6 g/h	Test No. 4 1.2 g/h	Test No. 5 1.8 g/h	Test No.6 2.1 g/h	Test No. 7 2.4 g/h
Regression Statistics					
R	1.00	1.00	1.00	1.00	1.00
R^2	1.00	1.00	1.00	1.00	1.00
Adjusted R^2	1.00	1.00	1.00	1.00	1.00
Standard error	0.06	0.06	0.05	0.03	0.05
No. of observations	16	24	20	12	11
Analysis of Variance					
Degrees of freedom					
Regression	1	1	1	1	1
Residual	14	22	18	10	9
Total	15	23	19	11	10
Sums of Squares					
Regression	27.36	405.14	522.82	156.75	160.23
Residual	0.05	0.08	0.04	0.01	0.02
Total	27.41	405.22	522.86	156.76	160.25
Mean Square					
Regression	27.36	405.14	522.82	156.75	160.23
Residual	0.00	0.00	0.00	0.00	0.00
Total					
F-statistic	8191	105451	251049	174732	72334
p-level	8.8 E-21	5.5 E-42	9.3 E-39	1.5 E-22	6.9 E-19
Regression Estimates					
Intercept, β_0 (Value ± *S.E.*[b])	0.09	-0.06	-0.01	-0.01	0.03
t-Statistic (H_0: $\beta_0 = 0$; H_A: $\beta_0 \neq 0$)	2.72	-2.24	-0.38	-0.64	0.73
p-level	0.17	0.35	0.71	0.54	0.49
Slope, β_1 (Value ± *S.E.*[b])	0.96	1.00	1.00	0.99	1.01
t-Statistic (H_0: $\beta_1 = 1$; H_A: $\beta_1 \neq 1$)	-3.49	1.12	0.38	-3.61	1.38
p-level	0.33	0.27	0.71	0.00	0.20

[a]Test nos. 1 and 2 were not included due to limited number of observations.
[b]*S.E.* = standard error

Table D.6. Comparison of means results from CO_2 absorption column tests.

Test No.[a]	$r^*_{CO_2}$ (g/h)	Mean		Variance		df^b	Summary (H_0: $\overline{\sum m_{CO_2}} - \overline{\sum m^*_{CO_2}} = 0$)		
		$\sum m_{CO_2}$ (g)	$\sum m^*_{CO_2}$ (g)	$\sum m_{CO_2}$ (g)	$\sum m^*_{CO_2}$ (g)		*t-Statistic*	*t-Critical*[c]	*p-value*
3	0.6	2.78	2.80	1.67	1.77	28	0.05	2.04	0.96
4	1.2	7.95	7.99	16.42	16.27	44	0.03	2.01	0.97
5	1.8	10.21	10.20	25.25	25.25	36	0.00	2.03	0.99
6	2.1	7.88	7.96	12.61	12.84	20	0.05	2.08	0.95
7	2.4	9.56	9.48	12.66	12.50	18	0.04	2.1	0.96

[a]Test nos. 1 and 2 were not included due to limited number of observations.

[b]*df* = degrees of freedom.

[c]Two-tailed, 5%.

Table D.7. Data from tests using various moisture contents of adsorbent and a fixed loading rate of 0.4 g/h.

MC_{ad} (%) =		6.8		8.1		9.2		11.3	
t (h)	$\sum m^*_{CO_2}$ (g)	$\sum m_{CO_2}$ (g)	η_{CO_2}	$\sum m_{CO_2}$ (g)	η_{CO_2}	$\sum m_{CO_2}$ (g)	η_{CO_2}	$\sum m_{CO_2}$ (g)	η_{CO_2}
1	0.4	0.70	1.89	0.50	1.35	0.6	1.62	0.5	1.35
2	0.7	1.10	1.48	1.00	1.35	1.0	1.35	0.9	1.21
3	1.1	1.40	1.26	1.30	1.17	1.4	1.26	1.2	1.08
4	1.5	1.90	1.28	1.60	1.08	1.7	1.15	1.7	1.15
5	1.9	2.40	1.29	1.90	1.03	2.0	1.08	2.1	1.13
6	2.2	2.90	1.30	2.30	1.03	2.3	1.03	2.4	1.08
7	2.6	3.10	1.19	2.60	1.00	2.6	1.00	2.9	1.12
8	3.0	3.10	1.05	2.80	0.94	2.9	0.98	3.0	1.01
9	3.3	3.10	0.93	2.90	0.87	3.1	0.93	3.1	0.93
Mean[a]	1.86	2.19	1.30	1.88	1.09	1.96	1.16	1.98	1.12
S.D.	1.01	0.95	0.27	0.84	0.17	0.86	0.22	0.96	0.12

[a]*S.D.* = standard deviation

Table D.8. Linear regression results for various moisture contents of adsorbent.

MC_{ad} (%)	6.8	8.1	9.2	11.3
Regression Statistics				
R	0.97	0.99	1.00	0.99
R^2	0.93	0.98	0.99	0.98
Adjusted R^2	0.92	0.98	0.99	0.97
Standard error	0.26	0.12	0.07	0.16
No. of observations	9	9	9	9
Analysis of Variance				
Degrees of freedom				
Regression	1	1	1	1
Residual	7	7	7	7
Total	8	8	8	8
Sums of Squares				
Regression	6.66	5.58	5.83	7.21
Residual	0.49	0.10	0.04	0.17
Total	7.15	5.68	5.86	7.38
Mean Square				
Regression	6.66	5.58	5.83	7.21
Residual	0.07	0.01	0.01	0.02
Total				
F-statistic	1.9 E-07	4.0 E+02	1.1 E+03	3.0 E+02
p-level	2.5 E-05	9.5 E+01	5.1 E-09	5.5 E-07
Regression Estimates				
Intercept, β_0 (Value ± *S.E.*[a])	0.53	0.36	0.40	0.25
t-Statistic (H_0: $\beta_0 = 0$; H_A: $\beta_0 \neq 0$)	2.74	4.17	7.73	2.20
p-level	0.03	0.00	0.00	0.06
Slope, β_1 (Value ± *S.E.*[a])	0.90	0.82	0.84	0.93
t-Statistic (H_0: $\beta_1 = 1$; H_A: $\beta_1 \neq 1$)	-1.11	-4.35	-6.46	-1.22
p-level	0.30	0.00	0.00	0.26

[a]*S.E.* = standard error

Table D.9. Comparison of means results for various moisture contents of adsorbent.

MC_{ad} (%)	Mean		Variance		Summary (H_0: $\overline{\sum m_{CO_2}} - \overline{\sum m^*_{CO_2}} = 0$), df[a] = 14)		
	$\sum m_{CO_2}$ (g)	$\sum m^*_{CO_2}$ (g)	$\sum m_{CO_2}$ (g)	$\sum m^*_{CO_2}$ (g)	*t-Statistic*	*t-Critical*[b]	*p-value*
6.8	2.16	2.04	0.70	0.83	0.28	2.14	0.77
8.1	2.05	2.03	0.51	0.82	0.03	2.14	0.97
9.2	2.12	2.03	0.54	0.82	0.21	2.14	0.83
11.3	2.16	2.04	0.70	0.83	0.28	2.14	0.77

[a]*df* = degrees of freedom.

[b]Two-tailed, 5%.

D.3. Soybean respiration tests

Table D.10. Data from tests using 14% moisture soybeans at 35°C.

Test No. 1					Test No. 2				
t (h)	$\sum m_{CO_2}$ (g)	Δm_{CO_2} (g)	r_{CO_2} (g/h)	r_{CO_2} (g/kg·h)[a]	t (h)	$\sum m_{CO_2}$ (g)	Δm_{CO_2} (g)	r_{CO_2} (g/h)	r_{CO_2} (g/kg·h)[a]
6	929.3	0.00	0.00	0.00	6	933.3	0.03	0.01	0.02
21	929.3	0.10	0.01	0.05	18	933.3	0.03	0.00	0.02
30	929.4	0.30	0.04	0.16	24	933.3	0.13	0.03	0.07
48	929.6	0.60	0.03	0.32	30	933.3	0.13	0.00	0.07
53	929.8	0.60	0.00	0.32	41	933.3	0.23	0.01	0.13
71	929.8	0.60	0.00	0.32	49	933.4	0.33	0.02	0.18
79	929.8	0.60	0.00	0.32	57	933.5	0.43	0.02	0.23
					64	933.5	0.43	0.00	0.23
					80	934.7	0.53	0.01	0.29
					89	934.7	0.53	0.00	0.29
					105	934.7	0.73	0.02	0.40
					111	934.9	0.83	0.03	0.45
					130	935.0	1.03	0.02	0.56
					153	935.0	1.33	0.02	0.72
		Mean	0.01	0.29				0.02	0.32
		± S.D.[b] =	± 0.02	± 0.07				± 0.01	± 0.19

[a]On a per kg dry matter basis.

[b]*S.D.* = standard deviation.