A STUDY OF GUSHING IN CIDERS: ITS MECHANISM AND CAUSATIVE EFFECTS

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ABSTRACT

A STUDY OF GUSHING IN CIDERS: ITS MECHANISM AND CAUSATIVE EFFECTS

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Recent interest in the commercial production of bottle-fermented (sparkling) cider from Ontario-grown apples instigated this study. Preliminary investigations indicated that certain pre-fermentation treatments of apples could produce gushing ciders. Gushing is characterized by the overfoaming of the cider when the cap is removed from the bottle, and cannot be attributed to overcarbonation or mishandling. Decades of research on gushing in beer have not fully elucidated the cause(s) of gushing.

Investigation of four methods of cider production identified the use of thawed apples as the only processing treatment which produced gushing ciders. Chemical analyses conducted over the course of primary and secondary fermentations permitted comparison of the three treatments against the control. Gushing ciders were particularly high in soluble pectin and low in phenolic substances. The concentrations of several divalent and trivalent metallic ions were also significantly different in gushing ciders.

The mechanism of gushing was investigated in the second part of the research. Pressure release from the bottled ciders revealed that bubbles originated only in the sediment. A mathematical model and computer simulation programs were constructed to predict the growth and ascent of the bubbles. In non-gushing ciders, bubbles were produced at low frequencies and ascended through the liquid as single bubbles. In

gushing ciders, bubbles were produced at high frequencies and ascended through the liquid as a cloud. Interaction of the bubbles within the cloud resulted in slower (hindrance) or faster velocities than predicted by the computer simulation program.

The higher rate of bubble production in ciders resulted in the phenomenon of gushing. High densities of bubbles within the bubble clouds restricted the movement of liquid through the clouds. Constriction of the bottle at the bottle neck compressed the cloud of bubbles, further slowing or preventing liquid movement through the bubble cloud; liquid above the cloud was lifted by the continuing rise of the bubble cloud, resulting in gushing.

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SYMBOLS AND UNITS OF MEASURE

Symbols

a	diameter of an ellipsoidal bubble, in the vertical plane
b	diameter of an ellipsoidal bubble, in the horizontal plane
c_{A1}	concentration of gas at the gas-liquid interface of the bubble
c_{A2}	concentration of gas in the bulk liquid
c_D	drag coefficient
d_e	effective diameter of an ellipsoidal bubble
d_{head}	interior diameter of the neck of the bottle
D_{AB}	diffusion of very dilute gas A through a solvent/liquid B
ξ	porosity of the bed
g	gravity = 9.81 m s^{-2}
H_{ij}	Henry's constant for component *i* in solvent *j*
γ	gas/liquid interfacial tension, LaPlace equation
kconst	mass transfer coefficient for rising small bubbles of gas in a liquid
kgas	volumetric mass transfer coefficient
k_{head}	mass transfer coefficient at the headspace
M_B	molecular weight of solvent/liquid B
μ_B	viscosity of solvent/liquid B
n_{bubble}	moles of gas inside the bubble
n_{gas}	total moles in the gas phase

NRe	Reynolds number
NSc	Schmidt number
NSh	Sherwood number
N_A	flux of gas in a dilute system
N_{head}	flux at the headspace
P	pressure
P_{bubble}	pressure inside the bubble
ΔP	pressure difference across the gas/liquid interface, LaPlace equation
θ	liquid contact angle at the bubble nucleation site
r	radius of the bubble
r_c	radius of curvature of the gas/liquid interface
R	gas constant = 8.3144 J K^{-1} mol^{-1}
ρ	density of the liquid
ρ_{bed}	density of a bubble bed
ρ_{bubble}	density of the bubble
σ	bubble surface energy
T	temperature, degrees Kelvin
v_A	molar volume of gas A, at its normal boiling point
vt	velocity of bubble at an instant in time
vt_{ave}	average bubble velocity in a bubble bed
vt_{gas}	superficial gas velocity through the bed
V_{bubble}	volume of the bubble

V_{gas}	total volume of the gas phase
ψ_B	association factor for solvent B, which accounts for hydrogen bonding
x_i	mole fraction of component *i* in the liquid phase
y_i	mole fraction of component *i* in the gas phase
^	to the power of; for example: q^3 = q^3

Units of measure

atm	atmospheres = 101325 Pa
cm	centimeters
cP	centipoise
erg	= 1 g cm^2 s^{-2}
g	gram
J	joules
K	degrees Kelvin
kg	kilogram
m	meters
mN	millinewton
N	newton
mol	moles
Pa, kPa	pascals and kilopascals, respectively
poise	= 1 g cm^{-1} s^{-1}
s	second

1. GENERAL INTRODUCTION

Traditionally, cider is the product of the natural fermentation of fresh apple juice, to which nothing is added to increase the alcoholic content (Giffard, 1979). Cider is a popular beverage in many countries, but has not achieved such status in Canada.

For centuries cider has been produced in European countries from varieties of apples specifically selected for cider production (Arengo-Jones, 1941; Beech, 1972) based on their sweetness, acidity and astringency (Bowen *et al.*, 1959). For example, British cider varieties such as Kingston Black, Knotted Kernel, Woodbine, Foxwhelp and Dabinett are classified as "bitter-sweets" and are valued in British cider production for their high astringency and sugar concentrations but relatively low acidity (Arengo-Jones, 1941). Apple varieties in North America are primarily cultivated for their fresh-eating or culinary qualities (Agriculture Canada, 1988; Arengo-Jones, 1941; Atkinson, 1959) and are much lower in astringency and bitterness than "true" cider apples (La Belle, 1979). In Ontario, Canada, experimental plantings of European cider apple varieties such as Brown's Apple, Güttingen, Stoke Red, Tremlett's Bitter and Yarlington Mill yielded mixed results (Agriculture Canada, 1988) and have not lead to commercial production.

Earlier work by other researchers concerning the production of cider in Canada focussed on the suitability of locally grown apple varieties for cider production (Arengo-Jones, 1941; Bowen *et al.*, 1959; Grove, 1930). An investigation of bottle-fermented (sparkling) cider produced from locally grown apples was initiated by recent interest in the commercial production of cider in Ontario. The unpredicted gushing tendency of some ciders produced in this preliminary investigation prompted the current study.

The term gushing has been used to describe beer that overfoams excessively, which cannot be attributed to overcarbonation or mishandling. Gushing in beer has been characterized as the sudden release of gas the instant the bottle is opened, creating an

enormous number of very tiny bubbles throughout the liquid which expand and ascend very quickly, resulting in a spout of foam which flows out of the bottle (Amaha and Kitabatake, 1981; Gray and Stone, 1956). Remedies for gushing have been sought since the bottling of beer began in the 16th century (Beattie, 1951). The presence of a particular soluble protein, produced by *Fusarium* infection of barley, has been linked to gushing in beer and work continues to characterize the protein and to identify the cause of gushing (Amaha *et al.*, 1978; Bellmer, H.-G., 1996; Munar and Sebree, 1997; Schwarz *et al.*, 1996). Gushing also occurs in cider (Beattie, 1951). However, the chemical characteristics of gushing ciders have not been reported and the cause of gushing has not been identified definitively.

The goal of the first part of this study was to produce gushing and non-gushing sparkling ciders and to compare the chemical and microbial characteristics of the juices and ciders of the gushing products with those of non-gushing products. The results from Part One revealed that gushing occurred only in ciders from thawed apples; gushing ciders are particularly high in soluble pectin and low in phenolic substances. The concentrations of several divalent and trivalent metallic ions were also significantly different in gushing ciders.

In Part Two of the research, the mechanism of gushing in cider was investigated. Although the chemical characteristics of a cider and its sediment are responsible for the numbers and sizes of bubbles produced in a cider, it is the behaviour of the bubbles as they ascend to the top of the bottle which ultimately causes gushing. Based on the results and observations of Part One, and on gushing studies by other researchers, a theory of the mechanism of gushing was developed. Differences in bubble nucleation, rather than foam formation, were hypothesized to be the principal mechanism causing gushing in cider. Experiments were conducted in Part Two to support and illustrate this hypothesis.

2. PART ONE: EFFECT OF APPLE TREATMENTS ON CIDER QUALITY

2.1. Introduction

For more than five hundred years cider has been produced in European countries in significant quantities. During this time certain varieties of apples have become recognized as superior cider varieties and different styles of cider have been developed (Arengo-Jones, 1941). In North America, disenchantment with cider began with its overuse many years ago (La Belle, 1979). This unfortunate circumstance has contributed to the lack of interest in cider research and cider production on this continent.

Cider can be produced as "still" or "sparkling". Still cider is free of carbonation. It is frequently fermented to dryness and can be preserved by pasteurization or by the addition of sulfur dioxide. Sparkling (carbonated) cider is produced when fermentation continues inside a closed container (Arengo-Jones, 1941). The sparkling effect improves the organoleptic quality of the cider, is visually appealing and may be more pleasing to North American consumers who are fond of carbonated soft drinks and "sparkling" beer (La Belle, 1979).

Recent interest in the commercial production of sparkling cider in Ontario, Canada initiated a preliminary study on cidermaking using Ontario apple varieties (data not shown). The results of the study indicated that the method of cider production strongly influences the quality of the cider. Although all ciders were made from apples of satisfactory quality, certain pre-fermentation treatments of the apples produced gushing ciders.

2.2. Review of Literature

2.2.1. Apple Characteristics

Varieties of cider apples differ from culinary and dessert varieties primarily in their higher content of tannin or astringency. Cider varieties often have higher concentrations of sugar and lower acidities than culinary varieties. Similar to the production of wines, certain European apple varieties have become recognized as particularly suited for the production of specific types of cider. In addition, the quality of the cider produced is governed by the vintage characteristics of the apples (Smock and Neubert, 1950).

Arengo-Jones (1941) indicated that North American culinary or dessert apples cannot be used to produce a European style of cider, but rather a much lighter style of cider which is still of satisfactory quality. Compared to European varieties of cider apples, the low concentration of tannic acid and higher concentration of malic acid in North American dessert and culinary varieties leads to a loss of body and flavour during fermentation, resulting in a product which is organoleptically unappealing. It was recommended that North American varieties only be used for blending, to decrease the astringency and increase the acidity of the cider.

The tannic acid concentration in the apples can also alter the pectin content of the juice. The higher tannin content in cider apples inhibits the enzymatic solubilization of pectin. As a consequence, the drier texture of the apples allows increased storage before fruit processing and the juice is expressed more readily (Beech, 1972a).

In documented methods of cider production, apples were picked at storage maturity (Bowen *et al.*, 1959) and stored for several days to allow aroma development (Amerine *et al.*, 1972) and the conversion of starch to sugar (Beech, 1972b). To produce a cider

of satisfactory quality, only sound fruit was then selected for cider production (Beech, 1972b; Bowen *et al.*, 1959).

2.2.2. Cider Production

Before the advent of modern technology the fruit was crushed in a stone mill. The apples were deposited into a horizontal circular stone channel through which moved an upright circular crushing stone. The crushing stone was pushed through the channel manually or by horse (Beech, 1972b). In some cases, crushed apples were not pressed immediately but allowed to rest for up to 24 hours. This "maceration" substantially improved the flavour, colour and aroma of the juice and, through the actions of the native pectic enzymes, assisted in the clarification of the juice and increased juice yield at pressing (Amerine *et al.*, 1972; Beech, 1972b; Smock and Neubert, 1950). Methods now used for crushing and pressing apples for cider production are those also used in the commercial juice industry (Smock and Neubert, 1950).

Keeving or défécation traditionally followed pressing, although this has been replaced in the modern cider industry by treatment of the juice with pectic enzymes (Amerine *et al.*, 1972; Smock and Neubert, 1950). Keeving, which is still occasionally used as a method of juice clarification, was first documented by Grignon in 1887 (Calvez *et al.*, 1977). During keeving, the juice is held at low temperatures (below 10°C) for a few days until a brown "scum" or cap is formed on the surface (Arengo-Jones, 1941). Keeving encourages the action of the native pectic enzymes in the juice (Charley, 1935), which de-esterify the pectin molecules, liberating methanol and rendering the molecules insoluble in the presence of calcium (Calvez *et al.*, 1977). The coagulation of the pectin entraps microorganisms and particles suspended in the juice (Calvez *et al.*, 1977).

Clumps of the brown pectin "jelly" form a thick brown cap, also known as the "chapeau brun", on the surface of the juice (Smock and Neubert, 1950). Successful keeving will result in a bright, limpid juice between the brown cap and the sediment, which is siphoned off and used for the production of the cider (Amerine *et al.*, 1972; Beech, 1972b; Charley, 1935). Keeving significantly decreases the nitrogen content of the juice (Smock and Neubert, 1950) which may be beneficial or detrimental, depending on the style of cider desired and the original nitrogen content of the juice prior to keeving.

The fermentation of the juice occurs spontaneously or is controlled by the addition of a selected yeast culture (Amerine *et al.*, 1972). Although spontaneous fermentation is very common in Europe, studies of native yeasts on Canadian apples revealed a lack of fermenting strains (Beech, 1972b) and inoculation with a yeast culture is recommended.

In a typical apple juice with sugar compositions of 62.5% fructose, 20% glucose and 17.5% sucrose, as percentages of the total sugar content, sucrose is rapidly inverted during fermentation. By the completion of fermentation, sucrose and glucose are entirely depleted; fructose is practically the only sugar remaining in the fermented product (Smock and Neubert, 1950). In studies with Canadian-grown apples, Arengo-Jones (1941) showed that the juice would produce a dry cider with six or seven percent alcohol. Canadian ciders were fermented to a specific gravity of 1.000 before the fermentation was arrested. To produce a champagne-style cider, the dry cider was then aged in an oak barrel for six months before blending, sugaring, inoculating with a champagne yeast and bottling. Secondary fermentation in the bottle occurred slowly, followed by one year of ageing to ensure complete absorption of the gas. As in the style of the méthode champenoise, disgorgement and dosage followed ageing. This process of making carbonated or sparkling cider required twelve to eighteen months.

Fermentation of the base wine to "dryness" has been recommended by Amerine and Joslyn (1970) to produce a finished sparkling product of high quality with low concentrations of acetaldehyde and acetal.

2.2.3. Use of Thawed Fruit for Fermentation

A consideration of the emerging commercial cider industry in Ontario is the need for extended storage of apples (freezing), due to the short harvest season in this province. During freezing and thawing of apple tissues, cell membranes and cell walls may both be adversely affected (Tregunno and Goff, 1996). Damage to cell membranes may cause irreversible dysfunction of the membrane (Uemura and Yoshida, 1986) and loss of membrane permeability (Alonso *et al.*, 1997), resulting in a diffusion of cations to the cell wall. Freezing and thawing of fruit prior to processing may, therefore, increase the cation content of the juice. Apple cell walls are composed primarily of polysaccharides, mainly pectins (28%) and cellulose (27%) (Renard *et al.*, 1990). Diffusion of the cations through the membrane to the cell wall would activate pectinesterase, increasing the de-esterification of pectins and consequently assisting in the formation of divalent bridges between pectin chains (Alonso *et al.*, 1997). Juice and subsequent cider characteristics would undoubtedly be modified by these changes in the cell walls and membranes of the apple tissue. However, the scientific literature does not provide information on the use of frozen and subsequently thawed apples in cider production.

In research conducted by Spayd *et al.* (1987), juice produced from thawed grapes was much browner than juice from fresh grapes. Acidities were lower and pH levels were higher in juices and wines produced from thawed grapes compared to those from fresh grapes. Potassium concentrations were elevated in wines from thawed grapes; this was

attributed to the rupture of the berry cells due to freezing and the prolonged skin contact during thawing. Sensory analysis of the wines produced in the study indicated no detrimental effects due to the freezing treatment.

2.2.4. Effect of Storage on Apple Characteristics

Prior to the beginning of the twentieth century, cider apples were not picked from the trees but fell as they ripened. Early varieties were collected from the orchard floor soon after since they quickly became over-ripe. Varieties which matured later were left to lie in the orchard grass until all of their starch was converted to sugar. Apples which were collected prematurely were spread on wooden frames to ripen. This extensive ripening period also decreased the acidity, tannin and soluble nitrogen content of the extracted juice (Beech, 1972b). English cider factories now use concrete silos for apple storage and ripening (Beech, 1972a).

Canadian researchers have documented changes in the chemical characteristics of apples resulting from storage (Dever *et al.*, 1991; Fuleki *et al.*, 1994). Cold storage (2°C, 94-96% relative humidity) of apples for six months caused a decrease in sucrose concentration with concomitant increases in fructose and glucose concentrations, indicating inversion of the sucrose. Some sugar loss was also attributed to respiration (Fuleki *et al.*, 1994). Dever *et al.* (1991) studied the effect of fruit storage (5°C, 3 to 6 months, 75 to 80% relative humidity) on the quality of the extracted juice. Increases in turbidity and suspended solids in the juice were attributed to increased cell wall fragmentation during processing as a result of the softening of the apple tissue during storage. Decreases in phenol concentration and titratable acidity accompanied by

increases in pH were observed in juices produced from stored apples compared to those produced from fresh apples. Decreases in total phenol concentration and acidity were similarly shown by Poll (1985) to occur in juice from stored McIntosh apples, along with increases in alcohol, ester and aldehyde concentrations. Blanco *et al.* (1992) reported that in five Asturian varieties of cider apples the sugar concentrations increased and the malic acid and polyphenol concentrations decreased during apple ripening.

The pectic substances of apples also undergo a significant change during storage and senescence: the amount of water-soluble pectin increases (Hatfield and Knee, 1988) and galactose residues are lost (O'Beirne *et al.*, 1981). Mangas *et al.* (1992) studied the changes in the water-soluble, chelate-soluble and hydrochloric acid-soluble fractions of cider apples during ripening because of the relationship of these pectin fractions with fruit softening. They observed that the water-soluble and chelate-soluble fractions increased in the final stages of ripening at the expense of the hydrochloric acid-soluble fraction. The concentration of soluble pectin in juice is important in that the pectin molecules may act as protective colloids, binding to proteins to form electronegative particles, thereby influencing juice clarification (Yamasaki *et al.*, 1964). In addition, increases in soluble pectin cause increases in juice viscosity which then decrease the rate of the particle sedimentation during juice clarification (Mangas *et al.*, 1992). Calcium ions, which bind to pectin molecules in the middle lamella of apple cells, have been shown to decrease in concentration during the storage of apples, likely due to binding site changes (Stow, 1993).

Without humidity control, long-term storage of apples usually causes extensive water loss. Water loss decreases the weight of the fruit; losses in excess of 6% of harvest weight often cause fruit shrivelling (Hatfield and Knee, 1988).

2.3. Materials and Methods

2.3.1. Apple Varieties and Processing Treatments

Five apple varieties which are commercially available in Ontario were chosen for this study. Selection was based on the differing chemical characteristics of the apples or on their documented use in cider production (Table 1). Crispin is a popular fresh-eating variety, with relatively high sugar concentrations and moderate acidity. Hyslop crabapples were chosen primarily for their high astringency. McIntosh is low in tannin but highly aromatic and is grown throughout Ontario as a fresh market variety (Agriculture Canada,1988). In the province of Québec, Golden Russet has been used for apple "champagne" (Agriculture Canada, 1988) because of the organoleptic qualities of the fermented product. Northern Spy is a popular culinary apple in Ontario and was selected for its higher level of acidity. Preliminary experiments in our laboratory also indicated that these varieties produce ciders of satisfactory quality, either singly or in blends (data not shown).

The research was conducted using apples from two sequential harvests: 1994 and 1995, to account for effects due to climatic differences. Freshly harvested apples (unwaxed) were supplied by The Norfolk Fruit Growers' Association in Simcoe, Ontario. Each variety of apple was obtained from the same orchard in each of the two years in order to minimize effects of soil conditions and geographical location. Hyslop was only available in 1994 as the trees are biennial bearers.

In both years, eight bushels (approximately 288 L) of each apple variety were received at the University of Guelph. The apples were rinsed with tap water to remove dirt and debris (leaves, grass, etc.), sorted to remove damaged fruit and divided evenly, by weight, for the four processing treatments. Processing treatments and subsequent

Table 1. Apple varieties selected for the production of cider

Variety	Reason for Selection	Remarks	Waxiness of Apple Bloom [d]
Crispin	production of satisfactory quality cider in preliminary experiments in our lab (data not shown), although low in flavour	also known as Mutsu [a]	moderately waxy
Hyslop	crabapple: high in acidity and astringency [a]; possible use in blends to increase astringency	biennial bearer [a]; limited availability in Ontario	moderately waxy
McIntosh	aromatic [b,c] with a good acid/sugar balance [a]	popular fresh-eating variety	moderately to highly waxy
Golden Russet	described as a good variety for the production of cider [a,c]	also known as Reinette Grise [a]	very little or no waxiness
Northern Spy	higher in acidity; used successfully in blends to yield a good quality cider [c]	widely available throughout Ontario	very waxy

[a] source: (Agriculture Canada, 1988)

[b] source: (Bowen *et al.*, 1959)

[c] source: (Arengo-Jones, 1941)

[d] personal observation only

fermentation steps are outlined in Figure 1.

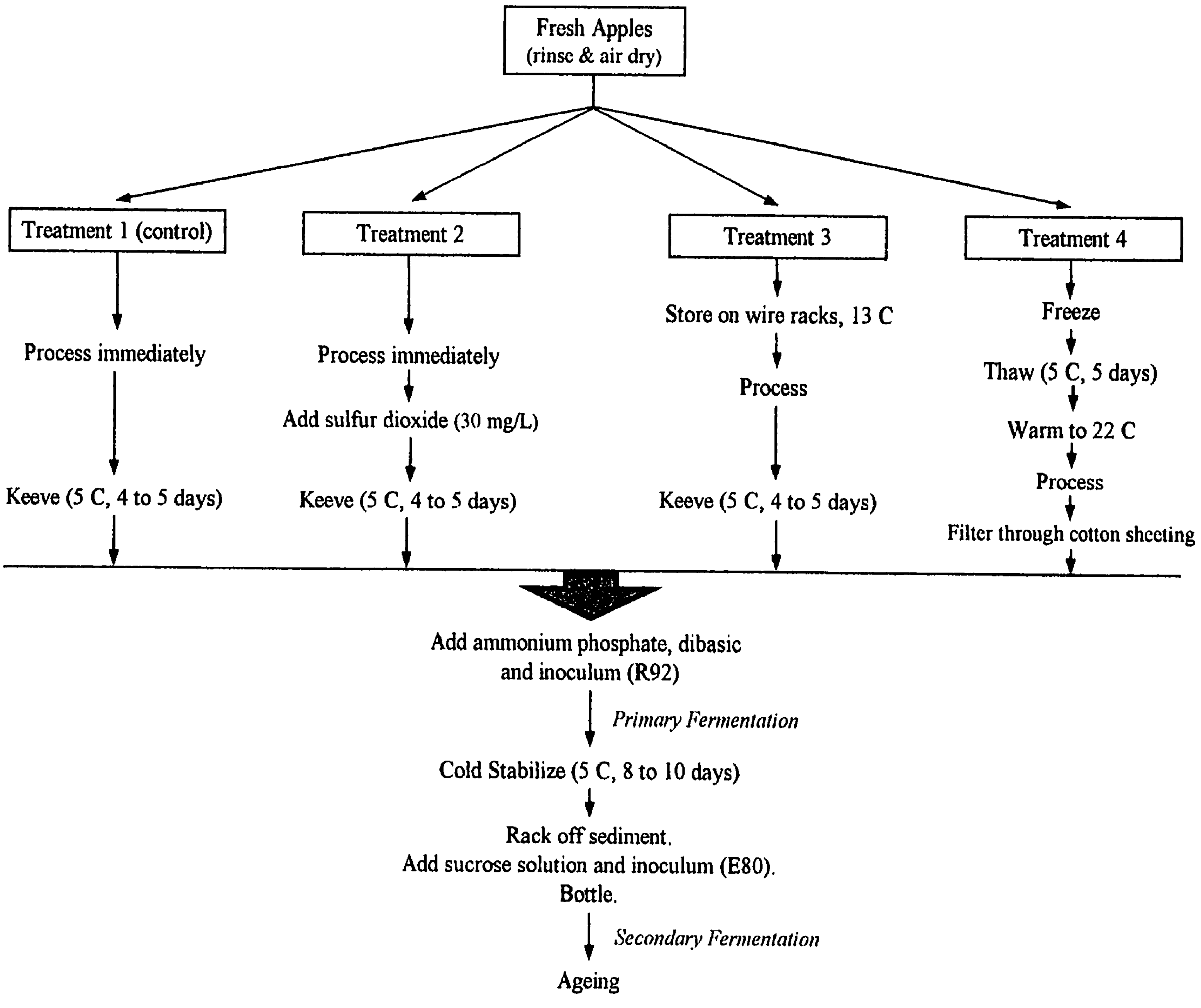
Treatment 1 was the control. The fresh apples were processed in a domestic Braun® juice extractor (Multipress Automatic MP80 Type 4290) and the juice transferred directly into 20 litre glass carboys; juice yield (L) was recorded per weight (kg) of apples. Compared to cider apples, the varieties of apples used in this study were expected to produce juices with higher amounts of solubilized pectin because of the low tannin content of the fruit (Beech, 1972a). The juice was not treated with pectinase because of the potential development of off-flavours (vinyl phenols) during fermentation (Chatonnet *et al.*, 1992). The juices were keeved (défécation) at 5°C for 4 to 5 days; the low temperature was used to discourage the growth of the native microflora and to promote the keeving action (Smock and Neubert, 1950). The juice between the sediment and the "brown cap" (chapeau brun) was siphoned off and used for the production of cider. Samples of the juices were taken for chemical analysis just prior to inoculation.

Treatment 2 was processed in the same fashion as Treatment 1, but 30 mg of sulfur dioxide ($K_2S_2O_5$; Fisher Scientific) was added per litre of juice during transfer to glass carboys. Keeving and juice sampling were as described for Treatment 1.

Treatment 3 apples were placed in a single layer on wire racks in a room maintained at 13°C. The purpose of this treatment was to imitate the maturation or storage of apples after picking (Amerine *et al.*, 1972; Beech, 1972b). Apples were processed when the fruit showed signs of shrivelling or the onset of senescence. Processing and keeving took place as described in Treatment 1. Juice yield was calculated per original weight of the fresh apples.

In Treatment 4, whole apples were sealed in ZiPLOC® plastic bags and frozen for 2 to 4 months at -27°C ± 5°C. Prior to processing, the apples were thawed at 5°C and

Figure 1. Processing treatments and vinification procedure. Apples in Treatments 1 and 2 were processed immediately, without storage. Treatment 3 apples were stored on wire racks until shrivelling was evident or until the onset of senescence. Treatment 4 apples were frozen for 2 - 4 months then thawed and processed.


Fresh Apples
(rinse & air dry)
Treatment 1 (control)
Process immediately
Keeve (5 C, 4 to 5 days)
Treatment 2
Process immediately
Add sulfur dioxide (30 mg/L)
Keeve (5 C, 4 to 5 days)
Treatment 3
Store on wire racks, 13 C
Process
Keeve (5 C, 4 to 5 days)
Treatment 4
Freeze
Thaw (5 C, 5 days)
Warm to 22 C
Process
Filter through cotton sheeting
Add ammonium phosphate, dibasic
and inoculum (R92)
Primary Fermentation
Cold Stabilize (5 C, 8 to 10 days)
Rack off sediment.
Add sucrose solution and inoculum (E80).
Bottle.
Secondary Fermentation
Ageing

then brought to ambient temperature (22°C). Apples were processed as in Treatment 1. As an increased amount of suspended material in the Treatment 4 juices prevented keeving from occurring, juices were filtered through cotton sheeting. Samples were then removed for analysis.

2.3.2. Primary Fermentation

Saccharomyces cerevisiae R92 from the culture collection in the Department of Food Science, University of Guelph, was chosen for the primary (alcoholic) fermentation because of its moderate tolerance to alcohol and for its low-foaming properties. To prepare the inoculum, the yeast from the slant was first tested for respiratory efficiency by streaking the culture on acidified Potato Dextrose Agar (PDA) containing Tetrazolium chloride (red) (Appendix 1) and growing for 48 hours at ambient temperature (22°C). Two respiratory efficient colonies were selected from each of two PDA plates and then transferred to yeast broth (Appendix 1). Yeast cells were grown in broth for 48 hours while stirring and subsequently transferred to an aerobic cyclone fermenter for an additional 48 hours (Wilson, 1992). The resulting biomass was used to inoculate sterile apple juice (1:10, volume:volume), to be used as the inoculum. All growth stages of the inoculum preparation were carried out at ambient temperature (22°C).

The primary fermentation was carried out in 10 and 20 L glass carboys. Juices were supplemented with 200 mg of ammonium phosphate, dibasic per liter and inoculated (1:20, volume:volume). Fermentation was carried out at 13°C and continued until the specific gravities of the ciders reached 0.997 or until no decrease in the specific gravity was observed for four days at which time the base cider was assumed to be "dry", having

no glucose or sucrose remaining for fermentation.

Ciders were racked off their lees and stabilized at 5°C for 8 to 10 days, followed by a final racking and removal of samples for analysis.

2.3.3. Secondary Fermentation

Saccharomyces cerevisiae strain E80, a champagne yeast, was selected from the culture collection in the Department of Food Science, University of Guelph for the secondary fermentation in the bottle. The yeast was examined for respiratory efficiency, as described in Section 2.3.2. Two respiratory efficient colonies were selected from each of two PDA plates, transferred to yeast broth (Appendix 1) and incubated at ambient temperature (22°C) for 48 hours, while stirring. This broth was used to inoculate (at 10%) 200 mL of sterile apple juice prepared from concentrate. After growth for 48 hours, the fermenting juice was used to inoculate (at 10%) the cider broth described in Appendix 2 which, after 48 hours of growth, served as the inoculum for the still ciders. Growth occurred at ambient temperature (22°C) in all stages of the inoculum preparation.

The purpose of the secondary fermentation in the bottle was to produce sufficient carbon dioxide for an internal pressure of 3 to 4 atmospheres (atm) in the final cider. Sugar additions required for the bottled cider to achieve these pressures were calculated according to Amerine and Joslyn (1970). A 50% sucrose solution was prepared and sterilized by autoclave (121°C, 103392.9 Pa for 15 minutes). The appropriate volume of the sucrose solution along with the inoculum for the secondary fermentation (added at 1% (v/v) of the still cider volume) were mixed with the still base cider. Ciders were then distributed into 750 mL champagne bottles and closed with crown caps. Secondary

fermentation and ageing took place at 13°C. Bottles of cider were selected for chemical and microbial analysis at two months and five months after bottling.

2.3.4. Experimental Design

2.3.4.1. *Description of the Design*

The experiment was carried out as a randomized complete block design (Cochran and Cox, 1957). Harvest years and apple varieties were combined to form nine Blocks (replicates). The four different treatments, as described in section 2.3.1., were applied to each of these Blocks. Samples were taken for the analyses at the following four times in the fermentation process: after keeving of the juice (Time 1); after cold stabilization of the still cider (Time 2); at two months in the bottle (Time 3); at five months in the bottle (Time 4).

The response criteria were selected to give an indication of the quality of the ciders. Response criteria for the juices and ciders included: specific gravity, mold and yeast populations, pH, titratable acidity, volatile acidity, free and total sulfur dioxide, ash, ash alkalinity, dry weight, phenols, pectin content and concentrations of sugars, glycerol and alcohols. Yield was also determined for the juices. Ciders were analyzed for mineral content. Gushing tendency was included for bottled ciders. Response criteria for the cider sediments were: weight per volume of cider, pectin content, mineral content and dry weight.

2.3.4.2. *Objectives*

The main objective of Part One was to compare the effects of the four different processing treatments on the quality characteristics of the cider and on the tendency of the bottled ciders to gush. Changes in the characteristics of the ciders from these different treatments over the course of the vinification period were also of interest. Apple varieties were chosen to represent a broad sample of Ontario apple varieties.

The objectives for Part One of the study were:

(i) to determine whether treatments influence the response criteria

(ii) to contrast the characteristics of Treatment 1 (control) against the three other processing treatments within each sampling time, as the methodology used for Treatment 1 was known to produce non-gushing ciders.

2.3.4.3. *Statistical Analysis*

The data were subjected to an analysis of variance using SAS (1989) according to the data analysis plan in Table 2. The data were analyzed separately for each sampling time, in order to emphasize the differences between the four treatments at each time. This format highlights new information obtained in this study regarding changes in the response criteria over the course of the fermentation; this information is not available in the literature.

The data (Appendix 3) from all analyses were processed and summarized so that treatment comparisons could be made based on individual degrees of freedom. Treatments 2, 3 and 4 were contrasted against the control (Treatment 1), as indicated in Figure 2. Treatment means were also computed. Analysis of variance tables as generated by SAS are in Appendix 4. Tests were conducted at a significance level of $\alpha = 0.05$.

Table 2. Analysis of variance (ANOVA) plan.

Source of variation	Degrees of Freedom		
Block [a]	8		
Treatment	3		
Treatment 1 vs. Treatment 2		1	
Treatment 1 vs. Treatment 3		1	
Treatment 1 vs. Treatment 4		1	
Experimental Error	24		(24)
(Sampling Error [b])			(36)
TOTAL	35		(71)

[a] Block = Year * Variety
[b] for some responses, two determinations were made on each experimental unit, allowing estimation of sampling error variance

Block effects are presented in summary form in Appendix 5a as much of this information is also not available in the literature. For the interest of the reader, non-significant Treatment means are reported in Appendix 5b.

2.3.5. Analytical Procedures

Juice and still cider samples were analyzed without further clarification. Samples of bottled ciders undergoing secondary fermentation and ageing were degassed (Amerine and Ough, 1980). Centrifugation for twenty minutes at 21600 g was used to separate sediments from the ciders; both sediments and ciders were analyzed.

Juice yield (L) was calculated per weight (kg) of fresh apples. Specific gravity,

titratable acidity, volatile acidity, free and total sulfur dioxide, ash and alkalinity of ash analyses were carried out according to Amerine and Ough (1980). The pH was determined with an Accumet model 1001 pH meter. Dry weight of juices, ciders and sediments was obtained by drying the sample at 45°C (to avoid sugar caramelization) in a gravity convection oven to constant weight and expressed as grams per gram of wet weight. Total phenols of the bottled ciders (1995 only) were determined by spectrometry (Beckman DB-G Grating Spectrometer) using the method of Somers and Evans (1977); the Folin-Ciocalteu method could not be used because of interference by sugars (Amerine and Ough, 1980) and also possibly by pectins. Pectins were analyzed by the *m*-hydroxydiphenyl method (Robertson, 1979) and expressed as uronic acid; Pectin Fraction 1 represents the water soluble fraction (high methoxy), Pectin Fraction 2 is the oxalate soluble fraction (low methoxy) and Pectin Fraction 3 is the fraction of pectin soluble only in hydroxide. Mold and yeast populations were estimated by plating on acidified Potato Dextrose Agar and enumerating after 3 to 5 days at ambient temperature (22°C).

Glucose, fructose, sucrose and glycerol concentrations in the juices and ciders were determined using a Waters 600E HPLC System with a 700 Satellite WISP sampler. Cider samples were passed through a 0.45 μm filter and injected directly (20 μL). Juice samples were diluted by 80% with Milli-Q water before filtration and injection. Separation of the sugars and glycerol was achieved with a Jones Chromatography Apex Amino column (JC4M25340, 4.6 x 250 mm) at 35°C and eluted with an acetonitrile solution (8:1, acetonitrile:Milli-Q water (v/v)) at 2.0 mL / min. Detection was carried out with a Waters 410 Differential Refractometer and recorded on a Waters Maxima 815 data station.

Ethanol and methanol were analyzed by a Hewlett Packard 5830A gas

chromatograph equipped with a Hewlett Packard 18850A GC terminal. Separation was achieved with a Porapak Q-S ethylvinylbenzenedivinylbenzene copolymer column from Chromatographic Specialties with a 100/120 mesh size. A flame ionization detector (FID) was used, with nitrogen as the carrier gas. Operating conditions of the GC were: injector temperature at 200°C, FID at 230°C, oven temperature at 150°C, FID hydrogen flow at 30 mL / min and FID air flow at 200 mL / min. Cider samples were diluted by 15% with Milli-Q water; juice samples required no dilution. All samples, along with 2-propanol as an internal standard, were passed through a 0.45 μm filter and injected directly (1 μL) into the chromatograph.

Minerals in the bottled ciders (Times 3 and 4) and their sediments (Time 4 only) were analyzed by Inductively Coupled Plasma (ICP) spectroscopy (AOAC, 1988) at A&L Canada Laboratories East, Inc., London, Ontario.

2.4. Results and Discussion

2.4.1. Observations During Processing

Although Treatment 2 juice was treated with sulfur dioxide immediately following juice extraction, the juice after keeving was not much lighter in colour (brown) than the juice of Treatment 1. During keeving it seemed that most of the sulfur dioxide reacted with material in the "brown cap" as the cap was not brown but rather yellow-green in colour, indicative of the anti-oxidative action of the sulfite. This observation was supported by the chemical analyses for free and total sulfur dioxide in that the concentrations in Treatment 2 juices were not significantly different from those in Treatment 1 juices (Section 2.4.3.1.1.; Appendices 3 and 4).

During storage of Treatment 3 apples, the varieties with a more waxy bloom (Table 1) showed lower levels of desiccation and shrivelling. Golden Russet apples shrivelled the most. Spy apples tended to reach senescence more quickly than the other varieties during storage. Moisture loss during storage resulted in significantly lower juice yields for Treatment 3 (Tables 3 and 4).

Treatment 4 apples required three or four days at 5°C to thaw thoroughly. In preliminary trials using frozen apples it was necessary to entirely thaw the apples for maximum juice yield (data not shown). In most cases, the apples exuded a thick sugary syrup during thawing, creating the opportunity for microbial growth. After thawing, the colour of the skin of the apples of all varieties was brown. The flesh of the apples remained similar in colour to that of fresh apples but the texture was soft, suggesting extensive cellular breakdown. Difficulties in juice clarification (lack of keeving) resulted in a slight decrease in the amount of juice available for the production of cider compared to the control (Treatment 1), as shown by the lower yield (Tables 3 and 4). Juices produced in Treatment 4 were more cloudy than juices from the other three treatments and appeared to be more viscous.

2.4.2. Observations During Primary and Secondary Fermentations

Juices of Treatments 1, 2 and 3 fermented in a similar manner during the primary fermentation, regardless of apple variety or harvest year. Fermentation was evident within 48 hours after inoculation and was completed within a month. The rate of fermentation of some of the Treatment 4 juices varied from those of the other treatments. In the first year, the fermentation rate of the Spy juice from Treatment 4

was quite rapid, the cider reaching "dryness" in less than three weeks. Conversely, Treatment 4 juices from Crispin, McIntosh and Russet in 1994 required five weeks to ferment to dryness. Treatment 4 Hyslop juice took four weeks to ferment to completion; by the end of the fermentation, approximately twenty-five percent of the glass carboy was filled with a dense, milky-coloured pectinaceous sediment but the cider was clear. This large amount of sediment reduced the volume of Hyslop cider available for bottling to just 1.4 L. In 1995, Treatment 4 juices of Crispin and McIntosh fermented to dryness in four weeks; Spy and Russet juices required five weeks to complete the fermentation.

Ciders which were cloudy at the end of primary fermentation also remained cloudy during the secondary fermentation; cloudy ciders became clear gradually during ageing, with the exception of Treatment 4 Spy cider in 1995, which never clarified. Several of the cloudy ciders produced significantly larger amounts of sediment in the bottle than those which were clear when bottled. McIntosh cider in 1995 was unusual for Treatment 4 -- after two months in the bottle, the cider became a semi-liquid carbonated gel when the bottle was opened, from which no sediment could be isolated (Appendix 3); at five months in the bottle, the gel had undergone seneresis and was surrounded by "still" cider, suggesting that the carbon dioxide had become trapped in the gel. As a result of the small volume of Hylsop Treatment 4 cider at the end of the primary fermentation, only about 650 mL of cider could be distributed into each of two 750 mL bottles at time of bottling.

None of the ciders from Treatments 1, 2 or 3 showed any tendency to gush (Appendix 3). Treatment 4 ciders gushed, often at two months in the bottle and invariably at five months in the bottle, despite cooling to 10°C prior to opening.

There were two Treatment 4 ciders which did not gush: Hylsop in 1994 and McIntosh in 1995. The smaller liquid volumes of the bottled Treatment 4 Hyslop ciders resulted in headspace volumes of approximately 100 mL which may have eliminated the gushing tendency. The gushing in the McIntosh cider was undoubtedly inhibited by the formation and seneresis of the pectinaceous gel. Treatment 4 Crispin ciders in both years were clear and showed very low levels of gushing, better described as slight overflowing of the cider rather than gushing. The Treatment 4 Spy cider produced in 1995 was the cloudiest of all the ciders and gushed explosively, resulting in the loss of most of the contents of the bottle when opened at 5 months after bottling.

2.4.3. Chemical and Microbiological Analyses

The raw data obtained from the chemical analyses of the juices, ciders and sediments are contained in Appendix 3. The analysis of variance (ANOVA) tables in Appendix 4 were generated by the SAS computer program. Statistical analysis of the data was conducted separately for each sampling time, so that the differences between the treatments at each sampling time could be examined more thoroughly. It was expected that most of the chemical analyses would change over the course of the fermentation, so the effect of the sampling time was not of interest in this study. As Block (Year x Variety) effects were not related to gushing tendency, they are summarized in Appendix 5a.

Significant treatment effects are presented in tables throughout Section 2.4.3.; non-significant treatment effects are presented only in the text, but are summarized in Appendix 5b.

2.4.3.1. *Sampling Time 1: Analysis of the Juices*

2.4.3.1.1. Chemical Analyses

The specific gravities of the juices of Treatments 2, 3 and 4 were not significantly different from the control, Treatment 1. The overall mean specific gravity of the juices was 1.059.

The pH and titratable acidity of Treatment 2 juices did not differ significantly from the control. A significant increase in the pH and decrease in the titratable acidity was observed in Treatment 3 juices (Tables 3 and 4). This is consistent with the results of research on Canadian apples by other authors (Bowen *et al.*, 1959; Dever *et al.*, 1991) who noted that fruit, when stored, tended to undergo these changes in acidity. The respiration of the fruit, which continued during storage, involves the decomposition of malic acid (Webb and Coombe, 1994) via oxidative decarboxylation and for gluconeogenesis (Blanco *et al.*, 1992). Respiration could, therefore, cause significant decreases in titratable acidity and increases in pH. A significant decrease in acidity was observed in juices from Treatment 4 apples; these trends have also been observed in musts produced from thawed grapes (Spayd *et al.*, 1987). As the mushy texture of the flesh of thawed apples indicated cellular breakdown, these changes in pH and titratable acidity were not unexpected; cell rupture would have released enzymes such as malic acid dehydrogenase, leading to a decrease in malic acid (Braverman, 1969). Apple cell walls are composed largely of polysaccharides, mainly cellulose and pectins with calcium ion cross-bridges, in addition to sugars (Renard *et al.*, 1990). Thawing damages both cell membranes and cell walls (Ahmed

Table 3. Juice analysis: significance[a] of Treatment contrasts[b].

Response Variable	Treat[c] 1 vs Treat 2	Treat 1 vs Treat 3	Treat 1 vs Treat 4	Error df[d]	Error mean square
Yield (L juice / 100 kg apples)	ns	**	*	24	25.24
Molds (colonies / mL)	ns	ns	*	24	9.55×10^{10}
Yeasts (colonies / mL)	ns	ns	*	24	5.43×10^{14}
pH	ns	**	**	24	0.01569
Titratable Acidity (g malic acid / 100 mL)	ns	**	**	24	0.003994
Volatile Acidity (g acetic acid / 100 mL)	ns	**	ns	24	0.0002955
Free Sulfur Dioxide (mg / L)	ns	*	ns	23	6.380
Ash (g / 100 g juice sample)	ns	*	*	24	0.0665
Pectin Fraction 1 (µg uronic acid / g juice)	ns	ns	**	24	413199
Pectin Fraction 3 (µg uronic acid / g juice)	ns	ns	*	24	68.85
Fructose (g / 100 mL)	ns	**	ns	21	0.9193
Glucose (g / 100 mL)	ns	*	ns	21	0.2515
Sucrose (g / 100 mL)	ns	**	**	20	0.236
Ethanol (g / 100 mL)	ns	ns	**	19	0.0299

[a] * , ** : significant at $\alpha = 0.05$ and 0.01 respectively   ns : not significant

[b] only the response variables having at least one significant contrast are contained in this table; response variables with no significant Treatment contrasts are discussed in the text only

[c] Treat = Treatment

[d] degrees of freedom, accounting for missing data and for outliers removed

Table 4. Juice analysis: Treatment means (adjusted)[a, b]. Means are of 9 observations.

Response Variable	Treatment 1	Treatment 2	Treatment 3	Treatment 4	Standard Error of Diff.[c]
Yield (L juice / 100 kg apples)	37.7	37.4	20.4	32.3	2.368
Molds (colonies / mL)	150	110	108	2.30×10^5	1.46×10^5
Yeasts (colonies / mL)	3	4	72	1.61×10^7	1.10×10^7
pH	3.25	3.30	3.64	3.53	0.1961
Titratable acidity (g malic acid / 100 mL)	0.665	0.658	0.470	0.604	0.02978
Volatile acidity (g acetic acid / 100 mL)	0.0063	0.0059	0.0245	0.0116	0.008097
Free sulfur dioxide (mg / L)	5.02	5.32	6.81	6.20	1.9006
Ash (g / 100 g juice)	0.456	0.482	0.680	0.252	0.1578
Pectin Fraction 1 (µg uronic acid / g juice)	90.0	95.6	290.1	1243	303.02
Pectin Fraction 3 (µg uronic acid / g juice)	6.96	8.36	9.45	12.87	3.9115
Fructose (g / 100 mL)	4.91	4.56	6.40	4.74	0.102
Glucose (g / 100 mL)	1.77	1.44	2.40	2.02	0.363
Sucrose (g / 100 mL)	4.03	4.12	3.33	3.51	0.696
Ethanol (g / 100 mL)	0.0001[d]	0.024	0.057	0.280	0.2601

[a] least-squares means, to adjust for missing data and outliers removed

[b] only the response variables having at least one significant contrast are contained in this table; response variables with no significant Treatment contrasts are discussed in the text only

[c] average standard error of the difference of two means

[d] Detection limit by HPLC

et al., 1991; Tregunno and Goff, 1996). Damage to the cell walls of the apple tissue would have released the polysaccharide components into the juice. Although cell damage undoubtedly occurred through the method of juice extraction, the extent of this damage was further increased by the action of freezing and thawing of the fruit in Treatment 4. The increase in pH and decrease in titratable acidity observed in Treatment 4 juices was possibly due to the reaction of malic acid with the calcium ions released during cell disruption.

Volatile acidity is a measure of the fatty acids in the juice, such as acetic, formic and butyric acids (Amerine and Ough, 1980). Higher levels of volatile acidity are usually associated with bacterial spoilage (Iland *et al.*, 1993). The increased time of storage of Treatment 3 apples provided an opportunity for spoilage bacteria to grow and to increase the volatile acidity (Tables 3 and 4). At such low levels, the volatile acidities of the juices have no practical consequence.

The Ripper method (Amerine and Ough, 1980), used to determine free and total sulfur dioxide in the juice, is based on the redox reaction in which iodine reacts with the sulfur dioxide (Iland *et al.*, 1993). Unfortunately, the iodine may also react with some of the phenols, sugars, aldehydes and other substances in the juices. The levels of total sulfur dioxide in Treatments 2, 3 and 4 were not significantly different from the control. The overall mean concentration of total sulfur dioxide in the juices was 16.34 mg / L. Free sulfur dioxide levels are related to the total sulfur dioxide concentration in the juice and are affected by the pH of the juice and the sulfite-binding capabilities of the juice constituents (Amerine and Ough, 1980); only free sulfur dioxide levels in Treatment 3 juices were significantly different from the control (Tables 3 and 4). In practical terms, this slight increase observed in Treatment 3

juices is inconsequential; it is suspected that this increase is the result of interference in the Ripper method by increased sugar concentrations (fructose and glucose).

Ash is the inorganic matter that remains after evaporation and incineration. During the ashing process cations in the juice are converted to carbonates and other anhydrous mineral salts and the ammonium ion is lost (Amerine and Ough, 1980). The significantly lower concentration of ash in the Treatment 4 juices would be consistent with the release of neutral sugars (Renard *et al.*, 1990) such as pectins (Tregunno and Goff, 1996) during the freezing and thawing procedures, thus increasing their concentration in the juice. The desiccation and shrivelling of Treatment 3 apples are indicative of water loss and this loss is reflected in the decreased juice yield and higher ash content (Tables 3 and 4). Despite the conversion of starch to sugar during storage of apples (Beech, 1972b), the results of the chemical analysis suggest that the water loss had a greater effect on the ash concentration (Tables 3 and 4).

The alkalinity of the ash of all juices, compared to the control, was not significant; the overall mean was 29.4 milliequivalents (meq.). Dry weight of the juices was also not significantly different between the treatments. The overall dry weight was 13.6 g per 100 g of "wet" juice sample.

Pectin Fractions 1 (water soluble) and 3 (hydroxide soluble) were in significantly higher concentrations in juices from Treatment 4 apples. The cell walls of apple tissue are composed of approximately 80% polysaccharide material, a high proportion of which is pectin (28%). Approximately 45% of this pectin material is highly methylated (Renard *et al.*, 1990), which in the chemical analysis of the pectin would be classified as Fraction 1 (Robertson, 1979). Low methoxy pectins (Fraction

2) and alkali soluble pectins (Fraction 3) are also present in the cell walls (Renard *et al.*, 1990). Disruption of the cell walls by the freezing and thawing process in Treatment 4 would have increased the release of these pectins from the cell wall material into the juice. Since a large proportion of the pectin in the cell wall is water soluble, the influence of the cell wall disruption is consequently more evident in Pectin Fraction 1 (Tables 3 and 4). The concentration of Pectin Fraction 3 is also slightly higher in juices from thawed apples. Pectin Fraction 2 was not significantly different in Treatments 2, 3 or 4, compared to Treatment 1; overall mean for this fraction was 47.81 μg / g of juice.

Sugar concentrations in Treatment 2 were not significantly different from those in Treatment 1. For Treatment 3 juices, all three sugars (fructose, glucose and sucrose) were significantly different from the control; fructose and glucose concentrations were much higher, and sucrose concentration was lower in Treatment 3 compared to Treatment 1 (Tables 3 and 4). These changes in sugar concentrations of juices from stored apples was also observed by Fuleki *et al.* (1994), who attributed the decrease in sucrose mainly to inversion of the sugar during storage, consequently increasing the glucose and fructose of the fruit. Some sugar may also have been lost through respiration during apple storage. In Treatment 4, sucrose was the only sugar significantly different from the control. Inversion of sucrose during thawing of fruit can be quite pronounced (Joslyn, 1966), although the decrease in the concentration of sucrose did not result in significant increases in glucose or fructose in this study (Table 3). Glycerol, a product of yeast fermentation (Amerine and Ough, 1980), was not detectable in any of the juices.

Methanol could not be detected in juices from Treatments 1, 2 and 3.

Treatment 4 juices contained very low but measurable amounts of methanol; the average methanol concentration in Treatment 4 juices was 4 mg / 100 mL. In cider production, methanol is produced exclusively through the enzymatic activity of pectin methylesterase (Cordonnier, 1987); pectin methylesterase has been detected in strains of *Hanseniaspora, Pichia, Brettanomyces* and *Dekkera spp.*, but not in *Saccharomyces cerevisiae* (Panon *et al.*, 1995). The large yeast population in the Treatment 4 juices (Tables 3 and 4) likely contained strains of yeast which possess pectin methylesterase. The high concentrations of pectin in Treatment 4 juices would have provided large amounts of substrate for this pectinase activity.

Compared to the control, the concentration of ethanol was significantly higher in only the Treatment 4 juices (Tables 3 and 4). Although present in very small quantities, the elevated concentration of ethanol supports our hypothesis that the length of thawing time and liquid exuded from the apples during the thawing encouraged the growth of yeasts and other microorganisms present in the sealed bags. Fermentation of sugars in the syrupy liquid exuded from the fruit by the yeasts would have produced ethanol (Webb, 1984).

In the first year of research, all apple juices were analyzed for starch using an enzymatic test kit (Boehringer Mannheim). Since no starch could be detected in any of the juices, this analysis was discontinued.

2.4.3.1.2. Microbiological Analyses

Mold and yeast populations were significantly higher in the Treatment 4 juices compared to the control (Tables 3 and 4; Appendix 3). The thick syrup released from

the apples over the thawing period would have provided an ideal substrate for a variety of microorganisms. The high native mold and yeast populations (10^5 to 10^7 colonies / mL) in the juices of Treatment 4 would undoubtedly have a significant influence on the organoleptic properties of the juice and on the fermentation of the juice.

2.4.3.2. *Sampling Time 2: Analysis of the Still Ciders*

2.4.3.2.1. Chemical Analyses

The specific gravities of Treatment 3 still ciders differed significantly from the control at the end of the fermentation (Tables 5 and 6). Specific gravity of a fermented beverage is influenced by organic acids, sugars and polysaccharides, proteins and other components including alcohols. As a result of the influences of such a large combination of factors, specific gravity should only be used as a rough estimation of the degree of completeness of the fermentation (Amerine and Ough, 1980). The higher ethanol concentration in the Treatment 3 ciders (Table 6) could be responsible for the significantly lower specific gravities.

The pH of Treatment 3 ciders was significantly higher and the titratable acidity significantly lower that those of the control ciders (Treatment 1; Tables 5 and 6). These results are consistent with those of the juice analysis for this treatment (Tables 3 and 4). The mean pH of Treatment 4 ciders was also significantly higher than that of Treatment 1 ciders; this too is consistent with the juice results. Treatment 4 ciders did not have significantly lower mean titratable acidities than the control as was the

Table 5. Analysis of still ciders: significance[a] of Treatment contrasts[b]

Response Variable	Treat[c] 1 vs. Treat 2	Treat 1 vs. Treat 3	Treat 1 vs. Treat 4	Error df[d]	Error Mean Square
Yeasts (colonies / mL)	ns	ns	*	24	1.83×10^{14}
Specific gravity	ns	*	ns	24	0.0000014
pH	ns	**	**	24	0.005811
Titratable acidity (g malic acid / 100 mL)	ns	**	ns	24	0.002761
Ash (g / 100 g cider)	ns	ns	ns	24	0.003553
Alkalinity of ash (milliequivalents)	ns	**	ns	24	29.205
Dry weight[e] (g / 100 g "wet" sample)	ns	*	*	8	0.01317
Pectin Fraction 1 (μg uronic acid / g cider)	ns	ns	**	24	326339
Pectin Fraction 3 (μg uronic acid / g cider)	ns	ns	*	24	53.22
Fructose (g / 100 mL)	ns	**	ns	29[f]	0.00524
Glycerol (g / 100 mL)	ns	ns	*	29	0.00390
Ethanol (g / 100 mL)	ns	ns	ns	24	0.61140

[a] * , ** : significant at $\alpha = 0.05$ and 0.01 respectively ns : not significant

[b] only the response variables having at least one significant contrast are contained in this table; response variables with no significant Treatment contrasts are discussed in the text only; exceptions: ethanol and ash, as their changes in concentration from the juice to the still cider are noteworthy

[c] Treat = Treatment

[d] degrees of freedom, accounting for missing data and for outliers removed

[e] Dry weight not determined in 1994

[f] a few samples were analyzed in duplicate for the sugars

Table 6. Analysis of still ciders: Treatment means (adjusted)[a, b]. Means are of 9 observations.

Response Variable	Treatment 1	Treatment 2	Treatment 3	Treatment 4	Standard Error of Diff. [c]
Yeasts (colonies / mL)	6.14×10^5	6.06×10^5	4.30×10^5	1.19×10^7	6.38×10^6
Specific gravity	0.9975	0.9975	0.9969	0.9978	0.000558
pH	3.52	3.52	3.75	3.61	0.03593
Titratable acidity (g malic acid / 100 mL)	0.555	0.555	0.433	0.532	0.0247
Ash (g / 100 g cider)	0.287	0.293	0.322	0.281	0.02810
Alkalinity of ash (milliequivalents)	24.04	23.16	29.84	27.28	2.5475
Dry weight [d] (g / 100 g "wet" sample)	1.82	1.78	1.92	1.92	0.08115
Pectin Fraction 1 (µg uronic acid / g cider)	125.3	119.2	328.4	1133.5	269.29
Pectin Fraction 3 (µg uronic acid / g cider)	3.32	2.66	3.83	9.37	3.439
Fructose (g / 100 mL)	0.045	0.081	0.147	0.081	0.0341
Glycerol (g / 100 mL)	0.365	0.375	0.358	0.434	0.02944
Ethanol (g / 100 mL)	5.56	6.00	6.19	5.41	0.3686

[a] least-squares means, to adjust for missing data and outliers removed

[b] only the response variables having at least one significant contrast are contained in this table; response variables with no significant Treatment contrasts are discussed in the text; exceptions: ethanol and ash, as their changes in concentration from the juice to the still cider are noteworthy

[c] average standard error of the difference of two means

[d] Dry weight was not determined in 1994; means are of 4 observations

case with the juice samples. It is usual for the titratable acidity to decrease during fermentation (Webb, 1994). As a result of the high microbial population in Treatment 4 juices prior to inoculation, it is likely that the fermentation of these juices progressed differently than those of the other treatments. The differences in fermentation would have resulted in changes in titratable acidity which were not the same in Treatment 4 ciders compared to those which occurred in Treatment 1 ciders, thus eliminating the significant difference between the two treatments over the course of the fermentation. Volatile acidity was not significantly different for Treatments 2, 3 and 4 compared to Treatment 1; the overall mean volatile acidity was 0.020 g acetic acid / 100 mL.

Free and total sulfur dioxide levels of Treatments 2, 3 and 4 were not significantly different from the control. The overall mean concentrations of free and total sulfur dioxide in the ciders were 9.58 mg / L and 16.70 mg / L respectively.

Ammonical nitrogen was added to all juices at the time of inoculation in the form of ammonium phosphate, dibasic (200 mg / L). By the end of the fermentation ammonical nitrogen could not be detected in ciders of Treatments 1, 2 and 4. A very small amount of ammonical nitrogen was detected in Treatment 3 ciders; the mean concentration of ammonical nitrogen in these ciders was 1.6 mg / L.

The ash content of the ciders was not significant for any of the Treatment contrasts; the overall mean for ash was 0.296 g / 100 g cider. The alkalinity of ash was significantly higher for Treatment 3 ciders when compared to the control ciders. Ash alkalinity is a measure of the quantity of organic acid salts present (Amerine and Ough, 1980) . This characteristic may be of interest in determining the balance between organic cations and anions in quality control aspects of cider production. The dry weights of Treatments 3 and 4 were significantly higher than the control; as a

higher non-alcohol residue is indicative of a higher initial sugar content of the juice (Amerine and Ough, 1980), this was not unexpected.

The significance of the treatment contrasts with respect to the three pectin fractions corresponds to the results obtained for the juices. None of the contrasts were significant for Pectin Fraction 2; the overall mean for this fraction was 9.85 μg / g cider, much less than in the juice (47.81 μg uronic acid / g juice). Pectin Fraction 1 of Treatments 2 and 3 was not significantly different than that of Treatment 1. Concentrations of Pectin Fraction 1 in Treatments 1, 2 and 3 increased from the juice to the cider in amounts approximately equal to the observed decreases in Pectin Fraction 2. Polygalacturonase activity has been detected in *Saccharomyces cerevisiae* (Panon *et al.*, 1995); this enzyme hydrolyzes the glycosidic chains of the pectin molecule between nonesterified residues of galacturonic acid (Canal-Llaubères, 1989) thus decreasing the molecular weight and increasing the solubility of the molecules (Pomeranz and Meloan, 1994). Therefore, as pectin chains originally measured in Fraction 2 decreased in molecular weight due to hydrolysis, they would have become part of the Fraction 1 pectins. Treatment 4 ciders had significantly higher concentrations of Pectin Fractions 1 (water soluble) and 3 (hydroxide soluble), which can be directly attributed to the processing treatment of the apples. However, there was a large decrease in the pectin concentration (Pectin Fraction 1) between the juices and ciders of Treatment 4 (Tables 4 and 6), indicating some degree of pectin precipitation or degradation during the fermentation period. Pectin can be precipitated by ethanol and methanol, depending on the concentration of the alcohol(s) and the degree of esterification of the pectin molecule (Pomeranz and Meloan, 1994). Methanol in Treatment 4 ciders increased slightly to 6 mg / L, compared to the

corresponding juices, which indicates that the pectin methylesterase activity continued after juice inoculation. Methanol was not detected in ciders produced in Treatments 1, 2 and 3.

Glucose and sucrose were depleted from the ciders during the course of the fermentation. Fructose concentrations in Treatment 3 ciders were significantly higher than in the control (Tables 5 and 6), although such low concentrations are of no practical importance; fructose concentrations were also initially significantly higher in Treatment 3 juices (Tables 3 and 4).

Glycerol is produced due to an excess of NADH in the cells during yeast fermentation. Its production is influenced by fermentation temperature, yeast strain, pH, initial sugar concentration and aeration conditions (Amerine and Ough, 1980), but none of these influences seem to apply to the increased glycerol production in Treatment 4 ciders. It is possible that sugars resulting from the degradation of pectin molecules by polygalacturonase activity provided the excess NADH required for higher levels of glycerol production.

Ethanol concentrations in Treatments 2, 3 and 4 were not significantly different from those of Treatment 1 (Tables 5 and 6) despite the differences in sugar concentrations in the original juices. The overall mean ethanol concentration of the ciders was 5.79 g / 100 mL.

2.4.3.2.2. Microbiological Analyses

Molds were not detected in any of the ciders. The molds in the juices were

likely killed by the alcohol produced during the fermentation. There were significantly more yeasts in Treatment 4 ciders compared to the control (Tables 5 and 6). This was probably due to the significantly larger yeast population present in Treatment 4 juices prior to inoculation.

2.4.3.2.3. Mineral Analyses of Ciders

Results of the mineral analysis of the ciders are presented in Tables 7 and 8. The nitrogen concentration in Treatment 4 ciders was significantly higher than in the control. Disruptions to the cell walls and membranes of the apple tissue during the freezing/thawing process of Treatment 4 would have resulted in the release of cellular components, including enzymes (Braverman, 1969; Heber and Schmitt, 1981), increasing the total nitrogen content in the juice and, subsequently, the ciders. The higher nitrogen concentration in the Treatment 4 ciders may also reflect the significantly larger microbial population in this treatment (Tables 5 and 6). Magnesium, calcium, sodium, aluminum, manganese and copper were in significantly higher concentrations in Treatment 4 ciders (Tables 7 and 8). In the cell walls of apples, divalent ions bridge residues of galacturonic acid attached to adjacent pectic chains. These divalent ion-pectin complexes act as intercellular cement to give firmness to the apple tissue (Alonso *et al.*, 1997). Disruption of the cell walls would have released these divalent ions along with the pectin. The other minerals would also likely have been released due to cell disruption by the processing treatment, thus increasing their concentration in the juice and subsequently in the cider.

Table 7. Mineral analysis of still ciders: significance [a] of Treatment contrasts.

Response Variable	Treat [c] 1 vs Treat 2	Treat 1 vs Treat 3	Treat 1 vs Treat 4	Error df [d]	Error mean square
Nitrogen	ns	ns	**	23	96989.8
Sulfur	*	ns	ns	24	104.9
Phosphorous	ns	**	ns	24	177.4
Potassium	ns	**	ns	24	13981.8
Magnesium	ns	ns	**	24	49.9
Calcium	ns	*	**	24	117.5
Sodium	ns	*	*	24	387.9
Aluminum	ns	ns	**	24	23.9
Manganese	ns	*	**	24	0.031
Copper	ns	*	*	24	0.0089

[a] * , ** : significant at $\alpha = 0.05$ and 0.01 respectively ns : not significant

[b] only the response variables containing at least one significant contrast are contained in this table; response variables with no significant Treatment contrasts are discussed in the text

[c] Treat = Treatment

[d] degrees of freedom; outlier removed for nitrogen

Table 8. Mineral analysis of still ciders: Treatment means (adjusted) [a, b], expressed as mg/L. Means are of 9 observations.

Response Variable	Treatment 1	Treatment 2	Treatment 3	Treatment 4	Standard Error of Diff. [c]
Nitrogen	500.9	483.7	513.3	1175.2	146.81
Sulfur	22.3	35.1	26.1	30.49	4.828
Phosphorous	110.8	112.9	128.6	111.6	6.279
Potassium	997.9	1026.2	1210.2	1061.0	55.741
Magnesium	25.5	25.7	32.3	43.1	3.33
Calcium	28.2	26.3	39.3	62.3	5.110
Sodium	20.0	12.4	43.5	44.0	9.284
Aluminum	7.6	8.9	10.3	16.5	2.305
Manganese	0.3	0.3	0.4	0.6	0.0830
Copper	0.2	0.2	0.4	0.4	0.0445

[a] least-squares means to adjust for missing data and outliers removed

[b] only the response variables having at least one significant contrast are contained in this table; response variables with no significant Treatment contrasts are discussed in the text

[c] average standard error of the difference of two means

Several minerals were also significant for Treatment 3 ciders (Table 7). Microbial and enzymatic reactions occurring over the course of the storage period may have caused some cellular disruption in the apples, although not to the same degree as the freezing/thawing of Treatment 4.

Sulfur was slightly but significantly higher in concentration in Treatment 2 ciders. This significance can be attributed to the sulfur dioxide added to the juices at time of processing. The greater sensitivity of the ICP spectroscopy over the iodine titration of the Ripper method revealed the small increase of sulfur in Treatment 2.

Iron, boron and zinc were not significant for any of the treatment contrasts; overall means were 1.9 mg / L, 2.0 mg / L and 0.4 mg / L respectively.

2.4.3.3. *Sampling Time 3: Analysis of the Ciders after Two Months in the Bottle*

2.4.3.3.1. Chemical Analyses

Specific gravities of the ciders of Treatments 2, 3 and 4 were not significantly different from the control, Treatment 1, after two months in the bottle. The overall mean specific gravity of the ciders was 0.9971.

As in the case of the still ciders, the Treatment 2 ciders at this sampling time did not differ significantly from the control. Ciders of Treatments 3 and 4 had significantly higher levels of pH and lower titratable acidities than Treatment 1 ciders (Tables 9 and 10). These results are consistent with those of the still cider analyses for these treatments (Tables 5 and 6). In all treatments, pH increased and titratable acidity decreased over the course of the secondary fermentation; it is usual for these

changes to occur during fermentation (Webb, 1994). Volatile acidity was not significantly different for Treatments 2, 3 and 4 compared to Treatment 1. The overall mean volatile acidity was 0.025 g acetic acid / 100 mL.

Free and total sulfur dioxide levels of Treatment 2, 3 and 4 were not significantly different from the control. The overall mean concentrations of free and total sulfur dioxide in the ciders were 7.95 mg / L and 16.59 mg / L respectively.

Neither the ash nor ash alkalinity was significant for any of the Treatment contrasts. The overall mean for ash was 0.292 g / 100 g cider, which corresponds to the concentration of ash in the still ciders. The overall mean for ash alkalinity was 23.4 meq.

Ammonical nitrogen was not significantly different from the control for Treatments 2, 3 or 4. Overall mean ammonical nitrogen concentration was 0.5 mg / L.

Dry weight of the Treatment 3 ciders was significantly higher than in the control (Tables 9 and 10). A higher non-alcohol residue is indicative of a higher initial sugar content in the juice, but is also influenced by the alcohol concentration, ash content and acidity of the wine. Typical values for sugar-free extracts range from 0.7 g / 100 mL for low-alcohol German wines, to more than 3 g / 100 mL for late-harvest red wines; the Office International de la Vigne et du Vin (OIV) defines "extract" as the non-volatile components of the wine (Amerine and Ough, 1980). The ciders in this research were expected to have extracts similar to those of low-alcohol German wines, although the amount of extract was likely increased by the addition of sugar for the secondary fermentation. The differences in dry weights observed in the ciders (Table 10) are consistent with the differences in the concentrations of sugars in the original juices (Table 4), wherein Treatment 3 juices contained the highest

Table 9. Analysis of ciders at 2 months in the bottle: significance[a] of Treatment contrasts[b].

Response Variable	Treat[c] 1 vs. Treat 2	Treat 1 vs. Treat 3	Treat 1 vs. Treat 4	Error df[d]	Error Mean Square
pH	ns	**	**	24	0.030622
Titratable acidity (g malic acid / 100 mL)	ns	**	**	24	0.015047
Dry weight[e] (g / 100 g "wet" sample)	ns	*	ns	9	0.09280
Pectin Fraction 1 (μg uronic acid / g cider)	ns	ns	**	24	352838
Ethanol (g / 100 mL)	ns	*	ns	23	0.19807
Total Phenols[e] (absorbance units)	ns	ns	**	16	0.08946

Table 10. Analysis of ciders at 2 months in the bottle: Treatment means (adjusted)[b, g].
Means are of 9 observations.

Response Variable	Treatment 1	Treatment 2	Treatment 3	Treatment 4	Standard Error of Diff.[h]
pH	3.59	3.60	3.90	3.82	0.0825
Titratable acidity (g malic acid / 100 mL)	0.517	0.496	0.358	0.367	0.0578
Dry weight[e] (g / 100 g "wet" sample)	1.63	1.54	2.11	1.30	0.2154
Pectin Fraction 1 (μg uronic acid / g cider)	71.23	70.62	213.5	1014.9	280.02
Ethanol (g / 100 mL)	6.06	6.01	6.58	6.14	0.2098
Total Phenols[e] (absorbance units)	10.35	11.39	10.28	2.43	0.2115

[a] * , ** : significant at $\alpha = 0.05$ and 0.01 respectively   ns : not significant

[b] only response variables having at least one significant contrast are contained in these tables; response variables with no significant Treatment contrasts are discussed in the text only

[c] Treat = Treatment

[d] degrees of freedom, accounting for missing data and for outliers removed

[e] Dry weights and total phenols were not determined in 1994; means are of 4 observations

[f] a few samples were analyzed in duplicate for the sugars

[g] least-squares means, to adjust for missing data and outliers removed

[h] average standard error of the difference of two means

concentrations of fructose and glucose.

The concentration of Pectin Fraction 1 was significantly higher in Treatment 4 ciders compared to the control; this corresponds to the results of the analysis of still ciders (Tables 5 and 6). However, concentrations of Pectin Fraction 1 decreased over the course of the secondary fermentation. This decrease could in part be attributable to the continuing polygalacturonase activity of *Saccharomyces cerevisiae*, which may have cleaved the pectin molecules into small sugar units. Some precipitation of the pectin also occurred, as was evident from the analysis of the sediment (Appendix 3; Tables 13 and 14). The slight increase observed in the methanol concentration (8 mg / L) of Treatment 4 ciders two months after bottling indicates that the pectin methylesterase activity continued during the secondary fermentation in these ciders. Methanol was not detectable in the ciders of the other three treatments.

Pectin Fraction 2 of Treatments 2, 3 and 4 did not differ significantly from that of Treatment 1. The overall mean of Pectin Fraction 2 in the ciders two months after bottling was 2.86 μg uronic acid / g cider, which is less than in the still cider. This decrease during the course of the secondary fermentation also indicates continued degradation of the pectin molecules by the polygalacturonase activity of the yeast. In addition, Pectin Fraction 2 was also precipitated during this fermentation, as it was detected in the sediment (Appendix 3). There was no significant difference in the concentration of Pectin Fraction 3 in Treatments 2, 3 and 4 compared to that in Treatment 1; the overall mean of this fraction was 3.15 μg uronic acid / g cider. Hydrolysis of water-insoluble pectic substances (Pectin Fraction 3) yields water soluble pectins (Fractions 1 and 2) (Pomeranz and Meloan, 1994). There may have been a sufficient concentration of Pectin Fraction 3 present in Treatment 4 still ciders

(Table 6) for enzymatic hydrolysis by the yeast during the secondary fermentation to decrease the concentration of this fraction to a level not significantly different from the control.

The total phenol content of ciders two months after bottling was only determined for 1995 ciders (Tables 9 and 10). Treatments 2 and 3 did not differ significantly in their total phenol content compared to the control. Treatment 4 ciders had significantly lower concentrations of phenolic substances compared to Treatment 1. During processing, Treatment 4 juices were passed through cotton sheeting because keeving did not occur. This additional processing step substantially increased the time during which the juice was exposed to air, which undoubtedly encouraged the oxidation of the phenolic substances. Oxidation of phenols leads to the condensation (Wilson, 1992) and polymerization (Meistermann, 1990) of their oxidation products, which may combine with proteins and precipitate (Macheix *et al.*, 1991; Meistermann, 1990; Müller-Späth, 1988). Once precipitated, the phenols would have been removed when the still ciders were racked off their lees (sampling Time 2).

The ethanol concentration in Treatment 3 ciders was significantly higher than in the control ciders (Tables 9 and 10). The reason for this slight difference is two-fold: although not significantly different, the ethanol concentration in the still ciders of Treatment 3 was higher than in the other ciders (Table 6); in addition, the decrease in Pectin Fraction 1 during secondary fermentation (114.9 µg uronic acid / g; Tables 6 and 10) is approximately twice the amount of the decrease observed in Treatments 1 and 2. If the polygalacturonase activity of the yeasts yielded fermentable sugar residues through hydrolysis of the pectin molecules, this would have increased the amount of carbohydrate available for fermentation and consequently increased the amount of alcohol produced.

No significance is noted in the Treatment 4 ciders with the equivalent decrease in Pectin Fraction 1 because of the lower ethanol concentration initially in the corresponding still ciders (Tables 6 and 10). Treatment 2 ciders contained slightly, but not significantly, less ethanol than Treatment 1 ciders (Tables 9 and 10). Higher sulfur dioxide concentrations, as indicated by the higher amounts of sulfur in Treatment 2 ciders (Tables 8 and 12) would likely have provided slightly less favourable conditions for metabolic activity of the yeasts at the higher alcohol concentrations and pressures inside a closed bottle, compared to Treatment 1.

None of the treatment contrasts were significant for glycerol, fructose and glucose; overall means were 0.395, 0.257 and 0.019 g / 100 mL respectively. Sucrose could not be detected in the ciders.

2.4.3.3.2. Microbiological Analyses

Yeast concentrations in Treatments 2, 3 and 4 were not significantly different from the control, Treatment 1. The overall mean was 2.62×10^4 colonies / mL.

Molds were not detected in any of the ciders.

2.4.3.3.3. Mineral Analyses of Ciders

The nitrogen concentration in Treatments 2, 3 and 4 was not significantly different from that of Treatment 1. The overall mean nitrogen concentration was 987.4 mg / L. Yeasts added as inoculum for the secondary fermentation would have increased the nitrogen content of the ciders, as reflected in the higher concentrations in Treatments 1, 2 and 3 compared to those of the still ciders (Tables 8 and 12); however, the concentration of nitrogen decreased in Treatment 4 compared to the previous sampling period. At two months after bottling, Treatment 4 ciders contained more sediment (Tables 13 and 14) than the other treatments. Precipitation of the pectinaceous components from the cider would also have caused the co-precipitation of some yeasts, although this is not reflected by the concentration of the yeasts in the sediment (Table 14) as the method of analysis measures only viable yeast cells. Once the yeast cells were trapped in the structure of the gelatinous sediment, products of their lysis would also likely remain trapped there.

The concentration of sulfur in Treatment 2 was significantly higher than that in Treatment 1 (Tables 11 and 12); this is consistent with the results observed in the still ciders (Table 8). Treatment 4 ciders were also significantly higher in sulfur concentration compared to the control (Tables 11 and 12). Lysis of yeast cells would have released minerals, including sulfur, into the cider medium. The number of viable yeast cells decreased from 10^5 cells / mL of cider to 10^4 cells / mL for Treatments 1, 2 and 3 between the sampling of the still cider (Table 6; Section 2.4.3.2.2.) and the sampling at two months in the bottle (Section 2.4.3.3.2.). Treatment 4 ciders decreased in viable yeast concentration from 10^7 cells / mL (Table 6) to 10^4 cells / mL, a much larger decrease than

the other three treatments. Lysis of the larger number of yeast cells in Treatment 4 would have significantly increased the concentration of sulfur, which is an important component of proteins, and several other minerals.

Although it is difficult to discern trends for specific minerals, the results do indicate that significantly higher concentrations of minerals are present in Treatment 4 ciders compared to the control. Pectic substances are known to interact with ions of polyvalent metals and in particular with calcium (Ca^{2+}) (Braudo *et al.*, 1992). Transition metals (Groups IVa through IIIb in the periodic table) such as iron, in concentrations as low as 2 mg / L, have been linked to gushing in beer; manganese, magnesium, aluminum, boron, sodium and calcium reportedly do not promote gushing in beer (Gray and Stone, 1956). In other work, calcium has been implicated in gushing (Kieninger, 1983).

Treatment contrasts were not significant for boron, copper and zinc. The overall means for these minerals were 2.2, 0.4 and 0.5 mg / L respectively.

2.4.3.3.4. Sediment Analysis

Significantly larger amounts of sediment were isolated from Treatment 4 ciders compared to the control (Tables 13 and 14). The flocculant, jelly-like appearance of the sediments from Treatment 4 ciders suggested significantly higher concentrations of pectin; this was confirmed by the pectin analysis (Tables 13 and 14).

Dry weights of the sediments of Treatments 2, 3 and 4 were not significantly different from the control, Treatment 1. This suggests that the significantly larger weight of wet sediment of Treatment 4 is due primarily to water. The hydrophillic nature of the

Table 11. Mineral analysis of ciders at 2 months in the bottle: significance[a] of Treatment contrasts.

Response Variable	Treat[c] 1 vs Treat 2	Treat 1 vs Treat 3	Treat 1 vs Treat 4	Error df[d]	Error mean square
Sulfur	**	ns	*	24	120.3
Phosphorous	*	ns	**	24	1010.7
Potassium	**	ns	*	24	84316.9
Magnesium	ns	ns	**	24	111.0
Calcium	ns	ns	**	24	90.80
Sodium	ns	ns	**	24	630.4
Iron	ns	ns	**	24	1.65
Aluminum	ns	ns	**	24	66.5
Manganese	ns	ns	**	24	0.014

[a] * , ** : significant at $\alpha = 0.05$ and 0.01 respectively   ns : not significant

[b] only the response variables having at least one significant contrast are contained in this table; response variables with no significant Treatment contrasts are discussed in the text

[c] Treat = Treatment

[d] df = degrees of freedom

Table 12. Mineral analysis of ciders at 2 months in the bottle: Treatment means (adjusted)[a,b], expressed as mg/L.

Response Variable	Treatment 1	Treatment 2	Treatment 3	Treatment 4	Standard Error of Diff.[c]
Sulfur	23.4	49.2	23.2	37.6	5.170
Phosphorous	113.8	151.5	129.1	158.8	14.987
Potassium	1022.0	1411.9	1132.7	1390.0	136.88
Magnesium	30.7	39.5	34.7	61.9	24.667
Calcium	35.6	42.5	38.9	82.2	4.4920
Sodium	43.2	53.0	62.9	93.3	11.836
Iron	1.1	1.8	1.4	2.8	0.6055
Aluminum	8.3	6.7	10.2	22.2	3.844
Manganese	0.5	0.5	0.6	0.8	0.05578

[a] least-squares means to adjust for missing data and outliers removed; means are of 9 observations

[b] only the response variables having at least one significant contrast are contained in this table; response variables with no significant Treatment contrasts are discussed in the text

[c] average standard error of the difference of two means

Table 13. Analysis of sediments of ciders at 2 months in the bottle: significance [a] of Treatment contrasts [b].

Response Variable	Treat [c] 1 vs Treat 2	Treat 1 vs Treat 3	Treat 1 vs Treat 4	Error df [d]	Error mean square
Yeasts (colonies / g)	*	ns	ns	57	6.47×10^{17}
Wet weight (g / 750 mL bottle)	ns	ns	*	58	0.67072
Pectin Fraction 1 (μg uronic acid / g sediment)	ns	ns	**	58	3020289.7
Pectin Fraction 2 (μg uronic acid / g sediment)	ns	ns	**	58	1144002.3
Pectin Fraction 3 (μg uronic acid / g sediment)	ns	ns	**	58	772924.7

[a] * , ** : significant at $\alpha = 0.05$ and 0.01 respectively   ns : not significant

[b] only the response variables having at least one significant contrast are contained in this table; response variables with no significant Treatment contrasts are discussed in the text only

[c] Treat = Treatment

[d] degrees of freedom, accounting for missing data and for outliers removed

Table 14. Analysis of sediments of ciders at 2 months in the bottle: Treatment means (adjusted) [a, b]. Means are of 9 observations.

Response Variable	Treatment 1	Treatment 2	Treatment 3	Treatment 4	Standard Error of Diff. [c]
Yeasts (colonies / g)	8.86×10^{8}	1.53×10^{9}	9.02×10^{8}	1.35×10^{9}	3.92×10^{8}
Wet weight (g / 750 mL bottle)	0.8033	0.8114	0.6176	1.9073	0.39205
Pectin Fraction 1 (μg uronic acid/g wet sediment)	686.4	1016	771.1	2951	831.955
Pectin Fraction 2 (μg uronic acid/g wet sediment)	418.8	529.9	864.8	2131.8	512.023
Pectin Fraction 3 (μg uronic acid/g wet sediment)	2454	2275	2223	1252	420.866

[a] least-squares means, to adjust for missing data and outliers removed

[b] only the response variables having at least one significant contrast are contained in this table; response variables with no significant Treatment contrasts are discussed in the text only

[c] average standard error of the difference of two means

pectins would have resulted in a larger water content in Treatment 4 sediments which would have been removed during drying. The overall mean dry weight of the sediments was 24.57 g / 100 g wet sample.

The concentration of viable yeasts was significantly higher in Treatment 2 ciders after two months in the bottle. However, a visual check of the Treatment means (Table 14) indicates that in practice these differences would be inconsequential.

2.4.3.4. *Sampling Time 4: Analysis of the Ciders after Five Months in the Bottle*

2.4.3.4.1. Chemical Analyses

Specific gravities of the ciders of Treatments 2, 3 and 4 were not significantly different from Treatment 1. The overall mean specific gravity of ciders after five months in the bottle was 0.9961.

The ciders of Treatments 3 and 4 had significantly higher levels of pH and lower titratable acidities (Tables 15 and 16). This is consistent with the trends observed in the ciders after two months in the bottle (Tables 9 and 10). Treatment contrasts were not significant for volatile acidity; the overall mean volatile acidity was 0.0291 g acetic acid / 100 mL. Ammoniacal nitrogen could not be detected in the ciders.

Unfortunately, the Ripper method (Amerine and Ough, 1980) is adversely affected by the presence of sugars, phenols, aldehydes and other substances capable of reacting with iodine. Although this method provides a rapid estimate of the sulfur dioxide content of the cider, the interferences caused by other cider constituents can decrease the accuracy of the results (Iland *et al.*, 1993). Therefore, despite the small but significant differences in the free sulfur dioxide concentration of Treatment 3 and the free and total sulfur

Table 15. Analysis of ciders at 5 months in the bottle: significance[a] of Treatment contrasts[b]					
Response Variable	Treat[c] 1 vs. Treat 2	Treat 1 vs. Treat 3	Treat 1 vs. Treat 4	Error df[d]	Error Mean Square
pH	ns	**	*	24	0.048929
Titratable acidity (g malic acid / 100 mL)	ns	*	*	24	0.020542
Free sulfur dioxide (mg / L)	ns	**	ns	24	19.9491
Total sulfur dioxide (mg / L)	ns	**	**	24	54.3119
Alkalinity of ash (milliequivalents)	ns	ns	**	24	270.54
Pectin Fraction 1 (µg uronic acid / g cider)	ns	ns	**	24	220476
Pectin Fraction 2 (µg uronic acid / g cider)	ns	*	ns	24	11.9361
Glucose (g / 100 mL)	--[e]	*	--	24	0.02648
Total Phenols[f] (absorbance units)	ns	ns	*	9	0.26955

[a] * , ** : significant at $\alpha = 0.05$ and 0.01 respectively   ns : not significant

[b] only the response variables having at least one significant contrast are contained in this table; response variables with no significant Treatment contrasts are discussed in the text only

[c] Treat = Treatment

[d] degrees of freedom, accounting for missing data and for outliers removed

[e] glucose was not detected in Treatments 2 and 4 (Table 16)

[f] not determined in 1994

dioxide concentrations of Treatment 4 (Tables 15 and 16), these differences most likely reflect the differences in the interfering components of the ciders.

The ash content of the ciders, compared to the control, was not significant; the overall mean was 0.257 g / 100 g cider. The alkalinity of the ash of Treatment 4 ciders was significantly higher from that of the control. Ash alkalinity is a measure of the quantity of organic acid salts

Table 16. Analysis of ciders at 5 months in the bottle: Treatment means (adjusted)[a, b]. Means are of 9 observations.

Response Variable	Treatment 1	Treatment 2	Treatment 3	Treatment 4	Standard Error of Diff. [c]
pH	3.72	3.74	3.93	3.91	0.10428
Titratable acidity (g malic acid / 100 mL)	0.437	0.408	0.336	0.327	0.06756
Free sulfur dioxide (mg / L)	12.72	12.59	7.83	9.76	2.1056
Total sulfur dioxide (mg / L)	24.49	22.56	17.35	12.84	3.474
Alkalinity of ash (milliequivalents)	26.38	30.03	21.84	41.97	7.7536
Pectin Fraction 1 (μg uronic acid / g cider)	52.28	51.91	277.4	689.7	221.34
Pectin Fraction 2 (μg uronic acid / g cider)	0.134	0.010	2.87	2.34	5.667
Glucose (g / 100 mL)	0.001	nd [d]	0.057	nd	0.02427
Total Phenols [e] (absorbance units)	10.33	11.36	10.21	2.80	0.36712

[a] least-squares means, to adjust for missing data and outliers removed

[b] only the response variables having at least one significant contrast are contained in this table; response variables with no significant Treatment contrasts are discussed in the text

[c] average standard error of the difference of two means

[d] not detectable: < 0.001 g / 100 mL

[e] not determined in 1994; means are of 4 observations

present and has theoretical interest in winemaking in determining the balance of total organic cations against the total organic anions (Amerine and Ough, 1980). The differences observed in the ash alkalinity (Tables 15 and 16) are reflected in the differences observed in the results of the mineral analysis of the ciders (Tables 17 and 18).

Pectin Fraction 1 was in a significantly higher concentration in ciders of Treatment 4 compared to the control after five months in the bottle (Tables 15 and 16). This is consistent with the results observed in ciders at the previous sampling time (Tables 9 and 10). The concentration of Pectin Fraction 1 decreased by approximately thirty percent between the sampling at two months in the bottle (Table 10) and the sampling at five months in the bottle (Table 16) for Treatments 1, 2 and 4, indicating continued degradation of the pectin by polygalacturonase activity or precipitation of the pectin molecules. Comparison of the pectin concentrations in the ciders to those in the sediments indicates that both of these processes may have occurred (Tables 10, 14, 16 and 20). Pectin Fraction 1 in Treatment 3 does not appear to have undergone degradation or precipitation (Tables 10 and 16) but rather increased during time between the two samplings. This phenomenon cannot be explained from the changes in Pectin Fractions 2 or 3 in the Treatment 3 ciders (Tables 10 and 16; Appendix 3) nor from the changes in the pectin concentrations in the sediments (Tables 14 and 20); some interference by cider's residual sugars (Table 15) in the pectin determination may have been possible.

The concentration of Pectin Fraction 2 in Treatment 3 ciders was significantly higher than in the control (Tables 15 and 16). At two months in the bottle (sampling Time 3), the mean of Pectin Fraction 2 was 2.86 μg of uronic acid / 100 mL; the concentration of Pectin Fraction 2 in Treatment 3 ciders did not change by five months in the bottle (Table 16). The concentrations of Pectin Fraction 2 in Treatments 1, 2 and 4 decreased between the samplings at two months and at five months after bottling (Table 10 and 16). These changes in pectin concentration in the ciders are due to the precipitation of the pectinaceous material, as reflected in the increase in pectin concentration in the sediments of Treatments 1, 2 and 4 (Tables 14 and 20); the concentration of pectin in the sediment of Treatment 3 remained relatively constant

between sampling at two months and at five months in the bottle.

No treatment contrasts were significant for Pectin Fraction 3. The overall mean concentration for this fraction was 2.88 μg uronic acid / g cider, slightly lower than at the previous sampling time (3.15 μg uronic acid / g cider). Some residual polygalacturonase activity by the yeasts may have caused this slight decrease.

Treatment 3 ciders had significantly more glucose than the control (Tables 15 and 16). At such extremely low concentrations, this significant difference is inconsequential. Fructose in Treatments 2, 3 and 4 did not differ significantly from the control; the overall mean concentration of fructose was 0.118 g / 100 mL of cider. Sucrose could not be detected in the ciders. No treatment contrasts were significant for glycerol; the overall concentration was 0.396 g / 100 mL. The dry weight of the ciders did not differ significantly from the control; the overall mean dry weight was 1.38 g / 100 g of cider.

The methanol concentration in Treatment 4 ciders had increased to 10.9 mg / L by five months after bottling, indicating that pectin methylesterase continued to be active. Methanol was not detected in any of the other ciders.

The concentration of ethanol in Treatments 2, 3 and 4 was not significantly different from Treatment 1. The overall ethanol concentration was 6.23 g / 100 mL. This concentration was comparable to those determined at 2 months after bottling (Table 16). As it was expected that the ciders would have completed the secondary fermentations in the bottles prior to the 5-month sampling time, a large change in the ethanol concentrations between the 2 sampling times was not anticipated.

As mentioned (section 2.4.2.), all Treatment 4 ciders gushed after five months in the bottle (Appendix 3) with the exception of Hyslop cider in 1994 and McIntosh in 1995. Observations concerning the differences between the fermentations of these non-gushing ciders and the other ciders of Treatment 4, which may have eliminated the gushing

tendency, have been described previously (section 2.4.2.).

2.4.3.4.2. Microbiological Characteristics

Viable yeast concentrations of Treatments 2, 3 and 4 did not differ significantly from the control. The overall mean concentration of yeasts in the ciders was 793 colonies per mL, which is a notable decrease from sampling time, at two months after bottling, and indicates that yeasts die when nutrient sources are depleted.

Molds were not detected in any of the ciders.

2.4.3.4.3. Mineral Analyses of Ciders

The nitrogen concentrations in Treatments 2, 3 and 4 were not significantly different from those of Treatment 1 after five months in the bottle; this result is consistent with that of the previous sampling period (Time 3). The overall mean nitrogen concentration was 1072.9 mg / L. Similarly, treatment contrasts for boron, copper and zinc remained nonsignificant; overall means were 2.8, 0.4 and 0.4 mg / L respectively.

Concentrations of iron (1.94 mg/L), phosphorous (159.9 mg/L) and potassium (1367.6 mg/L) were not significantly different in ciders of Treatments 2, 3 and 4 compared to Treatment 1 ciders; these concentrations differ little from those in the previous sampling period (Tables 11 and 12).

It is expected that during the course of the secondary fermentation and ageing (storage) of the bottled ciders that some exchange of materials, including metallic ions, would occur between the ciders and the sediments. Changes in the binding or interaction

sites of the biological materials in the sediments, for example pectins, would presumably cause the release of some metallic ions which would then be "redissolved" in the cider. Thus, fluctuations in the concentrations of the metallic ions from one sampling period to the next were not unexpected. Although one of the objectives of Part One of this research was to determine the differences between gushing and non-gushing ciders, these fluctuations between sampling periods within the same cider Treatments are interesting but not the focus of this study.

Concentrations of magnesium and calcium were significantly higher in Treatment 4 ciders compared to the control (Tables 17 and 18), consistent with the previous sampling period (Tables 11 and 12). The significantly higher concentrations of these ions in gushing ciders are contradictory to the findings of Gray and Stone (1956) in which the addition of magnesium or calcium to beer did not promote gushing. The higher concentrations of these divalent ions may be the result of their strong binding capabilities with pectin molecules (Braudo, *et al.*, 1992; Garnier *et al.* 1993; Joslyn and Phaff, 1947), a property which is utilized in industry and research in the formation of pectate gels. As pectin concentrations are significantly higher in Treatment 4 ciders (Tables 15 and 16), it follows that ions which strongly bind to pectin would also remain in the cider.

2.4.3.4.4. Sediment Analysis

Significantly larger amounts of sediment were isolated from Treatment 4 ciders compared to the control (Tables 19 and 20). The sediments of Treatment 4 ciders were flocculant and gel-like, as they had been at 2 months after bottling. Wet weights of the sediments decreased in Treatments 1 and 2 compared to the previous sampling period

Table 17. Mineral analysis of ciders at 5 months in the bottle: significance[a] of Treatment contrasts.

Response Variable	Treat[c] 1 vs Treat 2	Treat 1 vs Treat 3	Treat 1 vs Treat 4	Error df[d]	Error mean square
Sulfur	**	*	ns	24	78.9
Magnesium	ns	ns	*	24	124.2
Calcium	ns	ns	**	24	192.0
Sodium	*	ns	ns	24	824.5
Aluminum	ns	*	ns	24	193.4
Manganese	ns	*	ns	24	0.038

[a] * , ** : significant at $\alpha = 0.05$ and 0.01 respectively ns : not significant

[b] only the response variables having at least one significant contrast are contained in this table; response variables with no significant Treatment contrasts are discussed in the text

[c] Treat = Treatment

[d] df = degrees of freedom

Table 18. Mineral analysis of ciders at 5 months in the bottle: Treatment means (adjusted)[a,b], expressed as mg/L.

Response Variable	Treatment 1	Treatment 2	Treatment 3	Treatment 4	Standard Error of Diff.[c]
Sulfur	31.6	50.2	20.2	31.3	4.1873
Magnesium	41.3	40.8	39.4	55.2	5.2536
Calcium	42.8	45.5	32.7	63.6	6.352
Sodium	44.4	81.6	28.6	47.1	13.536
Aluminum	17.3	18.2	3.0	23.7	6.556
Manganese	0.6	0.6	0.4	0.4	0.0919

[a] least-squares means to adjust for missing data and outliers removed; means are of 9 observations

[b] only the response variables having at least one significant contrast are contained in this table; response variables with no significant Treatment contrasts are discussed in the text

[c] average standard error of the difference of two means

(Tables 13 and 14), and increased in Treatments 3 and 4. These changes in sediment weight accompanied changes in the total pectin content of the sediments; the treatments containing lower amounts of pectin decreased in weight while treatments whose sediments increased in total pectin also increased in sediment wet weight. However, treatment contrasts for the dry weights show that sediments from Treatments 3 and 4 have significantly lower dry weights than the control. This further supports the hypothesis put forward for the previous sampling period (Section 2.4.3.3.4.), that the wet weight differences could be attributed to the differences in water content of the sediments caused by the hydrophillic properties of the pectins.

Concentrations of viable yeasts were significantly lower in Treatment 2 and Treatment 4 sediments compared to the control. However, a visual comparison of the treatment means (Table 20) shows that the differences between the treatments are not of *practical* significance.

At five months after bottling, the sediments of Treatments 1, 2 and 3 were compact; this characteristic caused difficulty in dissolution of the sediment for the pectin analysis which may have decreased the accuracy of the analysis. Sediments of Treatment 4 dissolved readily during pectin analysis.

Pectin Fractions 1 and 2 were significantly higher in sediments of Treatment 4 compared to the control (Tables 19 and 20). The concentration of Pectin Fraction 1 in Treatment 4 was in fact more than four times higher per gram of sediment than in any of the other treatments (Table 20). The increases in the concentrations of Fraction 2 pectins in Treatments 1, 2 and 4 sediments corresponded to a decrease in the concentrations of Fraction 2 pectins in ciders (Table 18). In comparing the Treatment means of the pectin concentrations, it should be noted that the means of Table 20 are expressed per gram of "wet" sediment, rather than per 750 mL bottle. Comparisons of

total concentrations of pectin per bottle are presented graphically in Figure 2.

The concentration of Pectin Fraction 3 was significantly higher in Treatment 3 ciders than the control (Tables 19 and 20); this significance was probably caused by sampling error as the sediments of Treatment 3 and of the control did not dissolve well during the pectin analysis. Treatment 4 had the lowest concentration of Pectin Fraction 3, although this difference from the control was not significant (Tables 19 and 20).

2.4.3.4.5. Mineral Analysis of Sediments

Mineral analysis of the sediments was only conducted five months after bottling. Interestingly, the minerals having significant treatment contrasts for sediment samples (Tables 21 and 22) were different than the minerals having significant contrasts for ciders (Tables 17 and 18), which the exception of sulfur. As Treatment 4 ciders gushed after five months in the bottle (Appendix 3), the primary purpose for the mineral analysis of the sediments was to investigate differences between gushing and non-gushing ciders, to determine if minerals could have an effect on gushing.

Sulfur was significantly higher in Treatments 3 and 4 compared to Treatment 1. This result is inconsistent with those of the ciders, in which Treatment 2 ciders usually contained the higher concentration of sulfur (Tables 15 and 16) because of the processing treatment of the apples. Higher concentrations of sulfur in the sediments of Treatments 3 and 4 may result from differences in cell lysis during ageing.

The concentration of phosphorous was significantly lower in Treatment 4 ciders compared to the control. However, if the phosphorous in the sediment was recalculated as the total amount rather than per kg of sediment (Table 20 and 22), the sediment of

Table 19. Analysis of sediments of ciders at 5 months in the bottle: significance[a] of Treatment contrasts[b].

Response Variable	Treat[c] 1 vs Treat 2	Treat 1 vs Treat 3	Treat 1 vs Treat 4	Error df[d]	Error mean square
Yeasts (colonies / g)	*	ns	**	60	1.57×10^{16}
Wet weight (g / 750 mL bottle)	ns	ns	*	22	0.65690
Dry weight (g / 100 g "wet" sample)	ns	**	**	60	36.620
Pectin Fraction 1 (µg uronic acid / g sediment)	ns	ns	**	60	3296285.3
Pectin Fraction 2 (µg uronic acid / g sediment)	ns	ns	*	60	1362160.5
Pectin Fraction 3 (µg uronic acid / g sediment)	ns	**	ns	60	1304342.4

[a] * , ** : significant at $\alpha = 0.05$ and 0.01 respectively   ns : not significant

[b] only the response variables having at least one significant contrast are contained in this table; response variables with no significant Treatment contrasts are discussed in the text only

[c] Treat = Treatment

[d] degrees of freedom, accounting for missing data and for outliers removed

Table 20. Analysis of sediments of ciders at 5 months in the bottle: Treatment means (adjusted)[a, b]. Means are of 9 observations.

Response Variable	Treatment 1	Treatment 2	Treatment 3	Treatment 4	Standard Error of the Mean[c]
Yeasts (colonies / g)	1.73×10^{8}	8.31×10^{7}	1.03×10^{8}	1.47×10^{7}	5.19×10^{7}
Wet weight (g / 750 mL bottle)	0.4787	0.4939	0.7180	2.0542	0.38799
Dry weight (g / 100 g "wet" sample)	30.12	27.67	22.63	16.48	2.8527
Pectin Fraction 1 (µg uronic acid/g sediment)	567.3	394.4	820.1	3328.7	855.867
Pectin Fraction 2 (µg uronic acid/g sediment)	607.8	642.8	845.9	1766.1	550.18
Pectin Fraction 3 (µg uronic acid/g sediment)	2231.1	2716.7	3712.8	1726.1	583.38

[a] least-squares means, to adjust for missing data and outliers removed

[b] only the response variables having at least one significant contrast are contained in this table; response variables with no significant Treatment contrasts are discussed in the text only

[c] average standard error for the comparison of two means

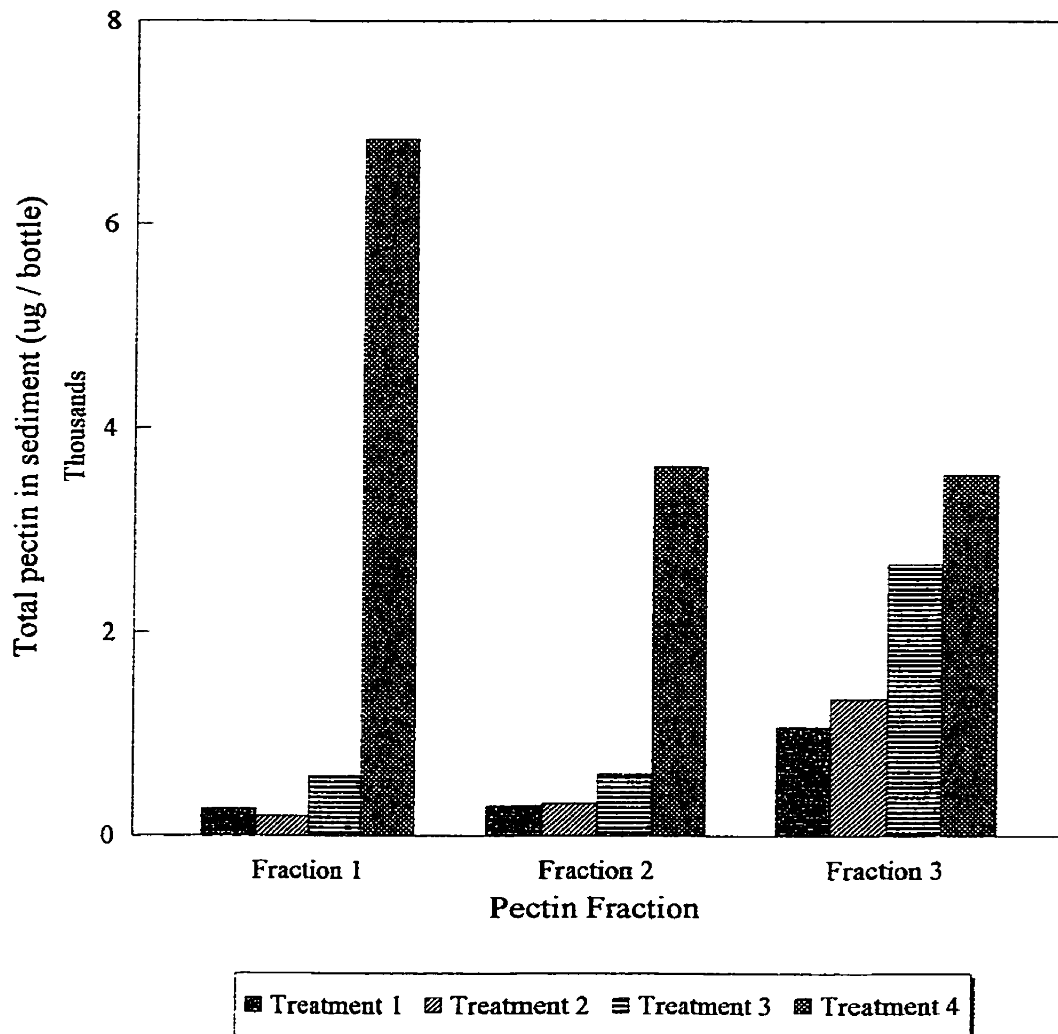


Figure 2. Pectin concentrations in sediments of ciders at 5 months after bottling. Concentrations are expressed as ug of uronic acid per bottle of cider; refer to Materials and Methods for a description of the three pectin fractions.

Treatment 1 ciders contained 0.839 mg of phosphorous compared to 1.9 mg of phosphorous in the sediment of Treatment 4 ciders. This raises the question as to whether the concentrations of the minerals in the sediments are more or less important than the total amount present -- a question which can not be fully answered without investigating the binding properties and roles of each mineral in the sediment. Phosphorous was not tested by Gray and Stone (1956) to determine its gushing activity.

The concentrations of potassium, magnesium and sodium in the sediments of Treatments 2, 3 and 4 were not significantly different from those of the control (Tables 21 and 22). The overall mean concentrations of these minerals were 1292.2, 101.46 and 168.2 mg / kg respectively.

Iron was in a significantly lower concentration in sediments of Treatments 3 and 4 than in Treatment 1 (Tables 21 and 22). Although iron was determined to be a strong promoter in the gushing of beer by Gray and Stone (1956), it can not be linked to gushing in cider (Treatment 4) (Section 2.4.3.4.3.; Table 22).

Concentrations of aluminum and manganese in sediments of Treatments 2, 3, and 4 did not differ significantly from those in the control; overall mean concentrations were 75.9 and 7.3 mg / kg respectively. Calcium, despite its affinity for binding with pectin molecules (Braudo, *et al.*, 1992; Garnier *et al.* 1993; Joslyn and Phaff, 1947) was not in significantly different concentrations in Treatment 2, 3 or 4 compared to Treatment 1, regardless of the pectin concentration of the sediment (Table 20). Overall, the mean concentration of calcium in the sediments was 289.6 mg / kg.

In the research conducted by Gray and Stone (1956), boron did not promote gushing in beer; copper showed a slight tendency to promote gushing. However, both boron and copper were in significantly lower concentrations in sediments of gushing ciders (Treatment 4) compared to the non-gushing control (Tables 21 and 22).

Table 21. Mineral analysis of sediments of ciders at 5 months in the bottle: significance[a] of Treatment contrasts.

Response Variable	Treat[c] 1 vs Treat 2	Treat 1 vs Treat 3	Treat 1 vs Treat 4	Error df[d]	Error mean square
Nitrogen	*	ns	ns	22	9175796
Sulfur	ns	*	**	24	7848.1
Phosphorous	ns	ns	**	24	290094
Iron	ns	**	**	24	182.33
Boron	ns	*	*	24	51.35
Copper	ns	ns	**	24	6073.4

[a] * , ** : significant at $\alpha = 0.05$ and 0.01 respectively   ns : not significant

[b] only the response variables having at least one significant contrast are contained in this table; response variables with no significant Treatment contrasts are discussed in the text only

[c] Treat = Treatment

[d] degrees of freedom, accounting for missing data and for outliers removed

Table 22. Mineral analysis of sediments of ciders at 5 months in the bottle: Treatment means (adjusted)[a, b], expressed as mg/kg.

Response Variable	Treatment 1	Treatment 2	Treatment 3	Treatment 4	Standard Error of Diff.[c]
Nitrogen	10277.8	13941.1	9777.0	7293.1	1471.91
Sulfur	82.4	105.2	179.6	213.9	41.761
Phosphorous	1753.6	1762.0	1398.7	943.6	253.90
Iron	35.6	28.5	10.1	11.0	6.363
Boron	20.5	19.2	12.4	12.6	11.411
Copper	179.0	176.0	163.0	41.8	36.736

[a] least-squares means to adjust for missing data and outliers removed; means are of 9 observations

[b] only the response variables having at least one significant contrast are contained in this table; response variables with no significant Treatment contrasts are discussed in the text

[c] average standard error of the difference of two means

Treatment contrasts were not significant for the concentrations of zinc in the sediments. The overall mean zinc concentration was 42.4 mg / L.

The results of Gray and Stone (1956) differed from those obtained through this research, with respect to the presence of specific metallic ions in gushing and non-gushing ciders. In their studies, Gray and Stone (1956) added solutions of the salts of metals to bottles of beer and subjected the bottles to a gushing test which involved shaking the bottles. In the current cider research, the metals were inherent components of the cider and undoubtedly were incorporated into the macromolecular structure of the sediment. This suggests that metal ions added to bottle will exhibit different effects than those of inherent metals.

2.5. Conclusions

The design of Part One allowed new information to be obtained on several aspects of cidermaking. There are very few published accounts, and no recent reports, of cider production using Canadian-grown apples. In Ontario, the focus of apple production is primarily on culinary and fresh-eating varieties; these apples are higher in pectin and lower in astringency and acidity than traditional cider apple varieties grown in Europe. Consequently, the characteristics of ciders produced from the varieties of apples available in Ontario will be unique. Repeated sampling over the course of the vinification in this study provided information on the changes in chemical characteristics during cider production and allowed comparisons between ciders produced from four different pre-fermentative treatments.

Ontario has a short apple harvest season and apples for juice production may be subsequently stored out-of-doors for extended periods of time. Differences observed in

the ciders produced from the different treatments indicate that the length and type of apple storage will have a significant effect on the quality of the cider; this must be considered when storing apples prior to processing for cider production.

The results of Part One confirmed that the occurrence of gushing in ciders is related to the pre-fermentation treatment of apples. Only ciders produced from thawed apples (Treatment 4) gushed; none of the ciders produced from the other three treatments showed any gushing tendency. Treatment 4 ciders frequently gushed two months after bottling; all ciders which gushed did so by five months after bottling.

Gushing ciders contained significantly more water-soluble (Fraction 1) pectin than any of the other treatments, and had lower concentrations of polyphenols. At the time of bottling, Treatment 4 ciders appeared cloudier than ciders of the other treatments. During the course of the secondary fermentation and ageing Treatment 4 ciders became clear, generating a greater amount of sediment in the bottles compared to the other ciders; Treatment 4 Spy cider in 1995 was the one exception: it remained cloudy with little sediment throughout the secondary fermentation and ageing.

Treatment 4 ciders contained significantly more magnesium and calcium than the control ciders. Divalent and trivalent ions bind to pectin molecules; greater concentrations of these two minerals in ciders with high pectin concentrations was not unexpected.

Treatment 4 ciders had significantly higher amounts of sediment in the bottle when sampled at five months after bottling; the sediments also contained significantly greater concentrations of water soluble (Fraction 1) and oxalate soluble (Fraction 2) pectins. Iron and copper were in lower concentrations in Treatment 4 sediments compared to the control, Treatment 1. These results are in contrast to research by Gray and Stone (1956) which indicated that iron and copper were strong gushing promoters when added to beer; metals added to the liquid may exhibit different effects on gushing than inherent metals.

3. PART TWO: MECHANISM OF GUSHING

3.1. Introduction

In Part One, gushing occurred only in Treatment 4 ciders: those which were made from thawed apples. Part Two of this study was designed to investigate the mechanism of gushing in the Treatment 4 ciders, and to compare the evolution and behaviour of bubbles in the gushing ciders with those in non-gushing ciders. Gushing in beer has received much attention from the commercial brewing industry in recent years (Bellmer, 1996) and has been extensively investigated. Despite occurrences of gushing in other beverages (Beattie, 1951), the focus of research has not expanded beyond the phenomenon as it occurs in beer.

Foam in carbonated beverages is caused by bubble formation (nucleation), growth of the bubbles as they ascend through the liquid, and subsequently the creation of the layer of foam at the surface of the liquid. The foam layer is composed of bubbles separated from each other by a continuous phase of thin liquid layers (lamellae). The structure of the foam is stabilized by favourable conditions of surface tension, surface viscosity and surface activity (Walstra, 1989). During gushing, an enormous number of very tiny bubbles are formed in the liquid which expand and ascend very quickly, resulting in a spout of beer which flows out of the bottle (Amaha and Kitabatake, 1981; Gray and Stone, 1956). In gushing, the foam layer cannot be created at the liquid surface because of the violent, disruptive action of the creaming phase.

The formation and stability of foam in beer has been studied extensively (Bamforth, 1985; Lusk *et al.*, 1995; Roberts, 1977). Researchers have also studied effervescence in sparkling wines (champagnes and Spanish cavas) because of the acknowledged impact of the quality of the foam on the overall perception of the product by the consumer (Casey, 1995; Pueyo *et al.*, 1995; Robillard *et al.*, 1993; Viaux *et al.*, 1984). Foam is most often

described as the dispersion of gas bubbles in a liquid (Prins and van't Riet, 1987; Walstra, 1989). In the case of food foams, such as beer foams or whipped cream, air or carbon dioxide is the gas dispersed in an aqueous solution or suspension containing proteins (Cheftel *et al.*, 1985). The bubbles in a foam are polyhedral and form a honeycomb structure; the gas-to-liquid volume ratio is usually greater than 1:1 and often greater than 3:1 (Prins and van't Riet, 1987). In carbonated beverages, foam is formed through supersaturation of the liquid, under pressure, with the gas, followed by a release of the pressure. Foam cannot form in a pure liquid; there must be nucleation sites within the liquid from which bubbles can form (Walstra, 1989). The presence of surfactants in the liquid is necessary to generate a stable foam (Bamforth, 1985; Roberts, 1977).

The formation of foam in beer is responsible for the typical "head" on a poured beer. The foam is largely dependent on the gas content of the beer and/or that introduced when dispensing the beer, together with the tendency of the gas to leave the solution (Bamforth, 1989). Unlike beer, the foam in sparkling wines is normally meager and short-lived, providing an evanescent ring of foam at the perimeter of the liquid surface (Casey, 1995).

The term gushing has been used interchangeably in the past with fobbing, wildness, boiling-over, kicking, flushing, foaming and lifting. However, gushing has become the accepted term to describe the overfoaming of a beverage in the absence of pre-agitation, over-carbonation or high concentrations of air (Beattie, 1951). Gushing is said to be characterized by the immediate formation of a large number of fine bubbles throughout the liquid which ascend rapidly when the bottle is opened, creating foam which overflows the bottle (Munar and Sebree, 1997). The degree of gushing may range from a mild overflow to a more catastrophic eruption causing substantial loss of liquid from the bottle (Beattie, 1951; Munar and Sebree, 1997). The occurrence of gushing in a commercial product thus

has a detrimental effect on consumer acceptance of that product, which in turn seriously affects the business of the companies concerned (Bellmer, 1996).

Gushing in beer was first documented by Dr. Y. Worth in 1692 (Beattie, 1951) and has been the focus of many research studies since the 1950's (Amaha and Kitabatake, 1981; Beattie, 1951; Gray and Stone, 1956; Piratzky *et al.*, 1955; Thorne and Helm, 1957). It has been linked to fungal infection of barley crops (Gjertsen *et al.*, 1963; Gyllang *et al.*, 1977), specifically to a protein produced by *Fusarium* (Bellmer, 1996; Gjertsen *et al.*, 1965; Munar and Sebree, 1997). Some researchers suggest that presence of this protein in gushing beer may be independent of the phenomenon of gushing (Munar and Sebree, 1997; Schwarz *et al.*, 1996) and that more research is necessary to determine the cause and prevention of gushing (Bellmer, 1996).

There is no indication in the literature that gushing occurs in sparkling wines. Gushing in cider has been acknowledged (Amaha and Kitabatake, 1981; Beattie, 1951) but not investigated.

3.2. Review of Literature

3.2.1. Gushing

3.2.1.1. *Gushing in Beer*

Gushing in bottled beer is considered an undesirable phenomenon whose remedy has been sought for much of this century (Curtis and Martindale, 1961; Kitabatake, 1978; Munar and Sebree, 1997; Thorne and Helm, 1957). One of the first detailed investigations of gushing beer was carried out by Krause (1936) who suggested that gushing was not caused by overcarbonation of the beer but rather to bubble formation sites, or "nuclei" which

were already formed before the bottle was opened. Krause studied beer which had been subjected to extensive periods of shaking, jolting or vibration during transport, causing "bubbles" of gas from the headspace of the bottle to be mixed into the beer. Krause theorized that these gas bubbles adsorbed to colloidal surface-active particles in the beer. The bubbles diminished in size over time in the closed bottle, but it was suspected that the "coating" of surfactant particles around the gas bubbles remained as compact colloidal micelles, with a small pocket of the gas possibly trapped inside. When the bottle of beer was opened and the liquid became supersaturated with carbon dioxide gas due to the immediate decrease in pressure, Krause hypothesized that these micelles could then act as bubble nucleation sites. Although Krause's theory of bubble nucleation in gushing beer was considered to be theoretically plausible, it lacked direct experimental proof (Thorne and Helm, 1957).

Several years later, Schmith (1952) was able to provide experimental data to support Krause's theories. In Schmith's research, model solutions were used to investigate the effect of trace amounts of several surfactants on gushing; the addition of colloidal aluminum hydroxide ($Al(OH)_3$) or ferric oxide (Fe_2O_3) to the solution at pH 4.4 (positively charged ions) caused strong gushing, but the addition of silicon dioxide (SiO_2) to the solution at the same pH (negatively charged ions) did not cause gushing. Schmith (1952) also demonstrated that some adsorption of carbon dioxide occurred with the colloidal $Al(OH)_3$ or Fe_2O_3 but not with the SiO_2. Overfoaming occurred in bottles of a model solution or beer which had a gas-liquid boundary present but bottles which were completely filled did not gush; this was consistent with Krause's theories on gushing (Thorne and Helm, 1957).

Description of gushing beer has been divided into three categories: mishandled beer, wild beer and gushing beer. In most cases, bottled beer will gush if shaken before opening

the bottle; this is classified as mishandled beer. Overcarbonated beer or beer with an excessive air content which overfoams on opening is defined as wild beer. The term gushing designates beer that cannot be categorized as overcarbonated or mishandled but overfoams excessively on opening (Amaha and Kitabatake, 1981).

Gushing beer can be described as "winter-type" and "summer-type" gushing (Amaha and Kitabatake, 1981). Winter-type gushing occurs in bottled beer shaken or stored at refrigeration temperatures before opening at room temperature. Summer-type gushing occurs in bottled beer that has been shaken or stored at temperatures between 25°C and 40°C. Contrary to winter-type gushing, in summer-type gushing no overfoaming is observed when bottles are shaken or stored at 0°C prior to opening at 20°C. Most reported occurrences of gushing in European countries are best described as summer-type gushing since the gushing phenomenon occurs without subjecting the beer to low temperatures. Summer-type gushing appears to be associated with defects in malt quality, particularly when the barley is infected with mold. Winter-type gushing is more prevalent in countries where beer is chilled before consumption (Amaha *et al.*, 1978).

3.2.1.2. *Winter-type gushing*

Gray and Stone (1956; 1960) investigated metal-induced gushing in beer. They added 41 metals at levels of 2 mg/L to bottles of non-gushing beer. The bottle size and shape were standardized so that the results not would be affected by differences in the surface cross section or the length of path through which the bubbles travelled. The closed bottles were stored for varying lengths of time at -2°C before sampling or subjected to a rapid shake test at -2°C for 24 hours. Their results indicated that heavy metals such as iron, tin, nickel and cobalt, which are often also present in high concentrations in chill haze

substances, could cause gushing at concentrations of 2 mg/L. Copper, silver, mercury and lead caused only slight gushing. Other metals such as boron, sodium, magnesium, aluminum, calcium, potassium, manganese and zinc did not induce gushing (Gray and Stone, 1956). Treatment of the beer with ethylenediaminetetraacetic acid (EDTA) to chelate the metals was reported to prevent haze formation and metal-induced gushing (Gray and Stone, 1960). Absence of haze in the beer did not necessarily indicate that gushing would not occur (Gray and Stone, 1956).

Studies on gushing in Australian beer attributed the phenomenon to a triggering action by trace metals and excess oxygen; agitation and storage at low temperatures accelerated gushing tendency but treatment with EDTA and reducing substances such as ascorbates inhibited or considerably reduced gushing (Beckley, 1958). Other researchers suggested that microcrystals of calcium oxalate could act as sites for bubble formation, causing gushing (Amaha *et al.*, 1978), although this was not supported by Gray and Stone (1956).

Investigation of gushing in Japanese beer by Amaha *et al.* (1978) indicated that the winter-type gushing they observed could not be attributed to heavy metals or oxalate. The gushing in bottles of pasteurized beer usually did not become evident until after at least one month of storage and reached a maximum after three months of storage. All gushing beers exhibited some residual proteolytic activity by chill-proofing enzymes; beers which did not gush did not exhibit any proteolytic activity. Amaha *et al.* (1978) conducted further experiments in which they added papain, a common chill-proofing enzyme, to beer. They hypothesized that the proteolytic action of the enzyme remained active, despite pasteurization, and that it could attack proteinaceous components of the beer, yielding protein fragments which could then play a role as nuclei and cause gushing. If the papain

was added in an autolyzed, heat-denatured or chemically-inactive form, gushing was not observed. Addition of acid proteases to gushing beers to further cleave the protein fragments effectively reduced the gushing potential of the beers.

3.2.1.3. *Summer-type gushing*

Summer-type gushing is not related to chill haze-forming compounds. Research by Curtis and Martindale (1961) confirmed that in some cases gushing beer was as clear as normal beer. Gjertsen *et al.* (1963) reviewed publications on gushing and suggested that gushing in beer is not related to proteolytic degradation nor to any other enzymatic activity. In conducting their own investigations, Gjertsen and his colleagues divided gushing into two further categories: primary and secondary gushing. Primary gushing occurred sporadically and appeared to be related to the microbiological quality of the malt. Secondary gushing was due to faults during beer production or storage of bottled beer and was often easily corrected. Gjertsen *et al.* (1963) proposed techniques to discourage the occurrence of gushing such as maintaining adequately high concentrations of isohumulones and treatment of the beer with bleaching earth.

From the domestic barley crop in Japan, Kitabatake and Amaha (1977) isolated a protein produced by *Nigrospora* which could induce gushing in beer. The isolated protein contained relatively high amounts of hydrophobic amino acid residues; addition of the purified form to non-gushing beer at concentrations as low as 0.05 mg/L induced vigorous gushing. Cleavage of the disulfide bonds of the protein, either by oxidative or reductive means, resulted in the elimination of gushing-inducing activity. They concluded that the maintenance of the disulfide bonds and of the molecular conformation was essential for the protein to retain its gushing-inducing activity.

Kitabatake (1978) also was successful in extracting and purifying a gushing-active substance from commercial malts produced in northern Europe. Analysis of the purified substance revealed that it was composed mainly of a peptide associated with some carbohydrates and polyphenols. The amino acid composition of the component was characterized by high levels of acidic residues and proline and relatively low levels of basic residues, and thus was acidic in nature. In contrast to the gushing-inducing protein from Japanese barley whose activity was sensitive to enzymatic degradation (Kitabatake and Amaha, 1977), the gushing-active substance in the European malts was resistant to several types of enzymes, including proteases, carbohydrases and a polyphenoloxidase (Kitabatake, 1978).

Swedish researchers (Gyllang *et al.*, 1977) studied the microflora of barley and malt at a brewery whose beers gushed periodically. It was determined that there was a heavy contamination of the malt by *Aspergillus, Penicillium* and *Rhizopus*. Although no gushing-inducing proteins were isolated in this work, the researchers determined that malt and wort samples of gushing beers had a number of significantly different characteristics compared to non-gushing beers, including higher extract yields, soluble nitrogen and α-amino nitrogen. Gushing, it was hypothesized, is dependent on an interaction between the fungus and the germinating barley.

A high occurrence of gushing in German beers in 1987 led to a joint interdisciplinary four-year project to investigate the causes of gushing and to offer practical solutions to the problem (Bellmer, 1996). Many difficulties were encountered in the project, including the lack of reliable procedures for determining gushing potential and a shortage of raw material with gushing potential. Although the substances which caused gushing in beer could not be isolated, identified or their sources detected, the researchers maintained that there must be

a relationship between the fungal infection of barley or wheat and subsequent gushing tendency of beers made from them. At the conclusion of the project, it was recommended that further research be conducted to identify the causative agent of gushing and to develop a reliable method for determining gushing potential.

Epidemics of *Fusarium* head blight in American Midwest barley crops in 1993 and 1994 prompted studies on gushing in beer in the United States (Munar and Sebree, 1997; Schwarz *et al.*, 1996). Fifty barley samples with varying degrees of *Fusarium* infection were studied during the harvest of 1994 (Schwarz *et al.*, 1996). After malting on a micro-scale, samples were analyzed for a number of quality parameters and for the fungal metabolites deoxynivalenol and ergosterol. *Fusarium* infection and concentrations of the metabolites were used to predict gushing potential. The results of their research indicated that although approximately 90% of the malts with detectable levels of deoxynivalenol exhibited some level of gushing potential, it was unlikely that the mold metabolites were the compounds responsible for gushing. It was suggested that the production of the mold metabolites may closely parallel the production of components which are responsible for gushing. In addition, although *Fusarium* infested samples did exhibit a strong gushing tendency, the level of *Fusarium* infection was a poor predictor of the severity of gushing. It was suggested that further research was required to identify the actual compound(s) responsible for gushing and that until such compound(s) could be identified, prediction of gushing potential would be difficult.

A study by Munar and Sebree (1997) also focussed on *Fusarium* infestation of barley and deoxynivalenol levels in malted samples. Barley samples with a range of deoxynivalenol levels were collected and pilot-malted. Results of the study indicated that the factors causing gushing were present in the malt and that a minimum concentration was

necessary to induce gushing. Malts that exhibited a tendency to gush were not necessarily produced from barley with gushing tendencies. In gushing malts produced from barley with no gushing tendency, the evolution of gushing factors occurred prior to the increase in deoxynivalenol concentrations, suggesting that the gushing factors and the deoxynivalenol were formed independently during the malting process. The impact of the gushing factors was precise: beer either gushed or did not gush. The induction of gushing appeared to have a slight varietal dependence. Although all gushing samples did contain deoxynivalenol, the researchers concluded that deoxynivalenol was not a reliable indicator of gushing tendency.

3.2.1.4. *Other Factors*

Several researchers have suggested other factors which may be the cause of or supportive of gushing in beer (Amaha and Kitabatake, 1981). Other materials, particularly from hops, have exhibited some tendencies to inhibit gushing (Curtis *et al.*, 1961).

Amaha and Kitabatake (1981) reviewed previous studies on sporadic gushing in beer. They reported on incidents of gushing in which severely etched ("weathered") bottles were determined to be the cause of the gushing phenomenon. Residue particles which remained in the bottles after cleaning could also function as nucleation sites in the beer, promoting gushing. Gray and Stone (1956) suggested that slight increases in the pH of the beer accelerated the development of gushing. Conversely, decreasing the pH of the beer to low levels inhibited gushing, possibly due to inhibition of the development of bubble nucleation sites. High levels of dissolved air or nitrogen in the beer have also been implicated in gushing (Amaha and Kitabatake, 1981). Siebert *et al.* (1996) suggested that colloidal haze particles in wines may function as nucleation sites and may promote gushing.

Colloidal materials which formed micelles in beer were also suggested by Beattie (1951) to be gushing promoters. High surface viscosity in beer does not cause gushing, but stabilized nuclei in such an environment may lead to gushing (Gardner, 1972). Amaha and Kitabatake (1981) reported that isomerized hop extracts introduced in the early 1970s could also cause gushing. In particular, dehydrated humulinic acid and the oxidation products of humulone and isohumulone were identified as the factors which promoted gushing.

Gushing was inhibited in beers with higher quantities of hops (Curtis *et al.*, 1961). This presumably explains why stouts and brown ales were observed to gush more readily than lagers. Studies on hop resin components indicated that lupuloxinic acid, cohulupone, α-acids and β-acids suppressed gushing in beer (Amaha and Kitabatake, 1981). Beattie (1951) reported that antioxidants such as ascorbic acid and reductone may have an appreciable preventative action on gushing. The addition of foam-inhibiting agents in his study had a negligible effect on the occurrence of gushing but a significant effect on the severity of gushing.

3.2.1.5. *Gushing in Cider*

Very little information exists on gushing in cider; nor has the phenomenon of gushing been investigated in any detail. Beattie (1951) reported on several limited investigations of gushing cider. In most cases, gushing was attributed to excessive fermentation in the bottled cider. On occasion, gushing was believed to be caused by: faulty clarification, contact with air at bottling, too much headspace in the bottle, or the violent evolution of gas from precipitated solids.

3.2.2. Bubble Nucleation, Growth and Velocity

The study of gushing requires an examination of the formation of bubbles and their subsequent growth and speed of ascent through the liquid. Many studies of these topics have concentrated on bubbles of air or pure gas in water or simple aqueous solutions (Atchley and Prosperetti, 1989; Bernath, 1952; Blander, 1979; Liebermann, 1957; Lubetkin, 1989; Wilt, 1986; Yount, 1982). More recently these studies have been extended to bubble formation, growth and velocity in fermented beverages (Casey, 1995; Codrington, 1986; Shafer and Zare, 1991).

3.2.2.1. *Bubble Nucleation*

The nucleation of bubbles is the first process which must occur in foam formation (Walstra, 1989) or for any type of effervescence in carbonated beverages (Casey, 1995; Wilt, 1986). Release of pressure, such as the removal of the cap from bottled beer, causes the solution (beer) to be supersaturated with respect to carbon dioxide. Jordan and Napper (1986) indicated that the opening of a bottle of sparkling wine reduced the pressure from 606 kPa to approximately 101 kPa. This reduction in pressure decreases the solubility of carbon dioxide in the liquid from 14 g / L to approximately 2 g / L; for equilibrium to be established at this new pressure, approximately 5 L of carbon dioxide must be released from solution -- a process which could take years to complete if diffusion through the surface of the wine was the only avenue for gas release. Consequently, bubbles form in the solution and increase in size as they ascend through the liquid, thus increasing the rate of gas release from the liquid.

Nucleation implies the formation of nuclei within a metastable mother phase which may develop spontaneously into large fragments of a new and more stable phase (Gardner,

1973). Thus, in carbonated beverages bubbles are produced in the liquid which is supersaturated with carbon dioxide. Classical nucleation theory divides bubble formation into two mechanisms: homogeneous and heterogeneous nucleation (Wilt, 1986).

When nucleation is homogeneous, bubbles form spontaneously in the liquid without the existence of an interface from which to form (Lubetkin, 1989). Homogeneous nucleation may occur in superheated liquids. Once bubble formation begins, the liquid boils explosively (Blander and Katz, 1975; Casey, 1995). Sparkling wines at room temperature would require pressures of 1000 atmospheres (atm) for homogeneous nucleation to take place (Casey, 1995). The energy requirements necessary for homogeneous nucleation preclude it from occurring in carbonated beverages (Wilt, 1986).

Heterogeneous bubble nucleation occurs at pre-existing gas-liquid interfaces within the liquid (Lubetkin, 1989; Wilt, 1986) and can take place at temperatures much lower than those required for homogeneous nucleation (Blander and Katz, 1975). Conditions for heterogeneous nucleation are dependent on the properties of the surface of the nucleation site and on the surface and interfacial tensions (Blander, 1979). In general, sites for heterogeneous nucleation are regions whose surface is poorly wetted by the liquid (Blander, 1979) and where the size, shape and liquid contact angle of the non-wetted area can support micro-cavities of a size capable of generating bubbles; narrower, deeper and more hydrophobic regions are more likely to resist liquid penetration, retain small quantities of gas and thus function as nucleation sites (Casey, 1995). The postulated presence of small pockets of gas stabilized at the bottom of cracks or crevices found on hydrophobic solid particles in the liquid has given rise to the crevice model of bubble nucleation (Atchley and Prosperetti, 1989). The diameter of the cavity perimeter is reported to be the main determinant of bubble size (Casey, 1995).

An alternative, less popular theory for heterogeneous bubble nucleation is the varying-permeability model (Atchley and Prosperetti, 1989), based on principles put forward by Krause (1936). Free floating bubbles cannot pre-exist in the liquid (Liebermann, 1957; Wilt, 1986; Yount, 1982); pre-existing nuclei are required for heterogeneous nucleation. However, if a skin of surface-active molecules stabilizes the bubble within the liquid, preventing its dissolution, the stabilized bubble may be able to serve as a nucleation site (Schmith, 1952; Yount, 1982). These bubbles must be small enough to prevent floatation to the surface of the liquid and strong enough to resist collapse, the mechanical compression strength being provided by the elastic skin or membrane composed of surface-active molecules (Yount, 1982). Other researchers maintain that stabilized bubbles cannot exist and that this method of bubble nucleation is therefore not possible (Atchley and Prosperetti, 1989; Wilt, 1986).

Surface tension reportedly increases the gas pressure in a bubble. In a hydrophobic, non-wetted crevice, the effect of surface tension can be reversed (Liebermann, 1957). The pressure exerted by the tension in the liquid surface varies inversely with the radius of curvature of the trapped gas, as described by the LaPlace equation:

$$\Delta P = 2\gamma/r_c \quad (1)$$

where ΔP represents the pressure difference across the gas/liquid interface, γ is the liquid/gas interfacial tension, and r_c is the radius of curvature of the gas/liquid interface (Casey, 1995). If the external pressure is counterbalanced by the surface tension and radius of curvature of the trapped gas, stability results and the gas pocket may remain stable indefinitely (Liebermann, 1957). Release of pressure from a carbonated beverage, for example the removal of the cap from a bottle of beer, causes an immediate disruption of the equilibrium between gases in the vapour phase and that dissolved in the liquid phase. The

presence of a gas/liquid interface at an unwetted surface allows carbon dioxide dissolved in the liquid to enter the gas cavity until the partial pressures of the carbon dioxide are once again in equilibrium between the gas and liquid phases (Casey, 1995).

The potential nucleation activity of several crevice shapes was examined by Wilt (1986). Through a series of mathematical evaluations of varying bubble surface energies, σ, and liquid contact angles, θ (Figure 3), Wilt demonstrated that conical cavities of various geometries could theoretically support observable nucleation rates. For example, bubble surface energies of $\sigma = 65$ erg / cm^2 and $\sigma = 75$ erg / cm^2 and contact angles in the range of 94° to 130° were shown, in theory, to support bubble nucleation in water / carbon dioxide solutions with supersaturation levels typical of freshly opened carbonated beverages. Evaluation of conical projections, spherical cavities and spherical projections indicated that these geometries would not function as bubble nucleation sites.

Growth at the nucleation site is initiated by the loss of mechanical stability of the balance of forces, which occurs, for example, when the cap is removed from a bottled carbonated beverage. The gas in the cavity expands due to the loss of mechanical stability; this growth would be indefinite if other effects such as buoyancy did not interfere (Atchley and Prosperetti, 1989). As the radius of the gas/liquid interface expands, the pressure exerted by the tension in its liquid surface decreases and no longer inhibits the continued expansion of the bubble (Casey, 1995).

The size of the sites capable of forming bubbles depends on the surface tension of the liquid in contact with the gas and solid material (Figure 3) and inversely on the vapour pressure of the dissolved gas. Thus, liquids with high gas partial pressures and low surface tensions will allow bubble formation from smaller sites. The surface tensions of still wines have been reported to be in the range of 48 to 50 mN / m while those of non-alcoholic

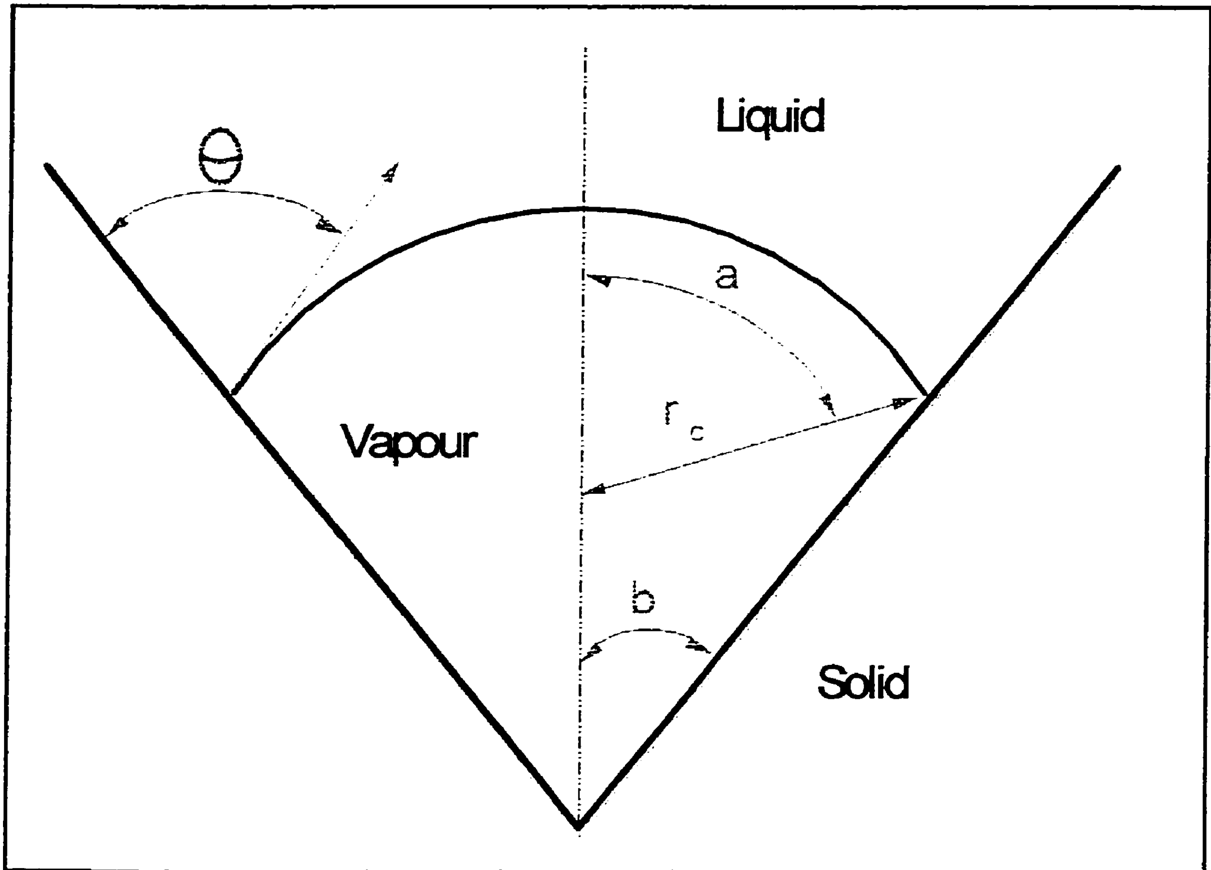


Figure 3. Geometric parameters for heterogeneous nucleation at conical cavities:
θ = contact angle as measured in the liquid;
r_c = radius of curvature of the gas/liquid interface;
a = contact angle;
b = cone half-angle

(Atchley and Prosperetti, 1989; Wilt, 1986)

beverages are approximately 70 to 72 mN / m. High concentrations of carbon dioxide in both the liquid and gas phases of effervescent beverages likely cause a reduction in the interfacial tensions, although this has been difficult to determine. Alcohol in carbonated beverages causes a decrease in the solubility of carbon dioxide and thus an increase in the gas partial pressure. These differences in surface tension and gas solubility allow bubbles to be produced in alcoholic drinks at nucleation sites which are 1.5 to 1.8 times smaller than active nucleation sites in soft drinks (Casey, 1995).

The diffusion of gas into a nucleus is a very complex phenomenon, about which little is known (Atchley and Prosperetti, 1989). For a bubble to be released from its nucleation site, it must grow sufficiently so that the buoyant forces of the bubble overcome the surface tension of the liquid surface anchoring it to the nucleation cavity (Casey, 1995). Lubetkin (1989) suggested that nucleation sites may be composite in nature: hydrophobic regions of the site would encourage the nucleation phenomenon while hydrophilic regions would facilitate bubble release from the nucleation site. Upon detachment, the bubble may leave behind a significant portion of attached gas, allowing the crevice to once again act as a nucleation site (Walstra, 1989) or alternatively, blocking of the nucleation site from producing further bubbles (Lubetkin, 1989).

The frequency of bubble generation from a nucleation site is dependent upon the time required for a bubble to expand from its embryonic size to one whose buoyant forces allow it to separate from the nucleation site. Bubble frequency from a single site is, therefore, inversely related to bubble size and to the density of the liquid and directly dependent upon the circumference of the cavity perimeter and the surface tension of the liquid (Casey, 1995).

La Mer (1952) reviewed nucleation, from the point of view of chemical kinetics, in

a variety of contexts including the production of new phases in metallurgy applications, and fog formation and the artificial production of rain by seeding. Nucleation, like other illustrations of chemical kinetics, involves an activation process, which leads to the formation of unstable intermediate states which La Mer identified as embryos; a critical rate-determining embryo is called a nucleus. At the nucleus, the boundary layer separating the liquid phase from the trapped pocket of gas should be considered as a transition layer in which the properties of the liquid are able to pass continuously into the properties of the gas phase. Therefore, a catalytic event must occur for heterogeneous nucleation to take place. At contact angles of $\theta = 180°$ (Figure 3), the work required to activate the nucleus is equivalent to that required for homogeneous nucleation. As the contact angle θ decreases, the energy required to activate the nucleation site also decreases significantly. Once the nucleation site is activated and the bubble expands beyond the critical radius for an (unstable) equilibrium, the reaction continues spontaneously without further energy or work input until the potential in the mother phase (liquid) becomes equal to that in the new, more stable phase (gas).

3.2.2.2. *Bubble Ascent and Growth*

Once bubbles are released from their nucleation sites, they continue to expand as they rise through the liquid (Casey, 1995; Walstra, 1989). Casey (1995) indicated that in bottles and glasses of sparkling wines, the hydrostatic pressure due to the depth of the liquid and the pressure exerted by the now enlarged liquid/gas interface could be considered to be negligible. The pressure inside the bubble can be assumed to be equal to the pressure at the surface of the liquid; in an opened bottle or in a glass this pressure would be atmospheric pressure. If the pressure at the surface of the liquid and the concentration gradient in the

liquid remains constant, the rate at which bubbles expand depends solely on the rate at which the carbon dioxide passes from the liquid into the bubble, and thus is directly dependant on the difference in the partial pressures of the gas in the liquid and vapour phases and on the area of the gas/liquid interface of the bubble. Any surfactants which adsorb to the surface of the growing bubble will also affect (decrease) the rate of gas diffusion into the bubble (Jordan and Napper, 1986).

In a solution supersaturated with carbon dioxide, the partial pressure of the carbon dioxide dissolved in the liquid is larger than the pressure of the gas inside the bubble. Therefore, as the bubble rises through the liquid, it accumulates carbon dioxide until it reaches the surface. The rate of growth of the bubble is affected by the rate of diffusion of the carbon dioxide to the bubble, the temperature of the liquid and the surfactants adsorbed at the growing bubble surface which affect the rate of diffusion into the bubble (Jordan and Napper, 1986). Although carbon dioxide is not a totally inert gas, in most applications of brewing, it is regarded as such (Kuzniarski, 1983); this consideration is also applicable to other fermented carbonated beverages. Thus, if it is assumed that the gas inside the bubble obeys the ideal gas law, the bubble can be described as:

$$P_{bubble} \bullet V_{bubble} = n_{bubble} \bullet R \bullet T \qquad (2)$$

where P_{bubble}, V_{bubble} and n_{bubble} are the pressure in the bubble, the volume of the bubble and the number of moles of gas in the bubble, respectively. The symbol R denotes the gas constant; T is the temperature in Kelvin. Therefore, if the bubble is small enough to be spherical, the growth of the bubble with respect to time is:

$$\frac{dn_{bubble}}{dtime} = \left(\frac{P_{bubble}}{R \bullet T}\right) \bullet \frac{dV_{bubble}}{dtime}$$

or

$$\frac{dn_{bubble}}{dtime} = \left(\frac{P_{bubble}}{R \bullet T}\right) \bullet 4\pi r^2 \bullet \frac{dr}{dtime} \tag{3}$$

where r is the radius of the bubble (Shafer and Zare, 1991). In a solution supersaturated with carbon dioxide, the partial pressure of the gas in the liquid will remain virtually unchanged during the lifetime of the bubble (Casey, 1995) and, therefore, does not need to be incorporated into equation 3, above. Several researchers (Casey, 1995; Shafer and Zare, 1991) have demonstrated that for bubbles rising in a glass of beer or sparkling wine, the increase in the radius of the bubble is linear with respect to time.

Diffusion of carbon dioxide and the growth of bubbles in pure water have been extensively researched and mathematical equations describing the phenomena are well established (Bird *et al.*, 1960; Geankoplis, 1983; Sakiadis, 1984). Diffusion is defined by Fick's first law as the ratio of flux to the concentration gradient. The diffusion (D_{AB}) of very dilute gas A through a solvent B, as in the case of carbon dioxide in beer or wine, can be described by the Wilke-Chang equation (Sakiadis, 1984):

$$D_{AB} = \frac{7.4 \bullet 10^{-8}(\psi_B M_B)^{.5} \bullet T}{\mu_B \bullet v_A^{.6}} \tag{4}$$

where ψ_B is an association factor for solvent B which accounts for hydrogen bonding. M_B and μ_B are the molecular weight and viscosity of solvent B, respectively. The term v_A denotes the molar volume of the gas A at its normal boiling point.

The growth of bubbles is due to the mass transfer of carbon dioxide into the bubble from the surrounding liquid and is dependent on the surface area, and hence the size, of the bubble. Therefore, the growth of bubbles is also related to their velocity, or speed of ascent,

through the liquid. The velocity of a bubble at any instant in time (*vt*) can be calculated from the Stokes law if its Reynolds number is less than 0.1 (Sakiadis, 1984; Walstra, 1989):

$$vt = \frac{2g \bullet \rho \bullet r^2}{9\mu_B} \tag{5}$$

which includes the friction or drag force attributable to the shape of the bubble (Sakiadis, 1984 and g is acceleration due to gravity, r is the radius of the bubble and ρ is the mass density of the liquid. The mass density of the gas is very small compared to the mass density of the liquid and thus is negligible. The Reynolds number (NRe) is related to the bubble velocity by (Walstra, 1989):

$$NRe = \frac{2r \bullet vt \bullet \rho}{\mu_B} \tag{6}$$

The Sherwood number (NSh) for the bubbles with NRe < 2 can then be calculated (Sakiadis, 1984):

$$NSh = 1.01 \bullet NRe^{\frac{1}{3}} \bullet NSc^{\frac{1}{3}} \tag{7}$$

where NSc denotes the Schmidt number (Geankoplis, 1983):

$$NSc = \frac{\mu_B}{\rho \bullet D_{AB}} \tag{8}$$

The mass transfer coefficient for rising small bubbles of gas in a liquid is a function of the Sherwood number (Sakiadis, 1984):

$$kconst = \frac{NSh \bullet D_{AB}}{2r} \tag{10}$$

where *kconst* is the average over the entire surface of the bubble. The flux in a dilute system can expressed as (Geankoplis, 1983; Sakiadis, 1984):

$$N_A = kgas \bullet \left|(c_{A1} - c_{A2})\right| \tag{11}$$

where c_{A1} is the concentration of the gas at the gas-liquid interface of the bubble, c_{A2} is the concentration of the gas in the bulk liquid and kgas is the volumetric mass transfer coefficient. According to Geankoplis (1983), since the gas is dilute within the "stagnant" (non-flowing) liquid, $kgas \cong kconst$. In addition, c_{A1} can be equated to the concentration of the gas inside the bubble because the partial pressure of the gas in the liquid is much larger than the partial pressure of the gas inside the bubble.

Once the Reynolds number becomes larger than 0.1, the velocity of the bubble is governed by the intermediate law and can no longer be calculated according to equation (5). At $0.1 < NRe < 1000$, the velocity of the bubble is determined by (Sakiadis, 1984):

$$vt = \sqrt{4g \bullet 2r \bullet \frac{(\rho - \rho_{bubble})}{3 \bullet \rho \bullet c_D}} \tag{12}$$

where ρ_{bubble} is the density of the bubble and the drag coefficient, c_D, is calculated by:

$$c_D = \frac{24}{NRe} \bullet \left(1 + 0.14 \bullet NRe^{.7}\right) \tag{13}$$

If $1000 \leq NRe \leq 350{,}000$ then $c_D = 0.445$ and the velocity of the bubble becomes:

$$vt = 1.73 \bullet \sqrt{g \bullet 2r \bullet \frac{(\rho - \rho_{bubble})}{\rho}} \tag{14}$$

according to Newton's law.

The Sherwood number, NSh, is also affected by the Reynolds number. For $1 \leq NRe \leq 48{,}000$ the calculation for NSh becomes (Geankoplis, 1983):

$$NSh = 2 + 0.552 \bullet NRe^{.53} \bullet NSc^{\frac{1}{3}} \tag{15}$$

An important consideration for determining the velocity and growth rate of a bubble is its shape. When the radius of the bubble is less than 1.5 mm, the bubble is essentially spherical and will rise in a straight line in the water. Once the radius exceeds 1.5 mm, the bubble becomes ellipsoidal, flattened in the horizontal plane. These medium-sized bubbles tend to rise with rocking, oscillating or spiral movements. Bubbles which have radii larger than 4 mm become greatly deformed, often mushroom-like in shape, and although they rise in a relative straight line, they are unstable in water and tend to break into smaller bubbles. To calculate drag coefficients for bubbles which are no longer spherical, the diameter of the bubble is taken to the diameter of a sphere having the same volume as the bubble (Sakiadis, 1984).

3.2.2.3. *Bubble Swarms*

The characteristics of velocity and growth discussed in the previous section (Section 3.2.2.2.) are applicable only to bubbles which are produced at sufficient distances from each other and in sufficiently low quantities that they may be considered as single bubbles. When

bubbles are produced in swarms or clouds, as by a porous disperser for example, their behaviour during rising is influenced by their interaction with each other. In water, such bubbles tend to coalesce if small or disintegrate if large; in aqueous systems, coalescence also depends on the liquid properties such as liquid depth and the presence of surfactants. In addition, there are two opposing influences which affect the rate of rise of bubbles of any particular size: (i) the close proximity of the bubbles to one another can result in a hindered-settling condition, which will reduce bubble velocity; (ii) a "chimney" effect can occur in which a massive current upward appears at the axis of the bubble stream, leading to an increase in the net bubble velocity (Fair, 1984).

Houghton *et al.* (1957) studied the size, number and size-distribution of bubbles in bubble-beds. The researchers reported that small bubbles emerging from a porous plate in water and organic liquids showed coalescence but that this could be suppressed by the addition of small quantities of acetic acid. Since the pressure at a nucleation site, or in this research, at a gas jet first increases during bubble formation as the radius of the bubble expands to that of the radius of the jet, and then decreases as the bubble grows, the researchers were able to calculate the average pore diameter of the nucleation site. The average pore size was determined to be a function of the physical properties of the liquid, particularly the surface tension; the lower the surface tension, the lower the average active pore size for the same porous plate. They inferred that, in general, there was a tendency for the largest pores to operate during bubble formation but that smaller pores could be activated by using liquids with lower surface tensions. As the flow of gas was increased through the porous plate, the bubble bed density decreased and the gas hold-up increased until a constant value was reached. Addition of glycerine to the water tended to lower the bubble density in the bed and to cause the formation of a layer of foam at the surface of the

liquid. Acetic acid in small quantities also significantly decreased the bed density. Sea water containing surface-active agents tended to decrease the bed density and to promote foam formation. In general, however, the bed density was determined to be a function of the bubble size and the number of bubbles per unit volume of the bed. Photographic examination of the bubbles in the bubble beds indicated that for viscosities of 0.5 to 1.3 cP (= 10^{-3} kg/m/s), bubble shape was not affected by viscosity; the effective diameter (d_e) of the bubble as a oblate spheroid could be calculated as:

$$d_e = 1.13\ a \qquad (16)$$

where a is the diameter of the bubble in the vertical plane. Bubble size in the bubble bed was not uniform but rather followed a typical probability (normal) distribution; bubble size was determined to be a function of the plate porosity, gas velocity and the properties of the liquid phase. In all solutions, bubble size increased with increases in gas velocity and surface tension; the bubble bed thus behaved more as a foam than as a fluidized bed.

The velocity rise of bubbles in a bubble bed was also determined by Houghton *et al.* (1957). The velocity of rise was not constant for a particular bubble size, but was varied according to the density of the bed. The hindrance of the motion of the bubbles due to their close proximity with each other caused the rate of rise of the bubbles in the bubble bed to be significantly lower than that of single bubbles. The average velocity of rise of bubbles in the bubble bed was expressed as:

$$vt_{ave} = vt_{gas}(\rho / (\rho - \rho_{bed})) \qquad (17)$$

where vt_{ave} is the average bubble velocity in the bed, vt_{gas} is the average superficial gas-velocity through the bed, ρ is the liquid density and ρ_{bed} is the density of the bubble bed. The rise velocities were also observed to be affected by the presence of surfactants. In addition, the researchers observed an interesting phenomenon in which the rise velocities of the bubble bed occasionally were greater than the velocities of single bubbles, which was not in accordance with the theory of hindered rise. Such increased velocities were attributed to the formation of large bubbles or "plugs" of gas in the liquid such that the vt_{gas} of equation (17) becomes large while the bed density (ρ_{bed}) remains unchanged; plug formation occurred more frequently when the rate of bubble generation was high and the rise velocity was low. These increased velocities were confirmed by the observation that high bubble-velocities in the bed were always observed in the region of "bumping" where the plugs of gas caused the bed level to rise and fall about an average value.

3.2.2.4. *Effect of Alcohol, Polysaccharides, Proteins and other Factors*

Not surprisingly, bubble formation, growth and rise velocity may be affected by some of the components in the liquid medium and thus these bubble characteristics may deviate slightly from those which would be observed in pure water.

Liebermann (1957) studied the diffusion of gas from bubbles in sea water and in water with various hydrophobic and surface-active contaminants added. He concluded that diffusion rates were not significantly affected by the sea water or by any of the added contaminants in comparison to pure water. In support of this, Jordan and Napper (1986) concluded that although the binding of carbon dioxide by some components in wine cannot be ruled out, this binding can be regarded as minor.

Gardner (1973) suggested that if bubble nucleation in gushing occurred according

to the varying-permeability model, colloidal changes in beer during storage could affect the degree of gushing. For example, if colloidal changes in the beer produced micelles, these micelles could "pick up" gas and become nucleation sites for bubble formation. The influence of colloids on gushing in beer was also proposed by Schmith (1952).

A possible connection between surface viscosity and gushing was suggested by Gardner (1973); Jordan and Napper (1986) also indicated that surface viscosity plays a role in effervescence. Gardner (1973) noted that the addition of metal ions to the beer, such as nickel, caused a large increase in surface viscosity and tended to promote gushing. Surfactants, which lower the interfacial tension at a gas/liquid interface, have a significant effect on bubble formation and growth, but these effects are usually very difficult to measure (Jordan and Napper, 1986). Shafer and Zare (1991) reported that the presence of even a small amount of surfactant significantly reduced the rise velocity of an air bubble in water. The surface contamination theory (Clift *et al.*, 1978) implies that in the absence of surfactants, gases inside the bubble circulate, lubricating the bubble and promoting mass transfer through the gas-liquid interface. It has been suggested that surfactants form a rigid wall around the bubble, eliminating the lubricating effect of the circulation of the gas, thus decreasing the rise velocity of the bubble and also decreasing the mass transfer rate through the gas-liquid interface (Clift *et al.*, 1978; Shafer and Zare, 1991).

Alcohol has a significant impact on bubble formation and growth in carbonated beverages (Casey, 1995). Ethanol in sparkling wine lowers the surface tension and the solubility of the carbon dioxide, and increases the viscosity (Casey, 1995; Jordan and Napper, 1986). These changes due to the presence of the alcohol lead to a slower evolution of bubbles from the wine. The presence of polysaccharides is also reported to influence the viscosity of wine, but the influence of such components on bubble generation and bubble

size is controversial.

3.2.3. Techniques to Count and Size Bubbles

Amaha and Kitabatake (1981) describe gushing as the sudden release of carbon dioxide in beer at the instant the container is opened, creating an enormous number of tiny bubbles in the liquid which ascend and expand quickly. The investigation of gushing, therefore, requires a study of the bubbles in the liquid as they are formed and their behaviour as they ascend. Several techniques are reported in the literature for counting and sizing bubbles.

3.2.3.1. *Ultrasound*

Ultrasound has been used extensively to study bubbles in a variety of materials. The detection of bubbles in vivo, particularly resulting from decompression sickness, is often conducted by ultrasound (Rubissow and Mackay, 1971). This technique has also been applied to the study of cavitation (Iyengar and Richardson, 1958; Katz and Acosta, 1982), specifically with respect to ship propellers (Lauterborn, 1982). Ultrasound can be combined with other methods of bubble detection, such as photography (Leighton *et al.*, 1989).

Low-intensity ultrasound can provide information on the physico-chemical properties of food; higher levels of intensity have been used to physically or chemically alter the structure of food (McClements, 1995). Ultrasound has been used to study the gelation process of polysaccharides (Audebrand *et al.*, 1995) and for the in-line measurement of sugar and alcohol concentrations in beer and wort (Forrest, 1996).

When liquids are subjected to ultrasound, bubbles in the liquid are forced to oscillate, thus emitting a detectable, well-defined resonance frequency (Leighton *et al.*, 1989). This

acoustic resonance frequency is then used to calculate the equilibrium radius of the bubble (Leighton *et al.*, 1996). Ultrasound can be used to determine the number of bubbles in a given sample (Medwin, 1977) and has been adapted to provide an estimate of the bubble size distribution in bioreactors (Boyd and Varley, 1997) and bubble columns (Koller and Shankar, 1994).

Many difficulties can arise when employing ultrasound in situations other than model solutions with tethered bubbles (Leighton *et al.*, 1996). Ultrasound "treatment" may lead to the generation of new bubbles or bubble nuclei and to the expansion (Suslick, 1989) or collapse of existing bubbles (Leighton *et al.*, 1996). It may also cause a significant number of highly reactive free radicals to be formed (Didenko *et al.*, 1994; Suslick, 1989). In addition, although the bubbles may resonate as desired, this resonance may cause microstreaming to occur (Watmough *et al.*, 1992), with unpredictable effects.

3.2.3.2. *Laser Light Scattering*

Several researchers have used the scattering of light by bubbles to determine their sizes (Breña de la Rosa *et al.*, 1991); this technique has been extended to bubble size determination by measurement of the critical-angle scattering of laser light by bubbles (Langley and Marston, 1984).

Sizing of particles and bubbles by light scattering measurements is based on the phase shift of light as it is transmitted through or reflected from spherical particles (Breña de la Rosa *et al.*, 1991; Hallett, 1996). Typically this technique is used for measurements of particles ranging in size from 50 nm to 5 μm, but size approximations for larger particles are possible (Hallett, 1996).

3.2.3.3. *Photographic Techniques*

Gushing beer was studied by high speed stroboscopic motion-picture photography at Wallerstein Laboratories in the 1940's (Anonymous, 1948). In stroboscopic photography, flashes of light at a pre-determined frequency replace the mechanical opening and closing of the camera shutter; this allowed the researchers to use exposure times as small as 1/50,000 of a second. The camera was placed at a distance to allow viewing of the whole bottle as the cap was removed and as gushing proceeded. Stroboscopic photography allowed researchers to observe minute bubbles throughout the beer within 0.3 seconds after cap removal; gushing ceased within 2.3 seconds.

3.3. Preliminary Experimental Methods and Screening Tests

Preliminary experiments were conducted to determine the most appropriate methods for the analysis of ciders in Part Two of the research. Screening tests were also conducted to determine whether gas compositions and viscosities of the ciders might be different in gushing ciders compared to those which did not gush.

3.3.1. Gas Composition

Published reports of gushing indicate that excess fermentation (ie. too much carbon dioxide in the bottle) was frequently the cause (Beattie, 1951). An investigation of gushing ciders, therefore, requires an analysis of the gas composition in the bottles. Several randomly selected gushing and non-gushing ciders were analyzed in a preliminary gas analysis test at Molson's Center for Innovation in Etobicoke, Ontario, Canada. An Orbisphere Sampling Device was used to remove samples for analysis; air was used as the

counter-pressure gas for the carbon dioxide determinations and carbon dioxide was used as a counter-pressure for oxygen analysis. Carbon dioxide in the cider was determined with a LAN-IaZ Laboratory Carbonization Analyzer by gac (general analysis corporation; model 203-852-8999) which uses an infrared detection system. The oxygen concentrations in the ciders were determined with a Dr. Thiedig DIGOX EC-401 oxygen analyzer which uses an electro-chemical cell containing a silver (Ag) electrode as the method of detection. Nitrogen in the headspace was determined by Fourier Transform-Infrared (FTIR) spectroscopy. The results of this screening test are presented in Appendix 6.

If the gushing of ciders was caused by excess fermentation in the bottle, higher concentrations of carbon dioxide would have been detected in the gushing ciders compared to the non-gushing ciders. A distinct trend was not observed (Appendix 6).

Gushing has also been attributed to excess air contact at the time of bottling (Beattie, 1951); the nitrogen concentration in the headspace and the dissolved oxygen in the cider were determined to evaluate such a possibility. Yeasts do not produce oxygen or nitrogen during fermentation (Webb, 1994); the only source of these gases is the ingress of air during bottling. There was no notable difference observed in the concentrations of nitrogen and oxygen in gushing versus non-gushing ciders.

The results of this screening test for gas composition indicated that an analysis for the composition of these three separate gases was not necessary to determine the mechanism of gushing.

3.3.2. Cider Viscosities

The viscosities of two gushing and two non-gushing ciders from Part One were

determined with a Carri-Med Rheometer (model CSL^2 500, TA Instruments) at 20°C, using a 2 cm stainless steel cone with a 4° angle and 109 μm truncation. The viscosity affects the diffusivity of carbon dioxide through the liquid and the ascent velocity of the bubbles (equations (4) and (5), Section 3.2.2.2.); a higher liquid viscosity would therefore slow bubble growth and bubble ascent. If viscosity were to be a factor in gushing, the ciders which gushed should have notably lower viscosities than those which did not gush. This trend was not observed (Table 23); the average viscosity of the ciders was 1.22 cP.

Table 23. Viscosities of gushing and non-gushing ciders selected from Part One of the study.

Cider (from Part One)	Treatment	Gushing?	Viscosity (cP)
Crispin, 1995	3	no	1.21
Crispin, 1995	4	yes	1.22
Spy, 1995	2	no	1.22
Spy, 1995	4	yes	1.23

3.3.3. Evaluation of Techniques to Count and Size Bubbles

3.3.3.1. *Ultrasound*

The many difficulties that can arise when employing ultrasound in situations other than model solutions (Leighton *et al.*, 1996) were of significant concern when considering its use for counting and sizing bubbles. In addition, the adaption of ultrasonic techniques and selection of ultrasound frequencies to use with the bottles of ciders would have been difficult. As a result, an alternative bubble detection method was sought for this study.

3.3.3.2. *Laser Light Scattering*

Static laser light scattering (SLS) was considered as a method for determining bubble size distribution in gushing ciders compared to those in non-gushing ciders. A sampling device (Section 3.4.2.) was designed to allow the controlled release of gases from the headspace of the cider bottles, to provide an environment in which to study gushing without loss of liquid from the bottle. Several difficulties with the use of laser light scattering for bubble size determination quickly became apparent. Under the controlled-release conditions permitted by the sampling device, bubbles were observed to originate only in the sediment of the cider regardless of the gushing tendency of the sample; this contradicts published accounts that bubbles are formed throughout the liquid in gushing beer (Amaha and Kitabatake, 1981; Anonymous, 1948; Gray and Stone, 1956). Bubble release was observed to take place at different frequencies and at unevenly distributed locations across the sediment. An even distribution of particles, or bubbles, throughout the liquid is desirable for SLS, to ensure that particles detected within the small volume defined by the laser beam provide a representative sample. In gushing ciders bubble release was rapid, producing an enormous number of bubbles at the instant the headspace gas was released; closure of the gas release valve caused bubble formation to cease within a few seconds. However, bubble release in non-gushing ciders was observed to be much slower, producing only a few large bubbles per second -- a process which continued for hours in some ciders despite the closure of the gas release valve. In addition, irregularities in the glass of the cider bottles caused significant variations in the bubble size determinations and in the determinations of "background" particle sizes in the cider before bubble formation. It was determined, therefore, that laser light scattering was also not appropriate for studying bubbles in this research.

3.3.3.3. *Photographic Techniques*

Photographic techniques have been used successfully by other researchers to observe bubbles during gushing (Anonymous, 1948). Videography was considered as an alternative to high speed motion-picture photography because of the availability of video taping equipment. In addition, video tapes may be digitized and the images analyzed by computer, facilitating determination of bubble sizes, numbers and velocities.

A preliminary analysis of the use of video cameras to study bubbles in gushing and non-gushing ciders indicated that with cameras placed at positions close to the bottle, useful information and analyzable images could be obtained. Therefore, videography was selected as the method to use in this study for the enumeration and sizing of bubbles.

3.3.4. Investigation of Nucleation Sites

A thorough investigation of gushing in ciders should undoubtedly include a study of bubble nucleation sites, to determine if they are different in gushing ciders compared to non-gushing ciders. Current mathematical models predict that nucleation sites are most likely conical crevices in solid materials, containing small pockets of gas (Atchley and Prosperetti, 1989). Casey (1995) suggested that the radii of such cavities in sparkling wines may be approximately 0.5 μm.

Transmission electron microscopy (TEM) was investigated as a technique to examine structures at the sizes suggested for nucleation sites. Sediments were separated from the cider by decanting the liquid; attempts were made to retain the structure of the sediment. Samples of the sediment were drawn into agar sleeves and fixed in a glutaraldehyde solution (2% in pH 4 (citrate) buffer) overnight. Removal of the samples

from the glutaraldehyde solution was followed by three rinses in citrate buffer and staining, by soaking in an osmium tetroxide solution (1% OsO_4 in deionized water) for one hour. Dehydration of the samples was carried out by rinsing with a series of acetone solutions (in deionized water: 50%, 70%, 90% and finally 100% acetone), followed by propylene oxide (100%). Samples were then embedded in Spurr's resin and cut for viewing by TEM.

Several structures which conformed to the size suggested by Casey (1995) and the structure as predicted by the crevice model (Atchley and Prosperetti, 1989; Wilt, 1986) were identified in each sediment sample. However, severe dehydration techniques required for TEM may have distorted the structure of the sediment; the conical crevices observed under the microscope may not necessarily be present in the original sediment structure. In addition, the preparation of samples for TEM removed any pockets of gas from the sediment; therefore, it could not be determined whether the crevices had ever contained pockets of gas required for bubble nucleation, or if the nucleation sites had been active. Concentrations of these conical crevices in the sediments were difficult to determine by microscopy, but did not appear to be more abundant in sediments from gushing ciders.

The ambiguity in interpreting results indicated that TEM would not provide useful information about the structure of the sediment and the nucleation sites contained therein.

3.4. Materials and Methods

3.4.1. Experimental Design

3.4.1.1. *Description of the Design*

Part Two was designed as an observational study, using ciders remaining from Part One research. Ciders were divided into three "treatments": Treatment A (non-gushing), Treatment B (low gushing) and Treatment C (high gushing). Treatment A was composed of Treatment 1 and Treatment 2 ciders from Part One (non-gushing). Treatment B consisted of Crispin Treatment 4 ciders from 1994 and 1995; low gushing ciders were defined as those which lost less than 15% of the contents of the bottle when the cap was removed at 10°C. The remainder of the gushing ciders from Treatment 4 in Part One were designated as Treatment C -- high gushing ciders, resulting in the loss of more than 15% of the bottle contents when the cap was removed from the bottle cooled to 10°C (Appendix 7).

The experimental design for Part Two was regarded as a 1-factor design, with three treatments and thirteen replicates each for non-gushing and gushing ciders. Subdivision of the gushing ciders into low and high gushers resulted in five replicates for Treatment B (low gushers) and eight replicates for Treatment C (high gushers). One experimental unit consisted of one 750 mL bottle of cider. The replicates within treatments served as the error term for the statistical analysis (Table 24).

Table 24. Analysis of Variance Plan for Part Two.

Source of Variation	Degrees of Freedom
Treatments	2
Replicates (Treatments)	23
Total	25

3.4.1.2. *Objectives*

The primary focus of Part Two of the study was to construct mathematical models to describe the growth and ascent of bubbles in bottles created after pressure release from gushing and non-gushing ciders. In order to construct the models, initial headspace pressures, sediment thicknesses and headspace volumes were measured for each bottle and analyzed (Table 24; Appendix 7).

The objectives for the second part of the study were:

(i) to determine if there is a difference in headspace pressure between unopened bottles of gushing and non-gushing ciders

(ii) to determine if there is a difference in the thickness of the sediments between unopened bottles of gushing and non-gushing ciders

(iii) to determine if there is a difference in the rate of bubble formation and growth between gushing and non-gushing ciders

(iv) to develop mathematical models to describe bubble growth and ascent

(v) to determine if there is a difference in bubble growth and ascent between gushing and non-gushing ciders, using the mathematical models developed in (iv).

3.4.1.3. *Statistical Analysis*

The data collected for the headspace pressures and sediment thicknesses were subjected to an analysis of variance (ANOVA) using SAS (1989) according to the data analysis plan in Table 24; Treatment means were also computed. Results were used to construct the mathematical model. The data and results of the statistical analyses are contained in Appendices 8 and 9 respectively.

Data collected during the recovery of the headspace pressure after a brief pressure release were also analyzed using SAS. Curve fitting of the recovery data was not carried out as the complexity of the curve fitting would have resulted in the incorporation of much subjectivity into the models.

All tests were conducted at a level of significance of $\alpha = 0.05$.

3.4.2. Experimental Equipment

3.4.2.1. *Sampling Device and Monitoring Equipment*

In order to facilitate the study of the phenomenon of gushing, a sampling device was required which would allow small, controlled amounts of gas to be released from the headspace of the bottle. The brewing industry often uses devices which puncture the crown cap and a pressure gauge attached to the puncturing needle is used to measure headspace pressures in bottles of beer (Gray and Stone, 1938). Unfortunately, these types of devices would have required extensive modification to be applicable to this study, and the nature of the sealing gasket around the needle might have allowed gas to leak from the bottle during the sampling period. Other sampling devices commercially available were cost prohibitive and would also have required modification.

A sampling device[1] (Figure 4) was designed which could be adapted to this and many other applications. Electronically controlled pressure release allowed a small amount of gas to be released from the headspace in the bottle and the bottle subsequently resealed. Controlled gas release permitted video cameras to be placed at close range for all bottled ciders, including those which gushed severely. Headspace pressure changes and external bottle temperatures were monitored electronically using a Labmate Data Acquisition and Control System (Sciemetric Instruments Inc., model 7000).

3.4.2.2. *Video Taping and Analysis Equipment*

Two Panasonic video cameras (model AG-195) were used to videotape the activity in the ciders resulting from pressure release from the headspace of the bottle. One camera was used to monitor the bottom of the bottle, while the second camera was positioned to videotape the activity in the neck of the bottle. Videotaping at the bottom camera was carried out through a Panasonic SVHS Time Lapse Video Cassette Recorder (model AG-6370). Connection to the cassette recorder provided a means to add a time stamp to the recorded images, which is useful for large data sets such as those provided by the cameras. Videotaping at the top was carried out within the video camera. Timers on the two cameras could not be synchronized, thus creating difficulties in the tracking of bubbles through the entire height of the bottle. However, the top camera was useful in verifying bubble behaviour observed in the bottom camera.

The bottom camera was positioned to focus on a 6 cm height of the bottle, beginning 2.6 cm above the bottom of the bottle. This height above the bottle bottom

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[1] under patent application

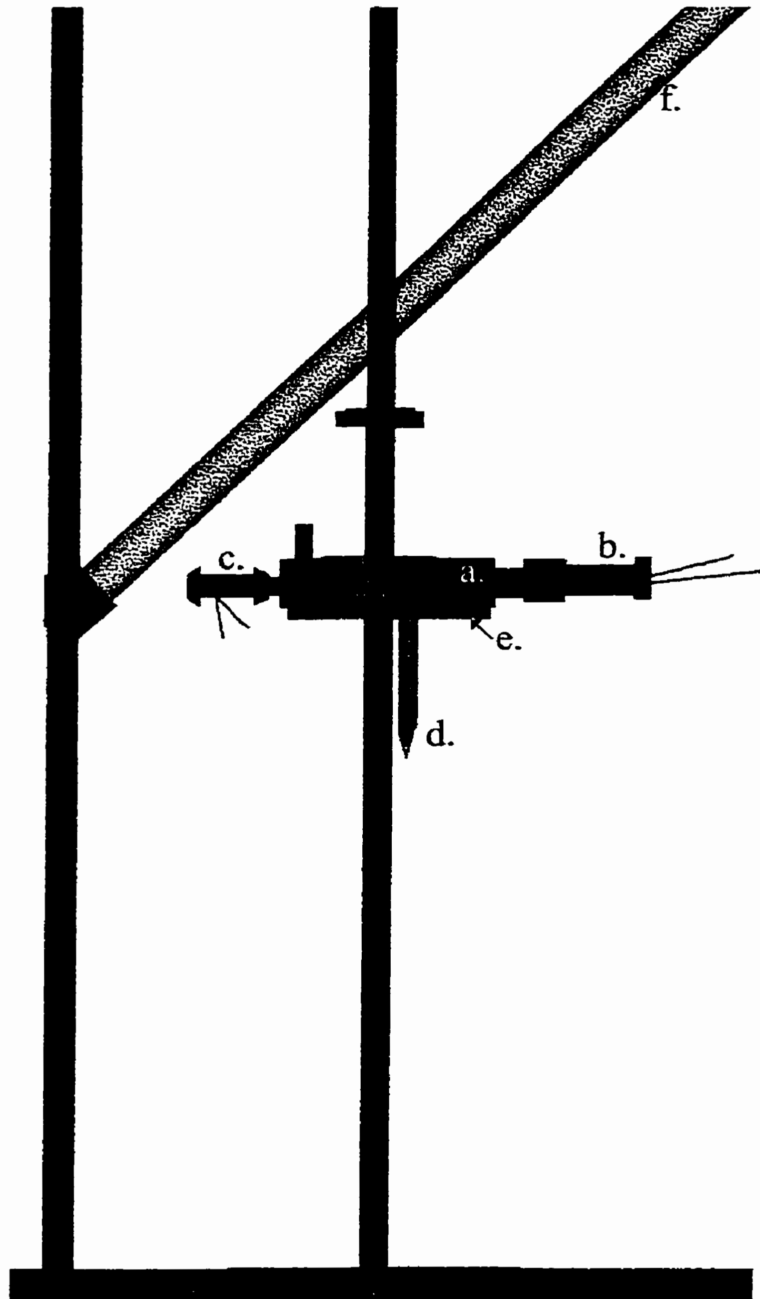


Figure 4. Sampling device for pressure release (patent pending).

a. Aluminum housing, containing piercing needle and components for pressure release/measurement. Slides up/down verticle pole and locks in place by set screw.
b. Solenoid valve for pressure release.
c. Pressure transducer, to measure pressure in bottle.
d. Hollow piercing needle, to penetrate crown cap.
e. Silicone seal.
f. Lever for driving piercing needle through crown cap.

allowed a full view of cider, regardless of the thickness of the sediment. The top camera was positioned to video tape a 4 cm high portion of the neck of the bottle.

3.4.3. Experimental Methods

3.4.3.1. *Laboratory Procedures*

Cameras were carefully aligned and adjusted to the same position daily, to ensure that any slight changes in positioning of the cameras would have a minimal effect on the accuracy of the results obtained from the camera data. In order to account for the refraction from the glass and the cider (Snell's Law), calibration measurements were made using a ruler in a bottle of still cider, positioned at varying distances from the camera lens. Calibrations for the bottom camera were carried out by using a bottle which had been cut at the shoulder and the top half of the bottle removed. Video tape recordings were made of the calibrations for each day, so that they could be analyzed in the computer programs and thus be used to determine bubble size and the velocity rates within the programs.

Using a water bath, bottles of cider were adjusted to 22°C (room temperature), to avoid condensation on the bottle exterior during video taping. The bottles were carefully removed and dried to avoid disturbance of the sediment. Headspace height and sediment thickness were measured just prior to insertion of the bottle into the sampling device.

The data acquisition unit and the two cameras were started just prior to headspace pressure release from the bottle. Headspace pressure was released using an electronic switch; the length of time of gas release was typically less than 1 second.

Data were collected by the cameras and the data acquisition unit for 20 minutes after the pressure release. The recovery of headspace pressures after the brief pressure release was monitored, to be used as an indirect measure of bubble generation and growth

in the cider. In most cases, the pressure release was only carried out once, as the sediment particles had a tendency to float over time. The data were transferred to the appropriate software packages for analysis.

3.4.3.2. *Mathematical Modelling and Computer Applications*

Videotapes were captured for computer analysis by a MATROX Marvel G200-TV system. The video clips were digitized and separated into individual frames with an Adobe Premier version 5.1 software package. Conversion of the images to grayscale, image processing and data collection were conducted in Adobe PhotoShop.

Automated measurements could not be carried out as the computer had difficulty differentiating bubbles from the background (green cider bottle) and single bubbles from those appearing to overlap in the two-dimensional image. Individual bubbles were identified and their diameters measured manually using the on-screen ruler within Adobe PhotoShop. Distances travelled by individual bubbles through a series of frames were measured to calculate the rise velocity of the bubbles. Corrections for image distortion from the bottom camera were computed. To determine bubble sizes, numbers and rates of ascent, frames positioned at every 0.1 second were analyzed within a video clip; in a 10 second clip, this constituted a series of 100 frames (30 frames / s). Preliminary trials indicated that this number of frames was required for image analysis, to account for variations in bubble sizes, populations and rates of ascent.

Mathematical models for bubble growth and ascent and for headspace recovery following pressure release were constructed from information in the literature and incorporated into computer simulation programs in MathCad and Visual Basic.

Results of the camera recordings and the data acquisition unit measurements for gushing and non-gushing ciders were used to determine the validity of the mathematical models.

3.5. Results and Discussion

3.5.1. Observations during Pressure Release from the Bottles

Gushing ciders varied in the severity of their gushing. In bottles of low gushing ciders, liquid loss from the bottle at approximately 10°C when the cap was removed ranged from a slight overfoam to a loss of 15%; this corresponds to a wildness scale of 5 - 9, according to characterizations by Beattie (1951). High gushing ciders lost more than 15%, and frequently as much as 75%, of the bottle capacity when opened under the same conditions; this corresponds to a wildness number of 10 (Beattie, 1951). Non-gushing ciders produced only a small collar of foam at the top of the liquid, usually less than 1 cm in height, when the bottle was opened.

When pressure was released from the bottled ciders under controlled conditions using the sampling device, the bubbles which formed in high and low gushing ciders appeared to be similar in size (small), but there were many more bubbles produced in the high gushing ciders compared to low gushing ciders. Non-gushing ciders had strikingly fewer bubbles than the gushing ciders, and the sizes of the bubbles varied from one bottle of cider to the next. In some instances, the bubble sizes produced in non-gushing ciders appeared to be similar to those produced in gushing ciders. In other bottles, the bubbles

produced were large and were produced less frequently than the smaller bubbles. In all bottles, the bubbles originated the sediment rather than throughout the liquid.

The recovery of the headspace pressure of the bottled cider was monitored after a brief pressure release carried out in the sampling device (Appendix 10). Examples of the recoveries of the headspace pressures during the first five minutes (300 s) in the three ciders treatments are in Figure 5. Pressures are reported per second, as this was the sampling frequency of the data acquisition unit.

A 15 second time interval was selected for analysis as initial testing of samples indicated that the first 10 to 15 seconds after pressure release was the most important with respect to observable differences between gushing and non-gushing ciders. The headspace pressures in non-gushing ciders did not recover to initial levels during the 15 second time interval because of the slow rate of bubble release from the sediment. Low gushing ciders (Appendix 7) recovered headspace pressures more quickly than non-gushing ciders although not all recovered to the initial pressures during the 15 second sampling time; occasionally the recovered pressure exceeded the initial value. The rate of bubble generation was greater in low gushing ciders than in non-gushing ciders. High gushing ciders recovered headspace pressures quickly and in most cases the recovered pressures exceeded the initial value (Appendix 10; Figure 5). It was observed that pressure release from high gushing ciders resulted in the instantaneous formation of a large cloud of minute bubbles and that during the pressure recovery time, the liquid interface in the neck of the bottle lifted up as the bubbles surged up through the cider. Once pressures exceeded the initial value, bubble formation gradually ceased over the course of a few seconds. In several high gushing ciders, headspace pressures in the high gushing bottles exceeded the initial pressure values by as much as 20 - 25% (Appendix 10; Figure 5); pressures

eventually started to decrease after approximately 30 minutes, at which time numbers of bubbles began to be released from the sediment once again.

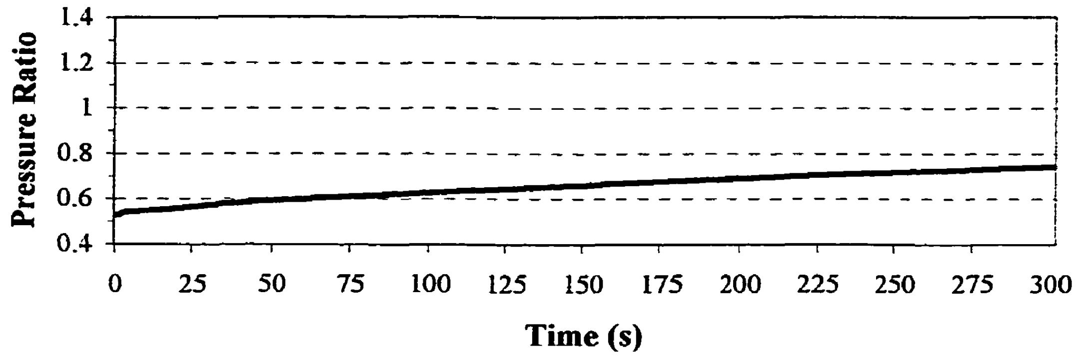
Ciders, both gushing and non-gushing, were clear with varying thicknesses of deposit (sediment) at the bottom of the bottle. In Treatment C (high gush) ciders, replicates 3, 4 and 5 (Appendix 7), a distinct haze was observed in the neck of the bottle; due to the low polyphenol but very high concentration of Pectin Fraction 1 in these ciders (Appendix 3), it was suspected that the haze was of a pectinaceous nature. Upon pressure release from the bottle, minute bubbles appeared to form within this haze. Treatment C, replicates 7 and 8 (Appendix 7) were the only ciders which were not clear; the cider in these cases appeared uniformly opaque and there was little sediment. The opacity of the cider impaired visual and computer-image analysis and thus it was difficult to determine if bubbles were generated solely in the sediment.

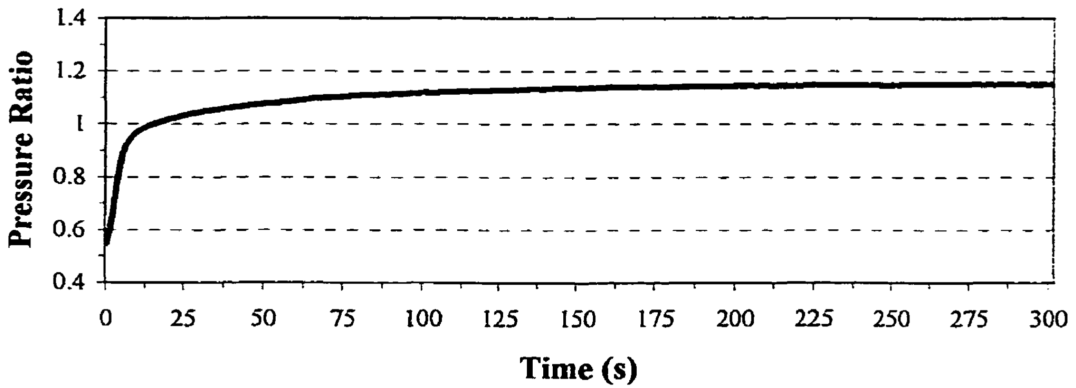
3.5.2. Sediment Thickness, Headspace Volume and Initial Pressure

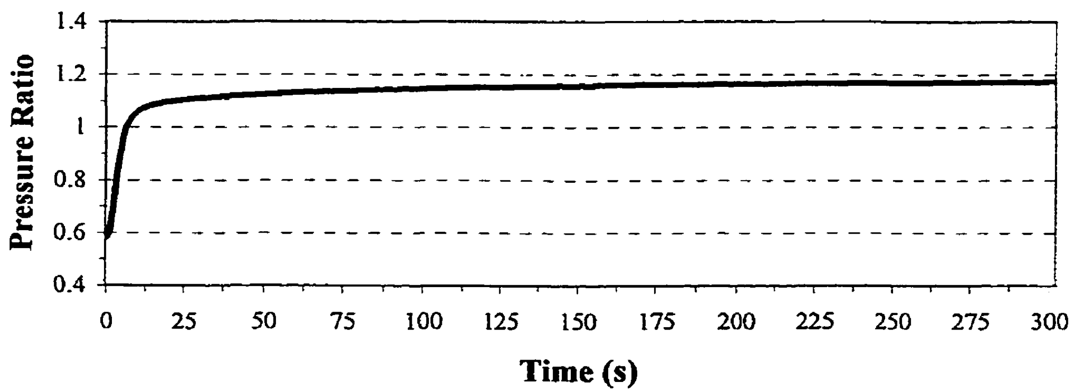
Measurements of sediment thickness, headspace volume and initial headspace pressure in the closed bottles prior to pressure release were taken to determine if there was a difference between gushing and non-gushing ciders (Appendix 8). The analysis of variance (ANOVA) tables in Appendix 9A were generated by the SAS computer program. Treatment means are presented in Table 25.

High gushing ciders had significantly larger amounts of sediment (Table 25) than those which did not gush; low gushing ciders did not have larger amounts of sediment compared to non-gushing ciders. These results are corroborated by the sediment wet weights reported in Part One of this study (Appendix 3; Tables 18 and 19) and suggest that the amount of sediment in the bottle does not determine the occurrence of gushing

Figure 5. Examples of pressure recoveries during the first 5 minutes (300 s) after a brief pressure release, as measured in headspace of the bottles of cider. Pressure ratio refers to the ratio of the recorded pressure compared to the initial pressure *before* the pressure release; pressures were measured in atm.


Non-gushing cider: Treatment A, rep. 5
Pressure Ratio
1.4
1.2
1
0.8
0.6
0.4
0 25 50 75 100 125 150 175 200 225 250 275 300
Time (s)


Low gushing cider: Treatment B, rep. 1
Pressure Ratio
1.4
1.2
1
0.8
0.6
0.4
0 25 50 75 100 125 150 175 200 225 250 275 300
Time (s)


High gushing cider: Treatment C, rep. 6
Pressure Ratio
1.4
1.2
1
0.8
0.6
0.4
0 25 50 75 100 125 150 175 200 225 250 275 300
Time (s)

but may be associated with the severity of the gushing. Headspace volume was not significantly different between the treatments (Table 25).

Headspace pressures in the closed bottles were determined with the use of the sampling device, as the equipment was designed to allow pressure determinations to be conducted independently from any headspace pressure release. High gushing ciders had significantly higher pressures than non-gushing ciders; low gushing ciders did not have significantly higher bottle pressures than non-gushing ciders (Table 25). Since all ciders were fermented to dryness in the primary fermentation and equivalent amounts of sucrose added for the secondary fermentation (Part One, Section 2.3.2.), this observed increase in pressure in ciders containing larger amounts of pectin (Appendix 3) supports the hypothesis that pectin fractions were degraded to smaller sugar units which could be fermented during the secondary fermentation (Section 2.4.3.3.1.). The headspace pressures of low gushing ciders were not significantly different from those of non-gushing ciders. This indicates that higher headspace pressures are associated with the severity of gushing but do not determine its occurrence. The ciders, which were produced in a champagne style, had pressures well below the maximum of 6 atmospheres expected for champagne (Robinson, 1994); this indicates that gushing is not caused by over carbonation, but by other factors.

The lack of significance in the thicknesses of the sediments of low gushing ciders compared to those of non-gushing ciders indicated that the composition of the sediment must play a significant role in determining the occurrence of gushing. The chemical analyses conducted on the sediments in Part One of the study (Appendix 3; Section 2.4.3.4.4.) were reviewed in light of these findings.

Table 25. Treatment means and significance[a] of treatment contrasts for the sediment thickness, headspace volume and headspace pressure in the closed bottle.

Response Variable	Treatment A Means	Treatment B Means[b]	Treatment B SED[c]	Treatment C Means	Treatment C SED[c]	EMS[d]
Sediment Thickness (cm)	0.431	0.300[ns]	0.2771	1.386[**]	0.2131	0.4802
Headspace Volume (mL)	7.87	7.14[ns]	0.4566	7.25[ns]	0.3511	3.5405
Pressure (atm)	4.09	4.42[ns]	0.2233	5.10[**]	0.1717	0.2024

[a] significance: *, ** : significant at $\alpha = 0.05$ and 0.01 respectively; ns : not significant

[b] Treatment: A = non-gush B = low gush C = high gush;
Treatment B and Treatment C were contrasted against Treatment A (Treat A vs Treat B.; Treat A vs Treat C)

[c] standard error of the difference of the means for Treatments B or C minus A

[d] error mean square; error degrees of freedom = 25

The raw data (Appendix 3) obtained from analyses of the sediments at 5 months in the bottle were selected for the ciders used in the Part Two research (Appendix 7). The results of the pectin analyses for non- , low and high gushing ciders were re-analyzed in SAS, to investigate the hypothesis that composition of the sediment, particularly its pectin content, is important in the phenomenon of gushing. The number of samples of the low gushing ciders (only 1994 and 1995 Crispin ciders from thawed apples; n = 2) prevented the contrasting of the gushing treatments to the non-gushing treatment. Pectin Fractions 1 (water soluble) and 2 (oxalate soluble) were significantly different for the treatments; treatment means are reported in Table 26 (Appendix 9B), suggesting that higher pectin concentrations in the sediment are associated with the occurrence *and* severity of gushing.

Table 26. Significance of the main effect of Treatment and Treatment means of sediment pectin composition of ciders used in Part Two research. Analysis of variance was conducted using data obtained at 5 months in the bottle (Appendix 3).

Response Variable	Significance [a]	Error Mean Square	Error degrees of freedom (df)	Treatment means[b]		
				A	B	C
Pectin Fraction 1 (μg/g wet sediment)	**	3.885×10^6	12	148	765	2936
Pectin Fraction 2 (μg/g wet sediment)	**	5.891×10^5	12	166	870	2028
Pectin Fraction 3 (μg/g wet sediment)	ns	4.163×10^5	12	1757	1800	1873

[a] significance of Treatment main effect: *, ** : significant at $\alpha = 0.05$ and 0.01 respectively; ns : not significant

[b] Treatment: A = non-gush B = low gush C = high gush; means are expressed as μg of uronic acid / g of wet sediment

3.5.3. Headspace Pressure Recovery after Pressure Release

At the low pressures used in this study, it can be assumed that the cider behaves as an incompressible liquid. Therefore, the rate of recovery of the headspace pressures following a pressure release is directly related to the rate of mass transfer of the carbon dioxide from the liquid to the gas phase, primarily due to bubble formation and growth. The data acquisition unit used in this study collected pressure and temperature readings once per second; therefore, headspace recovery pressures and rates of recovery were reported per second (Appendices 10 and 11).

The amount of gas released by the sampling device is a function of the headspace pressure of the bottle and the length of time of the pressure release. As neither one of these parameters could be precisely controlled in this experiment, the pressure release could not be standardized. If it is assumed that carbon dioxide (CO_2) is inert, as has been

assumed in studies of beer (Kuzniarski, 1983), the amount of gas released can be estimated by the ideal gas law from the headspace pressure which was recorded immediately following the pressure release (Appendix 10).

The rate of change of the pressure following the pressure release, as measured in the headspace, was used as an indirect estimate of the rate of bubble formation and growth, to indicate if a significant difference may exist between gushing and non-gushing ciders. The rate of the change in headspace pressure during the 15 seconds following the pressure release was calculated from the data in Appendix 10, at one-second intervals (Appendix 11). The pressure was expressed as a fraction of the initial pressure value. The means of the recovery data for each second were plotted (Figure 6) to provide a clearer presentation of the headspace pressure recovery rates. From Figure 6, it is evident that the rate of pressure recovery is much faster in the first three seconds in the high gushing ciders than in low gushing ciders.

Changes in headspace pressure were determined for each 1 second interval following pressure release. Statistical analysis was carried out to determine if there was a difference in the rates of headspace pressure recovery between the treatments (Appendices 11 and 12). The rate of pressure recovery was significantly faster in gushing ciders for the first nine seconds only (Table 27; Appendix 12); these differences are evident in the plot of the raw data (Figures 5 and 6). The results indicate that gushing develops very rapidly, within the first second following pressure release from the bottled cider; this is in agreement with studies of gushing in beer (Anonymous, 1948). A large amount of gas must be transferred from the liquid to the gas phase in gushing ciders compared to non-gushing ciders, to provide the significantly different rates of pressure recovery in the headspace noted in the first 9 seconds following the release of headspace pressure (Table

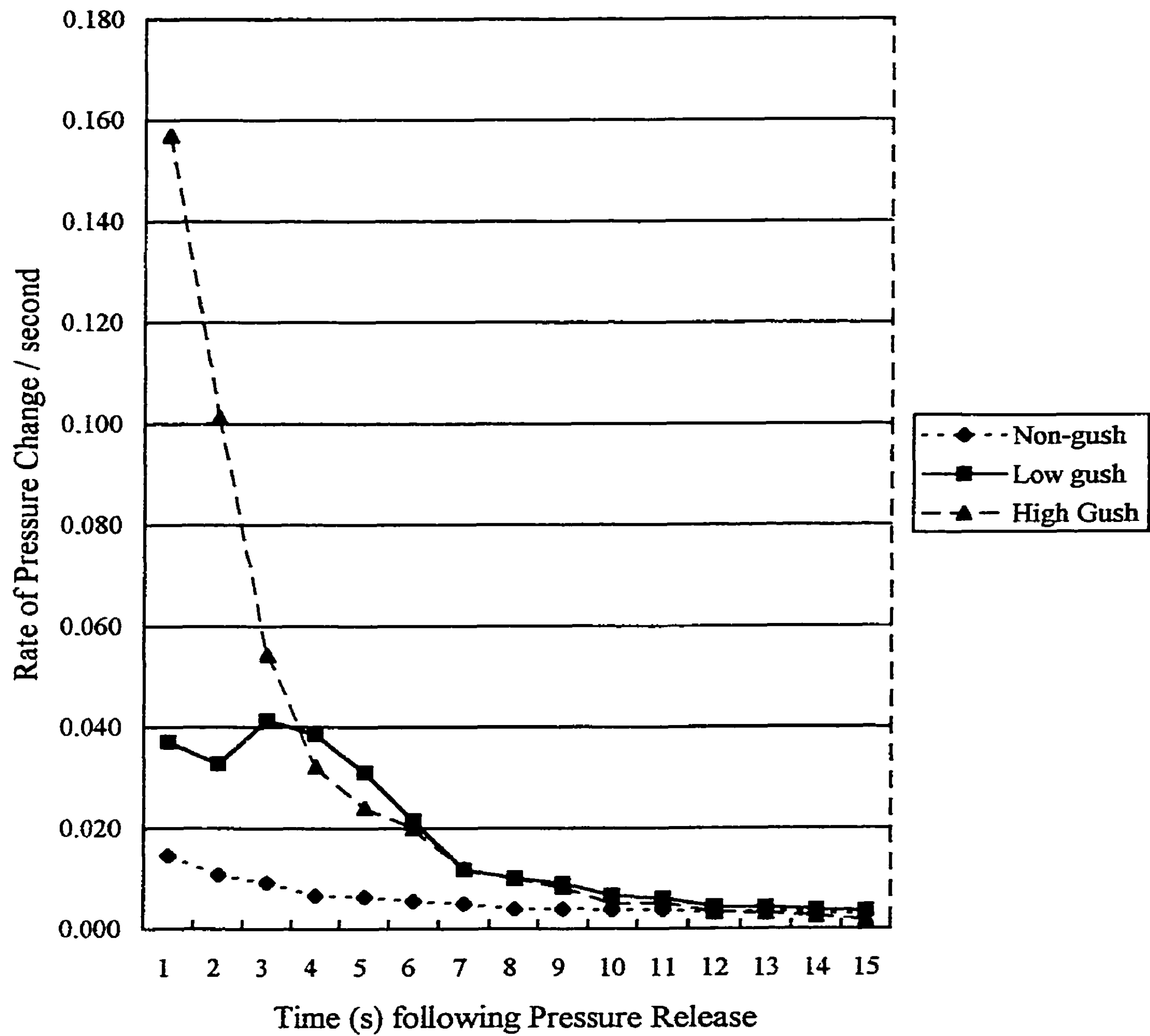


Figure 6. Recovery rates of headspace pressures in bottled ciders after a brief pressure release (Appendix 11). Pressures are as fractions of their initial values.

27). Observations during pressure release (Section 3.5.1.) indicated that large bubbles are *not* the cause of increased gas release in gushing ciders; therefore, the higher rate of pressure recovery is due to a larger *number* of bubbles produced per unit of time.

Table 27. Treatment means and significance [a] of treatment contrasts of the recovery rates of the headspace pressure following a brief pressure release. Pressures are expressed fractions of their initial pressures.

Time (s) after Pressure Release	Treatment A	Treatment B		Treatment C		
	Means	Means[b]	SED[c]	Means	SED	EMS[d]
1	0.01462	0.0371 ns	0.08210	0.157 **	0.06315	0.003703
2	0.01077	0.0327 ns	0.05482	0.101 **	0.04216	0.000736
3	0.00917	0.0414 *	0.04935	0.054 **	0.03795	0.000483
4	0.00662	0.0386 **	0.04764	0.032 *	0.03664	0.000420
5	0.00638	0.0309 **	0.04190	0.024 *	0.03223	0.000251
6	0.00547	0.0214 *	0.03735	0.020 *	0.02872	0.000159
7	0.00496	0.0116 ns	0.02820	0.012 *	0.02169	0.000052
8	0.00397	0.0100 *	0.02273	0.010 **	0.01748	0.000022
9	0.00386	0.0090 *	0.02132	0.008 *	0.01640	0.000017
10	0.00380	0.0066 ns	0.01893	0.005 ns	0.01456	0.000010
11	0.00379	0.0060 ns	0.01809	0.005 ns	0.01391	0.000009
12	0.00315	0.0045 ns	0.01680	0.003 ns	0.01292	0.000006
13	0.00359	0.0043 ns	0.01665	0.003 ns	0.01280	0.000006
14	0.00314	0.0038 ns	0.01641	0.003 ns	0.01262	0.000006
15	0.00280	0.0035 ns	0.01514	0.002 ns	0.01164	0.000004

[a] significance: *, ** : significant at $\alpha = 0.05$ and 0.01 respectively; ns : not significant

[b] Treatment: A = non-gush B = low gush C = high gush; Treatment B and Treatment C were contrasted against Treatment A (Treat A vs Treat B.; Treat A vs Treat C)

[c] standard error of the difference of the two means for the treatment contrasts

[d] error mean square; error degrees of freedom = 23

3.5.4. Mechanism of Gushing

Gushing ciders differed significantly from those which do not gush in the recovery rate of the headspace pressure after a brief release of pressure (Section 3.5.3.). Thus, the rate of carbon dioxide transfer from the liquid to the gas phase was significantly greater in gushing ciders compared to non-gushing ciders. In order to propose a mathematical model to describe the gushing phenomenon, the numbers and behaviour of the bubbles in the ciders were studied using image analysis of the video tapes. "Normal" bubble frequency and behaviour were determined from the data of non-gushing ciders. Differences in bubble formation and behaviour in gushing ciders were then used to modify the model to explain the action of gushing.

3.5.4.1. *Non-gushing Ciders*

3.5.4.1.1. Image Analysis

A series of images constituting a ten-second video "clip" were analyzed for each of three ciders, for bubble size, bubble frequency and velocity of the rising bubbles. Video recordings were chosen randomly for analysis. Bubble size, growth rate and velocity were determined from the images. Despite being positioned approximately 3 centimeters above the bottom of the bottle, image analysis of the tapes from the bottom camera allowed estimation of the initial sizes of the bubbles at departure from the nucleation sites by back calculation. The number of bubbles produced per second ("bubble frequency") could also be estimated.

Calibration of the cameras was carried out in Adobe Photoshop, so that the on-screen rulers in the software program could be used directly to determine the diameters of the bubbles and their distances travelled. Variations in the calibrations between days was not unexpected as the equipment was disassembled after each day's work. The impact of the variations in calibration was reduced by calculating the image analysis results of each day using only the calibrations of that day. Although it was first believed that a volume of cider within the bottle could be defined by the focus of the camera, analysis of the images revealed that whether or not a bubble was in focus could not be determined accurately, particularly in the case of the very small bubbles produced in gushing ciders. Therefore, the volume of cider analyzed was defined by the width of the bottle and the height of the camera view. In the top camera, the volume within the view of the video camera was calculated as 16.3 ± 0.8 mL. For the bottom camera, this volume was calculated as 267 ± 35 mL. The large variation in the measurements for the bottom camera is due to the calibration differences between the front and back walls of the inside of the bottle, with respect to the camera position, as the focus of the camera could not be used to define a smaller volume within the bottle. Calibrations for the bottom camera were also affected by the taping procedure in which the recording was carried out in the video cassette recorder to improve the tracking of the elapsed time during the recording, but this caused a slight distortion of the image: the size of objects was magnified slightly in the center of the frame of the image. All measurements were, therefore, adjusted for the position within the frame. The video recording in the top camera was made directly by the camera and distortions were not observed.

Bubble sizes, ascent velocities and estimated bubble frequencies were calculated from analysis of the video tapes. A non-gushing cider often contained bubbles of different

sizes, which were generated at different frequencies; bubble sizes and frequencies usually varied over the course of the 15 second time interval during which the analysis took place. Therefore, single bubbles were tracked for several frames in the different ciders, at different pressures, and average values were computed.

3.5.4.1.2. Modelling the Single Bubble

Studies of the diffusion of carbon dioxide, bubble nucleation and bubble growth are usually conducted in pure water, lacking surfactants (Geankoplis, 1983; Houghton *et al.*, 1957). The presence of surface contaminants, including surfactants, affects both mass transfer of gas into the bubble and bubble velocity (Clift *et al.*, 1978), but appears to have little effect on the diffusion of gases through the liquid (Houghton *et al.*, 1957). To build a model to describe the growth of a single bubble and its velocity as it rises through the cider, it is necessary to first assume that the surface contaminants present in the ciders do not affect mass transfer or bubble motion.

Four ciders randomly selected from Treatment A were used to provide experimental data for affirmation of the single bubble modelling (Appendix 13). For each cider, single bubbles were selected and their ascent and growth determined over a series of frames from the video clip(s).

To construct the model and computer simulation of the rising bubble, the amounts of nitrogen, oxygen and carbon dioxide present in the bottled cider were first calculated (Appendix 14). Due to their lower solubilities compared to that of carbon dioxide (Tinoco *et al.*, 1985), oxygen and nitrogen in the cider will tend to move from the liquid phase to the gas phase more quickly than the carbon dioxide, which may in turn lead to

more bubbles being formed more quickly within the cider. The only source of oxygen and nitrogen gases in the bottle would be at the time of bottling, as yeasts cannot produce these gases de novo. Secondary fermentation consumes oxygen and produces carbon dioxide (Webb, 1994); thus, at the end of the secondary fermentation, oxygen concentrations would have decreased to negligible levels.

In a mixed gas system, such as in the cider, Henry's Law (Carroll, 1991) can be used to calculate mole fractions of the gases in the liquid and the headspace:

$$x_i H_{ij} = y_i \mathrm{P} \tag{18}$$

where x_i is the mole fraction of the solute, component i (oxygen or nitrogen) , in the liquid phase j, y_i is the mole fraction of component i in the gas phase, H_{ij} is the Henry's constant, as taken from published tables (Tinoco *et al.*, 1985) and P represents the pressure of the system. Oxygen would have been depleted at the completion of the secondary fermentation, and the concentration of nitrogen in the bottle would be so low compared to the concentration of carbon dioxide that it can be considered negligible (Appendix 14). These expectations were corroborated by the very low concentrations of oxygen and nitrogen that were detected in the screening test for gas composition (Appendix 6).

Equations from the literature (Section 3.2.2.) were assembled to construct a computer program in Visual Basic (Figure 7; Appendix 15) to simulate the growth and velocity of a single bubble in a non-gushing cider. The temperature of the bottled cider at time of pressure release and the change in pressures during the recovery after pressure release were incorporated into the computer program, as both these parameters will affect

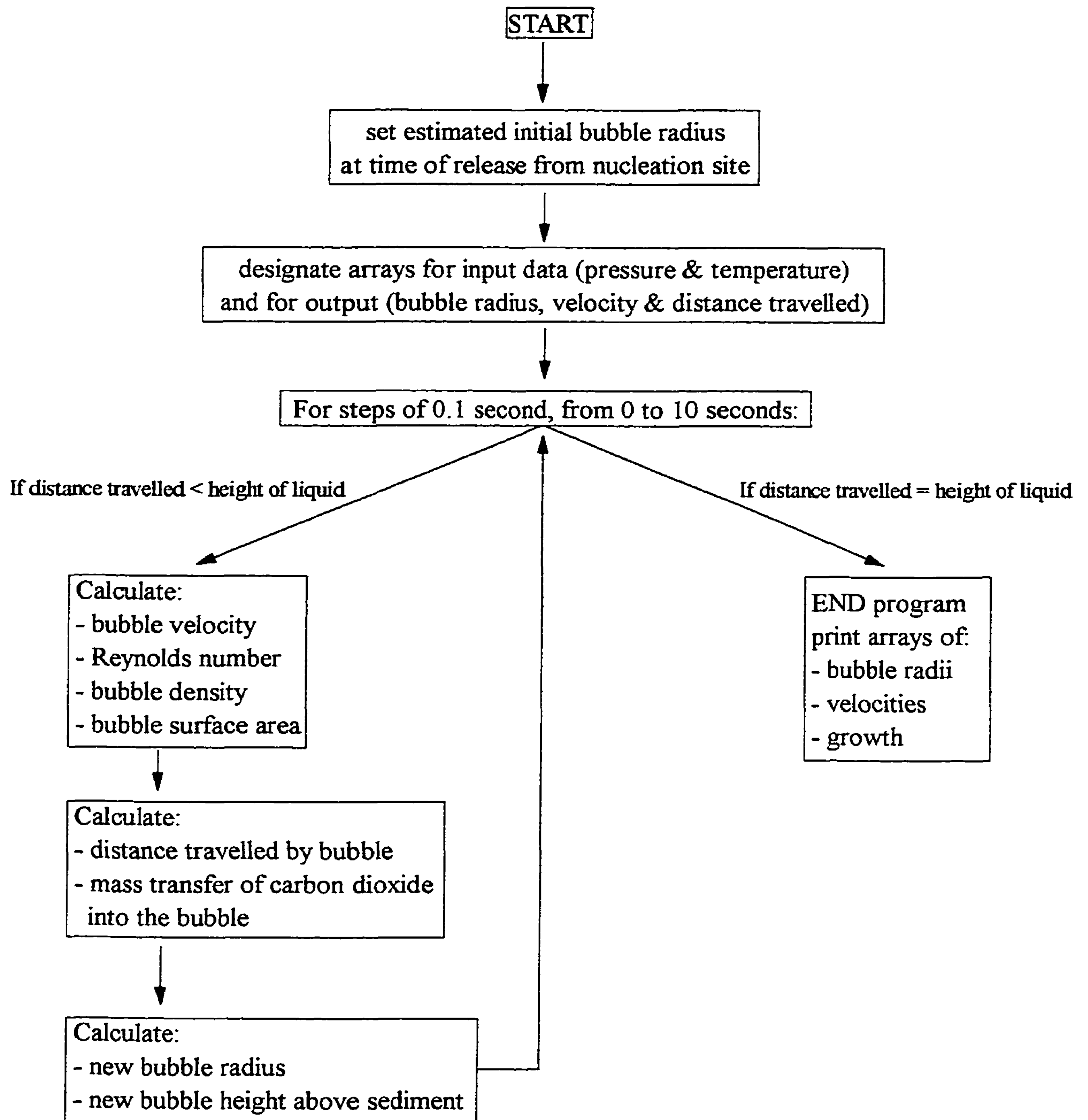


Figure 7. Flow diagram of the computer program used to calculate the increase in size and velocity of a single bubble during ascention from the nucleation site in the sediment to the headspace of the bottle.

the growth and velocity of the bubble. Data obtained from analysis of the images from the video tapes (Appendix 13) were used to test the model and computer simulation program.

The initial radius of the bubble can be estimated from the data collected from the image analysis (Appendix 13), as the bottom camera was situated such that the bottom of the camera's view was 2.6 cm above the bottom inside the bottle, noting that the focussing error is ± 14% of the measured value. Sediment thickness measured for each bottle (Appendix 8) allowed calculation of the height of the bubble above the sediment. Estimations of initial bubble radius (±14%) of the examples from Appendix 13 are in Table 28, below, along with the heights of the ciders; these data are necessary to simulate the bubble growth and rise by the computer program (Appendix 15).

Table 28. Cider liquid height and estimated initial bubble radius at detachment of the bubble from the nucleation site from data in Appendix 13 in non-gushing ciders. Radii were estimated using velocity (equation 5) and mass transfer (equation 11) estimations from changes in radii (Appendix 13).

Treatment A	Liquid height (cm)[a]	Bubble Number	Initial bubble radius (mm)
replicate 1	27.3	1	0.8
		2	0.7
replicate 4	26.5	1	0.3
		2	2.6
replicate 5	27.2	1	0.1
		2	0.6
replicate 13	27.5	1	0.4

[a] Liquid height = total bottle height - (sediment thickness + headspace height)

A study of the entire process of gushing should include the investigation of the structure of active nucleation sites; conceivably, there may be different types and shapes of nucleation sites in gushing ciders compared to non-gushing ciders. Technological limitations did not allow comparison of the sites themselves in this study. However, the number, frequency and size(s) of bubbles generated from the nucleation sites within a bottle of cider are ultimately responsible for the gushing action, and some information about the physical or physico-chemical properties of the sites may be gained from the examination of size of the bubbles released from the nucleation sites.

Once the bubble leaves its nucleation site, it begins an ascent through the cider during which it grows and increases in velocity. In a closed system such as the bottle of cider, it can be assumed that the pressure inside the bubble is equivalent to the pressure of the gas phase in the headspace; the number of moles of gas in the bubble can be calculated from the ideal gas law, as outlined in Section 3.2.2.2.

$$n_{bubble} = \frac{P_{bubble} \bullet V_{bubble}}{R \bullet T} \tag{2}$$

The initial velocity (*vt*) and Reynolds number (NRe) can be calculated by the previously reported equations:

$$vt = \frac{2g \bullet \rho \bullet r^2}{9\mu_B} \tag{5}$$

$$NRe = \frac{2r \bullet vt \bullet \rho}{\mu_B} \tag{6}$$

Diffusion of carbon dioxide through the cider was calculated from equation (4), where values for ψ_B and M_B were those for water, as Houghton *et al.* (1957) indicated that diffusion did not vary significantly at low viscosities (0.5 - 1.3 cP):

$$D_{AB} = \frac{7.4 \bullet 10^{-8} \left(\psi_B M_B\right)^{.5} \bullet T}{\mu_B \bullet V_A^{.6}}$$

and thus:

$$D_{AB} = \frac{7.4 \bullet 10^{-8} (2.26 \bullet 18.02)^{.5} \bullet T}{1.22 \bullet 10^{-2} \bullet 94.0^{.6}} \text{ cm}^2 \text{ per second}$$

Average viscosities of the ciders were previously determined as 1.22 cP (Table 23; Section 3.3.2.). Equations (7) through (15) of Section 3.2.2.2. were then used to construct the computer program (Appendix 15) for the bubble simulation. The effective diameters for bubbles with radii larger than 1.0 mm were computed (Appendix 13) in order to calculate bubble radii required for velocity and mass transfer determinations (Houghton *et al.*, 1957):

$$d_e = (a \bullet b^2)^{1/3} \qquad (19)$$

Houghton *et al.* (1957) were able to model the relationship of the two diameters of the ellipsoidal bubble according to:

$$b = 1.2\,a \tag{20}$$

for viscosities in the range of 0.5 to 1.3 cP. Although the ciders in this study had viscosities of approximately 1.22 cP, this relationship between the two ellipsoidal diameters did not hold true for the bubbles in the cider.

Although Treatment A, replicate 5 was the example used to illustrate the computer program in Appendix 15, trials with data in Appendix 13 were also conducted, to test the computer program and thus the mathematical model. Figure 8 shows the results of the simulation for Bubble 1 (Table 28) of Treatment A, replicate 5, with initial radius of 0.2 mm; the error bars on the graph indicate the variation of ±14% due to the focussing difficulties in the bottom portion of the cider bottle. Figure 9 shows the results of the simulation for Bubble 2 (Table 28) in Treatment A, replicate 5, with an initial radius of 0.6 mm, also with the error bars. Data produced from the simulation for both bubbles are in Appendix 16.

Simulated data agreed with measured values within the margin of error (focus error of ±14%) due to the camera focus in the bottom camera. Therefore, for the short distance that the bubble travels through the liquid in the bottle, modelling using equations constructed for bubble studies in pure water is sufficient to predict the growth and speed of ascent of the bubble through the liquid. For ascent through greater heights of liquid, it is expected that the decreased velocity and lower rate of bubble growth would be significant as a result of the surface contaminants; this is suggested by the lower values of velocity and bubble growth observed in the smaller bubbles (Appendix 13 D., for example) compared to those calculated (Appendix 16). If the bubble travelled up the wall of the bottle rather than through the liquid in the center of the bottle the velocity of the bubble

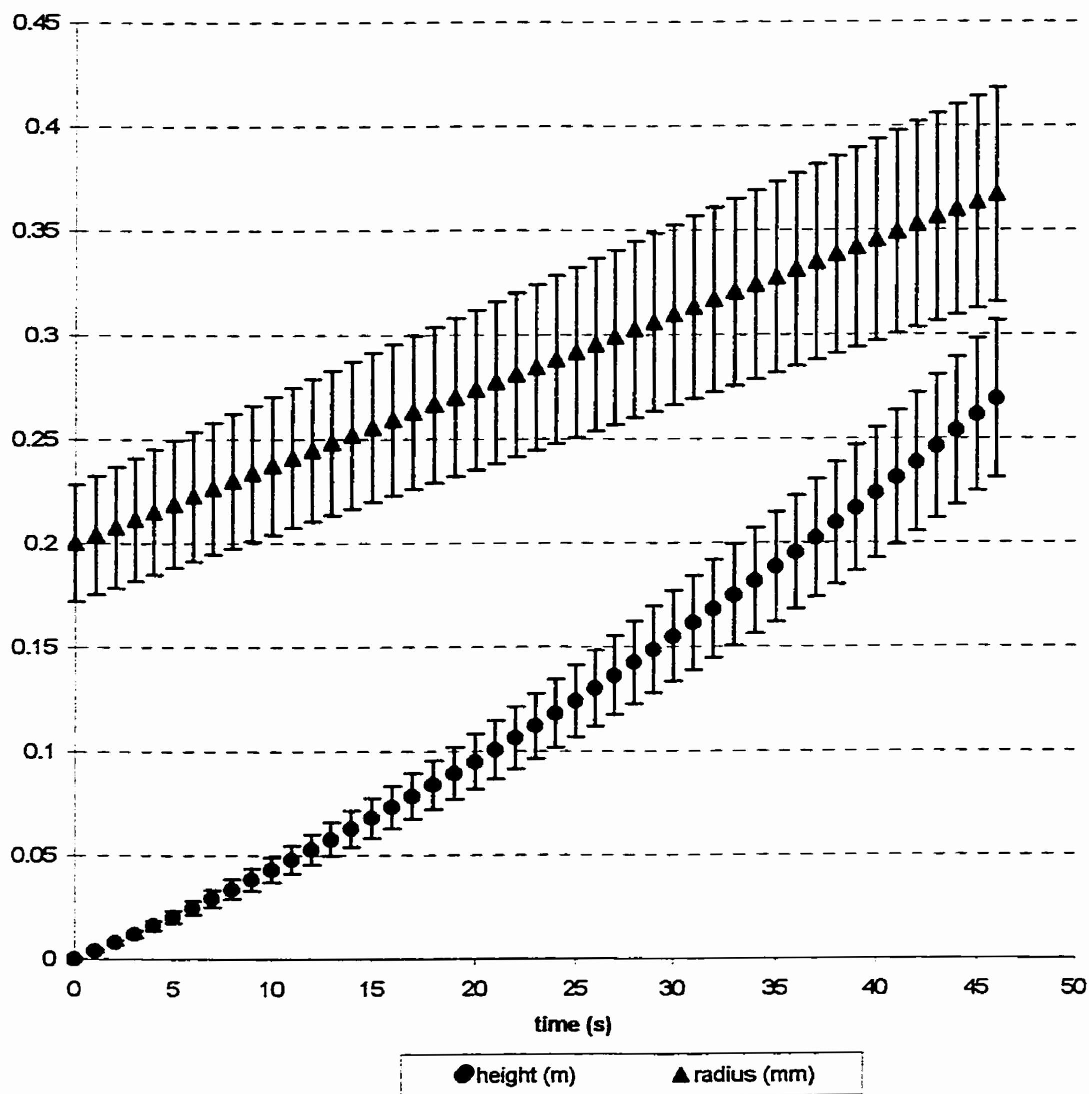


Figure 8. Computer simulation of the velocities and bubble growth by a single bubble in Treatment A, replicate 5 with an initial radius of 0.2 mm. Error bars represent the variation (± 14%) in measurement caused by the difficulties in the focussing of the bottom camera. A bubble with an initial radius of 0.2 mm would reach the headspace at the top of the bottle in approximately 48 s.

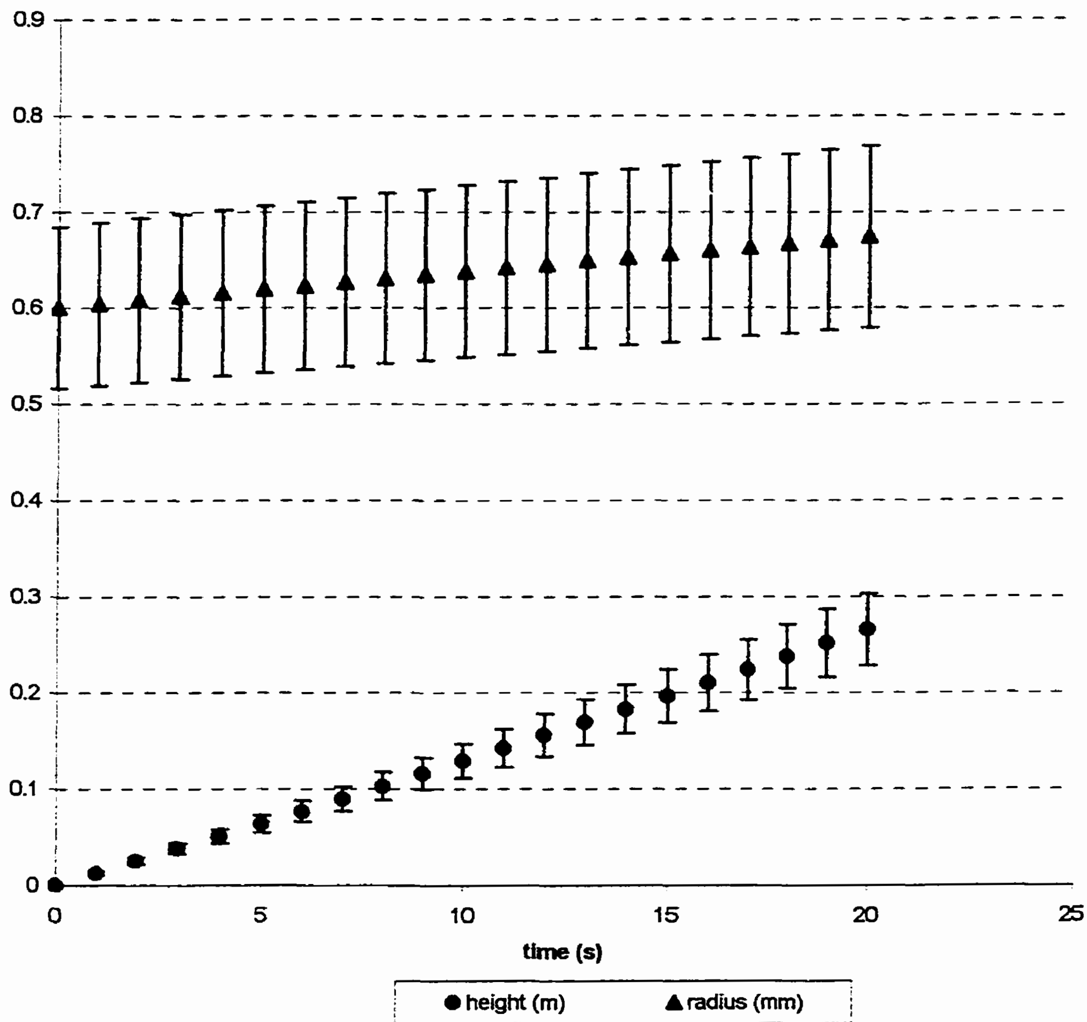


Figure 9. Computer simulation of the velocities and bubble growth by a single bubble in Treatment A, replicate 5 with an initial radius of 0.6 mm. Error bars represent the variation (± 14%) in measurement caused by the difficulties in the focussing of the bottom camera. A bubble with an initial radius of 0.6 mm would reach the headspace at the top of the bottle in approximately 20 s.

was lower; an example of this occurrence is the Bubble 1 of Treatment A, replicate 1 (Appendix 13) when it reached the view of top camera. This reduced rate of ascent is not unlike liquid laminar flow in pipes, which is due to shear of the liquid at the pipe wall (McCabe, 1976).

3.5.4.1.3. Model of Headspace Pressure Recovery

Knowledge of bubble size and the frequency of bubble production provided information for the prediction of the headspace recovery rates by computer simulation. To obtain these data, images from the video tapes of the three randomly selected non-gushing ciders were analyzed (Appendix 17). The image analyses were conducted from the video tapes for the first ten seconds after pressure release, as it was determined that the changes in headspace pressure that were significantly different between the treatments occurred within this period of time (Table 27; Section 3.5.3.).

By following the ascent paths of the bubbles, it was observed that bubbles were seldom released more than once from a single location in the sediment during the 10 seconds. This suggests that a single nucleation site may only release one bubble during the 10 seconds; therefore, in order to model the rate of the recovery of the headspace pressure following pressure release, the bubble frequency per unit surface area of the sediment and the frequency for the whole bottle were determined, rather than from a single nucleation site (Appendix 17). Frequencies (numbers of bubbles generated / cm^2 of sediment/ s) were calculated from the averaged velocities and bubble populations per frame of the video tape, over a one second time period:

$$\text{frequency} = (\text{average number of bubbles per unit volume}) \cdot (\text{average velocity}) \tag{21}$$

The frequency of bubble evolution in a bottle of cider is a function of the number of nucleation sites within the bottle and the rate of growth of the embryonic bubble at the nucleation site, until it reaches a size with sufficient buoyancy to break away from the nucleation site; the geometry and physico-chemical nature of the site govern the mass transfer rate of carbon dioxide into the embryonic bubble and the surface tension binding the bubble to the nucleation site. Estimates of the average sizes of the bubbles as they lifted from the nucleation site in the sediment allowed calculation of the average volume of the gas phase evolved per second due to bubble generation (Appendix 17). Figure 10 shows a series of frames for a non-gushing cider, from which the average bubble size and velocity and the number of bubbles may be calculated. In Treatment A ciders, bubble frequency was low and the number of bubbles produced per second remained relatively constant; this is consistent with the gradual but continuous increase in headspace pressure measured by the data acquisition unit (Appendix 10) and the relatively constant rate of pressure recovery observed in Figure 6, for non-gushing ciders. Larger bubbles (Figure 11) were observed occasionally in non-gushing ciders. Treatment A replicate 3 cider was different from other Treatment A ciders as it produced bubbles in group bursts rather than at a more constant frequency.

Once the pressure was released from the bottle of cider through the sampling device, the release valve was closed and the total volume of the bottle remained fixed during the recovery of the headspace pressure. The incompressibility of the liquid in the confined volume of the bottle dictates that changes in pressure in the headspace are

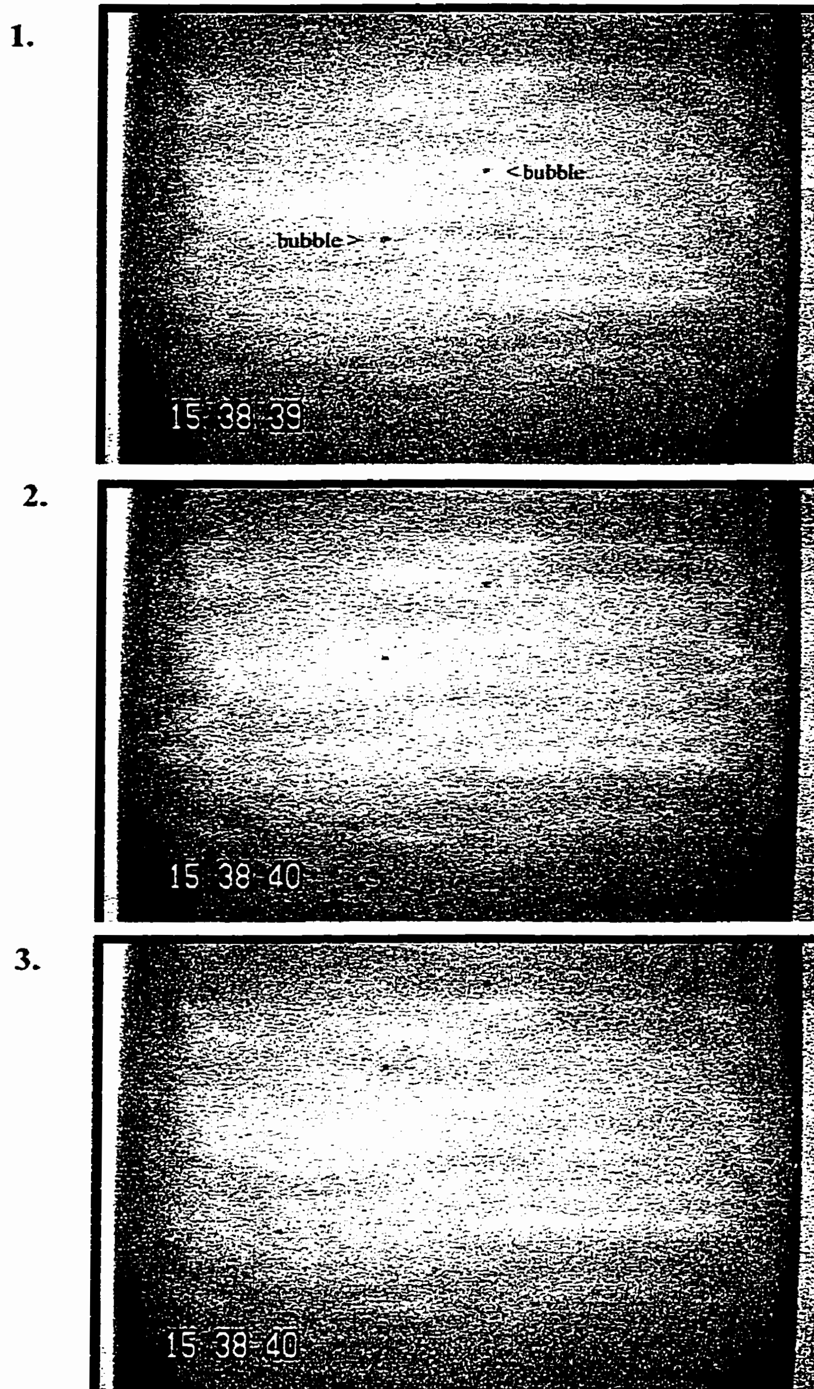
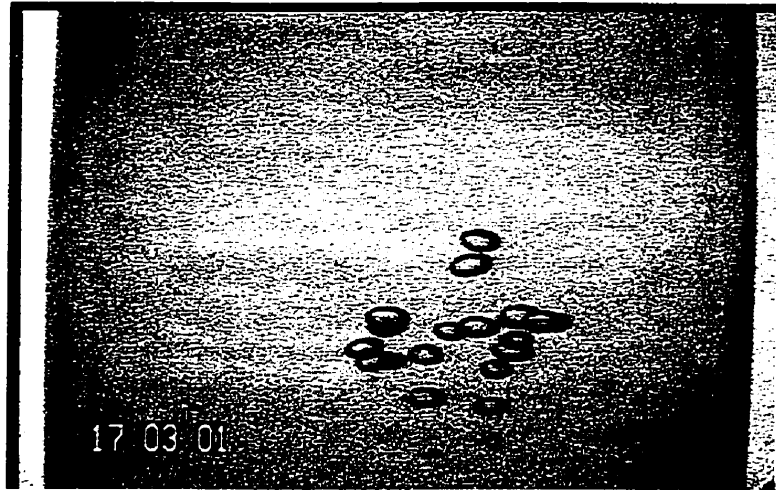
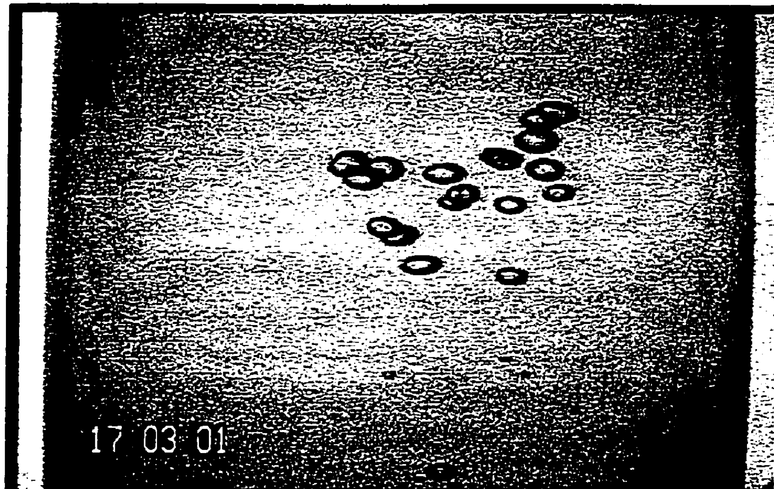


Figure 10. Ascent of bubbles through cider of Treatment A, rep.5 (non-gush), as viewed through the bottom camera. Frames are numbered in sequence and are 0.1 seconds apart. Bubbles are very small (0.2 mm radius) and only two are clearly identifiable in the center of the frames, as indicated in Frame 1. Frame sequence begins approximately 2 seconds after pressure release.

1.



2.



3.

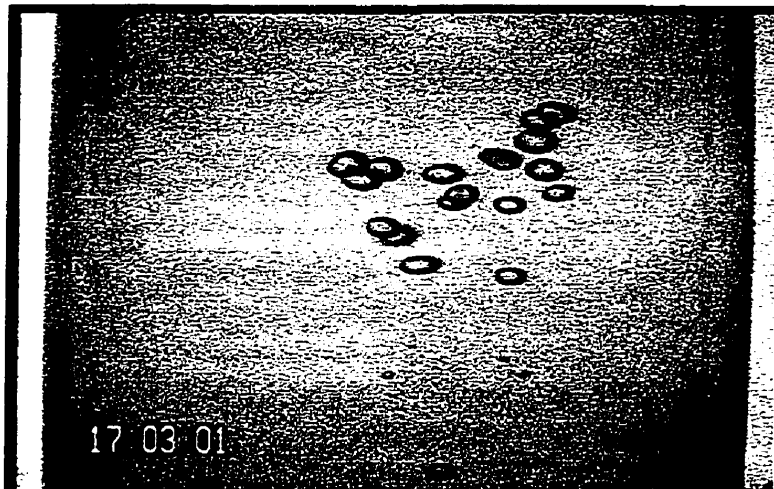


Figure 11. Ascent of bubbles through cider of Treatment A, rep. 3, as viewed through the bottom camera. Frames are numbered in sequence and are 0.1 seconds apart. This group of bubbles appeared approximately 1 second after pressure release.

attributed only to changes in the number of moles of carbon dioxide in the gas phase; as the volumes of the bottle and of the liquid are both constant, the *total* volume of the gas phase remains constant. Although the nucleation and growth of the bubbles as they rise through the cider is the primary site of mass transfer of carbon dioxide from the liquid to the gas phase, mass transfer also takes place at a slower rate at the liquid/gas interface in the neck of the bottle. The surface area of the interface was constant between bottles, as it is defined by the interior circumference of the neck. The mass transfer coefficient for the headspace can be described as (Sakiadis, 1984):

$$k_{head} = \frac{8 \bullet D_{AB}}{\pi \bullet \mathrm{d}_{\mathrm{head}}} \tag{22}$$

where k_{head} is the mass transfer constant, D_{AB} is the diffusivity of carbon dioxide in the cider, as defined previously in equation (4), and $\mathrm{d}_{\mathrm{head}}$ is the interior diameter of the neck of the bottle. The rate of mass transfer at the headspace interface is dependent upon the difference in the concentration of the carbon dioxide in the cider and the headspace, as derived from equation (11):

$$N_{head} = k_{head} \bullet (\mathrm{c}_{\mathrm{A1}} - \mathrm{c}_{\mathrm{A2}}) \tag{23}$$

where N_{head} is the flux at the headspace, c_{A1} is the concentration of carbon dioxide in the liquid phase, as calculated by the computer program in Appendix 14 and c_{A2} is the concentration of the gas in the headspace. The pressure inside the growing bubbles can be considered to be instantaneously equivalent to the pressure in the headspace at any point in time. Therefore, the pressure as measured in the headspace reflects the combined

increase in the number of moles of carbon dioxide in the bubbles and in the headspace. According to the Ideal Gas Law:

$$P \bullet V_{gas} = n_{gas} \bullet R \bullet T \qquad (24)$$

where R, the gas constant, and T, the temperature, are constant over the 10 second time period, P is the pressure as measured at the headspace, V_{gas} is the total volume of the gas phase and n_{gas} is the total number of moles in the gas phase. Differentiation of equation (24) expresses the change in the number of moles in the gas phase as a function of time:

$$\frac{dn_{gas}}{dtime} = \left(\frac{dP}{dtime} \bullet V_{gas} + \frac{dV_{gas}}{dtime} \bullet P\right) \bullet \left(\frac{1}{R \bullet T}\right)$$

and

$$\frac{dn_{gas}}{dtime} = \frac{d}{dtime}\left(P \bullet V_{gas}\right) \bullet \left(\frac{1}{R \bullet T}\right) \qquad (25)$$

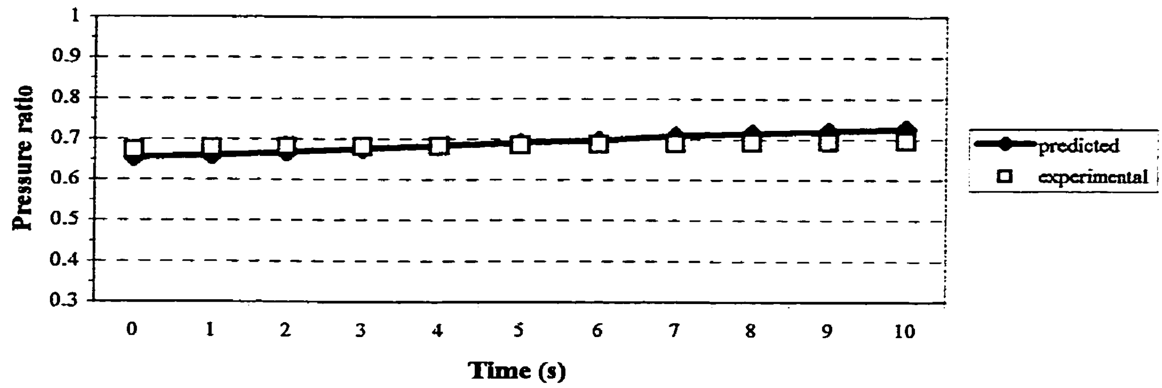
To predict the pressure recovery in the headspace of a bottle of cider from the measured sizes and frequencies of the bubbles produced in a cider (Appendix 17), a computer program was developed (Appendix 18) based on the computer simulation for the rise and growth of a single bubble (Appendix 15). Three of the ciders, which were randomly selected for the modelling of the ascent of the single bubbles (Section 3.5.4.1.2.), were chosen to evaluate the model. Bubbles examined through the image analysis of the video tapes showed no signs of coalescence, and the distance between the

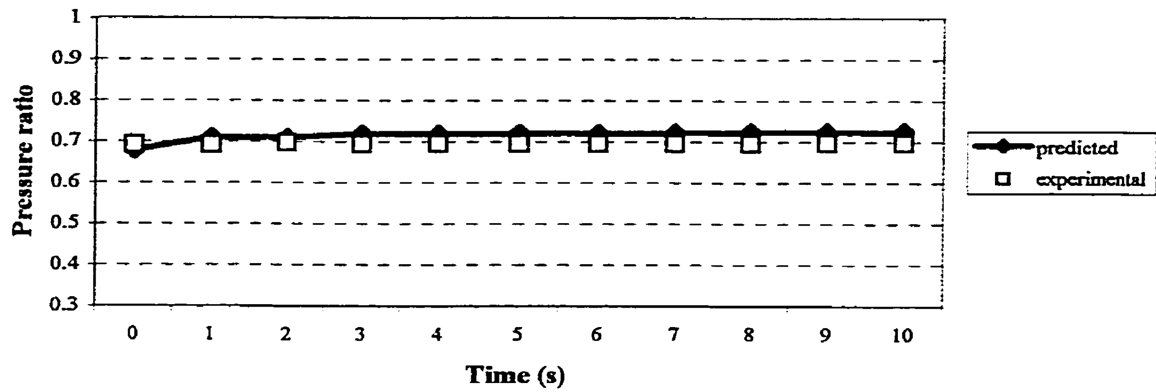
bubbles in the non-gushing ciders was sufficiently large such that interactions between the bubbles, in terms of growth rate, ascent path and velocity, were negligible. Growth of the bubbles at the nucleation sites before their release was not included in the model as such experimental data was not acquired in this research due to technological constraints and information is not available in the literature.

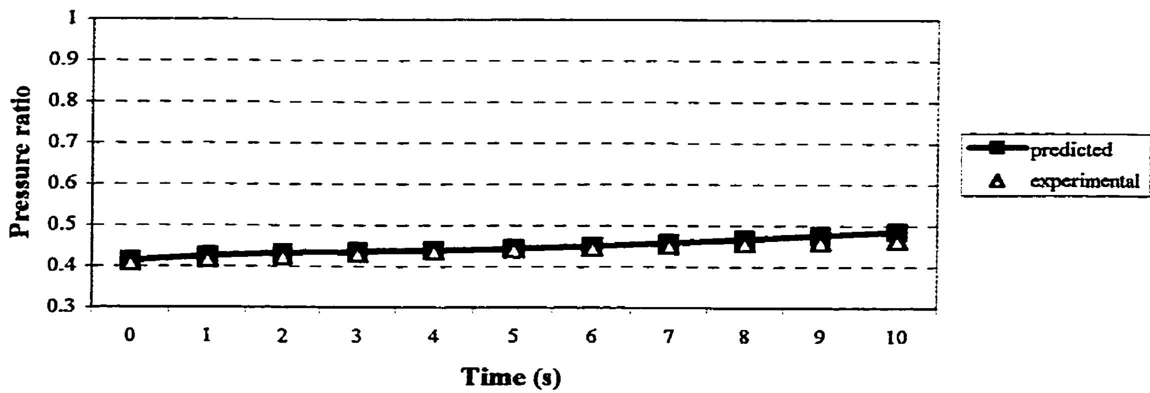
Despite the large measurement error (±14%) in the determination of the radii of the bubbles from the analysis of the video images, the computer simulation of the increase in headspace pressure from the modelled bubble growth and ascent produced pressure values which differed by less than 5% from the experimental headspace pressure readings (Appendix 19a; Figure 12). If the distance the bubbles ascended had been larger than that defined by the height of the bottle, as in this study, the predicted values might have differed more from experimental readings as the mass transfer rate of the gas into the bubbles and the ascent of the bubbles may be affected more significantly by the surface contaminants in the liquid. However, due to the relatively short path of ascent of the bubbles in this study, the difference between predicted and experimental values was expected to be low. The predicted number of moles in the gas phase (headspace + bubbles) during the 10 second time interval was also computed (Appendix 19b; Figure 13). Negation of the volume of the gas phase at the nucleation sites was acceptable, likely as a result of the low rate of bubble production which thus would have contributed little volume to the total gas volume of the bottle.

The mathematical model and ensuing computer simulation program for the recovery of headspace pressure after pressure release are based on the model of a single bubble. The small difference between the predicted pressure and the experimental pressure readings (Appendix 19a) indicate that bubbles in non-gushing ciders must behave

Figure 12. Experimental and predicted headspace pressures for three Treatment A ciders (non-gushing) during pressure recovery following pressure release from the bottle. Pressure predicted values were generated from the computer simulation program (Appendix 18). Data for the graphs are in Appendix 19a. The y-axis value, pressure ratio, is the ratio of the measured or predicted pressure to the initial pressure in the bottle before the release.


Treatment A, replicate 1
Pressure ratio
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0 1 2 3 4 5 6 7 8 9 10
Time (s)
predicted
experimental


Treatment A, replicate 3
Pressure ratio
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0 1 2 3 4 5 6 7 8 9 10
Time (s)
predicted
experimental


Treatment A, replicate 5
Pressure ratio
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0 1 2 3 4 5 6 7 8 9 10
Time (s)
predicted
experimental

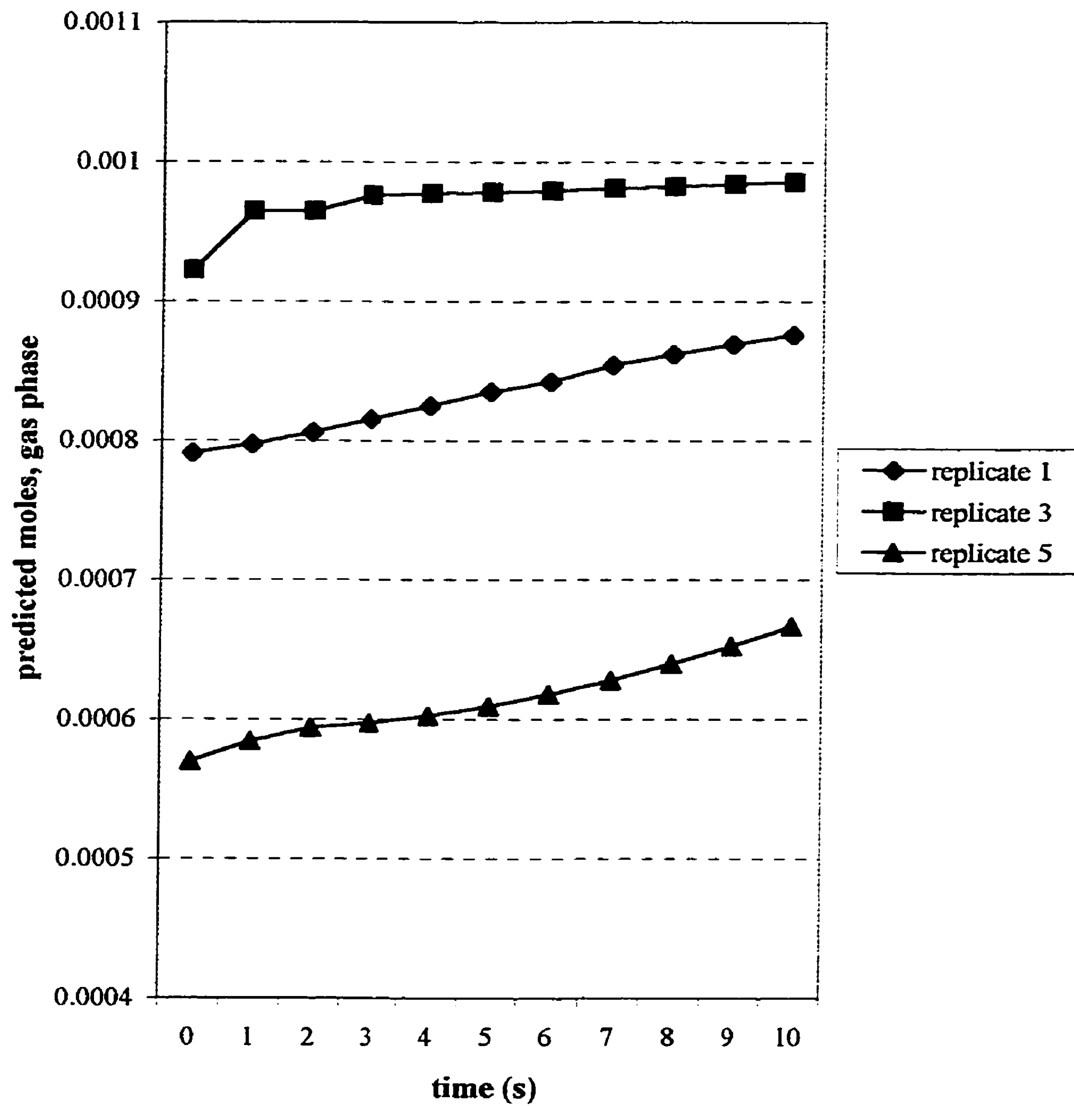


Figure 13. Number of moles of carbon dioxide in the gas phase of the three bottles of non-gushing cider, as predicted by computer simulation (Appendix 16).

as individual bubbles, without interaction amongst themselves as they rise through the cider. The rate at which the pressure recovers in the headspace of non-gushing ciders is therefore directly dependent on the frequency of bubble production and on the mass transfer rate of carbon dioxide from the liquid to the gas phase, in the bubbles and the headspace.

3.5.4.2. *Gushing Ciders*

3.5.4.2.1. Image Analysis

Image analysis of gushing ciders was conducted as described for non-gushing ciders (Section 3.5.4.1.1.). A ten second clip of images (300 frames; 30 frames per second) was captured from the video tapes for each gushing cider and processed with Adobe Photoshop. Bubble sizes and velocities were determined from on-screen measurement of bubble diameters and the distances travelled between frames (Appendices 19 and 20); frequencies of bubble generation were calculated using equation (21).

Ciders were easily identified as high or low gushers when conducting image analysis of the video tapes. The production of bubbles in low gushing ciders was similar to that of non-gushing ciders for the first second following pressure release. However, within two or three seconds, the front of a cloud of bubbles became evident in the bottom camera (Figure 14) and remained as a well-defined plateau as it ascended through the cider. The front edge of the cloud travelled through the 6 cm height of the view of the bottom camera in approximately 1 second; the trailing bottom edge of the cloud was not as well defined as the leading edge. It was immediately evident when viewing the images that the density, or concentration, of bubbles within the bubble cloud was markedly higher

in the cloud than above (Figure 14-1) or below (Figure 14-6) it.

The images of high gushing ciders were very difficult to analyze. Bubbles formed immediately after pressure release at higher generation rates than in either non-gushing or low-gushing ciders (Figure 15). A very dense bubble cloud ascended through the liquid immediately at a fast rate of ascent. In most high gushing ciders, the density of bubbles within the cloud was so high that individual bubbles were difficult to discern and the entire volume of the camera view was filled with a dark mass of liquid; this was observed in both the top and bottom cameras for very high gushing ciders. Occasionally, such bubble clouds were so dense that the lighting used for the video taping procedure could not adequately penetrate the bottle of cider to illuminate its contents.

3.5.4.2.2. Modelling the Gushing Ciders

Modelling of single bubbles of low gushing ciders was based on the model and computer simulation program developed for the non-gushing ciders (Appendices 14 and 15). Bubbles sizes and distances travelled were measured from the computer images (Appendix 20) for use in the computer program.

Image analysis of low gushing ciders indicated that no increase in the size of the bubbles was detected as they ascended through the liquid; this is in agreement with the values for the bubble radii as predicted by the computer model (Table 29). Therefore, with respect to bubble growth, the bubbles in the low gushing ciders behave as those in non-gushing ciders. However, measured velocities of single bubbles were not accurately predicted by the simulation program (Table 29), but were much slower than predicted above the bubble clouds and much faster than predicted within the clouds; bubbles trailing

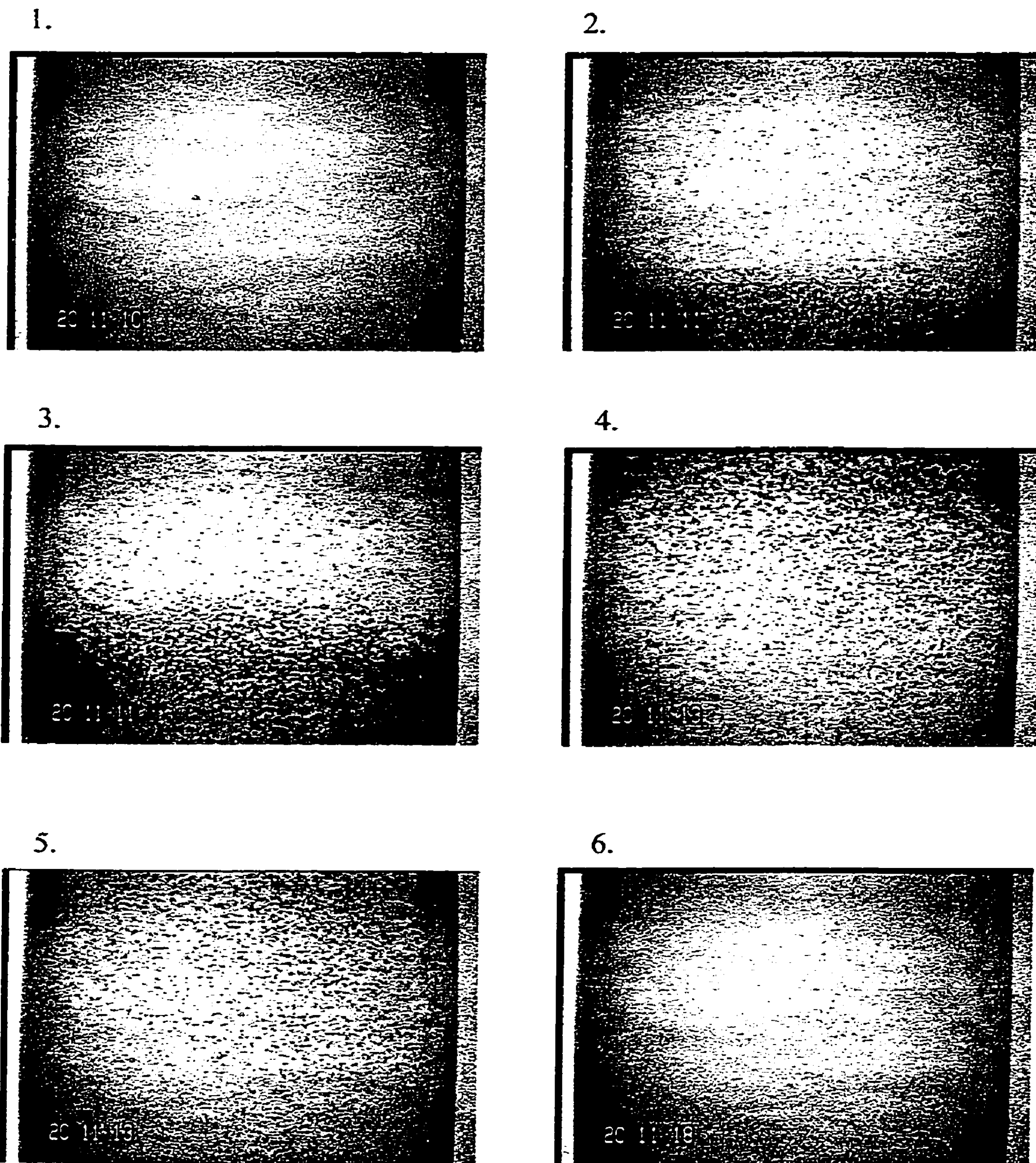


Figure 14. Ascent of bubbles in low gushing cider.
Note appearance of bubble cloud by Frame number 2.
Frames are approximately 1 second apart. Frame 1
shows image in bottom camera less than one second
after the pressure release; the frames are numbered in
sequence.

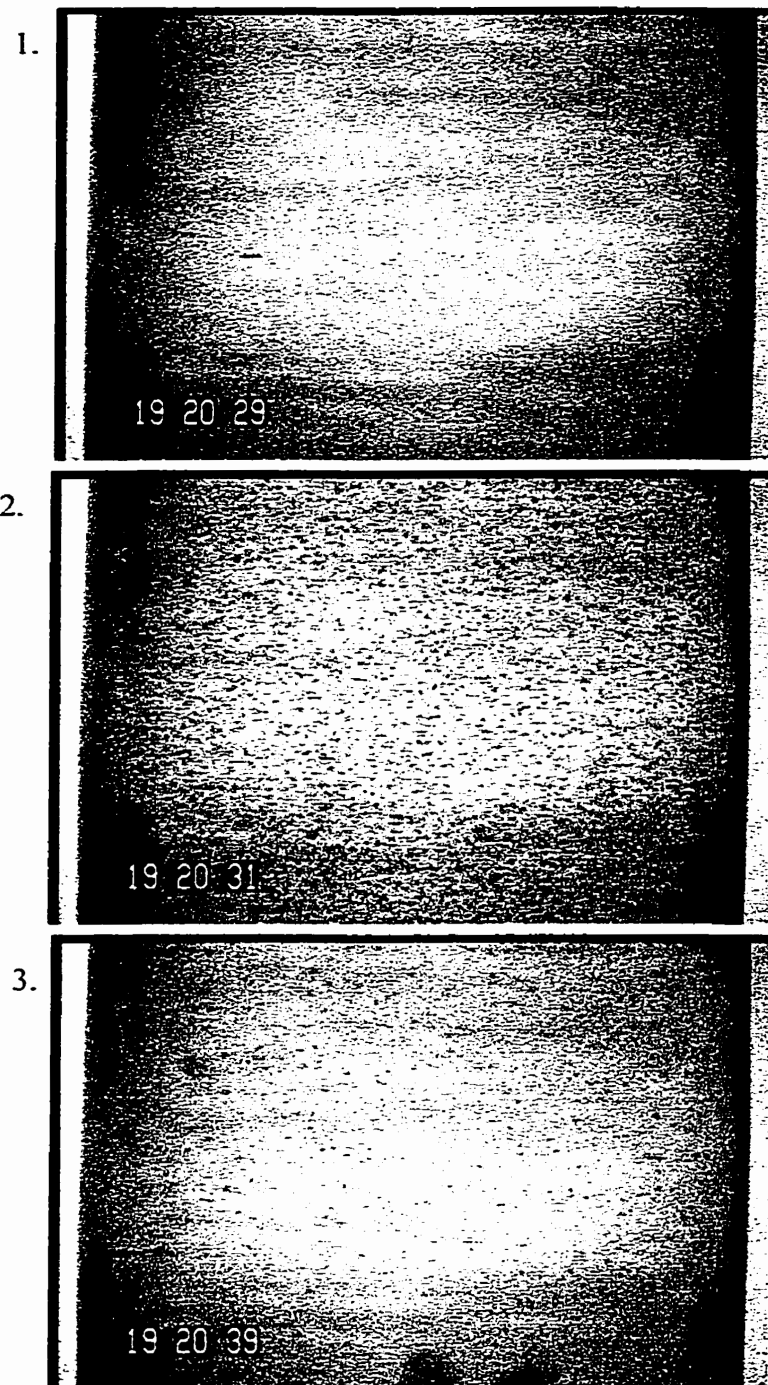


Figure 15. Frames from image analysis of moderately high gushing cider. (1.) immediately following pressure release; (2.) mid-way through the 10 s interval and (3.) at the end of 10 s. The front of the bubble cloud was not usually evident in high gushing ciders.

at the back ends of the bubble clouds tended to ascend more quickly, possibly due to a slip stream effect created by the quickly rising bubbles in the cloud above them. Only the velocity of the large single bubble measured in replicate 4 (Table 29) with a diameter of 0.6 mm was accurately predicted by the computer model; this accurate prediction may have been possible because the bubble ascended through the liquid at least 1 second before the appearance of the bubble cloud (frame 49 - frame 16 = 33 frames ahead of the bubble cloud), and thus avoided the interfering effects of other bubbles in close proximity.

In their study of bubble clouds, Houghton *et al.* (1957) observed that at lower densities, bubbles in the clouds tended to hinder each other with respect to growth and speed of ascent, while bubbles at higher densities tended to coalesce, creating a plug of gas which ascended rapidly through the liquid. Houghton and his colleagues studied bubble clouds, created by a porous plate sparging device, which had as few as 2 bubbles / mL in the case of water, to several hundred bubbles per mL in more viscous solutions; very high bubble densities of 50 - 300 bubbles / mL were observed in glycerine solutions. Typical bubble clouds studied were in the order of 1 - 7 bubbles / mL; due to the sizes of the pores in the sparging plate, the bubbles studied were larger than 1 mm in diameter.

The results tabulated in Table 29 indicate that hindrance and acceleration effects may also be observed in clouds of much smaller bubbles. Densities of bubbles inside and outside the bubble clouds were calculated for the three ciders which had been randomly selected for the modelling portion of the study (Table 30), at the locations of the bubbles which were reported in Table 29.

Table 29. Measured (Appendix 20) and predicted velocities of bubbles in low gushing ciders. Predicted values were computed from the computer program for the growth and ascent of a single bubbles, Appendix 15.

Treatment B	Height (cm) [a]	Frame[b]	Bubble radius (mm)	Measured Velocity (cm/s)	Predicted radius (mm)	Predicted Velocity (cm/s)
rep 2	5.4	45	0.2	1.7 ± 0.2	0.2	4.2
- single bubble	5.5	48	0.2	1.8 ± 0.3	0.2	4.3
- at cloud edge	2.9	75	0.2	2.4 ± 0.3	0.2	4.0
rep 4	5.8	16	0.6	11.5 ± 1.61	0.6	12.6
- single bubble	7.0	19	0.6	10.8 ± 1.51	0.6	12.6
	8.0	21	0.6	12.5 ± 1.75	0.6	12.6
- at cloud edge	3.4	49	0.2	2.5 ± 0.4	0.2	3.8
	3.7	52	0.2	2.5 ± 0.4	0.2	3.8
	4.6	55	0.2	4.7 ± 0.7	0.2	3.8
	5.5	58	0.2	5.0 ± 0.7	0.2	3.7
	6.5	65	0.2	4.4 ± 0.6	0.2	3.7
- at end of cloud	5.4	103	0.2	4.6 ± 0.6	0.2	3.5
- single bubble	6.1	256	0.2	5.2 ± 0.7	0.2	2.9
rep 5 - single bubble	5.7	82	0.2	2.4 ± 0.3	0.2	4.5
- at cloud edge	3.0	105	0.2	5.6 ± 0.8	0.2	4.3
	4.2	111	0.2	4.8 ± 0.7	0.2	4.4
	5.1	117	0.2	6.5 ± 0.9	0.2	4.5

[a] height of bubble above sediment

[b] frame number in video clip (Appendix 20); frames are numbered sequentially; rate = 30 frames per second

Table 30. Bubble densities of low gushing ciders: inside and outside observed bubble clouds.

Treatment B	Location of Measurement	Average Bubble Radius (mm)	Bubble Density (bubbles / mL)
rep 2	- above bubble cloud	0.2	1.4
	- within bubble cloud	0.2	1.7
rep 4	- 1 second before cloud appearance	0.6	0.03
	- at front of cloud	0.2	41.0
	- at trailing end of cloud	0.2	7.6
	- 4 seconds after cloud moved out of camera view	0.2	1.8
rep 5	- above bubble cloud	0.2	4.3
	- at front of cloud	0.2	5.2

The velocity of the rising bubbles in a bubble bed is governed by the density of the bubbles and that of the surrounding liquid. Compared to bubble densities studied by Houghton *et al.* (1957), high bubble densities were observed in all measurement locations in the low gushing ciders, with the exception of the bubble reported in replicate 4 which appeared more than one second before the bubble cloud (Table 30). The observed velocities were slower than those predicted from the computer simulation (Table 29) for the low gushing cider, replicate 2. This was most likely caused by hindrance in the rise of the bubbles due to their close proximity with each other, despite the small size of the bubbles. Bubbles may rise in spiral and other non-linear ascent trajectories, depending on their size (Clift *et al.*, 1978) and on the rigidity of the structure containing the nucleation

sites (Houghton *et al.*, 1957); the similarities or differences in the trajectories of adjacent bubbles may also affect the overall movement of the bubble cloud. Gases are reported to circulate within the bubble, the amount of circulation being related to the gas-liquid interface and the surfactant composition of the liquid (Clift *et al.*, 1978). Whether the circulation of the gas inside a bubble would contribute to the interactions of one bubble with another within the cloud has not been reported.

Houghton *et al.* (1957) noted that the rise velocity of the bubbles in the bubble bed was not constant for a particular size of bubble but rather varied with the density of the bubbles. They reported that for sea-water bubble-beds, the velocities were less than half that of single bubbles in the same medium. This is consistent with the results of replicate 2 low gushing cider, in which the observed velocities were less than half that of the predicted velocities.

Replicate 4 and replicate 5 ciders had much higher bubble densities, both inside and outside the observed bubble clouds. The density of bubbles in the cloud of replicate 4 cider was approximately 41 bubbles / mL (Table 30), a very high concentration according to the definition of Houghton *et al.* (1957). Initially the observed velocity of the bubbles at the leading edge of the cloud was lower than predicted by computer simulation; this velocity increased as the cloud rose through the cider, contrary to the predicted rates for the velocity. In dense bubble beds, Houghton *et al.* (1957) reported that occasionally the velocity of rise in a bubble bed was greater than that of a single bubble, which was due to plugs of gas forming which, with a greater buoyant force, could rise more quickly than the smaller bubbles in the bed. Scrutiny of the images from the video taped ciders did not reveal coalescence of bubbles to form plugs of gas in any of the ciders. Examination of tapes from the top video camera, which was focussed on the neck of the bottle, revealed

that frequently in gushing ciders the bubbles forced into close proximity with each other by the smaller cross-sectional area of the neck became attached as they ascended through the cider, but did not coalesce to form a larger bubble; the stability of the bubbles can be attributed to the surface active components in the cider, which would serve to stabilize the gas/liquid interface of the bubble and thus deter bubble coalescence.

It is hypothesized, from the velocities observed in this research that, despite the lack of coalescence, bubbles in very high concentrations in bubble clouds may begin to interact and exhibit some adherence, which becomes more pronounced in the smaller diameter of the neck of the bottle. This adherence allows the bubbles to imitate, to a limited extent, a larger bubble with a greater buoyant force. The drag force experienced by a particle (bubble) rising through a liquid is dependent on the shape of the particle and on its orientation with respect to its path of ascent (McCabe, 1976). Therefore, bubbles which adhere to each other in a plane parallel to the path of ascent (vertical) will experience less drag than those which adhere to each other on a horizontal plane. However, since the bubbles in the ciders generally did not come directly in contact with one another until the headspace interface was reached, the orientation and extent of adherence between the bubbles could not be determined under the conditions of this study. Bubbles did not collect at the surface of the cider but rather burst quickly, thus forming very little foam.

Bubble sizes and velocities were measured in two randomly selected high gushing ciders (Appendix 21) and compared to velocities predicted by the computer simulation program (Table 31).

Table 31. Measured (Appendix 21) and predicted velocities of bubbles in high gushing ciders. Predicted values were computed from the computer program for the growth and ascent of a single bubbles, Appendix 15.

Treatment C	Height (cm) [a]	Frame [b]	Bubble radius (mm)	Measured Velocity (cm/s)	Predicted radius (mm)	Predicted Velocity (cm/s)
rep 2 - in cloud	3.8	76	0.2	3.8 ± 0.5	0.2	3.9
rep 6 - single bubble	6.6	67	0.2	3.3 ± 0.5	0.2	3.9
- in cloud	5.5	150	0.2	5.1 ± 0.7	0.2	3.7
- in cloud	4.5	210	0.2	5.1 ± 0.7	0.2	3.4
- in cloud	4.4	240	0.2	5.1 ± 0.7	0.2	3.2

[a] height of bubble above sediment

[b] frame number in video clip (Appendix 21)

As with the low gushing ciders, the computer simulation was able to satisfactorily predict ascent velocities immediately after pressure release, but the model predicted much lower velocities than those which were observed at subsequent time periods (Table 31). Interaction of the bubbles with each other due to their close proximities in gushing ciders must take place, as hypothesized for low gushing ciders. Bubble densities (Table 32) within the bubble clouds of high gushing ciders were similar to those in the low gushing ciders. However, bubble clouds in high gushing ciders appeared immediately after pressure release from the bottle, and continued to be produced for much longer after the pressure release. For example, Treatment C replicate 6 cider (Table 32; Appendix 22) images indicated that the bubble cloud decreased in density but continued to be produced for most of the 10 second time interval examined.

Table 32. Bubble densities of high gushing ciders: inside and outside observed bubble clouds.

Treatment C	Location of Measurement	Average Bubble Radius (mm)	Bubble Density (bubbles / mL)
rep 2	- within bubble cloud	0.2	1.7
rep 6	- above bubble cloud	0.2	21.8
	- within cloud (time = 5 s)	0.2	9.0
	- within cloud (time = 7 s)	0.2	4.8
	- within cloud (time = 8 s)	0.2	3.8

3.5.4.2.3. Headspace Pressure Recovery and Gushing

The computer program developed to simulate headspace pressure recoveries (Appendix 18) after pressure release in non-gushing ciders was also employed to examine the behaviour of the pressure recovery in the headspace of gushing bottles of cider.

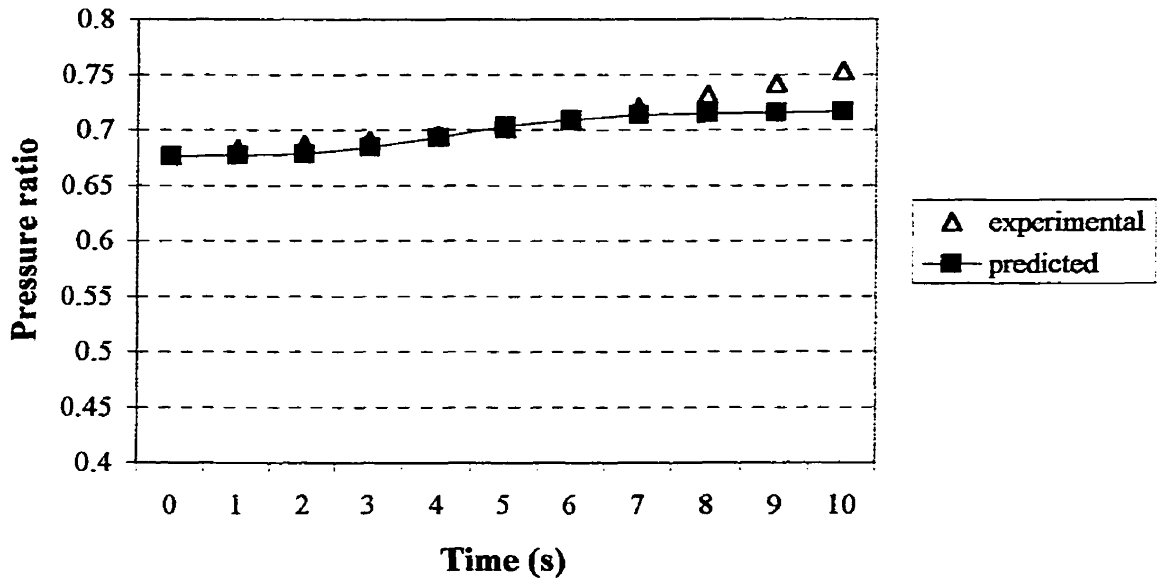
In very low gushing ciders (<5% overflow) such as Treatment B, replicate 2 (Figure 16), the computer simulation program adequately predicted the recovery of the headspace pressure in the bottle. However, for moderate (Treatment B, replicate 5; Figure 16) and high gushing ciders, the model developed for non-gushing ciders underestimated the headspace pressure recovery after pressure release.

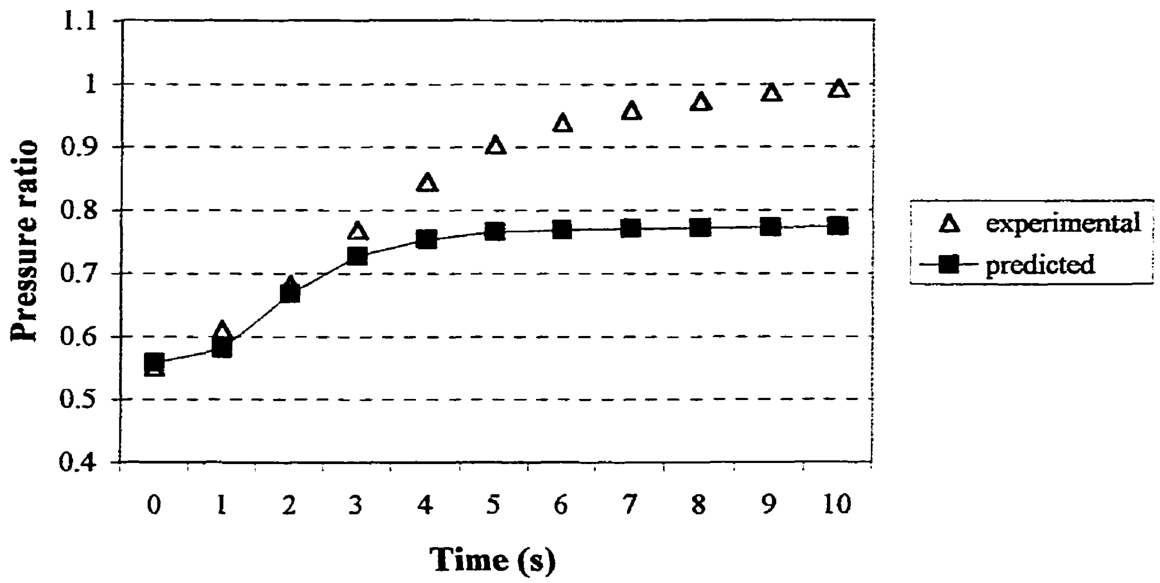
A second analysis of the video images confirmed the numbers and frequencies of bubbles recorded in Appendix 22. Mass transfer rates are based on carbon dioxide in pure water. Therefore, the rate of mass transfer into the rising bubbles and into the headspace would be slightly overestimated compared to their mass transfer rates in cider; the significantly lower predicted values for Treatment B, rep. 5 (Figure 16) could not result from incorrect mass transfer rates.

The assumption in the computer-generated modelling that the volumes of gas at the nucleation sites during bubble formation are negligible with respect to contributions to the pressure recovery was examined. For bubbles that are released from the sediment very quickly after pressure release from the headspace, the length of time that the volume of the embryonic bubble at the nucleation site may contribute to the total volume of gas in the bottle is very short. However, if a bubble is released from a nucleation site after eight seconds (Appendix 21), for example, there are seven previous seconds during which the bubble grows at the nucleation site and may contribute significantly to the total gas volume; alternatively, the embryonic bubble at the nucleation site may grow over time but may never be reach a size sufficient to allow the bubble's release. The number of nucleation sites which may contribute to the rate of pressure recovery cannot be determined from the data gathered in this study. However, the overall rate of mass transfer of carbon dioxide from the liquid phase to the gas phase can be estimated from the rate of the pressure recovery in the headspace of the bottle (Appendices 10 and 11); the overall mass transfer rate would include those at the headspace interface, at the nucleation sites and into the rising bubbles.

The slope of the pressure recovery curve at the first second after pressure release was used to estimate the initial overall rate of mass transfer of carbon dioxide, expressed in Appendix 22 as the number of moles of carbon dioxide added to the gas phase. Since the closed bottle dictates a fixed volume and the liquid (cider) is incompressible, an increase in the number of moles of carbon dioxide in the gas phase will *not* change the *total volume* of gas in the bottle but will only increase the pressure as recorded in the headspace; slight variations in the *partitioning* of the total volume of gas in the bottle may occur between the nucleation sites, the bubbles and the headspace, due to the

Figure 16. Predicted and experimental headspace pressure recovery rates following pressure release from the bottle of cider. Pressure recoveries in very low gushing ciders (eg. Treatment B, replicate 2) were well predicted by the computer simulation. Pressures of more moderately gushing ciders (eg. Treatment B, replicate 5) and high gushing ciders deviated substantially from the predicted values, likely due to the assumption within that computer program that the mass transfer of carbon dioxide at the nucleation sites


Treatment B, replicate 2
0.8
0.75
0.7
0.65
0.6
0.55
0.5
0.45
0.4
Pressure ratio
0
1
2
3
4
5
6
7
8
9
10
Time (s)
experimental
predicted


Treatment B, replicate 5
1.1
1
0.9
0.8
0.7
0.6
0.5
0.4
Pressure ratio
0
1
2
3
4
5
6
7
8
9
10
Time (s)
experimental
predicted

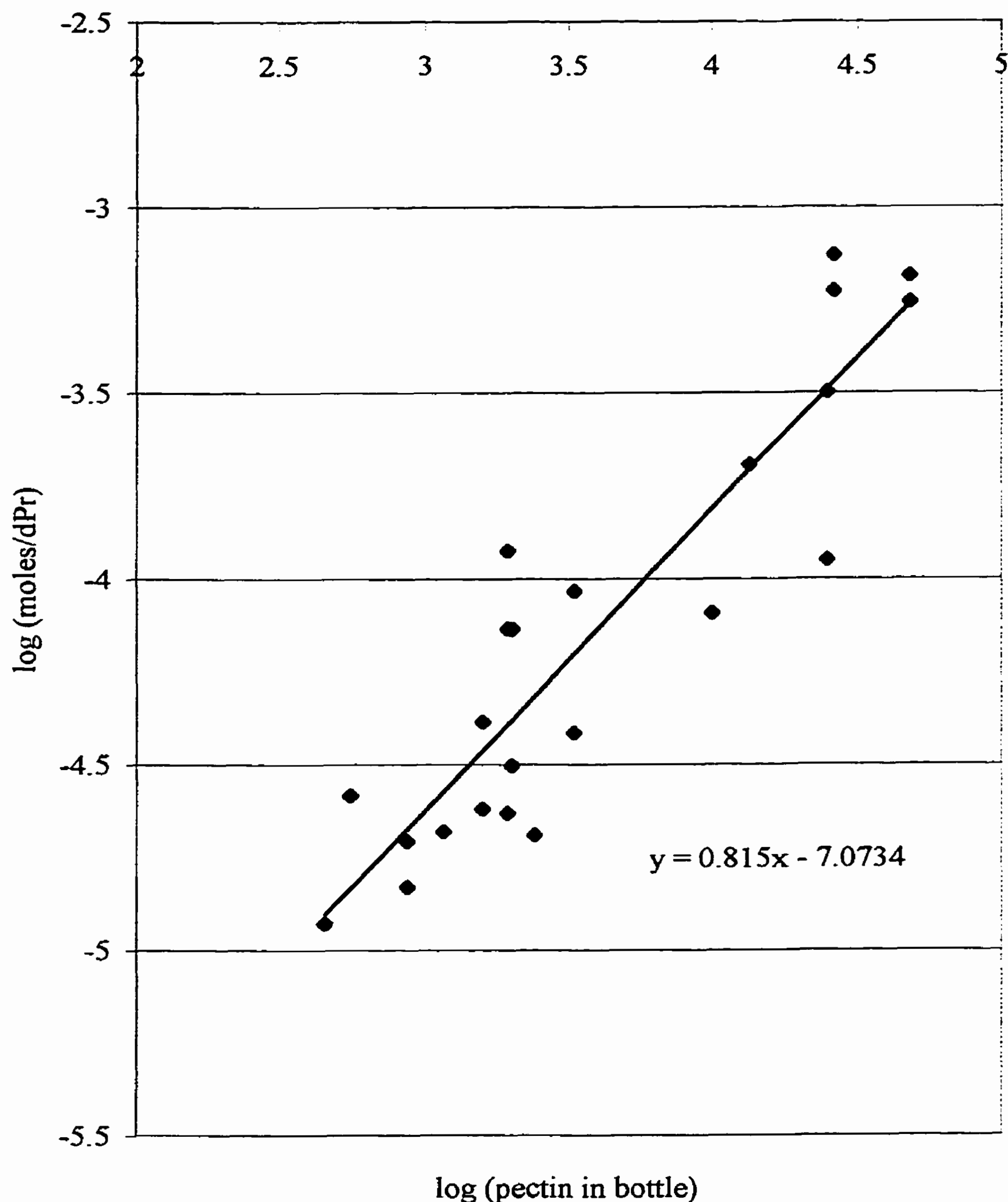


Figure 17. The relationship of the number of moles of carbon dioxide ("moles"), which undergoes mass transfer to the gas phase per second, with the total pectin in the sediment in the bottled cider ("pectin in bottle"); "dPr" indicates the ratio of the current headspace pressure reading to the original pressure prior to pressure release, which is a measure of the mechanical distruption, or energy, put into the system. The relationship between "x" (= log (moles/dPr)) and "y" (= log (pectin in bottle)) can be described by the above linear regression equationwith an R^2 value of 0.82.

increasing moles of carbon dioxide in the gas phase.

Evaluation of chemical and physical data of gushing and non-gushing ciders determined that a relationship exists between the number of moles of carbon dioxide transferred to the gas phase from the liquid after pressure release, as a function of the mechanical disruption exerted on the system, and the total pectin (the sum of all three fractions) contained in the sediment in the bottle. This relationship can be described by the equation:

$$\text{new moles} = (\text{delta P})\cdot 10^{(0.815\cdot\log(\text{pectin}) - 7.0734)}$$

where "new moles" indicates the number of moles of carbon dioxide which are transferred from the liquid to the gas phase, per second; "delta P" represents the ratio of the current headspace pressure reading to the original pressure prior to pressure release, which is a measure of the mechanical distruption, or energy, put into the system; "pectin" refers to the total pectin in the sediment of one 750 mL bottle. This equation is represented graphically in Figure 17, using the data from Appendix 22.

Further analysis of the video tapes revealed that in a few cases in which the headspace volume was sufficiently large to allow the liquid interface in the neck of the bottle to be viewed in the top video camera, the liquid interface lifted as the cloud of bubbles rapidly ascended through the liquid. This lifting coincided with the pressure of the headspace exceeding its initial value (Appendix 10).

A schematic representation of the hypothetical mechanisms involved in gushing ciders, with respect to bubble ascent, was developed (Figure 18). Bubbles which are produced in gushing ciders include bubble clouds, which, as with all the bubbles produced in cider, originate in the sediment of the bottle. At low bubble densities, as in non-

gushing ciders, bubbles generally ascend and grow as single bubbles, with little interaction between the bubbles. However, as suggested by the increased velocities of bubbles during their rise in gushing ciders, bubbles in these ciders do not act independently. Bubble densities as low as 1.8 bubbles / mL (Tables 29 and 30) caused increased velocities of the bubbles within the bubble cloud, thus indicating some interaction amongst the bubbles.

The density of bubbles in the liquid is determined by the frequency of bubble production. Observation of the gushing ciders (Section 3.5.1.) and indirect measurement of bubble formation through pressure recovery rates after pressure release, indicated that the number of bubbles produced in gushing ciders was much higher than non-gushing ciders. Analysis of the first three seconds of the video tapes provided an average rate of bubble production which supported the hypothesis (Appendix 23). Statistical analysis of the data (Table 33) confirmed the hypothesis that the "treatment" significantly affects the rate of bubble production, and consequently the bubble density in the liquid. The mean values of sediment Fraction 1, Fraction 2 and bubble frequency are presented Figure 19.

Table 33. Treatment means of the frequency of bubble production in gushing and non-gushing ciders. Raw data and analysis of variance (ANOVA) table are in Appendix 23.

Response Variable	Significance [a]	Treatment A[b]	Treatment B	Treatment C
Frequency (bubbles produced / s / bottle)	**	140	441.5	2371.2

[a] significance: ** : significant at $\alpha =$ 0.01

[b] Treatment: A = non-gush B = low gush C = high gush

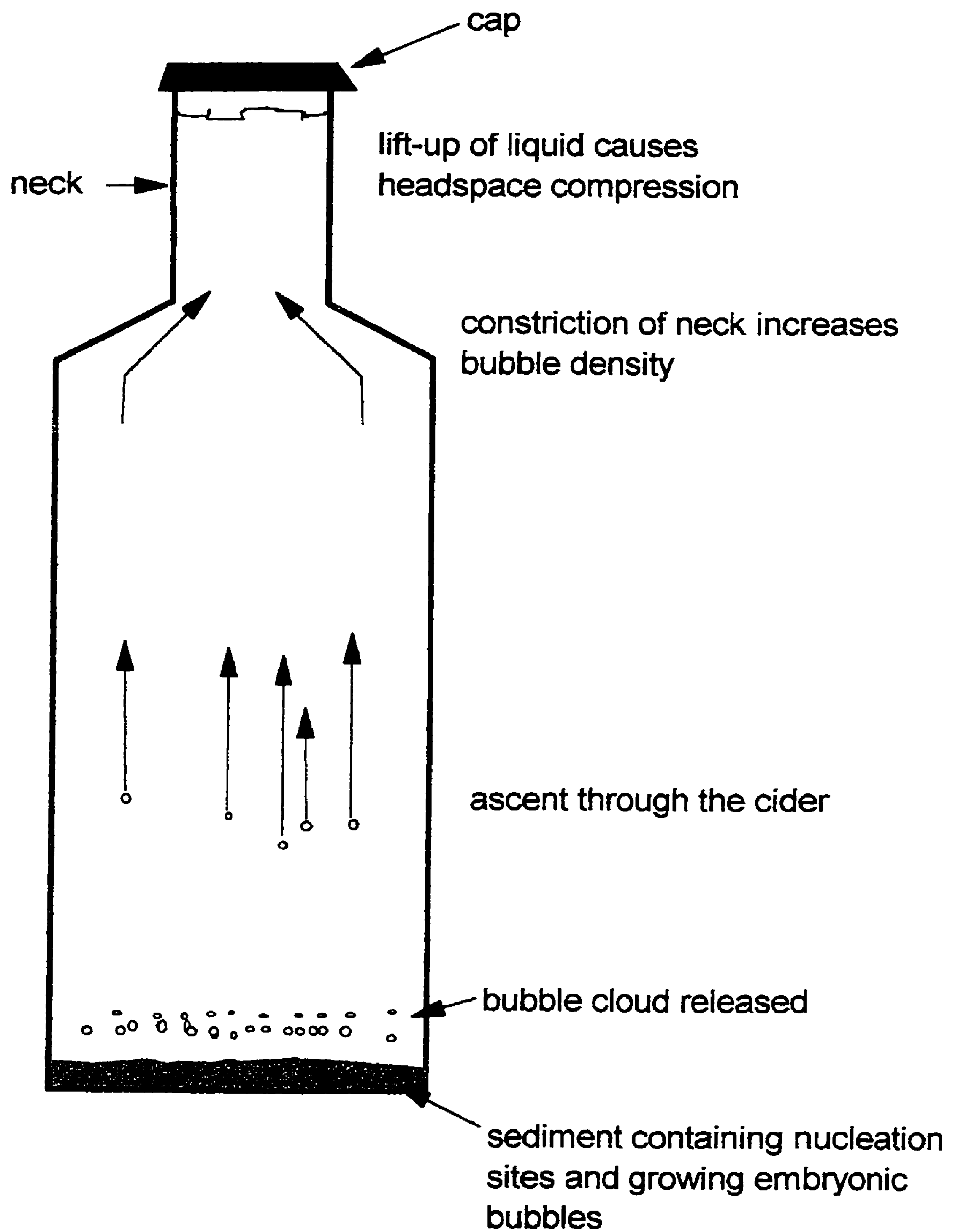


Figure 18. Schematic representation of bubble behaviour in gushing cider

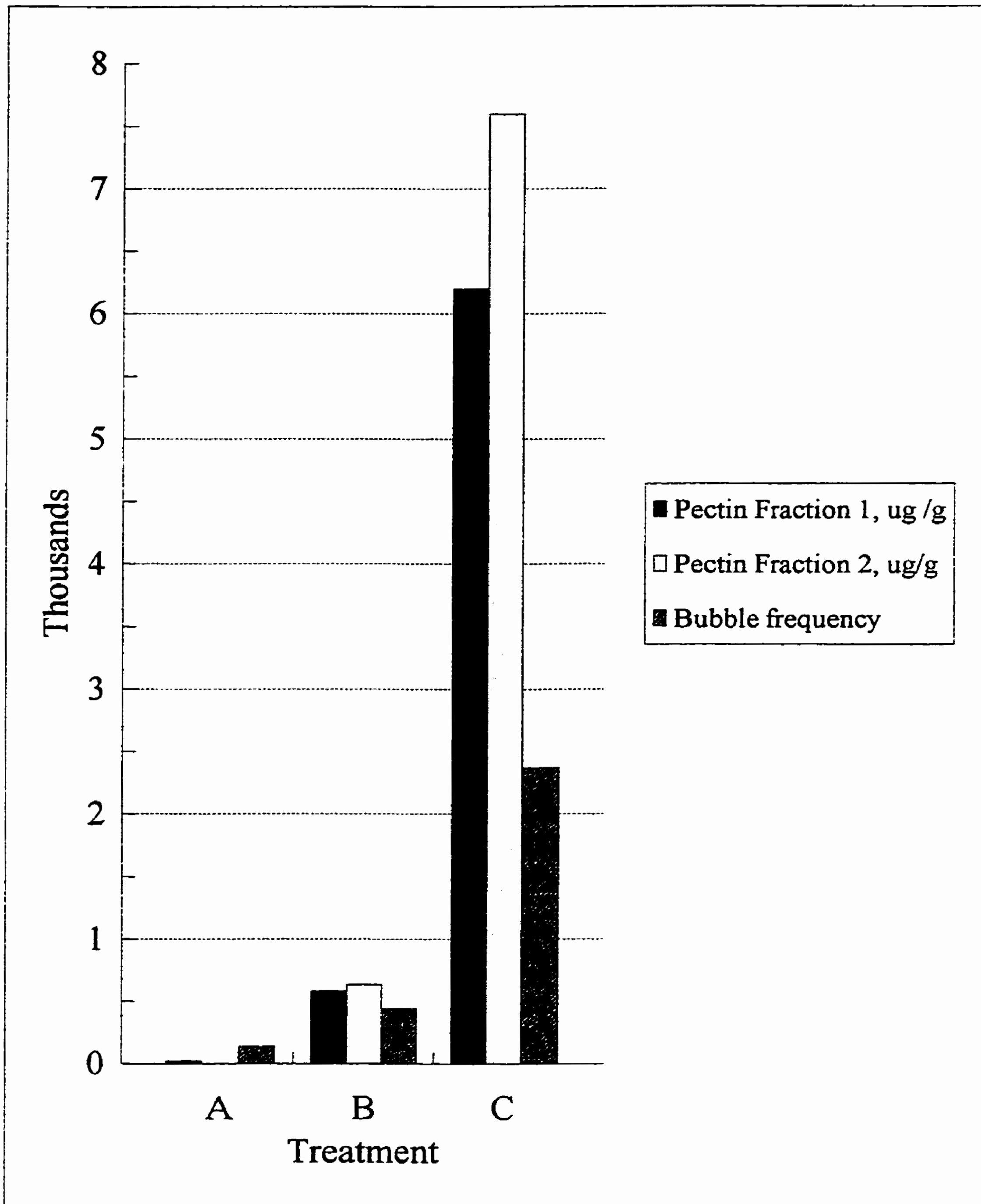


Figure 19. Average pectin concentrations per bottle and bubble frequencies per bottle for the three treatments, during the first three (3) minutes following pressure release.

The bubble density of gushing ciders is the determinant factor in the physical aspects of the gushing phenomenon. For example, in replicate 4 a bubble cloud was produced which contains 41 bubbles per mL (Table 30). The surface area of the sediment, as defined by the perimeter of the bottle at the base, was 43.0 cm^2; during production of the bubbles in the bubble cloud, 39 bubbles were thus produced per cm^2 of the sediment, per second. When released from the sediment, the bubbles ascended through the liquid as predicted, with a small increase in velocity due to the interaction amongst the bubbles. Once the shoulder and neck regions of the bottle were reached by the bubble cloud, the density of the cloud was forced to increase because of the smaller cross-sectional area of the neck, compared to the base of the bottle. This constriction is substantial: the surface area across the neck through which the bubbles "flow" is 2.5 cm^2. According to Houghton *et al.* (1957) the average velocity of the rise of bubbles in a bubble bed is expressed as:

$$vt_{ave} = vt_{gas}\left(\frac{\rho}{\rho - \rho_{bed}}\right) \qquad (26)$$

where vt_{ave} is the average velocity of the bubble cloud, vt_{gas} is the superficial velocity of the gas through the bed, ρ is the density of the liquid and ρ_{bed} is the density of the bubble bed. If the mass transfer rate of the carbon dioxide from the liquid to the bubbles is assumed to be equivalent to the gas flow used to generate the bubbles in the study by Houghton *et al.* (1957) and assumed to be at a constant level, and the liquid does not change its density, as the cider is considered to be an incompressible liquid, changes in the density of the bubble bed will directly affect the velocity of the bubbles within the

bed. However, decreases in velocity were not observed with increases in bed density in gushing ciders. Therefore, it must considered that increases in bubble cloud density increase the possible interactions of the bubbles with one another and thus possibly lead to increases in velocity.

The constricted volume at the shoulder and neck of the bottle through which the bubbles must rise is critical to the phenomenon of gushing. If the bottle of cider is considered to be "slices" through which the bubbles rise, a horizontal "slice" of cider, with a thickness equivalent to the diameter of the bubble (0.04 cm), contains 269 bubbles within a volume of 6.88 mL, as calculated by: volume = height·area

$$= 0.04 \text{ cm} \cdot \pi \cdot r^2$$

$$= 0.04 \text{ cm} \cdot \pi \cdot (3.7 \text{ cm})^2$$

As the bubble approaches the neck of the bottle, the bubbles within the slice continue to rise at the same rate, but the volume of the slice decreases due to the shape of the bottle. By the time the bubbles reach the neck, the volume within the 0.04 cm slice of liquid has decreased to 0.102 mL ($= 0.04 \text{ cm} \cdot \pi \cdot (0.95 \text{ cm})^2$), but as many as the 269 bubbles may remain within this volume.

Houghton *et al.* (1957) indicated that bubble beds resemble fluidized beds. In fluidized beds, gas or liquid is passed through a bed of solid spheres to facilitate mass transfer; the fluid passes through small, tortuous channels between the spheres, losing pressure energy (McCabe, 1976). Fluidization of the bed occurs when velocity of the gas or liquid flowing through the spheres is gradually increased until the spheres no longer remain stationary but are "fluidized" by the action of the liquid or gas. The onset of fluidization is determined by a minimum porosity, which can be expressed as:

$$\varepsilon = \frac{\text{volume of voids in the bed}}{\text{total volume of the bed}}$$

(27)

Relating this to the bed of bubbles, porosity can be expressed as:

(28)

$$\varepsilon = \frac{\text{volume of liquid in the bed}}{\text{total volume of the bed}}$$

Continuing with the example of Treatment B replicate 4, this would yield a porosity of 0.991 if the diameters (and consequently the volumes) of the bubbles remained unchanged at 0.2 mm. Fluidization of a bed of sphere occurs when the porosity approaches unity. In the case of the bubble cloud in the cider, however, compression of the volume at the neck of the bottle causes a decrease in the porosity of the bed.

Bubble clouds are similar but not entirely equivalent to fluidized beds. In ciders, for example, the "bed of spheres" is the cloud of bubbles; bubbles move upwards because of their buoyancy but overall movement of the liquid. In fluidized beds, the spheres of the bed become "fluidized" when the flow of the gas or liquid through the bed causes the bed particles to be lifted. Despite the differences in bed types, the porosity can be used as a gauge to determine the flow of the liquid through the bed. Increases in porosity cause increases in the concentration of the bed materials: either particles or spheres. The higher the concentration of spheres, the greater the length of path will be for the liquid to pass through the bed, as it winds its way around the particles. Similarly, as the porosity of the bubble cloud in the cider decreases with the volume constriction in the neck of the bottle, the flow of the cider through the rising bubbles is hindered by the

increased bubble density. If the rise of the cloud of bubbles is faster than the rate at which the cider can flow through the cloud, the cider remaining above the bubbles will be carried up with the bubbles. If this volume is sufficient, gushing will result when the volume of the bottle is not controlled.

If the system remains as a closed volume, such as the bottle in the closed sampling device, the rise of the bubble cloud will be counteracted by an increase in the pressure in the headspace of the bottle. Increasing pressure decreases the rise velocity of the bubbles and reduces the volume of the bubbles and decreases the mass transfer of the carbon dioxide into the bubbles. However, if the cloud of bubbles carries a volume of the incompressible cider along as it rises because of the decreased porosity in the bubble cloud, this cider will be forced against the gas in the headspace of the bottle at some velocity which is less than the rise velocity of the bubble cloud. This forces a compression of the headspace of the bottle, as is observed by the rise of the liquid interface in the high gushing bottles of cider. According to the Ideal Gas Law, such a decrease in volume is translated into an increase in pressure in the headspace.

The severity of gushing appears to be attributable to the period of time during which large numbers of bubbles are released from the sediment, as high gushing ciders tended to have bubble clouds which took several seconds to completely pass through the view of the bottom camera. Longer periods of production of bubbles would have produced a much deeper bubble bed, extending the path through which the liquid must travel around the bubbles and thus increasing the effect of the bubble cloud on the velocity of the liquid.

3.6. Conclusions

Release of gas from the headspaces of gushing and non-gushing ciders under controlled conditions by the use of a sampling device allowed an in-depth study of the growth, ascent and interactions of the bubbles as they rose through the cider. The rate of recovery of the headspace pressures was indicative of the amount of gas released from the cider into bubbles and into the headspace.

Comparison of initial headspace pressures indicated that higher pressures are not the cause of gushing in ciders, but may contribute to the severity of gushing. Measurement of the sediment thicknesses in non-, low and high gushing ciders similarity indicated that amount of sediment in the bottles may influence the extent of gushing but that small amounts of sediment would not necessarily indicate a lack of gushing tendency.

Mathematical modelling and computer simulations provided tools by which to differentiate bubble behaviour in gushing and non-gushing ciders, and a novel approach to the study of gushing. The bubbles produced in non-gushing ciders behaved as single bubbles rising through the liquid, exhibiting no interaction with other bubbles in the liquid. Mass transfer rates and ascent velocities in non-gushing ciders were very similar to those of bubbles in water; bubbles rising through greater heights of liquid would be expected to experience reduced mass transfer rates and a slower rise velocity due to surface contaminants in the liquid.

Bubbles in gushing ciders deviated from the velocities predicted by the computer simulation. In gushing ciders bubbles were produced in clouds, and rose from the sediment en masse. Bubbles in the clouds were expected to rise more slowly than single bubbles because of the hindrance caused by the interactions of the bubbles with one another. However, the velocities of the bubble clouds were observed to increase during

the rise through the bottle, without changes in the sizes of the bubbles. It was hypothesized that, although coalescence of the bubbles did not take place, the interaction of bubbles with each other provided a degree of adherence, which could increase the overall buoyant force and thus increase the velocity of the bubbles. Non-linear ascent patterns of bubbles and internal circulation of gas within the bubbles may also have some effect on the rise velocity of bubble clouds.

Reduction of the cross-sectional area of the bottle in the shoulder and neck areas leads to the physical action of gushing. The constricted area through which the bubbles must flow causes an increase in the bubble density. If bubble density is sufficiently low, the flow of the liquid around the rising bubbles is not interrupted, despite the increase in bubble density and no cider will be lost from the bottle. However, if the density of bubbles is high enough to interfere with the flow of the liquid through the cloud of bubbles, the rate of bubble ascent may be greater than the flow of liquid through the bubbles. Cider which is carried up with cloud of bubbles will inevitably "gush" from the bottle if it ascends beyond the mouth of the uncapped bottle. Under controlled conditions, the sudden lifting of the incompressible liquid into the headspace volume translates to an immediate decrease in volume in the headspace and consequently and increase in pressure.

Although difficult to determine, particularly in gushing ciders with high bubble densities, it appeared that only one bubble was released from each active nucleation site during the 10 second monitoring period in this study. Therefore, the increased numbers of bubbles in gushing ciders are due to a greater number of active nucleation sites in the sediments, compared to non-gushing ciders.

4. GENERAL CONCLUSIONS

This investigation of bottle-fermented (sparkling) cider produced from locally grown apples was initiated by recent interest in the commercial production of cider in Ontario. In North America, apple varieties are cultivated for their fresh-eating or culinary qualities and "true" cider apples, which are higher in astringency and bitterness, are not readily available. Preliminary experiments on ciders produced from Ontario apples provided information on the suitability of locally available varieties for cider production and indicated that some ciders produced from these apples had a tendency to gush, a phenomenon which was dependent upon the pre-fermentation treatment of the apples.

Investigation of four methods of cider production identified the use of thawed apples as the only processing treatment which produced gushing ciders. Chemical analyses of the juice and ciders over the course of the primary and secondary fermentations permitted comparisons of the characteristics of the three treatments against a control. Gushing was observed in several ciders at 2 months in the bottle; all ciders which gushed exhibited the phenomenon at 5 months in the bottle.

Gushing ciders contained more total pectin than non-gushing ciders. In particular, the ciders and sediments of gushing ciders contained significantly higher concentrations of the water soluble pectin fraction (Fraction 1), compared to the control; the sediments also contained higher concentrations of oxalate-soluble pectin (Fraction 2). The results demonstrate that there is a correlation between the phenomenon of gushing and the pectin content of the ciders.

Iron, boron and copper were present in lower concentrations in gushing ciders than in those which did not gush. Other researchers (Gray and Stone, 1956) have indicated that the addition of salts of some metals to beer, including iron and copper, induced

gushing but that the addition of salts of other metals such as boron did not promote gushing. The effect of metals which were added to beer may be different than the effects of metals inherently present. Most likely, metals inherently present in the ciders would be bound to other molecules, such as pectin, and would be involved more with the three dimensional structures of molecules rather than functioning individually as nucleation sites.

Bubbles originated from the sediment of the cider. In non-gushing ciders, bubbles were produced at low frequencies and ascended through the liquid as single bubbles. In gushing ciders, bubbles were produced at high frequencies and ascended through the liquid as a cloud. Clouds of bubbles released from the sediment did not ascend as predicted from the model obtained by the study of single bubbles. The velocities of the clouds were slower or faster than predicted as a result of the interaction of the bubbles with one another. Bubbles in close proximity may hinder the ascent of one another, possibly as a result of their individual ascent trajectories (spiral or linear) or interactions of effects of the internal circulations of the bubbles (Clift *et al.*, 1978). High densities of bubbles caused lift-up of the liquid interface at the headspace. Constriction of the bottle at the bottle neck leads to compression of the bubble bed and lift-up of the liquid above the bed, and subsequently to gushing in an open system.

An increased rate of bubble production resulted in the phenomenon of gushing. Characteristics such as sediment thickness and pressure inside the bottle are associated with the severity of gushing but do not determine its occurrence. Pectin concentrations in the sediments of bottles of high gushing ciders were significantly higher than those in the sediments of low gushers; both high and low gushing ciders contained more pectin than non-gushing ciders. Therefore, both the occurrence and severity of gushing are

directly associated with the pectin concentrations of the sediments.

To clearly connect the chemical characteristics of the ciders to the underlying physical mechanism of the gushing phenomenon, further work is required to resolve the technological difficulties involved with observing and chemically analyzing nucleation sites, which is beyond the scope of this current study. Until the technology is available to observe the activity of the nucleation *in situ* following pressure release from the bottle and to examine the physical (three-dimensional structure) and the chemical (hydrophobicity and hydrophillicity) characteristics of the active nucleation sites, the connection between chemical and physical characteristics determined in this study cannot be fully resolved.

5. RECOMMENDATIONS

Further research on several aspects of gushing should be conducted, provided the technological hurdles can be resolved. The chemical and physical structure of the active nucleation sites should be elucidated in order to determine the effect of the differences in the composition of the sediments of high, low and non-gushing ciders on the nucleation sites. The release of the bubbles from the nucleation sites should be studied *in situ* at the microscopic level, to determine if bubble release from sites at differing orientations in the sediment affects the trajectories of ascent of the bubbles. The release of carbon dioxide from yeast cells and the possibility that yeasts may possess bubble nucleation sites should be investigated.

The roles of minerals in gushing and non-gushing ciders requires further investigation. Minerals added to solution to induce gushing may not reflect the activity of minerals inherent in the solution. It should also be determined whether differences

exist between minerals which promote gushing and those which promote pectin gelation.

It is recommended that thawed apples not be used to produce cider. If thawed apples are used in the production, the removal of macromolecules (pectin) will be necessary to eliminate the gushing potential; ultrafiltration may be an appropriate method to remove the pectins and other colloids which may be involved in gushing. Enzymatic degradation of the pectins with pectinolytic enzymes is not advised because of the possible formation of vinyl phenols during fermentation (Chatonnet *et al.*, 1992). The severity of gushing may be controlled by decreasing the amount of pressure in the bottled ciders and reducing the amount of sediment.

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APPENDICES

Appendix 1. Formulae for the preparation of microbiological media.

A. Tetrazolium chloride solution

1. Combine: 0.0013 g tetrazolium chloride (red) powder (Sigma)
   50.0 mL distilled water

2. Filter (0.2 μm) into a sterile container. Store in the dark at refrigeration temperatures (5 - 10 °C) until required.

3. Add to 0.1 mL sterile Tetrazolium chloride solution to each 100 mL Potato Dextrose Agar (PDA), to determine respiratory efficient (pink) yeast colonies.

B. Yeast Broth

1. Combine: 1.0 L deionized water
   50.0 g glucose
   7.5 g yeast extract
   5.0 g KH_2PO_4
   2.5 g K_2HPO_4

2. Sterilize at 121°C, 105.5 kg / cm^2 for 15 minutes.

3. Just prior to use, to each 200 mL of yeast broth add:
   - 4.0 mL of a 20% $(NH_4)_2HPO_4$ solution

Solution (20%) of Ammonium Phosphate, dibasic

1. Combine: 20.0 g $(NH_4)_2HPO_4$ powder (Fisher)
   100.0 mL distilled water

2. Sterilize at 121°C, 105.5 kg / cm^2 for 15 minutes.

Appendix 2. Formula for the preparation of the cider broth.

Combine:			
	540	mL	sterile[1] cider
	540	mL	sterile deionized water
	180	mL	sterile apple juice concentrate[2]
	144	mL	sterile 50% (w/w) sucrose solution
	27	mL	95% ethanol
	0.4	g	$(NH_4)_2HPO_4$ powder (Fisher Scientific)

[1] Cider, juice concentrate and the sucrose solution were sterilized by autoclave (121°C, 105.5 kg / cm^2 for 15 minutes).

[2] commercial brand frozen juice concentrate; no preservatives

Appendix 3. Results (raw data) of chemical analyses.
Year 94 = 1994; Year = 1995
Treat = Treatments as described in Materials and Methods of Part One.
Time 1 = juice; Time 2 = still cider; Time 3 = 2 months in bottle; Time 4 = 5 months in bottle
md = missing data

A. Chemical analyses of juices and ciders: specific gravity, mold and yeast populations, pH, titratable and volatile acidities, sulfur dioxide
All analyses except specific gravity were done in duplicate.

Year	Apple	Treat	Time	Specific Gravity	Molds (colonies/mL)	Yeasts (colonies/mL)	pH	Titratable acidity (g/100 mL)	Volatile acidity (g/100 mL)	Free Sulfur dioxide (mg/L)	Total Sulfur dioxide (mg/L)
94	Crispin	1	1	1.0623	8.40E+01	1.60E+08	3.06	0.599	0.0060	2.76	11.01
94	Crispin	1	1		7.20E+01	1.60E+08	md	0.599	0.0057	2.91	12.11
94	Crispin	1	2	0.9962	0.00E+00	7.50E+05	3.51	0.491	0.0186	6.27	14.80
94	Crispin	1	2		0.00E+00	7.40E+05	3.51	0.496	0.0144	8.36	10.81
94	Crispin	1	3	0.9955	0.00E+00	4.00E+01	3.53	0.492	0.0216	6.40	12.16
94	Crispin	1	3		0.00E+00	4.90E+01	3.54	0.490	0.0174	7.68	11.52
94	Crispin	1	4	0.9940	0.00E+00	0.00E+00	3.90	0.243	0.0264	15.36	32.64
94	Crispin	1	4		0.00E+00	0.00E+00	3.90	0.245	0.0300	15.49	30.72
94	Crispin	2	1	1.0513	3.90E+01	1.60E+08	3.31	0.578	0.0054	3.16	18.04
94	Crispin	2	1		3.10E+01	1.60E+08	3.03	0.579	0.0053	2.91	15.47
94	Crispin	2	2	0.9962	0.00E+00	7.70E+05	3.49	0.471	0.0179	9.38	13.88
94	Crispin	2	2		0.00E+00	7.70E+05	3.49	0.474	0.0186	8.17	11.66
94	Crispin	2	3	0.9955	0.00E+00	2.10E+01	3.52	0.482	0.0216	6.40	11.20
94	Crispin	2	3		0.00E+00	1.40E+01	3.52	0.486	0.0180	7.36	15.04
94	Crispin	2	4	0.9935	0.00E+00	0.00E+00	3.85	0.257	0.0300	11.78	25.92
94	Crispin	2	4		0.00E+00	0.00E+00	3.85	0.241	0.0377	12.03	24.64
94	Crispin	3	1	1.0415	3.90E+01	1.50E+06	3.62	0.387	0.0387	6.14	14.19
94	Crispin	3	1		3.30E+01	1.50E+06	3.62	0.385	0.0438	6.57	13.30
94	Crispin	3	2	0.9957	0.00E+00	5.80E+05	3.62	0.386	0.0276	9.59	20.94
94	Crispin	3	2		0.00E+00	5.70E+05	3.66	0.371	0.0188	9.27	23.79

Year	Apple	Treat	Time	Specific Gravity	Molds (colonies/mL)	Yeasts (colonies/mL)	pH	Titratable acidity (g/100 mL)	Volatile acidity (g/100 mL)	Free Sulfur dioxide (mg/L)	Total Sulfur dioxide (mg/L)
94	Crispin	3	3	0.9956	0.00E+00	9.00E+01	3.92	0.255	0.0234	5.50	13.12
94	Crispin	3	3		0.00E+00	9.10E+01	3.91	0.259	0.0215	5.38	12.48
94	Crispin	3	4	0.9941	0.00E+00	1.60E+01	3.99	0.194	0.0276	14.08	13.76
94	Crispin	3	4		0.00E+00	3.00E+01	4.00	0.189	0.0240	5.25	19.20
94	Crispin	4	1	1.0542	8.00E+03	2.20E+06	3.41	0.547	0.0084	4.35	13.24
94	Crispin	4	1		1.10E+04	2.10E+06	3.41	0.538	0.0101	4.08	14.18
94	Crispin	4	2	0.9962	0.00E+00	9.10E+05	3.58	0.496	0.0181	7.02	8.04
94	Crispin	4	2		0.00E+00	9.00E+05	3.56	0.489	0.0157	6.14	10.19
94	Crispin	4	3	0.9971	0.00E+00	7.40E+03	3.70	0.343	0.0216	5.95	6.24
94	Crispin	4	3		0.00E+00	4.90E+03	3.69	0.348	0.0252	8.77	6.40
94	Crispin	4	4	0.9957	0.00E+00	3.00E+00	3.89	0.273	0.0269	12.80	9.92
94	Crispin	4	4		0.00E+00	0.00E+00	3.89	0.275	0.0311	12.48	12.80
94	Hyslop	1	1	1.0580	3.00E+01	1.30E+06	3.49	0.991	0.0102	6.48	30.17
94	Hyslop	1	1		1.00E+02	1.30E+06	md	1.000	0.0074	5.87	27.95
94	Hyslop	1	2	1.0020	0.00E+00	8.60E+05	3.60	0.855	0.0211	13.99	27.95
94	Hyslop	1	2		0.00E+00	8.60E+05	3.59	0.845	0.0193	14.59	23.51
94	Hyslop	1	3	1.0006	0.00E+00	1.20E+03	3.67	0.823	0.0485	16.32	25.28
94	Hyslop	1	3		0.00E+00	1.60E+03	3.63	0.817	0.0329	15.68	24.96
94	Hyslop	1	4	1.0008	0.00E+00	3.70E+03	3.68	0.804	0.0161	20.10	21.76
94	Hyslop	1	4		0.00E+00	4.10E+03	3.68	0.812	0.0161	23.55	23.36
94	Hyslop	2	1	1.0607	2.50E+01	1.30E+06	3.47	1.003	0.0096	7.85	22.97
94	Hyslop	2	1		2.40E+01	1.30E+06	md	1.058	0.0061	8.15	24.67
94	Hyslop	2	2	1.0030	0.00E+00	8.50E+05	3.56	0.853	0.0151	19.95	34.73
94	Hyslop	2	2		0.00E+00	8.50E+05	3.56	0.872	0.0187	15.73	37.98
94	Hyslop	2	3	1.0011	0.00E+00	2.70E+03	3.64	0.823	0.0335	14.08	29.44
94	Hyslop	2	3		0.00E+00	3.20E+03	3.63	0.823	0.0365	18.24	28.80
94	Hyslop	2	4	1.0013	0.00E+00	1.40E+04	3.66	0.843	0.0449	21.50	20.96
94	Hyslop	2	4		0.00E+00	1.40E+04	3.65	0.824	0.0227	26.88	24.48
94	Hyslop	3	1	1.0632	6.90E+01	1.50E+06	3.71	0.792	0.0524	11.13	26.10

Year	Apple	Treat	Time	Specific Gravity	Molds (colonies/mL)	Yeasts (colonies/mL)	pH	Titratable acidity (g/100 mL)	Volatile acidity (g/100 mL)	Free Sulfur dioxide (mg/L)	Total Sulfur dioxide (mg/L)
94	Hyslop	3	1		5.20E+01	1.50E+06	3.71	0.787	0.0603	12.71	25.25
94	Hyslop	3	2	1.0011	0.00E+00	6.30E+05	3.94	0.686	0.0139	13.26	38.78
94	Hyslop	3	2		0.00E+00	6.30E+05	3.94	0.683	0.0152	19.60	43.01
94	Hyslop	3	3	1.0001	0.00E+00	4.30E+03	3.97	0.666	0.0167	19.20	18.40
94	Hyslop	3	3		0.00E+00	2.10E+03	3.98	0.647	0.0168	13.12	24.32
94	Hyslop	3	4	1.0001	0.00E+00	3.70E+02	4.00	0.635	0.0174	12.32	26.88
94	Hyslop	3	4		0.00E+00	2.90E+02	3.99	0.630	0.0198	13.28	29.12
94	Hyslop	4	1	1.0647	4.40E+03	2.00E+06	3.49	0.977	0.0118	20.74	39.69
94	Hyslop	4	1		7.40E+03	1.90E+06	3.47	0.985	0.0123	24.14	40.66
94	Hyslop	4	2	1.0021	0.00E+00	7.00E+05	3.65	0.822	0.0156	11.40	23.85
94	Hyslop	4	2		0.00E+00	7.20E+05	3.65	0.817	0.0204	9.65	17.83
94	Hyslop	4	3	1.0016	0.00E+00	3.20E+04	3.62	0.808	0.0173	14.66	20.80
94	Hyslop	4	3		0.00E+00	4.00E+04	3.62	0.812	0.0131	19.26	25.60
94	Hyslop	4	4	1.0002	0.00E+00	5.60E+02	3.78	0.717	0.0239	17.60	19.20
94	Hyslop	4	4		0.00E+00	4.20E+02	3.79	0.720	0.0257	17.28	19.20
94	McIntosh	1	1	1.043	2.30E+02	1.30E+06	3.24	0.708	0.0061	6.93	10.81
94	McIntosh	1	1		3.00E+02	1.30E+06	md	0.702	0.0050	7.39	10.23
94	McIntosh	1	2	0.9991	0.00E+00	8.50E+05	3.33	0.605	0.0205	5.03	9.41
94	McIntosh	1	2		0.00E+00	8.50E+05	3.36	0.614	0.0270	4.93	9.44
94	McIntosh	1	3	0.9991	0.00E+00	1.40E+02	3.41	0.565	0.0365	6.08	17.92
94	McIntosh	1	3		0.00E+00	1.60E+02	3.39	0.634	0.0413	6.40	16.96
94	McIntosh	1	4	0.998	0.00E+00	2.50E+02	3.42	0.591	0.0143	6.08	11.04
94	McIntosh	1	4		0.00E+00	2.40E+02	3.42	0.583	0.0126	6.08	9.12
94	McIntosh	2	1	1.0436	8.30E+01	1.30E+06	3.24	0.704	0.0096	3.47	13.70
94	McIntosh	2	1		5.30E+01	1.30E+06	md	0.705	0.0051	4.35	12.63
94	McIntosh	2	2	0.9991	0.00E+00	8.60E+05	3.34	0.625	0.0181	6.51	14.29
94	McIntosh	2	2		0.00E+00	8.60E+05	3.33	0.629	0.0187	5.88	14.45
94	McIntosh	2	3	1.0001	0.00E+00	3.60E+01	3.40	0.598	0.0257	4.16	16.64
94	McIntosh	2	3		0.00E+00	4.20E+01	3.40	0.590	0.0564	5.44	15.68

Year	Apple	Treat	Time	Specific Gravity	Molds (colonies/mL)	Yeasts (colonies/mL)	pH	Titratable acidity (g/100 mL)	Volatile acidity (g/100 mL)	Free Sulfur dioxide (mg/L)	Total Sulfur dioxide (mg/L)
94	McIntosh	2	4	0.9978	0.00E+00	2.50E+02	3.40	0.595	0.0173	5.06	18.40
94	McIntosh	2	4		0.00E+00	3.30E+02	3.40	0.590	0.0144	4.54	11.52
94	McIntosh	3	1	1.0389	1.50E+01	1.50E+06	3.75	0.375	0.0358	8.39	15.46
94	McIntosh	3	1		2.60E+01	1.50E+06	3.76	0.368	0.0359	6.63	14.19
94	McIntosh	3	2	0.9981	0.00E+00	5.60E+05	3.71	0.387	0.0157	8.64	16.19
94	McIntosh	3	2		0.00E+00	5.60E+05	3.72	0.392	0.0218	8.00	12.38
94	McIntosh	3	3	0.9956	0.00E+00	8.70E+03	4.06	0.204	0.0290	4.61	9.92
94	McIntosh	3	3		0.00E+00	6.80E+03	4.05	0.204	0.0287	6.14	10.24
94	McIntosh	3	4	0.9955	0.00E+00	2.50E+02	3.99	0.216	0.0318	4.99	12.80
94	McIntosh	3	4		0.00E+00	1.90E+02	3.99	0.213	0.0342	4.10	15.36
94	McIntosh	4	1	1.0438	4.40E+04	1.80E+06	3.42	0.603	0.0055	3.56	9.65
94	McIntosh	4	1		4.00E+04	1.80E+06	3.43	0.599	0.0073	3.68	10.87
94	McIntosh	4	2	0.9987	0.00E+00	2.30E+06	3.56	0.543	0.0128	5.75	8.04
94	McIntosh	4	2		0.00E+00	2.30E+06	3.56	0.537	0.0163	6.39	13.23
94	McIntosh	4	3	0.9961	0.00E+00	1.20E+04	3.84	0.277	0.0234	4.16	14.56
94	McIntosh	4	3		0.00E+00	1.50E+04	3.83	0.306	0.0281	4.80	12.64
94	McIntosh	4	4	0.9962	0.00E+00	1.10E+01	3.92	0.283	0.0287	13.44	6.40
94	McIntosh	4	4		0.00E+00	1.00E+01	3.91	0.283	0.0293	14.72	10.56
94	Russet	1	1	1.0652	4.70E+01	1.60E+08	3.22	0.674	0.0067	4.65	16.69
94	Russet	1	1		3.20E+01	1.60E+08	md	0.682	0.0073	5.02	17.55
94	Russet	1	2	0.9977	0.00E+00	1.20E+06	3.70	0.561	0.0274	11.53	14.99
94	Russet	1	2		0.00E+00	1.10E+06	3.70	0.570	0.0222	10.71	17.53
94	Russet	1	3	0.9983	0.00E+00	5.00E+00	3.78	0.544	0.0378	7.68	15.36
94	Russet	1	3		0.00E+00	5.00E+00	3.81	0.547	0.0347	11.52	18.56
94	Russet	1	4	0.9965	0.00E+00	0.00E+00	4.10	0.275	0.0318	15.74	40.96
94	Russet	1	4		0.00E+00	0.00E+00	4.10	0.281	0.0348	16.13	34.56
94	Russet	2	1	1.0637	7.40E+01	1.60E+08	3.58	0.650	0.0071	4.74	15.16
94	Russet	2	1		7.30E+01	1.60E+08	3.56	0.650	0.0064	5.02	20.69
94	Russet	2	2	0.9972	0.00E+00	9.90E+05	3.72	0.549	0.0274	12.74	15.75

Year	Apple	Treat	Time	Specific Gravity	Molds (colonies/mL)	Yeasts (colonies/mL)	pH	Titratable acidity (g/100 mL)	Volatile acidity (g/100 mL)	Free Sulfur dioxide (mg/L)	Total Sulfur dioxide (mg/L)
94	Russet	2	2		0.00E+00	1.00E+06	3.70	0.549	0.0226	12.04	17.18
94	Russet	2	3	0.9971	0.00E+00	7.00E+00	3.95	0.373	0.0366	6.40	27.84
94	Russet	2	3		0.00E+00	8.00E+00	3.96	0.328	0.0372	9.28	25.60
94	Russet	2	4	0.9950	0.00E+00	3.00E+00	4.10	0.267	0.0354	18.30	38.08
94	Russet	2	4		0.00E+00	3.00E+00	4.09	0.273	0.0366	20.74	33.92
94	Russet	3	1	1.0859	3.90E+02	1.50E+06	3.66	0.586	0.0529	7.90	16.80
94	Russet	3	1		3.50E+02	1.50E+06	3.64	0.586	0.0614	7.90	15.07
94	Russet	3	2	0.9964	0.00E+00	7.20E+05	3.97	0.528	0.0214	7.88	23.57
94	Russet	3	2		0.00E+00	7.30E+05	3.97	0.528	0.0220	9.46	19.77
94	Russet	3	3	0.9986	0.00E+00	1.40E+03	3.99	0.516	0.0234	8.48	12.96
94	Russet	3	3		0.00E+00	1.40E+03	3.99	0.516	0.0234	8.00	14.56
94	Russet	3	4	0.9981	0.00E+00	4.70E+01	4.02	0.484	0.0263	7.84	20.80
94	Russet	3	4		0.00E+00	4.80E+01	4.01	0.481	0.0252	11.20	16.96
94	Russet	4	1	1.0713	9.00E+02	1.50E+06	3.56	0.647	0.0066	5.08	20.26
94	Russet	4	1		9.00E+02	1.50E+06	3.56	0.632	0.0078	6.45	26.31
94	Russet	4	2	0.9972	0.00E+00	4.00E+06	3.82	0.541	0.0205	18.43	20.46
94	Russet	4	2		0.00E+00	4.10E+06	3.81	0.568	0.0186	11.84	15.26
94	Russet	4	3	0.9976	0.00E+00	3.80E+02	3.95	0.391	0.0186	8.06	16.00
94	Russet	4	3		0.00E+00	3.60E+02	3.94	0.393	0.0216	6.66	15.20
94	Russet	4	4	0.9967	0.00E+00	0.00E+00	4.13	0.284	0.0311	16.00	16.32
94	Russet	4	4		0.00E+00	0.00E+00	4.13	0.291	0.0311	12.80	19.52
94	Spy	1	1	1.0499	3.00E+01	1.60E+08	2.97	0.494	0.0058	4.23	16.97
94	Spy	1	1		9.00E+01	1.60E+08	md	0.535	0.0074	3.62	15.26
94	Spy	1	2	0.9952	0.00E+00	7.60E+05	3.34	0.434	0.0322	11.60	15.57
94	Spy	1	2		0.00E+00	7.60E+05	3.34	0.450	0.0280	9.76	13.69
94	Spy	1	3	0.9976	0.00E+00	2.10E+02	3.37	0.433	0.0179	6.40	16.00
94	Spy	1	3		0.00E+00	1.50E+02	3.37	0.433	0.0204	6.40	20.80
94	Spy	1	4	0.9945	0.00E+00	0.00E+00	3.37	0.431	0.0329	25.28	57.28
94	Spy	1	4		0.00E+00	0.00E+00	3.37	0.422	0.0210	16.64	34.88

Year	Apple	Treat	Time	Specific Gravity	Molds (colonies/mL)	Yeasts (colonies/mL)	pH	Titratable acidity (g/100 mL)	Volatile acidity (g/100 mL)	Free Sulfur dioxide (mg/L)	Total Sulfur dioxide (mg/L)
94	Spy	2	1	1.0485	8.30E+01	1.60E+08	2.98	0.486	0.0061	4.16	16.45
94	Spy	2	1		7.60E+01	1.60E+08	md	0.486	0.0067	3.88	16.61
94	Spy	2	2	0.9952	0.00E+00	7.50E+05	3.32	0.435	0.0197	11.41	14.80
94	Spy	2	2		0.00E+00	7.50E+05	3.33	0.426	0.0155	11.28	14.49
94	Spy	2	3	0.9966	0.00E+00	4.70E+02	3.35	0.446	0.0234	6.72	20.80
94	Spy	2	3		0.00E+00	3.60E+02	3.37	0.441	0.0203	8.00	15.68
94	Spy	2	4	0.9945	0.00E+00	0.00E+00	3.36	0.441	0.0222	18.56	30.08
94	Spy	2	4		0.00E+00	4.00E+00	3.36	0.434	0.0228	18.05	28.80
94	Spy	3	1	1.0465	3.50E+01	1.50E+06	3.44	0.346	0.0671	6.87	25.04
94	Spy	3	1		3.40E+01	1.50E+06	3.46	0.362	0.0757	7.48	19.60
94	Spy	3	2	0.9952	0.00E+00	5.70E+05	3.41	0.382	0.0336	5.47	16.50
94	Spy	3	2		0.00E+00	5.70E+05	3.42	0.382	0.0247	8.00	21.89
94	Spy	3	3	0.9974	0.00E+00	7.00E+05	3.41	0.370	0.0221	4.99	14.08
94	Spy	3	3		0.00E+00	6.70E+05	3.42	0.377	0.0287	6.02	18.24
94	Spy	3	4	0.9946	0.00E+00	9.20E+01	3.38	0.386	0.0150	7.04	18.56
94	Spy	3	4		0.00E+00	1.10E+02	3.38	0.382	0.0162	7.04	18.24
94	Spy	4	1	1.0504	2.50E+03	1.60E+06	3.34	0.464	0.0096	4.38	18.38
94	Spy	4	1		2.50E+03	1.60E+06	3.34	0.469	0.0089	4.74	15.34
94	Spy	4	2	0.9968	0.00E+00	4.60E+05	3.42	0.437	0.0239	11.63	14.00
94	Spy	4	2		0.00E+00	4.60E+05	3.42	0.441	0.0298	3.91	15.26
94	Spy	4	3	0.9956	0.00E+00	2.00E+02	3.60	0.251	0.0132	6.14	13.60
94	Spy	4	3		0.00E+00	1.80E+02	3.61	0.383	0.0162	5.76	12.64
94	Spy	4	4	0.9942	0.00E+00	0.00E+00	3.84	0.256	0.0300	12.80	18.88
94	Spy	4	4		0.00E+00	0.00E+00	3.84	0.257	0.0282	5.44	17.92
95	Crispin	1	1	1.0449	2.40E+01	1.40E+06	3.39	0.519	0.0077	4.31	14.36
95	Crispin	1	1		2.50E+01	1.40E+06	3.39	0.526	0.0065	6.20	14.06
95	Crispin	1	2	0.9969	0.00E+00	2.90E+05	3.57	0.443	0.0150	8.38	13.87
95	Crispin	1	2		0.00E+00	2.80E+05	3.57	0.451	0.0121	7.88	18.63
95	Crispin	1	3	0.9951	0.00E+00	2.80E+04	3.59	0.414	0.0108	8.19	14.40

Year	Apple	Treat	Time	Specific Gravity	Molds (colonies/mL)	Yeasts (colonies/mL)	pH	Titratable acidity (g/100 mL)	Volatile acidity (g/100 mL)	Free Sulfur dioxide (mg/L)	Total Sulfur dioxide (mg/L)
95	Crispin	1	3		0.00E+00	2.70E+04	3.59	0.406	0.0108	9.60	15.68
95	Crispin	1	4	0.9941	0.00E+00	1.80E+02	3.93	0.221	0.0156	7.62	15.20
95	Crispin	1	4		0.00E+00	1.70E+02	3.92	0.214	0.0191	6.46	15.36
95	Crispin	2	1	1.0463	7.00E+00	1.40E+06	3.36	0.509	0.0065	5.45	16.34
95	Crispin	2	1		4.00E+00	1.40E+06	3.36	0.500	0.0071	4.92	14.82
95	Crispin	2	2	0.9969	0.00E+00	2.90E+05	3.55	0.424	0.0132	4.77	21.95
95	Crispin	2	2		0.00E+00	2.90E+05	3.56	0.430	0.0145	6.93	18.47
95	Crispin	2	3	0.9941	0.00E+00	2.60E+04	3.56	0.399	0.0090	7.04	8.64
95	Crispin	2	3		0.00E+00	2.80E+04	3.57	0.398	0.0108	9.73	17.92
95	Crispin	2	4	0.9941	0.00E+00	0.00E+00	3.96	0.209	0.0233	6.40	22.08
95	Crispin	2	4		0.00E+00	0.00E+00	3.96	0.209	0.0186	6.66	20.81
95	Crispin	3	1	1.0436	6.10E+01	1.30E+05	3.71	0.373	0.0039	5.39	4.90
95	Crispin	3	1		5.60E+01	1.30E+05	3.70	0.371	0.0068	5.27	6.24
95	Crispin	3	2	0.9968	0.00E+00	1.60E+05	3.80	0.322	0.0163	11.21	13.04
95	Crispin	3	2		0.00E+00	1.60E+05	3.80	0.328	0.0145	11.21	11.14
95	Crispin	3	3	0.9976	0.00E+00	2.50E+03	3.86	0.330	0.0804	4.48	12.64
95	Crispin	3	3		0.00E+00	2.10E+03	3.86	0.330	0.0636	4.86	11.04
95	Crispin	3	4	0.9966	0.00E+00	1.00E+00	3.81	0.338	0.0870	5.76	11.36
95	Crispin	3	4		0.00E+00	1.00E+00	3.83	0.346	0.0790	5.76	12.64
95	Crispin	4	1	1.0475	2.00E+03	3.00E+06	3.72	0.465	0.0135	9.39	24.01
95	Crispin	4	1		3.00E+03	3.00E+06	3.71	0.467	0.0140	8.60	25.22
95	Crispin	4	2	0.9968	0.00E+00	2.80E+05	3.59	0.426	0.0117	7.08	6.50
95	Crispin	4	2		0.00E+00	2.60E+05	3.59	0.425	0.0134	7.85	7.26
95	Crispin	4	3	0.9956	0.00E+00	1.70E+04	3.90	0.217	0.0185	4.86	9.92
95	Crispin	4	3		0.00E+00	1.80E+04	3.91	0.218	0.0210	4.99	12.48
95	Crispin	4	4	0.9951	0.00E+00	0.00E+00	3.92	0.222	0.0270	4.16	9.44
95	Crispin	4	4		0.00E+00	0.00E+00	3.92	0.217	0.0192	4.48	8.48
95	McIntosh	1	1	1.0425	4.80E+01	1.40E+06	3.29	0.456	0.0094	5.47	17.86
95	McIntosh	1	1		5.10E+01	1.40E+06	3.29	0.448	0.0054	8.57	21.66

Year	Apple	Treat	Time	Specific Gravity	Molds (colonies/mL)	Yeasts (colonies/mL)	pH	Titratable acidity (g/100 mL)	Volatile acidity (g/100 mL)	Free Sulfur dioxide (mg/L)	Total Sulfur dioxide (mg/L)
95	McIntosh	1	2	0.9962	0.00E+00	3.00E+05	3.51	0.422	0.0206	4.88	13.63
95	McIntosh	1	2		0.00E+00	3.00E+05	3.51	0.423	0.0157	8.05	12.68
95	McIntosh	1	3	0.9956	0.00E+00	4.80E+02	3.43	0.422	0.0162	3.97	12.48
95	McIntosh	1	3		0.00E+00	4.70E+02	3.43	0.423	0.0137	5.63	9.60
95	McIntosh	1	4	0.9946	0.00E+00	6.40E+03	3.51	0.442	0.0180	10.88	18.88
95	McIntosh	1	4		0.00E+00	6.50E+03	3.50	0.415	0.0258	10.24	19.20
95	McIntosh	2	1	1.0430	6.00E+00	1.40E+06	3.27	0.454	0.0083	6.93	20.44
95	McIntosh	2	1		6.00E+00	1.40E+06	3.27	0.455	0.0059	7.41	18.46
95	McIntosh	2	2	0.9962	0.00E+00	4.40E+05	3.46	0.416	0.0139	13.51	30.82
95	McIntosh	2	2		0.00E+00	4.30E+05	3.47	0.422	0.0144	14.15	54.58
95	McIntosh	2	3	0.9951	0.00E+00	1.30E+04	3.45	0.415	0.0156	7.55	15.04
95	McIntosh	2	3		0.00E+00	1.20E+04	3.44	0.418	0.0150	7.68	15.68
95	McIntosh	2	4	0.9951	0.00E+00	2.80E+02	3.47	0.429	0.0287	11.97	18.40
95	McIntosh	2	4		0.00E+00	2.60E+02	3.47	0.426	0.0323	7.30	14.24
95	McIntosh	3	1	1.0484	5.00E+00	1.30E+05	3.65	0.333	0.0051	5.39	4.78
95	McIntosh	3	1		6.00E+00	1.30E+05	3.66	0.344	0.0034	4.54	6.24
95	McIntosh	3	2	0.9963	0.00E+00	1.50E+05	3.68	0.343	0.0127	7.47	16.21
95	McIntosh	3	2		0.00E+00	1.50E+05	3.68	0.340	0.0144	6.59	16.21
95	McIntosh	3	3	0.9976	0.00E+00	2.10E+04	3.80	0.303	0.0137	5.70	12.80
95	McIntosh	3	3		0.00E+00	2.50E+04	3.80	0.297	0.0156	6.59	13.12
95	McIntosh	3	4	0.9941	0.00E+00	1.30E+03	4.00	0.233	0.0222	6.46	13.28
95	McIntosh	3	4		0.00E+00	1.20E+03	4.00	0.230	0.0227	6.59	15.68
95	McIntosh	4	1	1.0460	1.00E+06	5.40E+07	3.59	0.373	0.0237	9.49	23.86
95	McIntosh	4	1		1.00E+06	5.10E+07	3.58	0.380	0.0277	9.73	22.34
95	McIntosh	4	2	0.9968	0.00E+00	8.50E+06	3.59	0.357	0.0182	8.98	7.51
95	McIntosh	4	2		0.00E+00	8.70E+06	3.59	0.355	0.0139	11.52	8.27
95	McIntosh	4	3	0.9960	0.00E+00	4.80E+02	3.95	0.212	0.0264	8.19	15.68
95	McIntosh	4	3		0.00E+00	5.00E+02	3.96	0.214	0.0318	7.42	13.21
95	McIntosh	4	4	0.9956	0.00E+00	0.00E+00	3.87	0.355	0.0132	4.00	10.88

Year	Apple	Treat	Time	Specific Gravity	Molds (colonies/mL)	Yeasts (colonies/mL)	pH	Titratable acidity (g/100 mL)	Volatile acidity (g/100 mL)	Free Sulfur dioxide (mg/L)	Total Sulfur dioxide (mg/L)
95	McIntosh	4	4		0.00E+00	0.00E+00	3.87	0.214	0.0324	7.28	9.60
95	Russet	1	1	1.0606	6.80E+02	1.40E+06	3.41	0.694	0.0066	4.74	19.07
95	Russet	1	1		7.30E+02	1.40E+06	3.41	0.687	0.0059	5.59	21.66
95	Russet	1	2	0.9966	0.00E+00	3.70E+05	3.74	0.500	0.0174	10.09	24.80
95	Russet	1	2		0.00E+00	3.70E+05	3.74	0.504	0.0210	11.48	22.90
95	Russet	1	3	0.9951	0.00E+00	1.30E+03	4.09	0.264	0.0408	6.66	22.72
95	Russet	1	3		0.00E+00	9.90E+02	4.08	0.265	0.0330	6.27	17.60
95	Russet	1	4	0.9955	0.00E+00	4.70E+01	4.06	0.288	0.0551	7.49	17.44
95	Russet	1	4		0.00E+00	7.10E+01	4.08	0.281	0.0384	6.66	18.08
95	Russet	2	1	1.0615	7.80E+02	1.40E+06	3.40	0.665	0.0054	8.93	22.57
95	Russet	2	1		5.10E+02	1.40E+06	3.40	0.654	0.0060	4.44	20.59
95	Russet	2	2	0.9962	0.00E+00	2.90E+05	3.78	0.504	0.0253	7.23	15.21
95	Russet	2	2		0.00E+00	2.90E+05	3.78	0.503	0.0276	8.24	13.00
95	Russet	2	3	0.9946	0.00E+00	1.50E+04	4.07	0.259	0.0294	5.25	11.52
95	Russet	2	3		0.00E+00	1.50E+04	4.06	0.251	0.0348	6.40	12.48
95	Russet	2	4	0.9951	0.00E+00	3.80E+02	4.04	0.281	0.0420	8.06	20.80
95	Russet	2	4		0.00E+00	3.40E+02	4.04	0.276	0.0522	12.42	19.84
95	Russet	3	1	1.0739	3.70E+02	1.30E+05	3.68	0.508	0.0055	5.52	8.19
95	Russet	3	1		3.20E+02	1.30E+05	3.67	0.494	0.0056	5.88	9.40
95	Russet	3	2	0.9955	0.00E+00	1.90E+05	3.93	0.414	0.0251	9.37	18.11
95	Russet	3	2		0.00E+00	1.90E+05	3.94	0.408	0.0245	6.46	19.38
95	Russet	3	3	0.9961	0.00E+00	1.40E+04	4.17	0.269	0.0174	7.74	20.48
95	Russet	3	3		0.00E+00	1.10E+04	4.18	0.268	0.0204	7.30	17.60
95	Russet	3	4	0.9951	0.00E+00	0.00E+00	4.15	0.272	0.0474	6.98	16.32
95	Russet	3	4		0.00E+00	0.00E+00	4.15	0.268	0.0432	6.34	17.44
95	Russet	4	1	1.0660	2.30E+03	2.70E+06	3.76	0.586	0.0089	8.30	22.18
95	Russet	4	1		4.00E+03	2.70E+06	3.75	0.591	0.0078	7.26	22.34
95	Russet	4	2	0.9976	0.00E+00	4.50E+07	3.76	0.500	0.0145	8.99	20.29
95	Russet	4	2		0.00E+00	4.50E+07	3.76	0.504	0.0199	8.36	18.07

Year	Apple	Treat	Time	Specific Gravity	Molds (colonies/mL)	Yeasts (colonies/mL)	pH	Titratable acidity (g/100 mL)	Volatile acidity (g/100 mL)	Free Sulfur dioxide (mg/L)	Total Sulfur dioxide (mg/L)
95	Russet	4	3	0.9961	0.00E+00	4.00E+02	4.11	0.239	0.0246	6.66	18.88
95	Russet	4	3		0.00E+00	4.30E+02	4.11	0.243	0.0246	8.96	14.08
95	Russet	4	4	0.9961	0.00E+00	0.00E+00	4.02	0.261	0.0288	4.48	9.60
95	Russet	4	4		0.00E+00	0.00E+00	4.02	0.264	0.0306	5.12	10.40
95	Spy	1	1	1.0506	5.80E+01	1.40E+06	3.16	0.836	0.0105	6.08	19.68
95	Spy	1	1		8.40E+01	1.40E+06	3.17	0.823	0.0072	4.31	20.14
95	Spy	1	2	0.9973	0.00E+00	2.10E+05	3.44	0.663	0.0181	9.49	9.80
95	Spy	1	2		0.00E+00	2.10E+05	3.44	0.657	0.0182	9.99	9.04
95	Spy	1	3	0.9976	0.00E+00	1.80E+04	3.45	0.666	0.0204	9.73	23.36
95	Spy	1	3		0.00E+00	3.50E+04	3.46	0.669	0.0276	8.45	21.44
95	Spy	1	4	0.9966	0.00E+00	0.00E+00	3.49	0.657	0.0174	9.47	14.40
95	Spy	1	4		0.00E+00	0.00E+00	3.49	0.659	0.0186	9.60	25.92
95	Spy	2	1	1.0520	1.90E+01	1.40E+06	3.19	0.856	0.0066	6.97	22.42
95	Spy	2	1		8.60E+01	1.40E+06	3.19	0.857	0.0077	7.35	23.94
95	Spy	2	2	0.9980	0.00E+00	2.10E+05	3.45	0.696	0.0163	9.11	6.88
95	Spy	2	2		0.00E+00	2.10E+05	3.46	0.707	0.0164	9.36	7.39
95	Spy	2	3	0.9970	0.00E+00	1.40E+04	3.48	0.697	0.0150	7.17	20.48
95	Spy	2	3		0.00E+00	1.80E+04	3.48	0.695	0.0174	7.81	22.40
95	Spy	2	4	0.9951	0.00E+00	0.00E+00	3.80	0.375	0.0276	9.86	17.12
95	Spy	2	4		0.00E+00	0.00E+00	3.80	0.379	0.0246	6.46	16.00
95	Spy	3	1	1.0522	3.50E+01	1.30E+05	3.48	0.543	0.0068	5.15	9.15
95	Spy	3	1		3.90E+01	1.30E+05	3.47	0.532	0.0073	6.24	9.53
95	Spy	3	2	0.9968	0.00E+00	3.20E+05	3.66	0.454	0.0121	8.36	16.23
95	Spy	3	2		0.00E+00	3.00E+05	3.66	0.461	0.0138	5.83	19.71
95	Spy	3	3	0.9996	0.00E+00	7.10E+02	3.94	0.315	0.0191	9.15	16.80
95	Spy	3	3		0.00E+00	9.00E+02	3.93	0.322	0.0192	9.28	15.52
95	Spy	3	4	0.9971	0.00E+00	3.10E+02	4.00	0.269	0.0281	8.32	16.80
95	Spy	3	4		0.00E+00	2.60E+02	4.01	0.283	0.0299	7.55	17.12
95	Spy	4	1	1.0520	1.00E+06	8.30E+07	3.53	0.734	0.0193	16.00	27.96

Year	Apple	Treat	Time	Specific Gravity	Molds (colonies/mL)	Yeasts (colonies/mL)	pH	Titratable acidity (g/100 mL)	Volatile acidity (g/100 mL)	Free Sulfur dioxide (mg/L)	Total Sulfur dioxide (mg/L)
95	Spy	4	1		1.00E+06	9.60E+07	3.52	0.736	0.0197	11.75	30.54
95	Spy	4	2	0.9980	0.00E+00	4.50E+07	3.50	0.657	0.0365	11.05	19.34
95	Spy	4	2		0.00E+00	4.50E+07	3.51	0.664	0.0365	15.01	13.32
95	Spy	4	3	0.9946	0.00E+00	2.50E+03	3.72	0.478	0.0378	7.68	23.04
95	Spy	4	3		0.00E+00	2.20E+03	3.72	0.476	0.0258	8.83	27.20
95	Spy	4	4	0.9966	0.00E+00	0.00E+00	3.82	0.360	0.0438	4.99	10.56
95	Spy	4	4		0.00E+00	0.00E+00	3.81	0.362	0.0408	5.76	11.36

Appendix 3. (continued)

B. Chemical analyses of juices and ciders: juice yield, ammonical nitrogen, ash, ash alcalinity, dry weight, pectin concentrations and total phenolics
All analyses except yield were done in duplicate. Dry weight was only measured in 1995. Total phenolics of bottled ciders were only determined in 1995.

Year	Apple	Treat	Time	Yield	Ammonical nitrogen (mg/L)	Ash (g/100g)	Alkalinity of ash (meq.)	Dry weight (g/100g)	Pectin Fraction 1 (ug/g)	Pectin Fraction 2 (ug/g)	Pectin Fraction 3 (ug/g)	Total Phenolics (absorbance units)
94	Crispin	1	1	45.7	0.0	0.323	25.8		76.3	18.5	1.13	
94	Crispin	1	1		1.3	0.294	26.4		86	24.6	35.8	
94	Crispin	1	2		0.0	0.259	23.5		214.2	0.37	13.91	
94	Crispin	1	2		0.0	0.229	22.4		90.6	0.37	0.43	
94	Crispin	1	3		0.0	0.253	23.1		91.6	7.23	5.67	
94	Crispin	1	3		0.0	0.258	22.6		105.3	0.01	0.01	
94	Crispin	1	4		0.0	0.224	28.8		82.7	0.01	0.01	
94	Crispin	1	4		0.0	0.214	31.2		87.9	0.01	0.01	
94	Crispin	2	1	44.7	0.0	0.389	22.3		114	0.86	1.13	
94	Crispin	2	1		0.0	0.260	24.4		74.1	3.39	10.58	
94	Crispin	2	2		0.0	0.221	19.8		217	69.5	0.43	
94	Crispin	2	2		0.0	0.201	18.7		98.5	0.37	0.43	
94	Crispin	2	3		0.0	0.225	20.7		90.1	0.01	0.01	
94	Crispin	2	3		0.0	0.264	19.7		92.4	0.01	0.01	
94	Crispin	2	4		0.0	0.217	51.7		86.6	0.01	0.01	
94	Crispin	2	4		0.0	0.215	50.9		80.6	0.01	0.01	
94	Crispin	3	1	29.2	20.7	0.671	22.6		177.7	1.49	7.18	
94	Crispin	3	1		22.0	0.605	23.2		181.8	3.35	8.46	
94	Crispin	3	2		0.0	0.300	22.2		207.6	5.74	7.67	
94	Crispin	3	2		0.0	0.337	21.2		210.2	5.65	4.11	
94	Crispin	3	3		0.0	0.232	20.0		244.3	0.01	3.62	
94	Crispin	3	3		0.0	0.230	17.7		205.5	3.82	2.07	
94	Crispin	3	4		0.0	0.214	31.0		278.6	4.5	9.66	
94	Crispin	3	4		0.0	0.203	31.3		183.1	2.17	9.86	

Year	Apple	Treat	Time	Yield	Ammonical nitrogen (mg/L)	Ash (g/100g)	Alkalinity of ash (meq.)	Dry weight (g/100g)	Pectin Fraction 1 (ug/g)	Pectin Fraction 2 (ug/g)	Pectin Fraction 3 (ug/g)	Total Phenolics (absorbance units)
94	Crispin	4	1	35	0.0	0.200	26.4		80.9	15.66	16.4	
94	Crispin	4	1		0.0	0.197	24.4		73.9	13.37	18.9	
94	Crispin	4	2		0.0	0.271	23.9		260.2	1.74	0.14	
94	Crispin	4	2		0.0	0.228	24.2		196.6	0.11	2.62	
94	Crispin	4	3		0.0	0.318	27.1		112.1	0.01	0.01	
94	Crispin	4	3		0.0	0.293	26.9		113.8	0.01	0.01	
94	Crispin	4	4		0.0	0.180	35.9		219	0.01	0.01	
94	Crispin	4	4		0.0	0.215	37.1		197.2	0.01	0.01	
94	Hyslop	1	1	17.8	0.0	1.102	44.0		237.9	0.93	22.7	
94	Hyslop	1	1		0.0	1.206	47.1		144	0.93	3.2	
94	Hyslop	1	2		0.0	0.599	38.9		163.9	0.51	0.368	
94	Hyslop	1	2		0.0	0.709	41.2		164	0.98	13.21	
94	Hyslop	1	3		0.0	0.481	44.0		45.2	5.94	4.96	
94	Hyslop	1	3		0.0	0.551	31.5		45.3	4.42	6.85	
94	Hyslop	1	4		0.0	0.496	5.3		19.7	0.01	0.01	
94	Hyslop	1	4		0.0	0.455	5.6		8.28	0.01	0.01	
94	Hyslop	2	1	21.3	0.0	1.054	43.2		160.9	0.93	20	
94	Hyslop	2	1		0.0	0.931	44.7		101.2	0.93	6.8	
94	Hyslop	2	2		0.0	0.697	42.0		101.5	0.19	0.92	
94	Hyslop	2	2		0.0	0.694	38.9		116.7	0.19	1.36	
94	Hyslop	2	3		0.0	0.563	43.4		29	4.55	7.05	
94	Hyslop	2	3		0.0	0.555	42.2		33.9	6.07	6.07	
94	Hyslop	2	4		0.0	0.518	7.0		15.3	0.01	0.01	
94	Hyslop	2	4		0.0	0.448	5.5		11.7	0.01	0.01	
94	Hyslop	3	1	7.1	18.1	1.070	56.9		619.2	7.38	12.8	
94	Hyslop	3	1		11.7	0.973	57.1		597.9	9.59	10.9	
94	Hyslop	3	2		0.0	0.662	54.0		549.7	6.32	8.23	
94	Hyslop	3	2		0.0	0.648	52.6		547.1	0.15	0.25	
94	Hyslop	3	3		0.0	0.713	46.4		187.6	6.75	2.28	

Year	Apple	Treat	Time	Yield	Ammonical nitrogen (mg/L)	Ash (g/100g)	Alkalinity of ash (meq.)	Dry weight (g/100g)	Pectin Fraction 1 (ug/g)	Pectin Fraction 2 (ug/g)	Pectin Fraction 3 (ug/g)	Total Phenolics (absorbance units)
94	Hyslop	3	3		0.0	0.665	49.1		133.9	0.01	0.01	
94	Hyslop	3	4		0.0	0.699	2.8		506.9	0.01	0.01	
94	Hyslop	3	4		0.0	0.661	2.3		515.3	0.01	0.01	
94	Hyslop	4	1	12.6	0.0	0.563	54.0		2330.1	881.85	29.9	
94	Hyslop	4	1		0.0	0.485	54.0		943.9	1641.2	5.78	
94	Hyslop	4	2		0.0	0.443	40.0		747.6	3.46	5.71	
94	Hyslop	4	2		0.0	0.539	31.2		571.5	0.71	3.62	
94	Hyslop	4	3		0.0	0.516	2.6		505.1	0.01	0.01	
94	Hyslop	4	3		0.0	0.508	2.8		542.9	0.01	0.01	
94	Hyslop	4	4		0.0	0.463	22.5		510.2	0.01	0.01	
94	Hyslop	4	4		0.0	0.471	21.9		435.2	0.01	0.01	
94	McIntosh	1	1	37.7	0.0	0.750	21.9		119.1	0.93	20.6	
94	McIntosh	1	1		0.0	0.617	24.8		119	0.93	4.96	
94	McIntosh	1	2		0.0	0.248	22.4		113	1.6	2	
94	McIntosh	1	2		0.0	0.258	11.7		120.6	3.04	0.844	
94	McIntosh	1	3		0.0	0.303	19.5		107.6	0.01	4.49	
94	McIntosh	1	3		0.0	0.305	22.0		72.4	0.01	5.9	
94	McIntosh	1	4		0.0	0.220	28.6		105.2	0.01	0.01	
94	McIntosh	1	4		0.0	0.231	27.7		93.5	0.01	0.01	
94	McIntosh	2	1	37.7	0.0	0.532	22.6		172.7	0.93	19	
94	McIntosh	2	1		0.0	0.351	23.8		150	1.73	5.57	
94	McIntosh	2	2		0.0	0.148	13.5		152.3	2.14	5.27	
94	McIntosh	2	2		0.0	0.283	18.5		149.8	2	1.87	
94	McIntosh	2	3		0.0	0.319	21.0		107.4	0.01	0.01	
94	McIntosh	2	3		0.0	0.302	21.5		127.5	5.59	4.59	
94	McIntosh	2	4		0.0	0.232	29.7		125.8	0.01	0.01	
94	McIntosh	2	4		0.0	0.231	29.3		111.1	0.01	0.01	
94	McIntosh	3	1	14.8	23.0	0.668	23.4		215.1	4.26	17.8	
94	McIntosh	3	1		24.2	0.685	26.5		320.3	12.87	9.81	

Year	Apple	Treat	Time	Yield	Ammonical nitrogen (mg/L)	Ash (g/100g)	Alkalinity of ash (meq.)	Dry weight (g/100g)	Pectin Fraction 1 (ug/g)	Pectin Fraction 2 (ug/g)	Pectin Fraction 3 (ug/g)	Total Phenolics (absorbance units)
94	McIntosh	3	2		0.0	0.298	26.0		353.4	3.32	2.75	
94	McIntosh	3	2		0.0	0.286	26.4		350.6	4.69	5.1	
94	McIntosh	3	3		0.0	0.228	10.3		342.2	3.53	0.01	
94	McIntosh	3	3		0.0	0.218	19.8		284.4	1.43	0.268	
94	McIntosh	3	4		0.0	0.219	27.9		294.7	0.01	13	
94	McIntosh	3	4		0.0	0.224	26.2		306.1	9.17	10.7	
94	McIntosh	4	1	28.8	0.0	0.228	28.8		1812.2	18.5	9.18	
94	McIntosh	4	1		0.0	0.230	30.2		1825.5	13.81	8.04	
94	McIntosh	4	2		0.0	0.272	28.5		1672.8	123.6	6.83	
94	McIntosh	4	2		0.0	0.263	27.3		1453.3	253.8	4.95	
94	McIntosh	4	3		0.0	0.251	23.4		1662.8	9.21	0.01	
94	McIntosh	4	3		0.0	0.261	21.9		1596	5.46	5.46	
94	McIntosh	4	4		0.0	0.218	43.1		950.9	0.01	0.01	
94	McIntosh	4	4		0.0	0.224	43.5		881.9	0.01	0.01	
94	Russet	1	1	38.7	0.0	0.470	38.8		161.2	11.2	8.82	
94	Russet	1	1		0.0	0.525	39.1		114.2	0.86	6.13	
94	Russet	1	2		0.0	0.375	32.3		486.8	0.37	0.43	
94	Russet	1	2		0.0	0.384	35.0		207.7	0.37	0.43	
94	Russet	1	3		0.0	0.421	34.0		188.4	0.01	4.09	
94	Russet	1	3		0.0	0.434	33.7		187.4	0.01	0.01	
94	Russet	1	4		0.0	0.410	17.3		172.7	0.01	3.19	
94	Russet	1	4		0.0	0.383	16.5		182.9	0.01	0.01	
94	Russet	2	1	38.7	0.0	0.440	37.3		88.9	0.86	39.7	
94	Russet	2	1		0.0	0.770	33.8		144.8	4.88	9.1	
94	Russet	2	2		0.0	0.371	34.4		424.3	0.37	13.91	
94	Russet	2	2		0.0	0.393	34.0		206.4	0.37	0.43	
94	Russet	2	3		0.0	0.470	33.4		184.6	4.67	4.67	
94	Russet	2	3		0.0	0.445	32.6		164.4	0.01	0.01	
94	Russet	2	4		0.0	0.347	36.7		168	0.01	0.36	

Year	Apple	Treat	Time	Yield	Ammonical nitrogen (mg/L)	Ash (g/100g)	Alkalinity of ash (meq.)	Dry weight (g/100g)	Pectin Fraction 1 (ug/g)	Pectin Fraction 2 (ug/g)	Pectin Fraction 3 (ug/g)	Total Phenolics (absorbance units)
94	Russet	2	4		0.0	0.354	36.9		147.5	0.01	0.01	
94	Russet	3	1	13.5	0.4	0.456	44.9		301.1	5.24	7.2	
94	Russet	3	1		0.4	0.683	43.9		313.2	6.38	10.92	
94	Russet	3	2		0.0	0.470	42.8		333.8	0.15	0.25	
94	Russet	3	2		0.0	0.496	42.9		339.1	0.15	0.25	
94	Russet	3	3		0.0	0.631	37.6		84.7	2.09	0.01	
94	Russet	3	3		0.0	0.603	38.5		80.8	7.72	0.01	
94	Russet	3	4		0.0	0.489	12.2		254	0.01	0.01	
94	Russet	3	4		0.0	0.503	11.2		258.3	0.01	0.01	
94	Russet	4	1	17.4	0.0	0.315	40.1		2188	352.13	13.8	
94	Russet	4	1		0.0	0.333	40.0		2373.3	42.34	11.78	
94	Russet	4	2		0.0	0.344	36.6		2435.7	11.04	2.79	
94	Russet	4	2		0.0	0.395	37.3		2761.4	9.28	9.3	
94	Russet	4	3		0.0	0.425	10.3		2554.2	0.01	0.01	
94	Russet	4	3		0.0	0.403	9.9		2673.6	5.06	0.01	
94	Russet	4	4		0.0	0.357	31.9		2145.7	0.01	0.01	
94	Russet	4	4		0.0	0.355	30.3		2343.5	0.01	0.01	
94	Spy	1	1	44.7	0.0	0.137	12.9		25.9	0.86	1.13	
94	Spy	1	1		0.0	0.235	16.0		39.5	32.1	5.63	
94	Spy	1	2		0.0	0.198	13.2		159.9	0.37	16.7	
94	Spy	1	2		0.0	0.198	13.5		53.7	0.37	0.43	
94	Spy	1	3		0.0	0.222	13.2		47.3	0.01	4.19	
94	Spy	1	3		0.0	0.204	13.0		49.4	0.01	0.01	
94	Spy	1	4		0.0	0.181	39.3		45.9	0.01	0.01	
94	Spy	1	4		0.0	0.161	59.8		45.3	0.01	0.01	
94	Spy	2	1	42.8	0.0	0.228	15.4		89.9	0.86	1.13	
94	Spy	2	1		0.0	0.168	18.5		45	6.36	7.61	
94	Spy	2	2		0.0	0.177	12.8		146.1	12.46	15.3	
94	Spy	2	2		0.0	0.176	12.0		35.3	0.37	0.43	

Year	Apple	Treat	Time	Yield	Ammonical nitrogen (mg/L)	Ash (g/100g)	Alkalinity of ash (meq.)	Dry weight (g/100g)	Pectin Fraction 1 (ug/g)	Pectin Fraction 2 (ug/g)	Pectin Fraction 3 (ug/g)	Total Phenolics (absorbance units)
94	Spy	2	3		0.0	0.154	12.9		62.2	0.01	5.44	
94	Spy	2	3		0.0	0.131	11.6		53.7	0.01	0.01	
94	Spy	2	4		0.0	0.179	38.0		60	0.01	0.01	
94	Spy	2	4		0.0	0.174	38.0		52.7	0.01	0.01	
94	Spy	3	1	17.9	29.4	0.415	11.9		109.8	3.24	15.3	
94	Spy	3	1		9.2	0.233	16.6		132.5	4.37	17.68	
94	Spy	3	2		0.0	0.139	12.7		133.7	0.23	0.16	
94	Spy	3	2		0.0	0.136	12.8		146.7	3.84	4.27	
94	Spy	3	3		0.0	0.353	8.2		127.7	0.01	0.01	
94	Spy	3	3		0.0	0.282	5.4		121.7	0.85	0.01	
94	Spy	3	4		0.0	0.148	40.7		303.3	0.01	8.6	
94	Spy	3	4		0.0	0.165	39.5		308.2	4.32	9.26	
94	Spy	4	1	49.5	0.0	0.143	18.0		788.9	13.1	14.8	
94	Spy	4	1		0.0	0.147	18.6		761	13.55	15.71	
94	Spy	4	2		0.0	0.198	16		753.9	8.96	7.26	
94	Spy	4	2		0.0	0.185	7.9		844.5	6.53	5.87	
94	Spy	4	3		0.0	0.247	35		903.8	0.01	0.01	
94	Spy	4	3		0.0	0.249	34.5		770.4	0.01	0.511	
94	Spy	4	4		0.0	0.119	58.8		769.6	6.91	0.01	
94	Spy	4	4		0.0	0.118	60.3		819.2	0.01	0.01	
95	Crispin	1	1	42.4	0.0	0.192	23.9	md	7.34	0.57	1.76	
95	Crispin	1	1		0.0	0.405	23.1	md	8.94	0.57	1.76	
95	Crispin	1	2		0.0	0.194	18.7	md	4.86	0.02	0.11	
95	Crispin	1	2		0.0	0.202	18.3	md	8.48	0.02	0.11	
95	Crispin	1	3		3.7	0.201	24.6	1.26	3.08	0.01	0.01	5.74
95	Crispin	1	3		9.2	0.214	25.3	1.27	1.59	0.01	0.01	5.44
95	Crispin	1	4		0.0	0.159	20.9	0.81	3.5	0.76	0.01	5.54
95	Crispin	1	4		0.0	0.157	19.1	0.80	4.29	1.49	0.01	5.89
95	Crispin	2	1	42.4	0.0	0.18	47.3	12.10	14.24	0.57	6.53	

Year	Apple	Treat	Time	Yield	Ammonical nitrogen (mg/L)	Ash (g/100g)	Alkalinity of ash (meq.)	Dry weight (g/100g)	Pectin Fraction 1 (ug/g)	Pectin Fraction 2 (ug/g)	Pectin Fraction 3 (ug/g)	Total Phenolics (absorbance units)
95	Crispin	2	1		0.0	0.183	43.5	12.20	8.15	0.57	1.76	
95	Crispin	2	2		0.0	0.21	16	1.40	2.29	0.02	1.21	
95	Crispin	2	2		0.0	0.183	15.4	1.40	5.94	0.02	0.11	
95	Crispin	2	3		1.4	0.184	20.8	1.26	6.73	0.01	0.01	6.4
95	Crispin	2	3		3.4	0.214	21.3	1.25	2.35	0.01	0.01	5.95
95	Crispin	2	4		0.0	0.153	19.3	0.82	4.44	0.01	7.09	6.61
95	Crispin	2	4		0.0	0.158	20	0.79	0.8	0.01	2.26	6.51
95	Crispin	3	1	35.9	25.8	0.542	26.1	11.60	109.7	1.08	5.57	
95	Crispin	3	1		19.4	0.645	25.6	11.60	154.81	1.08	1.63	
95	Crispin	3	2		4.5	0.217	25.6	1.46	156.91	2.06	3.94	
95	Crispin	3	2		6.5	0.255	25.1	1.45	145.62	2.63	3.87	
95	Crispin	3	3		4.1	0.192	24.3	1.45	180.8	6.83	0.01	3.24
95	Crispin	3	3		3.4	0.19	24.3	1.47	193.2	5.84	0.01	3.4
95	Crispin	3	4		0.0	0.188	17.4	1.46	13.4	2.51	2.51	3.19
95	Crispin	3	4		0.0	0.188	19.2	1.46	85.4	14.88	0.01	2.83
95	Crispin	4	1	48.4	0.0	0.199	19.3	12.20	158.3	5.9	13.48	
95	Crispin	4	1		0.0	0.184	18.4	12.10	51.2	6.5	18.5	
95	Crispin	4	2		0.0	0.228	25.8	1.46	145.6	5.11	11.18	
95	Crispin	4	2		0.0	0.196	24.9	1.50	142	0.05	3.43	
95	Crispin	4	3		0.0	0.158	19.2	0.89	102.6	0.01	0.01	0.28
95	Crispin	4	3		0.0	0.166	22.7	0.89	107.9	0.01	4.76	0.01
95	Crispin	4	4		0.0	0.162	56.3	0.87	42.9	0.01	0.01	0.01
95	Crispin	4	4		0.0	0.161	59.2	0.86	52.9	0.01	0.01	0.49
95	McIntosh	1	1	36.9	0.0	0.146	31.5	11.70	96.7	5	7.3	
95	McIntosh	1	1		0.0	0.15	18.4	11.70	93.7	3.23	1.76	
95	McIntosh	1	2		0.0	0.116	7.4	1.46	86.1	1.79	3.16	
95	McIntosh	1	2		0.0	0.116	9.4	1.44	93.8	1.92	1.21	
95	McIntosh	1	3		0.0	0.132	11.8	1.54	67.4	1.88	2.62	9.72
95	McIntosh	1	3		0.0	0.132	10.6	1.51	57.1	1.14	0.01	10.33

Year	Apple	Treat	Time	Yield	Ammonical nitrogen (mg/L)	Ash (g/100g)	Alkalinity of ash (meq.)	Dry weight (g/100g)	Pectin Fraction 1 (ug/g)	Pectin Fraction 2 (ug/g)	Pectin Fraction 3 (ug/g)	Total Phenolics (absorbance units)
95	McIntosh	1	4		0.0	0.14	11	1.21	28.4	0.01	0.01	10.18
95	McIntosh	1	4		0.0	0.149	10.8	1.19	24.7	0.01	0.01	10.23
95	McIntosh	2	1	33.7	0.0	0.154	18.1	11.50	123.1	7.53	9.98	
95	McIntosh	2	1		0.0	0.156	16.9	10.80	115.2	0.57	4.13	
95	McIntosh	2	2		0.0	0.152	14.5	1.42	85.8	0.01	0.03	
95	McIntosh	2	2		0.0	0.119	9.75	1.42	85.6	0.01	0.03	
95	McIntosh	2	3		0.0	0.138	13.1	1.22	53.2	7.41	0.01	11.45
95	McIntosh	2	3		0.0	0.131	12.8	1.23	49	0.01	0.01	11.91
95	McIntosh	2	4		0.0	0.135	10.7	1.24	13.3	0.01	0.01	12.22
95	McIntosh	2	4		0.0	0.134	9.39	1.24	14.8	0.01	0.01	12.12
95	McIntosh	3	1	18.9	9.7	0.478	22.5	12.70	232.6	7.73	14.5	
95	McIntosh	3	1		4.9	0.401	23.1	12.70	232.2	8.05	10	
95	McIntosh	3	2		8.9	0.187	20.5	1.73	228.9	4.92	4.96	
95	McIntosh	3	2		3.1	0.198	21.6	1.68	262.8	7.66	4.27	
95	McIntosh	3	3		0.0	0.17	19.2	1.80	76.2	5.15	7.81	14.51
95	McIntosh	3	3		0.0	0.172	19	1.79	75.4	6.8	5.41	14.87
95	McIntosh	3	4		0.0	0.165	13.1	1.11	174.7	3.11	2.5	12.12
95	McIntosh	3	4		0.0	0.167	14.8	1.18	190	3.05	2.45	11.91
95	McIntosh	4	1	27.2	0.0	0.165	16.1	11.60	1652.1	4.92	2.4	
95	McIntosh	4	1		0.0	0.165	15.4	11.60	1741.1	7.22	8.42	
95	McIntosh	4	2		0.0	0.142	19.4	1.59	1736.2	12.7	0.08	
95	McIntosh	4	2		0.0	0.162	18.7	1.59	1725.3	33	7.7	
95	McIntosh	4	3		0.0	0.146	15.7	1.04	1447	19	48.9	1.76
95	McIntosh	4	3		0.0	0.13	16.7	1.07	1630.4	19.36	24.9	1.66
95	McIntosh	4	4		0.0	0.14	66.2	0.86	177	0.01	0.01	2.43
95	McIntosh	4	4		0.0	0.141	60.8	0.78	167.9	0.01	0.01	2.12
95	Russet	1	1	29.3	0.0	0.271	36.3	16.30	182	4.67	6.54	
95	Russet	1	1		0.0	0.305	36	16.20	179.9	0.57	3.48	
95	Russet	1	2		0.0	0.294	34	2.49	134	0.01	0.03	

Year	Apple	Treat	Time	Yield	Ammonical nitrogen (mg/L)	Ash (g/100g)	Alkalinity of ash (meq.)	Dry weight (g/100g)	Pectin Fraction 1 (ug/g)	Pectin Fraction 2 (ug/g)	Pectin Fraction 3 (ug/g)	Total Phenolics (absorbance units)
95	Russet	1	2		0.0	0.271	34.6	2.32	132.6	0.01	0.03	
95	Russet	1	3		0.0	0.25	32.6	1.57	94.4	0.01	0.01	10.48
95	Russet	1	3		0.0	0.252	32.7	1.57	106.9	4.41	6.7	10.89
95	Russet	1	4		0.0	0.246	31.7	1.64	19.3	0.01	0.01	10.59
95	Russet	1	4		0.0	0.247	29	1.57	16.7	0.01	0.01	10.48
95	Russet	2	1	29.3	0.0	0.26	33.4	16.60	181	5.8	8.79	
95	Russet	2	1		0.0	0.264	33.6	16.50	184.3	1.3	6.59	
95	Russet	2	2		0.0	0.332	27.5	2.25	149.6	0.49	0.46	
95	Russet	2	2		0.0	0.34	26.3	2.25	158.7	1.75	4.8	
95	Russet	2	3		0.0	0.243	28.6	1.68	107.1	3.33	3.33	12.32
95	Russet	2	3		0.0	0.238	29.1	1.61	102.9	3.36	1.13	13.19
95	Russet	2	4		0.0	0.265	27.3	1.83	26.8	0.01	0.01	13.29
95	Russet	2	4		0.0	0.264	27.5	1.63	14.9	0.01	0.01	12.73
95	Russet	3	1	14.4	0.0	1.152	30.8	19.10	598.8	9.28	14	
95	Russet	3	1		0.0	1.864	30.4	19.10	653.2	13.59	14.1	
95	Russet	3	2		2.5	0.334	37.3	2.62	704.2	4	3.41	
95	Russet	3	2		4.1	0.329	38.2	2.40	659.3	4.28	4.32	
95	Russet	3	3		0.0	0.278	34.5	2.55	522.3	5.82	5.15	12.42
95	Russet	3	3		0.0	0.278	35	2.68	498.6	5.86	7.2	12.58
95	Russet	3	4		0.0	0.258	33.3	2.52	353.6	3.56	3.56	10.33
95	Russet	3	4		0.0	0.26	29.9	2.39	455	4.25	1.86	10.74
95	Russet	4	1	25.1	0.0	0.275	27	16.80	2341.8	12.63	8.5	
95	Russet	4	1		0.0	0.274	30.2	16.80	2324.7	23.59	18.4	
95	Russet	4	2		0.0	0.354	34.9	2.51	1996.3	16.69	27.4	
95	Russet	4	2		0.0	0.325	35.6	2.54	1924	16.24	18.3	
95	Russet	4	3		7.8	0.247	15	1.79	1489.8	0.01	0.01	2.12
95	Russet	4	3		6.8	0.249	14	1.77	1463.2	0.01	25.9	2.32
95	Russet	4	4		0.0	0.25	39.8	1.81	1021.3	9.26	13.8	2.27
95	Russet	4	4		0.0	0.247	33.5	1.81	1197.3	11.4	13.6	2.48

Year	Apple	Treat	Time	Yield	Ammonical nitrogen (mg/L)	Ash (g/100g)	Alkalinity of ash (meq.)	Dry weight (g/100g)	Pectin Fraction 1 (ug/g)	Pectin Fraction 2 (ug/g)	Pectin Fraction 3 (ug/g)	Total Phenolics (absorbance units)
95	Spy	1	1	46.4	0.0	0.69	27.7	13.70	24.9	4.26	7.9	
95	Spy	1	1		0.0	0.231	30.3	13.70	22.1	0.57	1.9	
95	Spy	1	2		0.0	0.275	28.2	2.03	14.5	0.05	6.17	
95	Spy	1	2		0.0	0.245	28.1	2.03	7.4	0.05	0.14	
95	Spy	1	3		0.0	0.218	27.1	2.14	5.47	0.01	4.69	15.23
95	Spy	1	3		0.0	0.223	24.1	2.15	6.33	7.92	0.01	14.97
95	Spy	1	4		0.0	0.235	42	1.89	0.01	0.01	0.01	14.87
95	Spy	1	4		0.0	0.228	50.2	1.79	0.01	0.01	0.01	14.87
95	Spy	2	1	46.4	0.0	1.023	20.6	13.70	35.6	4.03	6.36	
95	Spy	2	1		0.0	1.147	28.6	13.80	31.1	0.57	1.76	
95	Spy	2	2		0.0	0.272	31.2	2.06	4.74	0.05	0.08	
95	Spy	2	2		0.0	0.298	31.7	2.05	4.4	0.05	0.73	
95	Spy	2	3		0.0	0.237	28.3	2.03	4.59	0.01	0.01	15.02
95	Spy	2	3		0.0	0.249	28.7	2.03	0.01	4.76	0.01	14.87
95	Spy	2	4		0.0	0.251	52.4	1.17	0.01	0.01	0.01	15.02
95	Spy	2	4		0.0	0.243	50.3	1.13	0.01	0.01	0.01	12.34
95	Spy	3	1	32.3	0.0	0.884	29.6	13.70	266.3	5.55	7.64	
95	Spy	3	1		0.0	0.618	28.5	13.70	260.6	1.88	3.16	
95	Spy	3	2		0.0	0.253	27.6	2.00	285.9	4.81	4.98	
95	Spy	3	2		0.0	0.251	27.7	1.99	295.3	4.8	6.14	
95	Spy	3	3		0.0	0.207	26.2	2.56	232	1.97	0.01	10.99
95	Spy	3	3		0.0	0.219	25	2.57	252.3	0.01	0.01	10.23
95	Spy	3	4		0.0	0.208	20.7	1.93	240.3	0.01	0.01	15.02
95	Spy	3	4		0.0	0.212	19.6	1.95	272.5	0.01	0.01	15.53
95	Spy	4	1	46.4	md	0.246	19.7	12.60	228.7	5.14	24.3	
95	Spy	4	1		md	0.222	21.5	12.60	251.9	11.14	21	
95	Spy	4	2		0.0	0.241	30.2	2.05	310.3	18.9	31.7	
95	Spy	4	2		0.0	0.269	28.7	2.08	725.2	19.61	19.7	
95	Spy	4	3		0.0	0.217	21.5	1.49	300.2	10.53	0.01	5.49

Year	Apple	Treat	Time	Yield	Ammonical nitrogen (mg/L)	Ash (g/100g)	Alkalinity of ash (meq.)	Dry weight (g/100g)	Pectin Fraction 1 (ug/g)	Pectin Fraction 2 (ug/g)	Pectin Fraction 3 (ug/g)	Total Phenolics (absorbance units)
95	Spy	4	3		0.0	0.228	20.6	1.44	293	0.01	0.01	5.79
95	Spy	4	4		0.0	0.208	25.5	1.19	241.9	6.98	11.1	6.3
95	Spy	4	4		0.0	0.218	28.8	1.18	241.4	7.38	81.5	6.3

Appendix 3. (continued)

C. Sugar and glycerol concentrations (g / 100 mL) as determined by HPLC.

YEAR	APPLE	TREAT	TIME	GLYCEROL	FRUCTOSE	GLUCOSE	SUCROSE
94	Crispin	1	1	0	5.7	1.63	4.69
94	Crispin	1	2	0.38	0.00291	0	0
94	Crispin	1	3	0.422	0.215	0	0
94	Crispin	1	4	0.412	0.0314	0	0
94	Crispin	2	1	0	5.03	1.29	3.85
94	Crispin	2	2	0.39	0.0679	0	0
94	Crispin	2	3	0.419	0.271	0	0
94	Crispin	2	4	0.409	0.0316	0	0
94	Crispin	3	1	0	6.13	1.84	3.26
94	Crispin	3	2	0.327	0.207	0	0
94	Crispin	3	2	0.33	0.19	0	0
94	Crispin	3	3	0.339	0.27	0	0
94	Crispin	3	4	0.332	0	0	0
94	Crispin	4	2	0.453	0.0135	0	0
94	Crispin	4	2	0.457	0	0	0
94	Crispin	4	3	0.469	0.41	0.243	0
94	Crispin	4	4	0.44	0.151	0	0
94	Hyslop	1	1	0	2.21	1.07	7.64
94	Hyslop	1	2	0.361	0	0	0
94	Hyslop	1	3	0.403	0.027	0	0
94	Hyslop	1	4	0.355	0	0	0
94	Hyslop	2	1	0	2.48	1.49	8.17
94	Hyslop	2	2	0.361	0	0	0
94	Hyslop	2	3	0.422	0.112	0	0
94	Hyslop	2	4	0.406	0	0	0
94	Hyslop	3	1	0	3.54	2.38	7.82
94	Hyslop	3	2	0.316	0	0	0
94	Hyslop	3	3	0.323	0.0156	0	0
94	Hyslop	3	4	0.283	0.666	0	0
94	Hyslop	4	1	0	2.97	3.09	6500
94	Hyslop	4	2	0.33	0	0	0
94	Hyslop	4	4	0.325	0.0366	0	0
94	McIntosh	1	2	0.339	0.114	0	0
94	McIntosh	1	3	0.352	0.448	0	0
94	McIntosh	1	4	0.355	0.118	0	0
94	McIntosh	1	4	0.346	0.104	0	0
94	McIntosh	2	1	0	5.12	0.618	3.1

YEAR	APPLE	TREAT	TIME	GLYCEROL	FRUCTOSE	GLUCOSE	SUCROSE
94	McIntosh	2	2	0.333	0.0884	0	0
94	McIntosh	2	3	0.349	0	0	0
94	McIntosh	2	3	0.336	0.457	0	0
94	McIntosh	2	4	0.361	0.185	0	0
94	McIntosh	3	1	0	5.61	1.76	1.42
94	McIntosh	3	2	0.267	0.277	0	0
94	McIntosh	3	3	0.342	0.0423	0	0
94	McIntosh	3	4	0	0	0	0
94	McIntosh	4	1	0	4.71	1.26	2.11
94	McIntosh	4	2	0.412	0	0	0
94	McIntosh	4	3	0	0	0	0
94	McIntosh	4	4	0.351	0.191	0	0
94	Russet	1	2	0.457	0.029	0	0
94	Russet	1	3	0.46	0.634	0	0
94	Russet	1	4	0.495	0.421	0	0
94	Russet	2	1	0	3.47	1.08	2.51
94	Russet	2	2	0.428	0.181	0	0
94	Russet	2	3	0.46	0.522	0	0
94	Russet	2	4	0.482	0.244	0	0
94	Russet	3	1	0	10.3	3.97	3.85
94	Russet	3	2	0.549	0.345	0	0
94	Russet	3	3	0.552	0.825	0	0
94	Russet	4	2	0.536	0.0303	0	0
94	Russet	4	4	0.532	0.372	0	0
94	Spy	1	1	0	5.83	1.55	3.37
94	Spy	1	2	0.333	0.196	0	0
94	Spy	1	3	0.349	0.386	0	0
94	Spy	1	4	0.349	0.09	0	0
94	Spy	2	1	0	5.68	1.81	3.07
94	Spy	2	2	0.409	0.128	0	0
94	Spy	2	2	0.358	0.102	0	0
94	Spy	2	3	0.365	0.389	0	0
94	Spy	2	4	0.374	0.0927	0	0
94	Spy	3	1	0	6.19	2.27	1.8
94	Spy	3	2	0.339	0.129	0	0
94	Spy	3	3	0.349	0.584	0	0
94	Spy	3	4	0.279	0.154	0.179	0
94	Spy	4	1	0	5.83	2.22	1.87
94	Spy	4	2	0.434	0.116	0	0
94	Spy	4	3	0.434	0.466	0	0
94	Spy	4	4	0.438	0.21	0	0

YEAR	APPLE	TREAT	TIME	GLYCEROL	FRUCTOSE	GLUCOSE	SUCROSE
95	Crispin	1	1	0	4.21	2.2	2.15
95	Crispin	1	2	0.261	0	0	0
95	Crispin	1	3	0.346	0	0	0
95	Crispin	1	4	0.355	0	0	0
95	Crispin	2	1	0	4.68	2.08	2.88
95	Crispin	2	2	0.308	0.224	0	0
95	Crispin	2	3	0.342	0	0	0
95	Crispin	2	4	0.303	0.189	0	0
95	Crispin	3	1	0	5.43	1.72	1.77
95	Crispin	3	2	0.303	0.0186	0	0
95	Crispin	3	3	0.365	0	0	0
95	Crispin	3	4	0.358	0	0	0
95	Crispin	4	1	0	4.65	2.26	1.97
95	Crispin	4	2	0.415	0	0	0
95	Crispin	4	3	0.46	0.0135	0	0
95	Crispin	4	4	0.453	0	0	0
95	Crispin	1	1	0	5.58	1.57	2.32
95	McIntosh	1	1	0	5.68	1.56	1.96
95	McIntosh	1	2	0.3	0.0305	0	0
95	McIntosh	1	3	0.365	0.241	0	0
95	McIntosh	1	4	0.374	0	0	0
95	McIntosh	2	1	0	5.31	1.29	2.18
95	McIntosh	2	2	0.358	0.0376	0	0
95	McIntosh	2	3	0.387	0	0	0
95	McIntosh	2	4	0.358	0	0	0
95	McIntosh	3	1	0	7.31	1.82	1.46
95	McIntosh	3	2	0.365	0.0988	0	0
95	McIntosh	3	3	0.393	0.383	0.13	0
95	McIntosh	3	4	0.412	0.0349	0	0
95	McIntosh	4	1	0	5.11	1.55	1.62
95	McIntosh	4	2	0.282	0.178	0	0
95	McIntosh	4	2	0.221	0	0	0
95	McIntosh	4	4	0.434	0	0	0
95	Russet	1	1	0	6.43	2.55	3.93
95	Russet	1	2	0.444	0	0	0
95	Russet	1	3	0.404	0	0	0
95	Russet	1	4	0.45	0	0	0
95	Russet	2	1	0	6.78	2.47	4.11
95	Russet	2	2	0.425	0.0109	0	0
95	Russet	2	3	0.457	0.103	0	0
95	Russet	2	4	0.472	0.0184	0	0

YEAR	APPLE	TREAT	TIME	GLYCEROL	FRUCTOSE	GLUCOSE	SUCROSE
95	Russet	3	1	0	9.37	4.21	3.06
95	Russet	3	2	0.495	0.0438	0	0
95	Russet	3	3	0.44	0.364	0	0
95	Russet	3	4	0.507	0.187	0	0
95	Russet	4	1	0	7.01	3.21	3.14
95	Russet	4	1	0	7.13	2.85	3.66
95	Russet	4	2	0.472	0	0	0
95	Russet	4	3	0.491	0.00926	0	0
95	Russet	4	4	0.51	0.013	0	0
95	Spy	1	1	0	5.22	1.49	4.13
95	Spy	1	2	0.409	0.033	0	0
95	Spy	1	3	0.434	0.301	0	0
95	Spy	1	4	0.431	0.125	0	0
95	Spy	2	1	0	5.15	1.49	3.89
95	Spy	2	2	0.371	0.0252	0	0
95	Spy	2	3	0.406	0.202	0	0
95	Spy	2	4	0.399	0.0436	0	0
95	Spy	3	1	0	6.43	2.35	2.21
95	Spy	3	2	0.349	0.109	0	0
95	Spy	3	2	0.358	0.185	0	0
95	Spy	3	3	0.317	0.475	0.307	0
95	Spy	3	3	0.368	0.769	0	0
95	Spy	3	4	0.399	0.545	0.281	0
95	Spy	4	1	0.247	3.71	1.19	2.98
95	Spy	4	2	0.672	0.0221	0	0
95	Spy	4	3	0.707	0.0769	0	0
95	Spy	4	4	0.717	0	0	0

Appendix 3. (continued)

D. Alcohol concentrations (g / 100 mL) determined by Gas Chromatography.

YEAR	APPLE	TREAT	TIME	ETHANOL	METHANOL
94	Crispin	1	1	0.00	0
94	Crispin	1	2	5.57	0
94	Crispin	1	3	6.44	0
94	Crispin	1	4	6.49	0
94	Crispin	2	1	0.00	0
94	Crispin	2	2	5.45	0
94	Crispin	2	3	6.11	0
94	Crispin	2	4	6.37	0
94	Crispin	3	1	0.05	0
94	Crispin	3	2	5.73	0
94	Crispin	3	3	5.92	0
94	Crispin	3	4	6.42	0
94	Crispin	4	1	6.35	0.0122
94	Crispin	4	2	5.56	0.0108
94	Crispin	4	3	6.39	0.0143
94	Crispin	4	4	5.85	0.0125
94	Hyslop	1	1	0.00	0
94	Hyslop	1	2	5.95	0
94	Hyslop	1	3	6.26	0
94	Hyslop	1	4	5.89	0
94	Hyslop	2	1	0.00	0
94	Hyslop	2	2	5.51	0
94	Hyslop	2	3	6.53	0
94	Hyslop	2	4	6.65	0
94	Hyslop	3	1	0.04	0
94	Hyslop	3	2	6.62	0
94	Hyslop	3	3	7.46	0
94	Hyslop	3	4	7.06	0
94	Hyslop	4	1	0.02	0.0180
94	Hyslop	4	2	6.08	0.0288
94	Hyslop	4	3	6.85	0.0321
94	Hyslop	4	4	6.12	0.0288
94	McIntosh	1	2	4.51	0
94	McIntosh	1	3	4.95	0
94	McIntosh	1	4	5.24	0
94	McIntosh	2	1	0.00	0

YEAR	APPLE	TREAT	TIME	ETHANOL	METHANOL
94	McIntosh	2	2	4.52	0
94	McIntosh	2	3	4.81	0
94	McIntosh	2	4	4.54	0
94	McIntosh	3	1	0.13	0
94	McIntosh	3	2	4.70	0
94	McIntosh	3	3	5.12	0
94	McIntosh	3	4	4.57	0
94	McIntosh	4	1	0.01	0
94	McIntosh	4	2	4.14	0.0023
94	McIntosh	4	3	5.03	0.0056
94	McIntosh	4	4	5.39	0.0123
94	Russet	1	2	7.40	0
94	Russet	1	3	7.47	0
94	Russet	1	4	7.15	0
94	Russet	2	2	7.53	0
94	Russet	2	3	7.28	0
94	Russet	2	4	7.62	0
94	Russet	3	1	0.02	0
94	Russet	3	2	9.32	0
94	Russet	3	3	9.30	0
94	Russet	3	4	9.18	0
94	Russet	4	2	7.30	0
94	Russet	4	3	7.98	0
94	Russet	4	4	8.14	0.0226
94	Spy	1	1	0.05	0
94	Spy	1	2	5.66	0
94	Spy	1	3	5.64	0
94	Spy	1	4	5.92	0
94	Spy	2	1	0.01	0
94	Spy	2	2	5.67	0
94	Spy	2	3	5.59	0
94	Spy	2	4	6.27	0
94	Spy	3	1	0.03	0
94	Spy	3	2	5.94	0
94	Spy	3	3	5.70	0
94	Spy	3	4	5.84	0
94	Spy	4	1	0.22	0
94	Spy	4	2	5.01	0
94	Spy	4	3	5.84	0
94	Spy	4	4	5.86	0

YEAR	APPLE	TREAT	TIME	ETHANOL	METHANOL
95	Crispin	1	1	0.00	0
95	Crispin	1	2	4.99	0
95	Crispin	1	3	5.68	0
95	Crispin	1	4	5.78	0
95	Crispin	2	1	0.00	0
95	Crispin	2	2	4.67	0
95	Crispin	2	3	5.79	0
95	Crispin	2	4	5.58	0
95	Crispin	3	1	0.06	0
95	Crispin	3	2	4.54	0
95	Crispin	3	3	5.04	0
95	Crispin	3	4	5.18	0
95	Crispin	4	1	0.21	0
95	Crispin	4	2	4.07	0
95	Crispin	4	3	5.45	0
95	Crispin	4	4	5.04	0
95	McIntosh	1	1	0.01	0
95	McIntosh	1	2	4.82	0
95	McIntosh	1	3	5.17	0
95	McIntosh	1	4	5.30	0
95	McIntosh	2	1	0.22	0
95	McIntosh	2	2	8.46	0
95	McIntosh	2	3	4.53	0
95	McIntosh	2	4	4.82	0
95	McIntosh	3	1	0.13	0
95	McIntosh	3	2	5.09	0
95	McIntosh	3	3	5.63	0
95	McIntosh	3	4	5.89	0
95	McIntosh	4	1	0.47	0
95	McIntosh	4	2	4.49	0
95	McIntosh	4	3	4.62	0
95	McIntosh	4	4	5.02	0.0072
95	Russet	1	1	0.00	0
95	Russet	1	2	5.48	0
95	Russet	1	3	7.15	0
95	Russet	1	4	7.41	0
95	Russet	2	1	0.00	0
95	Russet	2	2	7.03	0
95	Russet	2	3	7.45	0
95	Russet	2	4	7.31	0

YEAR	APPLE	TREAT	TIME	ETHANOL	METHANOL
95	Russet	3	1	0.01	0
95	Russet	3	2	8.06	0
95	Russet	3	3	8.68	0
95	Russet	3	4	8.70	0
95	Russet	4	1	0.09	0
95	Russet	4	2	6.84	0.0131
95	Russet	4	3	7.35	0.0202
95	Russet	4	4	7.43	0.0147
95	Spy	1	1	0.00	0
95	Spy	1	2	5.68	0
95	Spy	1	3	5.80	0
95	Spy	1	4	5.84	0
95	Spy	2	1	0.00	0
95	Spy	2	2	5.23	0
95	Spy	2	3	6.03	0
95	Spy	3	1	0.06	0
95	Spy	3	2	5.69	0
95	Spy	3	4	5.97	0
95	Spy	4	1	1.00	0
95	Spy	4	2	5.17	0
95	Spy	4	3	5.73	0
95	Spy	4	4	6.03	0

Appendix 3. (continued)

E. Minerals in ciders (mg/L).

Year	Apple	Treat	Time	Nitrogen	Sulfur	Phosphorous	Potassium	Magnesium	Calcium	Sodium	Iron	Aluminum	Manganese	Boron	Copper	Zinc
94	Crispin	1	2	356	21.9	93.5	778.3	21.0	23.1	10.7	1.9	8.5	0.3	3.3	0.3	0.1
94	Crispin	1	3	1290	24.5	90.6	972.1	26.4	35.7	58.8	2.4	4.5	0.7	3.0	0.3	0.3
94	Crispin	1	4	1500	16.2	88.5	996.3	28.2	21.3	10.5	0.8	9.0	0.6	3.0	0.3	0.4
94	Crispin	2	2	208	27.9	86.0	782.2	22.4	25.0	10.3	4.4	19.3	0.4	3.1	0.3	0.4
94	Crispin	2	3	1310	31.1	81.9	929.7	24.8	18.3	10.6	0.3	4.4	0.7	2.7	0.3	0.3
94	Crispin	2	4	1350	30.2	88.2	1000.7	27.7	22.1	9.9	1.1	7.0	0.6	2.9	0.2	0.3
94	Crispin	3	2	370	16.4	80.7	792.3	16.4	16.6	8.1	2.1	5.2	0.3	2.6	0.3	0.3
94	Crispin	3	3	1230	20.8	80.6	960.2	27.6	39.5	64.2	1.1	7.6	0.8	2.6	0.5	0.4
94	Crispin	3	4	1200	12.5	78.6	801.4	18.8	16.0	5.2	2.9	1.0	0.3	2.7	0.3	0.2
94	Crispin	4	2	1483	26.3	89.5	981.8	45.8	63.8	49.8	1.3	14.0	1.0	2.7	0.4	0.7
94	Crispin	4	3	1060	23.7	90.4	1006.1	45.9	60.3	51.3	3.6	8.4	1.0	2.8	0.3	0.3
94	Crispin	4	4	1650	23.6	85.8	777.0	35.8	44.2	23.9	1.2	11.3	0.2	3.0	0.2	0.1
94	Hyslop	1	2	17521	30.1	155.5	1689.9	36.6	33.9	10.2	7.3	6.1	0.4	2.9	0.3	0.2
94	Hyslop	1	3	1430	47.5	170.0	1844.7	56.3	66.0	59.7	1.2	9.4	0.8	2.9	0.5	0.6
94	Hyslop	1	4	1990	33.9	163.9	1900.8	52.1	46.0	12.8	0.9	15.2	0.8	2.8	0.3	0.4
94	Hyslop	2	2	592	37.9	150.5	1734.3	35.5	28.6	10.8	2.7	5.8	0.3	2.8	0.2	0.4
94	Hyslop	2	3	1360	56.6	167.6	1877.8	54.9	62.3	83.8	1.6	12.0	0.8	2.6	0.4	0.5
94	Hyslop	2	4	2140	49.0	154.2	1843.7	46.8	61.4	75.9	1.9	9.0	0.8	2.7	0.4	1.2
94	Hyslop	3	2	1504	42.9	219.9	2231.1	68.0	67.7	77.0	1.8	17.4	0.8	3.4	0.5	0.9
94	Hyslop	3	3	2110	41.0	225.0	2313.2	78.7	73.2	74.7	3.0	29.7	1.1	3.6	0.5	0.6
94	Hyslop	3	4	2100	24.5	217.3	2168.1	63.9	40.7	13.9	6.1	3.8	0.4	3.5	0.2	0.3
94	Hyslop	4	2	2117	81.1	174.7	1894.1	61.3	78.8	62.4	1.1	5.1	0.9	2.9	0.4	0.4
94	Hyslop	4	3	1200	80.7	178.7	2002.0	67.0	92.2	90.9	1.0	14.0	1.1	3.1	0.5	0.4
94	Hyslop	4	4	1180	51.6	148.7	1525.8	48.7	53.4	42.9	0.7	7.1	0.2	3.0	0.2	0.3
94	McIntosh	1	2	215	21.2	112.5	852.4	21.3	22.4	14.7	2.0	11.2	0.4	2.3	0.3	0.1

Year	Apple	Treat	Time	Nitrogen	Sulfur	Phosphorous	Potassium	Magnesium	Calcium	Sodium	Iron	Aluminum	Manganese	Boron	Copper	Zinc
94	McIntosh	1	3	680	22.2	111.9	1052.1	28.6	45.8	64.8	1.2	8.6	0.8	2.2	0.4	0.6
94	McIntosh	1	4	1390	26.2	118.6	1057.8	29.4	40.1	54.1	1.2	5.4	0.8	2.2	0.3	0.3
94	McIntosh	2	2	87	30.9	116.2	863.4	20.4	22.5	10.5	3.2	7.3	0.3	2.3	0.3	0.2
94	McIntosh	2	3	1280	31.5	120.5	1057.8	28.1	47.4	70.4	2.9	6.7	0.8	2.2	0.5	0.7
94	McIntosh	2	4	1420	36.3	127.2	1097.6	29.8	44.0	59.2	1.1	10.1	0.8	2.3	0.4	0.3
94	McIntosh	3	2	58	28.4	128.6	1174.4	31.4	43.4	70.5	3.1	6.7	0.8	2.0	0.6	0.4
94	McIntosh	3	3	910	24.3	127.1	1192.6	31.7	43.7	77.8	2.3	17.7	1.0	2.1	0.4	0.5
94	McIntosh	3	4	1725	8.5	120.9	921.9	20.4	14.9	9.9	3.5	1.1	0.4	2.0	0.2	0.2
94	McIntosh	4	2	1255	25.8	112.9	1063.0	51.0	75.2	63.6	2.0	19.0	1.1	1.7	0.7	0.5
94	McIntosh	4	3	1280	25.8	123.2	1078.4	52.2	76.8	71.7	4.2	21.5	1.1	2.0	0.4	0.4
94	McIntosh	4	4	880	22.0	112.1	842.4	38.0	41.5	20.8	1.1	19.2	0.3	2.0	0.2	0.3
94	Russet	1	2	129	30.4	135.1	1249.2	30.1	35.9	19.8	2.3	5.3	0.3	2.0	0.2	0.2
94	Russet	1	3	1290	37.9	144.0	1522.3	38.0	54.7	73.2	3.4	16.9	0.8	1.6	0.3	0.4
94	Russet	1	4	1450	40.5	141.5	1485.2	39.0	62.7	77.3	1.1	14.0	0.8	1.8	0.4	0.4
94	Russet	2	2	168	40.2	133.3	1266.8	28.7	36.1	11.7	4.0	7.4	0.4	2.2	0.3	0.2
94	Russet	2	3	550	52.8	130.7	1444.7	35.2	56.6	65.8	1.2	9.8	0.6	1.6	0.3	0.4
94	Russet	2	4	1480	54.8	138.7	1469.3	39.7	68.8	91.6	2.3	9.6	0.8	1.9	0.4	0.7
94	Russet	3	2	55	43.3	176.7	1760.0	45.5	62.6	78.8	1.7	10.5	0.8	1.7	0.6	0.4
94	Russet	3	3	1730	50.8	173.1	1767.7	45.1	60.9	75.3	0.8	6.9	1.0	1.8	0.5	0.3
94	Russet	3	4	1725	22.7	177.2	1643.9	40.5	40.6	14.4	3.4	2.8	0.4	1.9	0.4	0.1
94	Russet	4	2	1265	46.8	150.4	1496.9	57.6	85.3	53.3	0.9	13.6	1.0	1.5	0.5	0.3
94	Russet	4	3	1240	34.6	159.1	1594.1	57.2	95.0	72.9	3.5	16.5	1.0	1.8	0.7	0.4
94	Russet	4	4	1460	39.4	151.9	1360.8	48.1	71.4	32.4	1.3	15.3	0.2	2.0	0.2	0.2
94	Spy	1	2	327	12.1	77.4	502.2	16.1	26.1	6.5	4.8	6.8	0.3	2.2	0.3	0.1
94	Spy	1	3	1450	19.4	84.5	670.7	21.7	38.4	54.3	1.2	5.3	0.6	2.2	0.3	0.3
94	Spy	1	4	1350	35.8	87.3	688.2	23.5	58.1	89.9	3.5	3.8	0.7	2.4	0.4	0.5
94	Spy	2	2	198	28.3	89.6	552.9	18.1	27.3	7.2	1.6	8.1	0.3	2.1	0.2	0.2
94	Spy	2	3	1270	38.7	88.4	730.9	22.0	43.1	58.6	3.6	3.8	0.7	2.1	0.3	0.4
94	Spy	2	4	1130	35.8	88.8	723.7	23.7	51.6	67.7	1.0	3.1	0.7	2.2	0.3	0.5

Year	Apple	Treat	Time	Nitrogen	Sulfur	Phosphorous	Potassium	Magnesium	Calcium	Sodium	Iron	Aluminum	Manganese	Boron	Copper	Zinc
94	Spy	3	2	133	26.0	92.9	677.2	27.4	54.7	75.7	2.9	6.9	0.7	1.8	0.5	0.3
94	Spy	3	3	1050	20.8	94.6	677.7	26.0	39.9	40.0	2.3	6.6	0.9	1.8	0.4	0.3
94	Spy	3	4	2464	7.5	84.6	502.0	13.9	21.0	7.1	1.6	1.7	0.3	1.8	0.2	0.2
94	Spy	4	2	1057	24.9	95.7	641.6	35.9	86.0	61.9	1.3	13.1	0.8	1.8	0.4	0.5
94	Spy	4	3	1410	30.9	93.1	695.0	40.2	91.5	56.4	4.0	17.3	0.9	1.9	0.4	0.3
94	Spy	4	4	730	20.5	104.7	579.5	41.0	86.5	21.4	1.6	16.0	0.8	2.0	0.3	1.8
95	Crispin	1	2	600	19.1	73.4	798.0	24.4	17.4	23.9	0.7	5.5	0.2	2.1	0.2	0.2
95	Crispin	1	3	400	15.1	73.6	724.0	24.4	15.5	11.5	0.8	18.8	0.2	1.7	0.3	0.2
95	Crispin	1	4	670	30.1	139.6	1500.5	46.0	28.3	41.1	2.5	80.6	0.3	3.0	0.3	0.1
95	Crispin	2	2	700	38.4	75.1	847.2	26.5	19.9	13.5	1.2	13.4	0.2	1.9	0.2	0.3
95	Crispin	2	3	1570	63.1	132.7	1421.6	45.8	30.8	34.5	5.1	13.7	0.5	9.9	0.3	0.2
95	Crispin	2	4	590	63.8	142.8	1478.5	49.9	36.7	166.8	3.6	59.4	0.3	2.9	0.3	0.1
95	Crispin	3	2	700	17.5	99.5	954.8	24.2	22.7	18.1	0.9	10.5	0.2	2.3	0.2	0.4
95	Crispin	3	3	420	8.2	93.2	748.3	22.9	18.9	51.3	0.0	2.9	0.1	0.9	0.3	0.5
95	Crispin	3	4	680	13.2	97.9	656.1	25.0	17.4	29.7	0.0	2.7	0.2	2.6	0.9	0.4
95	Crispin	4	2	700	16.7	52.0	635.7	29.0	33.1	16.9	1.2	14.5	0.2	1.9	0.1	0.3
95	Crispin	4	3	220	29.9	114.9	1210.5	67.6	63.1	100.8	1.1	24.1	0.5	3.0	0.3	0.7
95	Crispin	4	4	520	22.2	107.6	1270.8	68.6	61.9	46.0	1.7	65.0	0.6	2.8	0.3	0.4
95	McIntosh	1	2	500	8.8	99.8	578.5	18.9	22.3	17.7	0.6	1.4	0.1	1.1	0.1	0.3
95	McIntosh	1	3	160	12.7	94.7	507.6	19.3	19.1	13.4	0.0	4.8	0.2	0.8	0.3	0.3
95	McIntosh	1	4	550	18.5	182.3	1107.4	36.9	38.3	28.7	2.7	17.1	0.3	1.7	0.3	0.5
95	McIntosh	2	2	800	34.6	101.1	659.7	19.7	19.5	10.0	0.5	2.8	0.1	1.1	0.1	0.3
95	McIntosh	2	3	1070	52.7	182.7	1101.9	34.9	34.0	28.1	0.0	1.8	0.2	1.3	0.3	0.4
95	McIntosh	2	4	370	49.1	188.8	1002.3	35.7	32.1	94.9	3.2	3.1	0.3	1.2	0.3	0.2
95	McIntosh	3	2	900	16.8	108.1	751.0	20.0	22.6	12.8	0.8	8.8	0.1	1.0	0.2	0.3
95	McIntosh	3	3	170	11.2	103.2	596.0	20.5	20.2	31.6	1.6	13.5	0.1	0.8	0.3	0.5
95	McIntosh	3	4	580	25.5	228.5	1282.7	46.2	38.2	30.5	1.9	6.0	0.3	2.5	0.8	0.3
95	McIntosh	4	2	1200	10.8	98.0	613.1	31.0	46.7	29.8	1.1	16.1	0.2	1.3	0.2	0.4
95	McIntosh	4	3	250	38.3	209.7	1118.1	69.4	89.3	113.6	1.8	21.8	0.5	1.7	0.4	0.4

Year	Apple	Treat	Time	Nitrogen	Sulfur	Phosphorous	Potassium	Magnesium	Calcium	Sodium	Iron	Aluminum	Manganese	Boron	Copper	Zinc
95	McIntosh	4	4	540	25.4	182.1	904.7	47.4	36.6	35.8	1.2	7.3	0.3	7.7	0.3	0.2
95	Russet	1	2	800	39.9	130.2	1244.0	36.8	50.3	59.6	1.2	11.7	0.2	1.7	0.3	0.6
95	Russet	1	3	510	17.5	129.9	1029.0	34.9	28.2	17.8	0.0	4.1	0.2	1.0	0.3	0.5
95	Russet	1	4	640	27.8	238.6	1964.4	46.4	33.2	43.1	0.0	9.0	0.4	2.6	0.3	0.2
95	Russet	2	2	900	48.0	130.3	1249.8	33.4	33.9	17.1	1.1	12.5	0.2	1.5	0.1	0.7
95	Russet	2	3	1356	69.3	245.3	2169.3	67.3	57.5	83.1	1.4	1.8	0.2	1.9	0.3	0.7
95	Russet	2	4	300	70.0	245.2	2134.1	63.8	56.1	54.1	0.3	7.1	0.4	1.9	0.3	0.8
95	Russet	3	2	500	21.4	123.9	1381.1	37.2	42.6	36.3	1.2	15.9	0.2	1.0	0.2	0.6
95	Russet	3	3	450	17.9	134.2	1045.1	38.8	36.4	88.2	1.0	5.9	0.2	1.5	0.5	0.4
95	Russet	3	4	620	39.3	282.7	1815.9	82.6	71.1	67.4	1.2	6.0	0.6	3.6	1.4	0.7
95	Russet	4	2	600	21.9	116.8	1244.4	45.9	54.3	24.8	2.1	32.5	0.3	1.5	0.2	0.5
95	Russet	4	3	320	39.9	223.5	1972.1	93.1	100.8	140.9	3.6	44.0	0.6	1.7	0.4	1.0
95	Russet	4	4	640	47.5	257.9	2360.2	107.1	111.7	96.3	5.1	29.8	0.7	9.8	0.3	1.1
95	Spy	1	2	400	17.4	120.4	1108.2	24.6	22.2	17.3	1.1	11.7	0.2	1.3	0.2	0.8
95	Spy	1	3	590	14.0	125.4	875.6	26.3	17.3	35.6	0.0	2.6	0.2	1.7	0.5	0.5
95	Spy	1	4	490	55.7	253.3	2305.2	70.2	56.8	42.3	0.1	2.3	0.5	2.6	0.3	0.8
95	Spy	2	2	700	30.0	134.0	1281.3	27.0	23.6	20.7	0.6	3.5	0.2	2.1	0.2	0.4
95	Spy	2	3	890	47.1	214.1	1973.7	42.6	32.1	42.4	0.1	6.1	0.3	2.6	0.3	0.4
95	Spy	2	4	190	62.9	247.5	2089.9	49.7	36.5	114.6	2.2	55.0	0.3	2.8	0.3	0.3
95	Spy	3	2	400	22.0	127.1	1169.8	20.5	20.5	14.2	1.0	11.0	0.1	1.7	0.2	0.2
95	Spy	3	3	210	13.4	130.5	893.3	20.6	17.4	63.2	0.3	1.4	0.1	1.2	0.4	0.3
95	Spy	3	4	380	28.5	255.3	2162.7	43.0	34.7	79.6	2.2	1.8	0.3	2.8	0.3	0.1
95	Spy	4	2	900	19.3	114.8	978.8	30.7	37.7	33.6	1.6	20.3	0.2	1.6	0.3	0.4
95	Spy	4	3	1830	34.6	236.6	1833.9	64.9	70.8	141.0	2.6	31.9	0.5	1.9	0.3	0.8
95	Spy	4	4	550	29.2	228.2	1811.1	62.2	65.6	104.2	3.8	42.2	0.5	2.1	0.4	0.2

Appendix 3. (continued)

F. Chemical analyses of sediments from bottled ciders and gushing tendency of ciders.
All determinations, except wet weight of sediments and gushing tendency of the ciders, were conducted in duplicate.
Gushing: 1 = no gushing; 2 = gushing

Year	Apple	Treat	Time	Yeasts (colonies / g)	Wet Weight (g / 750 mL bottle)	Dry Weight (g / 100 g)	Pectin Fraction 1 (ug/g)	Pectin Fraction 2 (ug/g)	Pectin Fraction 3 (ug/g)	Gushing Tendency
94	Crispin	1	3	3.90E+08	1.8	19.9	6.0E+02	0.0E+00	1.6E+03	1
94	Crispin	1	3	4.20E+08		13.7	7.3E+02	5.2E+02	2.4E+03	
94	Crispin	1	4	4.40E+04	0.8877	51.9	0.0E+00	0.0E+00	7.5E+02	1
94	Crispin	1	4	3.30E+04		55.5	6.9E+02	4.0E+02	2.0E+03	
94	Crispin	2	3	9.50E+08	1.7	19.9	5.3E+02	2.6E+02	1.8E+03	1
94	Crispin	2	3	8.90E+08		14.2	5.7E+02	3.2E+02	1.7E+03	
94	Crispin	2	4	6.70E+04	0.7521	32.7	0.0E+00	0.0E+00	2.6E+03	1
94	Crispin	2	4	5.80E+04		22.2	5.3E+02	0.0E+00	2.2E+03	
94	Crispin	3	3	1.40E+09	1.2155	20.4	7.3E+01	8.1E+01	1.4E+02	1
94	Crispin	3	3	1.50E+09		25.5	4.5E+02	3.0E+02	1.1E+03	
94	Crispin	3	4	4.00E+06	1.2199	16.1	0.0E+00	4.7E+01	1.9E+03	1
94	Crispin	3	4	4.90E+06		17.5	0.0E+00	0.0E+00	7.6E+02	
94	Crispin	4	3	2.50E+09	0.4354	36.5	0.0E+00	0.0E+00	0.0E+00	1
94	Crispin	4	3	2.20E+09		29.6	0.0E+00	0.0E+00	0.0E+00	
94	Crispin	4	4	1.00E+06	0.4581	18.5	8.2E+02	1.1E+03	2.1E+03	2
94	Crispin	4	4	8.30E+05		18.5	7.9E+02	1.4E+03	2.2E+03	
94	Hyslop	1	3	6.70E+08	0.5	23.6	0.0E+00	0.0E+00	2.9E+03	1
94	Hyslop	1	3	5.10E+08		23.5	0.0E+00	0.0E+00	0.0E+00	
94	Hyslop	1	4	5.10E+08	0.334	31	0.0E+00	0.0E+00	2.6E+03	1
94	Hyslop	1	4	4.40E+08		31.1	0.0E+00	0.0E+00	1.7E+03	
94	Hyslop	2	3	6.00E+08	0.3	33.6	0.0E+00	0.0E+00	0.0E+00	1

Year	Apple	Treat	Time	Yeasts (colonies / g)	Wet Weight (g / 750 mL bottle)	Dry Weight (g / 100 g)	Pectin Fraction 1 (ug/g)	Pectin Fraction 2 (ug/g)	Pectin Fraction 3 (ug/g)	Gushing Tendency
94	Hyslop	2	3	5.70E+08		32.6	3.3E+02	0.0E+00	2.7E+03	
94	Hyslop	2	4	3.30E+08	0.4446	31.8	0.0E+00	0.0E+00	2.6E+03	1
94	Hyslop	2	4	3.90E+08		31	0.0E+00	0.0E+00	4.0E+03	
94	Hyslop	3	3	2.70E+08	0.3206	25.7	3.7E+03	1.2E+03	7.7E+02	1
94	Hyslop	3	3	4.40E+08		26.1	3.8E+03	2.7E+02	2.7E+03	
94	Hyslop	3	4	1.50E+08	1.3773	25.2	3.9E+03	0.0E+00	4.3E+03	1
94	Hyslop	3	4	1.80E+08		26.7	2.5E+02	0.0E+00	5.2E+03	
94	Hyslop	4	3	3.40E+09	0.488	39.6	9.5E+03	2.4E+03	0.0E+00	1
94	Hyslop	4	3	4.00E+09		41.3	1.1E+04	6.3E+02	0.0E+00	
94	Hyslop	4	4	1.50E+08	0.4209	31.6	5.7E+03	2.5E+03	2.5E+03	1
94	Hyslop	4	4	1.10E+08		31.3	7.4E+03	5.0E+03	1.9E+03	
94	McIntosh	1	3	1.10E+08	0.9	14.8	4.6E+02	2.2E+02	1.4E+03	1
94	McIntosh	1	3	1.00E+08		15.3	0.0E+00	0.0E+00	3.3E+03	
94	McIntosh	1	4	3.00E+08	0.9989	18.1	0.0E+00	0.0E+00	2.0E+03	1
94	McIntosh	1	4	4.40E+08		17.7	5.8E+02	0.0E+00	5.9E+02	
94	McIntosh	2	3	3.30E+08	1.2	16	0.0E+00	0.0E+00	2.5E+03	1
94	McIntosh	2	3	2.60E+08		14.2	0.0E+00	1.1E+03	2.7E+03	
94	McIntosh	2	4	2.70E+08	1.5027	16	2.3E+02	3.2E+02	1.9E+03	1
94	McIntosh	2	4	1.20E+08		16.1	0.0E+00	3.2E+02	2.3E+03	
94	McIntosh	3	3	2.60E+08	1.2554	23.6	6.2E+02	6.0E+02	1.2E+03	1
94	McIntosh	3	3	3.50E+08		23	6.9E+02	3.6E+02	1.0E+03	
94	McIntosh	3	4	1.60E+06	1.0387	17.4	0.0E+00	0.0E+00	2.7E+02	1
94	McIntosh	3	4	1.90E+06		21.1	0.0E+00	2.7E+02	1.7E+03	
94	McIntosh	4	3	1.00E+09	1.9074	14	4.7E+03	5.7E+03	4.1E+02	2
94	McIntosh	4	3	1.10E+09		11.2	4.8E+03	4.6E+03	2.7E+02	
94	McIntosh	4	4	1.00E+05	22.569	4.2	8.8E+03	1.2E+03	1.2E+03	2
94	McIntosh	4	4	9.90E+04		3.9	9.4E+03	6.5E+02	5.3E+02	

Year	Apple	Treat	Time	Yeasts (colonies / g)	Wet Weight (g / 750 mL bottle)	Dry Weight (g / 100 g)	Pectin Fraction 1 (ug/g)	Pectin Fraction 2 (ug/g)	Pectin Fraction 3 (ug/g)	Gushing Tendency
94	Russet	1	3	2.90E+08	1.3	46.7	9.0E+02	4.0E+02	2.3E+03	1
94	Russet	1	3	3.30E+08		33.3	7.1E+02	7.1E+02	2.6E+03	
94	Russet	1	4	5.60E+06	0.5421	28	0.0E+00	0.0E+00	2.0E+03	1
94	Russet	1	4	6.90E+06		33.4	1.0E+01	1.1E+03	3.4E+03	
94	Russet	2	3	2.10E+09	1.6	32.3	7.4E+02	7.4E+02	1.9E+03	1
94	Russet	2	3	1.90E+09		34	8.9E+02	6.8E+02	2.2E+03	
94	Russet	2	4	3.70E+07	0.3821	22.2	8.0E+02	0.0E+00	1.6E+03	1
94	Russet	2	4	3.70E+07		36.6	0.0E+00	1.6E+03	2.1E+03	
94	Russet	3	3	1.90E+09	0.2528	19.8	1.9E+02	0.0E+00	1.7E+03	1
94	Russet	3	3	1.50E+09		19.8	6.5E+02	0.0E+00	2.1E+03	
94	Russet	3	4	5.80E+07	0.2086	31.4	0.0E+00	0.0E+00	5.9E+03	1
94	Russet	3	4	5.40E+07		31.4	0.0E+00	0.0E+00	2.9E+03	
94	Russet	4	3	1.10E+09	2.0244	20.4	4.7E+03	1.8E+03	0.0E+00	2
94	Russet	4	3	1.20E+09		19.5	2.3E+03	1.9E+03	2.4E+02	
94	Russet	4	4	1.10E+06	1.8378	20.1	1.5E+03	3.5E+03	2.9E+03	2
94	Russet	4	4	8.50E+05		20.7	1.7E+03	2.8E+03	2.4E+03	
94	Spy	1	3	1.70E+09	1.6	16.3	1.0E+03	5.0E+02	1.9E+03	1
94	Spy	1	3	1.50E+09		19.2	5.1E+02	8.1E+02	2.2E+03	
94	Spy	1	4	1.10E+05	0.3918	36	0.0E+00	0.0E+00	7.2E+02	1
94	Spy	1	4	4.90E+04		34.1	4.2E+02	0.0E+00	1.2E+03	
94	Spy	2	3	2.30E+09	1.2	35.5	9.8E+02	0.0E+00	2.9E+03	1
94	Spy	2	3	2.40E+09		24.4	6.4E+02	4.2E+02	2.2E+03	
94	Spy	2	4	2.20E+05	0.3604	33.2	0.0E+00	0.0E+00	2.1E+03	1
94	Spy	2	4	4.00E+05		29.9	0.0E+00	5.5E+02	2.7E+03	
94	Spy	3	3	1.10E+09	0.6289	17.8	0.0E+00	0.0E+00	1.9E+03	1
94	Spy	3	3	1.20E+09		19	0.0E+00	6.8E+02	2.7E+03	
94	Spy	3	4	2.60E+07	0.6768	18.4	0.0E+00	0.0E+00	1.9E+03	1

Year	Apple	Treat	Time	Yeasts (colonies / g)	Wet Weight (g / 750 mL bottle)	Dry Weight (g / 100 g)	Pectin Fraction 1 (ug/g)	Pectin Fraction 2 (ug/g)	Pectin Fraction 3 (ug/g)	Gushing Tendency
94	Spy	3	4	3.00E+07		13.9	0.0E+00	0.0E+00	1.8E+03	
94	Spy	4	3	1.90E+08	1.3029	39.5	6.4E+02	8.6E+02	1.0E+03	1
94	Spy	4	3	1.60E+08		37.4	9.9E+02	4.5E+03	0.0E+00	
94	Spy	4	4	3.00E+03	1.4632	15.5	6.4E+02	1.5E+03	1.6E+03	2
94	Spy	4	4	7.60E+03		16.9	6.6E+01	1.8E+03	1.8E+03	
95	Crispin	1	3	1.80E+09	0.1636	24.7	1.6E+02	0.0E+00	1.1E+03	1
95	Crispin	1	3	1.90E+09		25	0.0E+00	0.0E+00	4.7E+02	
95	Crispin	1	4	2.10E+06	0.1705	31.2	0.0E+00	3.2E+03	2.1E+03	1
95	Crispin	1	4	2.40E+06		28.9	2.1E+03	0.0E+00	3.9E+03	
95	Crispin	2	3	1.50E+09	0.2192	24.4	0.0E+00	0.0E+00	1.2E+02	1
95	Crispin	2	3	1.80E+09		26	0.0E+00	0.0E+00	6.3E+02	
95	Crispin	2	4	2.90E+04	0.1152	32.3	1.8E+03	2.7E+03	5.3E+03	1
95	Crispin	2	4	2.10E+04		32.2	2.5E+03	0.0E+00	1.9E+03	
95	Crispin	3	3	5.60E+07	0.5405	26.4	0.0E+00	0.0E+00	3.1E+03	1
95	Crispin	3	3	5.60E+07		27.3	0.0E+00	0.0E+00	2.9E+03	
95	Crispin	3	4	4.20E+04	0.5553	28.3	0.0E+00	3.1E+03	7.2E+03	1
95	Crispin	3	4	4.00E+04		29.8	0.0E+00	2.0E+03	3.7E+03	
95	Crispin	4	3	1.00E+09	2.157	20.8	1.4E+03	2.6E+03	2.6E+03	1
95	Crispin	4	3	8.60E+09		20.6	9.0E+02	0.0E+00	2.0E+03	
95	Crispin	4	4	1.30E+04	1.8274	20.7	6.6E+02	5.6E+02	1.5E+03	2
95	Crispin	4	4	1.50E+04		19.1	7.9E+02	4.2E+02	1.4E+03	
95	McIntosh	1	3	1.00E+09	0.4262	19.4	0.0E+00	0.0E+00	3.3E+03	1
95	McIntosh	1	3	1.30E+09		17	3.7E+02	3.7E+02	3.3E+03	
95	McIntosh	1	4	7.90E+08	0.4131	17.4	0.0E+00	0.0E+00	1.5E+03	1
95	McIntosh	1	4	6.00E+08		17.2	0.0E+00	0.0E+00	2.6E+03	
95	McIntosh	2	3	3.30E+09	0.4086	27	3.0E+03	2.5E+03	4.7E+03	1
95	McIntosh	2	3	2.90E+09		25.5	2.1E+03	1.7E+03	4.2E+03	

Year	Apple	Treat	Time	Yeasts (colonies / g)	Wet Weight (g / 750 mL bottle)	Dry Weight (g / 100 g)	Pectin Fraction 1 (ug/g)	Pectin Fraction 2 (ug/g)	Pectin Fraction 3 (ug/g)	Gushing Tendency
95	McIntosh	2	4	1.50E+08	0.2674	22.5	0.0E+00	0.0E+00	2.6E+03	1
95	McIntosh	2	4	1.40E+08		22.8	0.0E+00	2.0E+03	3.1E+03	
95	McIntosh	3	3	1.40E+09	0.4626	19.5	1.1E+03	3.7E+03	3.3E+03	1
95	McIntosh	3	3	1.40E+09		19.5	1.0E+03	3.2E+03	3.8E+03	
95	McIntosh	3	4	6.90E+08	0.5038	19.1	2.0E+03	2.0E+03	5.1E+03	1
95	McIntosh	3	4	6.60E+08		18.4	2.5E+03	2.3E+03	3.6E+03	
95	McIntosh	4	3	md	md	md	md	md	md	1
95	McIntosh	4	3	md		md	md	md	md	
95	McIntosh	4	4	2.00E+02	150.9	2.2	7.5E+03	2.5E+02	3.8E+02	1
95	McIntosh	4	4	0.00E+00		2.1	6.9E+03	2.8E+02	3.6E+02	
95	Russet	1	3	1.40E+08	0.4	28.7	9.1E+02	1.3E+03	3.4E+03	1
95	Russet	1	3	1.00E+08		29.6	1.4E+03	0.0E+00	4.3E+03	
95	Russet	3	3	7.40E+06		25.1	5.0E+02	3.0E+02	1.9E+03	
95	Russet	3	4	1.60E+05	0.578	26.2	3.6E+03	3.0E+03	5.6E+03	1
95	Russet	3	4	1.90E+05		27	2.5E+03	2.5E+03	5.4E+03	
95	Russet	4	3	5.50E+06	2.97	20.7	2.0E+03	2.4E+03	2.0E+03	2
95	Russet	4	3	6.50E+06		22.3	2.1E+03	2.5E+03	2.2E+03	
95	Russet	4	4	0.00E+00	3.189	17.7	3.3E+03	3.8E+03	2.1E+03	2
95	Russet	4	4	0.00E+00		18.8	2.6E+03	3.2E+03	1.4E+03	
95	Spy	1	3	1.80E+09	0.14	29.3	2.7E+03	2.7E+03	3.5E+03	1
95	Spy	1	3	1.90E+09		26.2	1.9E+03	0.0E+00	4.2E+03	
95	Spy	1	4	4.20E+04	0.146	29.5	3.7E+03	3.7E+03	4.3E+03	1
95	Spy	1	4	3.00E+04		30.3	2.7E+03	2.1E+03	5.1E+03	
95	Spy	2	3	1.90E+09	0.132	32.7	6.3E+03	0.0E+00	3.3E+03	1
95	Spy	2	3	1.70E+09		27.3	2.2E+03	1.8E+03	2.6E+03	
95	Spy	2	4	0.00E+00	0.194	34	1.2E+03	1.2E+03	6.0E+03	1
95	Spy	2	4	0.00E+00		32.8	0.0E+00	2.8E+03	3.4E+03	

Year	Apple	Treat	Time	Yeasts (colonies / g)	Wet Weight (g / 750 mL bottle)	Dry Weight (g / 100 g)	Pectin Fraction 1 (ug/g)	Pectin Fraction 2 (ug/g)	Pectin Fraction 3 (ug/g)	Gushing Tendency
95	Spy	3	3	1.90E+09	0.28	19.6	0.0E+00	1.2E+03	3.7E+03	1
95	Spy	3	3	1.50E+09		21.3	0.0E+00	4.7E+02	3.2E+03	
95	Spy	3	4	3.30E+05	0.304	20.2	0.0E+00	0.0E+00	4.8E+03	1
95	Spy	3	4	4.10E+05		19.3	0.0E+00	0.0E+00	4.8E+03	
95	Spy	4	3	3.40E+08	4.284	18.9	0.0E+00	1.6E+03	2.7E+03	2
95	Spy	4	3	4.30E+08		19.8	1.3E+03	0.0E+00	3.7E+03	
95	Spy	4	4	0.00E+00	4.736	18.7	8.6E+02	8.6E+02	2.5E+03	2
95	Spy	4	4	0.00E+00		16.2	4.9E+02	9.7E+02	2.3E+03	

Appendix 3. (continued)

G. Minerals in sediments (mg/kg).

Year	Apple	Treat	Time	Nitrogen	Sulfur	Phosphorous	Potassium	Magnesium	Calcium	Sodium	Iron	Aluminum	Manganese	Boron	Copper	Zinc
94	Crispin	1	4	8960	3.6	1042.8	801.9	29.7	85.5	49.5	32.3	18.3	4.6	32.8	133.5	12.0
94	Crispin	2	4	11350	46.6	1320.1	1297.8	94.1	623.6	70.4	8.3	17.5	11.1	32.9	58.1	90.9
94	Crispin	3	4	6340	124.2	541.5	752.9	4.4	145.8	67.2	4.4	40.3	0.6	4.5	77.7	21.1
94	Crispin	4	4	8900	28.6	1116.6	1094.7	60.8	150.4	179.8	5.5	39.8	25.5	19.0	122.0	7.8
94	Hyslop	1	4	11850	59.7	1060.9	1412.1	69.6	166.0	68.3	53.7	15.1	2.2	31.2	150.5	52.1
94	Hyslop	2	4	11220	101.8	1078.4	1385.8	85.5	66.0	52.9	42.5	9.5	2.0	26.3	196.3	11.7
94	Hyslop	3	4	7220	500.4	535.0	2291.1	81.1	190.0	85.9	8.4	29.3	0.0	31.6	81.9	28.4
94	Hyslop	4	4	md	392.7	961.3	1906.3	41.5	1066.2	361.7	4.0	18.8	20.0	16.8	19.8	85.5
94	McIntosh	1	4	7220	205.1	662.7	1007.8	47.0	71.3	53.4	64.1	10.3	2.3	24.7	85.1	13.8
94	McIntosh	2	4	4830	68.9	656.7	927.9	32.8	94.4	31.6	45.2	7.6	2.1	20.2	58.5	26.0
94	McIntosh	3	4	5310	113.0	1008.4	1237.2	33.7	246.6	67.8	3.6	28.6	6.8	11.5	109.3	28.9
94	McIntosh	4	4	3440	149.5	74.3	541.3	29.9	277.4	31.7	1.9	6.6	0.3	5.6	2.0	5.2
94	Russet	1	4	11210	0.0	1676.1	1180.2	60.0	124.0	60.0	26.4	15.1	5.4	23.4	107.9	1.6
94	Russet	2	4	16400	124.7	1984.8	1364.5	82.9	438.3	582.7	46.6	20.5	6.1	23.8	201.2	14.6
94	Russet	3	4	md	171.7	1418.8	1702.7	47.7	332.0	322.4	14.4	23.8	11.8	12.7	151.1	66.8
94	Russet	4	4	8660	250.7	724.0	1132.1	55.0	393.2	73.0	7.8	18.2	1.9	3.6	30.4	50.6
94	Spy	1	4	9860	15.5	978.3	655.5	21.5	184.1	48.5	36.7	19.6	2.3	29.5	149.5	72.4
94	Spy	2	4	7670	0.0	938.5	795.9	45.7	168.7	57.1	29.3	41.1	2.2	32.8	149.9	46.2
94	Spy	3	4	6960	96.1	665.7	905.1	37.7	378.4	65.1	6.7	13.6	0.0	7.9	116.5	74.8
94	Spy	4	4	6580	22.1	771.1	647.0	85.9	543.8	48.8	12.5	41.2	7.4	27.0	31.9	4.4
95	Crispin	1	4	16100	58.1	2861.7	1074.2	118.7	585.5	415.7	57.2	102.9	17.7	11.4	116.3	158.9
95	Crispin	2	4	20800	2.2	2224.9	805.7	83.0	139.0	207.5	29.6	525.0	6.9	8.4	98.3	8.0
95	Crispin	3	4	18700	5.7	445.4	156.8	18.2	58.3	72.3	2.2	34.7	0.6	1.9	14.7	6.9
95	Crispin	4	4	10700	137.2	1859.4	1064.7	158.9	415.4	257.7	14.6	128.2	3.6	15.8	64.1	15.2

Year	Apple	Treat	Time	Nitrogen	Sulfur	Phosphorous	Potassium	Magnesium	Calcium	Sodium	Iron	Aluminum	Manganese	Boron	Copper	Zinc
95	McIntosh	1	4	200	118.1	1693.2	1378.8	158.2	141.1	324.1	8.1	21.7	2.0	8.4	250.5	27.6
95	McIntosh	2	4	11900	176.8	1796.8	839.7	83.8	400.5	155.2	27.0	46.0	2.6	5.9	166.5	180.9
95	McIntosh	3	4	6400	297.6	2077.3	2224.8	321.2	260.6	214.1	11.5	26.3	18.9	10.3	235.4	40.1
95	McIntosh	4	4	200	296.1	185.4	480.4	113.6	349.8	197.5	15.0	11.6	2.3	6.4	4.1	4.2
95	Russet	1	4	18900	122.0	3394.6	1788.0	158.4	352.8	182.4	20.4	104.3	3.7	12.3	382.9	72.0
95	Russet	2	4	26200	159.2	3520.2	1897.6	189.6	272.7	411.4	18.6	96.9	6.5	12.9	250.8	18.6
95	Russet	3	4	17100	157.2	3202.9	2408.6	259.5	398.7	144.9	16.7	193.2	11.2	18.5	204.2	7.8
95	Russet	4	4	9600	394.5	1514.6	1741.5	236.8	787.3	187.1	11.3	94.9	5.0	11.7	57.6	41.2
95	Spy	1	4	8200	159.1	2412.0	2145.5	136.7	266.4	155.7	21.6	388.9	3.5	10.9	235.1	93.0
95	Spy	2	4	15100	266.5	2337.9	1662.3	139.6	324.9	479.8	9.8	160.5	31.7	9.6	404.2	6.1
95	Spy	3	4	8600	150.6	2692.9	2356.5	316.3	445.2	160.9	22.8	144.5	28.8	12.7	476.6	103.0
95	Spy	4	4	11500	253.6	1285.6	1452.7	113.7	258.9	111.0	26.5	218.8	3.3	7.5	44.1	26.4

Appendix 4. Analysis of variance (ANOVA) tables, analyzed by sampling time as described in Material and Methods of Part One. ANOVA tables contain the mean squares for the factors as determined using the SAS computer program (* = significant at $\alpha = 0.05$). In cases in which cider analyses were conducted in duplicate the Experimental Error served as the error term for Blocks and for Treatments.
Note: Treat = Treatment

1. Chemical analysis of Juices and Ciders

a. Specific Gravity

Source of Variation	df	Time 1	Time 2	Time 3	Time 4
Block	8	0.000454 *	0.0000153 *	0.0000113 *	0.0000151 *
Treatment	(3)	0.0000085	0.0000014 *	0.0000014	0.0000005
Treat 1 vs. Treat 2	1	0.0000024	0.00000004	0.0000006	0.0000005
Treat 1 vs. Treat 3	1	0.0000074	0.0000016 *	0.0000008	0.00000003
Treat 1 vs. Treat 4	1	0.0000066	0.0000005	0.0000010	0.0000002
Experimental Error	24	0.0000269	0.0000002	0.0000017	0.0000008
Total	35				

b. pH

Source of Variation	df	Time 1	Time 2	Time 3	Time 4
Block	8	0.10842 *	0.16325 *	0.28511 *	0.29312 *
Treatment	(3)	0.52362 *	0.20647 *	0.44246 *	0.22186 *
Treat 1 vs. Treat 2	1	0.01456	0.000625	0.001469	0.00321
Treat 1 vs. Treat 3	1	1.0897 *	0.44667 *	0.87734 *	0.39690 *
Treat 1 vs. Treat 4	1	0.57434 *	0.05601 *	0.48071 *	0.33063 *
Experimental Error	24	0.01569 *	0.00581 *	0.03062 *	0.04893 *
Sampling Error	36	0.001655	0.0000611	0.0000736	0.0000264
Total	71				

c. Molds

Source of Variation	df	Time 1	Time 2	Time 3	Time 4
Block	8	9.540E+10			
Treatment	(3)	2.370E+11			
Treat 1 vs. Treat 2	1	1.505E+04			
Treat 1 vs. Treat 3	1	1.690E+04			
Treat 1 vs. Treat 4	1	4.738E+11 *	No molds were detected after Time 1.		
Experimental Error	24	9.549E+10			
Sampling Error	36	5.276E+05			
Total	71				

d. Yeasts

Source of Variation	df	Time 1	Time 2	Time 3	Time 4
Block	8	5.432E+14	1.700E+14	2.396E+10	2.028E+07
Treatment	(3)	1.173E+15	5.820E+14 *	2.470E+10	1.053E+07
Treat 1 vs. Treat 2	1	3.361E+00	7.111E+08	3.036E+07	1.864E+06
Treat 1 vs. Treat 3	1	4.244E+00	3.062E+11	5.117E+10	8.170E+06
Treat 1 vs. Treat 4	1	2.346E+15 *	1.151E+15 *	4.253E+07	1.185E+07
Experimental Error	24	5.432E+14 *	1.825E+14 *	2.641E+10*	1.131E+07 *
Sampling Error	36	2.848E+12	8.597E+08	1.841E+07	3.081E+03
Total	71				

e. Titratable acidity

Source of Variation	df	Time 1	Time 2	Time 3	Time 4
Block	8	0.24908 *	0.13792 *	0.18235 *	0.19102 *
Treatment	(3)	0.14760 *	0.06065 *	0.12545 *	0.05022
Treat 1 vs. Treat 2	1	0.00046	0.00000003	0.00412	0.00737
Treat 1 vs. Treat 3	1	0.34379 *	0.13310 *	0.22705 *	0.09151 *
Treat 1 vs. Treat 4	1	0.03404 *	0.00456	0.20220 *	0.10780 *
Experimental Error	24	0.00399 *	0.00276 *	0.01505 *	0.02054 *
Sampling Error	36	0.00001	0.00004	0.00036	0.00031
Total	71				

f. Volatile acidity

Source of Variation	df	Time 1	Time 2	Time 3	Time 4
Block	8	0.000184	0.000114	0.000197	0.000353
Treatment	(3)	0.001355 *	0.000012	0.000067	0.000219
Treat 1 vs. Treat 2	1	0.000001	0.000034	0.000019	0.000222
Treat 1 vs. Treat 3	1	0.002987 *	0.000012	0.00000002	0.000650
Treat 1 vs. Treat 4	1	0.000258	0.000004	0.000015	0.000168
Experimental Error	24	0.000295 *	0.0000499	0.000331 *	0.000321 *
Sampling Error	36	0.000005	0.000008	0.000028	0.000025
Total	71				

g. Free sulfur dioxide

Source of Variation	df	Time 1	Time 2	Time 3	Time 4
Block	8	49.339 *	47.515 *	86.679 *	161.769 *
Treatment	(3)	36.236	5.036	1.533	100.551 *
Treat 1 vs. Treat 2	1	0.760	10.433	0.526	0.147
Treat 1 vs. Treat 3	1	28.569	0.050	4.354	214.964 *
Treat 1 vs. Treat 4	1	84.303	0.444	1.460	78.736
Experimental Error	24	16.256*	12.010 *	2.687	19.949 *
Sampling Error	36	1.258	3.379	1.984	4.823
Total	71				

h. Total sulfur dioxide

Source of Variation	df	Time 1	Time 2	Time 3	Time 4
Block	8	236.413 *	267.590 *	150.770 *	280.949 *
Treatment	(3)	200.351 *	188.331	50.139	498.856 *
Treat 1 vs. Treat 2	1	10.726	154.008	5.507	33.466
Treat 1 vs. Treat 3	1	130.302	195.068	65.286	458.53 *
Treat 1 vs. Treat 4	1	165.037	366.663	41.452	1222.202 *
Experimental Error	24	41.402 *	89.711 *	19.973 *	54.312 *
Sampling Error	36	2.855	12.680	5.032	12.398
Total	71				

i. Juice Yield

Source of Variation	df	Time 1
Block	8	352.873 *
Treatment	(3)	588.336
Treat 1 vs. Treat 2	1	0.376
Treat 1 vs. Treat 3	1	1345.076 *
Treat 1 vs. Treat 4	1	134.480 *
Experimental Error	24	25.237
Total	35	

j. Ash

Source of Variation	df	Time 1	Time 2	Time 3	Time 4
Block	8	0.44894 *	0.16731 *	0.15525 *	0.12800 *
Treatment	(3)	0.66472 *	0.00596	0.00933	0.00852
Treat 1 vs. Treat 2	1	0.00598	0.00026	0.000002	0.00001
Treat 1 vs. Treat 3	1	0.63388 *	0.01089	0.01809	0.01120
Treat 1 vs. Treat 4	1	0.37434	0.00037	0.00005	0.00232
Experimental Error	24	0.11210 *	0.00355 *	0.00506 *	0.00310 *
Sampling Error	36	0.01831	0.00080	0.00028	0.00016
Total	71				

k. Ash alkalinity

Source of Variation	df	Time 1	Time 2	Time 3	Time 4
Block	8	951.72 *	806.88 *	268.62	880.79 *
Treatment	(3)	16.46	169.60 *	170.20	1337.76 *
Treat 1 vs. Treat 2	1	0.538	6.98	0.380	120.05
Treat 1 vs. Treat 3	1	11.90	302.76 *	6.33	185.64
Treat 1 vs. Treat 4	1	12.37	94.41	310.35	2187.12 *
Experimental Error	24	67.96 *	29.21 *	194.78 *	270.54 *
Sampling Error	36	5.726	4.843	4.314	8.813
Total	71				

l. Pectin Fraction 1

Source of Variation	df	Time 1	Time 2	Time 3	Time 4
Block	8	7.487E+05	5.958E+05	4.539E+05	3.397E+05
Treatment	(3)	5.447E+06 *	4.167E+06 *	3.698E+06 *	1.627E+06 *
Treat 1 vs. Treat 2	1	2.779E+02	3.433E+02	3.416E+00	1.221E+00
Treat 1 vs. Treat 3	1	3.602E+05	3.710E+05	1.822E+05	4.562E+05
Treat 1 vs. Treat 4	1	1.196E+07 *	9.147E+06 *	8.015E+06 *	3.657E+06 *
Experimental Error	24	4.132E+05 *	3.263E+05 *	3.528E+05 *	2.205E+05 *
Sampling Error	36	3.103E+04	7.742E+03	1.166E+03	1.542E+03
Total	71				

m. Pectin Fraction 2

Source of Variation	df	Time 1	Time 2	Time 3	Time 4
Block	8	9.393E+04	1.819E+03	3.443E+01	1.056E+01
Treatment	(3)	1.376E+05	3.333E+03	1.746E+01	3.929E+01 *
Treat 1 vs. Treat 2	1	1.433E+02	1.696E+02	1.281E+00	1.381E-01
Treat 1 vs. Treat 3	1	6.533E+00	7.856E+01	2.748E+01	6.721E+01 *
Treat 1 vs. Treat 4	1	2.701E+05	7.782E+03	3.538E+01	4.367E+01
Experimental Error	24	9.500E+04 *	1.883E+03 *	2.402E+01 *	1.194E+01 *
Sampling Error	36	1.037E+04	3.111E+02	7.279E+00	4.365E+00
Total	71				

n. Pectin Fraction 3

Source of Variation	df	Time 1	Time 2	Time 3	Time 4
Block	8	7.419E+01	3.622E+01	9.819E+01	9.900E+01
Treatment	(3)	1.147E+02	1.715E+02 *	7.504E+01	1.717E+02
Treat 1 vs. Treat 2	1	1.769E+01	3.942E+00	8.851E+00	1.174E+00
Treat 1 vs. Treat 3	1	5.592E+01	2.360E+00	7.409E+00	1.387E+02
Treat 1 vs. Treat 4	1	3.150E+02 *	3.29E+02 *	1.010E+02	3.788E+02
Experimental Error	24	6.885E+01	5.32E+01 *	7.781E+02*	1.445E+02
Sampling Error	36	6.642E+01	2.212E+01	2.138E+01	6.951E+01
Total	71				

o. Ammonical Nitrogen

Source of Variation	df	Time 2	Time 3	Time 4
Block	8	3.2718	10.4383	No ammonical nitrogen was detectable in any samples at Time 4
Treatment	(3)	12.0622 *	1.1790	
Treat 1 vs. Treat 2	1	0.0000	1.8496	
Treat 1 vs. Treat 3	1	24.1245 *	0.8220	
Treat 1 vs. Treat 4	1	0.0000	0.0803	
Experimental Error	24	3.2718 *	4.9963 *	
Sampling Error	36	0.5508	0.4897	
Total	71			

p. Dry weight

Source of Variation	df	Time 1	Time 2	Time 3	Time 4
Block	3	55.1653 *	1.5243 *	1.2649 *	1.4080 *
Treatment	(3)	1.0078	0.0360	0.9270 *	0.5427 *
Treat 1 vs. Treat 2	1	0.0000	0.0048	0.0306	0.0696
Treat 1 vs. Treat 3	1	1.5625	0.0729 *	0.9312 *	0.6018
Treat 1 vs. Treat 4	1	0.1406	0.0716 *	0.4330	0.1469
Experimental Error	9	1.2414 *	0.0132 *	0.0928	0.1248 *
Sampling Error	16	0.01719	0.00280	0.00086	0.00269
Total	35				

q. Total phenolics

Source of Variation	df	Time 3	Time 4
Block	3	89.4726 *	102.0282 *
Treatment	(3)	137.989 *	124.7829 *
Treat 1 vs. Treat 2	1	4.3160	4.1923
Treat 1 vs. Treat 3	1	0.0196	0.0600
Treat 1 vs. Treat 4	1	250.9848 *	226.8789 *
Experimental Error	24	9.3390 *	4.6206 *
Sampling Error	36	0.0896	0.2696
Total	71		

2. Sugar, glycerol and alcohol determinations of juices and ciders

a. Fructose

Source of Variation	df	Time 1	Time 2	Time 3	Time 4
Block	8	6.7916 *	0.0105	0.1440 *	0.0410
Treatment	(3)	6.3427 *	0.0279 *	0.0555	0.0371
Treat 1 vs. Treat 2	1	0.3330	0.0060	0.0072	0.0000004
Treat 1 vs. Treat 3	1	9.6140 *	0.0511 *	0.0604	0.0856
Treat 1 vs. Treat 4	1	0.0442	0.0007	0.0174	0.0017
Experimental Error	22	0.8838	0.00524	0.0267	0.0214
Total	33				

b. Glucose

Source of Variation	df	Time 1	Time 2	Time 3	Time 4
Block	8	1.2066 *	no glucose was detected in any samples at Time 2	0.00292	0.00262
Treatment	(3)	1.6108 *		0.00435	0.00656
Treat 1 vs. Treat 2	1	0.1530		0.00001	0.00001
Treat 1 vs. Treat 3	1	2.3582 *		0.00752	0.01372 *
Treat 1 vs. Treat 4	1	0.5570		0.00562	0.00001
Experimental Error	22	0.2741		0.00513	0.00265
Total	33				

c. Sucrose

Source of Variation	df	Time 1	Time 2	Time 3	Time 4
Block	8	8.9775 *	no sucrose was detected in any samples at Time 2	no sucrose was detected in any samples at Time 3	no sucrose was detected in any samples at Time 4
Treatment	(3)	1.6964 *			
Treat 1 vs. Treat 2	1	0.1261			
Treat 1 vs. Treat 3	1	3.4019 *			
Treat 1 vs. Treat 4	1	2.0496 *			
Experimental Error	22	0.2364			
Total	33				

d. Glycerol

Source of Variation	df	Time 1	Time 2	Time 3	Time 4
Block	8	no glycerol was detected in any samples at Time 1	0.0192 *	0.0170	0.0212 *
Treatment	(3)		0.0126 *	0.0055	0.0255 *
Treat 1 vs. Treat 2	1		0.0005	0.0010	0.0003
Treat 1 vs. Treat 3	1		0.0002	0.0017	0.0229
Treat 1 vs. Treat 4	1		0.0231 *	0.0077	0.0185
Experimental Error	22		0.00390	0.00912	0.00590
Total	33				

e. Ethanol

Source of Variation	df	Time 1	Time 2	Time 3	Time 4
Block	8	0.02996	4.5323 *	4.7419 *	4.4565 *
Treatment	(3)	0.11616 *	1.2101	0.5402	0.4061
Treat 1 vs. Treat 2	1	0.00399	0.8944	0.0102	0.0002
Treat 1 vs. Treat 3	1	0.01623	1.7558	1.1142 *	0.7901
Treat 1 vs. Treat 4	1	0.27832 *	0.1080	0.0261	0.0013
Experimental Error	19	0.02986	0.6114	0.1981	0.2244
Total	30				

f. Methanol

Source of Variation	df	Time 1	Time 2	Time 3	Time 4
Block	8	0.000011	0.000025	0.000035	0.000028
Treatment	(3)	0.000029	0.000084 *	0.000147 *	0.000271 *
Treat 1 vs. Treat 2	1	0.0000001	0.000000	0.000000	0.000001
Treat 1 vs. Treat 3	1	0.0000001	0.000000	0.0000005	0.000000
Treat 1 vs. Treat 4	1	0.000057	0.000168 *	0.000289 *	0.000534 *
Experimental Error	19	0.000013	0.000025	0.000035	0.000027
Total	30				

3. Cider minerals

a. Nitrogen

Source of Variation	df	Time 2	Time 3	Time 4
Block	8	1.055E+07	5.249E+05 *	1.194E+06 *
Treatment	(3)	6.622E+06	1.735E+05	2.290E+05
Treat 1 vs. Treat 2	1	1.512E+07	4.532E+05	6.242E+04
Treat 1 vs. Treat 3	1	1.463E+07	1.280E+04	1.158E+05
Treat 1 vs. Treat 4	1	5.861E+06	5.667E+04	1.964E+05
Experimental Error	24	7.509E+06	2.044E+05	9.658E+04
Total	35			

b. Sulfur

Source of Variation	df	Time 2	Time 3	Time 4
Block	8	393.25 *	445.43 *	353.04 *
Treatment	(3)	274.93	1416.37 *	1390.02 *
Treat 1 vs. Treat 2	1	738.56 *	2992.80 *	1553.10 *
Treat 1 vs. Treat 3	1	63.47	0.320	583.68 *
Treat 1 vs. Treat 4	1	293.63	904.54 *	0.605
Experimental Error	24	104.88	120.34	78.893
Total	35			

c. Phosphorous

Source of Variation	df	Time 2	Time 3	Time 4
Block	8	4084.29*	6274.06 *	15723.04 *
Treatment	(3)	641.08 *	3837.60 *	569.28
Treat 1 vs. Treat 2	1	18.61	6395.81 *	3.38
Treat 1 vs. Treat 3	1	1415.12 *	1041.20	930.24
Treat 1 vs. Treat 4	1	2.72	9094.51 *	66.51
Experimental Error	24	177.40	1010.75	301.15
Total	35			

d. Potassium

Source of Variation	df	Time 2	Time 3	Time 4
Block	8	6.946E+05 *	7.193E+05 *	1.154E+06 *
Treatment	(3)	9.036E+04 *	3.333E+05 *	6.153E+04
Treat 1 vs. Treat 2	1	1.060E+04	6.842E+05 *	1.531E+03
Treat 1 vs. Treat 3	1	2.429E+05 *	5.511E+04	6.138E+04
Treat 1 vs. Treat 4	1	3.114E+04	6.094E+05 *	1.346E+05
Experimental Error	24	1.398E+04	8.432E+04	4.249E+04
Total	35			

e. Magnesium

Source of Variation	df	Time 2	Time 3	Time 4
Block	8	352.80 *	597.68 *	1016.71 *
Treatment	(3)	613.69 *	1758.70 *	494.62 *
Treat 1 vs. Treat 2	1	0.201	352.89	1.33
Treat 1 vs. Treat 3	1	205.37	72.00	16.82
Treat 1 vs. Treat 4	1	1393.92 *	4405.48 *	820.84 *
Experimental Error	24	49.883	111.04	124.150
Total	35			

f. Calcium

Source of Variation	df	Time 2	Time 3	Time 4
Block	8	576.96 *	835.50 *	757.41 *
Treatment	(3)	2469.77 *	4269.62 *	1494.11 *
Treat 1 vs. Treat 2	1	16.44	209.44	33.35
Treat 1 vs. Treat 3	1	553.34 *	48.02	452.00
Treat 1 vs. Treat 4	1	5246.29 *	9758.05 *	1963.56 *
Experimental Error	24	117.54	90.801	191.99
Total	35			

g. Sodium

Source of Variation	df	Time 2	Time 3	Time 4
Block	8	436.53	814.31	1867.64
Treatment	(3)	2359.96 *	4220.25 *	4488.22 *
Treat 1 vs. Treat 2	1	261.44	432.18	6231.00 *
Treat 1 vs. Treat 3	1	2475.73 *	1744.44	1121.80
Treat 1 vs. Treat 4	1	2584.81 *	11270.01 *	31.73
Experimental Error	24	378.92	630.45	824.54
Total	35			

h. Iron

Source of Variation	df	Time 2	Time 3	Time 4
Block	8	3.1063	1.9806	0.3286
Treatment	(3)	1.8699	4.9996 *	1.8837
Treat 1 vs. Treat 2	1	0.3756	2.0000	0.8450
Treat 1 vs. Treat 3	1	2.2756	0.2689	5.5556
Treat 1 vs. Treat 4	1	4.8050	12.8356 *	1.3339
Experimental Error	24	1.6270	1.6453	2.5004
Total	35			

i. Aluminum

Source of Variation	df	Time 2	Time 3	Time 4
Block	8	39.914	42.530	876.36 *
Treatment	(3)	138.993 *	444.390 *	702.46 *
Treat 1 vs. Treat 2	1	7.867	12.334	2.722
Treat 1 vs. Treat 3	1	33.894	16.436	931.68 *
Treat 1 vs. Treat 4	1	355.556 *	861.125 *	179.24
Experimental Error	24	23.919	66.451	193.397
Total	35			

j. Manganese

Source of Variation	df	Time 2	Time 3	Time 4
Block	8	0.18778 *	0.37736 *	0.05028
Treatment	(3)	0.27583 *	0.16333 *	0.10222
Treat 1 vs. Treat 2	1	0.00000	0.00500	0.00222
Treat 1 vs. Treat 3	1	0.14222 *	0.03556	0.22222 *
Treat 1 vs. Treat 4	1	0.60500 *	0.40500 *	0.10889
Experimental Error	24	0.03083	0.01375	0.03806
Total	35			

k. Boron

Source of Variation	df	Time 2	Time 3	Time 4
Block	8	1.54382 *	2.91403	2.44403
Treatment	(3)	0.12741	2.58185	4.32769
Treat 1 vs. Treat 2	1	0.00222	5.33556	0.09389
Treat 1 vs. Treat 3	1	0.10889	0.03556	0.09389
Treat 1 vs. Treat 4	1	0.22222	0.43556	8.40500
Experimental Error	24	0.06595	1.90477	2.26644
Total	35			

l. Copper

Source of Variation	df	Time 2	Time 3	Time 4
Block	8	0.049861 *	0.013611	0.045000
Treatment	(3)	0.055185 *	0.016574	0.113611
Treat 1 vs. Treat 2	1	0.005000	0.002222	0.000000
Treat 1 vs. Treat 3	1	0.067222 *	0.020000	0.180000
Treat 1 vs. Treat 4	1	0.055556*	0.013889	0.013889
Experimental Error	24	0.008935	0.007407	0.047778
Total	35			

m. Zinc

Source of Variation	df	Time 2	Time 3	Time 4
Block	8	0.050000	0.050000	0.153611
Treatment	(3)	0.046204	0.022593	0.101019
Treat 1 vs. Treat 2	1	0.0138889	0.005000	0.035556
Treat 1 vs. Treat 3	1	0.0800000	0.0005556	0.672222
Treat 1 vs. Treat 4	1	0.108889	0.055556	0.055556
Experimental Error	24	0.032037	0.024259	0.121852
Total	35			

4. Sediment analysis

a. Sediment per 750 mL bottle (wet weight)

Source of Variation	df	Time 3	Time 4
Block	8	0.40571	604.440
Treatment	(3)	2.77801 *	923.548 *
Treat 1 vs. Treat 2	1	0.00030	0.0010
Treat 1 vs. Treat 3	1	0.15516	0.2576
Treat 1 vs. Treat 4	1	5.06260 *	1862.377 *
Experimental Error	58	0.67072	607.824
Total	69		

b. Dry Weight

Source of Variation	df	Time 3	Time 4
Block	8	132.09 *	264.49 *
Treatment	(3)	61.50	654.53 *
Treat 1 vs. Treat 2	1	76.27	54.27
Treat 1 vs. Treat 3	1	15.34	504.75 *
Treat 1 vs. Treat 4	1	24.48	1674.17 *
Experimental Error	58	42.88	36.62
Total	69		

c. Yeasts

Source of Variation	df	Time 3	Time 4
Block	8	2.803E+18	1.653E+17 *
Treatment	(3)	3.521E+18	7.650E+16 *
Treat 1 vs. Treat 2	1	3.667E+18	7.287E+16 *
Treat 1 vs. Treat 3	1	2.231E+15	4.363E+16
Treat 1 vs. Treat 4	1	6.920E+18 *	2.258E+17 *
Experimental Error	58	1.383E+18	1.570E+16
Total	69		

d. Pectin Fraction 1

Source of Variation	df	Time 3	Time 4
Block	8	7.891E+06 *	6.069E+06
Treatment	(3)	1.843E+07 *	3.420E+07 *
Treat 1 vs. Treat 2	1	9.775E+05	2.688E+05
Treat 1 vs. Treat 3	1	6.452E+04	5.753E+05
Treat 1 vs. Treat 4	1	4.259E+07 *	6.863E+07 *
Experimental Error	58	3.020E+06	3.296E+06
Total	69		

e. Pectin Fraction 2

Source of Variation	df	Time 3	Time 4
Block	8	2.924E+06 *	1.970E+06
Treatment	(3)	9.977E+06 *	5.324E+06 *
Treat 1 vs. Treat 2	1	1.110E+05	1.099E+04
Treat 1 vs. Treat 3	1	1.790E+06	5.103E+05
Treat 1 vs. Treat 4	1	2.438E+07 *	1.207E+07 *
Experimental Error	58	1.144E+06	1.362E+06
Total	69		

f. Pectin Fraction 3

Source of Variation	df	Time 3	Time 4
Block	8	5.991E+06 *	6.422E+06 *
Treatment	(3)	4.718E+06 *	1.291E+07 *
Treat 1 vs. Treat 2	1	2.880E+05	2.122E+06
Treat 1 vs. Treat 3	1	4.809E+05	1.976E+07 *
Treat 1 vs. Treat 4	1	1.201E+07 *	2.295E+06
Experimental Error	58	7.729E+05	1.304E+06
Total	69		

5. Sediment minerals at sampling Time 4 (5 months in the bottle).

Source of Variation	df	Nitrogen	Sulfur	Phosphorous	Potassium	Magnesium
Block	8	8.329E+07 *	2.916E+04 *	2.202E+06 *	9.099E+05 *	17528.3 *
Treatment	(3)	6.350E+07 *	3.436E+04 *	1.343E+06 *	3.226E+05	2283.0
Treat 1 vs. Treat 2	1	6.039E+07 *	2.346E+03	3.209E+02	1.211E+04	76.88
Treat 1 vs. Treat 3	1	1.042E+06	4.256E+04 *	5.669E+05	3.732E+05	5688.9
Treat 1 vs. Treat 4	1	3.700E+07	7.785E+04 *	2.952E+06 *	1.063E+05	515.2
Experimental Error	22	9.176E+06	7.848E+03	2.901E+05	1.409E+05	3289.0
Total	33					

Source of Variation	df	Calcium	Sodium	Iron	Aluminum	Manganese
Block	8	2.381E+04	2.899E+05	124.21	28744.03 *	71.360
Treatment	(3)	1.093E+05	1.529E+04	1467.27 *	3394.82	25.785
Treat 1 vs. Treat 2	1	1.689E+04	2.653E+04	224.72	2898.14	42.014
Treat 1 vs. Treat 3	1	1.274E+04	1.369E+03	2933.78 *	1456.20	68.056
Treat 1 vs. Treat 4	1	2.852E+05 *	4.570E+02	2723.22 *	774.87	36.409
Experimental Error	22	4.557E+04	1.753E+04	182.33	7661.77	74.048
Total	33					

Source of Variation	df	Boron	Copper	Zinc
Block	8	184.40 *	22010.3 *	762.86
Treatment	(3)	164.95 *	38989.9 *	1304.30
Treat 1 vs. Treat 2	1	7.74	42.01	560.01
Treat 1 vs. Treat 3	1	296.06 *	1150.40	876.41
Treat 1 vs. Treat 4	1	281.64 *	84775.9 *	3839.80
Experimental Error	22	51.35	6073.36	2301.33
Total	33			

Appendix 5.

a. Block means, adjusted for missing data and for outliers removed. Means are of 4 observations. Total phenolics were only measured in 1995. Dry weights of juices and ciders were not determined in 1994.

(i) Sampling Time 1: Juice analysis.

Response Variable	1994					1995			
	Crispin	Hyslop	McIntosh	Russet	Spy	Crispin	McIntosh	Russet	Spy
Juice yield (L / 100 kg)	38.6	14.7	29.8	27.1	38.7	42.3	29.2	24.5	42.9
Molds (10^3 colonies / mL)	2.4	1.5	10.6	0.4	0.7	0.6	250	1.2	250
Yeasts (10^3 colonies / mL)	155	115	75.0	2.0	22.1	83.7	13125	1.4	22750
Specific gravity	1.056	1.065	1.044	1.074	1.051	1.047	1.046	1.066	1.053
pH	3.32	3.55	3.42	3.51	3.18	3.55	3.45	3.57	3.33
Titratable acidity (g malic acid / 100 mL)	0.53	0.97	0.60	0.64	0.45	0.46	0.39	0.61	0.75
Volatile acidity (g acetic acid / 100 mL)	0.012	0.018	0.010	0.016	0.020	0.008	0.011	0.006	0.010
Free sulfur dioxide (mg / L)	3.82	8.79	5.46	5.64	4.67	5.43	6.48	5.58	7.31
Total sulfur dioxide (mg / L)	13.02	26.42	11.53	17.88	17.23	13.07	15.14	16.50	18.78
Ash (g / 100 g juice)	0.369	0.952	0.514	0.508	0.208	0.307	0.213	0.428	0.640
Alkalinity of ash (milliequivalents)	24.48	51.51	25.33	40.58	15.63	28.79	20.23	32.81	26.06
Dry weight (g / 100 g wet sample)						11.9	11.7	17.4	13.4
Pectin Fraction 1 (µg / g juice)	88.9	652	599	723	237	45.6	542	853	126
Pectin Fraction 2 (µg / g juice)	9.5	333	5.9	54.6	8.6	1.3	4.9	8.5	3.5
Pectin Fraction 3 (µg / g juice)	11.6	13.5	11.3	12.6	8.9	4.7	5.7	8.6	7.8
Fructose (g / 100 mL)	5.48	2.80	5.07	6.56	5.88	4.74	5.84	7.43	5.13
Glucose (g / 100 mL)	1.62	2.01	1.17	2.52	1.96	2.07	1.58	3.04	1.63
Sucrose (g / 100 mL)	3.83	7.85	2.37	3.27	2.53	2.19	1.81	3.64	3.30
Glycerol (g / 100 mL)	nd[a]	nd	nd	nd	nd	nd	nd	nd	nd
Ethanol (g / 100 mL)	0.08	0.01	0.01	0.05	0.08	0.07	0.21	0.05	0.27
Methanol (g / 100 mL)	0.003	0.005	nd	0.001	nd	nd	nd	nd	nd

[a] not detectable: less than 0.001 g / 100 mL for glycerol or 0.0001 g / 100 mL for methanol

(ii) Sampling Time 2: analysis of still ciders

Response Variable	1994					1995			
	Crispin	Hyslop	McIntosh	Russet	Spy	Crispin	McIntosh	Russet	Spy
Molds (colonies / mL)	nd[a]	nd	nd	nd	nd	nd	nd	nd	nd
Yeasts (10^5 colonies / mL)	7.5	7.6	11.4	17.3	6.4	2.5	23.7	115	114
Specific gravity	0.996	1.002	0.999	0.997	0.996	0.997	0.996	0.996	0.998
pH	3.55	3.69	3.49	3.80	3.38	3.63	3.56	3.80	3.52
Titratable acidity (g malic acid / 100 mL)	0.46	0.80	0.54	0.55	0.42	0.40	0.38	0.48	0.62
Volatile acidity (g acetic acid / 100 mL)	0.019	0.017	0.019	0.023	0.026	0.014	0.015	0.022	0.021
Free sulfur dioxide (mg / L)	8.03	14.77	6.39	11.83	9.13	8.16	9.39	8.78	9.78
Total sulfur dioxide (mg / L)	14.26	30.96	12.18	18.06	15.78	13.86	17.02	18.97	12.71
Ammonical nitrogen (mg / L)	nd	nd	nd	nd	nd	1.4	1.5	0.8	nd
Ash (g / 100 g cider)	0.256	0.624	0.257	0.404	0.176	0.211	0.149	0.332	0.263
Alkalinity of ash (milliequivalents)	21.99	42.35	21.79	36.91	12.61	21.23	15.16	33.55	29.18
Dry weight (g / 100 g wet sample)						1.45	1.54	2.42	2.04
Pectin Fraction 1 (µg / g cider)	186.8	370.3	545.7	899.4	284.2	76.46	538.0	732.3	206.0
Pectin Fraction 2 (µg / g cider)	1.8	1.6	2.8	2.8	4.1	1.2	7.8	5.4	6.0
Pectin Fraction 3 (µg / g cider)	3.7	4.2	3.7	3.5	6.3	3.0	2.7	7.3	8.7
Fructose (g / 100 mL)	0.08	nd	0.12	0.15	0.13	0.06	0.08	0.01	0.06
Glucose (g / 100 mL)	nd	nd	nd	nd	nd	nd	nd	nd	nd
Sucrose (g / 100 mL)	nd	nd	nd	nd	nd	nd	nd	nd	nd
Glycerol (g / 100 mL)	0.39	0.34	0.34	0.49	0.38	0.32	0.30	0.46	0.44
Ethanol (g / 100 mL)	5.57	6.04	4.47	7.89	5.57	4.57	5.71	6.85	5.44
Methanol (g / 100 mL)	0.003	0.007	0.001	nd	nd	nd	nd	0.003	nd

[a] Not Detectable: < 5 colonies / mL for molds; < 0.1 mg / L for ammonical nitrogen; < 0.001 g / 100 mL for sugars; < 0.0001 g / 100 mL for methanol

(iii) **Sampling Time 2: Analysis of minerals in still ciders. Means are expressed as mg/L.**

Response Variable	1994					1995			
	Crispin	Hyslop	McIntosh	Russet	Spy	Crispin	McIntosh	Russet	Spy
Nitrogen	604.3	1348.5	403.8	404.3	428.8	675.0	850.0	700.0	600.0
Sulfur	23.1	48.0	26.6	40.2	22.8	22.9	17.8	32.8	22.2
Phosphorous	87.4	175.2	117.6	148.9	88.9	75.0	101.8	125.3	124.1
Potassium	833.7	1887.4	988.3	1443.2	593.5	808.9	650.6	1279.8	1134.5
Magnesium	26.4	50.4	31.0	40.5	24.4	26.0	22.4	38.3	25.7
Calcium	32.1	52.3	40.9	55.0	48.5	23.3	27.8	45.3	26.0
Sodium	19.7	40.1	39.8	40.9	37.8	18.1	17.6	34.5	21.5
Iron	2.4	3.2	2.6	2.2	2.7	1.0	0.8	1.4	1.1
Aluminum	11.8	8.6	11.1	9.2	8.7	11.0	7.3	18.1	11.6
Manganese	0.5	0.6	0.7	0.6	0.5	0.2	0.1	0.2	0.2
Boron	2.9	3.0	2.1	1.9	2.0	2.1	1.1	1.4	1.7
Copper	0.3	0.4	0.5	0.4	0.4	0.2	0.2	0.2	0.2
Zinc	0.4	0.5	0.3	0.3	0.3	0.3	0.4	0.6	0.5

(iv) Sampling Time 3: analysis of ciders 2 months in the bottle.

Response Variable	1994					1995			
	Crispin	Hyslop	McIntosh	Russet	Spy	Crispin	McIntosh	Russet	Spy
Yeasts (10^3 colonies / mL)	1.6	10.9	5.4	0.45	171	18.6	9.1	7.3	11.4
Specific gravity	0.996	1.001	0.998	0.998	0.997	0.996	0.996	0.995	0.997
pH	3.67	3.72	3.67	3.92	3.44	3.73	3.66	4.11	3.65
Titratable acidity (g malic acid / 100 mL)	0.39	0.78	0.42	0.45	0.39	0.34	0.34	0.26	0.54
Volatile acidity (g acetic acid / 100 mL)	0.021	0.027	0.034	0.029	0.020	0.028	0.019	0.028	0.023
Free sulfur dioxide (mg / L)	6.68	16.32	5.22	8.26	6.30	6.72	6.59	6.91	8.51
Total sulfur dioxide (mg / L)	11.02	24.70	14.32	18.26	16.48	12.84	13.45	16.92	21.28
Ammonical nitrogen (mg / L)	nd [a]	3.14	nd	nd	nd	nd	nd	1.84	nd
Ash (g / 100 g cider)	0.259	0.569	0.273	0.479	0.230	0.190	0.144	0.254	0.225
Alkalinity of ash (milliequivalents)	22.23	32.74	19.93	28.75	16.73	22.81	14.86	27.69	25.19
Dry weight (g / 100 g wet sample)						1.22	1.40	1.90	2.05
Pectin Fraction 1 (µg / g cider)	131.9	190.4	537.5	764.8	267.0	74.78	432.0	548.2	136.7
Pectin Fraction 2 (µg / g cider)	1.4	3.5	3.2	2.4	0.1	1.6	7.6	2.9	3.2
Pectin Fraction 3 (µg / g cider)	1.4	3.4	2.6	1.1	1.3	0.6	11.2	6.2	0.6
Total phenolics (absorbance units)						3.8	9.5	9.5	11.6
Fructose (g / 100 mL)	0.29	0.03	0.20	0.64	0.46	0.003	0.18	0.12	0.34
Glucose (g / 100 mL)	0.06	0.007	0.004	0.007	nd	nd	0.05	nd	0.06
Sucrose (g / 100 mL)	nd	nd	nd	nd	nd	nd	nd	nd	nd
Glycerol (g / 100 mL)	0.41	0.39	0.28	0.50	0.37	0.39	0.39	0.45	0.45
Ethanol (g / 100 mL)	6.21	6.77	4.97	8.01	5.69	5.49	4.99	7.66	5.98
Methanol (g / 100 mL)	0.004	0.008	0.001	nd	nd	nd	nd	0.005	nd

[a] Not Detectable: < 0.1 mg / L for ammonical nitrogen; < 0.001 g / 100 mL for sugars; < 0.0001 g / 100 mL for methanol

(v) Sampling Time 3: Analysis of minerals (mg/L) in ciders 2 months in bottle.

Response Variable	1994					1995			
	Crispin	Hyslop	McIntosh	Russet	Spy	Crispin	McIntosh	Russet	Spy
Nitrogen	1222.5	1525.0	1037.5	1202.5	1295.0	652.5	412.5	659.0	880.0
Sulfur	25.0	56.5	26.0	44.0	27.5	29.1	28.7	36.2	27.3
Phosphorous	85.9	185.3	120.7	151.7	90.2	103.6	147.6	183.2	176.7
Potassium	967.0	2009.4	1095.2	1582.2	693.6	1026.1	830.9	1553.9	1394.1
Magnesium	31.2	64.2	35.2	43.9	27.5	40.2	36.0	58.5	38.6
Calcium	38.5	73.4	53.4	66.8	53.2	32.1	40.7	55.7	34.4
Sodium	46.2	77.3	71.2	71.8	52.3	49.5	46.7	82.5	70.6
Iron	1.9	1.7	2.7	2.2	2.8	1.8	0.9	1.5	0.8
Aluminum	6.2	16.3	13.6	12.5	8.3	14.9	10.5	14.0	10.5
Manganese	0.8	1.0	0.9	0.9	0.8	0.3	0.3	0.3	0.3
Boron	2.8	3.1	2.1	1.7	2.0	3.9	1.2	1.5	1.9
Copper	0.4	0.5	0.4	0.5	0.4	0.3	0.3	0.4	0.4
Zinc	0.3	0.5	0.6	0.4	0.3	0.4	0.4	0.7	0.5

(vi) Sampling Time 4: analysis of ciders 5 months in the bottle.

Response Variable	1994					1995			
	Crispin	Hyslop	McIntosh	Russet	Spy	Crispin	McIntosh	Russet	Spy
Yeasts (colonies / mL)	7	4680	191	13	27	45	1992	105	72
Specific gravity	0.996	1.001	0.998	0.998	0.997	0.996	0.996	0.995	0.997
pH	3.91	3.78	3.68	4.09	3.49	3.91	3.71	4.07	3.78
Titratable acidity (g malic acid / 100 mL)	0.24	0.75	0.42	0.33	0.38	0.25	0.34	0.28	0.42
Volatile acidity (g acetic acid / 100 mL)	0.029	0.023	0.023	0.032	0.024	0.036	0.024	0.042	0.029
Free sulfur dioxide (mg / L)	12.4	19.06	7.38	14.84	13.86	5.91	8.09	7.19	7.75
Total sulfur dioxide (mg / L)	21.20	23.12	11.90	27.64	28.08	14.42	15.02	16.24	16.16
Ammonical nitrogen (mg / L)	nd[a]	nd	nd	nd	nd	nd	nd	nd	nd
Ash (g / 100 g cider)	0.210	0.526	0.224	0.400	0.156	0.166	0.146	0.254	0.225
Alkalinity of ash (milliequivalents)	37.24	9.01	32.00	24.13	46.80	28.93	24.60	31.50	36.19
Dry weight (g / 100 g wet sample)						1.22	1.40	1.90	2.05
Pectin Fraction 1 (µg / g cider)	151.9	252.8	358.7	709.1	300.5	26.0	98.9	388.1	124.5
Pectin Fraction 2 (µg / g cider)	0.8	nd	1.2	nd	1.4	2.5	0.8	3.6	1.8
Pectin Fraction 3 (µg / g cider)	2.4	nd	3.0	0.5	2.2	1.5	0.6	4.1	11.6
Total phenolics (absorbance units)						3.9	9.2	9.1	12.9
Fructose (g / 100 mL)	0.05	0.17	0.11	0.34	0.13	0.04	0.003	0.05	0.17
Glucose (g / 100 mL)	nd	nd	nd	nd	0.04	nd	nd	nd	0.07
Sucrose (g / 100 mL)	nd	nd	nd	nd	nd	nd	nd	nd	nd
Glycerol (g / 100 mL)	0.42	0.36	0.31	0.52	0.38	0.39	0.42	0.51	0.51
Ethanol (g / 100 mL)	6.28	6.43	4.94	8.02	5.97	5.40	5.26	7.71	5.91
Methanol (g / 100 mL)	0.003	0.007	0.003	0.006	nd	nd	0.002	0.004	nd

[a] Not Detectable: < 0.1 mg / L for ammonical nitrogen; < 0.05 µg / g for pectin; < 0.001 g / 100 mL for sugars; < 0.0001 g / 100 mL for methanol

(vii) Sampling Time 4: Analysis of minerals (mg/L) in ciders 5 months in the bottle.

Response Variable	1994					1995			
	Crispin	Hyslop	McIntosh	Russet	Spy	Crispin	McIntosh	Russet	Spy
Nitrogen	1425.0	1852.5	1353.8	1528.8	1418.5	615.0	510.0	550.0	402.5
Sulfur	20.6	39.8	23.3	39.4	24.9	32.3	29.6	46.2	44.1
Phosphorous	85.3	171.0	119.7	152.3	91.4	122.0	195.4	256.1	246.1
Potassium	893.9	1859.6	979.9	1489.8	623.4	1226.5	1074.3	2068.7	2092.2
Magnesium	27.6	52.9	29.4	41.8	25.5	47.4	41.6	75.0	56.3
Calcium	25.9	50.4	35.1	60.9	54.3	36.1	36.3	68.0	48.4
Sodium	12.4	36.4	36.0	53.9	46.5	70.9	47.5	65.2	85.2
Iron	1.5	2.4	1.7	2.0	1.9	2.0	2.3	1.7	2.1
Aluminum	7.1	8.8	9.0	10.4	6.2	51.9	8.4	13.0	25.3
Manganese	0.4	0.6	0.6	0.6	0.6	0.4	0.3	0.5	0.4
Boron	2.9	3.0	2.1	1.9	2.1	2.8	3.3	4.5	2.6
Copper	0.3	0.3	0.3	0.4	0.3	0.5	0.4	0.6	0.3
Zinc	0.3	0.6	0.3	0.4	0.8	0.3	0.3	0.7	0.4

(viii) Sampling Time 3: analysis of the sediments from ciders 2 months in the bottle.

Response Variable	1994					1995			
	Crispin	Hyslop	McIntosh	Russet	Spy	Crispin	McIntosh	Russet	Spy
Yeasts (10^8 colonies / g)	12.8	13.1	4.4	12.9	13.2	20.9	20.6	2.9	14.3
Dry weight (g / 100 g wet sample)	22.5	30.8	16.5	28.2	26.1	24.4	21.6	26.1	24.4
Pectin Fraction 1 (µg / g wet sediment)	369.4	3542	1409	1385	595.3	308.1	1793	1002	1800
Pectin Fraction 2 (µg / g wet sediment)	185.5	563.0	1573	779.0	971.5	325.9	2294	1214	971.6
Pectin Fraction 3 (µg / g wet sediment)	1093	1134	1598	1630	1850	1615	3500	2675	3363

(ix) Sampling Time 4: analysis of the sediments from ciders 5 months in the bottle.

Response Variable	1994					1995			
	Crispin	Hyslop	McIntosh	Russet	Spy	Crispin	McIntosh	Russet	Spy
Yeasts (10^6 colonies / g)	1.4	283	142	25.1	7.1	0.58	379	4.8	0.10
Dry weight (g / 100 g wet sample)	29.1	30.0	14.3	28.0	24.7	27.8	15.2	23.8	25.1
Pectin Fraction 1 (μg / g wet sediment)	354.3	2157	2377	501.8	141.4	981.6	2363	1504	1119
Pectin Fraction 2 (μg / g wet sediment)	368.9	938.3	345.4	1126	481.9	1498	854.1	1625	1454
Pectin Fraction 3 (μg / g wet sediment)	1814	3100	1311	2900	1728	3375	2405	2588	4150

(x) Sampling Time 4: Analysis of minerals in the sediments of ciders 5 months in the bottle. Means are expressed as mg / kg.

Response Variable	1994					1995			
	Crispin	Hyslop	McIntosh	Russet	Spy	Crispin	McIntosh	Russet	Spy
Nitrogen	8887.5	9086.9	5200.0	11908	7767.5	16575	4675.0	17950	10850
Sulfur	50.8	263.7	134.1	136.8	33.4	50.8	222.2	208.2	207.5
Phosphorous	1005.3	908.9	600.5	1450.9	838.4	1847.9	1438.2	2908.1	2182.1
Potassium	986.8	1748.8	928.6	1344.9	750.9	775.4	1230.9	1958.9	1904.3
Magnesium	47.3	69.4	35.9	61.4	47.7	94.7	169.2	211.1	176.6
Calcium	251.3	372.1	172.4	321.9	318.8	299.6	288.0	452.9	323.9
Sodium	91.7	142.2	46.1	259.5	54.9	238.3	222.7	231.5	226.9
Iron	12.6	27.2	28.7	23.8	21.3	25.9	15.4	16.8	20.2
Aluminum	29.0	18.2	13.3	19.4	28.9	197.7	26.4	122.3	228.2
Manganese	10.5	6.1	2.9	6.3	3.0	7.2	6.5	6.6	16.8
Boron	22.3	26.5	15.5	15.9	24.3	9.4	7.8	13.9	10.2
Copper	97.8	112.1	63.7	122.7	112.0	73.4	164.1	223.9	290.0
Zinc	33.0	44.4	18.5	33.4	49.5	47.3	63.2	34.9	57.1

Appendix 5. (continued)

b. Summary of non-significant treatment effects. Means are adjusted for missing data and for outliers removed. Means are of 9 observations. Total phenolics and dry weights were not determined in 1994; means are of 4 observations. For some responses, two determinations were made on each experimental unit.

(i) Sampling Time 1: Juice analysis.

Response variable	Treatment 1	Treatment 2	Treatment 3	Treatment 4
Specific gravity	1.056	1.055	1.057	1.057
pH	3.25	3.30	3.64	3.53
Total sulfur dioxide (mg / L)	16.61	17.71	12.81	19.79
Alkalinity of ash (milliequivalents)	29.43	29.68	30.58	28.26
Dry weight (g / 100 g wet sample)	13.5	13.5	14.1	13.3
Pectin Fraction 2 (µg / g juice)	5.71	1.72	4.85	179.0
Glycerol (g / 100 mL)	nd [a]	nd	nd	nd
Methanol (g / 100 mL)	nd	nd	nd	0.004

[a] not detectable: less than 0.001 g / 100 mL for glycerol or 0.0001 g / 100 mL for methanol

(ii) Sampling Time 2: analysis of still ciders

Response Variable	Treatment 1	Treatment 2	Treatment 3	Treatment 4
Molds (colonies / mL)	nd [a]	nd	nd	nd
Volatile acidity (g acetic acid / 100 mL)	0.020	0.019	0.019	0.020
Free sulfur dioxide (mg / L)	9.28	10.36	9.20	9.50
Total sulfur dioxide (mg / L)	15.73	19.86	20.38	13.71
Ammonical nitrogen (mg / L)	nd	nd	1.65	nd
Ash (g / 100 g cider)	0.287	0.293	0.322	0.281
Pectin Fraction 2 (µg / g cider)	0.68	5.02	3.63	10.2
Glucose (g / 100 mL)	nd	nd	nd	nd
Sucrose (g / 100 mL)	nd	nd	nd	nd
Ethanol (g / 100 mL)	5.56	6.01	6.19	5.41
Methanol (g / 100 mL)	nd	nd	nd	0.006

[a] Not Detectable: < 5 colonies / mL for molds;
< 0.1 mg / L for ammonical nitrogen;
< 0.001 g / 100 mL for sugars;
< 0.0001 g / 100 mL for methanol

(iii) Sampling Time 2: Analysis of minerals in still ciders. Means are expressed as mg/L.

Response Variable	Treatment 1	Treatment 2	Treatment 3	Treatment 4
Iron	2.4	2.1	1.7	1.4
Boron	2.1	2.1	1.9	1.9
Zinc	0.3	0.3	0.4	0.4

(iv) Sampling Time 3: analysis of ciders 2 months in the bottle.

Response Variable	Treatment 1	Treatment 2	Treatment 3	Treatment 4
Yeasts (10^3 colonies / mL)	6.4	8.2	81.7	8.6
Specific gravity	0.997	0.997	0.998	0.997
Volatile acidity (g acetic acid / 100 mL)	0.027	0.025	0.027	0.023
Free sulfur dioxide (mg / L)	8.28	8.04	7.59	7.88
Total sulfur dioxide (mg / L)	17.60	18.38	14.91	15.45
Ammonical nitrogen (mg / L)	0.73	0.27	0.42	0.82
Ash (g / 100 g cider)	0.280	0.281	0.326	0.278
Alkalinity of ash (milliequivalents)	24.74	24.54	25.58	18.87
Pectin Fraction 2 (μg / g cider)	1.84	2.21	3.58	3.82
Pectin Fraction 3 (μg / g cider)	2.79	1.80	1.88	6.14
Fructose (g / 100 mL)	0.25	0.21	0.36	0.18
Glucose (g / 100 mL)	nd[a]	0.002	0.040	0.041
Sucrose (g / 100 mL)	nd	nd	nd	nd
Glycerol (g / 100 mL)	0.393	0.407	0.374	0.440
Methanol (g / 100 mL)	nd	nd	nd	0.008

[a] Not Detectable: < 0.001 g / 100 mL for sugars;
< 0.0001 g / 100 mL for methanol

(v) Sampling Time 3: Analysis of minerals (mg/L) in ciders 2 months in bottle.

Response Variable	Treatment 1	Treatment 2	Treatment 3	Treatment 4
Nitrogen	866.7	1184.0	920.0	978.9
Boron	1.9	3.0	1.8	2.2
Copper	0.4	0.3	0.4	0.4
Zinc	0.4	0.4	0.4	0.5

(viii) Sampling Time 3: analysis of the sediments from ciders 2 months in the bottle.

Response Variable	Treatment 1	Treatment 2	Treatment 3	Treatment 4
Dry weight (g / 100 g wet sample)	0.47	0.49	0.72	2.05

(vi) Sampling Time 4: analysis of ciders 5 months in the bottle.

Response Variable	Treatment 1	Treatment 2	Treatment 3	Treatment 4
Yeasts (colonies / mL)	1204	1659	251	57
Specific gravity	0.996	0.996	0.996	0.996
Volatile acidity (g acetic acid / 100 mL)	0.025	0.030	0.033	0.029
Ammonical nitrogen (mg / L)	nd [a]	nd	nd	nd
Ash (g / 100 g cider)	0.252	0.251	0.287	0.236
Dry weight (g / 100 g wet sample)	1.36	1.23	1.75	1.17
Pectin Fraction 3 (μg / g cider)	0.19	0.54	4.11	6.67
Fructose (g / 100 mL)	0.09	0.09	0.23	0.11
Sucrose (g / 100 mL)	nd	nd	nd	nd
Glycerol (g / 100 mL)	0.40	0.40	0.33	0.47
Ethanol (g / 100 mL)	6.11	6.11	6.53	6.10
Methanol (g / 100 mL)	nd	nd	nd	0.011

[a] Not Detectable: < 0.1 mg / L for ammonical nitrogen;
< 0.001 g / 100 mL for sugars;
< 0.0001 g / 100 mL for methanol

(vii) Sampling Time 4: Analysis of minerals (mg/L) in ciders 5 months in the bottle.

Response Variable	Treatment 1	Treatment 2	Treatment 3	Treatment 4
Nitrogen	1114.4	996.7	1274.9	905.6
Phosphorous	157.1	157.9	171.4	153.2
Potassium	1445.1	1426.6	1328.3	1270.3
Iron	1.4	1.9	2.5	2.0
Boron	2.5	2.3	2.6	3.8
Copper	0.3	0.3	0.5	0.3
Zinc	0.4	0.5	0.3	0.5

(ix) Sampling Time 4: Analysis of minerals in the sediments of ciders 5 months in the bottle. Means are expressed as mg / kg.

Response Variable	Treatment 1	Treatment 2	Treatment 3	Treatment 4
Potassium	1271.6	1219.7	1559.5	1117.9
Magnesium	88.9	93.0	124.4	99.6
Calcium	219.6	280.9	272.8	471.4
Sodium	150.8	227.6	133.4	160.9
Aluminum	77.4	102.7	59.4	64.2
Manganese	4.9	7.9	8.7	7.7
Zinc	55.9	44.8	42.0	26.7

Appendix 6. Preliminary analysis of gas composition in gushing and non-gushing ciders, as determined at Molson's Center for Innovation in Etobicoke, Ontario, Canada.

Dissolved Carbon Dioxide and Oxygen Determinations

Sample No.	Cider Type	Volumes[a] of CO_2	% CO_2 by weight ($g\ CO_2 / g$ liquid; approx.)	Oxygen (mg / L)
3	non-gush	4.04	0.792	0.29
6	non-gush	3.36	0.658	0.18
1	non-gush	3.34	0.653	0.25
7	non-gush	2.79	0.547	0.25
4	gush (high)[b]	4.58	0.894	0.18
8	gush (high)	4.10	0.802	0.33
5	gush (low)	3.96	0.774	0.15
2	gush (low)	6.26	1.222	0.16

[a] Volumes of CO_2 = volume of carbon dioxide per volume of liquid @ 0°C and 760 mm Hg
[b] high levels of gushing: > 15% of the contents of bottle are lost when cap is removed (at 10°C)
low levels: < 15% of the contents of the bottle are lost when cap is removed (bottle at 10°C)

Determination of Nitrogen in the Headspace

Sample No.	Cider Type	mg / L
3	non-gush	0.7
6	non-gush	0.8
1	non-gush	1.1
7	non-gush	1.1
4	gush (high)	1.7
8	gush (high)	1.4
5	gush (low)	0.8
2	gush (low)	1.0

Appendix 7. Ciders of Part One which were used in Part Two of the study.

Part One Label	Cider Type	Part Two treatment allocation
1994 Crispin, Treatment 2	non-gush	Treatment A, rep 1[a]
1994 Crispin, Treatment 2	non-gush	Treatment A, rep 2
1994 McIntosh, Treatment 1	non-gush	Treatment A, rep 3
1994 McIntosh, Treatment 1	non-gush	Treatment A, rep 4
1995 McIntosh, Treatment 1	non-gush	Treatment A, rep 5
1995 McIntosh, Treatment 1	non-gush	Treatment A, rep 6
1994 McIntosh, Treatment 2	non-gush	Treatment A, rep 7
1994 McIntosh, Treatment 2	non-gush	Treatment A, rep 8
1995 Russet, Treatment 1	non-gush	Treatment A, rep 9
1994 Russet, Treatment 2	non-gush	Treatment A, rep 10
1995 Russet, Treatment 2	non-gush	Treatment A, rep 11
1994 Spy, Treatment 1	non-gush	Treatment A, rep12
1994 Spy, Treatment2	non-gush	Treatment A, rep13
1994 Crispin, Treatment 4	gush (low)[b]	Treatment B, rep 1
1994 Crispin, Treatment 4	gush (low)	Treatment B, rep 2
1994 Crispin, Treatment 4	gush (low)	Treatment B, rep 3
1995 Crispin, Treatment 4	gush (low)	Treatment B, rep 4
1995 Crispin, Treatment 4	gush (low)	Treatment B, rep 5
1994 McIntosh, Treatment 4	gush (high)	Treatment C, rep 1
1994 Russet, Treatment 4	gush (high)	Treatment C, rep 2
1995 Russet, Treatment 4	gush (high)	Treatment C, rep 3
1995 Russet, Treatment 4	gush (high)	Treatment C, rep 4
1995 Russet, Treatment 4	gush (high)	Treatment C, rep 5
1994 Spy, Treatment 4	gush (high)	Treatment C, rep 6
1995 Spy, Treatment 4	gush (high)	Treatment C, rep 7
1995 Spy, Treatment 4	gush (high)	Treatment C, rep 8

[a] rep = replicate within Treatment

[b] high levels of gushing = more than ½ the liquid in bottle is lost when cap is removed (at 10°C)
low levels = less than ½ the liquid in bottle is lost when cap is removed (bottle at 10°C)

Appendix 8. Part 2: Raw data of initial headspace pressure, headspace volume and sediment thickness.

Treatment	Replicate	Headspace Pressure (atm)	Headspace Volume (mL)	Sediment (cm)
A	1	4.57	7.09	0.5
A	2	4.04	7.37	0.5
A	3	3.90	8.51	0.8
A	4	3.77	9.64	0.4
A	5	4.48	8.22	0.2
A	6	3.82	6.24	0.3
A	7	3.92	9.36	1.5
A	8	3.79	12.50	0.7
A	9	4.70	7.94	0.3
A	10	4.64	6.52	0.1
A	11	3.93	5.67	0.1
A	12	4.44	5.67	0.1
A	13	3.11	7.66	0.1
B	1	4.28	6.52	0.1
B	2	4.27	5.67	0.1
B	3	4.52	8.51	0.3
B	4	4.45	9.36	0.5
B	5	4.57	5.67	0.5
B	6	4.79	4.54	3.4
B	7	4.43	3.69	3.2
B	8	5.11	6.80	2.0
B	9	5.24	9.64	1.4
B	10	5.57	8.22	0.8
B	11	4.19	6.80	1.2
B	12	5.47	8.51	0.5
B	13	5.69	7.09	0.6

Appendix 9.

A. Analysis of variance (ANOVA) table for initial headspace pressure, headspace volume and sediment thickness (Appendix 8). The ANOVA table contains the mean squares for the factors as determined using the SAS computer program.
(* = significant at $\alpha = 0.05$) ; Treat = Treatment
Treat A = non-gush; Treat B = low gush; Treat C = high gush
Replicates within treatments served as the error term.

Source of Variation	df	Head. Pressure	Head. Volume	Sediment Thickness
Treatment	(2)	2.343 *	1.400	2.507 *
Treat A vs. Treat B	1	0.397	1.916	0.0620
Treat A vs. Treat C	1	1.360 *	0.032	3.438 *
Error	22	0.2079	3.400	0.3407
Total	24			

B. Analysis of variance (ANOVA) table for pectin concentrations of the sediments of ciders used in Part Two. Raw data used was for ciders at 5 months in the bottle. The ANOVA table contains mean squares for the factors as determined by SAS. (* = significant at $\alpha = 0.05$)
Treatment contrasts could not be accurately conducted because of the small number of ciders from Part One which were low gushers (n=2).
Replicates within treatments served as the error term.
Pectin Fractions were as described in Part One. Pectin is expressed as micrograms per gram of wet sediment (ug/g)

Source of Variation	df	Fraction 1 (ug/g)	Fraction 2 (ug/g)	Fraction 3 (ug/g)
Treatment	2	24266952 *	106637997 *	41496
Error	12	3885370	589125	416309
Total	14			

Appendix 10. Part Two: headspace pressure readings, in atm (raw data). Initial values and readings following pressure release. Time is in seconds (s); Time 0 = immediately following the pressure release; Treat = Treatment Rep = Replicate

				Time after pressure release														
Treat	Rep	Initial Value	Time 0	1 s	2 s	3 s	4 s	5 s	6 s	7 s	8 s	9 s	10 s	11 s	12 s	13 s	14 s	15 s
A	1	4.574	2.985	3.076	3.099	3.112	3.117	3.125	3.133	3.143	3.154	3.162	3.169	3.177	3.184	3.190	3.201	3.203
A	2	4.036	2.642	2.679	2.699	2.723	2.738	2.757	2.772	2.788	2.803	2.816	2.832	2.855	2.860	2.879	2.889	2.902
A	3	3.899	2.645	2.684	2.670	2.702	2.707	2.707	2.710	2.710	2.712	2.712	2.715	2.715	2.715	2.718	2.718	2.718
A	4	3.772	2.333	2.357	2.383	2.396	2.398	2.401	2.406	2.406	2.409	2.409	2.409	2.409	2.411	2.411	2.411	2.411
A	5	4.480	2.362	2.383	2.411	2.424	2.430	2.437	2.440	2.448	2.450	2.455	2.458	2.463	2.466	2.471	2.474	2.479
A	6	3.818	2.292	2.323	2.352	2.370	2.391	2.406	2.427	2.440	2.455	2.468	2.484	2.500	2.513	2.526	2.536	2.549
A	7	3.922	2.424	2.463	2.474	2.481	2.481	2.484	2.484	2.487	2.487	2.492	2.494	2.494	2.494	2.497	2.497	2.500
A	8	3.792	2.235	2.313	2.339	2.352	2.354	2.357	2.362	2.362	2.365	2.365	2.365	2.367	2.367	2.367	2.370	2.370
A	9	4.696	2.378	2.409	2.442	2.466	2.484	2.520	2.544	2.577	2.606	2.635	2.663	2.687	2.712	2.738	2.764	2.785
A	10	4.641	1.827	1.874	1.933	2.061	2.123	2.204	2.266	2.320	2.365	2.409	2.442	2.481	2.513	2.544	2.583	2.598
A	11	3.933	1.466	1.653	1.806	1.962	2.095	2.206	2.300	2.385	2.424	2.471	2.520	2.559	2.598	2.635	2.668	2.699
A	12	4.439	2.165	2.191	2.211	2.237	2.263	2.284	2.313	2.328	2.354	2.378	2.401	2.427	2.450	2.474	2.497	2.523
A	13	3.112	1.993	2.092	2.193	2.240	2.287	2.320	2.344	2.370	2.393	2.414	2.435	2.455	2.474	2.500	2.513	2.531
B	1	4.278	3.413	3.473	3.491	3.496	3.502	3.507	3.512	3.520	3.530	3.543	3.556	3.569	3.577	3.593	3.600	3.613
B	2	4.267	3.027	3.055	3.073	3.089	3.110	3.138	3.175	3.224	3.273	3.320	3.369	3.419	3.445	3.476	3.502	3.528
B	3	4.524	2.946	3.071	3.206	3.374	3.554	3.704	3.850	3.907	3.964	4.008	4.036	4.060	4.078	4.094	4.107	4.120
B	4	4.449	2.697	3.081	3.320	3.678	4.000	4.247	4.387	4.447	4.491	4.521	4.548	4.563	4.582	4.592	4.602	4.610
B	5	4.569	2.497	2.731	3.058	3.442	3.785	4.050	4.203	4.288	4.351	4.415	4.444	4.475	4.504	4.524	4.550	4.569
C	1	4.792	3.213	4.195	4.939	5.244	5.386	5.477	5.537	5.584	5.628	5.659	5.685	5.711	5.734	5.737	5.745	5.752
C	2	4.434	2.780	4.239	4.867	5.127	5.244	5.308	5.345	5.373	5.399	5.425	5.438	5.454	5.459	5.469	5.472	5.477
C	3	5.111	3.922	4.961	5.425	5.667	5.729	5.789	5.383	5.872	5.900	5.924	5.944	5.968	5.983	6.002	6.020	6.030
C	4	5.241	3.478	4.665	5.184	5.399	5.558	5.672	5.747	5.804	5.854	5.898	5.916	5.942	5.960	5.981	5.996	6.009
C	5	5.568	3.935	4.031	4.130	4.296	4.504	4.706	4.914	5.093	5.212	5.311	5.350	5.386	5.412	5.428	5.438	5.443
C	6	4.187	2.442	2.564	2.956	3.372	3.720	3.979	4.216	4.288	4.361	4.410	4.449	4.480	4.504	4.522	4.537	4.550
C	7	5.469	4.107	4.955	5.537	5.830	5.989	6.087	6.173	6.207	6.246	6.277	6.303	6.329	6.347	6.362	6.378	6.391
C	8	5.693	4.911	5.428	6.033	6.272	6.326	6.373	6.407	6.440	6.461	6.490	6.505	6.526	6.542	6.560	6.578	6.586

Appendix 11. Recovery rate of headspace pressure after a brief pressure release. Rates of pressure recovery are as fractions of their initial value (Appendix 8). Treat = treatment; Rep = replicate

Treat	Rep	Time interval (s) after Pressure Release							
		1 s	2 s	3 s	4 s	5 s	6 s	7 s	8 s
A	1	0.019865	0.005108	0.002838	0.001135	0.001703	0.001703	0.002270	0.002270
A	2	0.009004	0.005145	0.005788	0.003859	0.004502	0.003859	0.003859	0.003859
A	3	0.009988	0.003329	0.001332	0.001332	0.000001	0.000666	0.000001	0.000666
A	4	0.006195	0.006883	0.003441	0.000688	0.000688	0.001377	0.000001	0.000688
A	5	0.004635	0.006374	0.002897	0.001159	0.001738	0.000579	0.001738	0.000579
A	6	0.008158	0.007479	0.004759	0.005439	0.004079	0.005439	0.003399	0.004079
A	7	0.009928	0.002647	0.001986	0.000001	0.000662	0.000001	0.000662	0.000001
A	8	0.020536	0.006845	0.003423	0.000685	0.000685	0.001369	0.000001	0.000685
A	9	0.006634	0.007187	0.004976	0.003870	0.007740	0.004976	0.007187	0.006081
A	10	0.010068	0.012865	0.027407	0.013424	0.017339	0.013424	0.011746	0.009509
A	11	0.047529	0.038947	0.039608	0.033666	0.028385	0.023765	0.021784	0.009902
A	12	0.005848	0.004679	0.005848	0.005848	0.004679	0.006433	0.003509	0.005848
A	13	0.031697	0.032531	0.015014	0.015014	0.010844	0.007507	0.008341	0.007507
B	1	0.013957	0.004248	0.001214	0.001214	0.001214	0.001214	0.001821	0.002427
B	2	0.006692	0.004258	0.003650	0.004867	0.006692	0.008517	0.011558	0.011558
B	3	0.027541	0.029836	0.037295	0.039590	0.033279	0.032131	0.012623	0.012623
B	4	0.086355	0.053680	0.080520	0.072351	0.055430	0.031508	0.013420	0.009919
B	5	0.051140	0.071597	0.084098	0.075006	0.057959	0.033525	0.018751	0.013637
C	1	0.204782	0.155483	0.063385	0.029796	0.018961	0.012460	0.009752	0.009210
C	2	0.329066	0.141698	0.058553	0.026349	0.014638	0.008197	0.006441	0.005855
C	3	0.203163	0.090915	0.047235	0.012190	0.011682	0.009650	0.006603	0.005587
C	4	0.226365	0.099066	0.041112	0.030215	0.021794	0.014365	0.010897	0.009411
C	5	0.017251	0.017717	0.029839	0.037298	0.036366	0.037298	0.032170	0.021447
C	6	0.029141	0.093622	0.099203	0.083082	0.062002	0.056421	0.017360	0.017360
C	7	0.155207	0.106319	0.053634	0.028953	0.018036	0.015663	0.006170	0.007120
C	8	0.090708	0.106205	0.041935	0.009572	0.008205	0.005926	0.005926	0.003647

Appendix 11. continued

Treat	Rep	Time interval (s) after Pressure Release						
		9 s	10 s	11 s	12 s	13 s	14 s	15 s
A	1	0.001703	0.001703	0.001703	0.001703	0.001135	0.002270	0.000568
A	2	0.003216	0.003859	0.005788	0.001286	0.004502	0.002573	0.003216
A	3	0.000001	0.000666	0.000001	0.000001	0.000666	0.000001	0.000001
A	4	0.000001	0.000001	0.000001	0.000688	0.000001	0.000001	0.000001
A	5	0.001159	0.000579	0.001159	0.000579	0.001159	0.000579	0.001159
A	6	0.003399	0.004079	0.004079	0.003399	0.003399	0.002719	0.003399
A	7	0.001324	0.000662	0.000001	0.000001	0.000662	0.000001	0.000662
A	8	0.000001	0.000001	0.000685	0.000001	0.000001	0.000685	0.000001
A	9	0.006081	0.006081	0.004976	0.005528	0.005528	0.005528	0.004423
A	10	0.009509	0.007271	0.008390	0.006712	0.006712	0.008390	0.003356
A	11	0.011882	0.012542	0.009902	0.009902	0.009242	0.008582	0.007922
A	12	0.005264	0.005264	0.005848	0.005264	0.005264	0.005264	0.005848
A	13	0.006673	0.006673	0.006673	0.005839	0.008341	0.004171	0.005839
B	1	0.003034	0.003034	0.003034	0.001821	0.003641	0.001821	0.003034
B	2	0.010950	0.011558	0.011558	0.006083	0.007300	0.006083	0.006083
B	3	0.009754	0.006311	0.005164	0.004016	0.003443	0.002869	0.002869
B	4	0.007002	0.005835	0.003501	0.004084	0.002334	0.002334	0.001750
B	5	0.014206	0.006250	0.006819	0.006250	0.004546	0.005682	0.003978
C	1	0.006501	0.005418	0.005418	0.002709	0.002709	0.001625	0.001625
C	2	0.005855	0.002928	0.003513	0.001171	0.002342	0.000586	0.001171
C	3	0.004571	0.004063	0.004571	0.003047	0.003555	0.003555	0.002032
C	4	0.008421	0.003467	0.004953	0.003467	0.003963	0.002972	0.002477
C	5	0.017717	0.006993	0.006527	0.004662	0.002797	0.001865	0.000932
C	6	0.011780	0.009300	0.007440	0.005580	0.004340	0.003720	0.003100
C	7	0.005696	0.004746	0.004746	0.003322	0.002848	0.002848	0.002373
C	8	0.005014	0.002735	0.003647	0.002735	0.003191	0.003191	0.001367

Appendix 12. Analysis of variance (ANOVA) tables for headspace pressure recovery rates, following pressure release. Treatments B (low gushing) and C (high gushing) were contrasted against Treatment A (non-gushing). ANOVA tables contain mean squares for the factors as determined using SAS. Replicates within treatments served as the error term. (* = significant at $\alpha = 0.05$).

Source of Variation	df	1 s	2 s	3 s	4 s	5 s
Treatment	(2)	0.0522 *	0.0206 *	0.0055 *	0.0026 *	0.0014 *
Treat A vs Treat B	1	0.0018	0.0017	0.0037 *	0.0037 *	0.0021 *
Treat A vs Treat C	1	0.1003 *	0.0407 *	0.0101 *	0.0032 *	0.0015 *
Error	23	0.00370	0.00073	0.00048	0.00042	0.00025
Total	25					

Source of Variation	df	6 s	7 s	8 s	9 s	10 s
Treatment	(2)	0.0007 *	0.0002 *	0.0001 *	0.0001 *	0.00001
Treat A vs Treat B	1	0.0009 *	0.0002 *	0.0001 *	0.0001 *	0.00003
Treat A vs Treat C	1	0.0010 *	0.0002 *	0.0002 *	0.0001 *	0.00001
Error	24	0.00016	0.00005	0.00002	0.00002	0.000010
Total	25					

Source of Variation	df	11 s	12 s	13 s	14 s	15 s
Treatment	(2)	0.00001	0.00000	0.000002	0.000002	0.000004
Treat A vs Treat B	1	0.00002	0.00001	0.000002	0.000001	0.000002
Treat A vs Treat C	1	0.00001	0.00000	0.000001	0.000002	0.000004
Error	24	0.000009	0.000006	0.000006	0.000006	0.000004
Total	25					

Appendix 13. Examples of tracking of bubbles from a series of images obtained from the video tapes for one cider. Bubble numbers were assigned arbitrarily. "Time" indicates the time (s) elapsed since the pressure release. Rate of recording was 30 frames per second; "Frame" refers to the frame number within the video clip. Pressure is in atm. Ascent indicates the distance travelled from the position in the previously examined frame; for example, the distance travelled by bubble no. 1, in A below, between frames 25 and 28 (equivalent to 0.1 seconds) is 1.3 cm. "Height" indicates the distance of the bubble above the sediment. Since the area between the view of the bottom camera and the view of the top camera was not video taped, velocities and bubble growth BETWEEN the two camera views were not recorded; bubbles in non-gushing analyzed WITHIN the view of a camera.

A. Treatment A, replicate 1 (non-gush)

Bubble no.	Section	Pressure	Camera	Frame	Bubble radius (mm)	Velocity (cm/s)	Ascent (cm)	Height (cm)
1	1	2.99	bottom	25	0.8	13.1	---	2.4
				28	0.8	13.2	1.3	3.7
	2	3.08		31	0.8	13.1	1.3	5.0
				34	0.8	---	1.8	6.8
	3	3.11	top	87	0.8	13.7	---	24.7
				89	0.8	---	0.9	25.7
2	2	3.08	bottom	32	0.7	11.8	---	2.3
				35	0.7	12.7	1.2	2.5
				38	0.7	12.1	1.3	2.6
				41	0.7	11.7	1.2	2.7
				44	0.7	---	1.2	2.8
	3	3.11	top	87	0.8	13.7	---	24.3
				90	0.8	---	1.4	25.7

Appendix 13. continued.

B. Treatment A, replicate 4 (non-gush). Bubble radii larger than 1.0 mm were calculated from the effective diameter, according to Houghton et al. (1957).

Bubble no.	Section	Pressure	Camera	Frame	Bubble radius (mm)	Velocity (cm/s)	Ascent (cm)	Height (cm)
1	3	2.40	bottom	93	0.4	8.8	---	3.1
				96	0.4	10.5	0.9	4.0
				99	0.5	9.6	1.0	5.1
				102	0.6	10.7	1.0	6.0
				105	0.7	---	1.1	7.1
2	4	2.40	bottom	128	2.9	21.3	---	3.0
				131	2.6	18.7	2.1	5.1
				134	2.8	---	1.9	7.0
			top	145	3.2	19.9	---	23.2
				148	3.0	---	2.0	25.2

C. Treatment A, replicate 13 (non-gush). Bubble radii larger than 1.0 mm were calculated from the effective diameter, according to Houghton et al. (1957).

Bubble no.	Section	Pressure	Camera	Frame	Bubble radius (mm)	Velocity (cm/s)	Ascent (cm)	Height (cm)
1	1	2.09	bottom	3	0.4	3.1	---	4.9
				4	0.4	3.1	0.1	5.0
				5	0.4	---	0.1	5.1

Appendix 13. continued.

D. Treatment A, replicate 5 (non-gush).

Bubble no.	Section	Pressure	Camera	Frame	Bubble radius (mm)	Velocity (cm/s)	Ascent (cm)	Height (cm)
1	15	2.48	bottom	438	0.2	2.6	---	4.1
				441	0.2	---	0.3	4.4
2	2	2.38	bottom	31	0.6	13.7	---	2.9
				34	0.7	12.2	1.4	4.3
				40	0.7	12.8	2.4	6.7
				43	0.7	---	1.3	8.0

Appendix 14. MathCad program to calculate the initial concentrations of nitrogen,
oxygen and carbon dioxide in the bottle at time of bottling and after
secondary fermentation. Example is Treatment A, replicate 5.

Step 1. Calculate the volume of the headspace where the diameter of the inside of the bottle at the neck is 1.8 cm and the height of the headspace is 2.9 cm:

$$Vho := \frac{(1.8 \cdot cm)^2}{4} \cdot \pi \cdot 2.9 \cdot cm$$

Step 2. Input the value of the gas constant:

$$Rgas := 82.05 \cdot \frac{cm^3 \cdot atm}{K \cdot mol}$$

Step 3. Calculate gases in liquid and headspace at the time of bottling:

(i) the only source of nitrogen and oxygen is at the time of bottling, as yeasts cannot produce these gases de novo.

moles of nitrogen in the headspace at bottling (1atm, 13 C = 286.15 K); air is 78% nitrogen:

$$nN2 := (1 \cdot atm) \cdot \frac{Vho \cdot .78}{Rgas \cdot 286.15 \cdot K} \qquad nN2 = 2.452 \cdot 10^{-4} \cdot mol$$

moles of oxygen in the headspace at time of bottling; air contains 21% oxygen:

$$nO2 := (1 \cdot atm) \cdot \frac{Vho \cdot .21}{Rgas \cdot 286.15 \cdot K} \qquad nO2 = 6.601 \cdot 10^{-5} \cdot mol$$

Carbon dioxide concentration in air is less than 0.1% and therefore could be considered negligible at the time of bottling.

(ii) moles of nitrogen in the liquid at bottling can be calculated from Henry's Law for gas mixtures, where the Henry's constant for nitrogen at 13 C is 80.4*10^3 atm (Tinoco et al., 1985):

$$nN2liq := \frac{.78 \cdot 1 \cdot atm}{80.4 \cdot 10^3 \cdot atm} \cdot \frac{1000}{18} \cdot \frac{mol}{L} \qquad nN2liq = 0.539 \cdot m^{-3} \cdot mol$$

(iii) the total number of moles of nitrogen in the closed 750 mL bottle is:

$$TotalnN2 := nN2liq \cdot .75 \cdot L + nN2 \qquad TotalnN2 = 6.494 \cdot 10^{-4} \cdot mol$$

This amount of nitrogen remains constant over the secondary fermentation and ageing since the bottle remains closed.

Fermentation in the closed bottle consumes the oxygen and produces carbon dioxide.

Step 4. Use an iteration procedure to determine the concentration of nitrogen gas in the liquid phase, just prior to pressure release through the use of the sampling device:

(i) the total number of moles of nitrogen in the bottle is constant:

$$TotalnN2 = 6.494 \cdot 10^{-4} \cdot mol$$

(ii) set the number of moles of N2 in the headspace at an arbitrary level (the current value is the correct value to solve the iteration):

$$nN2b := 2.416 \cdot 10^{-4} \cdot mol$$

(iii) input pressure (Po) and temperature (Tp) measured in Part Two of this study:

$$Po := 4.53971 \cdot 10^{5} \cdot kg \cdot m^{-1} \cdot s^{-2} \qquad Tp := 292.9 \cdot K$$

(iv) from the Ideal Gas Law, the total number of moles in the headspace can be calculated as:

$$total_headsp_moles := \frac{Po \cdot Vho}{Rgas \cdot Tp} \qquad total_headsp_moles = 1.376 \cdot 10^{-3} \cdot mol$$

(v) the mole fraction of nitrogen in the gas phase can be estimated as that in the headspace (since no bubbles formed prior to the pressure release):

$$N2vapmole_fract := \frac{nN2b}{total_headsp_moles} \qquad N2vapmole_fract = 0.176$$

(vi) the mole fraction of nitrogen in the liquid phase can be calculated (Henry's Law for a mixture of gases):

$$N2liq_mole_fract := \frac{N2vapmole_fract \cdot Po}{80.4 \cdot 10^{3} \cdot atm} \qquad N2liq_mole_fract = 9.786 \cdot 10^{-6}$$

(vii) the concentration of nitrogen in the liquid is:

$$nN2liqb := N2liq_mole_fract \cdot \frac{1000}{18} \cdot mol \cdot L^{-1} \qquad nN2liqb = 0.544 \cdot m^{-3} \cdot mol$$

(viii) to verify the iteration, the total amount of nitrogen in the bottle is recalculated:

$$TotalnN2b := nN2liqb \cdot .75 \cdot L + nN2b \qquad TotalnN2b = 6.494 \cdot 10^{-4} \cdot mol$$

Step 5. Calculate total moles of all gases in the headspace by the Ideal Gas Law:

$$nheadsp_atPo := \frac{Po \cdot Vho}{Rgas \cdot Tp} \qquad nheadsp_atPo = 1.376 \cdot 10^{-3} \cdot mol$$

Step 6. Calculate concentrations of carbon dioxide:

(i) the number of moles of carbon dioxide in the headspace is:

$$nCO2 := nheadsp_atPo - nN2b \qquad nCO2 = 1.134 \cdot 10^{-3} \cdot mol$$

(ii) the mole fraction of carbon dioxide in the gas in the headspace can be calculated:

$$CO2vapmole_fract := \frac{nCO2}{total_headsp_moles} \qquad CO2vapmole_fract = 0.824$$

(iii) the mole fraction of carbon dioxide in the liquid phase can be calculated as follows (Henry's Law for mixture of gases), where 1.42*10^3 atm is the Henry's constant for carbon dioxide (Tinoco et al., 1985):

$$CO2liq_mole_fract := \frac{CO2vapmole_fract \cdot Po}{1.42 \cdot 10^{3} \cdot atm} \qquad CO2liq_mole_fract = 2.601 \cdot 10^{-3}$$

(iv) the concentration of carbon dioxide in the liquid (dilute solution) is:

$$nCO2liq := CO2liq_mole_fract \cdot \frac{1000}{18} \cdot \frac{mol}{L} \qquad nCO2liq = 144.505 \cdot m^{-3} \cdot mol$$

(v) the total moles of CO2 in whole bottle:

$$TotalnCO2 := nCO2liq \cdot .75 \cdot L + nCO2 \qquad TotalnCO2 = 0.11 \cdot mol$$

Step 7. Determine the relative concentration of nitrogen in the liquid:

$$percentN2gas := \frac{nN2liqb}{nCO2liq + nN2liqb} \cdot 100 \qquad percentN2gas = 0.375$$

Since the concentration of nitrogen in the liquid phase is so low (less than 0.4% of the total gas in the liquid), it should be considered as negligible.

Appendix 15. Computer program (Visual Basic) to simulate the growth and velocity during the ascention of a single bubble in a non-gushing cider. Pressure (P) and temperature (Tp) were taken from an array generated from the data acquisition unit recordings.

```
'Program for bubble growth of a single bubble in a non-gushing cider
'Step size is 0.1 second
'Example: Treatment A, replicate 5

Sub bubblegrow5()

'Pressure, temperature, diffusion of carbon dioxide and the Schmidt number are
'contained in arrrays

ReDim P(100), Tp(100), Diff(100), Sc(100)

Pi = 3.14159
g = 9.81 / 100              'gravity in meters /(0.1 s)^2
Rgas = 8.314 / 100          'gas constant:  Pa·m^3/K.mol adjusted to 0.1 second
visc = 0.00122 * 0.1        'viscosity of the cider:  kg/m·(0.1 s), adjusted to 0.1 s
dens = 994.6                'density of the cider:  kg/m^3

 'set the output parameters, to put into an array

ActiveCell.Offset(t, 4).Value = y          'y is the distance travelled, in meters
ActiveCell.Offset(t, 5).Value = rb         'rb is the radius of the bubble, in meters
ActiveCell.Offset(t, 6).Value = utpers     'bubble velocity:  meters per second
ActiveCell.Offset(t, 7).Value = Re         'Reynolds number
ActiveCell.Offset(t, 8).Value = nb         'moles of carbon dioxide in bubble

 'height of liquid (cider) in bottle, in meters
ymax = 0.272

'calculated concentration of carbon dioxide in liquid (Appendix 12): moles / cubic meter
co2liq = 144.51

Worksheets("one-tenths").Activate          'specify the input data
Range("C5").Select

'set the estimated initial radius of bubble, in meters
rb = 0.0002 'm
```

```
'starting height of the bubble, meters
y = 0

'calculate the initial number of moles of carbon dixoide in the bubble from the initial
'bubble radius
nb = 2.362 * 1013.25 * (4 * Pi * rb ^ 3 / 3) / (Rgas * 292.9)

For t = 0 To 100

   P(t) = ActiveCell.Offset(t, 0).Value * 1013.25       'convert pressure from atm to Pa
   Tp(t) = ActiveCell.Offset(t, 2).Value                'temperature in K
   Diff(t) = 0.0000000007557 * 0.2 * Tp(t) / 292.9      'diffusivity as a fn of Tp, time
   Sc(t) = visc / (dens * Diff(t))                      'Schmidt number for 0.1 s time step


ut = 2 * rb ^ 2 * dens * g / (9 * visc)                 'velocity: meters per 0.1 s
Re = 2 * rb * ut * dens / visc                          'Reynolds number
denb = P(t) * 0.044 / (Rgas * Tp(t))                    'density of bubble, kg/m^3
ab = 4 * Pi * rb ^ 2                                    'area of the bubble surface

If Re > 1 Then

'set previously calculated velocity as current velocity
      utp = ut

'set previously calculated Reynolds number as current Reynolds number
      Rep = Re

      Do
         Re = 2 * rb * ut * dens / visc                 'Reynolds #

         If Re < 1000 Then
            c = 24 / Re * (1 + 0.14 * Re ^ 0.7)
         Else
            c = 0.445
         End If
         utn = Sqr(8 * g * rb * (dens - denb) / (3 * dens * c))
         If Abs(utn - ut) / ut < 0.001 Then Exit Do
         ut = utn
      Loop

      If Re <= 1 Then                                   'Reynolds no. still not greater than 1
```

```
            ut = utp
            Re = Rep
        End If
End If

'calculation of Sherwood number, according to the value of Reynold's number

If Re <= 2 Then
    Sh = 1.01 * Re ^ (1 / 3) * Sc(t) ^ (1 / 3)

If Re > 2 And Re <= 48000 Then
   Sh = 2 + 0.552 * Re ^ 0.53 * Sc(t) ^ (1 / 3)

'calculation of mass transfer constant as meters per 0.1 s
kco2 = Sh * Diff(t) / (2 * rb)

'calculation of flux of carbon dioxide into the bubble, as moles per square meter per
'0.1 s
flux = kco2 * (co2liq - P(t) / (Rgas * Tp(t)))

'rate of mass transfer into the bubble, as moles per 0.1 s
mtr = flux * ab

'conversion of velocity from meters per 0.1 s to meters per 1.0 s
utpers = ut * 10

ActiveCell.Offset(t, 4).Value = y                  'sending output to spreadsheet
ActiveCell.Offset(t, 5).Value = rb
ActiveCell.Offset(t, 6).Value = utpers
ActiveCell.Offset(t, 7).Value = Re
ActiveCell.Offset(t, 8).Value = nb
ActiveCell.Offset(t, 9).Value = mtr

y = y + ut                              'total distance travelled by bubble (meters)
nb = nb + mtr                           'moles of carbon dioxide in bubble
vb = nb * Rgas * Tp(t) / P(t)           'new volume of bubble (m^3)
rbp = (vb * 0.75 / Pi) ^ (1 / 3)        'new bubble radius (meters)

End If

Next t                                  'start the next time step

End Sub
```

Appendix 16. Calculated results from computer simulation output for velocity and growth of a single bubble (Appendix 15) for initial bubble radius of 0.1 mm in a non-gushing cider. Measured values from the video images may vary as much as 14%, so this variation was calculated to allow comparison of the computer simulation to the measured values.

Time (s)	Radius, mm	radius+14%	radius -14%	Height (m)	velocity (m/s)	velocity + 14%	velocity -14%
0	0.10	0.11	0.09	0.000	0.014	0.016	0.012
1	0.10	0.12	0.09	0.001	0.015	0.017	0.013
2	0.11	0.12	0.09	0.003	0.016	0.018	0.014
3	0.11	0.13	0.09	0.004	0.017	0.019	0.014
4	0.11	0.13	0.10	0.006	0.017	0.020	0.015
5	0.12	0.13	0.10	0.008	0.018	0.021	0.016
6	0.12	0.14	0.10	0.010	0.019	0.022	0.016
7	0.12	0.14	0.11	0.012	0.020	0.023	0.017
8	0.13	0.15	0.11	0.014	0.021	0.024	0.018
9	0.13	0.15	0.11	0.016	0.022	0.025	0.019
10	0.13	0.15	0.12	0.018	0.022	0.026	0.019
11	0.14	0.16	0.12	0.020	0.023	0.027	0.020
12	0.14	0.16	0.12	0.022	0.024	0.028	0.021
13	0.14	0.17	0.12	0.025	0.025	0.029	0.022
14	0.15	0.17	0.13	0.027	0.026	0.030	0.022
15	0.15	0.17	0.13	0.030	0.027	0.030	0.023
16	0.16	0.18	0.13	0.033	0.028	0.031	0.024
17	0.16	0.18	0.14	0.035	0.028	0.032	0.024
18	0.16	0.18	0.14	0.038	0.029	0.033	0.025
19	0.17	0.19	0.14	0.041	0.030	0.034	0.026
20	0.17	0.19	0.15	0.044	0.031	0.035	0.027
21	0.17	0.20	0.15	0.047	0.032	0.036	0.027
22	0.18	0.20	0.15	0.050	0.033	0.037	0.028

Time (s)	Radius, mm	radius+14%	radius -14%	Height (m)	velocity (m/s)	velocity + 14%	velocity -14%
23	0.18	0.20	0.15	0.054	0.034	0.038	0.029
24	0.18	0.21	0.16	0.057	0.034	0.039	0.030
25	0.19	0.21	0.16	0.061	0.035	0.040	0.030
26	0.19	0.22	0.16	0.064	0.036	0.041	0.031
27	0.19	0.22	0.17	0.068	0.037	0.042	0.032
28	0.20	0.22	0.17	0.071	0.038	0.043	0.033
29	0.20	0.23	0.17	0.075	0.039	0.044	0.033
30	0.20	0.23	0.17	0.079	0.040	0.045	0.034
31	0.21	0.24	0.18	0.083	0.041	0.046	0.035
32	0.21	0.24	0.18	0.087	0.041	0.047	0.036
33	0.21	0.24	0.18	0.091	0.042	0.048	0.036
34	0.22	0.25	0.19	0.095	0.043	0.049	0.037
35	0.22	0.25	0.19	0.100	0.044	0.050	0.038
36	0.22	0.26	0.19	0.104	0.045	0.051	0.039
37	0.23	0.26	0.20	0.109	0.046	0.052	0.039
38	0.23	0.26	0.20	0.113	0.047	0.053	0.040
39	0.23	0.27	0.20	0.118	0.047	0.054	0.041
40	0.24	0.27	0.21	0.123	0.048	0.055	0.041
41	0.24	0.28	0.21	0.127	0.049	0.056	0.042
42	0.25	0.28	0.21	0.132	0.050	0.057	0.043
43	0.25	0.28	0.21	0.137	0.051	0.058	0.044
44	0.25	0.29	0.22	0.142	0.052	0.059	0.044
45	0.26	0.29	0.22	0.148	0.052	0.060	0.045
46	0.26	0.30	0.22	0.153	0.053	0.061	0.046
47	0.26	0.30	0.23	0.158	0.054	0.062	0.047
48	0.27	0.30	0.23	0.163	0.055	0.063	0.047

Time (s)	Radius, mm	radius+14%	radius -14%	Height (m)	velocity (m/s)	velocity + 14%	velocity -14%
49	0,27	0,31	0,23	0,169	0,056	0,064	0,048
50	0,27	0,31	0,24	0,175	0,057	0,065	0,049
51	0,28	0,32	0,24	0,180	0,057	0,065	0,049
52	0,28	0,32	0,24	0,186	0,058	0,066	0,050
53	0,28	0,32	0,24	0,192	0,059	0,067	0,051
54	0,29	0,33	0,25	0,198	0,060	0,068	0,052
55	0,29	0,33	0,25	0,204	0,061	0,069	0,052
56	0,29	0,34	0,25	0,210	0,062	0,070	0,053
57	0,30	0,34	0,26	0,216	0,062	0,071	0,054
58	0,30	0,34	0,26	0,222	0,063	0,072	0,054
59	0,31	0,35	0,26	0,228	0,064	0,073	0,055
60	0,31	0,35	0,27	0,235	0,065	0,074	0,056
61	0,31	0,36	0,27	0,241	0,066	0,075	0,056
62	0,32	0,36	0,27	0,248	0,066	0,076	0,057
63	0,32	0,36	0,27	0,255	0,067	0,077	0,058
64	0,32	0,37	0,28	0,261	0,068	0,078	0,058
65	0,33	0,37	0,28	0,268	0,069	0,078	0,059

Appendix 16. **continued.**

Calculated results from computer simulation output for velocity and growth of a single bubble (Appendix 15) for initial bubble radius of 0.6 mm. Measured values from the video images may vary as much as 14%, so this variation was calculated to allow comparison of the computer simulation to the measured values.

Time (s)	Radius (mm)	radius+14%	radius -14%	Height (m)	velocity (m/s)	velocity + 14%	velocity -14%
0	0.60	0.68	0.52	0.000	0.126	0.143	0.108
1	0.60	0.69	0.52	0.013	0.126	0.144	0.109
2	0.61	0.69	0.52	0.025	0.127	0.145	0.109
3	0.61	0.69	0.52	0.038	0.128	0.146	0.110
4	0.61	0.70	0.53	0.051	0.128	0.146	0.110
5	0.62	0.70	0.53	0.064	0.129	0.147	0.111
6	0.62	0.71	0.53	0.076	0.130	0.148	0.112
7	0.62	0.71	0.54	0.089	0.130	0.149	0.112
8	0.63	0.72	0.54	0.102	0.131	0.149	0.113
9	0.63	0.72	0.54	0.116	0.132	0.150	0.113
10	0.63	0.72	0.55	0.129	0.132	0.151	0.114
11	0.64	0.73	0.55	0.142	0.133	0.152	0.114
12	0.64	0.73	0.55	0.155	0.134	0.153	0.115
13	0.65	0.74	0.55	0.169	0.134	0.153	0.116
14	0.65	0.74	0.56	0.182	0.135	0.154	0.116
15	0.65	0.74	0.56	0.196	0.136	0.155	0.117
16	0.66	0.75	0.56	0.209	0.136	0.156	0.117
17	0.66	0.75	0.57	0.223	0.137	0.156	0.118
18	0.66	0.76	0.57	0.237	0.138	0.157	0.119
19	0.67	0.76	0.57	0.250	0.139	0.158	0.119
20	0.67	0.76	0.58	0.264	0.139	0.159	0.120

Appendix 17. Bubble sizes, frequencies and populations as determined through image analysis; "ave" indicates an average value. Bubbles in replicate (rep.) 3 were generated in group bursts; the numbers obtained from images are the total bubbles per second for this rep. Bubbles generated within one unit of elapsed time (s) was to be one "group" of bubbles, for the purposes of computer programming. "vol" = volume of gas evolved

cider	"group"	time (s)	ave radius (mm)	ave velocity (cm/s)	ave # / frame	frequency (#/cm^2/s)	frequency/bottle/s	vol.(cm^3)/bottle/s
rep. 5	1	0	0.21	2.61	77	2.014	87	16.005
	2	1	0.43	13.70	1	0.053	2	1.768
	3	2	0.20	2.44	2	0.019	1	0.136
	4	3	0.30	4.88	3	0.057	2	0.920
	5	4	0.26	7.08	3	0.082	4	1.002
	6	5	0.30	2.41	4	0.037	2	0.606
	7	6	0.27	6.30	5	0.122	5	1.603
	8	7	0.23	7.76	5	0.150	6	1.433
	9	8	0.26	6.18	5	0.120	5	1.458
	10	9	0.26	8.52	5	0.165	7	2.010
rep. 1	1	0	0.78	12.69	1	0.049	2	5.389
	2	1	0.31	5.94	192	4.419	190	76.504
	3	2	0.31	5.83	66	1.500	65	25.968
	4	3	0.33	5.73	46	1.032	44	20.245
	5	4	0.55	4.29	46	0.773	33	41.798
	6	5	0.55	4.92	40	0.759	33	41.071
	7	6	0.50	3.83	14	0.208	9	9.357
	8	7	0.63	13.49	16	0.836	36	59.798
	9	8	0.30	5.51	17	0.363	16	5.885
	10	9	0.31	4.56	15	0.265	11	4.588

Appendix 17. continued.

cider	"group"	time (s)	ave radius (mm)	ave velocity (cm/s)	ave # / frame	frequency (#/cm^2/s)	frequency/bottle/s	vol.(cm^3)/bottle/s
rep. 3	1	0	0.33	5.46	1	0.023	1	0.456
	2	1	1.78	17.92	18	0.419	18	238.892
	3	2	0.20	3.11	14	0.326	14	2.346
	4	3	1.03	18.67	22	0.512	22	98.336
	5	4	0.40	7.53	21	0.488	21	13.725
	6	5	0.26	7.13	35	0.814	35	9.911
	7	6	0.36	7.66	18	0.419	18	9.772
	8	7	0.47	8.18	12	0.279	12	11.056
	9	8	0.32	6.50	11	0.256	11	4.858
	10	9	0.26	7.10	20	0.465	20	5.663

Appendix 18. Computer program to predict the pressure recovery in the headspace of a non-gushing cider from evolution frequency and size of bubbles.

```
'Program for pressure recovery in headspace of a Treatment A rep. 5 cider
Sub pressuregrow()

'array of the experimental data contains the temperature and the number of bubbles produced at
'each consecutive time interval (s); data are grouped as averages per second based on analysis of
'images

ReDim  Tp(10), nob1(10), nob2(10), nob3(10), nob4(10), nob5(10), nob6(10), nob7(10)
ReDim  nob8(10),nob9(10), nob10(10)

'set up arrays of the calculations of diffusivity and the Schmidt number
ReDim  Diff(10), Sc(10)

'Define constants and initial conditions
Pi = 3.14159
g = 9.81 / 100              'gravity: meters /(.1 s)2
Rgas = 8.314 / 100                  'gas constant: Pa•m^3/(K•mol), adjusted to 0.1 seconds
visc = 0.00122 * 0.1                'viscosity of cider: kg/m.(0.1 s)
dens = 994.6                        'density of cider (specific gravity from Part One):  kg/m3
P = 1.84 * 1013.25                          'set initial pressure; convert to Pa, adjustec to 0.1 s
Vho = (0.018) ^ 2 / 4 * Pi * 0.029          ' initial headspace volume, cubic meters
nh = P * Vho / (Rgas * 292.9)               'initial moles in headspace
Vo = Vho                                    'initial gas volume is assumed to only be the headspace

y1 = 0      'all bubbles initiate at the sediment
y2 = 0
y3 = 0
y4 = 0
y5 = 0
y6 = 0
y7 = 0
y8 = 0
y9 = 0
y10 = 0

rb1 = 0.00021       'initial radii of bubbles
rb2 = 0.00043
```

```
rb3 = 0.0002
rb4 = 0.0003
rb5 = 0.00026
rb6 = 0.0003
rb7 = 0.00027
rb8 = 0.00023
rb9 = 0.00026
rb10 = 0.00026

ymax = 0.272         'height of liquid in meters
co2liq = 144.51      'concentration of CO2 in cider: mol/m^3

'specifying output content and destination
ActiveCell.Offset(t, 14).Value = Pout
ActiveCell.Offset(t, 15).Value = totalmoles

Worksheets("TreatA-rep5").Activate
Range("C5").Select

For t = 0 To 10        'Steps of pressure recovery are in time (s)

Tp(t) = ActiveCell.Offset(t, 0).Value            'temperature in Kelvin
nob1(t) = ActiveCell.Offset(t, 1).Value   'numbers of bubbles released in the first second
nob2(t) = ActiveCell.Offset(t, 2).Value   'numbers of bubbles released in second second
nob3(t) = ActiveCell.Offset(t, 3).Value   'numbers of bubbles released in third second
nob4(t) = ActiveCell.Offset(t, 4).Value   'numbers of bubbles released in fourth second
nob5(t) = ActiveCell.Offset(t, 5).Value   'numbers of bubbles released in fifth second
nob6(t) = ActiveCell.Offset(t, 6).Value   'numbers of bubbles released in six second
nob7(t) = ActiveCell.Offset(t, 7).Value   'numbers of bubbles released in seven second
nob8(t) = ActiveCell.Offset(t, 8).Value   'numbers of bubbles released in eight second
nob9(t) = ActiveCell.Offset(t, 9).Value   'numbers of bubbles released in nine second
nob10(t) = ActiveCell.Offset(t, 10).Value        'numbers of bubbles released in ten second


'calculation of the diffusivity of carbon dioxide as a function of temperature and time
Diff(t) = 0.000000007557 * 0.2 * Tp(t) / 292.9

'Schmidt number for 0.1 s
Sc(t) = visc / (dens * Diff(t))

'Steps of 0.1 s are required to more accurately predict growth, velocity and ascent of bubbles
```

```
For counter = 1 To 10

If y1 <= ymax Then             'growth and ascent of first group of bubbles, if they have not yet
                               'reached the headspace of the bottle

  If nob1(t) > 0 Then          'provided there are bubbles that have been generated, begin the
                               'modelling of the growth and ascent of the group of bubbles

ut1 = 2 * rb1 ^ 2 * dens * g / (9 * visc)          'velocity per 0.1 s
Re1 = 2 * rb1 * ut1 * dens / visc                           'Reynolds #
denb1 = P * 0.044 / (Rgas * Tp(t))                          'density of average bubble, kg/m^3
ab1 = 4 * Pi * rb1 ^ 2                                      'area of the average bubble surface, m^2
nb1 = P * (4 * Pi * rb1 ^ 3 / 3) / (Rgas * Tp(t))  'number of moles in the average bubble

If Re1 > 1 Then                          'velocity and Reynolds # are dependent on each other
      utp = ut1
      Rep = Re1
      Do
         Re1 = 2 * rb1 * ut1 * dens / visc

         If Re1 < 1000 Then
            c = 24 / Re1 * (1 + 0.14 * Re1 ^ 0.7)
         Else
            c = 0.445
         End If
         utn = Sqr(8 * g * rb1 * (dens - denb1) / (3 * dens * c))
         If Abs(utn - ut1) / ut1 < 0.001 Then Exit Do
         ut1 = utn
      Loop
      If Re1 <= 1 Then                   'Reynolds # still not greater than 1, after all
         ut1 = utp
         Re1 = Rep
      End If
End If

'to calculate the Sherwood #:
If Re1 <= 2 Then Sh1 = 1.01 * Re1 ^ (1 / 3) * Sc(t) ^ (1 / 3)
If Re1 > 2 And Re1 <= 48000 Then Sh1 = 2 + 0.552 * Re1 ^ 0.53 * Sc(t) ^ (1 / 3)

'Mass transfer coefficient for bubble, meters per 0.1 second:
kco21 = Sh1 * Diff(t) / (2 * rb1)
```

```
'movement of carbon dioxide into the bubble
flux1 = kco21 * (co2liq - P / (Rgas * Tp(t)))          'flux: moles / square meter / s
mtr1 = flux1 * ab1                                      'mass transfer rate for bubble: moles / s

y1 = y1 + ut1                                   'total distance travelled by bubble
nb1 = nb1 + mtr1                                'total moles per average bubble
nb1total = nb1 * nob1(t)                        'total moles in all bubbles in this "group"

  Else: y1 = 0                                  'if no bubbles are present, no growth or ascent
      nb1 = 0
End If

Else: nh = nh + nb1                                     'if bubbles reach the headspace, they join

End If


If y2 <= ymax Then              'growth and ascent of group of bubbles produced a 2 seconds

  If nob2(t) > 0 Then           'modelling equations are the same for each group of bubbles

ut2 = 2 * rb2 ^ 2 * dens * g / (9 * visc)          'velocity per 0.1 s
Re2 = 2 * rb2 * ut2 * dens / visc                          'Reynolds #
denb2 = P * 0.044 / (Rgas * Tp(t))                         'density of bubble, kg/m^3
ab2 = 4 * Pi * rb2 ^ 2                                     'area of the bubble surface
nb2 = P * (4 * Pi * rb2 ^ 3 / 3) / (Rgas * Tp(t))   'number of moles in the bubble

If Re2 > 1 Then
      utp = ut2
      Rep = Re2
      Do
         Re2 = 2 * rb2 * ut2 * dens / visc

         If Re2 < 1000 Then
            c = 24 / Re2 * (1 + 0.14 * Re2 ^ 0.7)
         Else
            c = 0.445
         End If
         utn = Sqr(8 * g * rb2 * (dens - denb2) / (3 * dens * c))
         If Abs(utn - ut2) / ut2 < 0.001 Then Exit Do
         ut2 = utn
```

```
      Loop
      If Re2 <= 1 Then
         ut2 = utp
         Re2 = Rep
      End If

End If

If Re2 <= 2 Then Sh2 = 1.01 * Re2 ^ (1 / 3) * Sc(t) ^ (1 / 3)                'Sherwood #
If Re2 > 2 And Re2 <= 48000 Then Sh2 = 2 + 0.552 * Re2 ^ 0.53 * Sc(t) ^ (1 / 3)

kco22 = Sh2 * Diff(t) / (2 * rb2)                  'Mass transfer coefficient for bubble, m/s
flux2 = kco22 * (co2liq - P / (Rgas * Tp(t)))      'for bubble, mol/m^2.s
mtr2 = flux2 * ab2                                 'mass transfer rate for ave. bubble, mol/s

y2 = y2 + ut2
nb2 = nb2 + mtr2
nb2total = nb2 * nob2(t)

  Else
     y2 = 0
     nb2 = 0

End If

Else
  nhead = nhead + nb2

End If


If y3 <= ymax Then                        'growth and ascent of 3rd group of bubbles

 If nob3(t) > 0 Then

ut3 = 2 * rb3 ^ 2 * dens * g / (9 * visc)           'velocity per 0.1 s
Re3 = 2 * rb3 * ut3 * dens / visc                           'Reynolds #
denb3 = P * 0.044 / (Rgas * Tp(t))                          'density of bubble, kg/m^3
ab3 = 4 * Pi * rb3 ^ 2                                      'area of the bubble surface
nb3 = P * (4 * Pi * rb3 ^ 3 / 3) / (Rgas * Tp(t))   'number of moles in the bubble
```

```
If Re3 > 1 Then
      utp = ut3
      Rep = Re3
      Do
         Re3 = 2 * rb3 * ut3 * dens / visc

         If Re3 < 1000 Then
            c = 24 / Re3 * (1 + 0.14 * Re3 ^ 0.7)
         Else
            c = 0.445
         End If
         utn = Sqr(8 * g * rb3 * (dens - denb3) / (3 * dens * c))
         If Abs(utn - ut3) / ut3 < 0.001 Then Exit Do
         ut3 = utn
      Loop
      If Re3 <= 1 Then
         ut3 = utp
         Re3 = Rep
      End If
End If


If Re3 <= 2 Then Sh3 = 1.01 * Re3 ^ (1 / 3) * Sc(t) ^ (1 / 3)                'Sherwood #
If Re3 > 2 And Re3 <= 48000 Then Sh3 = 2 + 0.552 * Re3 ^ 0.53 * Sc(t) ^ (1 / 3)

kco23 = Sh3 * Diff(t) / (2 * rb3)                    'Mass transfer coefficient for bubble, m/s
flux3 = kco23 * (co2liq - P / (Rgas * Tp(t)))        'for bubble, mol/m^2.s
mtr3 = flux3 * ab3                                   'mass transfer rate for bubble, mol/s

y3 = y3 + ut3
nb3 = nb3 + mtr3
nb3total = nb3 * nob3(t)

 Else: y3 = 0
     nb3 = 0

End If

Else: nh = nh + nb3

End If
```

```
If y4 <= ymax Then                          'growth and ascent of 4th group of bubbles

  If nob4(t) > 0 Then

ut4 = 2 * rb4 ^ 2 * dens * g / (9 * visc)             'velocity per 0.1 s
Re4 = 2 * rb4 * ut4 * dens / visc                             'Reynolds #
denb4 = P * 0.044 / (Rgas * Tp(t))                            'density of bubble, kg/m^3
ab4 = 4 * Pi * rb4 ^ 2                                        'area of the bubble surface
nb4 = P * (4 * Pi * rb4 ^ 3 / 3) / (Rgas * Tp(t))  'number of moles in the bubble

If Re4 > 1 Then
      utp = ut4
      Rep = Re4
      Do
         Re4 = 2 * rb4 * ut4 * dens / visc

         If Re4 < 1000 Then
            c = 24 / Re4 * (1 + 0.14 * Re4 ^ 0.7)
         Else
            c = 0.445
         End If
         utn = Sqr(8 * g * rb4 * (dens - denb4) / (3 * dens * c))
         If Abs(utn - ut4) / ut4 < 0.001 Then Exit Do
         ut4 = utn
      Loop
      If Re4 <= 1 Then
         ut4 = utp
         Re4 = Rep
      End If

End If

If Re4 <= 4 Then Sh4 = 1.01 * Re4 ^ (1 / 3) * Sc(t) ^ (1 / 3)              'Sherwood #
If Re4 > 2 And Re4 <= 48000 Then Sh4 = 2 + 0.552 * Re4 ^ 0.53 * Sc(t) ^ (1 / 3)

kco24 = Sh4 * Diff(t) / (2 * rb4)                        'Mass transfer coefficient for bubble, m/s
flux4 = kco24 * (co2liq - P / (Rgas * Tp(t)))            'for bubble, mol/m^2.s
mtr4 = flux4 * ab4                                       'mass transfer rate for bubble, mol/s
```

```
y4 = y4 + ut4
nb4 = nb4 + mtr4
nb4total = nb4 * nob4(t)

  Else
     y4 = 0
     nb4 = 0

End If

Else
  nhead = nhead + nb4

End If


If y5 <= ymax Then                        'growth and ascent of 5th group of bubbles

 If nob5(t) > 0 Then

ut5 = 2 * rb5 ^ 2 * dens * g / (9 * visc)          'velocity per 0.1 s
Re5 = 2 * rb5 * ut5 * dens / visc                     'Reynolds #
denb5 = P * 0.044 / (Rgas * Tp(t))                    'density of bubble, kg/m3
ab5 = 4 * Pi * rb5 ^ 2                                'area of the bubble surface
nb5 = P * (4 * Pi * rb5 ^ 3 / 3) / (Rgas * Tp(t))   'number of moles in the bubble

If Re5 > 1 Then
     utp = ut5
     Rep = Re5
     Do
        Re5 = 2 * rb5 * ut5 * dens / visc

        If Re5 < 1000 Then
           c = 24 / Re5 * (1 + 0.14 * Re5 ^ 0.7)
        Else
           c = 0.445
        End If
        utn = Sqr(8 * g * rb5 * (dens - denb5) / (3 * dens * c))
        If Abs(utn - ut5) / ut5 < 0.001 Then Exit Do
        ut5 = utn
     Loop
```

```
        If Re5 <= 1 Then
            ut5 = utp
            Re5 = Rep
        End If
End If


If Re5 <= 2 Then Sh5 = 1.01 * Re5 ^ (1 / 3) * Sc(t) ^ (1 / 3)                'Sherwood #
If Re5 > 2 And Re5 <= 48000 Then Sh5 = 2 + 0.552 * Re5 ^ 0.53 * Sc(t) ^ (1 / 3)

kco25 = Sh5 * Diff(t) / (2 * rb5)                        'Mass transfer coefficient for bubble, m/s
flux5 = kco25 * (co2liq - P / (Rgas * Tp(t)))            'flux for bubble, mol/m^2.s
mtr5 = flux5 * ab5                                       'mass transfer rate for bubble, mol/s

y5 = y5 + ut5
nb5 = nb5 + mtr5
nb5total = nb5 * nob5(t)

  Else: y5 = 0
      nb5 = 0

End If

Else: nh = nh + nb5

End If

 If y6 <= ymax Then                        'growth and ascent of 6th group of bubbles

 If nob6(t) > 0 Then

ut6 = 2 * rb6 ^ 2 * dens * g / (9 * visc)          'velocity per .1 s
Re6 = 2 * rb6 * ut6 * dens / visc                           'Reynolds #
denb6 = P * 0.044 / (Rgas * Tp(t))                          'density of bubble, kg/m3
ab6 = 4 * Pi * rb6 ^ 2                                      'area of the bubble surface
nb6 = P * (4 * Pi * rb6 ^ 3 / 3) / (Rgas * Tp(t))  'number of moles in the bubble

If Re2 > 1 Then
      utp = ut6
      Rep = Re6
      Do
```

```
            Re6 = 2 * rb6 * ut6 * dens / visc

            If Re6 < 1000 Then
              c = 24 / Re6 * (1 + 0.14 * Re6 ^ 0.7)
            Else
              c = 0.445
            End If
            utn = Sqr(8 * g * rb6 * (dens - denb6) / (3 * dens * c))
            If Abs(utn - ut6) / ut6 < 0.001 Then Exit Do
            ut6 = utn
          Loop
          If Re6 <= 1 Then
            ut6 = utp
            Re6 = Rep
          End If

      End If

      If Re6 <= 2 Then Sh6 = 1.01 * Re6 ^ (1 / 3) * Sc(t) ^ (1 / 3)          'Sherwood #
      If Re6 > 2 And Re6 <= 48000 Then Sh6 = 2 + 0.552 * Re6 ^ 0.53 * Sc(t) ^ (1 / 3)

      kco26 = Sh6 * Diff(t) / (2 * rb6)                   'Mass transfer coefficient for bubble, m/s
      flux6 = kco26 * (co2liq - P / (Rgas * Tp(t)))       'flux for bubble, mol/m^2.s
      mtr6 = flux6 * ab6                                  'mass transfer rate for bubble, mol/s

      y6 = y6 + ut6
      nb6 = nb6 + mtr6
      nb6total = nb6 * nob6(t)

        Else
          y6 = 0
          nb6 = 0
          volbub6 = 0
          ut6 = 0

      End If

      Else
        nhead = nhead + nb6

      End If
```

```
If y7 <= ymax Then                              'growth and ascent of 7th group of bubbles

 If nob7(t) > 0 Then

ut7 = 2 * rb7 ^ 2 * dens * g / (9 * visc)       'velocity per 0.1 s
Re7 = 2 * rb7 * ut7 * dens / visc                    'Reynolds #
denb7 = P * 0.044 / (Rgas * Tp(t))                   'density of bubble, kg/m3
ab7 = 4 * Pi * rb7 ^ 2                               'area of the bubble surface
nb7 = P * (4 * Pi * rb7 ^ 3 / 3) / (Rgas * Tp(t))  'number of moles in the bubble

If Re7 > 1 Then
      utp = ut7
      Rep = Re7
      Do
         Re7 = 2 * rb7 * ut7 * dens / visc

         If Re7 < 1000 Then
            c = 24 / Re7 * (1 + 0.14 * Re7 ^ 0.7)
         Else
            c = 0.445
         End If
         utn = Sqr(8 * g * rb7 * (dens - denb7) / (3 * dens * c))
         If Abs(utn - ut7) / ut7 < 0.001 Then Exit Do
         ut7 = utn
      Loop
      If Re7 <= 1 Then             'still not greater than 1, after all
         ut7 = utp
         Re7 = Rep
      End If
End If


If Re7 <= 2 Then Sh7 = 1.01 * Re7 ^ (1 / 3) * Sc(t) ^ (1 / 3)              'Sherwood #
If Re7 > 2 And Re7 <= 48000 Then Sh7 = 2 + 0.552 * Re7 ^ 0.53 * Sc(t) ^ (1 / 3)

kco27 = Sh7 * Diff(t) / (2 * rb7)               'Mass transfer coefficient for bubble, m/s
flux7 = kco27 * (co2liq - P / (Rgas * Tp(t)))   'for bubble, mol/m2.s
mtr7 = flux7 * ab7                              'mass transfer rate for bubble, mol/s

y7 = y7 + ut7
```

```
nb7 = nb7 + mtr7
nb7total = nb7 * nob7(t)

  Else: y7 = 0
      nb7 = 0
      volbub7 = 0
      ut7 = 0
End If

Else: nh = nh + nb7

End If


If y8 <= ymax Then                          'growth and ascent of 8th group of bubbles

  If nob8(t) > 0 Then

ut8 = 2 * rb8 ^ 2 * dens * g / (9 * visc)          'velocity per 0.1 s
Re8 = 2 * rb8 * ut8 * dens / visc                  'Reynolds #
denb8 = P * 0.044 / (Rgas * Tp(t))                 'density of bubble, kg/m3
ab8 = 4 * Pi * rb8 ^ 2                             'area of the bubble surface
nb8 = P * (4 * Pi * rb8 ^ 3 / 3) / (Rgas * Tp(t))  'number of moles in the bubble

If Re8 > 1 Then
      utp = ut8
      Rep = Re8
      Do
         Re8 = 2 * rb8 * ut8 * dens / visc         'Reynolds #

         If Re8 < 1000 Then
            c = 24 / Re8 * (1 + 0.14 * Re8 ^ 0.7)
         Else
            c = 0.445
         End If
         utn = Sqr(8 * g * rb8 * (dens - denb8) / (3 * dens * c))
         If Abs(utn - ut8) / ut8 < 0.001 Then Exit Do
         ut8 = utn
      Loop
      If Re8 <= 1 Then
         ut8 = utp
```

```
        Re8 = Rep
      End If

 End If

 If Re8 <= 4 Then Sh8 = 1.01 * Re8 ^ (1 / 3) * Sc(t) ^ (1 / 3)          'Sherwood #
 If Re8 > 2 And Re8 <= 48000 Then Sh8 = 2 + 0.552 * Re8 ^ 0.53 * Sc(t) ^ (1 / 3)

 kco28 = Sh8 * Diff(t) / (2 * rb8)              'Mass transfer coefficient for bubble, m/s
 flux8 = kco28 * (co2liq - P / (Rgas * Tp(t)))  'for bubble, mol/m^2.s
 mtr8 = flux8 * ab8                             'mass transfer rate for bubble, mol/s

 y8 = y8 + ut8
 nb8 = nb8 + mtr8
 nb8total = nb8 * nob8(t)

  Else
     y8 = 0
     nb8 = 0
     volbub8 = 0
     ut8 = 0

 End If

 Else
   nhead = nhead + nb8

 End If



 If y9 <= ymax Then                          'growth and ascent of 9th group of bubbles

  If nob9(t) > 0 Then

 ut9 = 2 * rb9 ^ 2 * dens * g / (9 * visc)          'velocity per 0.1 s
 Re9 = 2 * rb9 * ut9 * dens / visc                  'Reynolds #
 denb9 = P * 0.044 / (Rgas * Tp(t))                 'density of bubble, kg/m3
 ab9 = 4 * Pi * rb9 ^ 2                             'area of the bubble surface
 nb9 = P * (4 * Pi * rb9 ^ 3 / 3) / (Rgas * Tp(t))  'number of moles in the bubble
```

```
 If Re9 > 1 Then
       utp = ut9
       Rep = Re9
       Do
          Re9 = 2 * rb9 * ut9 * dens / visc

          If Re9 < 1000 Then
             c = 24 / Re9 * (1 + 0.14 * Re9 ^ 0.7)
          Else
             c = 0.445
          End If
          utn = Sqr(8 * g * rb9 * (dens - denb9) / (3 * dens * c))
          If Abs(utn - ut9) / ut9 < 0.001 Then Exit Do
          ut9 = utn
       Loop
       If Re9 <= 1 Then
          ut9 = utp
          Re9 = Rep
       End If
End If


If Re9 <= 2 Then Sh9 = 1.01 * Re9 ^ (1 / 3) * Sc(t) ^ (1 / 3)          'Sherwood #
If Re9 > 2 And Re9 <= 48000 Then Sh9 = 2 + 0.552 * Re9 ^ 0.53 * Sc(t) ^ (1 / 3)

kco29 = Sh9 * Diff(t) / (2 * rb9)                  'Mass transfer coefficient for bubble, m/s
flux9 = kco29 * (co2liq - P / (Rgas * Tp(t)))      'for bubble, mol/m^2.s
mtr9 = flux9 * ab9                                 'mass transfer rate for bubble, mol/s

y9 = y9 + ut9
nb9 = nb9 + mtr9
nb9total = nb9 * nob9(t)

 Else: y9 = 0
     nb9 = 0
     volbub9 = 0
     ut9 = 0
End If

Else: nh = nh + nb9
```

```
End If


If y10 <= ymax Then                          'growth and ascent of 10th group of bubbles

  If nob10(t) > 0 Then

ut10 = 2 * rb10 ^ 2 * dens * g / (9 * visc)                 'velocity per 0.1 s
Re10 = 2 * rb10 * ut10 * dens / visc                        'Reynolds #
denb10 = P * 0.044 / (Rgas * Tp(t))                         'density of bubble, kg/m3
ab10 = 4 * Pi * rb10 ^ 2                                    'area of the bubble surface
nb10 = P * (4 * Pi * rb10 ^ 3 / 3) / (Rgas * Tp(t))         'number of moles in the bubble

If Re10 > 1 Then
      utp = ut10
      Rep = Re10
      Do
         Re10 = 2 * rb10 * ut10 * dens / visc

         If Re10 < 1000 Then
            c = 24 / Re10 * (1 + 0.14 * Re10 ^ 0.7)
         Else
            c = 0.445
         End If
         utn = Sqr(8 * g * rb10 * (dens - denb10) / (3 * dens * c))
         If Abs(utn - ut10) / ut10 < 0.001 Then Exit Do
         ut10 = utn
      Loop
      If Re10 <= 1 Then
         ut10 = utp
         Re10 = Rep
      End If

End If

If Re10 <= 4 Then Sh10 = 1.01 * Re10 ^ (1 / 3) * Sc(t) ^ (1 / 3)          'Sherwood #
If Re10 > 2 And Re10 <= 48000 Then Sh10 = 2 + 0.552 * Re10 ^ 0.53 * Sc(t) ^ (1 / 3)

kco210 = Sh10 * Diff(t) / (2 * rb10)                    'Mass transfer coefficient for bubble, m/s
flux10 = kco210 * (co2liq - P / (Rgas * Tp(t)))    'for bubble, mol/m2.s
mtr10 = flux10 * ab10                              'mass transfer rate for bubble, mol/s
```

```
y10 = y10 + ut10
nb10 = nb10 + mtr10
nb10total = nb10 * nob10(t)

  Else
     y10 = 0
     nb10 = 0
     volbub10 = 0
     ut10 = 0

End If

Else
  nhead = nhead + nb10

End If

'calculation of moles added to headspace:

kprime = 8 * Diff(t) / (0.018 * Pi)                    'mass transfer coefficient at headspace
fluxhead = kprime * (co2liq - (P / (Rgas * Tp(t))))    'for headspace
mthead = fluxhead * Pi * (0.018) ^ 2 / 4               'mass transfer into headspace
nh = nh + mthead

'total moles of CO2 in the gas phase is now:
nbtotal = nb1total + nb2total + nb3total + nb4total + nb5total + nb6total + nb7total + nb8total +
nb9total + nb10total
totalmoles = nh + nbtotal

'calculation of new pressure and new volumes, which are interdependent

Pnew = totalmoles * Rgas * Tp(t) / Vo          'new pressure if volume doesn't change
'Pdiff = Pnew - P                              'difference between new and old pressures
'P = P + Pdiff                                 'best estimate of new pressure is midpoint
P = Pnew

Vo = totalmoles * Rgas * Tp(t) / P                   'new total gas volume, at new pressure
Vho = nh * Rgas * Tp(t) / P                    'new headspace volume

'calculating the new bubble radii based from the new pressure
```

```
If nob1(t) > 0 Then
volbub1 = nb1 * Rgas * Tp(t) / P
rb1 = (volbub1 * 0.75 / Pi) ^ (1 / 3)
Else
rb1 = rb1
End If

If nob2(t) > 0 Then
volbub2 = nb2 * Rgas * Tp(t) / P
rb2 = (volbub2 * 0.75 / Pi) ^ (1 / 3)
Else
rb2 = rb2
End If

If nob3(t) > 0 Then
volbub3 = nb3 * Rgas * Tp(t) / P
rb3 = (volbub3 * 0.75 / Pi) ^ (1 / 3)
Else
rb3 = rb3
End If

If nob4(t) > 0 Then
volbub4 = nb4 * Rgas * Tp(t) / P
rb4 = (volbub4 * 0.75 / Pi) ^ (1 / 3)
Else
rb4 = rb4
End If

If nob5(t) > 0 Then
volbub5 = nb5 * Rgas * Tp(t) / P
rb5 = (volbub5 * 0.75 / Pi) ^ (1 / 3)
Else
rb5 = rb5
End If

If nob6(t) > 0 Then
volbub6 = nb6 * Rgas * Tp(t) / P
rb6 = (volbub6 * 0.75 / Pi) ^ (1 / 3)
Else
rb6 = rb6
End If
```

```
If nob7(t) > 0 Then
volbub7 = nb7 * Rgas * Tp(t) / P
rb7 = (volbub7 * 0.75 / Pi) ^ (1 / 3)
Else
rb7 = rb7
End If

If nob8(t) > 0 Then
volbub8 = nb8 * Rgas * Tp(t) / P
rb8 = (volbub8 * 0.75 / Pi) ^ (1 / 3)
Else
rb8 = rb8
End If

If nob9(t) > 0 Then
volbub9 = nb9 * Rgas * Tp(t) / P
rb9 = (volbub9 * 0.75 / Pi) ^ (1 / 3)
Else
rb9 = rb9
End If

If nob10(t) > 0 Then
volbub10 = nb10 * Rgas * Tp(t) / P
rb10 = (volbub10 * 0.75 / Pi) ^ (1 / 3)
Else
rb10 = rb10
End If

Next counter


Pout = P / 1013.25                          'pressure, converted back to atm

'Send output data to a spreadsheet
ActiveCell.Offset(t, 14).Value = Pout       'pressure
ActiveCell.Offset(t, 15).Value = totalmoles 'moles of carbon dioxide in gas phase

Next t
End Sub
```

Appendix 19 a. Experimental and predicted (Appendix 16) pressures (atm) for headspace recoveries and the difference of the predicted from experimental values.

Replicate 1:

Time (s)	Experimental	Predicted	% Difference
0	3.0759072	2.994195	2.66
1	3.09927	3.018495	2.61
2	3.11225	3.050216	1.99
3	3.117	3.086111	0.99
4	3.12523	3.123446	0.06
5	3.13302	3.160297	0.87
6	3.14303	3.188215	1.44
7	3.1537874	3.233309	2.52
8	3.16158	3.262198	3.18
9	3.16936	3.289425	3.79
10	3.17715	3.315944	4.37

Replicate 3:

Time (s)	Experimental	Predicted	% Difference
0	2.69689	2.645037	1.92
1	2.7020824	2.766593	2.39
2	2.7172745	2.766731	1.82
3	2.7072745	2.799347	3.40
4	2.7098705	2.802645	3.42
5	2.7098705	2.805154	3.52
6	2.712467	2.808216	3.53
7	2.7124665	2.813339	3.72
8	2.7124665	2.817451	3.87
9	2.71506	2.822014	3.94
10	2.71506	2.826074	4.09

Replicate 5:

Time (s)	Experimental	Predicted	% Difference
0	1.8402088	1.854819	0.79
1	1.8739569	1.902938	1.55
2	1.910301	1.934172	1.25
3	1.936261	1.944934	0.45
4	1.9622211	1.96243	0.01
5	1.9829891	1.984121	0.06
6	2.006353	2.012563	0.31
7	2.024525	2.044373	0.98
8	2.0504852	2.083056	1.59
9	2.0634653	2.125139	2.99
10	2.0816373	2.170797	4.28

Appendix 19 b. Total moles of carbon dioxide in the gas phase (bubbles + headspace) as predicted by the computer simulation program (Appendix 16)

time (s)	replicate 1	replicate 3	replicate 5
0	0.0007908	0.0009221	0.0005695
1	0.0007972	0.0009645	0.0005843
2	0.0008056	0.0009645	0.0005939
3	0.0008151	0.0009759	0.0005972
4	0.0008249	0.0009771	0.0006026
5	0.0008347	0.0009779	0.0006092
6	0.000842	0.000979	0.000618
7	0.0008539	0.0009808	0.0006277
8	0.0008616	0.0009822	0.0006396
9	0.0008688	0.0009838	0.0006525
10	0.0008758	0.0009852	0.0006666

Appendix 20. Tracking of bubbles from a series of images obtained from the video tapes of low gushing ciders. Bubble numbers were assigned arbitrarily. Analyses were not always at equally spaced time intervals (s), but can be calculated from the frame number, as the rate of recording was 30 frames per second. "Frame" refers to the frame number within the video clip. Pressure is in atm. Ascent indicates the distance travelled from the position in the previously examined frame; for example, the distance travelled by bubble no. 1, in A below, between frames 16 and 19 (equivalent to 0.1 seconds) is 1.11 cm. "Height" indicates the distance of the bubble above the sediment.

A. Treatment B, replicate 4 (low gush)

Bubble no.	Time (s)	Pressure	Camera	Frame	Bubble radius (mm)	Velocity (cm/s)	Ascent (cm)	Height (cm)
1	0	2.70	bottom	16	0.6	11.5	---	5.8
				19	0.6	10.8	1.11	7.0
				21	0.7	12.5	1.06	8.0
2	1	3.08	bottom	49	0.6	13.2	---	3.8
				52	0.6	11.8	1.32	3.9
				55	0.6	12.1	1.18	5.1
				61	0.7	---	2.42	7.5
3 (at cloud front)	1	3.08	bottom	49	0.2	2.5	---	3.4
				52	0.2	2.5	0.32	3.7
				55	0.2	4.7	0.93	4.6
				58	0.2	5.0	0.85	5.5
	2	3.32		65	0.2	4.4	1.01	6.5
				68	0.2	---	0.45	6.9

Appendix 20. continued.

A. Treatment B, replicate 4 (low gush): continued.

Bubble no.	Time (s)	Pressure	Camera	Frame	Bubble radius (mm)	Velocity (cm/s)	Ascent (cm)	Height (cm)
4 (back end of cloud)	3	3.68	bottom	103	0.2	4.6	---	5.4
				106	0.2	---	0.46	5.4
5	8	4.49	bottom	256	0.2	5.2	---	6.1
				259	0.2	---	0.52	6.6
6	9	4.52	bottom	270	0.2	5.1	---	6.3
				273	0.2	---	0.51	6.8

Appendix 20. continued.

B. Treatment B, replicate 5 low gush.

Bubble no.	Time (s)	Pressure	Camera	Frame	Bubble radius (mm)	Velocity (cm/s)	Ascent (cm)	Height (cm)
1	2	3.06	bottom	82	0.2	2.4	---	5.7
				83	0.2	---	0.1	5.8
2 (at cloud front)	3	3.44	bottom	105	0.2	5.6	---	3.0
				111	0.2	4.8	1.1	4.2
				117	0.2	6.5	1.0	5.1
				123	0.2	---	1.3	6.4

Appendix 21. Tracking bubbles through images obtained from video tapes of high gushing ciders. Bubble number assignment was arbitrary. The high bubble density caused difficulties in tracking the bubbles for more than one or two frames. "Frame" refers to the frame number within the video clip. Pressure is in atm. Ascent indicates the distance travelled from the position in the previously examined frame. "Height" indicates the distance of the bubble above the sediment.

A. Treatment C, replicate 6 (high gush)

Bubble no.	Time (s)	Pressure	Camera	Frame	Bubble radius (mm)	Velocity (cm/s)	Ascent (cm)	Height (cm)
1 (above cloud)	2	2.44	bottom	67	0.2	3.3	---	6.59
				68	0.2	---	0.11	6.70
2 (in cloud)	5	3.98	bottom	150	0.2	5.1	---	5.47
				151	0.2	---	0.17	5.64
3 (in cloud)	7	4.29	bottom	210	0.2	5.1	---	4.49
				211	0.2	---	0.17	4.53
4 (in cloud)	8	4.36	bottom	240	0.2	5.1	---	4.44
				241	0.2	---	0.17	4.61

Appendix 21. continued.

B. Treatment C, replicate 6 (high gush)

Bubble no.	Time (s)	Pressure	Camera	Frame	Bubble radius (mm)	Velocity (cm/s)	Ascent (cm)	Height (cm)
1 (in cloud)	1	4.239	bottom	76	0.2	3.8	---	3.82
				77	0.2	---	0.13	3.94

Appendix 22.

Non-gushing and gushing ciders: initial mass transfer rate of carbon dioxide from the liquid to the gas phase. "New moles" indicates the overall mass transfer of carbon dioxide, per second, immediately following pressure release. "Delta P" represents the change (increase) in the ratio of the measured pressure to the original (before pressure release) pressure. Pectin (ug) is expressed as the total (all three fractions) contained in the sediment, per bottle.

Treatment	Replicate	New moles	Delta P	Sediment Pectin (ug)
A	1	2.71E-05	3.72E-01	2004
A	2	1.11E-05	3.55E-01	2004
A	3	1.37E-05	3.34E-01	1583
A	4	9.34E-06	3.90E-01	1583
A	5	7.10E-06	4.79E-01	874
A	6	8.06E-06	4.10E-01	874
A	7	1.51E-05	3.94E-01	3328
A	8	4.05E-05	4.37E-01	3328
A	9	1.03E-05	5.03E-01	2399
A	10	1.26E-05	6.06E-01	1165
A	11	1.40E-05	5.39E-01	554
A	12	6.11E-06	5.18E-01	458
B	1	1.61E-05	2.20E-01	1929
B	2	6.73E-06	2.89E-01	1929
B	3	4.39E-05	3.70E-01	1929
B	4	0.00015	4.70E-01	24853
B	5	5.49E-05	4.90E-01	24853
C	2	1.65E-04	8.12E-01	13600
C	3	0.00029	4.95E-01	26147
C	4	4.74E-04	6.38E-01	26147
C	6	3.45E-05	4.27E-01	10067
C	7	2.99E-04	4.57E-01	47666
C	8	1.52E-04	2.73E-01	47666

Appendix 23. Raw data and analysis of variance (ANOVA) table for average bubble frequencies during the first three minutes after pressure release. Frequencies are expressed as numbers of bubbles generated per second in one bottle.

A. Raw data obtained from analysis of the video tapes.

Treatment	Replicate	Frequency
A	1	25.5
A	2	107.9
A	3	40.0
A	4	24.4
A	5	2.0
A	6	9.2
A	7	10.4
A	8	7.9
A	9	24.4
A	10	79.5
A	11	1276.0
A	12	41.0
A	13	173.0
B	1	51.0
B	2	221.0
B	3	1383.0
B	5	111.0
C	2	3414.0
C	3	960.0
C	4	3869.5
C	5	11.0
C	6	2980.0
C	7	3537.9
C	8	1826.2

Appendix 23. continued.

B. Analysis of variance (ANOVA) table for bubble frequencies, averaged over the first 3 minutes following pressure release. The ANOVA table contains mean squares for the factors as determined by SAS. (* = significant at $\alpha = 0.05$)
df = degrees of freedom

Source of Variation	df	Frequency
Treatment	2	11708064 *
Error	21	740300
Total	23	