AN ABSTRACT OF THE THESIS OF

Carmen A. Velasco for the degree of Master of Science in Chemical Engineering presented on August 20, 2007.

Title: Microwave Extraction of Peppermint Oil and Comparison to the Current Practice of Steam Extraction.

Abstract approved:

David Hackleman

The increase of diesel fuels and natural gas has increased the energy cost of the mint oil extraction industry in the Willamette Valley. In this study the energy evaluation of a distillation facility in Oregon is considered. Solvent free microwave extraction of peppermint oil is introduced as a new technique to obtain the essential oils.

Technology from approximately fifty years ago was the common characteristic of all the farms visited at the beginning of this research. Three sets of data from the Setniker farm were collected; information from all the possible sample points were recorded to then evaluate the energy cost of pound of oil extracted. It was found that on average the energy usage cost is $1.26 per pound of oil obtained; the maximum fraction of oil recovered was reported to be 20% of all the oil available from the plant. Suggestions to improve the current setup without major modifications were done based on the findings of this part of this work.

Solvent free microwave extraction has been used as an analytical tool; the advantages and disadvantages on extraction of essential oils, specifically on the peppermint oil

extraction, were investigated in the second objective of this work. Dry peppermint hay was placed in a 100 mL distillation flask. Three different power settings were explored, 1120 W, 649W and 518W; the extraction time was the other variable investigated. Four combinations of the power applied to the plant material were also studied, 1120W-649W and 1120-518W, starting at 1.5 minutes and 2 minutes on the higher power setting and varying the lower power level. A Galanz WP700L17-8 (2.45 GHz) microwave was modified to direct the vapors to a condenser and which then allowed the liquids to be collected and then analyzed. The microwave cavity was modified with consideration of all safety precautions. The composition of the oil extracted was analyzed by gas chromatography. With the modest optimization of process performed, roughly three times more oil was extracted compared to the traditional process at an energy cost of approximately 3% lower than the energy cost from the steam distillation facilities.

The quality of the oil varies in some of its major components. One example is menthol which was 4% less than the ideal standard for peppermint oil. The microwave extracted material also was high in menthofuran content, 230% higher than the ideal standards created from blending. While in this study this fluctuation was shown to be overshadowed by normal mint crop oil composition variance, further investigation of how this behavior can affect the mint industry is recommended.

In general the solvent microwave extraction is more efficient than the steam distillation process. The microwave system was able to extract more essential oils than the steam process and do so in 3.25 minutes of extraction time. In comparison, the steam extraction process requires roughly 1.5 hours. This work offers the foundation for development of a pilot scale microwave system and an associated overall plant operations cost assessment.

Microwave Extraction of Peppermint Oil and Comparison to the Current Practice of Steam Extraction

by
Carmen A. Velasco

A THESIS

submitted to

Oregon State University

in partial fulfillment of
the requirements for the
degree of

Master of Science

Presented August 20, 2007
Commencement June 2008

Master of Science thesis of Carmen A. Velasco presented on August 20, 2007

APPROVED:

Major Professor, representing Chemical Engineering

Chair of the School of Chemical, Biological and Environmental Engineering

Dean of the Graduate School

I understand that my thesis will become part of the permanent collection of Oregon State University libraries. My signature below authorizes release of my thesis to any reader upon request.

Carmen A. Velasco, Author

ACKNOWLEDGEMENTS

I would like to thank my advisor Dr. David Hackleman for his constant support and for sharing his knowledge with me; his patience and guidance were priceless.

I would thank my family; they are my strength and my motivation. I especially would like to thank my mom; her support and understanding during this part of my life was immeasurable. I would like to thank Eilleen Hebert for her friendship and encouragement; they are invaluable. A special thank you to Amanda Grill, Zack Smith, Bill Brooks and Lane Edwards for being part of this project!

I would like to thank the Setniker family for letting me work at their facility and for enabling me to collect data. I would like to thank Labbeemint for helping with the GC analysis. Finally I would like to thank the Mint Industry Research Council for supporting this project.

TABLE OF CONTENTS

Page

1. Introduction 1

2. Literature Review 2
   2.1 Essential Oils 2
   2.2 Peppermint Oil Production and Storage 2
   2.3 Peppermint Essential Oil Composition 6
   2.4 Traditional Extraction Techniques of Essential Oils 10
   2.5 Peppermint Oil in Oregon 15
   2.6 Solvent Free Microwave Extraction 18

3. Materials 21
   3.1 Microwave Modification Design 21
   3.2 Microwave Reactor Design 22

4. Methods 25
   4.1 Experimental Design 25
   4.2 Sample Preparation Prior to Extraction 26
   4.3 Procedures after Extraction 27
   4.4 Quality Analysis 28

5. Results: Setniker Facility Evaluation 31
   5.1 Peppermint Hay Preparation 31
   5.2 Steam Production 31
   5.3 Extraction Process 36
   5.4 Condensation and Separation Process 40
   5.5 Distillate Composition 43
   5.6 Redistill Composition 45
   5.7 Total Peppermint Oil Extracted 46
   5.8 Boiler Feed Tank 49
   5.9 Conclusions and Recommendations to improve current operation 51

TABLE OF CONTENTS (Continued)

Page

6. Results: Solvent Free Microwave Distillation 55
6. 1 Material Balance 55
6.2 Energy Balance 56
6.3 Maximum Operating Conditions 58
6.4 Extractions at 1120 Watts (High Power) 58
6.5 Extractions at 697 Watts (Medium Power) 66
6.6 Extractions at 518 Watts (Medium Low Power) 73
6.7 Two Extraction Step (1.5 minutes at 1120 Watts - Medium) 79
6.8 Two Extraction Step (1.5 minutes at 1120 Watts- MediumLow) 86
6.9 Two Extraction Step (2 minutes at 1120 Watts- Medium) 92
6.10 Two Extraction Step (2 minutes at 1120 Watts- MediumLow) 98
6.11 Comparison of best extraction times at different power settings 104
6.12 Comparison of extraction efficiency using different peppermint hay 111

7. Conclusions 116

8. Future Work 121

9. Bibliography 123

APPENDICES 126

LIST OF FIGURES

Figure Page

2. 1Transmission electron micrograph of a peppermint peltate glandular trichome…..3
2. 2 Scanning electron micrograph 4
2. 3 Monoterpene biosynthesis in the secretory cells of peppermint leaves 7
2. 4 Hydro-Distillation Facility 11
2. 5 Water/Steam Distillation Facility 12
2. 6 Vapor Pressure-Boiling Point Relationship 14
2. 7 Steam Distillation Facility 15
2. 8 Distillation Facility with stationary tub open drip-type condenser 16
2. 9 Distillation unit with a portable tub and a submerged condenser 17
2. 10 Cardamom seed: (1) without any treatment, (2) after hydro-distillation, (3) after solvent free microwave extraction 20

3. 1 Microwave Oven 21
3. 2 Microwave Reactor Parts by Hidden View Glassworks 22
3. 3 Microwave Reactor Diagram 23
3. 4 Microwave Extractor Picture 24

5. 1 Boiler E-110 Temperature 32
5. 2 Boiler E-130 Temperature 33
5. 3 E-110 Pressure 33
5. 4 E-120 Pressure 34
5. 5 E-130 Boiler Pressure 34
5. 6 Boiler E-120 Internal Temperature based on Pressure Readings 36
5. 7 Mint Tub Dimensions 37
5. 8 Mint hay inside the mint tub 37
5. 9 External Wall Tub Temperature 39
5. 10 Internal Distillation Tub Temperature 39
5. 11 Mint Tub Internal Pressure 40
5. 12 Cooling H2O leaving the condenser 41

LIST OF FIGURES (Continued)

Figure Page

5. 13 Condensate Temperature Profile 42
5. 14 Separation Can Temperature 43
5. 15 Condensate Composition 44
5. 16 Condensate Flow rate 44
5. 17 Oil Flow rate 44
5. 18 Oil Recovered by the Redistill Unit 46
5. 19 Mass of Peppermint Oil Recovered 47
5. 20 Energy Cost (Trial 2) 48
5. 21 Energy Cost (Trial 3) 48
5. 22 Boiler Feed Tank Temperature (top) 49
5. 23 Boiler Feed Tank Temperature (bottom) 50

6. 1 Breakthrough Time vs. Extraction Time relationship (1120 W) 59
6. 2 Final Temperature of 1120 W Process 60
6. 3 Percentage of Oil Extracted (1120 W) 60
6. 4 Percentage of Water Extracted (1120 W) 61
6. 5 Mass Balance on the Liquid Phase (1120 W) 62
6. 6 Cineol, Menthol and Menthone Composition (1120 W) 63
6. 7 Neomenthol, Isomenthol and Esters Composition (1120 W) 63
6. 8 Germacrene-d, Terpenen-4-ol and Furan Composition(1120 W) 64
6. 9 Limonene, Pulegone and t-Sabine Hydrate Composition (1120 W) 64
6. 10 Breakthrough Time vs. Extraction Time relationship (697 W) 66
6. 11 Final Temperature of 697 W Process 67
6. 12 Percentage of Oil Extracted (697 W) 68
6. 13 Percentage of Water Extracted (697 W) 68
6. 14 Mass Balance on the Liquid Phase (697 W) 69
6. 15 Cineol, Menthol and Menthone Composition (697 W) 70
6. 16 Neomenthol, Isomenthol and Esters Composition (697 W) 70
6. 17 Germacrene-d, Terpenen-4-ol and Furan Composition (697 W) 71

LIST OF FIGURES (Continued)

Figure Page

6. 18 Limonene, Pulegone and t-Sabine Hydrate Composition (697 W)..... 71
6. 19 Breakthrough Time vs. Extraction Time relationship (518 W) 73
6. 20 Final Temperature of 518 W Process..... 74
6. 21 Percentage of Oil Extracted (518 W)..... 74
6. 22 Percentage of Water Extracted (518 W) 75
6. 23 Mass Balance on the Liquid Phase (518 W) 76
6. 24 Cineol, Menthol and Menthone Composition (518 W) 76
6. 25 Neomenthol, Isomenthol and Esters Composition (518 W) 77
6. 26 Germacrene-d, Terpenen-4-ol and Furan Composition (518 W)..... 77
6. 27 Limonene, Pulegone and t-Sabine Hydrate Composition (518 W)..... 78
6. 28 Breakthrough Time vs. Extraction Time relationship (1.5H-xM) 79
6. 29 Final Temperature of 1.5H-xM process..... 80
6. 30 Percentage of Oil Extracted (1.5H-xM)..... 81
6. 31 Percentage of Water Extracted (1.5H-xM) 82
6. 32 Mass Balance on the Liquid Phase (1.5H-xM)..... 82
6. 33 Cineol, Menthol and Menthone Composition (1.5H-xM) 83
6. 34 Neomenthol, Isomenthol and Esters Composition (1.5H-xM) 83
6. 35 Composition Germacrene-d, Terpenen-4-ol and Furan (1.5H-xM)..... 84
6. 36 Limonene, Pulegone and t-Sabine Hydrate Composition (1.5H-xM)..... 84
6. 37 Breakthrough Time vs. Extraction Time relationship (1.5H xML) 86
6. 38 Final Temperature 1.5H-xML process..... 87
6. 39 Percentage of Oil Extracted (1.5H xML)..... 88
6. 40 Percentage of Water Extracted (1.5H xML) 88
6. 41 Material Balance on the Liquid (1.5H xML) 89
6. 42 Cineol, Menthol and Menthone Composition (1.5H xML) 89
6. 43 Neomenthol, Isomenthol and Esters (1.5H xML)..... 90
6. 44 Germacrene-d, Terpenen-4-ol and Furan (1.5H xML) 90
6. 45 Limonene, Pulegone and t-Sabine Hydrate Composition (1.5H xML) 91
6. 46 Breakthrough Time vs. Extraction Time relationship (2H-xM) 92

LIST OF FIGURES (Continued)

Figure Page

6. 47 Final Temperature 2H-xM process 93
6. 48 Percentage of Oil Extracted (2H-xM) 93
6. 49 Percentage of Water Extracted (2H-xM) 94
6. 50 Material Balance on the Liquid (2H-xM) 95
6. 51 Cineol, Menthol and Menthone Composition (2H-xM) 95
6. 52 Neomenthol, Isomenthol and Esters Composition (2H-xM) 96
6. 53 Germacrene-d, Terpenen-4-ol and Furan Composition (2H-xM)..... 96
6. 54 Limonene, Pulegone and t-Sabine Hydrate Composition (2H-xM)..... 97
6. 55 Breakthrough Time vs. Extraction Time relationship (2H-xML) 98
6. 56 Final Temperature 2H-xML process 99
6. 57 Percentage of Oil Extracted (2H-xML)..... 99
6. 58 Percentage of Water Extracted (2H-xML) 100
6. 59 Mass Balance on the Liquid Phase (2H-xML)..... 100
6. 60 Cineol, Menthol and Menthone Composition (2H-xML) 101
6. 61 Neomenthol, Isomenthol and Esters Composition (2H-xML) 101
6. 62 Germacrene-d, Terpenen-4-ol and Furan Composition (2H-xML) 102
6. 63 Limonene, Pulegone and t-Sabine Hydrate Composition (2H-xML) 102
6. 64 Percentage of Oil Extracted (Best Extraction Settings) 104
6. 65 Percentage of Water Extracted (Best Extraction Settings) 105
6. 66 Mass Balance on the Liquid Phase (Best Extraction Settings) 106
6. 67 Cineol, Menthol and Menthone Composition (Best Extraction Settings)..... 107
6. 68 Neomenthol, Isomenthol and Esters Composition (Best Extraction Settings) . 108
6. 69 Limonene, Pulegone and t-Sabine Hydrate Composition (Best Extraction Settings) 108
6. 70 Germacrene-d, Terpenen-4-ol and Furan Composition (Best Extraction Settings) 109
6. 71 Comparison of Power Used and Needed by the Microwave System..... 110
6. 72 Percentage of Power Needed 111
6. 73 Comparison of percentage of oil extracted from different peppermint hay….. 112

LIST OF FIGURES (Continued)

Figure Page

6. 74 Comparison of percentage of water extracted from different peppermint hay . 113

6. 75 Cineol, Menthol and Menthone Composition (Comparison different hay) 113

6. 76 Germacrene-d and Furan Composition Composition (Comparison different hay) 114

6. 77 Limonene, Pulegone and t-Sabine Hydrate Composition Composition (Comparison different hay) 114

6. 78 Neomenthol, Isomenthol and Esters Composition Composition (Comparison different hay) 115

7. 1 SEM Peppermint leaf prior to extraction 117

7. 2 SEM Peppermint leaf image after microwave extraction 118

8. 1 Comparison of experimental data to theoretical model 122

LIST OF TABLES

Table Page

2. 1 Major monoterpene constituents of peppermint leaves 8

4. 1 Average Power Delivered 25
4. 2 DOE of Single Step Processes 25
4. 3 DOE of Two Step Processes Starting with 1.5 min at High Power 25
4. 4 DOE of Two Step Processes Starting with 2 min at High Power 26
4. 5 TOC experimental design 26
4. 6 GC Method and Specifications 29

5. 1 Data Summary..... 50
5. 2 Opportunities of savings using insulation on the pipes..... 51
5. 3 Opportunities of savings using insulation on the tubs 52

6. 1 Maximum Operating Conditions 58
6. 2 Composition Variation with respect to the Standard (1120 W)..... 65
6. 3 Composition Variation with respect to the Standard (697 W)..... 72
6. 4 Composition Variation with respect to the Standard (518 W)..... 78
6. 5 Composition Variation with respect to the Standard (1.5H-xM)..... 85
6. 6 Composition Variation with respect to the Standard (1.5H xML)..... 91
6. 7 Composition Variation with respect to the Standard (2H-xM)..... 97
6. 8 Composition Variation with respect to the Standard (2H-xML) 103
6. 9 Composition Variation with respect to the Standard (Best Extraction Settings) 109
6. 10 Comparison to the ideal mint oil sample of the extractions done at 3 minutes and 1120 Watts using hay from different farms 115

LIST OF APPENDICES

Appendix Page

A. Microwave Choke Design 127

B. Typical Chromatogram Of Willamette Valley Peppermint Oil 128

C. Total Organic Carbon Method 131

D. Setniker Facility Flow Sheet 132

E. Mint Tub Heat Loss Calculations 133

F. Pipes Heat Loss Calculations 135

G. Experimental Data and Calculations 136

Microwave Extraction of Peppermint Oil and Comparison to the Current Practice of Steam Extraction

1. Introduction

Peppermint farming has been a tradition in the northwest, especially in the Willamette Valley of Oregon. For nearly 120 years American farmers have used steam distillation to extract the essential oils from the peppermint hay. The extracted oil is then refined and blended before going into products from toothpaste to chewing gum.

The rising costs of natural gas and diesel have also increased the mint still operating costs in the past few years, cutting the profits and placing a considerable burden on operators. The intention of this research project was to find opportunities to make the peppermint oil extraction industry more efficient. The first objective was to assess the energy usage by the Oregon mint stills. Valuable data was collected at the Setniker mint still during the harvest of 2006 to perform mass and energy balance calculations in order to identify some opportunities to save resources and optimize the current operations. The second objective was to investigate a new extraction method that might be more environmentally friendly and more cost effective than the current operations used by the Oregonian mint farmers.

2. Literature Review

2.1 Essential Oils

Nowadays forage and fiber crops are not the only species considered for their agricultural and trade significance; plants whose secondary metabolites are extremely valuable due to their aromatic characteristics (Hay, Waterman 1993). Distilled volatile oils have been used since ancient times for culinary, perfumery and pharmaceutical purposes (Guenther 1949). In fact the world trade of essential oils is expected to continue expanding in the future, as a consequence of the growing number and preferences of consumers and the wider spectrum of the uses of these compounds (Sangwan, Farooqi 2001).

Volatile oils are obtained mainly from plants which belong to the labiates family, which is also known as “the mint family”. The labiate family includes around 200 genera and between 2000 and 5000 species of aromatic herbs; this family is one of the most highly evolved plant families with a world-wide distribution (Weiss 1997).

Because of its pleasant flavor and aroma and its cooling and anesthetic effect peppermint oil is used in many pharmaceutical, health care and cleaning products. This essential oil is used on cosmetics, teas, confectionary goods and tobacco products.

2.2 Peppermint Oil Production and Storage

Volatile oils are synthesized, stored and released by a variety of epidermal or mesophyl structures, whose morphology is a characteristic of the taxonomic group (O. GASIC 1987).These epidermal structures are distributed on the plant leaves, roots, stems, flowers and fruit. The epidermal structures include: oil cells, secretory glands, secretory ducts and trichomes (glandular hairs) (Maffei, Chialva et al. 1989). Labiates carry a great diversity of epidermal hairs which store volatile oils; it is known that glandular trichomes vary in morphology between species and it is been proved that

more than one gland type can be present on a single leaf but most are either capitate or peltate (Croteau and Hooper 1978).

The peppermint essential oil are produced and accumulated in the peltate glandular trichomes located on the aerial parts of the peppermint plant (Turner, Gershenzon et al. 2000). The epidermal oil glands are formed by eight secretory cells, radially distributed, in which the essential oil monoterpenes are produced (Croteau, Davis et al. 2005), (Turner, Gershenzon et al. 2000). Figure 2.1 shows how these cells sit upon a single stalk cell (ST) and a basal cell (B) that is embedded in the surface; the secretory cells (S) are surmounted by a shared subcuticular cavity (SC) into which the oil is secreted and stored (Turner, Gershenzon et al. 2000).

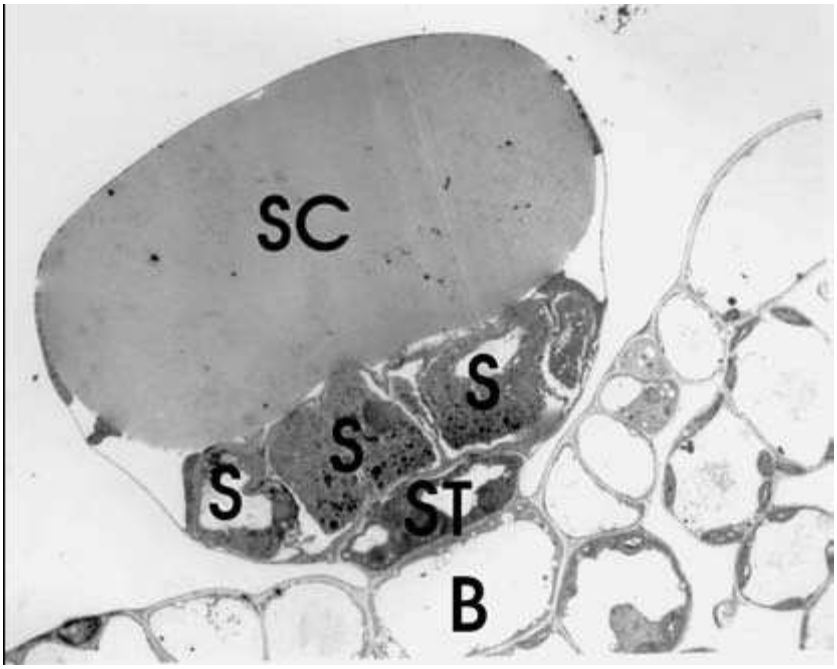


Figure 2. 1 Transmission electron micrograph of a peppermint peltate glandular trichome (Turner, Gershenzon et al. 2000)

In general the glandular trichome is made up of a basal cell which is located in the epidermis; a single head cell *capitate trichome* and a more complex head of three to ten cells *peltate trichome* (Burbott and Loomis 1969) . These two important groups of trichomes can be subdivide in smaller groups according to the number of stalk cells and whether the basal is continuous with the epidermal surface or sunk in an

epidermal pit. (Bruni and Modenesi 1983) . Figure 2.2 shows also the epidermal oils glands in the leaf where (P) are the peltate glandular trichomes where menthol and related monoterpenes are produced and accumulated that are interspersed with several smaller capitate trichomes (C) and non-glandular hairs (NG) that do not produce monoterpenes (Croteau, Davis et al. 2005).

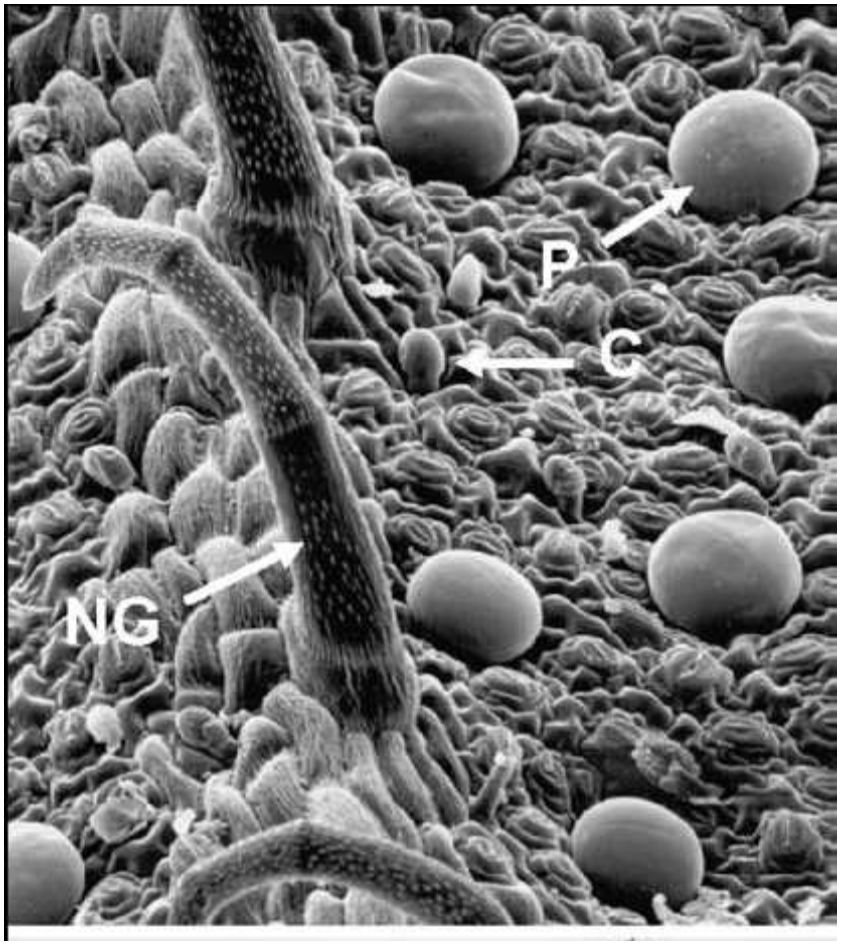


Figure 2. 2 Scanning electron micrograph (Croteau, Davis et al. 2005).

In the past it was thought that the trichome density decreased on both surfaces as the peppermint leaf expanded, however the total number of trichomes increased more rapidly on the abaxial surface. (Croteau and Hooper 1978) It was also discussed that young peppermint leaves have higher content of monoterpenes by weight than older leaves; which indicates that the monoterpene accumulation in the plant is more sensitive to the age of the leaf than to the size of the leaf. Literature suggests that the

oil glands of peppermint fill up when the leaves are young and unexpanded and synthesis does not occur in mature leaves (Loomis 1967). More recent studies state that trichomes growth initiate at different stages in the leaf development process, the creation and filling of oil reservoirs appear to be complete for all peltate trichomes by the time the leaf is fully expanded (Croteau and Winters 1982). Modern results report that peppermint peltate glands continue to grow until the leaf expansion process has been completed. Approximately 8000 peltate glands per leaf are observed once the plant has reached maturity (Croteau, Davis et al. 2005).

Oil storage capacity varies amongst trichomes and species. In peppermint the upper limit is near to 10 μL of oil extracted per individual peltate glands which have an approximate diameter of 90 μm (Denny 1991), (Croteau and Wildung 2005).

Once these reservoirs are filled with oil, it is not likely to be lost to the surrounding environment due to evaporation unless the wax-coated cuticle is physically damaged (Croteau and Wildung 2005). There is evidence that monoterpenes evaporate at a very low rate if the wax coated cells are not damaged. Less than 10% monoterpene loss was observed over fourteen months when dried peppermint hay was stored at room temperature; no change on the oil composition was found either (Burbott and Loomis 1969). This information was confirmed when oil glands of peppermint remained filled for several years after being frozen in air-dried state (Maffei, Chialva et al. 1989). Research reaffirms that the oil cells are coated by a resinous film which protects the oil from evaporation. This membrane seems to be broken by mechanical forces or by high temperatures (Guenther 1949).

The yield of oil per weight of plant material depends entirely upon the environment, the stage of dryness of the cut herb, and the plant development. It varies approximately from 0.3% to 0.4% per cent but it might be as high as 1% (Guenther 1949). According to Dr. Rod Croteau the fraction of oil in the plant could go as high as 2% percent by weight.

2.3 Peppermint Essential Oil Composition

Essential oils have several compounds which give the characteristic odor and taste, but they are mainly formed by terpenes. Terpene compounds are the constituent of labiates which provide the strongest aroma characteristics to the essential oils (Martinkus and Croteau 1981) Terpenoids generate from different primary metabolic precursors and through biosynthetic routes (Sangwan, Farooqi et al. 2001).

The building block of terpenes and terpenoids is the hydrocarbon isoprene, CH2=C(CH3)-CH=CH2 (Smith 1976). Terpenes are hydrocarbons with the molecular formula: (C5H8)n, they are classified according to the number of isoprene units that their molecule has. The most common types of terpenes are: monoterpenes (2), sesquiterpenes (3), diterpenes (4), sesterterpenes (5), triterpenes (6) and tetraterpenes (8) (Hay and Waterman 1993). Over a hundred monoterpenes are known primarily as the components of essential oils, they function in the crop as growth inhibitors, insecticidal principles and/or chemical attractants. (Smith 1976) This could be a reason why terpenoid levels in the plant can vary due to environmental changes such as temperature, mineral status of the substrate, etc. (Jean 1994).

From the economic standpoint, monoterpenes are the most important constituent of peppermint. As it was said before they accumulate in glandular trichomes on the epidermis of peppermint leaves (Gershenzon, McConkey et al. 2000). These chemical compounds are characterized because of their texture and aroma; they are colorless, lipophilic and volatile substances that have been implicated as defenses against herbivores and pathogens (Hay and Waterman 1993).

All monoterpenes of peppermint are derived from the methyl erythritol phosphate pathway (MEP). Menthol is the final product of the eight-step pathway from primary metabolism; however the rest of the monoterpenes present in peppermint oil are residual products from the series of enzymatic reactions of the pathway (Croteau and Wildung 2005),(Croteau, Davis 2005). Figure 2.3 shows the eight step pathway of

menthol in peppermint oil. ”The enzymatic steps are catalyzed by: (1) geranyl diphosphate synthase (GPPS), (2) (-)-(4S)-limonene synthase, (3) cytochrome (-)-limonene-3-hydroxylase, (4) (-)-trans-isopiperitenol dehydrogenase, (5) (-)-isopiperitenone reductase, (6) (+)-cis-isopulegone isomerase, (7) (+)-pulegone reductase (PR), (8) (-)-menthone reductase (MR), and (9) cytochrome P450 (+)-menthofuran synthase (MFS). The boxed MEP Pathway is the multistep methyl erythritol phosphate (MEP) pathway for supply of the isopentenyl diphosphate (IPP) and dimethylallyl diphosphate (DMAPP) precursors; OPP denotes the diphosphate moiety” (Croteau and Wildung 2005).

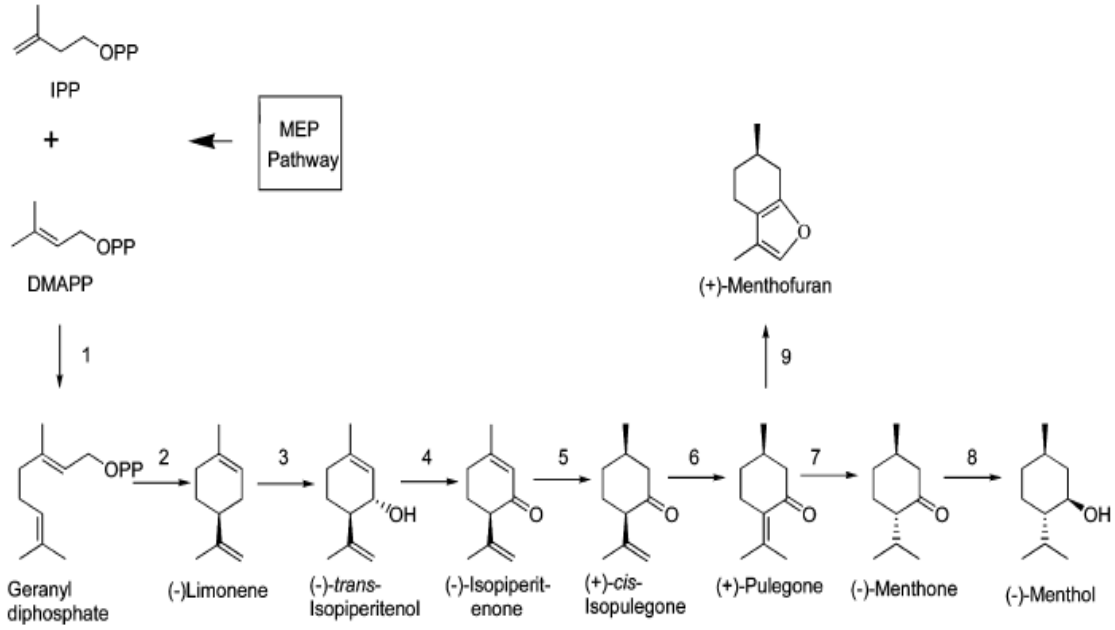
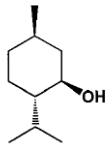
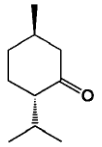
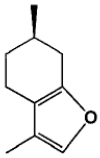


Figure 2. 3 Monoterpene biosynthesis in the secretory cells of peppermint leaves (Croteau and Wildung 2005).

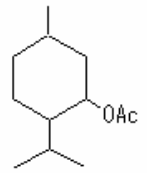
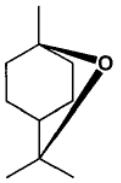
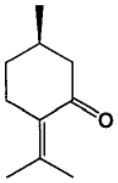
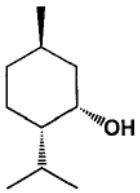
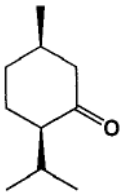
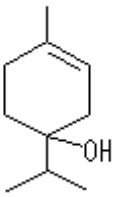
Menthol and all the related monoterpenes are representatives of the smallest members, monoterpenes (C_{10}), of a very extend class of terpenoid natural products (Buckingham 2004). Limonene is also one of the major monoterpenes present in the peppermint youngest leaves. The proportion of limonene declines rapidly with development, while menthone increases in prominence and declines only at later stages as menthol becomes the dominant monoterpene constituent (Gershenzon, McConkey et al. 2000).

It has been observed that as the peppermint plant matures menthone transforms into menthol, which is favorable. Menthone gives a bitter and harsh odor which is undesirable in high quality peppermint oils while menthol gives the “sweet” and “floral” characteristics to the high quality peppermint oil (Guenther 1949). The changes in terpenoid content within the leaves are quantitative. Developmental variation is considerable; menthofuran and ketones which dominate the oil of young peppermint leaves are replaced by methyl esters as the leaf ages (Turner, Gershenzon et al.), (Smith 1976). It has been proved that the peppermint oil composition and yield varies from year to year, which confirms the environmental influence on the plants (Jean 1994). Table 2.1 summarizes the most important peppermint oil components and their usual range.

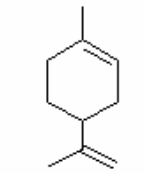
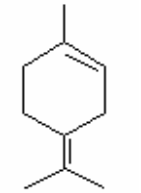
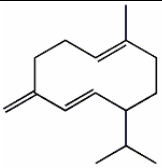
Table 2. 1 Major monoterpene constituents of peppermint leaves

	Compound	Chemical Structure	Percentage
Monoterpenes	(-)-Menthol		47% - 55%
	(-)-Menthone		6% - 32%
	(+)-Menthofuran		1% - 8%

Continued: Table 2.1 Major monoterpene constituents of peppermint leaves

	Compound	Chemical Structure	Percentage
	Esters (Menthyl Acetate)		3% - 29%
	1,8-Cineole		3% - 14%
	(+)-Pulegone		1% - 4%
	(+)-Neomenthol		1% - 3%
	(+)-Isomethone		1% - 3%
	4-Terpeniol		1% - 5%

Continued: Table 2.1 Major monoterpene constituents of peppermint leaves

	Component	**Chemical Structure**	**Percentage**
Monoterpene Olefins	Limonene		1 % - 6%
	Terpinolene		0.1% - 0.2%
Sesquiterpene	Germacrene-D		0.5% - 4.5 %

Additional compounds are also present in peppermint oil in a percentage of less than 1%. Some of them are: Isovaleraldhyde, a-Pinene, b-Pinene, Sabinene, b-Myrcene, a-Terpinene, b-Ocimene, g-Terpinene, para-Cymene, 3-Octanol, 1-Octen-3-ol, t-Sabinene Hydrate, b-Bourbonene, neomacetate, Linalool, isopulegol, neoisomenthol, pulegone, t-b-Farnescene, a-Terpineol, Germacrene-D, Piperitone, Carvone, Viridiflorol (Walter C. McCarthy 1963).

2.4 Traditional Extraction Techniques of Essential Oils

For an oil to be distinguished as an essential oil, it must be isolated by physical means only without the addition of any organic solvent. The physical methods are steam distillation, super- or sub-critical solvent extraction or hydro-distillation (Ramanadhan 2005).

Hydro distillation: This is the most ancient method of distillation and the most versatile. This method requires the simplest setup and it is used extensively by smallholder producers of essential oils (Figure 2.4). The herb is loaded into a tub and covered with enough water to ensure the plant material is suspended. This mixture is heated until it boils and the vapors rise from the tub and then condensed. Once the vapors are condensed the liquid mixture is poured in a separator where the oil and water separate by density difference (Denny 1991). The water sometimes is also used and is marketed as "floral waters" (also called hydrosol or sweet water) - such as rosewater, lavender water and orange water.

Some disadvantages are the variability on the distillation rate due to the uncontrolled heat rate input; possible overheated and eventually the aromatic materials can get burned. Improved distillation control can be obtained by using steam from a separate boiler. A further disadvantage of this system is that it requires the heating of a large quantity of water and the associated energy demand adds to the costs and time needed for each distillation. (Eikani and Rowshanzamir 2004)

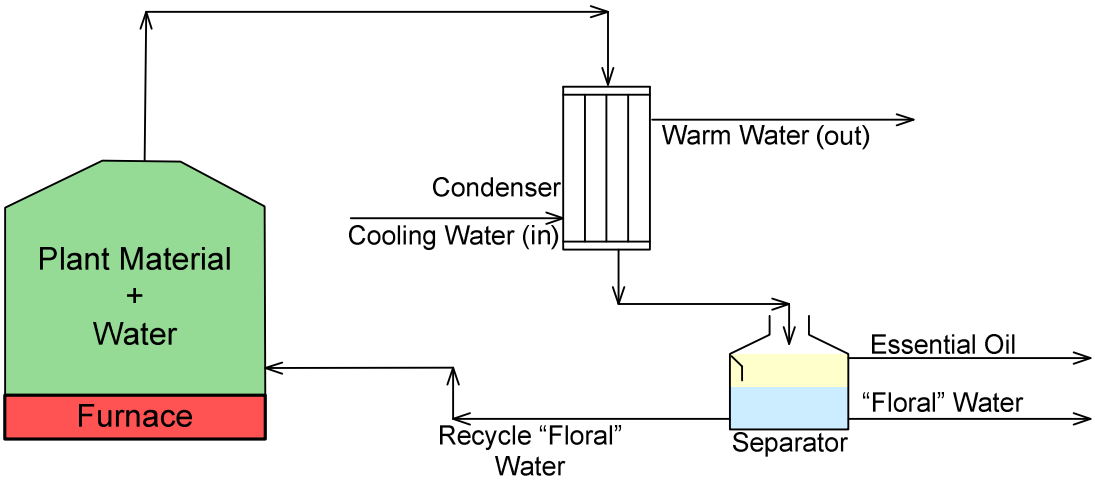


Figure 2. 4 Hydro-Distillation Facility

Water/steam distillation: This distillation is very similar to the hydro-distillation, the difference is that in this method the still contains a grid which keeps the plant material above the water level. This arrangement can be compared to a kitchen steamer basket,

the plant material is supported in a "basket" over boiling water, thus exposing the plant material only to the rising steam vapors. The water is boiled below the charge and wet steam passes through the plant material (Figure 2.5).

It is important in both water/steam and steam distillation that the still is packed evenly and not too tightly so that steam can extract from the complete charge efficiently. Over packing of the still can cause the steam to force "rat holes" through the charge and leave other parts of the charge unextracted. (E. Reverchon 1994)

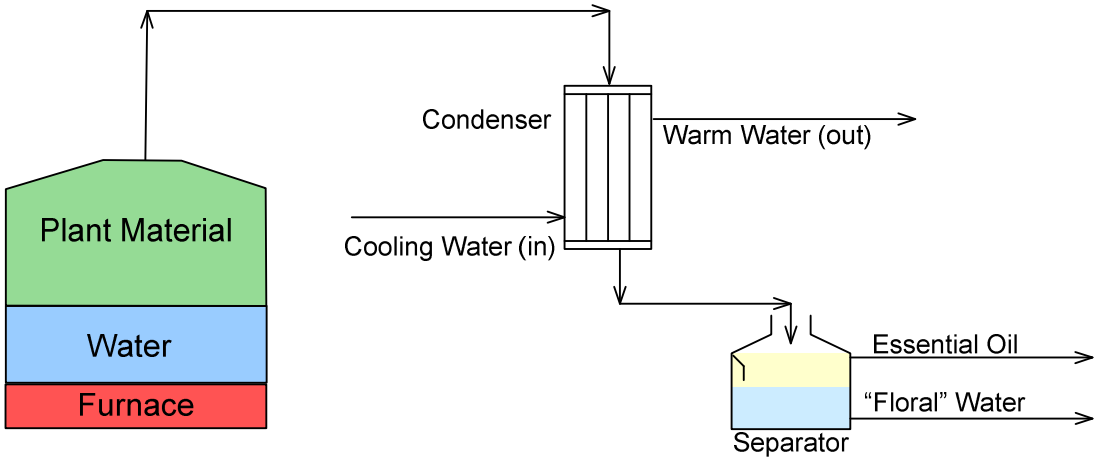


Figure 2. 5 Water/Steam Distillation Facility

Steam Distillation: This technique separates a mixture of water and an immiscible substance, peppermint oil in this specific case. The boiling point of peppermint oil is unknown but because menthol is its major component it could be assumed the peppermint oil mixture boiling point is close to the menthol boiling point of 212°C (CRC 1970-1971). The advantage of this technique is that mixture distillation temperature is approximately the lower boiling point component, which is water in this particular process (Adams 1963). This behavior is better explained by Raoult’s Law which states that the vapor pressure of a solute solution is equal to the vapor pressure of the pure solute (at an specific temperature) multiplied by its mole fraction, equation 1.

$$Pa = Xa \cdot Pa^{o} \qquad (1)$$

P is the vapor pressure of the solution, Pa^{o} is the vapor pressure of the pure solvent at a particular temperature and Xa is the mole fraction of the solvent.

Raoult's Law definition for an ideal mixture says the total vapor pressure of the mixture is equal to the sum of the individual partial pressures as equation (2) shows.

$$\begin{aligned} Pa &= Xa \cdot Pa^{o} \\ Pb &= Xb \cdot Pb^{o} \\ Pt &= Pa + Pb \end{aligned} \qquad (2)$$

Raoult's law applies only to an ideal solution which by definition is a solution in which the solvent-solvent and the solvent-solute interactions are the same. A solution is considered ideal when the intermolecular attractive forces between the molecules of the solvent are the same as those between the molecules in the separate components. This statement is true only for very dilute solutions. In this particular scenario because the concentration of the solute (peppermint oil) is 1%, it could be assumed that the concentration of the solution is very dilute and that the intermolecular forces between the peppermint oil and the water in the plant are the same; therefore the mixture water-peppermint oil is an ideal solution.

The vapor pressure of a mixture is closely related to its boiling point. If a liquid has a high vapor pressure at a particular temperature, it means that its molecules are escaping easily from the surface (its intermolecular forces are relatively weak). That means that relatively low amount of heat need to be provided to surpass the intermolecular forces and boil the liquid. Figure 2.6 shows the relationship between vapor pressure and boiling point of water and peppermint oil. The purpose of this figure is to illustrate the previous explanation. The vapor pressure of mint oil or menthol was not readily available in the literature. 1% of peppermint oil by mass in the liquid mixture represent 0.001 mole fraction of oil in the liquid solution (0.999 mole fraction of water in the liquid solution)

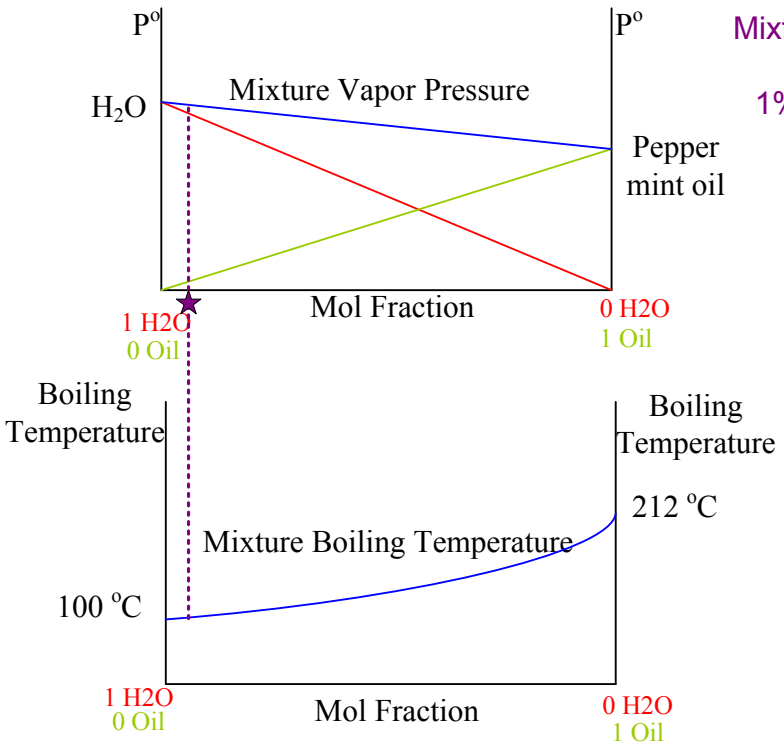


Figure 2. 6 Vapor Pressure-Boiling Point Relationship

This is how the addition of steam enables the transport of the menthol and water allowing them to evaporate at lower temperatures close to the boiling temperature of water at atmospheric pressure, 100 °C (Adams 1963). The steam then transports the mint oil way from the plant material; more steam must been generated to remove the mint oil vapors and to achieve equilibrium.

This is the most advanced type of distillation by direct steam provided from a separate boiler. The distillation trucks contain a grid plate under which an open steam pipe is fitted. The method is faster than any of the other methods explained before which is probably the most important advantage since the energy consumption is lower. The rapid distillation is also less likely to damage those oils which contain reactive compounds (Eikani and Rowshanzamir 2004). Figure 2.7 is a schematic representation of a steam distillation facility.

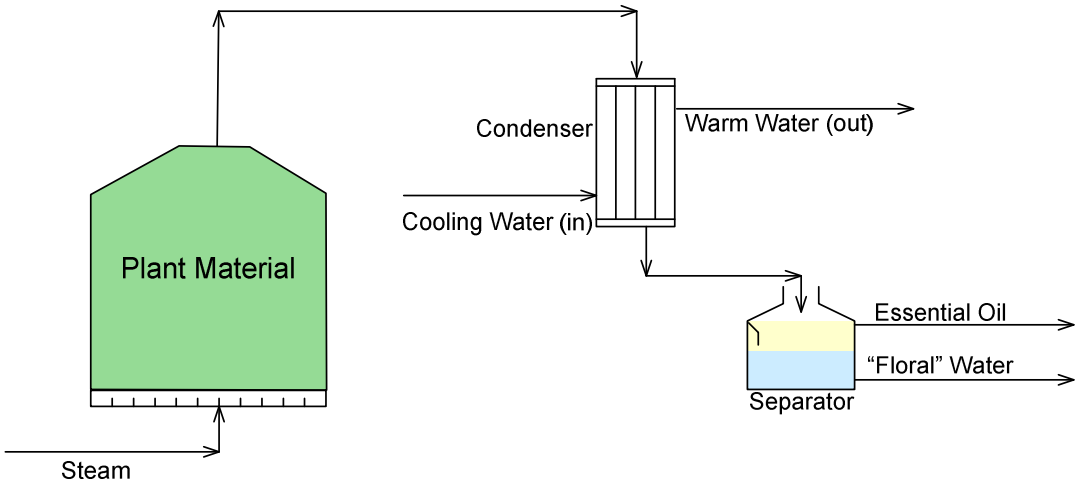


Figure 2. 7 Steam Distillation Facility

2.5 Peppermint Oil in Oregon

The first peppermint plants grown in the United States originated in England, they were planted in 1816 in the Wayne County, New York. Later on it was introduced to Ohio, Michigan and some small section of Indiana (Guenther 1949). In the west region the extraction of peppermint oil is small but an important industry. The Mint Industry Research Council (MIRC) confirmed that Washington and Oregon produce approximately 72% of the total world production and 86% of the total crop for the United States; similar information was found on the study done by Hughes on 1952. Washington and specially Oregon are favored by the temperature climate, ample supply of water and abundant land suitable for growing peppermint. In fact the yield of oil per acre since 1946 in Washington and Oregon are considerable higher than in any of the Midwest States. Another advantage that the western states have over the Midwestern region is that in general the peppermint plantations in Washington and Oregon have a longer life than those in the Midwest.

Distillation plants in Oregon

Steam distillation is the method used in Oregon to extract peppermint essential oil. With the objective to evaluate different stills in Oregon and to improve methods for the field distillation, a cooperative project started in 1949 at Oregon State University. A status report of the project written by Dr. Hughes a professor of the Mechanical Engineering from Oregon State University identifies some opportunities to improve the current methods. The following information is a compendium of that previous work.

Hughes identified two types of distillation facilities in Oregon. Figure 2.8 illustrates the older example where the tub is stationary and the condenser is an open drip type. The water used to condense the vapors is wasted; few facilities used that water as boiler feed.

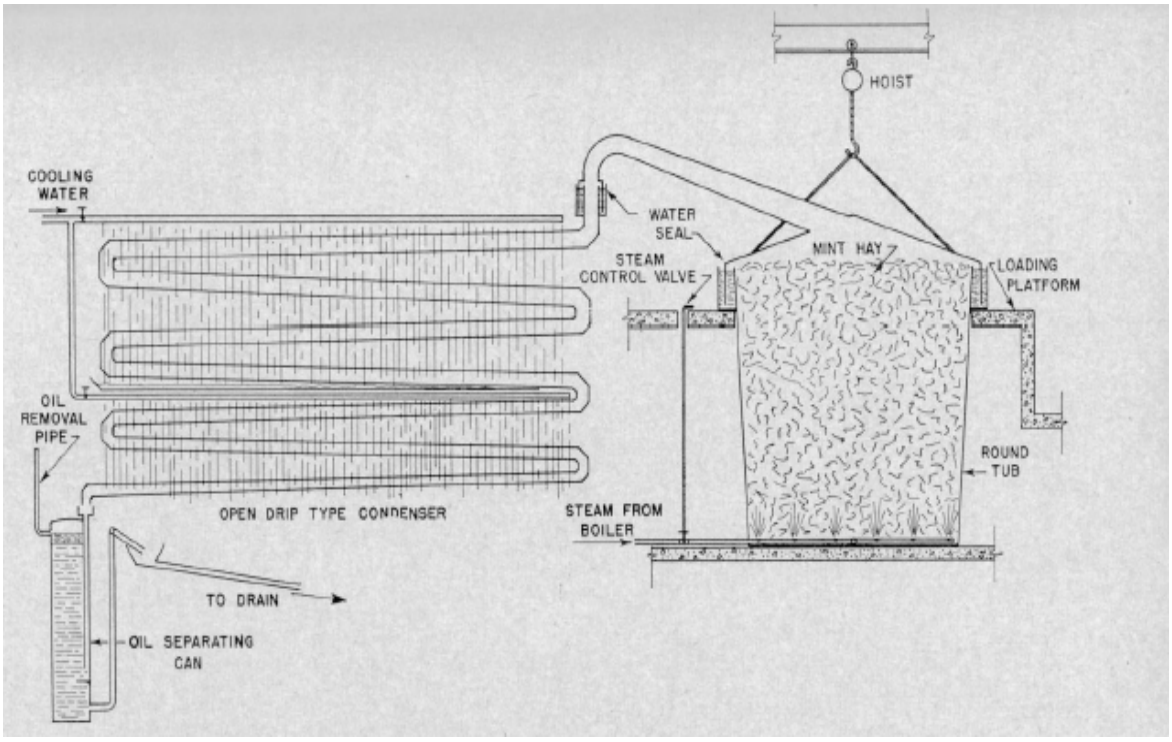


Figure 2. 8 Distillation Facility with stationary tub open drip-type condenser (Hughes 1952)

Figure 2.8 is an example of a facility with a non stationary tub and a submerged condenser. The separation can is the same that the other facility uses. This set-up helps to save water by using the submerged condenser.

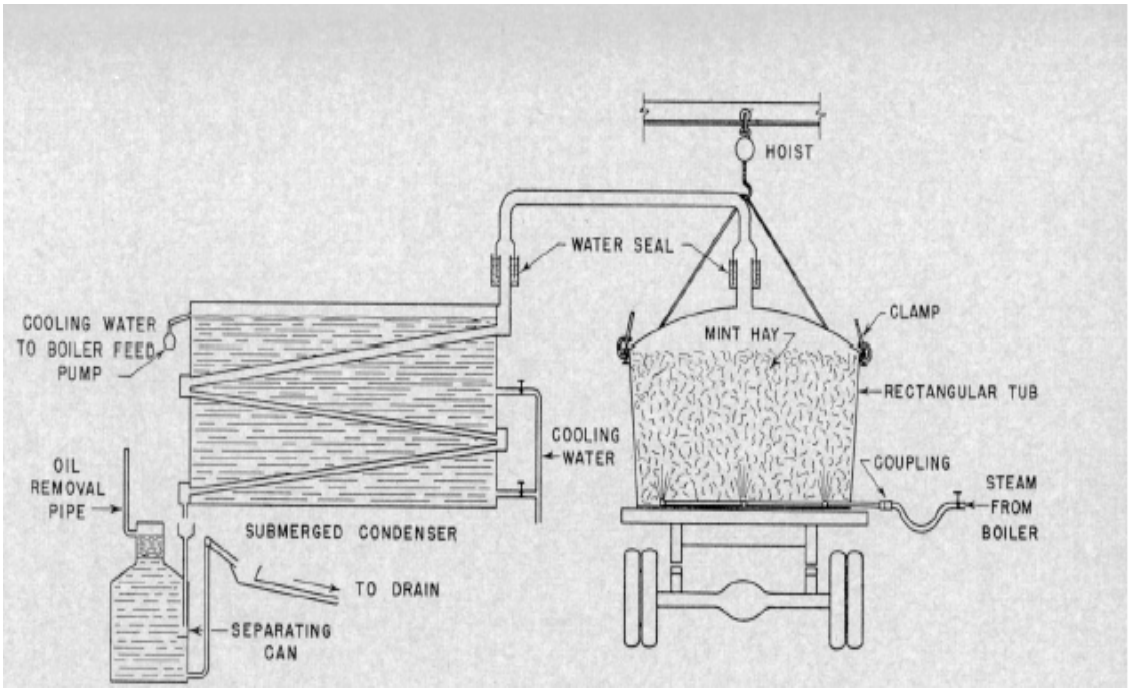


Figure 2. 9 Distillation unit with a portable tub and a submerged condenser (Hughes 1952)

Aiming a better water/oil separation the water from the separation cans is redistilled to extract the remaining oil. The oil obtained by this recovery process does not have the same quality as the oil extracted from the steam distillation process; however this oil brings the price of half to two thirds that of prime oil. This is mainly why at that time the recovery/redistill process was performed.

Based on the evaluations and data collected some suggestions were made, some of them are summarized as follows (Hughes 1952):

1. Installation of pressure gage as an accurate way to know the steam pressure going to the mint tub.
2. Installation of an automatic temperature control valve on the cooling water used by the condenser. Keeping the temperature at about 43.3 °C was

suggested since that seemed to be the optimal temperature that gives a rapid separation of oils without having evaporation losses.

3. Use a stopwatch to determine the optimal extraction time. The flow of mint oils should be used to determine the best extraction time.
4. Implement 2 inch heat insulation to the mint tubs

These are some of the suggestions made by Hughes in 1952 after analyzing several distillation facilities in the Willamette Valley (Hughes 1952). The mint stills in Oregon still use steam distillation to extract the essential oils and they still use the same technology that was used back in 1952. An evaluation of the current set up of the Setniker farm is analyzed later on CHAPTER 5, Setniker Facility Evaluation.

2.6 Solvent Free Microwave Extraction

Microwave ovens use radio waves to convey energy at a frequency which is approximately 2500 megahertz. Waves in this frequency range are absorbed by water, fats and sugars and other molecules with a sufficiently polar oxygen group. In the specific case of water which is an electric dipole (positive charge on one end and negative charge on the other), once the electric field is induced the molecules try to align within it; this motion and the collision with other molecules produce heat. In other words when microwaves excite the molecules producing rotational and translational motion; this motion is essentially heat (Buffler 1993). Heat is generated everywhere at once because the microwave energy applied excites molecules throughout the material. However radio waves penetrate unevenly in thick pieces, therefore depending on the sample the microwaves sometimes do not penetrate all the way to the middle, and there is also localized heat caused by wave interference (Buffler 1993).

Microwave energy is an advantageous alternative to several thermal applications due to its efficient volumetric heat production (Ramanadhan 2005). The volumetric

heating (heating of the bulk) as opposed to transferring heat from the surface inwards, is more efficient and uniform (Sau Soon Chen 1995). The ability to control and the rapid heat transfer are probably the greatest advantages of microwaves over conventional thermal technologies. In processing applications, the ability to instantaneously stop the heat source makes enormous difference to the product quality and hence the production economics (Wang, Ding et al. 2006). The nature of heating through the involvement of the raw material under processing (instead of using fossil fuels or less efficient, indirect electrical heating systems) brings about quality consistency as well as positive environmental impact. (Ramanadhan 2005), (Kwon, Belanger et al. 2003), (A. Brachet 2002).

Solvent Free Microwave Extraction (SFME) is a combination of microwave heating and distillation at atmospheric pressure. The benefit of this new alternative is mainly the reduction of extraction time which leads to a big opportunity in energy savings and improving the product quality (Michael Spiro 1995). Because of all these benefits in 1991 and 1992 general methods of microwave extraction of biological material were patented by Jocelyn Pare (Pare; J. R. Jocelyn 1991; Lucchesi, Smadja et al.). This technique is considered as the “green” technique in the essential oil extraction field since an isolated oil only be an essential oil if it was obtained only by using heat and water in the extraction process (Ramanadhan 2005).

Previous research investigates the essential oil extraction of fresh leaves of basil, garden mint and thyme. It was found that the microwave extraction time was 30 minutes while the time of the hydro-distillation was 4.5 hours. The total amount of energy used by this method was 0.25 kWh while the hydro-distillation used 4.5kWh which represent a considerable reduction of extraction cost (Lucchesi, Chemat et al. 2004).

Similar experiments were conducted using Ajowan, Cumin and Star Anise. Results show that the composition of essential oils extracted by SFME and HD has major differences in their aromatic profiles. Larger amount of desired compounds were

found in the oils extracted by SFME due to the diminution of thermal and hydrolytic effects since this method uses the in-situ water of the plant. (Lucchesi, Chemat et al. 2004). The potential of the SFME technique was compared with the conventional hydro-distillation method for the extraction of essential oil from cardamom seeds. It was found that extraction time, irradiation power or moisture content can be optimized to obtain a high yield of essential oil, or to obtain essential oils of differing composition (Kwon, Belanger et al. 2003).

Microwaves cause the physical rupture of the cells and the glands more rapidly than in conventional hydro-distillation or steam distillation.(Lucchesi, Smadja et al. 2007). Figure 2.9 shows Scanning Electron Microscope (SEM) images of the untreated cardamom, cardamom subjected to SFME and cardamom after hydro-distillation to understand the difference on the seeds between the two extraction methods used (Lucchesi, Smadja et al. 2007).

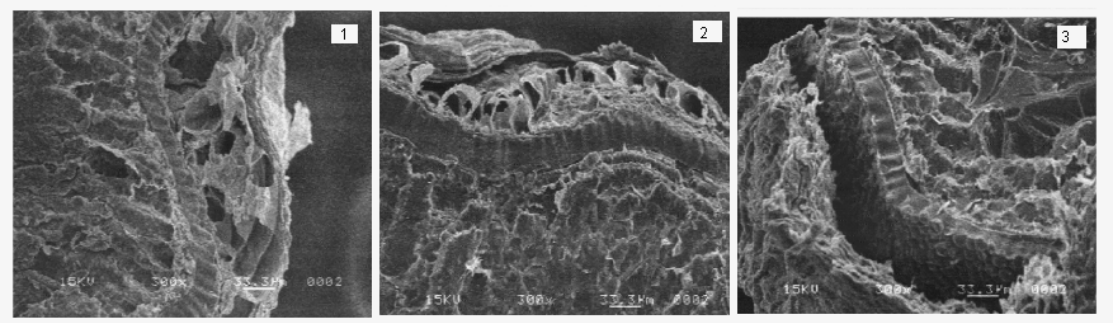


Figure 2. 10 Cardamom seed: (1) without any treatment, (2) after hydro-distillation, (3) after solvent free microwave extraction

Microwave extraction of rosemary and peppermint leaves was studied using ethanol and hexane as solvents. It was concluded that the extraction rate is a function of the plant material properties, the power level, duration of microwave radiation, solvent used, ratio of solid/solvent used and shape of extraction flask. Fast extractions were observed at high power level (Chen and Spiro 1994).

Among the various available methods, microwave assisted extractions show the highest promise due to the low extraction time which leads to low operating costs and high quality products.

3. Materials

3.1 Microwave Modification Design

A Galanz WP700L17-8 microwave produced by Shunde Galanz Electric Appliances Factory, Ltd, China was utilized in this research after the modification illustrated in Figure 3.1 was implemented.

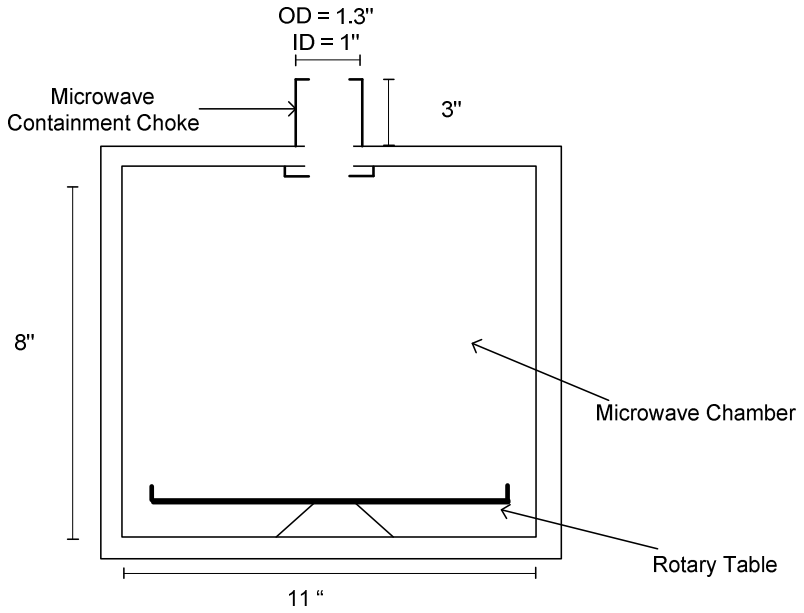


Figure 3. 1 Microwave Oven

The microwave was modified from its original condition to collect the water and oil vapors coming from the peppermint hay once it was heated. The hole and the microwave containment choke were centered above the turntable and approximately in the center of the microwave chamber. The design of the choke allows the safe usage of the modified microwave because as long as moderate to low dielectric materials pass through the choke, the design appears electrically as a quarter-wavelength at the microwave oven operation frequency of 2.45 GHz. For choke design, the reader is referred to general microwave design found in Electrical Engineering. For this specific design, internal communications with Professor Hackleman resulted in the

design. In spite of this fact, it is always a good idea to check for leakage during operation. A UEI MW1AK model microwave detector was utilized. An engineering design template for the first design is in the Appendix A including all the choke dimensions. For this design, Umpqua Research was contacted as they have performed like work on such devices and in addition, Mr. Andy Brickman (OSU CBEE Technician) and Mr. Manfred Diettrich (OSU Machinist) were directly involved.)

3.2 Microwave Reactor Design

Three pieces of glassware were designed by Hidden View Glassworks (Albany-Oregon) to fit the microwave modifications to facilitate the oil extraction process.

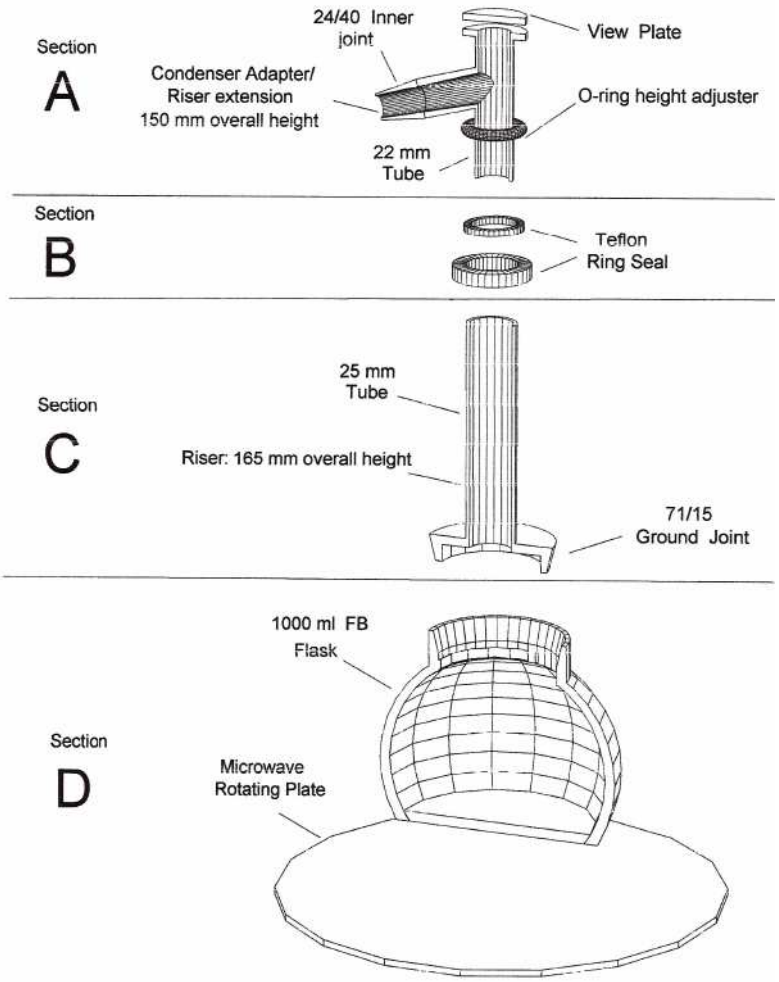


Figure 3. 2 Microwave Reactor Parts by Hidden View Glassworks

The reactor assembly consists of four pieces of glassware. The still pot (Section D) is a modified round-bottom flask so that it has a flat bottom and a wide mouth for ease of sample insertion and retrieval. A vertical riser (Section C) and two Teflon rings (Section B) allow the still pot to rotate with the turntable and still have a fairly sealed connection to "Y" connector (Section A). The "Y" connector is attached to the condenser and is equipped with a removable circular glass window situated directly above the still pot. This window was intended to be used to measure the temperature of the sample by using infrared transparent material and an infrared thermometer, however in this work, it was not found necessary. An O-ring in the "Y" connector (Section A) allows adjusting the height and the position of the condenser. The vapors travel from the still flask to the tubular condenser which has a supporting cooling water reservoir and recirculation pump that pumps water to condense the vapors. Extract vapors are then collected from the condenser in a separatory funnel for oil and water separation. A heating lamp was utilized to maintain the temperature of the condensates at a range from 30 °C to 40 °C which is the optimal separation temperature (Denny 1991). . Figures 3.3, 3.4 show the complete schematic of the microwave reactor assembly.

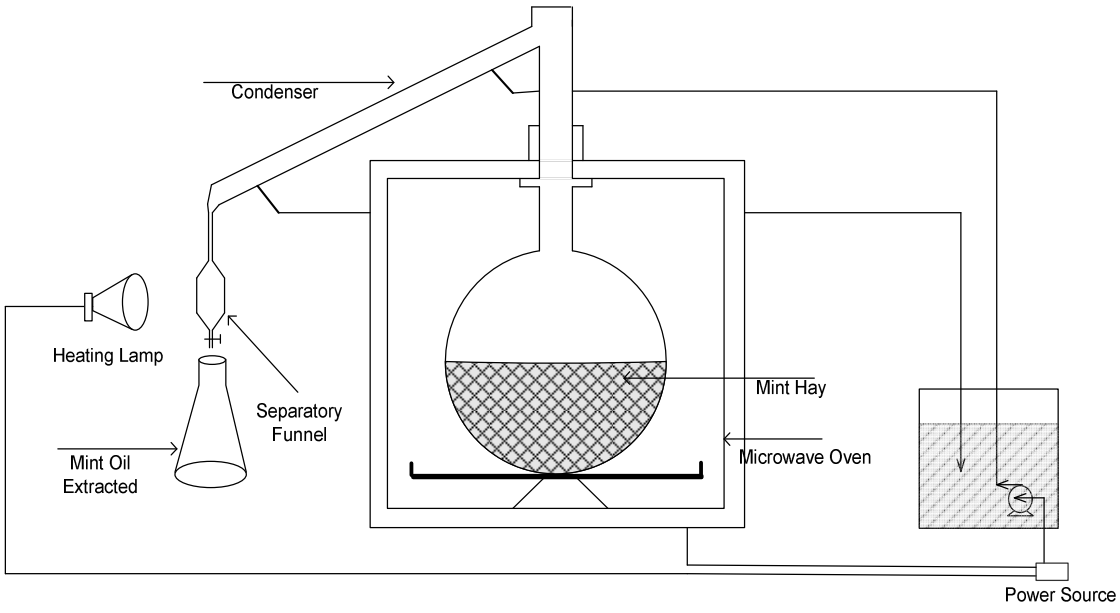


Figure 3. 3 Microwave Reactor Diagram

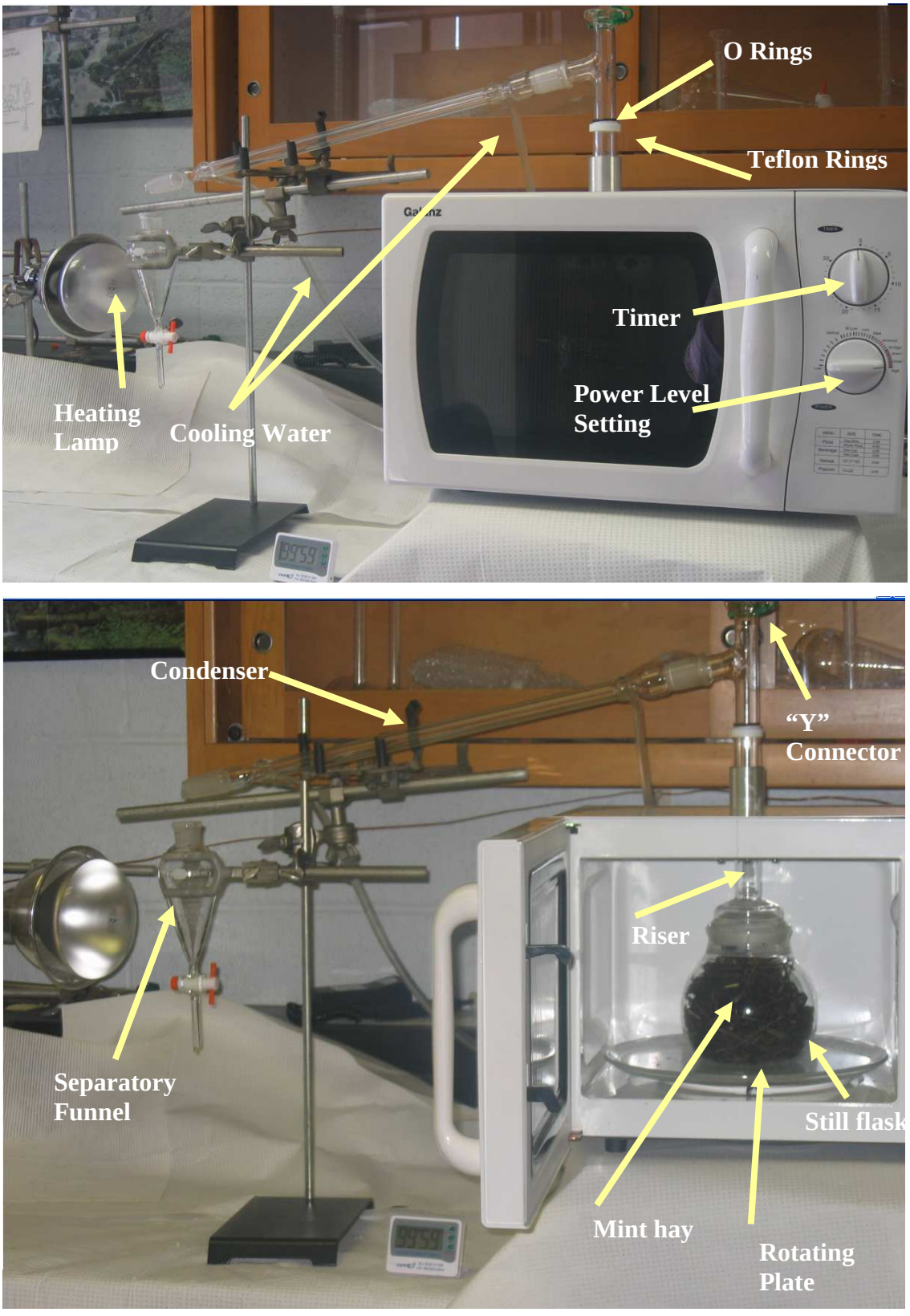


Figure 3. 4 Microwave Extractor Picture

4. Methods

4.1 Experimental Design

It was desired to explore the effects of the power level (Table 4.1) and the extraction time on the amount of oil distilled and its quality. This process is solvent free; no additional moisture was added to the samples of hay. Three power levels (Table 4.2) were chosen after running multiple samples at different power levels to explore the maximum distillation time. Tables 4.3, 4.4 and 4.5 summarize the experimental design space.

Table 4. 1 Average Power Delivered

Power Level	Equivalent Power [W]
High	1120
Medium High	870
Medium	697
Medium Low	518
Low	103

Table 4. 2 DOE of Single Step Processes

Power Level	Time [min]						
High	0.50	1.00	1.50	2.00	2.50	3.00	3.50
Medium	2.00	2.50	3.00	3.50	4.00	4.25	-
Medium Low	3.00	3.25	4.00	4.50	5.00	-	-

Table 4. 3 DOE of Two Step Processes Starting with 1.5 min at High Power

Power Level	Aditional Time [min]			
Medium	0.50	1.00	1.50	2.00
Medium Low	1.00	1.50	2.00	2.50

Table 4. 4 DOE of Two Step Processes Starting with 2 min at High Power

Power Level	Aditional Time [min]			
Medium	0.50	1.00	1.25	-
Medium Low	0.50	1.00	1.25	1.50

Each point was replicated at least three times unless it was a point to confirm the breakthrough time which is the time when the first liquid drop gets to the separatory funnel. All the experiments were done randomly to avoid any interactions between other factors that have not been explicitly accounted for in this experimental design.

Table 4.5 shows the sample collection plan to determine the total organic samples from the water extracted. Four samples at the highest and lowest power settings applied and extraction times were used.

Table 4. 5 TOC experimental design

Extraction Time [min]	Power Applied [W]	
	1120	518
2.5		
3.5		

4.2 Sample Preparation Prior to Extraction

Dry chopped peppermint hay collected from the Setniker farm (Independence-Oregon) was used in this research. The peppermint hay was stored at –10 °F (-23.3°C) in the OSU Department of Food Sciences facility in Wiegand Hall, OSU Campus. Freezing of the hay was necessitated by the fact that mint hay rapidly decomposes at normal ambient temperatures. The hay was dried for approximately two weeks and it was ready to be processed at the time it was collected. The dryness stage of the hay is not a variable in this research.

Before conducting experiments, the frozen peppermint hay was allowed to reach room temperature (21°C to 23°C) in order to avoid considering the hay initial temperature as

a factor that affects the efficiency of the process and also to simulate the starting temperature at the steam distillation facilities. Ice and water where placed in the condenser water reservoir and the recirculation pump was turned on to make sure the condenser coolant was circulating before vapors arrive.

A series of measurements were recorded to capture all the possible changes in mass of the hay. The still pot was massed and one hundred grams of mint hay was added. Because the hay was dried and chopped it was difficult to collect a homogeneous sample to be extracted. To improve the reproducibility based on the observation of the inhomogenity of the hay sample, approximately a fifty-fifty ratio of stems and leaf fragments were selected and massed in the still pot. The initial hay temperature was recorded as well as the temperature after extraction. It was assumed that the still pot and the mint hay reached equilibrium. All the temperatures were measured through use of a Fluke model 574 infrared thermometer and recorded. The still pot was then placed in the microwave and connected to the rest of the apparatus as figure 3.4 shows. The separatory funnel was placed under the condenser outlet stream to collect all of the extract condensate. The desired microwave power level was set and the microwave (along with a stopwatch) was started. While the experiment was running, the apparatus was under observation to ensure that the still pot was rotating and that the mint hay sample did not burn.

4.3 Procedures after Extraction

Once the desired extraction time was completed, the microwave was turned off; this temperature is assumed to be the final hay temperature after the distillation process. The temperature of the liquids extracted was recorded as well as the still pot with peppermint hay, again assumed to be in equilibrium, was read from the infrared thermometer and recorded. The entire system was then allowed to equilibrate for three to five minutes to ensure that all vapors were condensed to minimize vapor losses to the environment. Then the apparatus was partially disassembled to collect the liquid remaining within the condenser. The mass of the still flask was recorded to determine

the change in mass of the mint hay after the oil and water were extracted. The mint hay was collected from the still pot and saved in a plastic zip-loc® bag and put into frozen storage for later moisture analysis.

During this time the liquid extract collected was kept warm by a heat lamp to be close to the optimum separation temperature of about 40°C. The liquid extracted was then separated; the water was drained from the separatory funnel into a sample bottle (massed before and after the water was added) to determine the mass of water collected. The oil was left in the separatory funnel and collected using a Pasteur pipette into a sample vial which was massed before and after the oil was added to determine the mass of oil extracted. The masses and temperatures were all recorded in a lab notebook and the same procedure was performed for each desired power level and extraction time.

4.4 Quality Analysis

Several tests needed to be performed to analyze the chemical composition of the liquids extracted. The chemical composition of the oil and water extracted from the peppermint hay was analyzed using several techniques described in the following sections.

Gas Chromatography Analysis on Peppermint Oil

A Perkin-Elmer AutoSystem® Gas Chromatograph instrument with an auto sampler and flame ionization detector was used to determine the composition of the peppermint oil. The system was operated in the split mode with a polar, high resolution capillary column. The operation and data collection is carried out using Totalchrom® Data System software. Table 4.6 summarizes the conditions, methods used to run the GC as well the peak separation criteria.

Table 4. 6 GC Method and Specifications

Instrument Conditions	Run Time: 35.40 min. Sampling Rate: 3.1250 pts/min Offset: 5.0 mV
Autosampler Method	Syringe Capacity: 5.0 ul (0.5 ul) Injection Volume: 0.5 ul (0.1 ul) Injection Speed: Fast Viscosity Delay: 1 Sample Washes: 1 Sample Pumps: 6 Post-injection Solvent Washes (A): 5
Column Type	DB-Wax (Polyethylene Glycol) 30M x 0.25mm x 0.25um film
Carrier Gas	Helium UHP at 9.0 psig. (approx. 17 cm. /sec. flow)
Split Valve	ON (at 88 ml/min. flow)
Detector: Flame Ionization	Air flow at 270 ml/min. Hydrogen flow at 41 ml/min.
Detector B: ON	Time Range: 200
Heated Zones Oven Program	Injection Port: CAPILLARY; 250 C 70 °C - 0 min, 3.7°C / min, 120 °C - 6 min, 18.0 °C / min 190 °C - 12 min
Processing Parameters	Bunch Factor: 1 Noise Thresh: 1 uV Area Thresh: 5.00uV
Peak Separation Criteria	width ratio: 0.200 valley-to-peak ratio: 0.010
Exponential Skim Events	peak ht ratio: 5.00, Adj ht ratio: 4.00, Valley ht ratio: 3.00

This analysis was performed by Labbeemint (White Swan-Washington). Appendix B shows a typical chromatogram of peppermint oil from the Willamette Valley obtained using the method explained above at Labbeemint.

Total Organic Carbon Test

A total Organic Carbon (TOC) Reagent Set and a DRB 200 Portable Spectrophotometer manufactured by Hach Company were used to determine the percentage of organic compounds in the water extracted.

The total organic carbon (TOC) percentage in the samples is determined by first removing the inorganic carbon from the sample by exposing the sample under slightly acidic conditions. In the outside vial the organic carbon in the sample is digested by persulfate and acid to form carbon dioxide. During digestion, the carbon dioxide diffuses into a pH indicator reagent in the inner ampule. The adsorption of carbon dioxide into the indicator forms carbonic acid. Carbonic acid changes the pH of the indicator solution which, in turn, changes the color. The amount of color change is related to the original amount of carbon present in the sample. This method is used to quantify TOC levels between 15 mg/L to 150 mg/L with 95% confidence limits. The complete method developed by Hach is available in Appendix C.

Moisture Content Determination

The moisture content of the peppermint hay was determined by drying the samples in a convection oven. The samples were weighed before and after they were oven dried to calculate their moisture. Three replicates were run to determine the average moisture content of each sample. Moisture analysis was done on all the hay used for each extraction at different power and time settings.

5. Results: Setniker Facility Evaluation

The following sections describe the process of extracting peppermint essential oils. A process flow sheet which shows the current operations of the Setniker mint still facility was created. This flow sheet also displays the sample points from where data was collected (Appendix D).

5.1 Peppermint Hay Preparation

The peppermint plant is cut and left in the field to dry, typically for about three days. However, the drying time varies depending on the relative humidity of the hay, temperature and experience of the farmer. According to farmers, using dry hay is more economical to handle because the steam needed to extract the oils from the plant will be reduced as well as the overall extraction time. Retained water in the plant must be heated and evaporated at the same time that the retained oils are extracted; this is why distilling fresh hay means higher operating costs. Also dry hay is lighter and more compact which is beneficial since more mint hay can be processed per batch.

5.2 Steam Production

Steam is generated via the use of three commercial boilers. Boilers E-110 and E-130 have a maximum capacity of 300 hp. Boiler E-120 has a maximum capacity of 600 hp. Most facilities use natural gas for combustion however some farms use diesel in combination with natural gas; only one facility was observed using waste oil products effectively.

Typically, a mixture of fresh water and make-up water (coming from the condensers) is used to feed the boilers. It should be noted that if there is a large number of condensers not all water used in the cooling process will be needed for the boiler and should be captured to be used elsewhere.

The mixture of water is fed into the boiler using a pump activated by need based on the water level in the boiler. Inside of the boiler the water is fed into several tubes where the water gets vaporized and turned into saturated steam. Each boiler output stream combines into another stream which then divides to the bays.

Figures 5.1 and 5.2 show the temperature of the steam produced by boilers E-110 and E-130; boiler E-120 did not have a temperature indicator. The figures show the steam temperature during mint oil extraction cycles for each boiler. Similarly, the internal pressures of the boilers were recorded (Figures 5.3, 5.4 and 5.5).

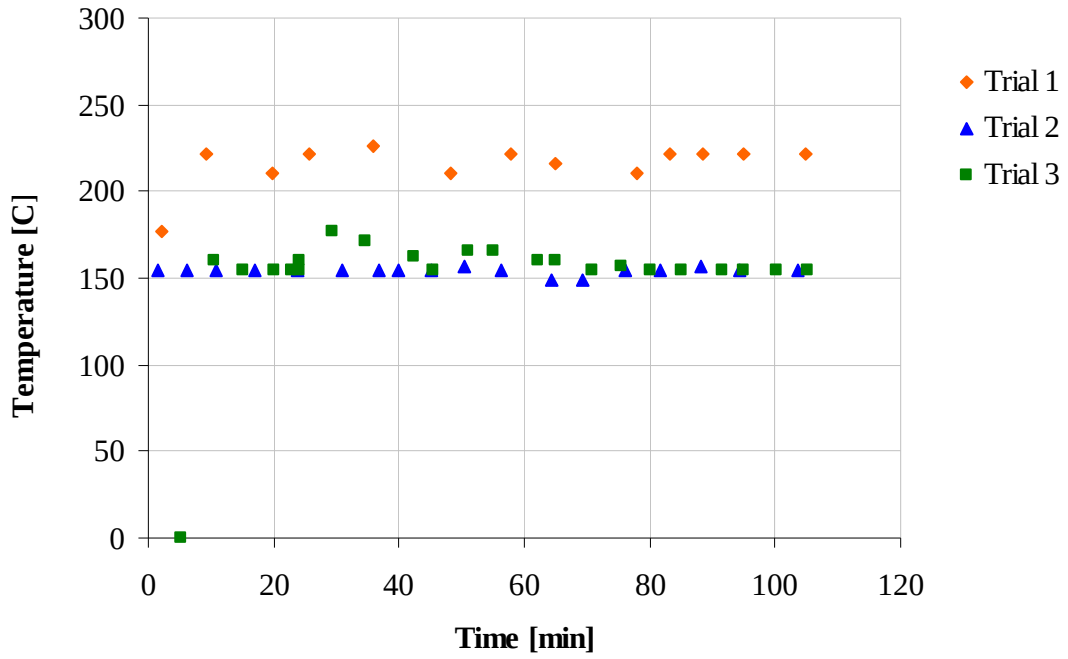


Figure 5. 1 Boiler E-110 Temperature

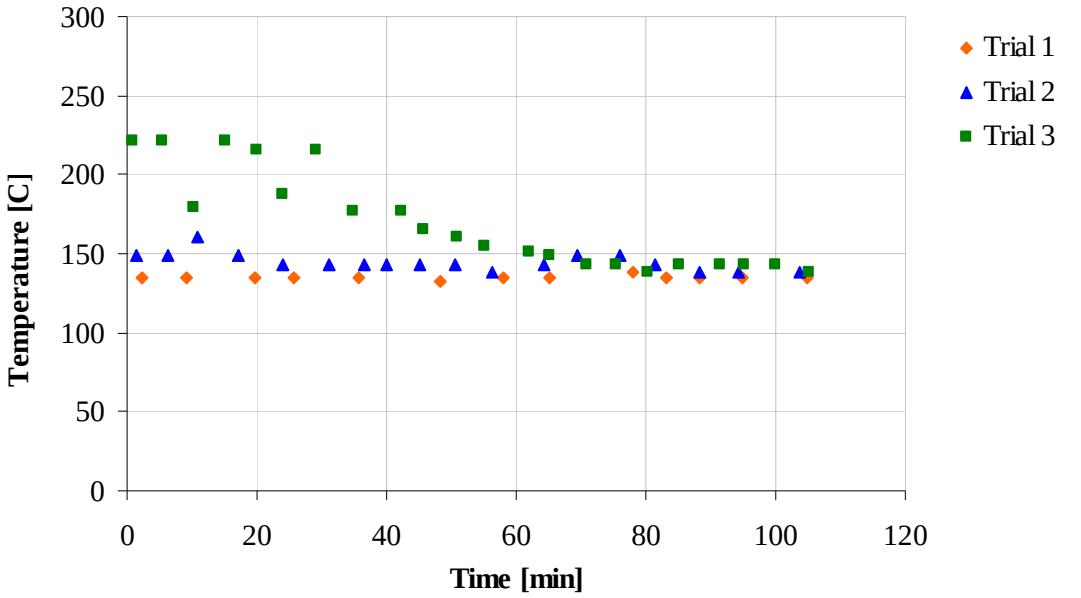


Figure 5. 2 Boiler E-130 Temperature

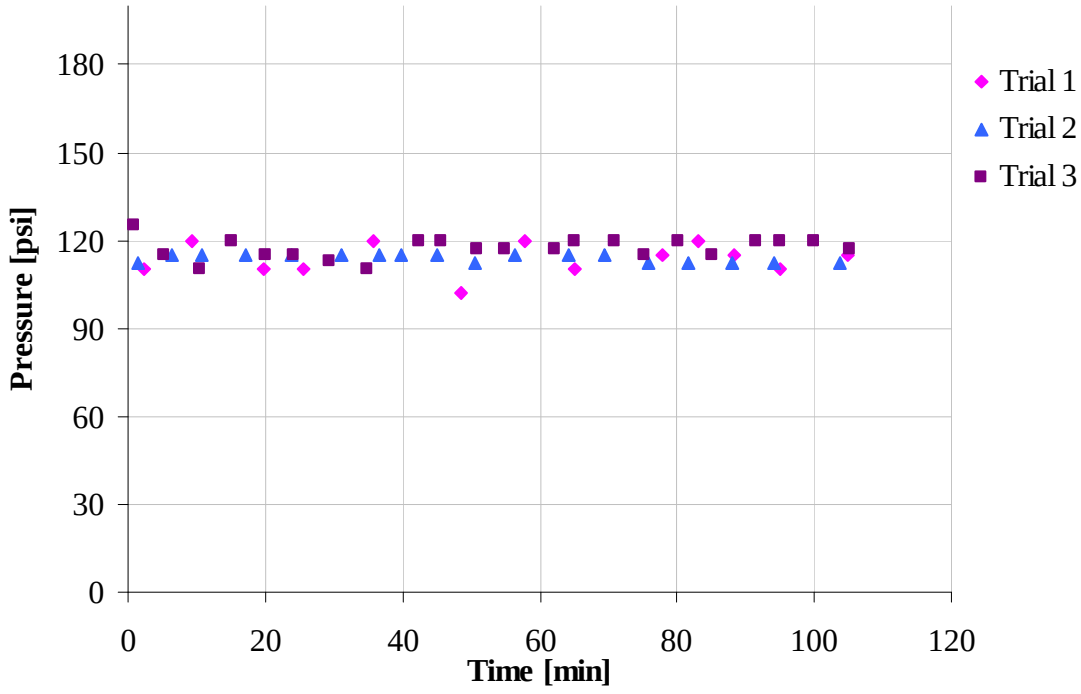


Figure 5. 3 E-110 Pressure

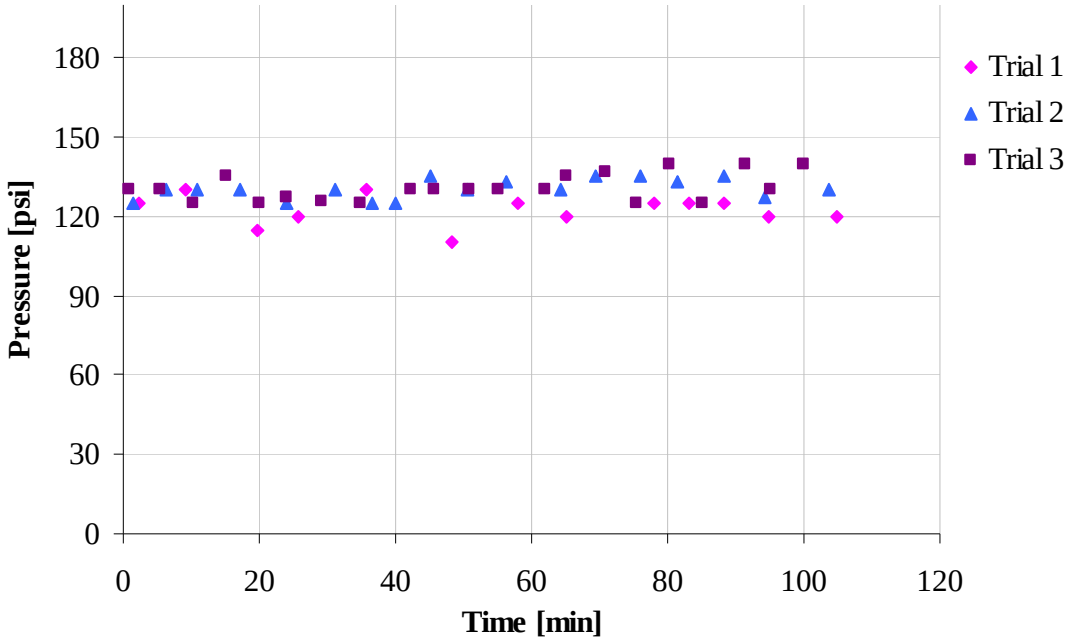


Figure 5. 4 E-120 Pressure

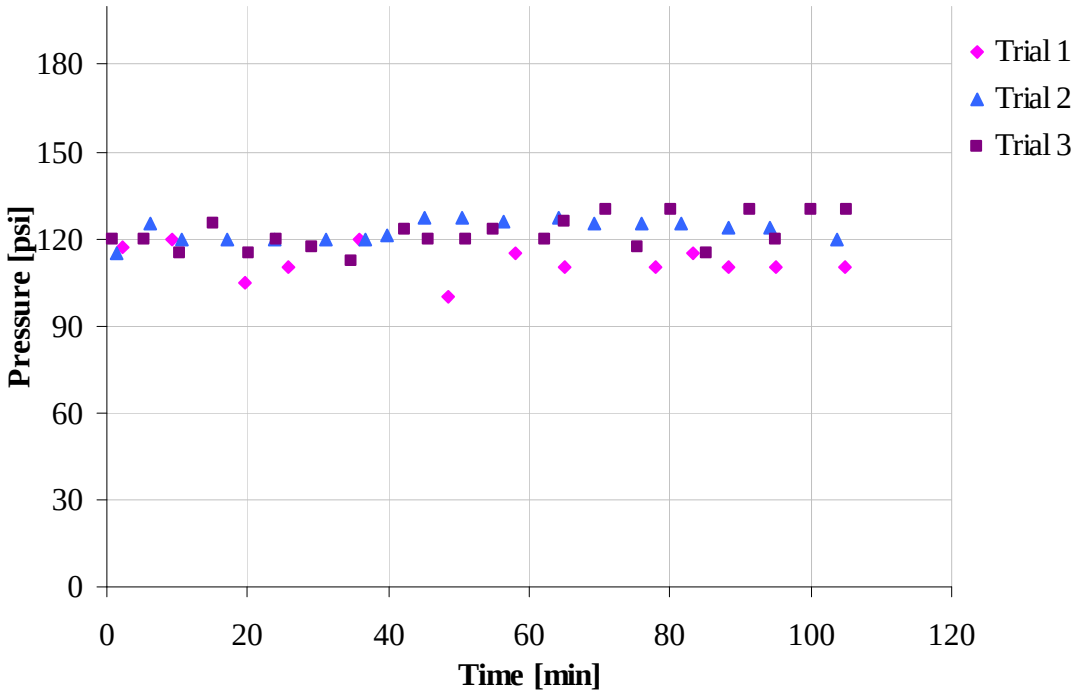


Figure 5. 5 E-130 Boiler Pressure

The previous figures show that the internal boiler pressures remain constant during the entire extraction period.

The temperature of **boiler E-110** changes in average from 200 °C at trial 1, 150 °C at trial 2 to 170 °C at trial 3. These temperatures correspond to the generation of superheated vapor at trials 1 and 3, and saturated steam in trial 2.

The internal temperature of **boiler E-130** varies for all the different trials. Trial 1 shows an average temperature of 137 °C which is too low to be even saturated steam. Trial 2 is at equilibrium at 150±2 °C which is saturated steam. Trial 3 shows high temperatures, 230°C, during the first forty minutes of the process, however its temperature also achieved "steady state" at 150 °C by the end of the process.

Since **boiler E-120** does not have a temperature indicator, the pressure readings were used to calculate the temperature using steam tables, calculations show that the boiler produces superheated steam, steam at approximately 170 °C, as Figure 5.6 shows.

The boilers need to be warmed up for approximately an hour before they start producing vapors. It was observed that when boilers are not in use they remain connected in the line which enables steam to travel into unused boilers and be spent heating the boiler and any associated water. Energy used heating the metal and water of unused boilers is not being used to process mint, but it increases the operating costs.

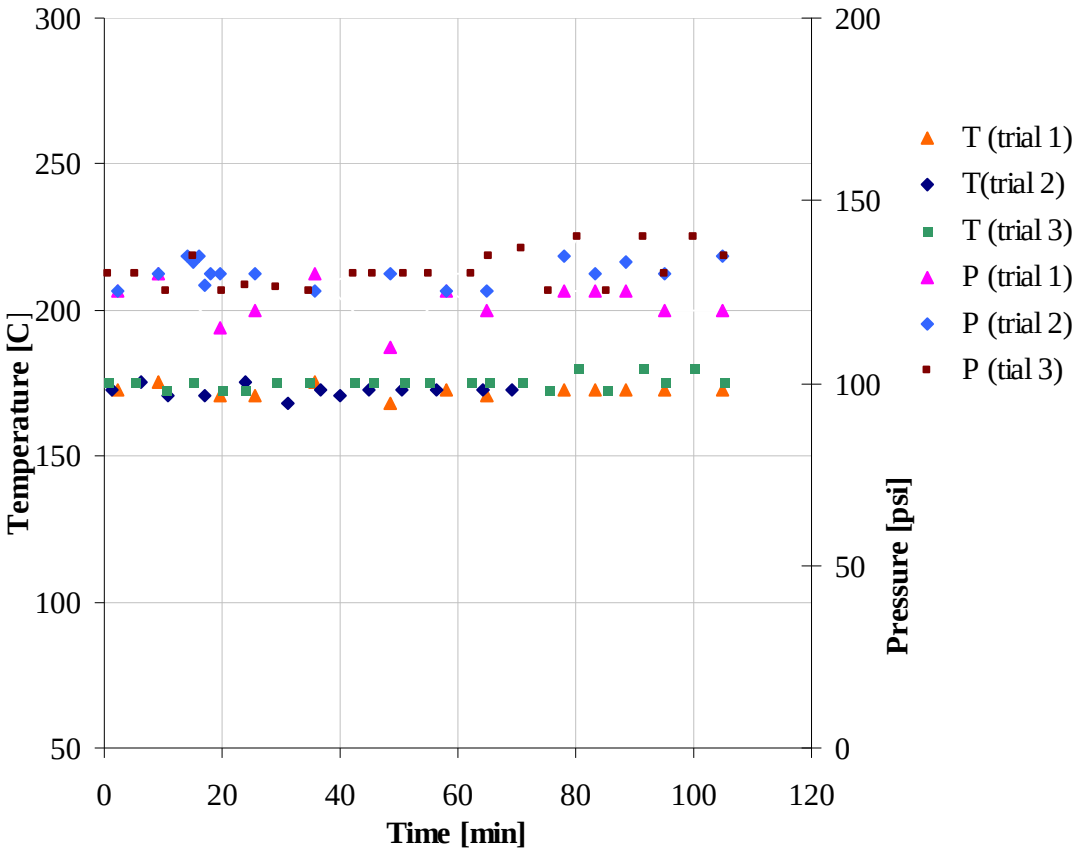


Figure 5. 6 Boiler E-120 Internal Temperature based on Pressure Readings

5.3 Extraction Process

After the mint is dry, it is chopped and loaded into the mint tubs (D-210 on the flow sheet). Figure 5.7 shows the dimensions of a distillation mint truck. The mint cookers are usually constructed of ¼" steel plate; the walls are 12 ga. sheet steel. None of the mint tubs are insulated.

It was observed that the hay packing inside of the tubs is not even (Figure 5.8). It is evident that the hay is often higher in the center than on the sides and uneven from front to back. Steam flows through the path of least resistance; hence unless some means of leveling the hay takes place, the hay near the sides of the tub will have the oil extracted much sooner than the center.

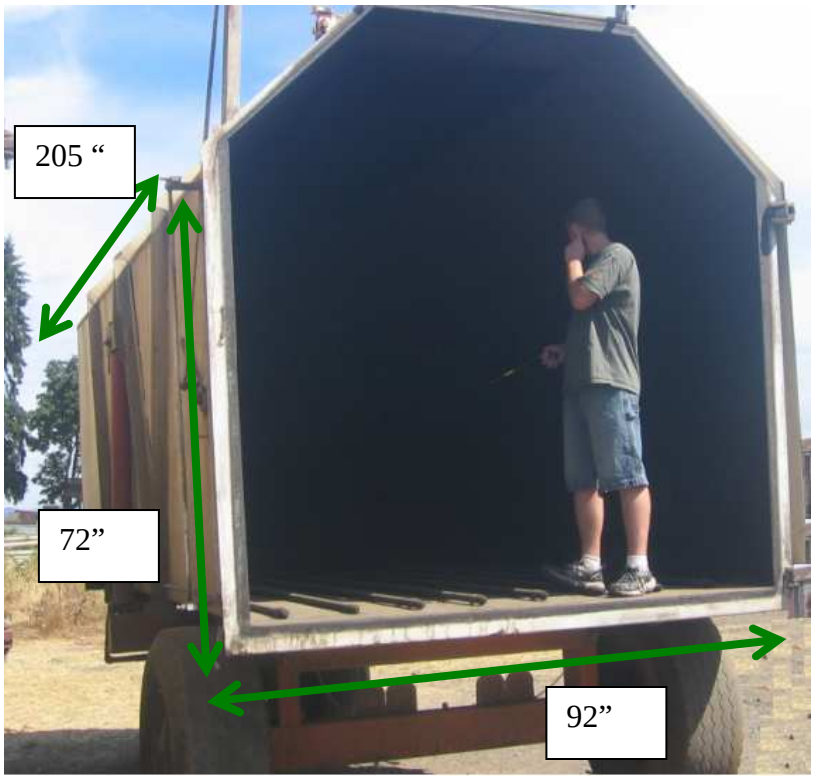


Figure 5. 7 Mint Tub Dimensions

Figure 5. 8 Mint hay inside the mint tub

Once the peppermint hay was filled into the tubs the steam lines are connected to the steam manifolds on the mint tubs to start pumping steam to the hay. The steam pumped to the mint trucks warms up the peppermint hay as well as the tub; the heat helps to vaporize the oil and water within the mint hay which then travels through the mint tub from bottom to top. Farmers agree that using higher pressure steam until the vapors “break through” facilitates the extraction process. However, each farmer uses different settings based on experience and what they consider is more efficient. Each still will have a different optimum setting due to the variance in the plumbing. “Break through time” is the time to obtain the first condensate drops. After the initial breakthrough, the steam gauge pressure is cut down to half. The breakthrough time varies depending on the temperature of the steam, the humidity of the hay, the ambient temperature, tub load, etc.

Temperature from the tub wall was recorded every 10 minutes starting when the steam line was connected to the bay (Figure 5.9).The temperature and pressure from the vapors coming out from the top of the tub were also measured and recorded every 5 seconds (Figures 5.10 and 5.11). Due to an equipment failure the first run data collected for this point cannot be used. However, the data obtained for the second and the third runs are consistent and reflect that the highest temperature of the steam leaving the tub is 100 °C and the pressure fluctuates between 103 and 101 KPa, which is consistent with experience and literature. The dip in Trial 2 was caused by the thermocouple falling out of position and not reflective of the process.

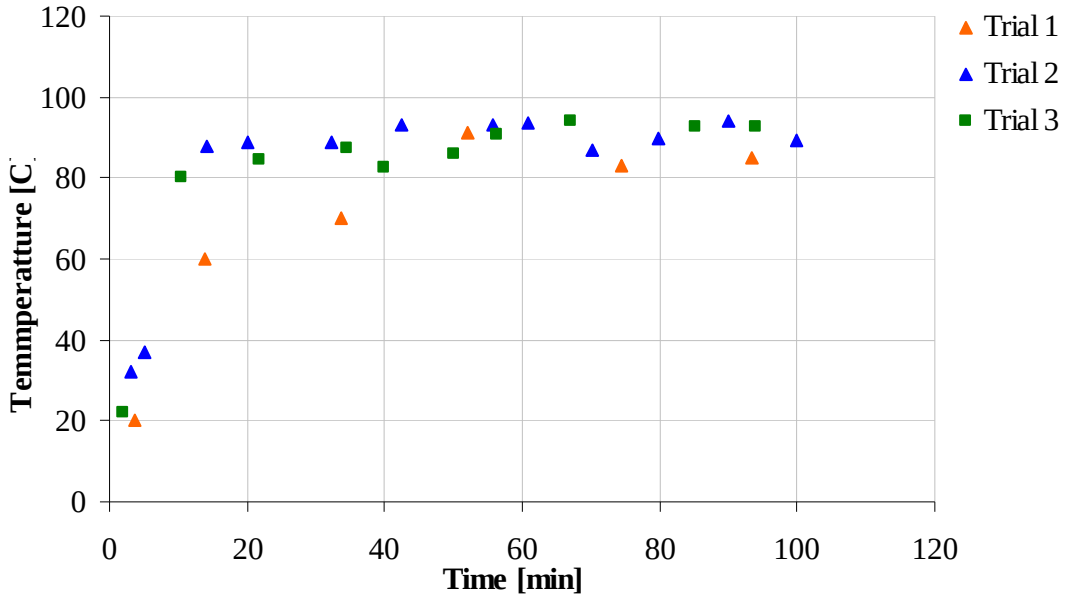


Figure 5. 91 External Wall Tub Temperature

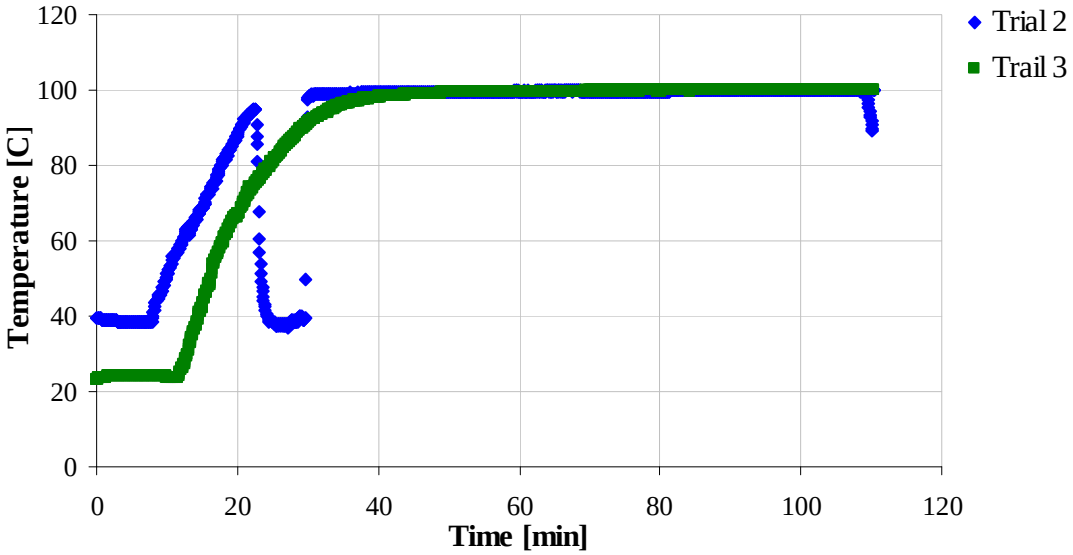


Figure 5. 10 Internal Distillation Tub Temperature

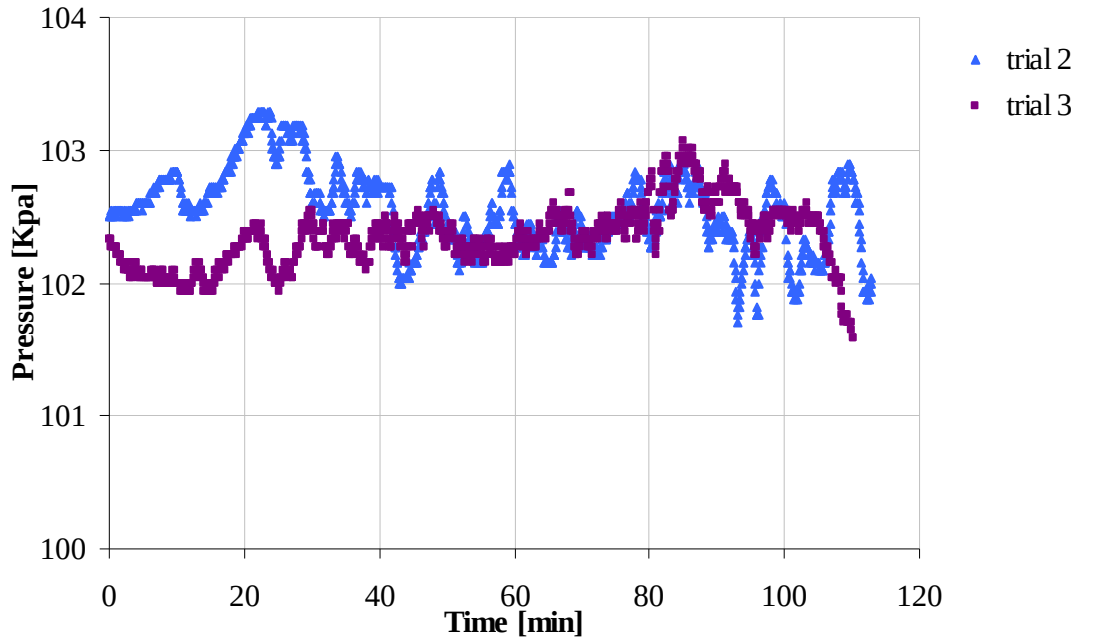


Figure 5. 11 Mint Tub Internal Pressure

As stated earlier, these mint tubs were uninsulated. We have heard that in some cases, the metal tub is processed with steam while rain is cooling its outer surface. This type of action significantly increases the amount of energy necessary, as the mint tub then offers conductive cooling to a temperature sink at the temperature of the rain, while the steam is attempting to heat the hay to a temperature of the vaporization of the mint oil.

5.4 Condensation and Separation Process

The water and peppermint vapor mixture flows through an 8” pipe to the vertical condenser (E-220 on the flow sheet). The condensers are located approximately 10ft. away from the distillation tubs. The condenser at this facility used ambient temperature water as coolant. Figure 5.12 shows the temperature profile of the cooling water going out of the condenser. This figure indicates the temperature of the water exiting the condenser does not remain constant. That was expected since the vapor flow rate to the condensers are not constant either. The cooling water fed to the condenser was not possible to measure, but according to the operators and the owner

of the still it is constant during the entire extraction process which could represent a problem to the condensation process. It was observed that vapors escaped from the condenser outlet which means that the coolant temperature is not low enough and that the coolant flow rate is too low. It was not possible to rearrange the pipes; quantitative information is not available on this observation.

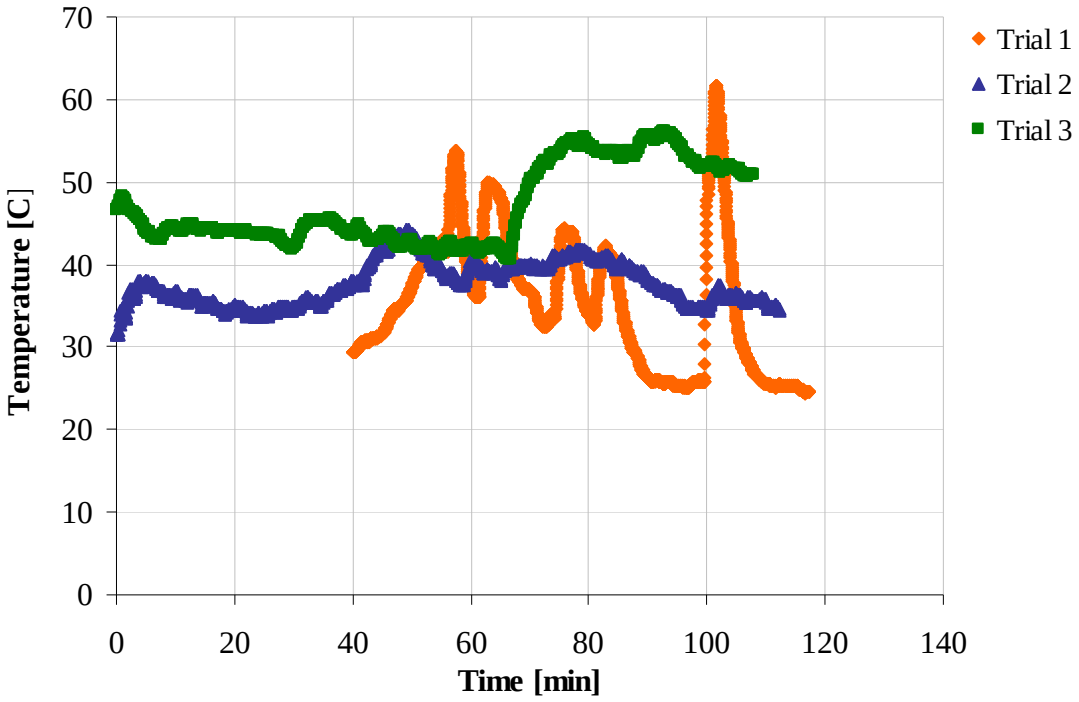


Figure 5. 12 Cooling H2O leaving the condenser

The temperature of the mixture of water and peppermint oil was measured immediately prior to the separation can. Figure 5.13 shows the temperature of the condensate at the condenser (E-220) exit. The data collected during the three runs show a lack of temperature control which affects directly the distillate flow rate. This behavior explains why the distill flow rate is not proportional to the fraction of oil extracted.

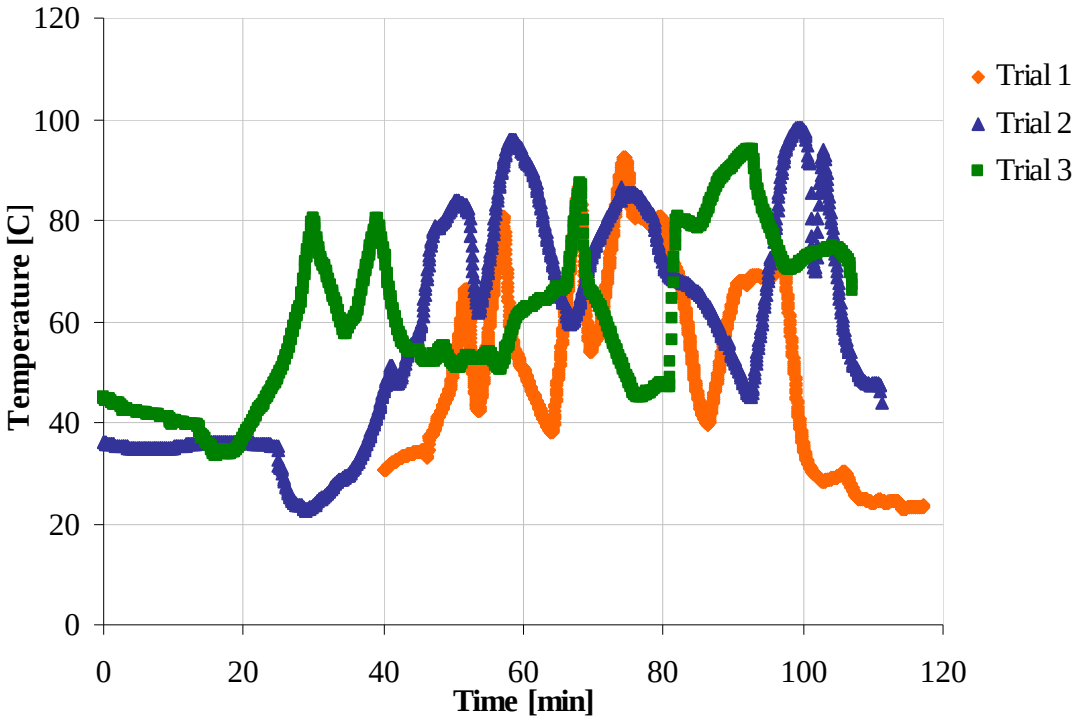


Figure 5. 23 Condensate Temperature Profile

The product outlet from the condenser goes to the receiving can where the oil and water are separated by gravity. It is known from literature and experience that the optimal separation of the mixture water/mint oil temperature is approximate 40 °C (Denny 1991). Figure 5.14 shows that the temperature varies between 60 °C and 35 °C with an average of 50 °C. Some oil can be lost in the separation process due to the high temperature of the distillate. This is another key that suggests that the condenser operating temperature needs better control to get a higher quality separation and to save resources.

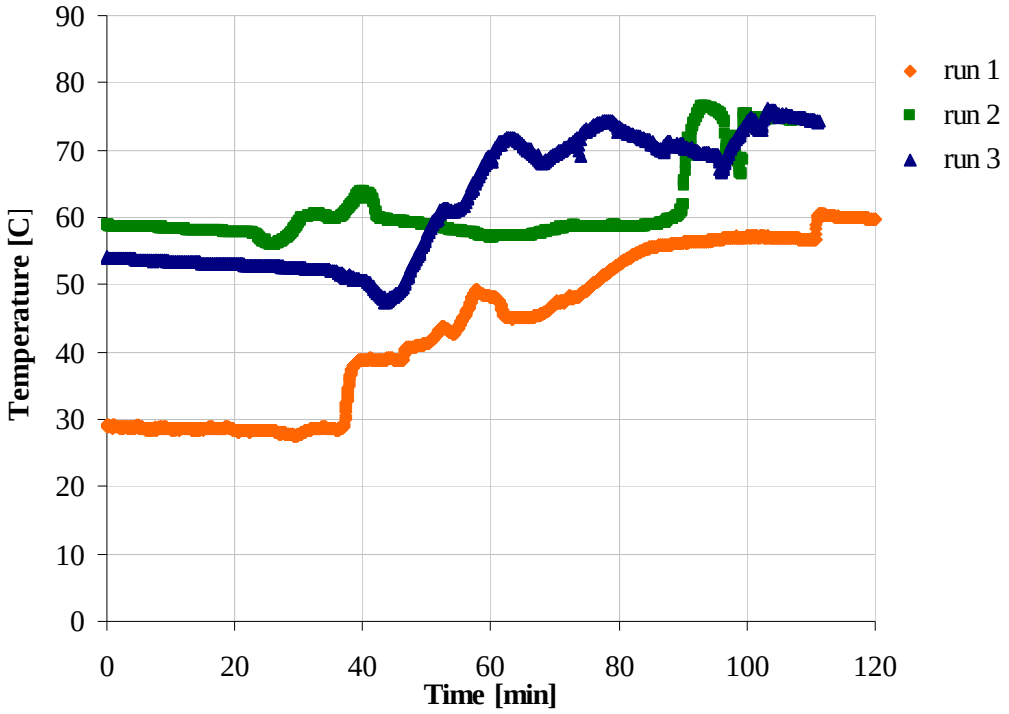


Figure 5. 34 Separation Can Temperature

The water from the separator can be redistilled to get the remaining oil out of the water and clean the water so it can be reused in the boiler.

5.5 Distillate Composition

Samples of the peppermint oil/water mixture were collected from the condenser outlet stream. The samples were taken at regular intervals throughout the entire extraction process. Figure 5.15 shows the condensate composition as a function of the extraction time. The data collected shows variability in the breakthrough time. It is known that the breakthrough occurs around forty five minutes after the steam is fed to the mint tub. According to Figure 5.16 the first oil drop comes around the minute twenty for the second and the third run and at minute forty for the first run. The high composition point at the minute seven on the first trial reflects the final composition of the previous run, therefore that point it is not considered as the breakthrough time. Figure 5.17 shows the oil flow rate of each trial. It was expected that the flow rate and the

composition curves would have the same behavior; however it does not occur, thus a high condensate flow rate does not imply a high mint oil composition.

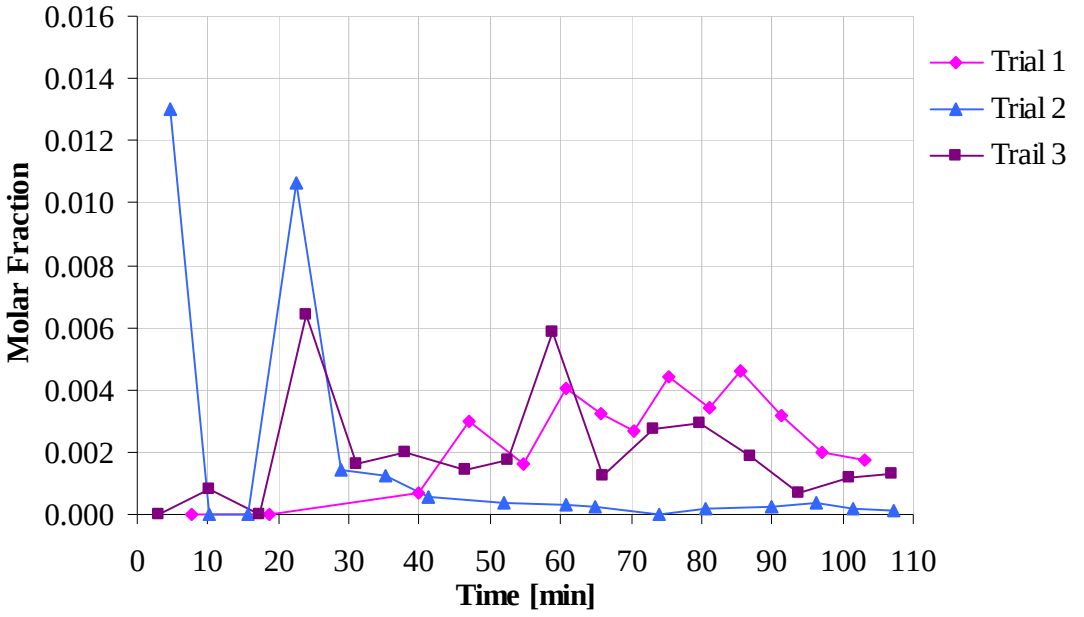


Figure 5. 15 Condensate Composition

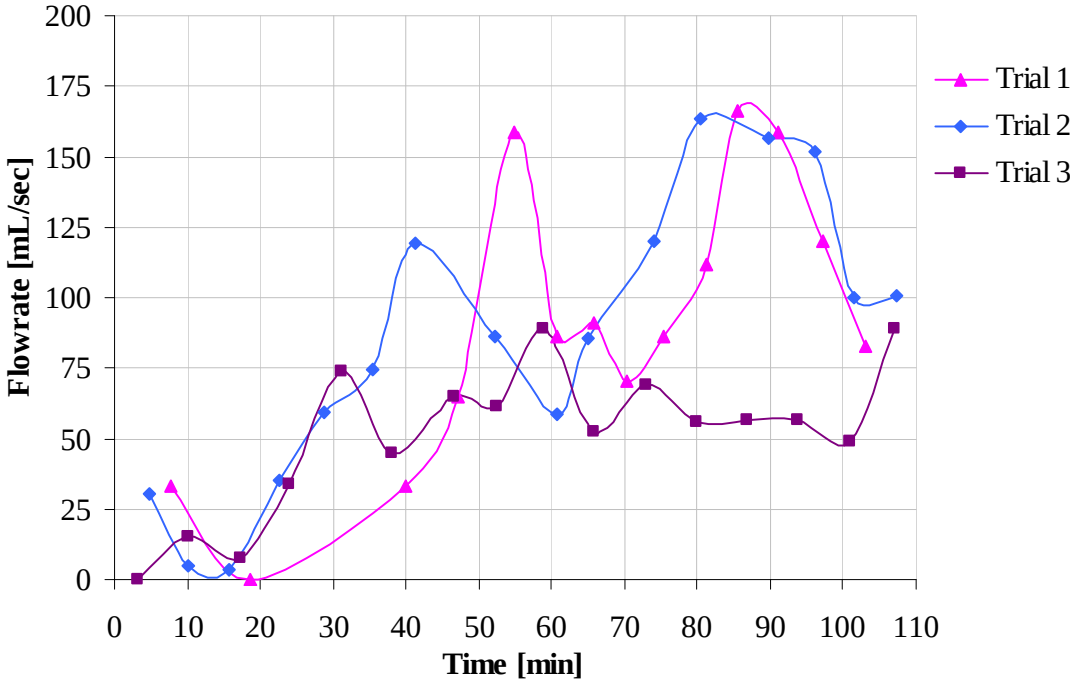


Figure 5. 16 Condensate Flow rate

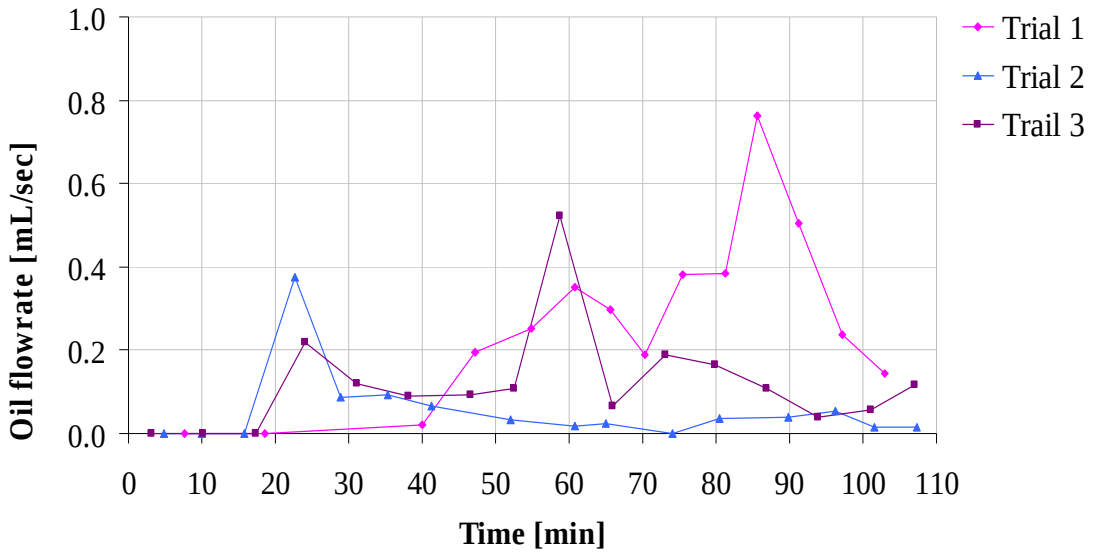


Figure 5. 47 Oil Flow rate

5. 6 Redistill Composition

Figure 5.18 shows the composition from the redistill unit. The water from all the separation cans is redistilled to recover the non-recovered oils; therefore it was not possible to get the data from only one line. The figure displays the information of this particular piece of equipment and is from the twelve tubs running at the same time.

Even though the amount of oil recovered from the redistill section is not considerable and its quality is low, this unit is used to clean the water so it can be reused as a boiler feed; clean water helps to avoid damage to the equipment due to presence of mint oil. Water treatment is the main objective of this unit because as Figure 5.18 shows the amount of mint oil collected varies between 0.1% and 0.01% of oil recovered. The total amount of oil recovered in the redistill unit at the Setniker farm is approximately one barrel per year, and this mint oil is considered very low quality by the buyers.

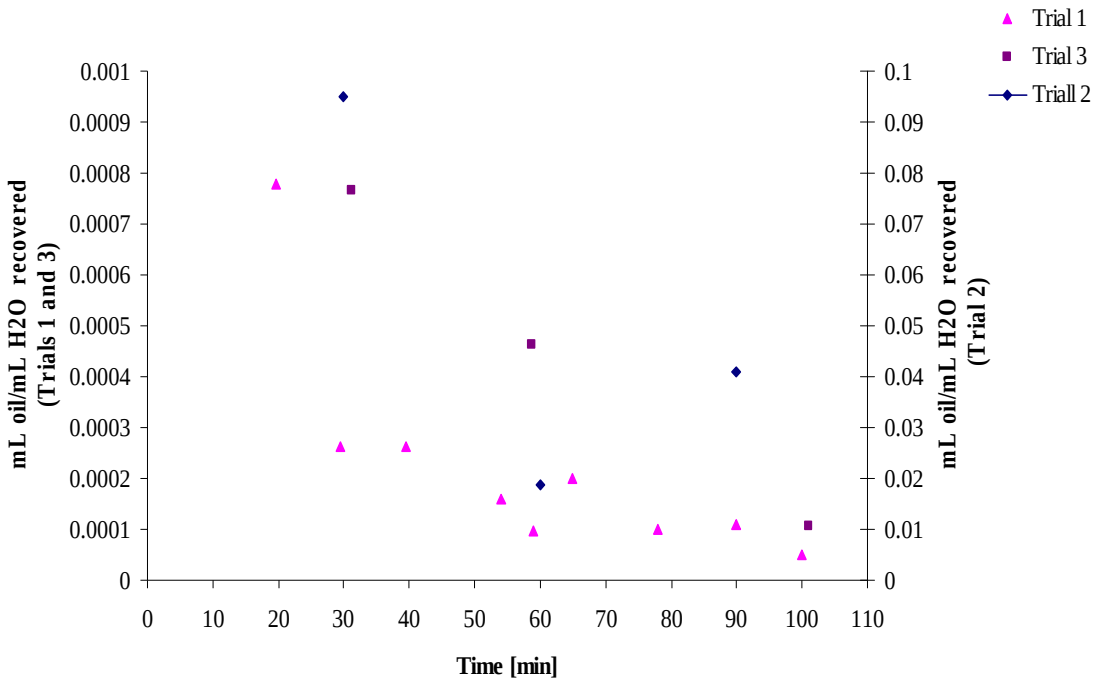


Figure 5. 5 Oil Recovered by the Redistill Unit

5.7 Total Peppermint Oil Extracted

Figure 5.19 shows the cumulative amount of mint oil obtained over the total extraction time process of the second and third runs. The green line illustrates when the oil collected in the separator is drained to the barrel; thus the last three points represent the amount of oil trapped in the separation can during the total extraction time. The amount of mint oil recovered is almost the same for all the three runs as Table 5.1 shows. The differences of the three runs are due to variations of the mint hay moisture before the steaming, mint hay packing inside the tub, the condenser operating temperature, etc.

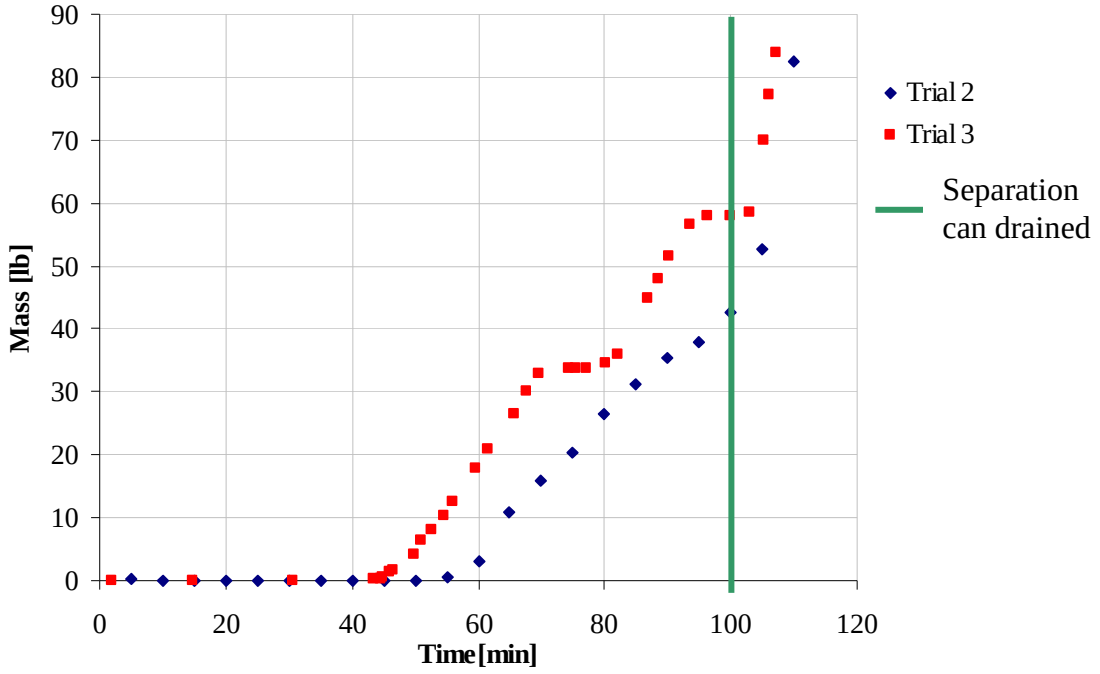


Figure 5. 6 Mass of Peppermint Oil Recovered

Figures 5.20 and 5.21 show the energy cost of extracting peppermint oil, gross revenue rate and the net revenue rate. These calculations were done assuming a cost of the natural gas of 0.8 $/therm and a selling price of peppermint oil at $14/lb. These graphs can be used to estimate the best time to stop steam flowing to a mint tub. The last data point of the oil flow rate is actually the draining of the separation funnel between mint tub runs as it is drained completely before the next run. This was done to enable quantification of the amount of oil in one tub of mint hay and does not represent an increase in oil coming from the hay at the end of the run. The flow of oil from the mint hay is at nearly zero at approximately the 90 minutes after the steam lines were connected. Therefore ninety minutes will be the optimal stop down time before the energy cost of extracting oil is higher than the net revenue. The graph from the first trial is not reported due to lack of data.

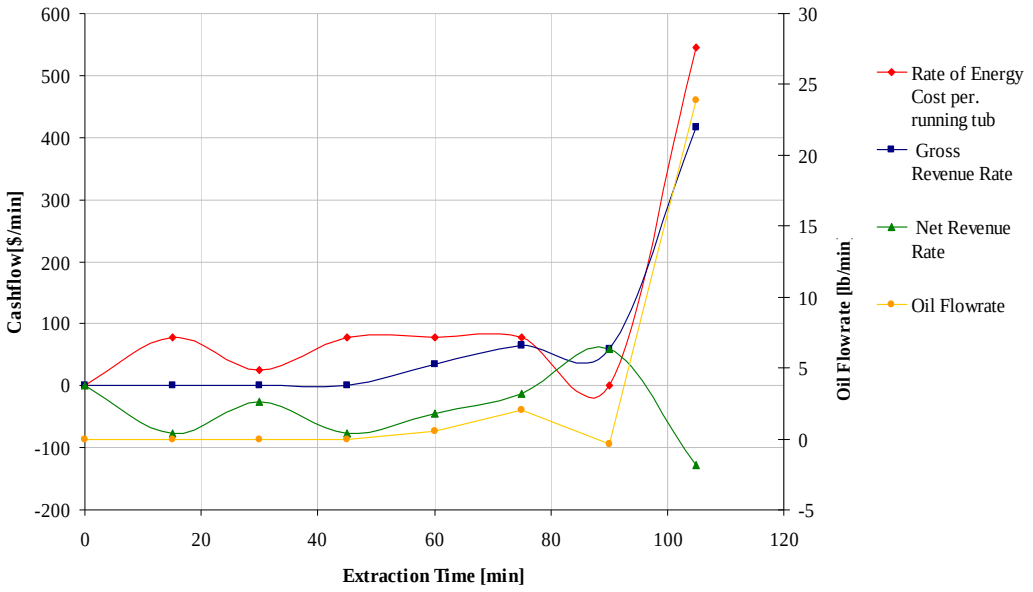


Figure 5. 7 Energy Cost (Trial 2)

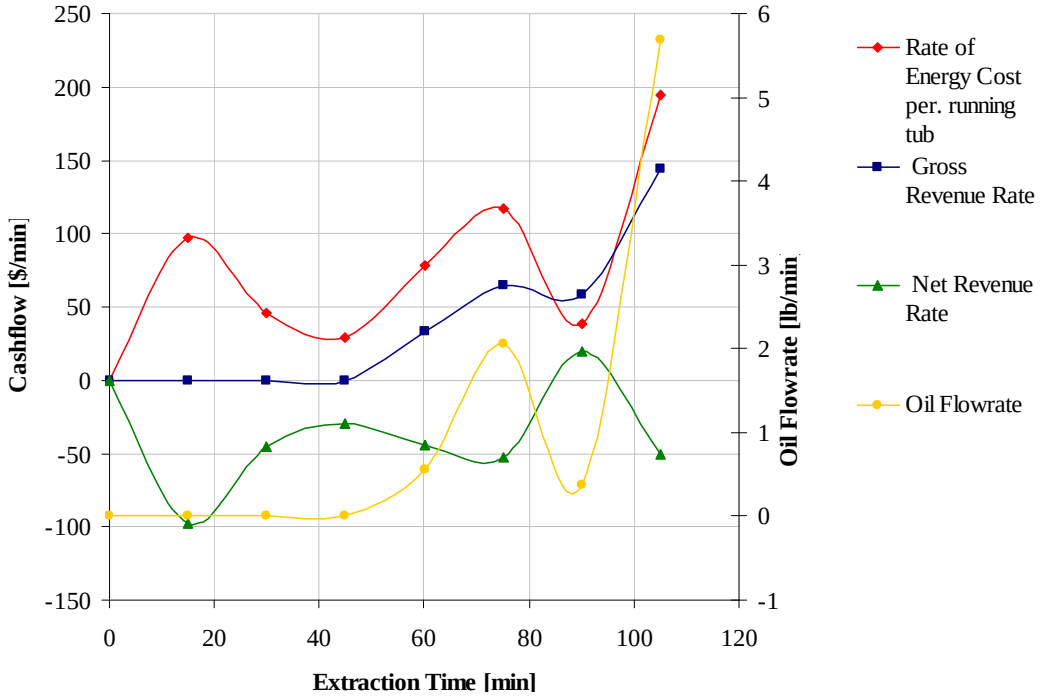


Figure 5. 8 Energy Cost (Trial 3)

5.8 Boiler Feed Tank

Water from the condensers is sent to a recycling tank which feeds the boilers. This stainless steel tank is not covered or insulated; its volume is approximately 3 m^3. It was observed that after the distillation has been running for approximately 40 minutes at its maximum capacity, the boiler tank overflows. The temperature of the water inside the tank was measured; the temperature at the top at times is much higher than the temperature at the bottom as figures 5.22 and 5.23 show. This means that the best place to draw make-up water for the boiler is from the top of the tank, for example with a floating siphon, and the best place to select water for the condenser is where the water temperature that the condensate (which will then flow into the separator) will be at the optimum separation temperature of 40° C. Such action would require a redesign of the tank to retain the higher temperature water instead of the current mixing process. In the case of the facility observed, no such automatic controls were in place. Table 5.1 is a stream summary of the measurements and calculations collected at the Setniker still.

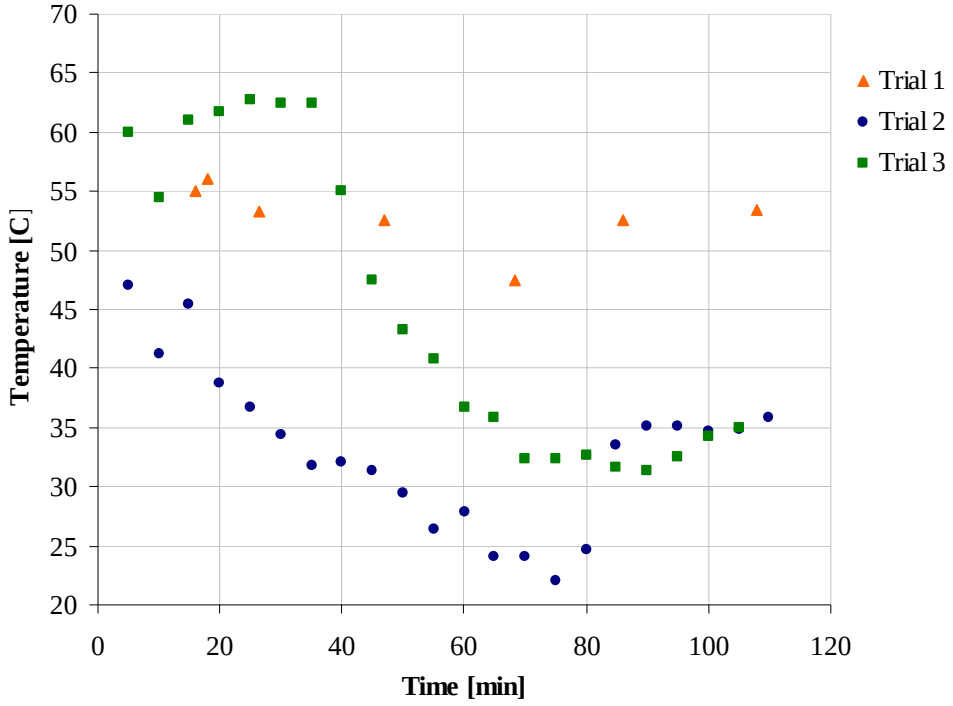


Figure 5. 9 Boiler Feed Tank Temperature (top)

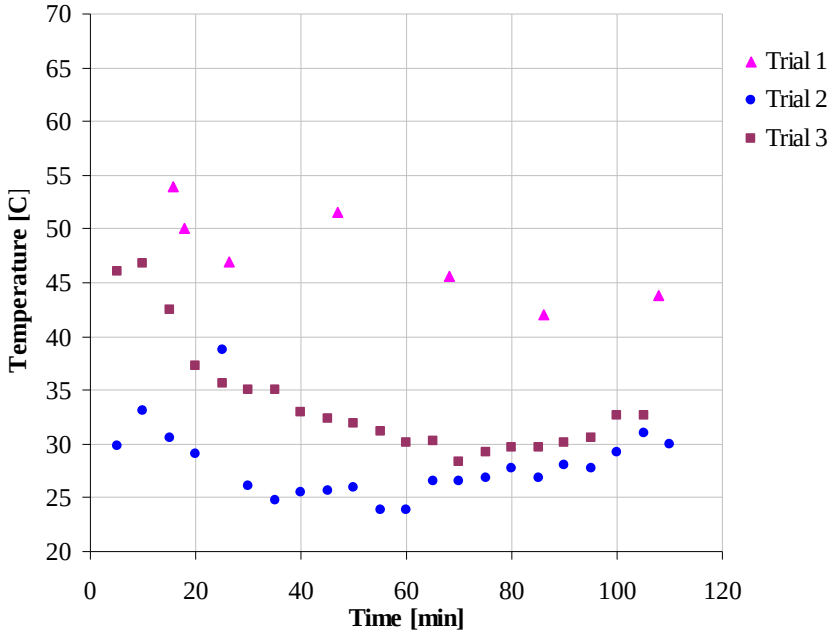


Figure 5. 10 Boiler Feed Tank Temperature (bottom)

Table 5. 1 Data Summary

		Run # 1	Run #2	Run # 3	Notes
Moisture Content	Overall Run Time	1:50	1:47	1:51	
	Breakthrough	0:40	0:28:50	0:23:06	
	Before	49.2%	55.6%	36.3%	
	After	67.2%	57.2%	50.7%	
Weights [kg]	Truck [kg]	24800	24800	-	
	Mint [kg]	16500	16600	16000	
	After steaming [kg]	19459	18100	-	
Peppermint oil Extracted	reading from scale [kg]	33.66	37.47	38.10	
	reading from scale [lb]	75.00	82.60	84.00	
	lb oil/lb of hay	20%	23%	24%	assuming 1% oil total
	$ obtained	1050.0	1156.40	1176.00	assume $14/lb
Natural Gas (NG) consumption	# Tubs running	8	3	4	
	NG used [m^3]	2203.16	1232.00	1240.00	
	NG / tub [m^3]	287.37	448.00	320.00	
	$ spend in NG only	83.60	130.33	93.09	2.75 m^3 produces 1therm
	[cost $/lb extracted]	1.11	1.58	1.11	$0.8/therm
Profit	$	**966.40**	**1026.07**	**1082.91**	
Left Boiler	Temperature [C]	215.13	153.89	158.74	superheated
	Pressure [bar]	7.83	7.85	8.09	vapor
Middle Boiler	Temperature [C]	172.32	174.63	175.45	T from Steam tables
	Pressure [bar]	8.43	8.93	9.03	assuming sat steam
Right Boiler	Temperature [C]	135	146	169.60	T and P lower than sat
	Pressure [bar]	8	8.48	8.39	conditions
average Temperatures [C]	T3	33.72	53.19	55.09	
	T5	15.45	16.08	13.88	
	T4	98.71	50.79	51.34	
	T2	63.67	64.67	57.99	
	T25	38.52	38.52	48.51	
	T13	42.44	37.71	47.07	

5.9 Conclusions and Recommendations to improve current operation

Due to difficulties in access to all the sample points it was not possible to evaluate the facility completely. However the production of peppermint oil in Oregon was well understood and practical suggestions that will help to save money in the operation of stills can be made. These suggestions do not imply any changes in the current still operations; they are only some adjustments that will help to get more out of the current process.

1. The hay should be leveled before steam comes through to have a uniform steam resistance and ensure a vapor rich in mint oil coming out from the top of the mint tub. This modification ensures a more effective use of the steam produced by the boilers.

2. Insulating all the pipes which carry the vapors will reduce the heat loss due to convection with the environment. Adding insulations will reduce the operating cost of the condensers as well. Table 5.2 shows the costs of insulated and no insulated pipes per running tub; and also the total cost assuming there are twelve running tubs. The calculations are available in Appendix E and F .

Table 5. 2 Opportunities of savings using insulation on the pipes

Heat loss due to:	$/running tub	$ / 12 running tubs	Cost Reduction
Convection only & no insulation	0.19	2.27	85.4%
Convection & 2cm foam insulation	0.03	0.33	

3. A rain shelter over the mint tub docking region should easily pay for itself after one rainstorm. Operating the still under cold or rainy environment will be prejudicial to the overall mint extraction process. Insulating the mint tubs would be the best action to take. This allows one to use all the steam produced by the boilers on only heating up the mint hay and reduces the heat losses of heating the

mint tub. Insulating all the mint tubs can be expensive for farmers; however covering the mint tubs from the rain is a simple action that would save money in the steam production unit. Table 5.3 shows the comparison between the cost per running the mint tubs with and without insulation; and also the total cost of running twelve tubs. The calculations are available in Appendix E.

Table 5. 3 Opportunities of savings using insulation on the tubs

Heat loss due to:	$/running tub	$ / 12 running tubs	Cost Reduction
Convection only & no insulation	24.50	294.05	98.5%
Convection & 2cm foam insulation	0.37	4.50	
Rain & no insulation	103.67	1244.04	99.6%
Rain & insulation	0.38	4.55	

4. The internal temperature does not correspond to the expected steam pressure under the conditions desired. From thermodynamic steam tables, one can deduce that at the observed pressure, the temperature should correspond to superheated vapor which would be around 170°C. The variation on temperature and pressure from boiler to boiler reflects that the optimal operating conditions are not well known. The fact that the boilers produce superheated vapor and sometimes they do not produce vapor puts in evidence the lack of process control in the facility and the poor performance of the boilers. It is also possible that the pressure gauges and/or the temperature indicators are not functioning as well. It is recommended to perform maintenance on the boilers to make sure they are delivering steam at the desired conditions.

5. Installing a flow meter to control the cooling water used by the condensers would be useful to ensure no vapors are lost due to poor condensation.

6. By using the condenser cooling water not needed for re-entry into the make-up tank, the water in the tank would be cooled less and hence the temperature of the

water entering the boiler would be higher. This would reduce the cost of the steam generation, and can be afforded by judicious placement of return pipes and a float valve which only opens to enable the pipe's use if the tank reaches a predetermined low level. The surplus water would be better diverted to other uses (agricultural irrigation, etc.) through simple use of an open pipe extension at the maximum fill height of the tank to act as a siphon break, after which the waste water could be returned to some cistern for use. The heated condenser water should be the primary feed of the boilers due to the fact that it is pre heated and will cost less to turn into steam.

7. On average the energy cost per running tub was determined to be 1.26 $/ lb of oil extracted based on 120 minute run time. Decreasing the running time to 90 minutes which is the time when the oil flow decreases enough to cause the cost of steam production to be higher than the net revenue should decrease the energy cost per running a tub and increase the net profit.

8. The lack of process control is evident in every single piece of equipment, however the fact that this facility has run successfully for decades indicates that one must first ensure that such additions will be cost effective. Installing efficient temperature and pressure indicators and controllers could be expensive, however this implementation represents saving to the operating cost of the mint sill and ensures a higher percentage of mint oil extracted. A recent observation of the Thacker facility in Bow Island, Alberta Canada proves that not only is it cost effective, it also dramatically increases the consistency and quality of the product (Hackleman, Velasco 2007). In this report a few opportunistic examples will be provided.

9. Further measured data would give more confident in the evaluation of the efficiency of the current process. This next phase may best be performed by individual extraction facilities utilizing the same means used in this study.

10. It is recommended that further investigation be performed on the optimal stage of the peppermint hay dryness.

11. Mint oil heat capacity for the liquid phase was determined: 3.358 J/g °C. The liquid mint oil density was determined as well: 0.89 g/mL. These values were not evident from the literature.

6. Results: Solvent Free Microwave Distillation

The microwaves applied to the hay break the oil cells and heat the water present in the stomata and the plant stems. The temperature of the water reaches its boiling point at atmospheric pressure, and as it was mention earlier the mixture is extracted at the minimum boiling point component. This method uses the steam produced by microwave heating of the water available in the plant; because of the Raoult's law behavior of the vapor composition, the steam carries the non miscible liquid portion in the plant as a vapor allowing the extraction to be possible.

6. 1 Material Balance

In order to determine the efficiency of this new extraction method, the following assumptions were done to perform the mass balance:

1. The material balance is performed only on the still flask taking into account the following species:
    a. Peppermint Oil (o)
    b. Water (w)
2. During extraction only the liquids trapped in the peppermint leaves are evaporated, the amount of plant material remains constant before and after extraction. (Mass of solids is constant before and after the extraction)
3. To determine the initial moisture content of the plant material, it was oven dried. It was assumed that all the liquid content was evaporated.
4. Literature states the approximate peppermint oil content in the plant is 1% by mass.
5. Assume optimal water-oil separation. The TOC tests were used to quantify the amount of carbon components left in the water extracted. The results from the four samples used reveled that the total carbon left in the water varied from 0.11% and 0.14%. This information allows assuming that the water extracted from the microwave process was free from peppermint.
6. No chemical reaction

7. No accumulation

The overall material balance on the liquid phase is described by equation

$$M_{before\_extraction} - M_{after\_extraction} + M_{lost} = 0 \qquad [\text{g}] \quad (3)$$

The material balance by species is modeled by equations 4 and 5:

$$M_{before\_extraction} = M_{o\_in} + M_{w\_in} \qquad [\text{g}] \quad (4)$$

$$M_{after\_extraction} = M_{o\_out} + M_{w\_out} \qquad [\text{g}] \quad (5)$$

The initial mass of water in the plant is calculated using equation 6 and assuming that the percentage of oil in the plant is 1% (Win).

$$\text{Initial Moisture Content} = W_{in} + O_{in} \qquad [\%] \quad (6)$$

Then, the initial mass of water and oil can be calculated by equations 7 and 8.

$$M_{w\_in} = M_{before\_extraction} \times W_{in} \qquad [\text{g}]$$
$$M_{o\_in} = M_{before\_extraction} \times O_{in} \qquad [\text{g}] \quad (7), (8)$$

The amounts of water and peppermint oil extracted (M_{w_out} and M_{o_out}) is known from the measurements of both the liquids after they are separated.

6.2 Energy Balance

The total energy (E) used by the microwave was calculated by equation 9, where P is the power used by the microwave and t is the extraction time.

$$E\ [\text{J}] = P\ [\text{W}] \cdot t\ [\text{sec}] \quad (9)$$

The cost of energy according to the Pacific Corp is 4.4 cents per kWh, using this factor is possible to calculate the cost of energy per run.

To calculate the total energy needed to extract the liquids from the plant the following assumptions were needed:

1. The value of the peppermint hay heat capacity was found on a previous study (Chen and Spiro 1994). It was assumed that this value includes the water and peppermint oil contained in the plant before extraction.
2. Due to the low concentration of peppermint oil in the liquid phase (1%); it was assume the mixture was very dilute, approximately 100% water. ΔH_{vap} of water was used.

The theoretical amount of energy needed was calculated by the following equation (10):

$$E' = \left(M_{hay} \cdot Cp_{hay} + M_{glass} \cdot Cp_{glass}\right) \cdot \left(T_f - T_o\right) + \left(Liq_{extracted} + Liq_{lost}\right) \cdot \Delta H_{vap} \quad (10)$$

where,

$$Cp_{hay} = 3.58\left[\frac{J}{g \cdot K}\right]$$

$$Cp_{glass} = 0.75\left[\frac{J}{g \cdot K}\right]$$

$$\Delta H_{vap} = 2270\left[\frac{J}{g}\right]$$

The efficiency of the microwave is determined by equation (11):

$$\eta = \frac{E'}{E} \cdot 100 \quad (11)$$

6.3 Maximum Operating Conditions

The operating conditions were determined by exploring the longest extraction time possible before the peppermint hay ignites. Three repetitions confirmed the ignition time at the power settings decided previously. Table 6.1 shows the upper limit operating conditions at the different power settings available. The experimental data is available in Appendix F

Table 6. 1 Maximum Operating Conditions

	First Step		Second Step		Total
	Power [W]	Time [min]	Power [W]	Time [min]	Energy Applied [KJ]
High	1120.0	3	-	-	201.6
Medium	697.1	4.5	-	-	188.2
Medium Low	518.2	6	-	-	186.6
High & Medium	1120.0	1.5	697.1	2	184.5
High & Medium Low	1120.0	1.5	518.2	2.5	178.5
High & Medium	1120.0	2	697.1	1.25	186.7
High & Medium Low	1120.0	2	518.2	1.5	181.0

6.4 Extractions at 1120 Watts (High Power)

The breakthrough time observations show that the first drops of liquid come out to the condenser on average at 1.2 minutes with a maximum variation coefficient of 10% (Figure 6.1). The first data point that was feasible to collect was at 1.5 minutes. The extraction temperature is equal to the boiling point of water at atmospheric pressure on average 100 °C with a variation coefficient of 2% (Figure 6.2).

Figure 6.3 shows the percentage of oil extracted calculated assuming there is 1% of essential oil available in the plant. Figure 6.3 also shows the cost of extracting the oil at each extraction time. The error bars represent the variation coefficient of the percentage of oil extracted. The fraction of oil collected at 2.5, 2.75 and 3 minutes is comparable; this shows that the best extraction time is 2.5 minutes because it requires less energy. Figure 6.4 shows how increasing the extraction time helps to extract more

water; the maximum amount of water extracted is 64% with a variance coefficient of 6% at 3 minutes extraction time.

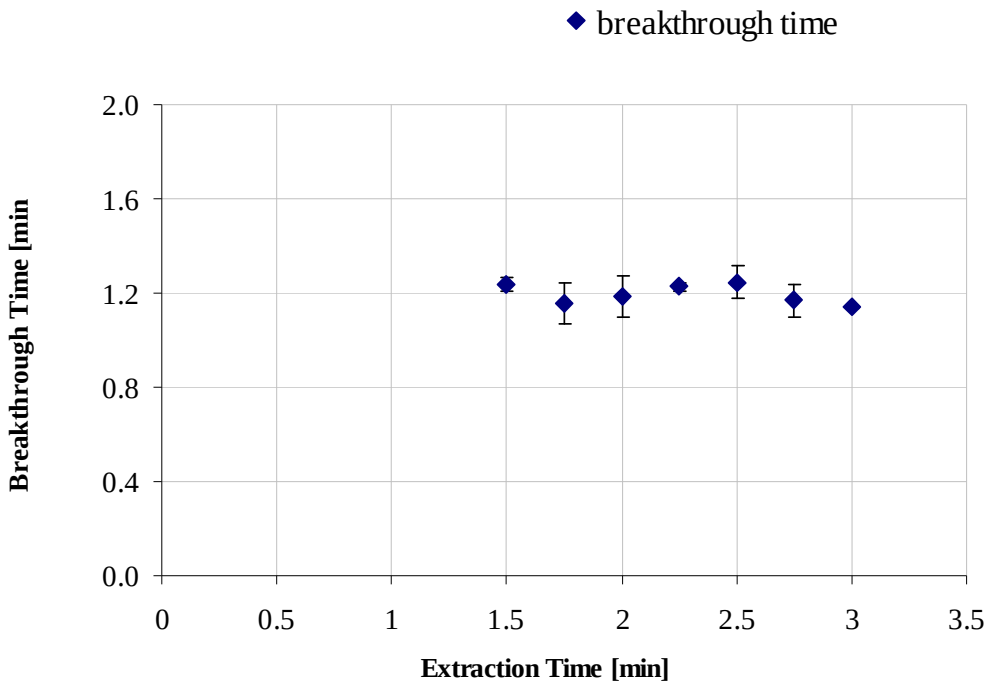


Figure 6. 1 Breakthrough Time vs. Extraction Time relationship (1120 W)

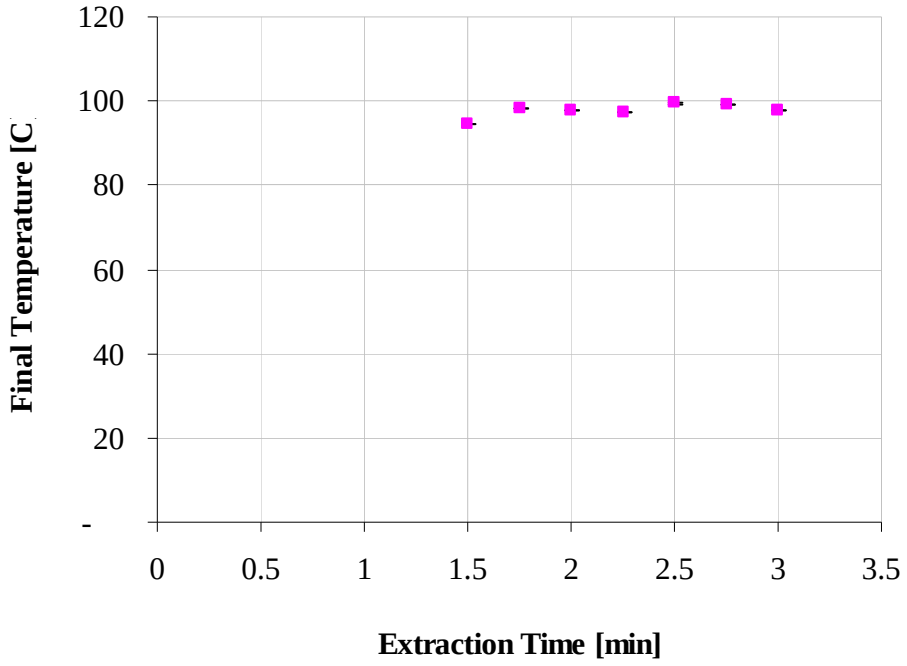


Figure 6. 2 Final Temperature of 1120 W Process (1120 W)

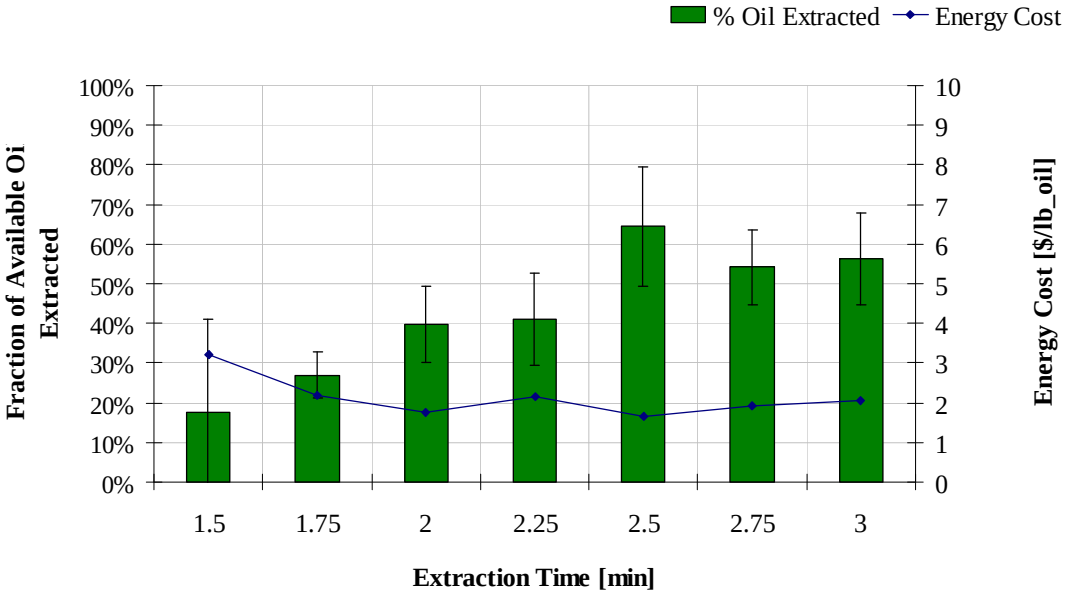


Figure 6. 3 Percentage of Oil Extracted (1120 W)

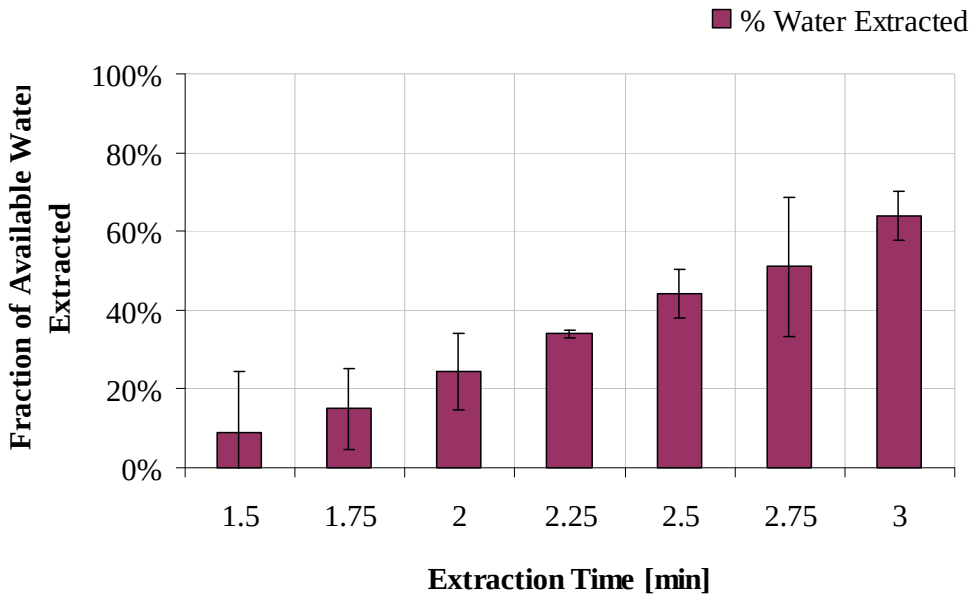


Figure 6. 4 Percentage of Water Extracted (1120 W)

Figure 6.5 shows the average mass balance on the liquid phase at each extraction time; as it was expected the amount of water and peppermint oil extracted is proportional to the extraction time. The quantity of liquids remaining in the plant material after extraction reduces as the extraction time increases. The amount of liquids unaccounted for vary between 9% and 24%. The liquids unaccounted for represents the sum of the liquids lost during extraction and variance.

The quality of the oil extracted is presented in the following figures which are the result of GC analysis. The twelve components selected to be monitored are distributed in 4 figures to make the observation easier. Figure 6.6 through 6.9 compare the average composition of peppermint oil extracted as a function of the extraction time with an ideal sample obtained from steam distillation.

It is observed that the concentrations of menthol, neomenthol, esters, terpenen-4-ol, pulegone and germacre-d are proportional to the extraction time increase. All these components seem to approach equilibrium at the three longer extraction times (2, 2.5 and 3 minutes).

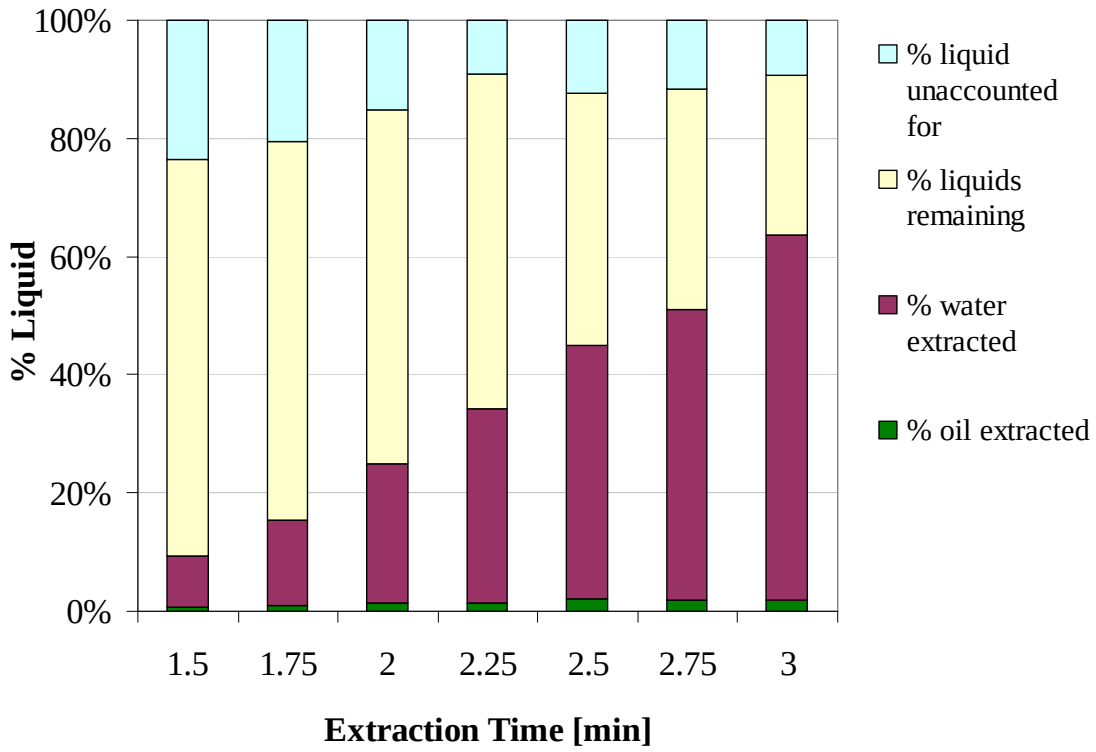


Figure 6. 5 Mass Balance on the Liquid Phase (1120 W)

The concentration of menthone, cineol, isomenthone, furan, limonene and t-sabine hydrate follow the opposite pattern; their concentration decreases as the extraction time increases (Figure 6.7)

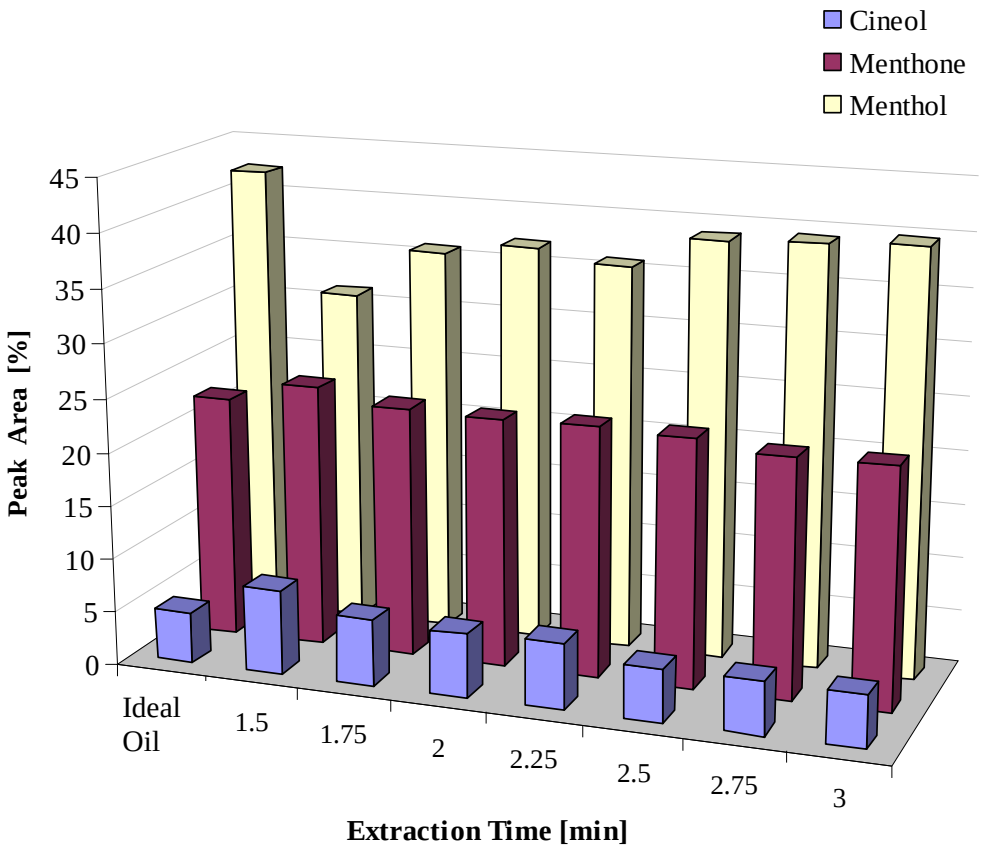


Figure 6. 6 Cineol, Menthol and Menthone Composition (1120 W)

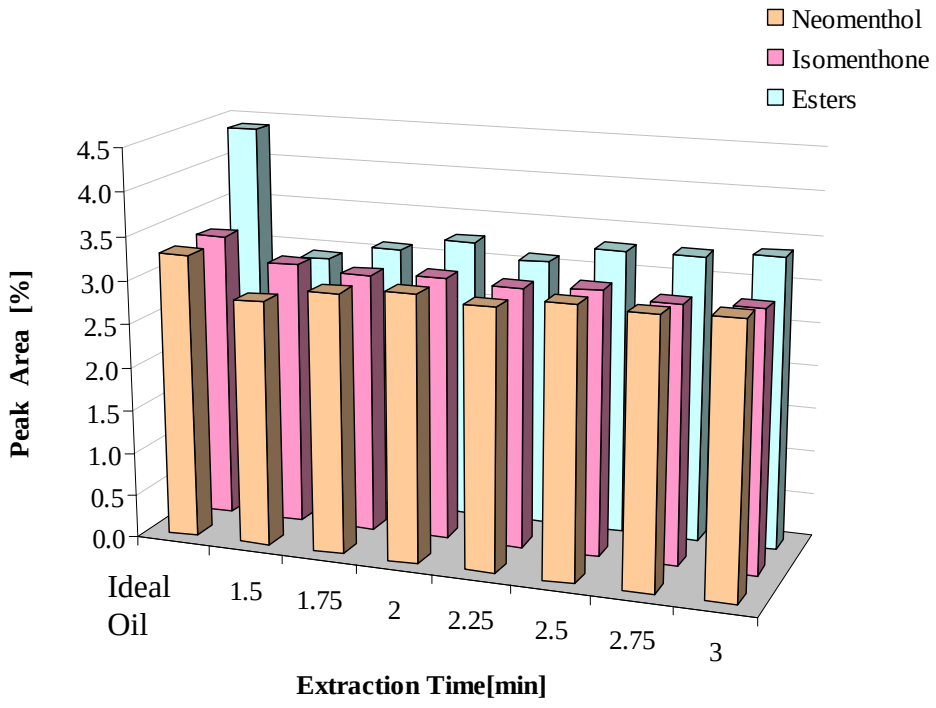


Figure 6. 7 Neomenthol, Isomenthol and Esters Composition (1120 W)

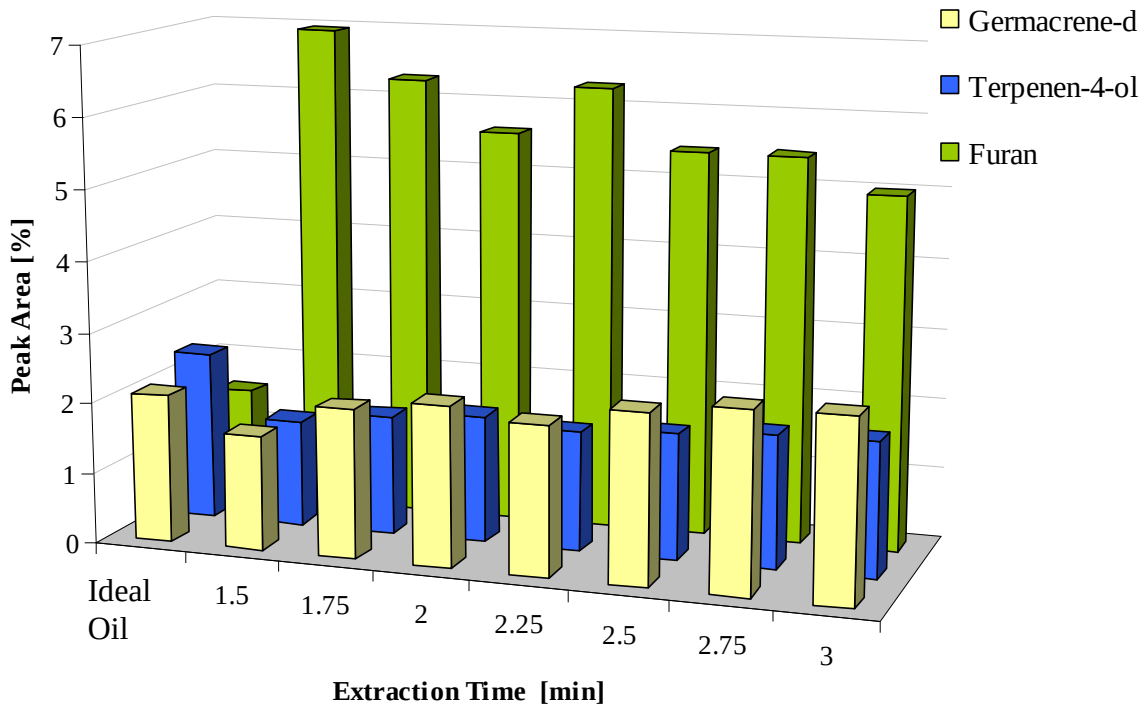


Figure 6. 8 Germacrene-d, Terpenen-4-ol and Furan Composition(1120 W)

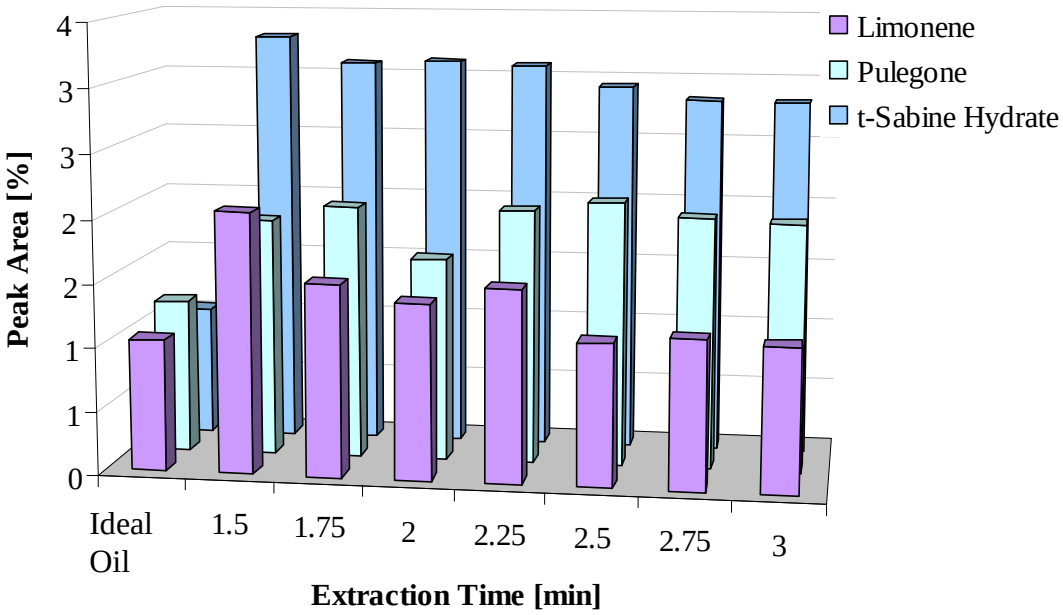


Figure 6. 9 Limonene, Pulegone and t-Sabine Hydrate Composition (1120 W)

The variation of the oil extracted composition was calculated as the variation of each component peak area with respect to the standard oil (equation 11)

$$\%\text{Variation} = \frac{\text{Observation Concentration-Standard Concentration}}{\text{Standard Concentration}} \quad (11)$$

Table 6.2 summarizes the variation of all the components concentration with respect to the standard. A negative variation reflects that the concentration of that component on the sample is lower than the standard concentration. A positive variation indicates that the concentration of the samples is higher than the standard concentration.

Table 6. 2 Composition Variation with respect to the Standard (1120 W)

	Extraction Time [min]						
Component	1.5	1.75	2	2.25	2.5	2.75	3
Limonene	98%	46%	33%	46%	8%	13%	9%
Cineol	65%	29%	23%	29%	3%	2%	2%
t-Sabine Hydrate	220%	200%	202%	200%	184%	175%	174%
Menthone	9%	3%	2%	3%	2%	-1%	-1%
Furan	347%	305%	260%	305%	250%	250%	221%
Isomenthone	-8%	-9%	-8%	-9%	-8%	-10%	-9%
Esters	-34%	-30%	-26%	-30%	-25%	-25%	-24%
Neomenthol	-14%	-9%	-7%	-9%	-5%	-6%	-5%
Terpenen-4-ol	-37%	-29%	-25%	-29%	-26%	-22%	-20%
Menthol	-26%	-15%	-13%	-15%	-8%	-7%	-6%
Pulegone	56%	65%	33%	65%	72%	63%	61%
Germacrene-d	-23%	1%	9%	1%	14%	22%	23%
Total	0%	1%	1%	1%	2%	2%	2%

6.5 Extractions at 697 Watts (Medium Power)

At 697 W the maximum extraction time is 4.5 minutes without causing ignition to the peppermint hay. Samples at every 0.5 minutes were collected. Figure 6.10 shows the breakthrough time at the different extraction times. As it was expected the breakthrough time remains constant the different extraction times; the average breakthrough time is 1.9 minutes and the variation is 3%.

Figure 6.11 shows the final temperature of the plant material after extraction.

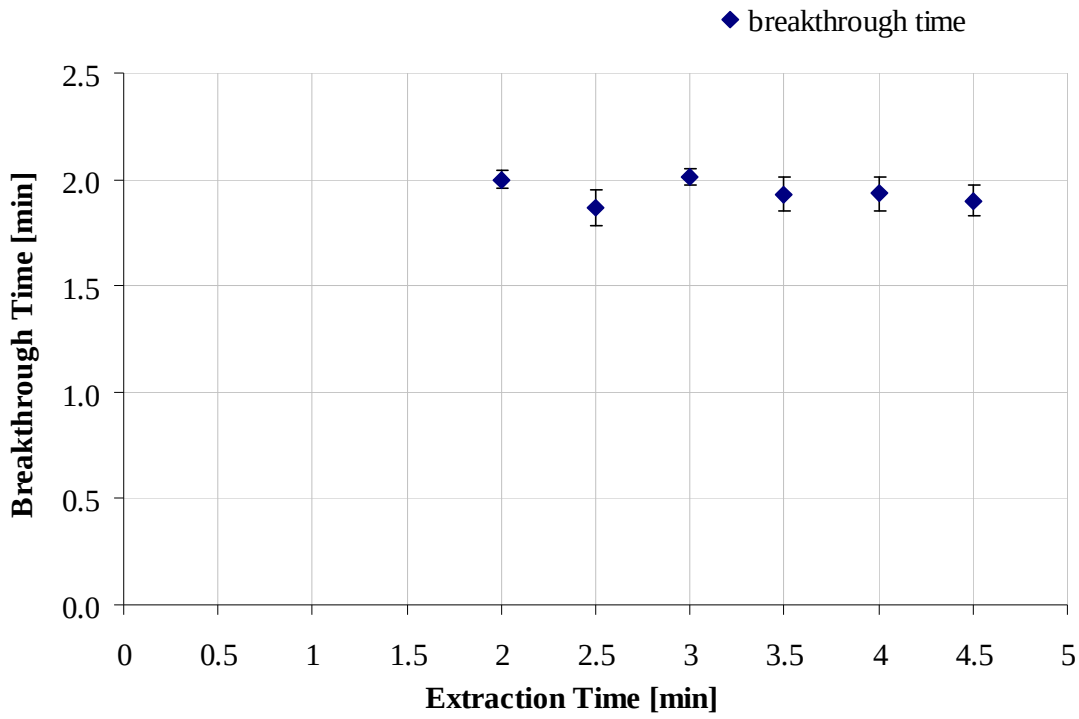


Figure 6. 10 Breakthrough Time vs. Extraction Time relationship (697 W)

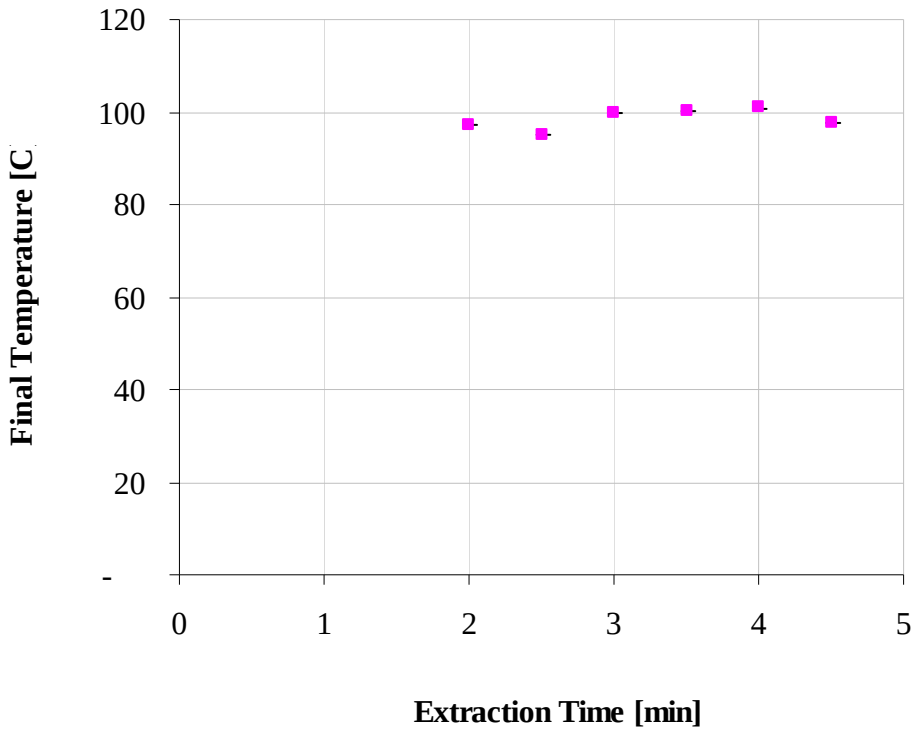


Figure 6. 11 Final Temperature of 697 W Process

Figure 6.12 shows percentage of oil extracted and the energy cost per pound of oil extracted. The error bars represent the variation coefficient of the percentage of oil extracted. The fraction of oil extracted at 3.5 and 4.5 minutes is similar on average; these two sets of experiments show the higher extraction yield (53% and 54%). The oil recovered at 4 minutes on average is lower than it was expected; the variation on the plant material and experimental error might have led to this result. Figure 6.13 shows how increasing the extraction time helps to extract more water; the maximum amount of water extracted is 60% with a variance coefficient of 10% at 4.5 minutes extraction time

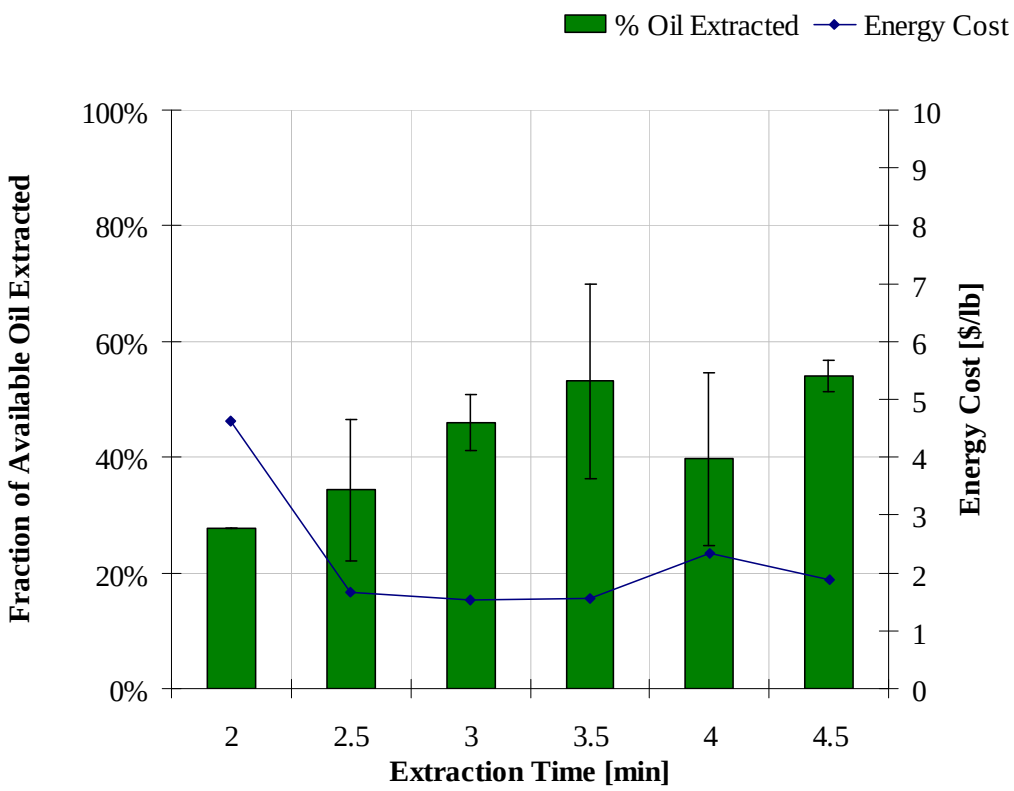


Figure 6. 12 Percentage of Oil Extracted (697 W)

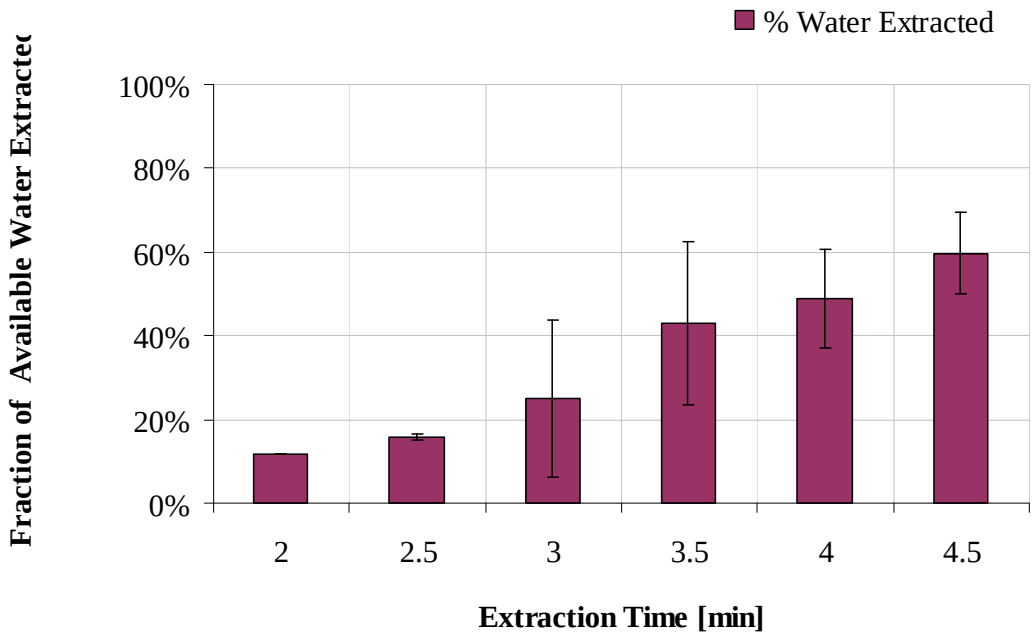


Figure 6. 13 Percentage of Water Extracted (697 W)

Figure 6.14 shows the average mass balance on the liquid phase as a function of the extraction time. The percentage of the liquids extracted increase as the extraction time increases while the percentage of liquid remaining in the plant material after extraction reduces. The amount of liquids unaccounted for varies between 4% and 17%.

Figures 6.15 to 6.18 represent the quality analysis of the peppermint oil extracted. It is observed that the concentration of menthol, neomenthol, esters, terpenen-4-ol, pulegone and germacre-d is proportional to the extraction time increase. The concentration of menthone, cineol, isomenthone, furan, limonene and t-sabine hydrate concentration decreases as the extraction increases.

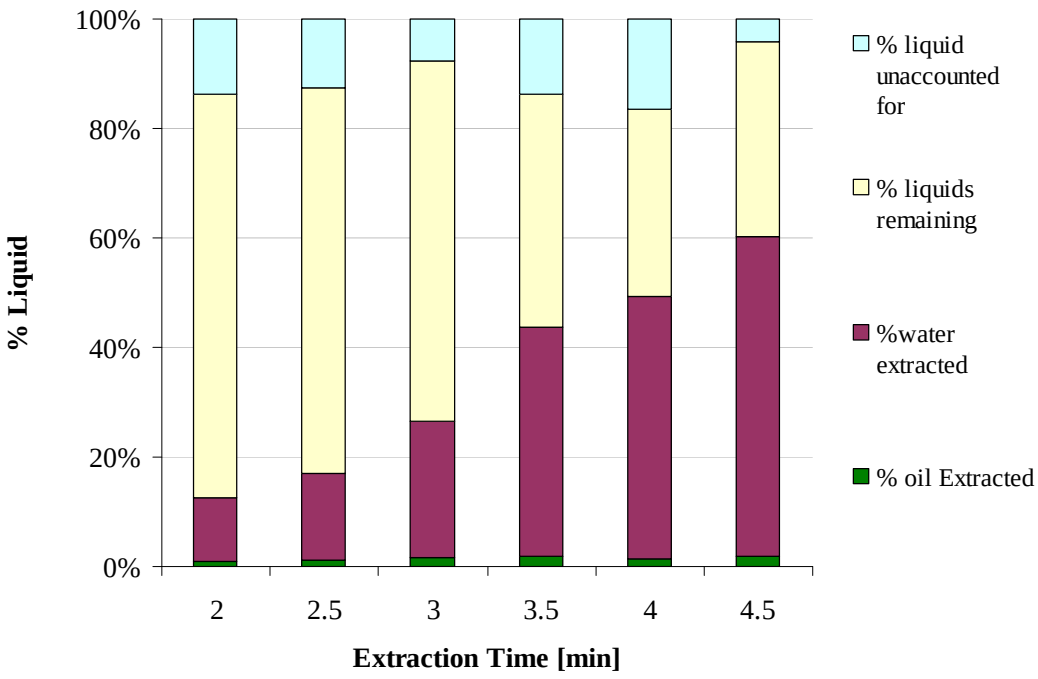


Figure 6. 14 Mass Balance on the Liquid Phase (697 W)

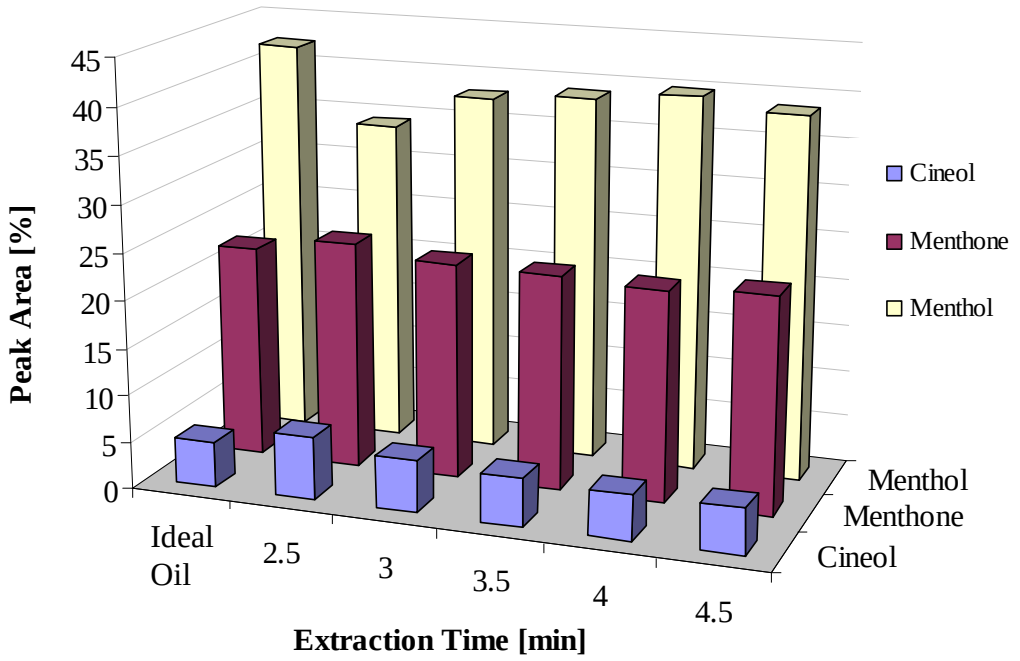


Figure 6. 15 Cineol, Menthol and Menthone Composition (697 W)

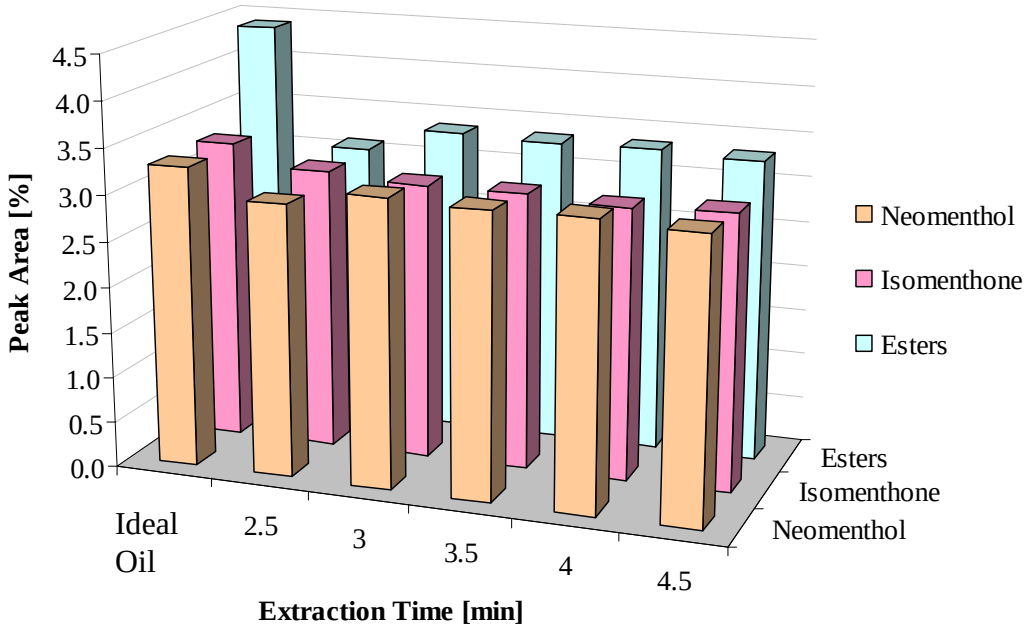


Figure 6. 16 Neomenthol, Isomenthol and Esters Composition (697 W)

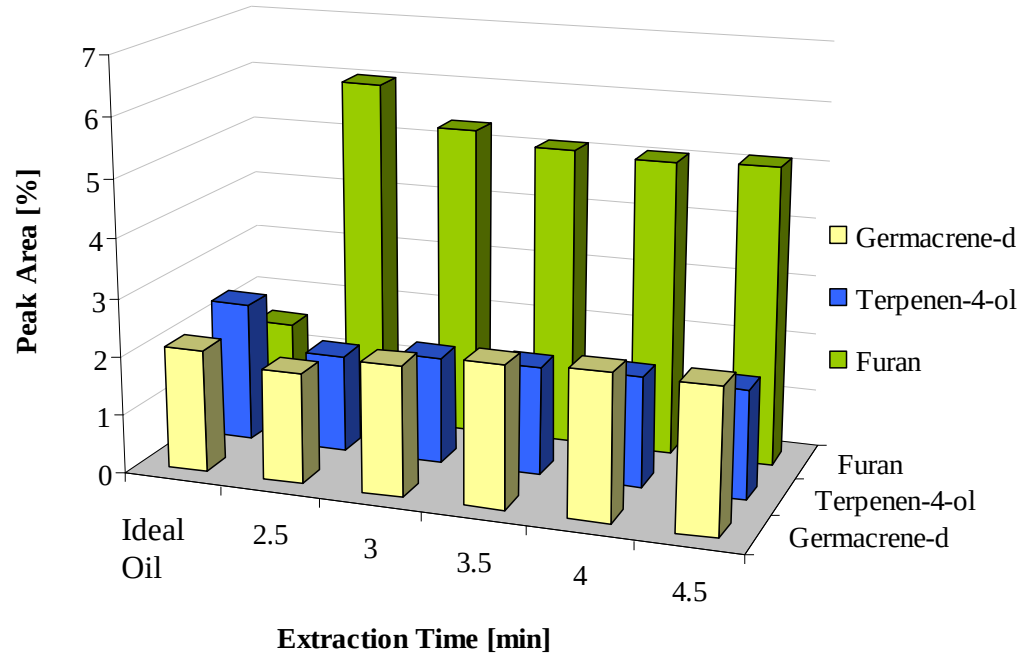


Figure 6. 17 Germacrene-d, Terpenen-4-ol and Furan Composition (697 W)

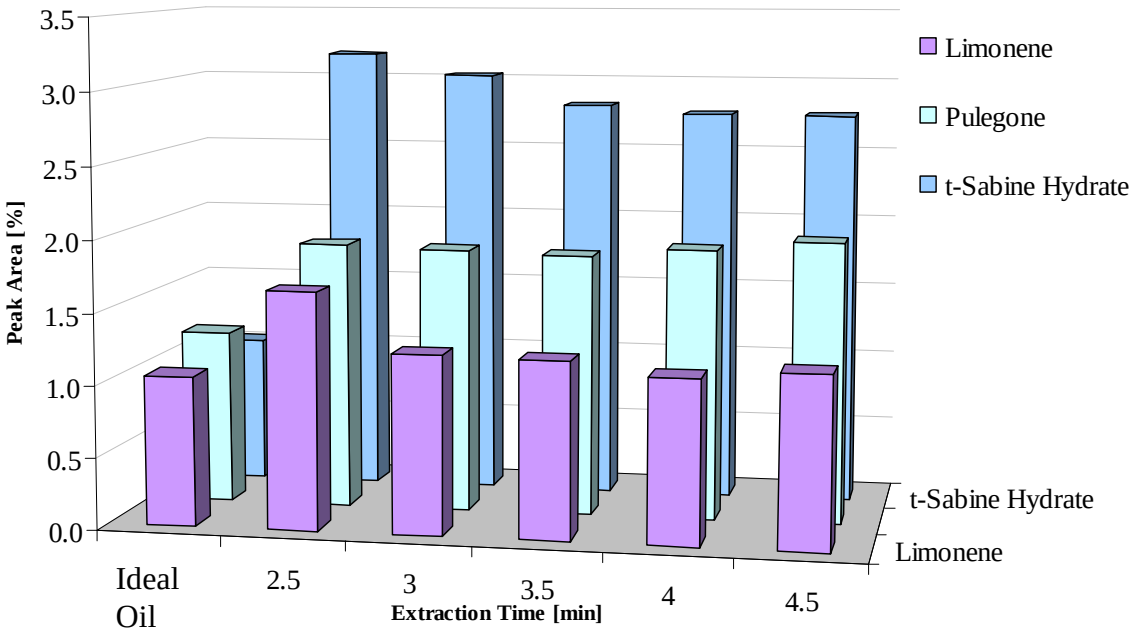


Figure 6. 18 Limonene, Pulegone and t-Sabine Hydrate Composition (697 W)

Table 6.3 summarizes the variation of all the components concentration with respect to the standard.

Table 6. 3 Composition Variation with respect to the Standard (697 W)

	Extraction Time [min]				
Component	2.5	3	3.5	4	4.5
Limonene	59%	20%	18%	10%	15%
Cineol	39%	15%	7%	-1%	1%
t-Sabine Hydrate	209%	195%	175%	169%	169%
Menthone	7%	2%	1%	-1%	2%
Furan	286%	243%	228%	224%	228%
Isomenthone	-7%	-9%	-9%	-10%	-9%
Esters	-29%	-24%	-24%	-24%	-25%
Neomenthol	-9%	-4%	-5%	-5%	-6%
Terpenen-4-ol	-30%	-24%	-23%	-21%	-22%
Menthol	-19%	-10%	-8%	-6%	-9%
Pulegone	54%	52%	51%	55%	61%
Germacrene-d	-9%	6%	15%	19%	17%
Total	1%	2%	2%	2%	1%

6.6 Extractions at 518 Watts (Medium Low Power)

At 518 W the first drops of liquid are obtained at 2.9 minutes with a variation of 1% variation between runs. The fraction of available oil extracted and the energy cost are presented on figure 6.19. The final temperature of the plant material does not achieve 100 °C; the maximum temperature recorded was 98 °C at 4.5 minutes of extraction time (Figure 6.20). The maximum percentage of oil extracted is obtained at 5 minutes of extraction; however the minimum energy cost of oil extracted is observed at 5 and 4.5 minutes. Since on average the amount of extracted is equivalent the optimal extraction time would be 4.5 or 5 minutes (Figure 6.21). Even though at 6 minutes it is observed a higher percentage of oil recollected, a yellow color was detected extracted oil and that characteristic might not be desired; also the operating cost is higher. Figure 6.22 shows the percentage of water extracted in function of the extraction time; it is observed that at 4.5 and 5 minutes the amount of water extracted is 43% and 48%.

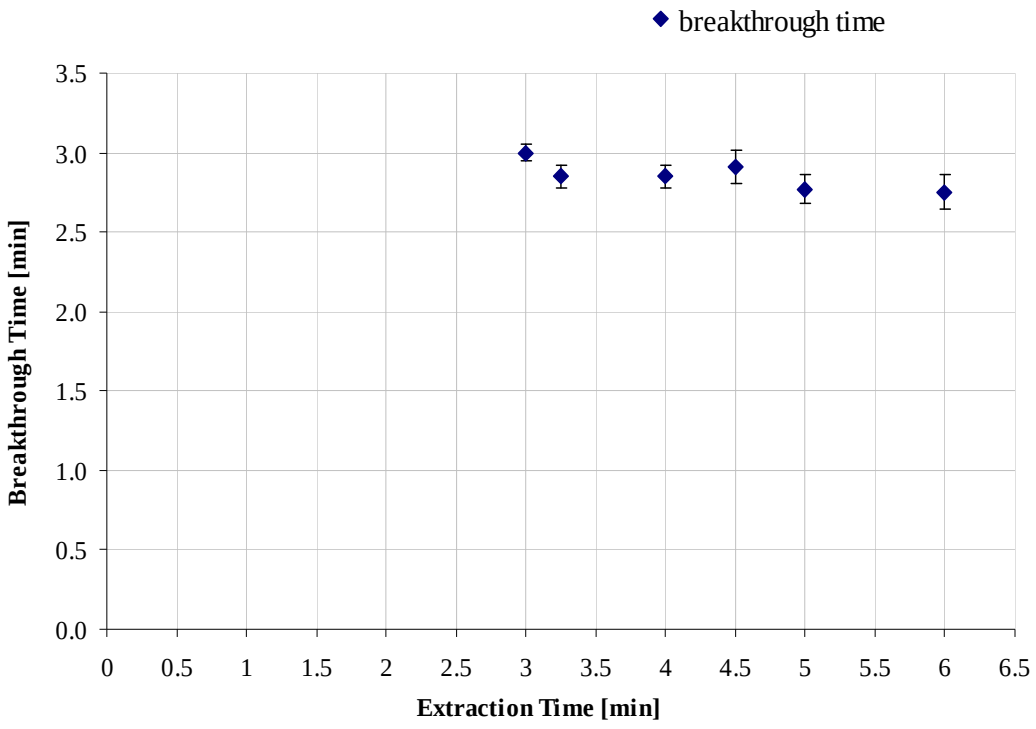


Figure 6. 19 Breakthrough Time vs. Extraction Time relationship (518 W)

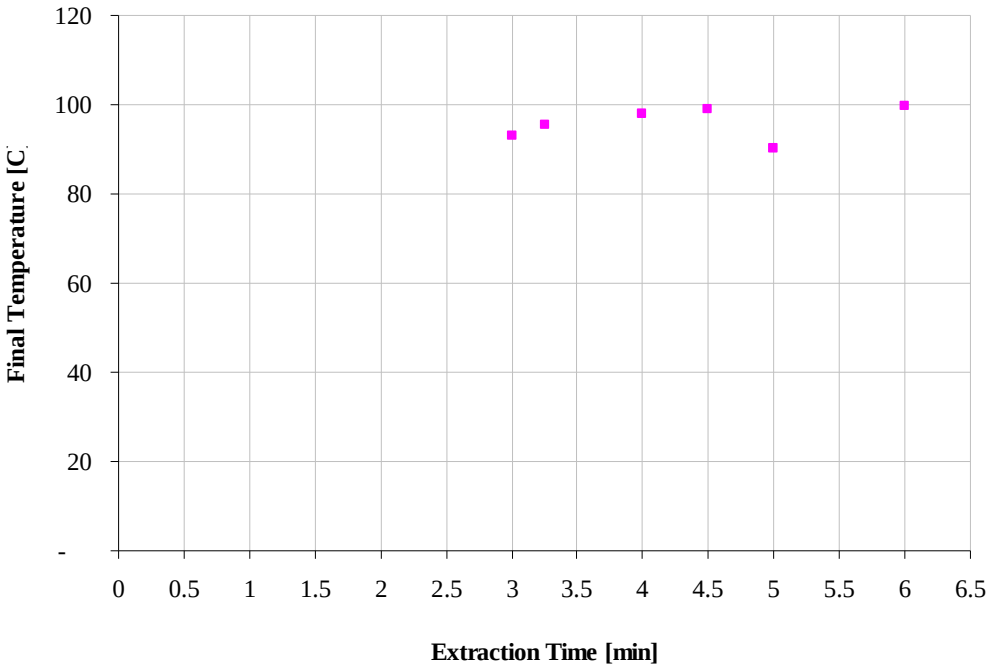


Figure 6. 20 Final Temperature of 518 W Process

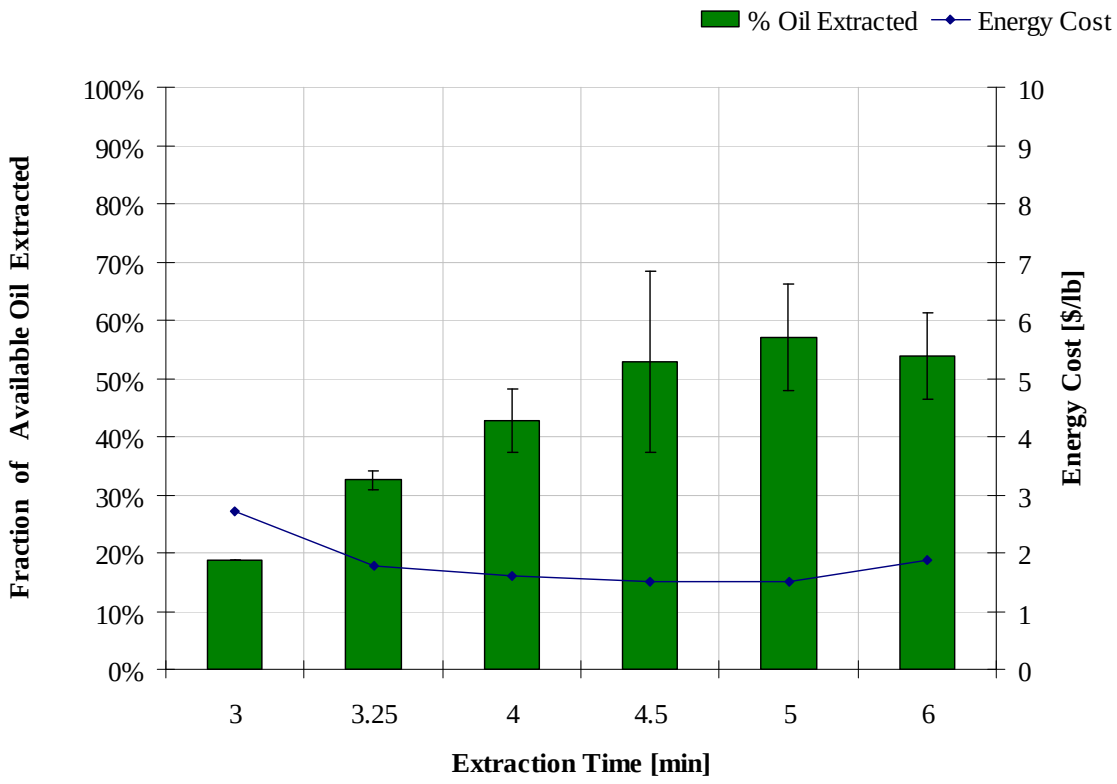


Figure 6. 21 Percentage of Oil Extracted (518 W)

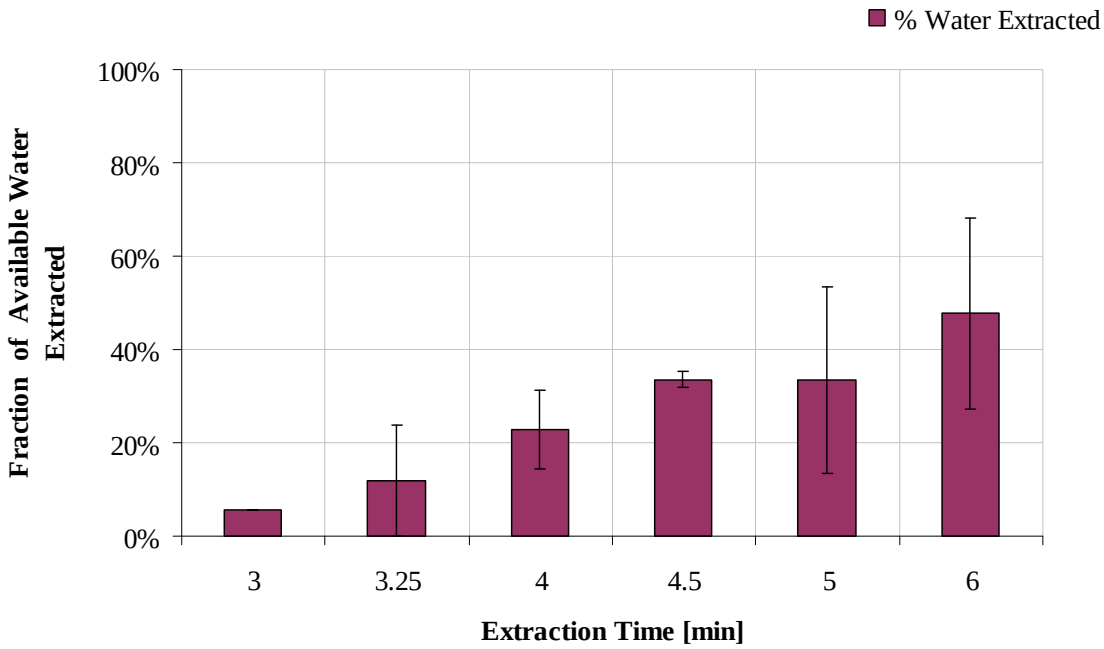


Figure 6. 22 Percentage of Water Extracted (518 W)

Figure 6.23 is the mass balance on the liquid phase. The same trend observed on the two previous power settings is observed in this case. The percentage of liquids unaccounted due to experimental error losses to the environment vary between 15% and 27%.

Figures 6.24 to 6.27 show the composition of oil extracted. As it was observed in the two previous power settings the same components concentration are proportional to the extraction time (menthol, neomenthol, esters, terpenen-4-ol, pulegone and germacre-d.) and decrease as extraction time increases (menthone, cineol, isomenthone, furan, limonene and t-sabine hydrate).

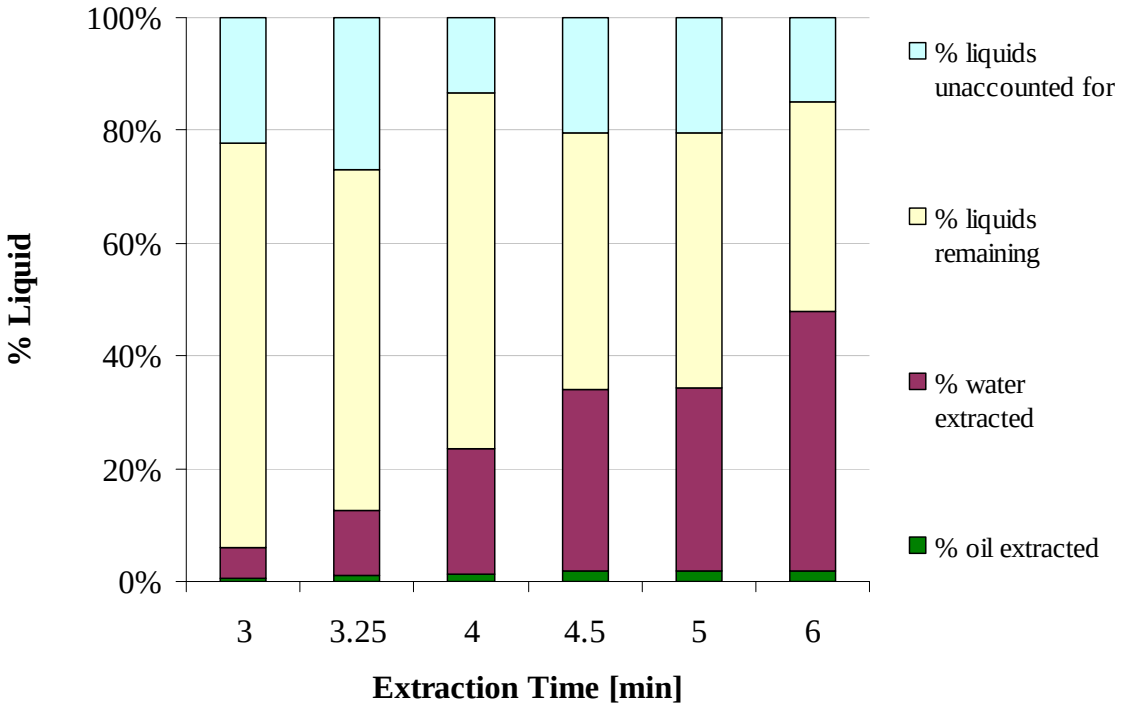


Figure 6. 23 Mass Balance on the Liquid Phase (518 W)

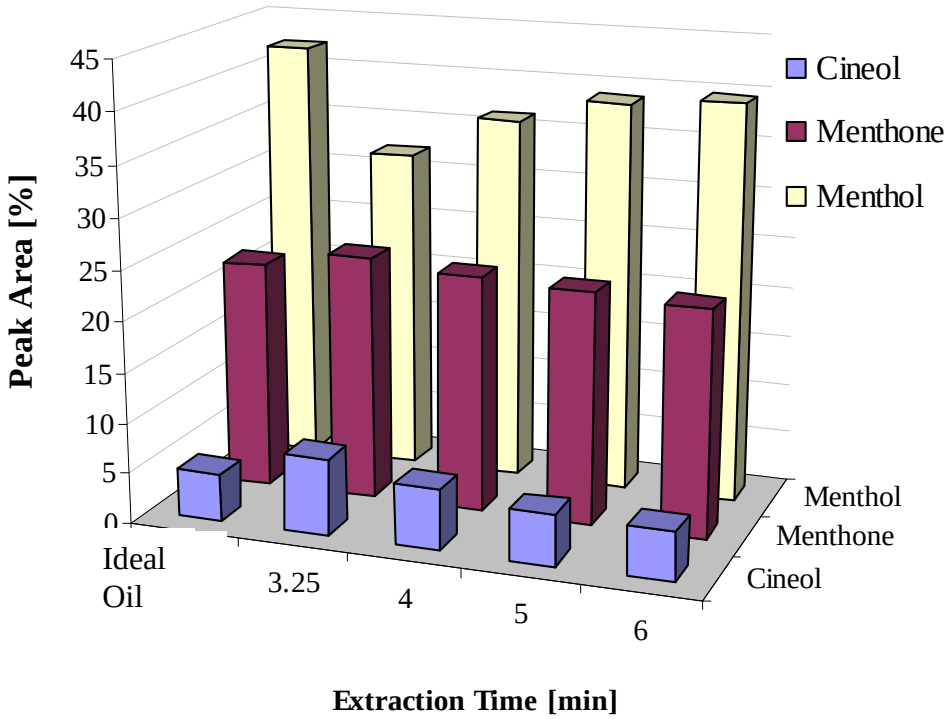


Figure 6. 24 Cineol, Menthol and Menthone Composition (518 W)

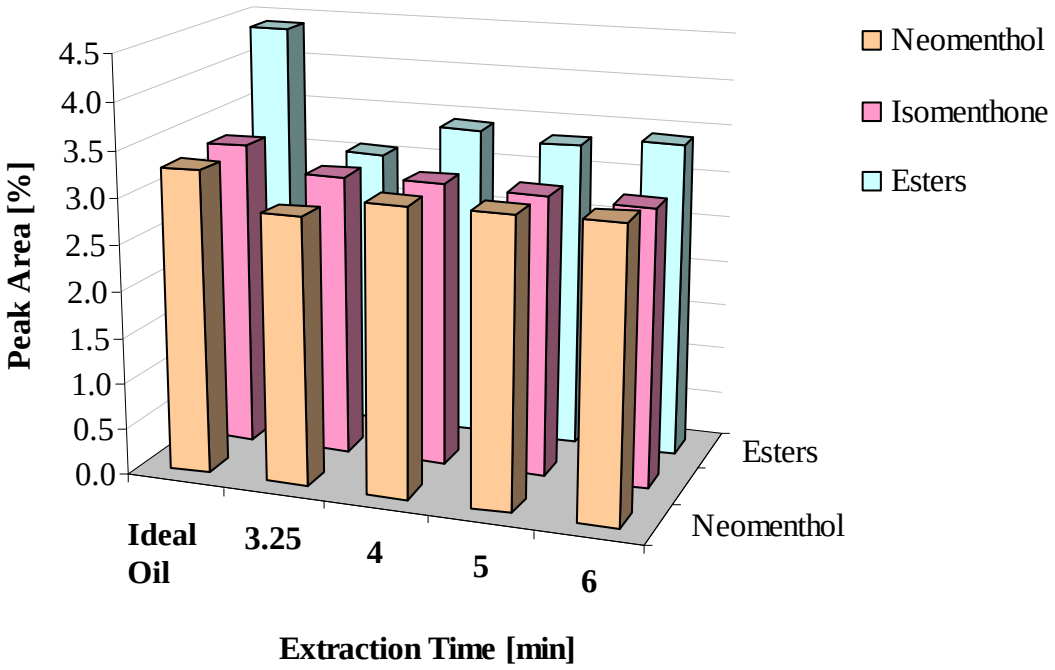


Figure 6. 25 Neomenthol, Isomenthol and Esters Composition (518 W)

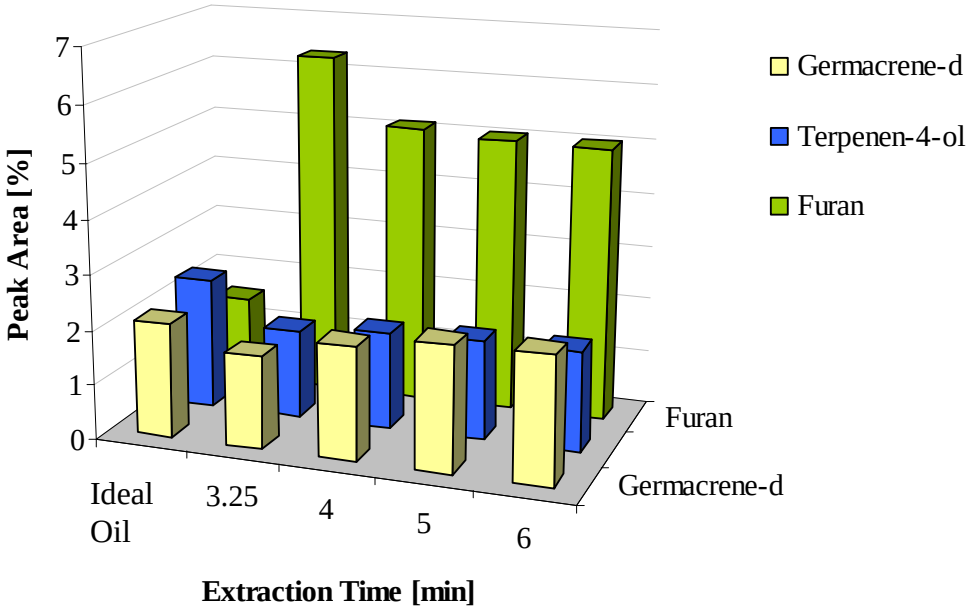


Figure 6. 26 Germacrene-d, Terpenen-4-ol and Furan Composition (518 W)

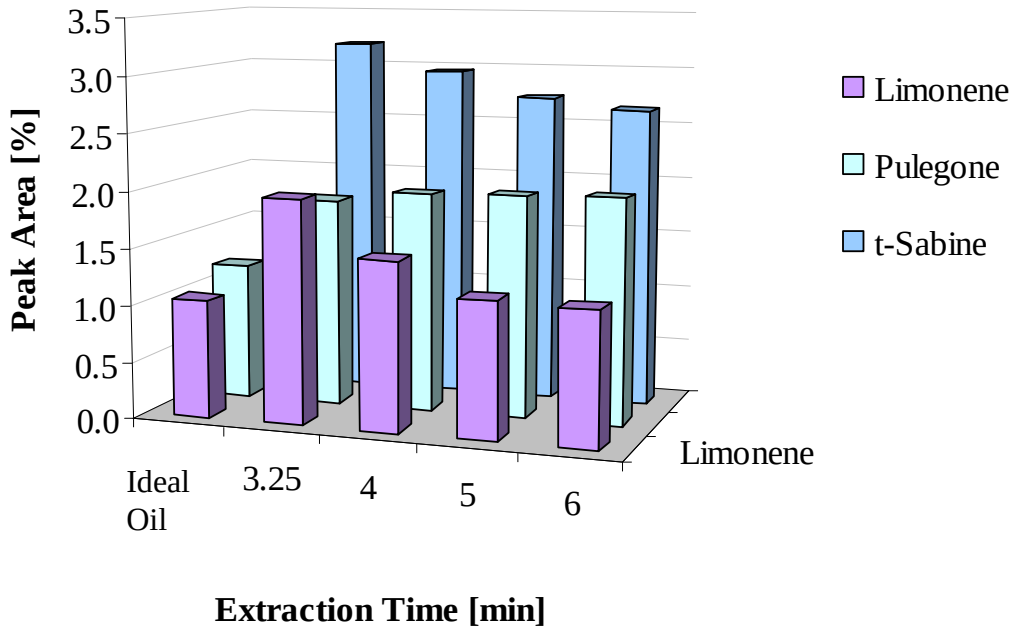


Figure 6. 27 Limonene, Pulegone and t-Sabine Hydrate Composition (518 W)

Table 6.4 summarizes the percentage on the concentration variation of the oils extracted with respect to the standard.

Table 6. 4 Composition Variation with respect to the Standard (518 W)

	Extraction Time [min]			
Component	3.25	4	5	6
Limonene	89%	43%	16%	13%
Cineol	58%	25%	4%	1%
t-Sabine Hydrate	211%	188%	166%	158%
Menthone	7%	4%	2%	-1%
Furan	306%	229%	224%	223%
Isomenthone	-8%	-7%	-8%	-9%
Esters	-30%	-22%	-24%	-22%
Neomenthol	-12%	-6%	-5%	-5%
Terpenen-4-ol	-32%	-26%	-23%	-23%
Menthol	-24%	-14%	-8%	-6%
Pulegone	52%	60%	62%	63%
Germacrene-d	-19%	-1%	10%	11%
Total	0%	1%	1%	2%

6.7 Two Extraction Step (1.5 minutes at 1120 Watts - Medium)

It was desired to study the combination of two different power settings in a single extraction. It was believed that more energy was needed until the breakthrough time was passed then less energy is needed to keep the hay warm to extract the rest of the volatiles.

The first step extraction was 1.5 minutes at 1120 W (High) and then different time intervals on 697W (Medium). All figures from the two step process have two horizontal axes: the total extraction time (bottom axis) and only the second step extraction time (top or secondary x axis) to make the observation of the second step easier. Figure 6.28 shows the breakthrough time as a function of the extraction and the information obtained is similar to the single step process at 1120 W; the breakthrough time is constant at approximately 1.2 minutes on average with a variation coefficient of 4% between runs.

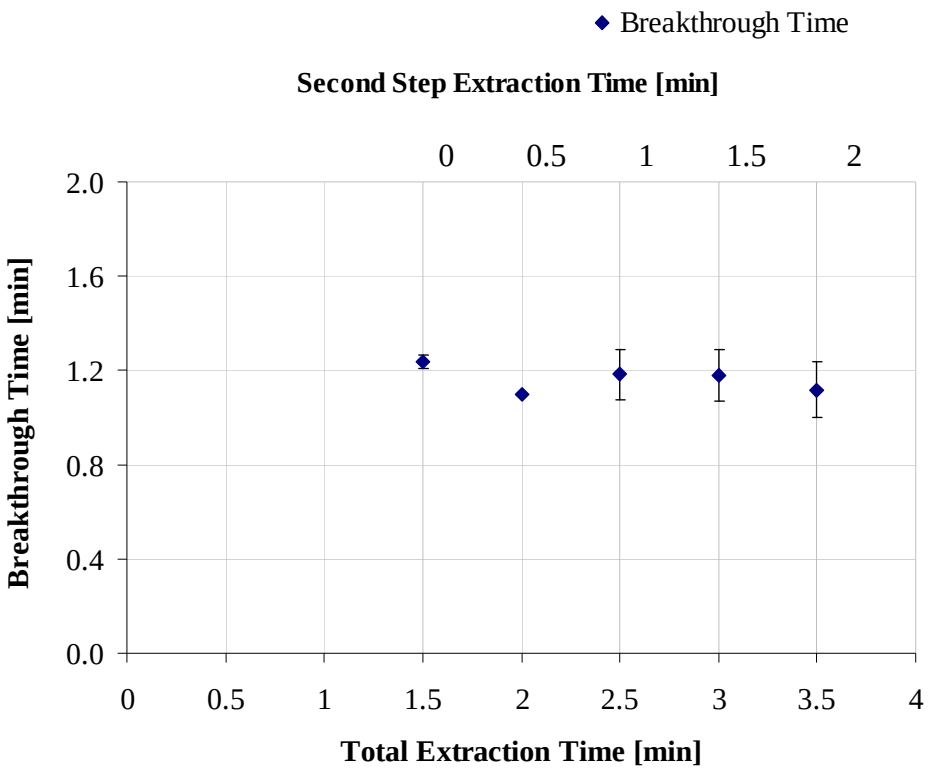


Figure 6. 28 Breakthrough Time vs. Extraction Time relationship (1.5H-xM)

Figure 6.29 shows the final temperature reached after extraction; as it was expected all temperatures reach the water boiling point easily.

Figure 6.30 shows the percentage of oil extracted as a function of the extraction time. This fraction represents the amount of oil recovered from all the oil available in the plant (assuming there is 1% by mass of oil in the plant material). As it was seen before the amount of oil extracted increases with the extraction time and it seems to reach a maximum limit. Because on average the last three points of this set of data are similar, it could be assumed hat a plateau starts at 2.5 minutes of total extraction time (1.5 minutes on 1120 W and 1 minute on 697W). The maximum percentage recovery is 63% however at 2.5 minutes 57% of the oil was extracted and at 3 minutes 60% with a variation of 12%.

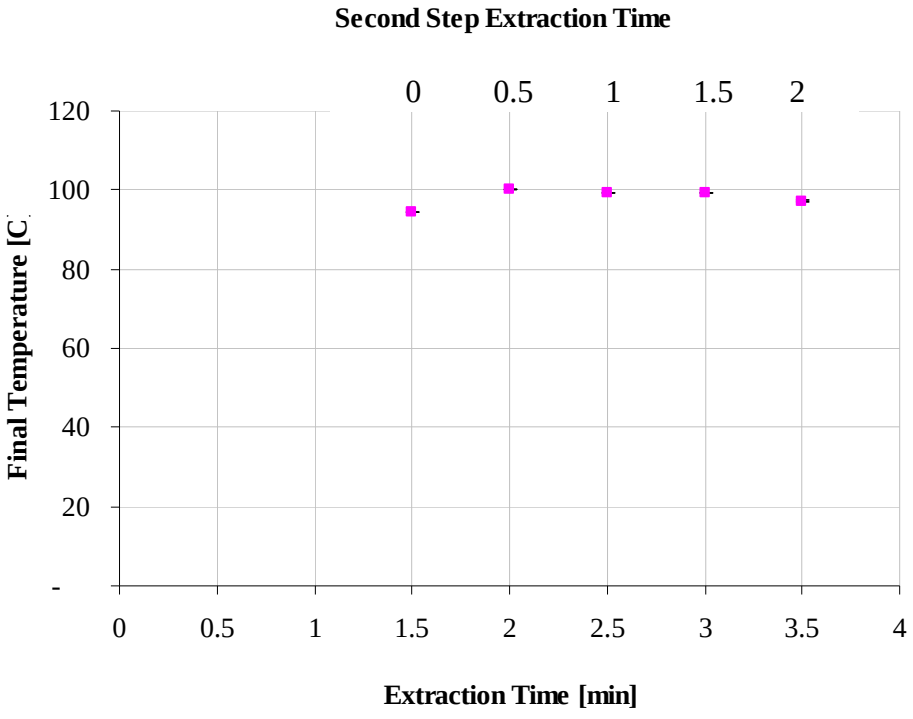


Figure 6. 29 Final Temperature of 1.5H-xM process

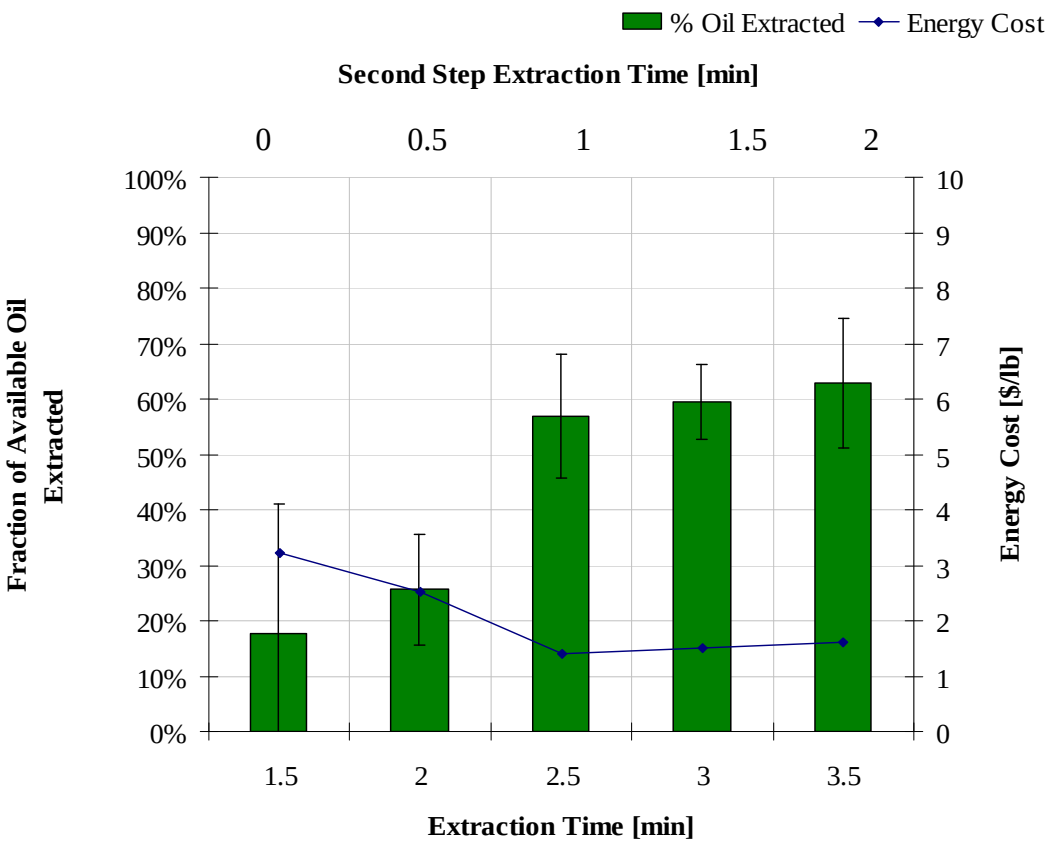


Figure 6. 30 Percentage of Oil Extracted (1.5H-xM)

Figure 6.31 shows the percentage of water extracted. A maximum limit is also reached on the percentage of water extracted, the two longer extraction times on average reach a maximum of 51% of water extracted. The comparison of figures 6.30 and 6.31 shows that the energy used on the last two extraction times help to extract more water than the oil. Figure 6.32 show the material balance on the liquids extracted. The percentage of liquids unaccounted for varies from 7% to 28%.

The composition of the oil extracted is shown on Figures 6.33 to 6.36. The same components are proportional to the extraction time (menthol, neomenthol, esters, terpenen-4-ol and germacre-d.) and decrease as extraction time increases (menthone, cineol, isomenthone, furan, limonene and t-sabine hydrate). The composition of pulegone does not follow any pattern with respect to the extraction time as it did in the previous settings.

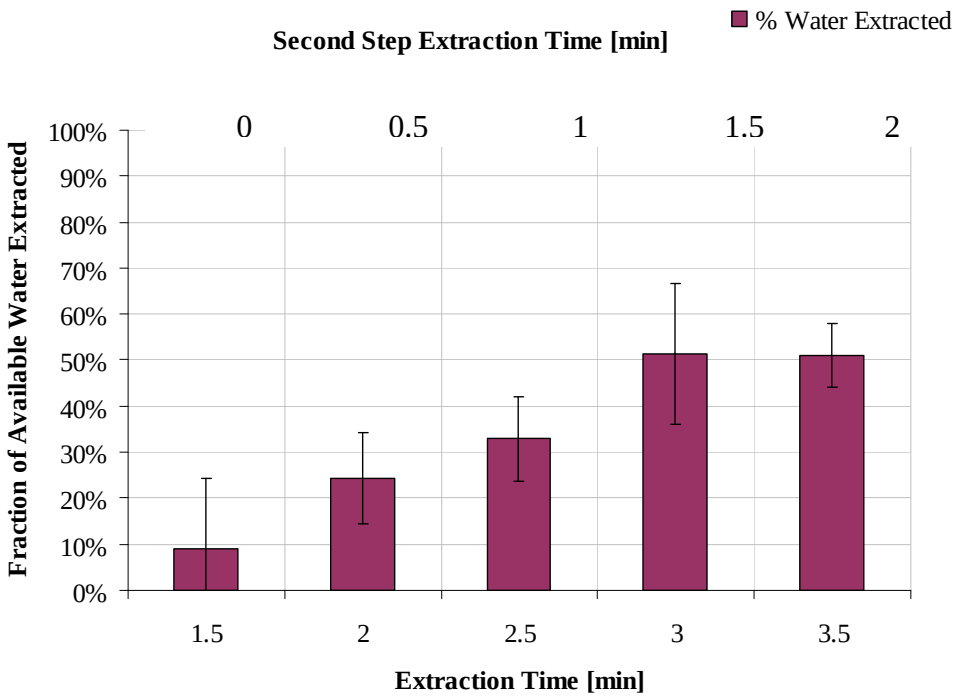


Figure 6. 31 Percentage of Water Extracted (1.5H-xM)

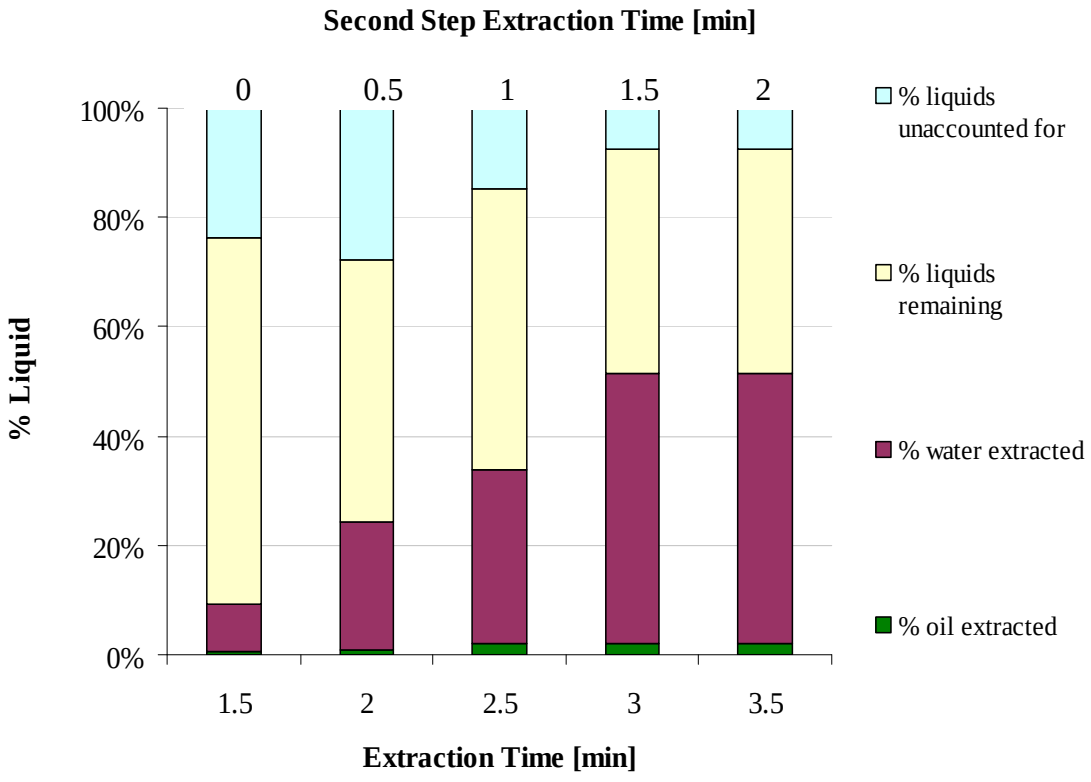


Figure 6. 32 Mass Balance on the Liquid Phase (1.5H-xM)

\

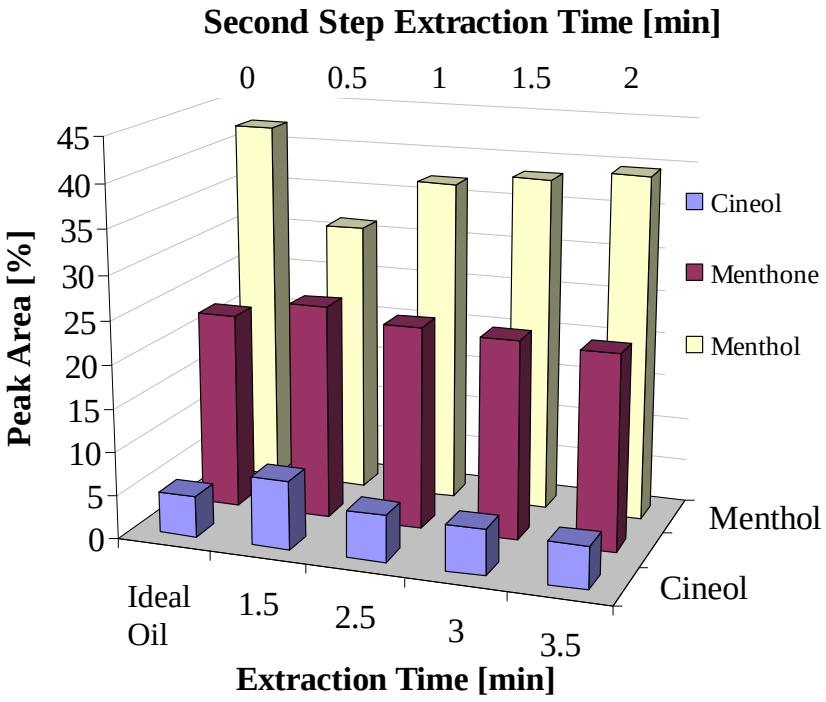


Figure 6. 33 Cineol, Menthol and Menthone Composition (1.5H-xM)

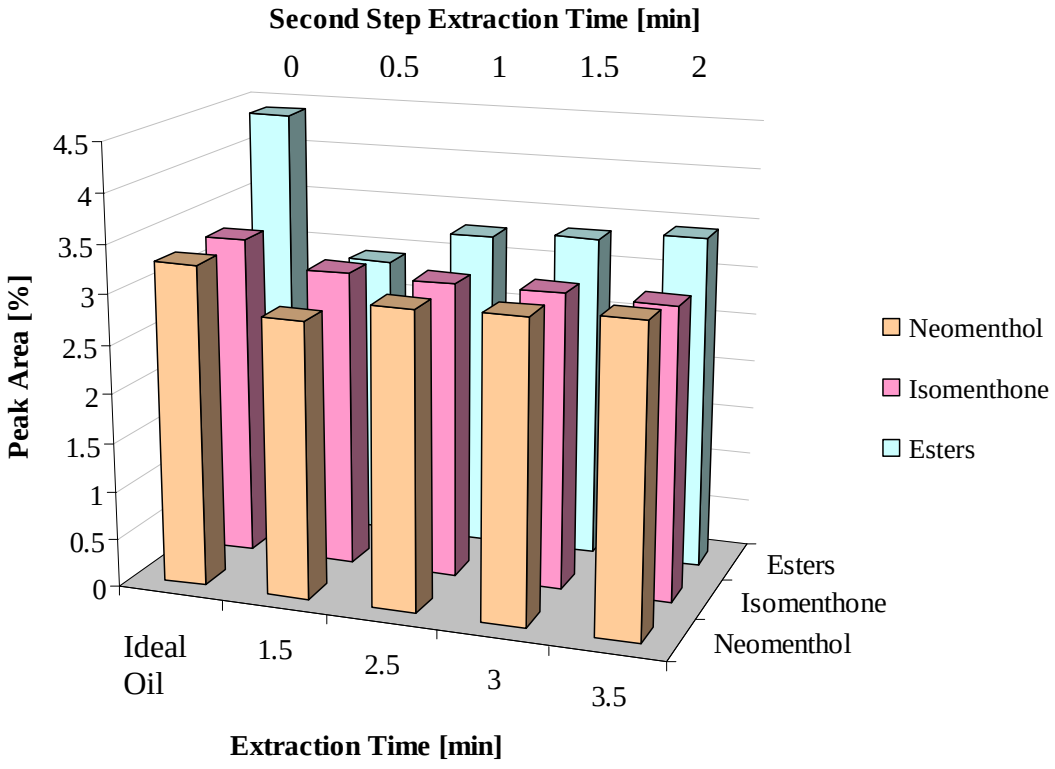


Figure 6. 34 Neomenthol, Isomenthol and Esters Composition (1.5H-xM)

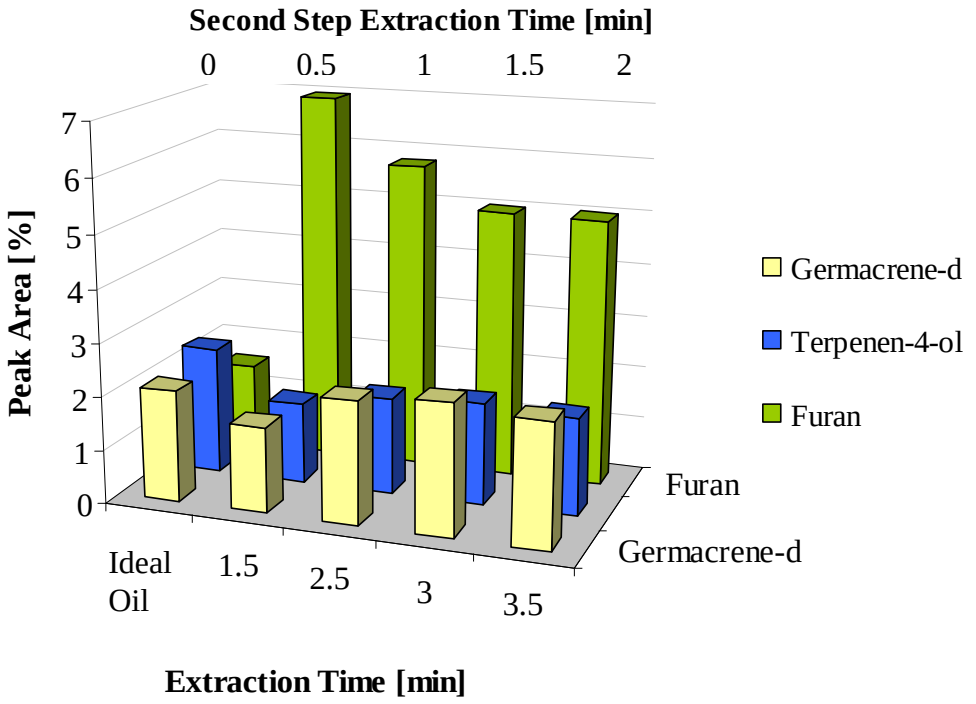


Figure 6. 35 Composition Germacrene-d, Terpenen-4-ol and Furan (1.5H-xM)

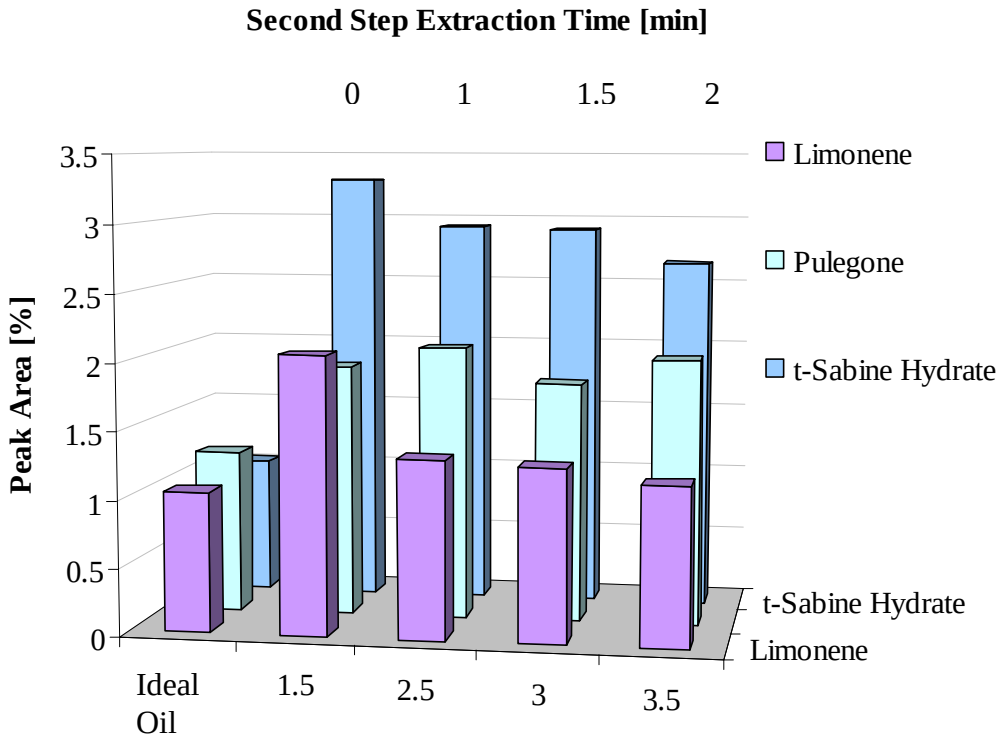


Figure 6. 36 Limonene, Pulegone and t-Sabine Hydrate Composition (1.5H-xM)

Table 6.5 summarizes the variation of the oil extracted per compound compared to the standard.

Table 6. 5 Composition Variation with respect to the Standard (1.5H-xM)

	Extraction Time [min]			
Component	1.5	2.5	3	3.5
Limonene	98%	27%	23%	13%
Cineol	65%	12%	9%	1%
t-Sabine Hydrate	220%	185%	182%	158%
Menthone	9%	3%	1%	-1%
Furan	347%	272%	223%	223%
Isomenthone	-8%	-8%	-8%	-9%
Esters	-34%	-26%	-24%	-22%
Neomenthol	-14%	-8%	-7%	-5%
Terpenen-4-ol	-37%	-24%	-20%	-23%
Menthol	-26%	-12%	-9%	-6%
Pulegone	56%	69%	47%	63%
Germacrene-d	-23%	10%	18%	11%
Total	0%	1%	1%	2%

6.8 Two Extraction Step (1.5 minutes at 1120 Watts- MediumLow)

This process keeps 1120 W constant for 1.5 minutes; the second step applies 518 W (Medium Low) for five different time intervals. The breakthrough is constant with extraction time at approximately 1.2 minutes as figure 6.37 shows.

Figure 6.38 shows how the final temperature remains constant at 100 °C at each two step process; the highest temperature observed is 101.7 °C at a total extraction time of 4 minutes (1.5H-2.5ML).

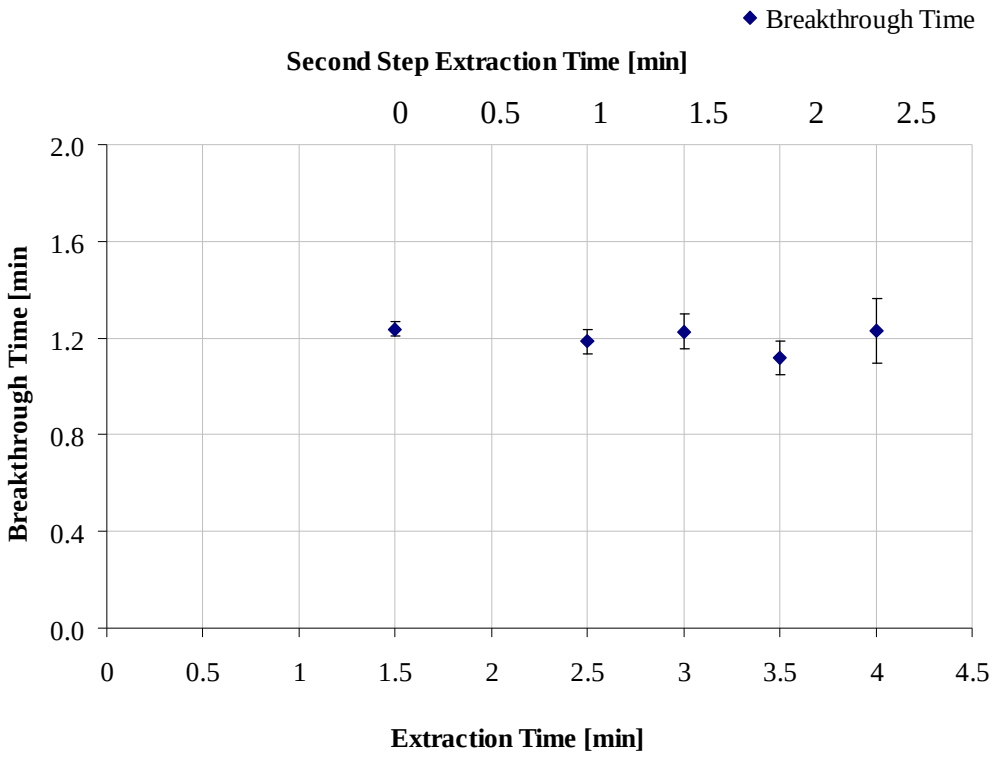


Figure 6. 37 Breakthrough Time vs. Extraction Time relationship (1.5H xML)

Figure 6.38 shows that the maximum percentage of oil collected is obtained after 3 minutes of extraction time. The highest extraction yield varies between 56% and 61% with a variation coefficient between 10% and 12%. The percentage of water extracted is presented on figure 6.39. The maximum limit is 47% and it is reached at 4.5 minutes of total extraction time.

The material balance of the liquids shows that the % of liquids unaccounted vary between 14% and 24% (Figure 6.40)

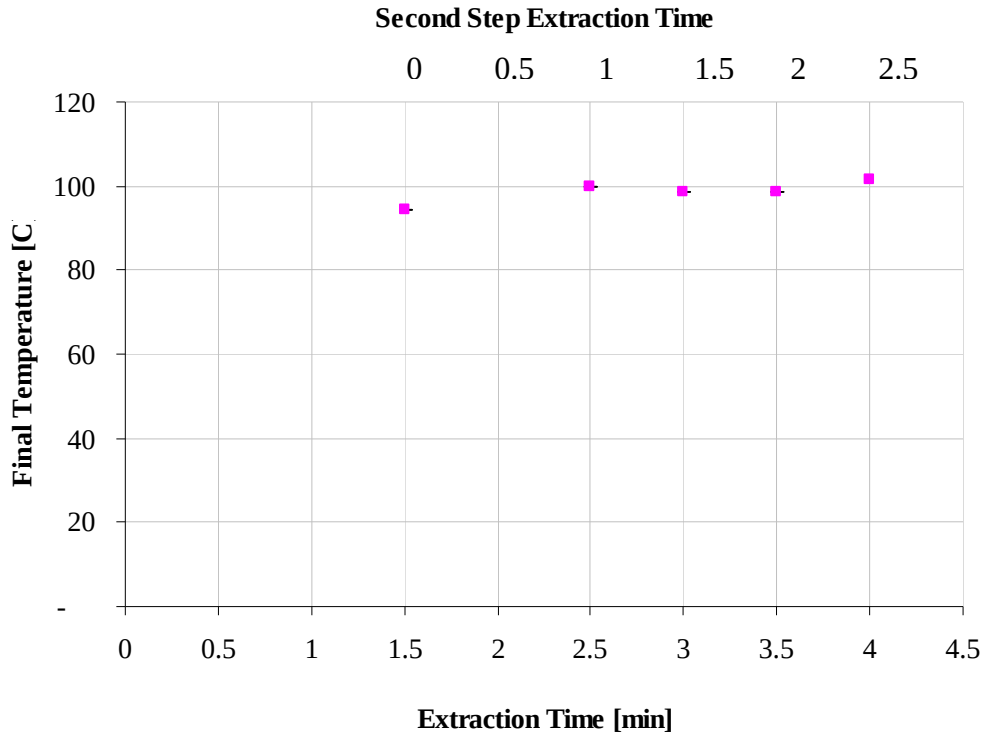


Figure 6. 38 Final Temperature 1.5H-xML process

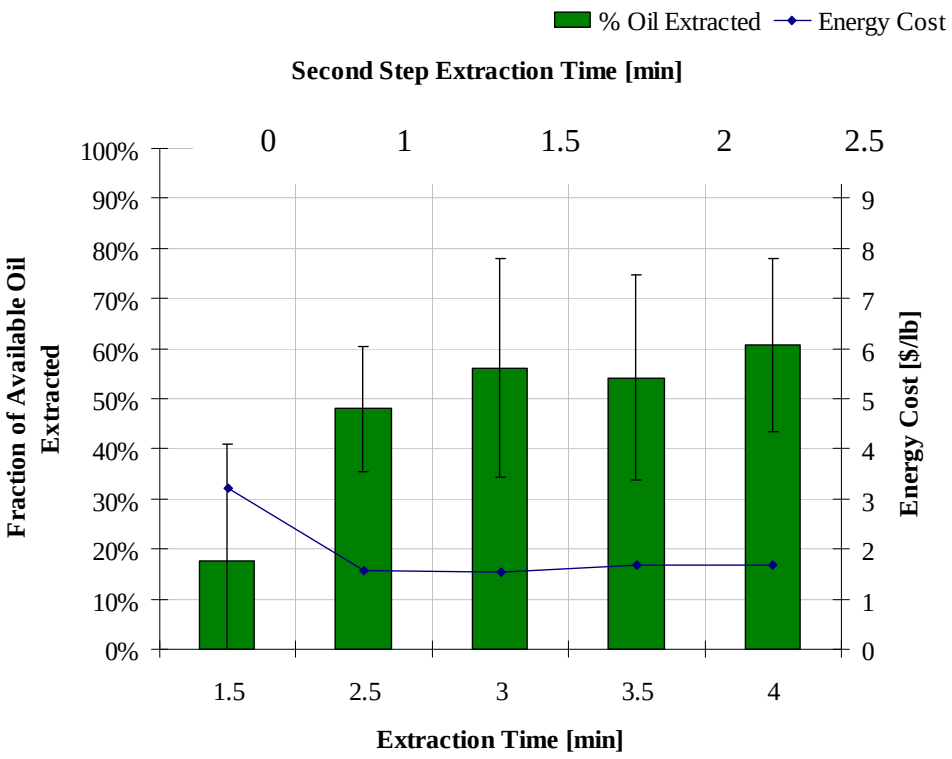


Figure 6. 39 Percentage of Oil Extracted (1.5H xML)

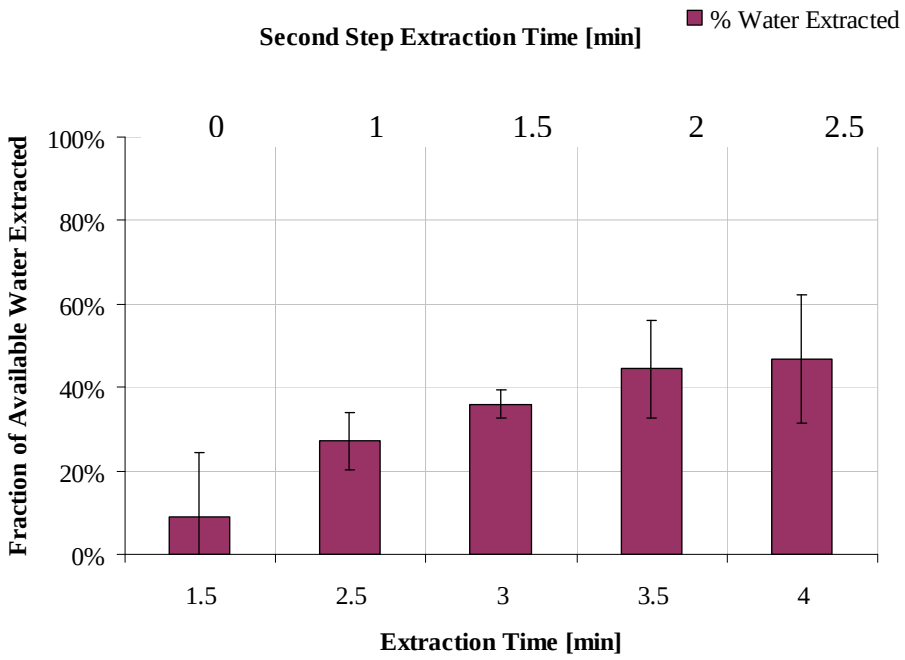


Figure 6. 40 Percentage of Water Extracted (1.5H xML)

Figures 6.42, 6.43, 6.44 and 6.45 show the extracted composition and table shows the variation on its composition with respect to the standard.

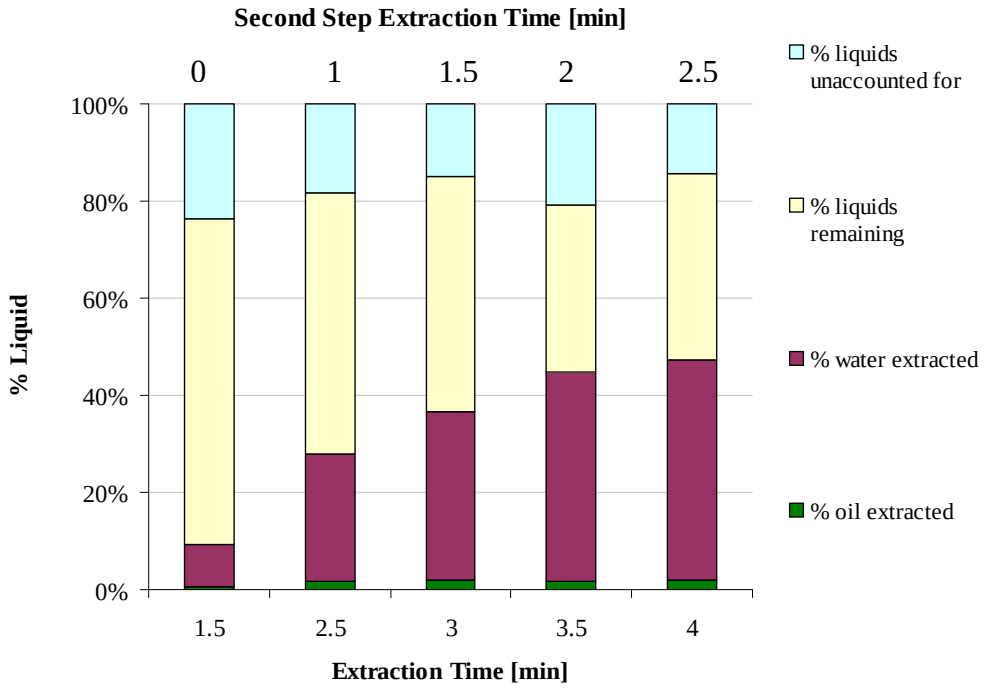


Figure 6. 41 Material Balance on the Liquid (1.5H xML)

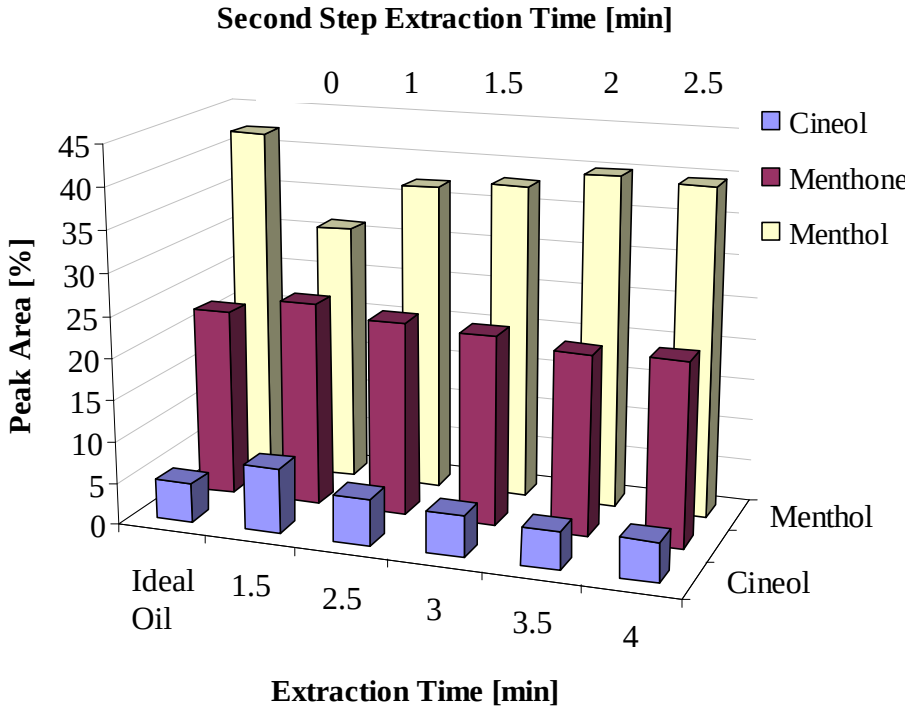


Figure 6. 42 Cineol, Menthol and Menthone Composition (1.5H xML)

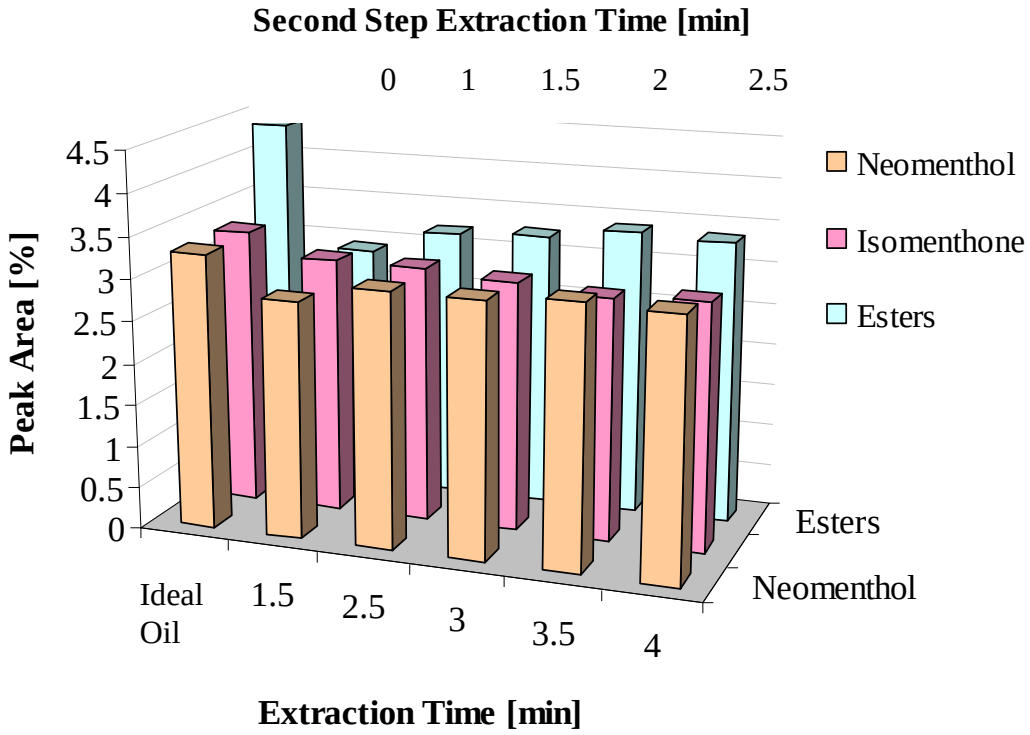


Figure 6. 43 Neomenthol, Isomenthol and Esters (1.5H xML)

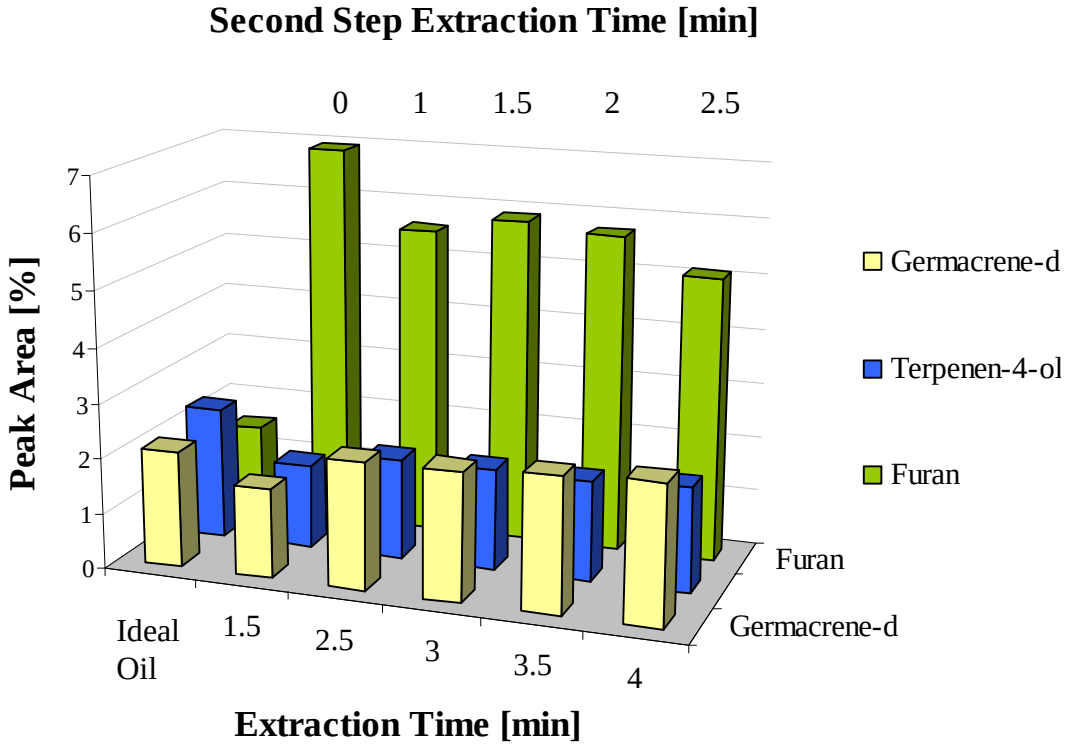


Figure 6. 44 Germacrene-d, Terpenen-4-ol and Furan (1.5H xML)

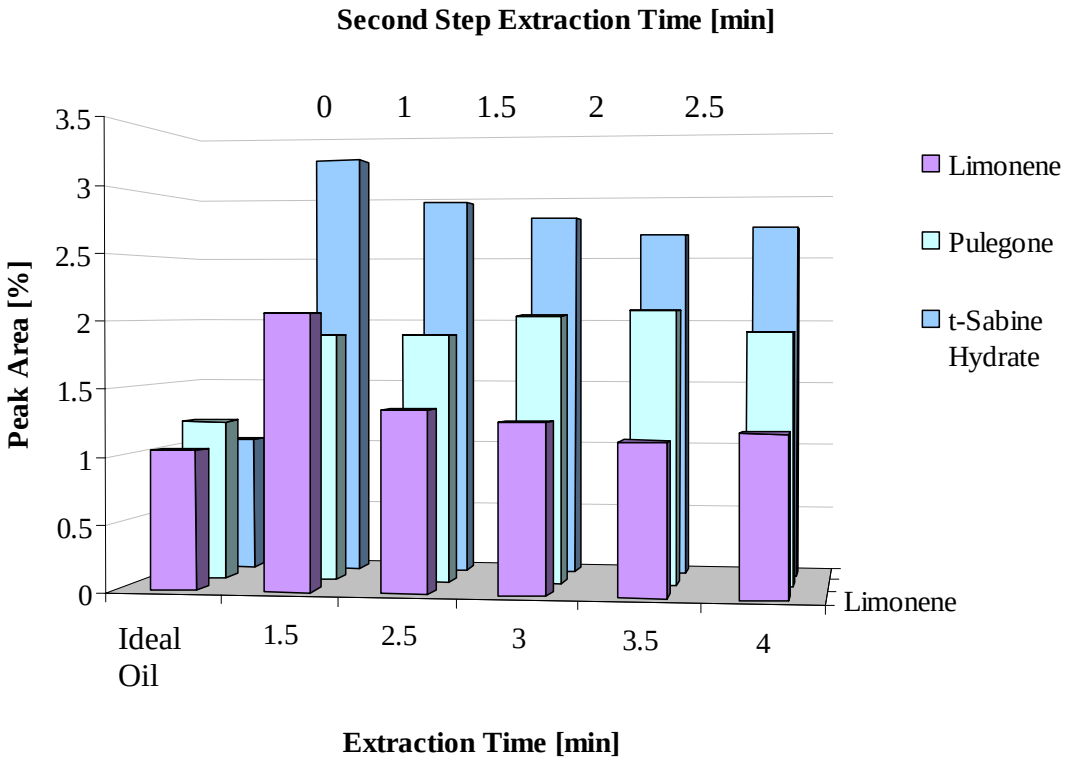


Figure 6. 45 Limonene, Pulegone and t-Sabine Hydrate Composition (1.5H xML)

Table 6. 6 Composition Variation with respect to the Standard (1.5H xML)

	Extraction Time [min]				
Component	**1.5**	**2.5**	**3**	**3.5**	**4**
Limonene	98%	30%	22%	9%	15%
Cineol	65%	15%	4%	-6%	-1%
t-Sabine Hydrate	220%	187%	174%	161%	166%
Menthone	9%	3%	1%	-4%	-2%
Furan	347%	259%	279%	269%	229%
Isomenthone	-8%	-8%	-10%	-13%	-11%
Esters	-34%	-27%	-26%	-23%	-23%
Neomenthol	-14%	-8%	-8%	-5%	-6%
Terpenen-4-ol	-37%	-24%	-24%	-24%	-21%
Menthol	-26%	-12%	-10%	-5%	-7%
Pulegone	56%	56%	68%	72%	58%
Germacrene-d	-23%	10%	11%	17%	20%
Total	0%	1%	1%	2%	1%

6.9 Two Extraction Step (2 minutes at 1120 Watts- Medium)

This set of experiments was chosen trying to obtain better results than that obtained from the two previous combinations processes. Figure 6.46 shows how the breakthrough time remains constant. Figure 6.47 shows the final temperature of the hay; it reaches 100 °C at all times.

Figure 6.48 show that the highest percentage of essential oil extracted was obtained at 3 minutes of extraction. It is observed that at 3 and 3.25 minutes the amount of oil extracted is similar.

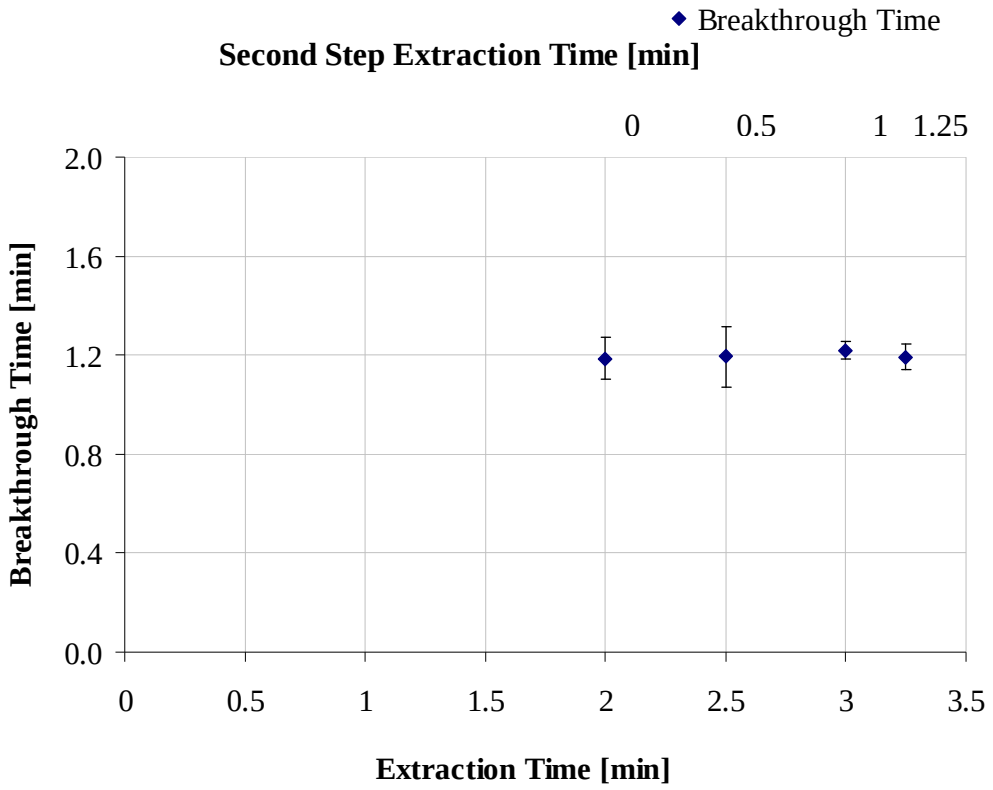


Figure 6. 46 Breakthrough Time vs. Extraction Time relationship (2H-xM)

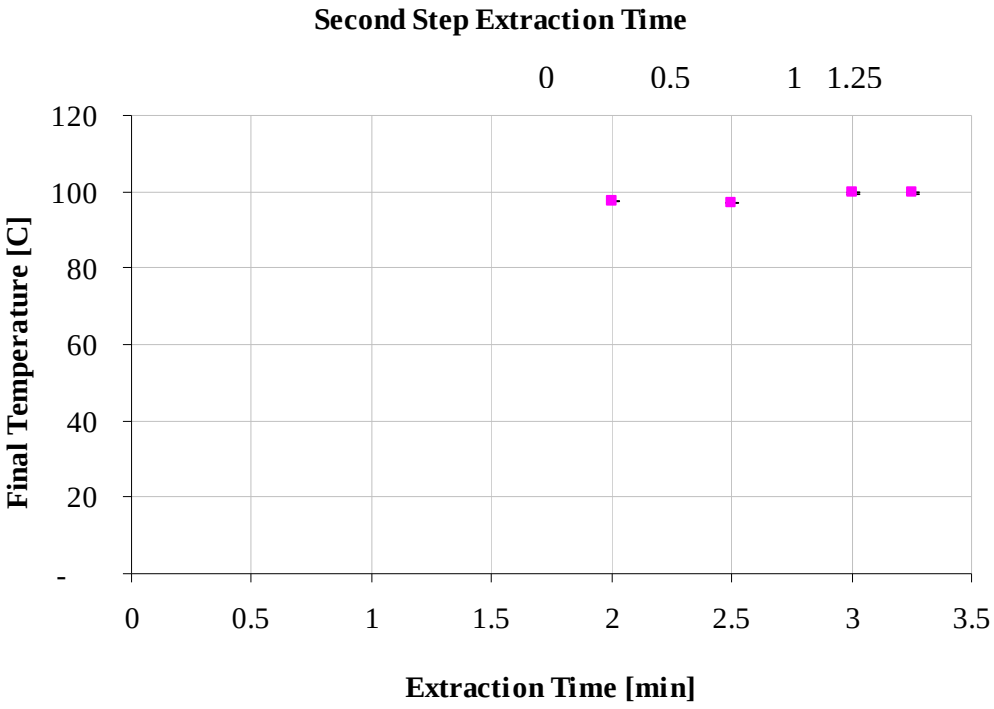


Figure 6. 47 Final Temperature 2H-xM process

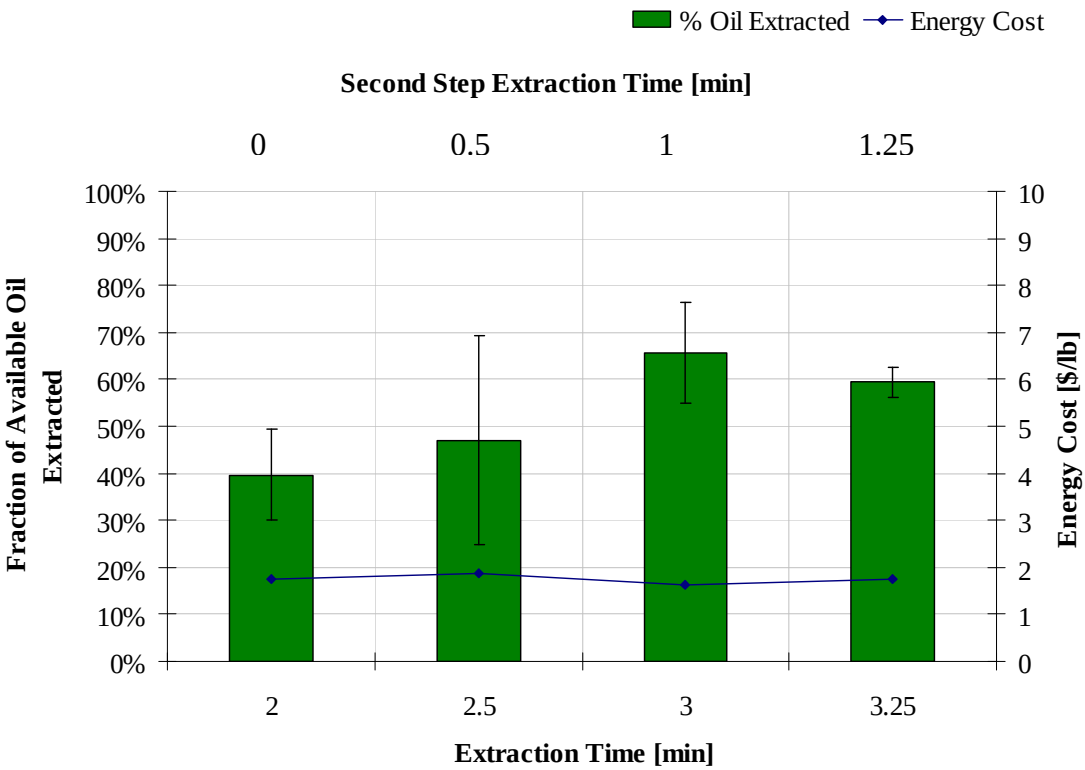


Figure 6. 48 Percentage of Oil Extracted (2H-xM)

Figure 6.49 shows that more water extracted was higher at 3 than at 3.25; however due to the small time extraction difference these two sets of data are giving the same information.

The material balance of the liquid phase is shown on figure 6.50 and the composition of the extracted is shown on figures 6.51, 6.52, 6.53 and 6.54. The same components are proportional to the extraction time (menthol, neomenthol, esters, terpenen-4-ol, pulegone and germacre-d.) and decrease as extraction time increases (menthone, cineol, isomenthone, furan, limonene and t-sabine hydrate).

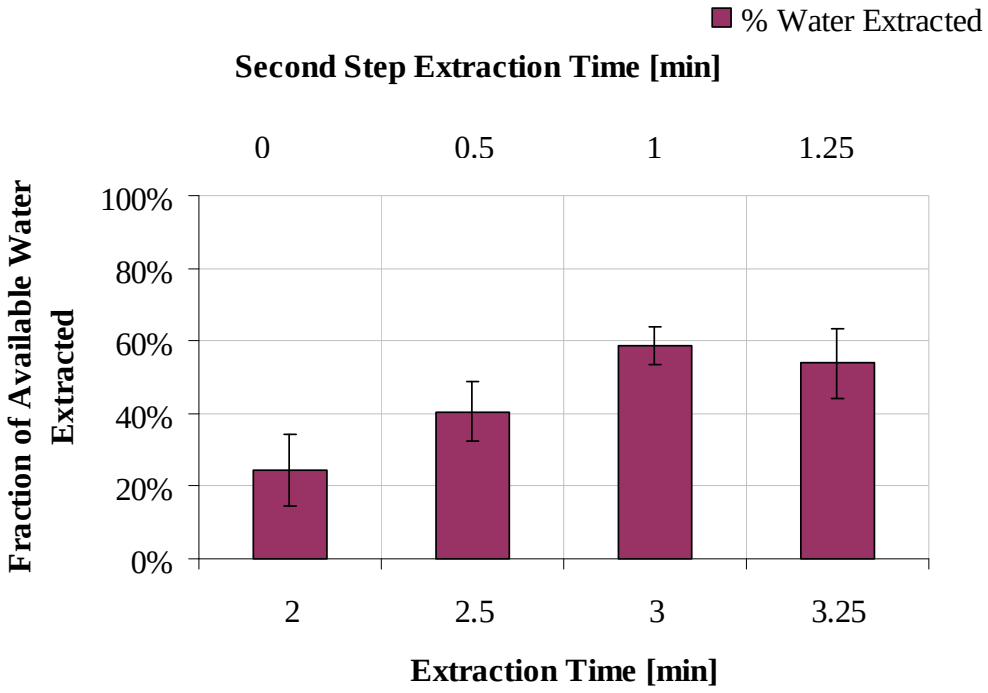


Figure 6. 49 Percentage of Water Extracted (2H-xM)

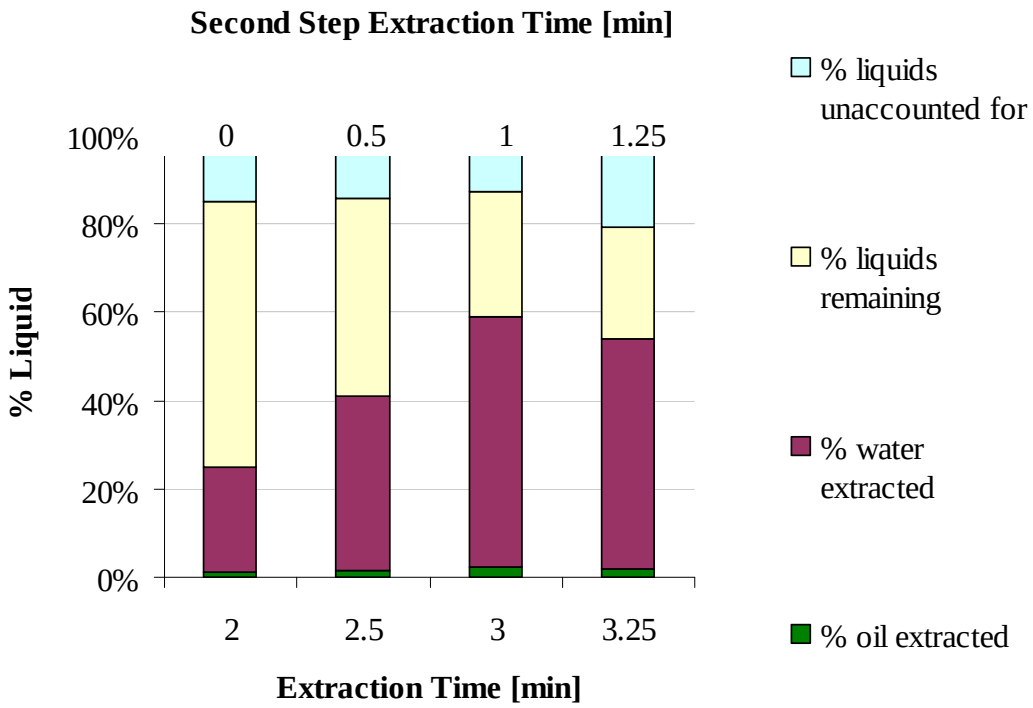


Figure 6. 50 Material Balance on the Liquid (2H-xM)

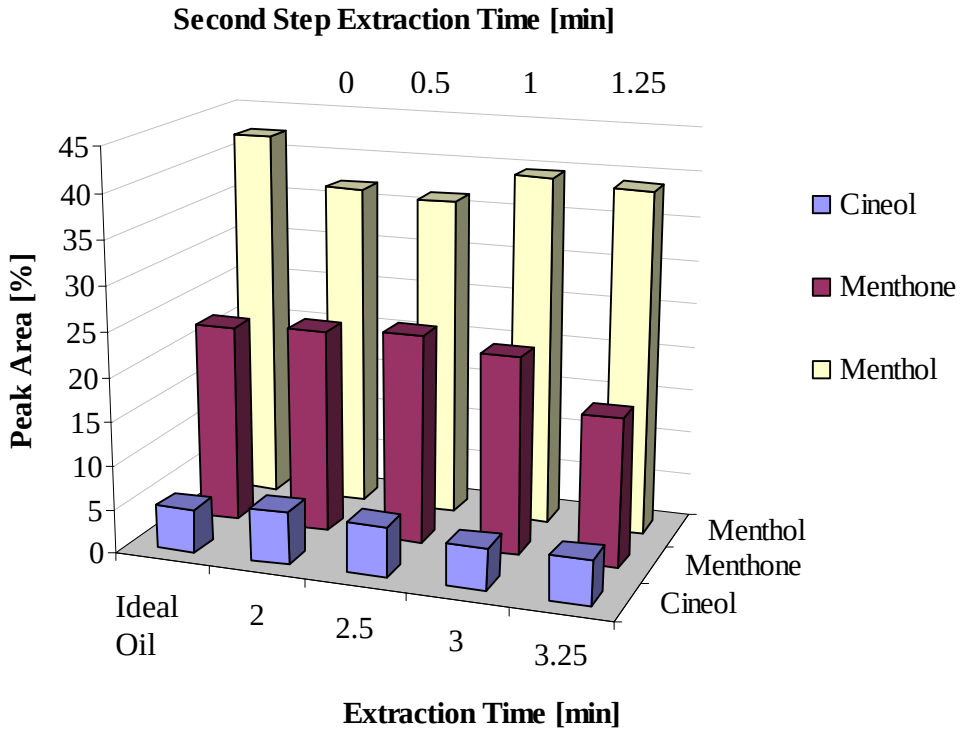


Figure 6. 51 Cineol, Menthol and Menthone Composition (2H-xM)

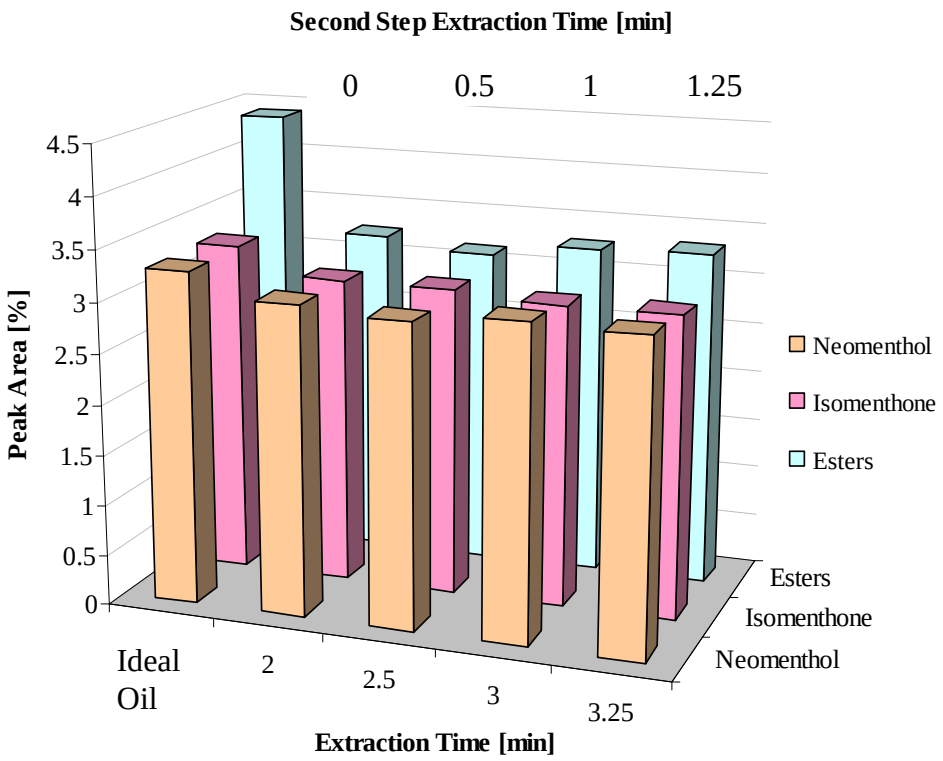


Figure 6. 52 Neomenthol, Isomenthol and Esters Composition (2H-xM)

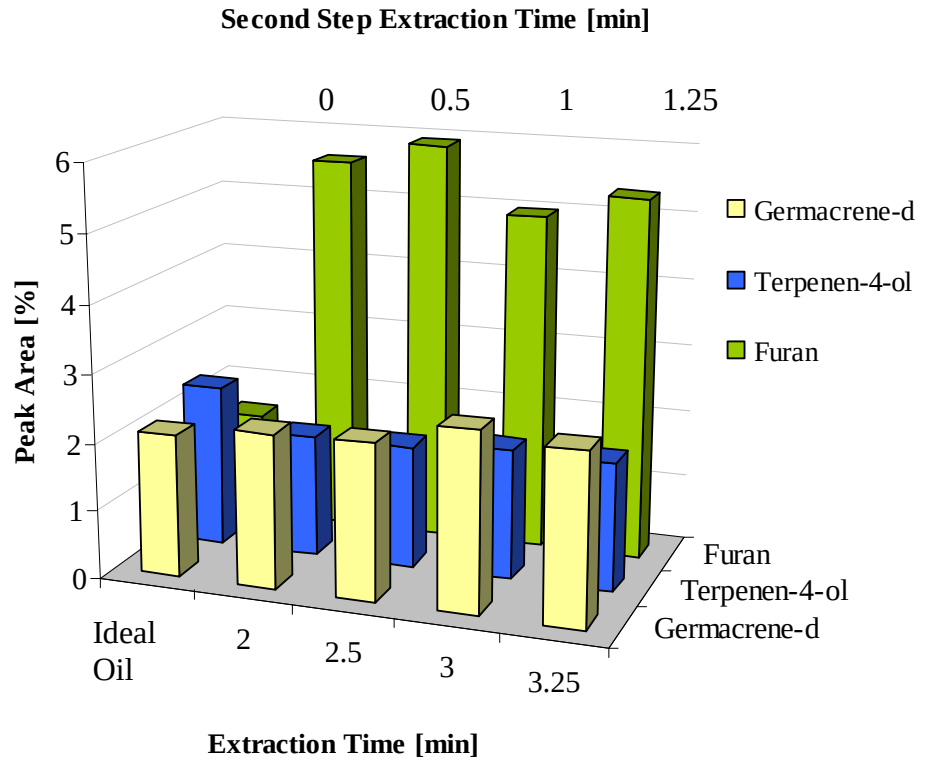


Figure 6. 53 Germacrene-d, Terpenen-4-ol and Furan Composition (2H-xM)

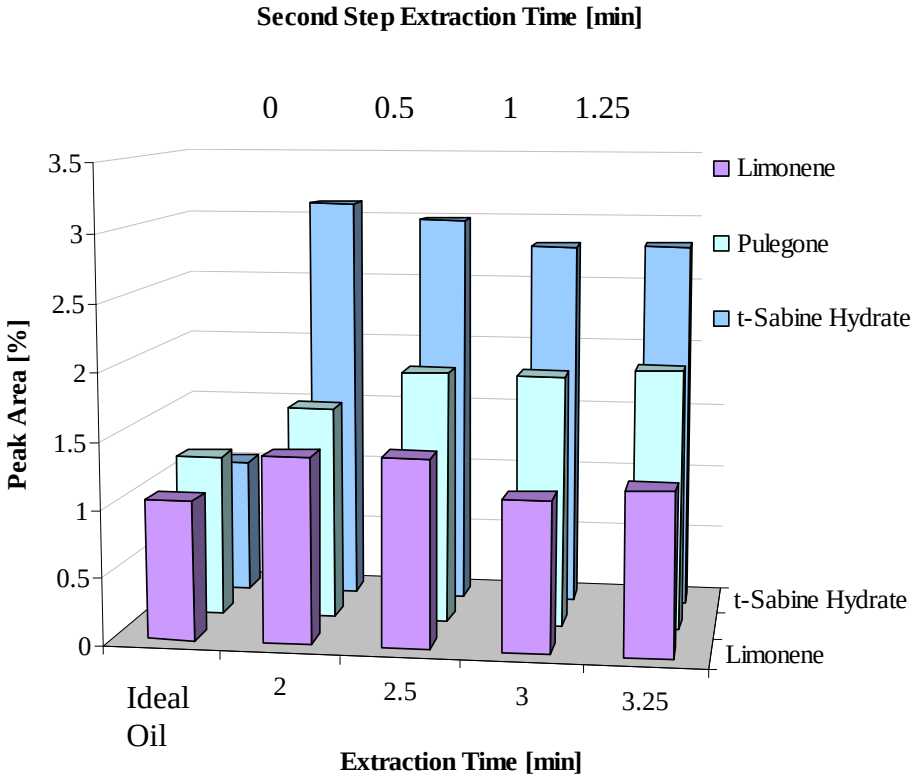


Figure 6. 54 Limonene, Pulegone and t-Sabine Hydrate Composition (2H-xM)

Table 6.7 is the summary of the variation of the composition of each component compared to the standard obtained from the steam distillation process.

Table 6. 7 Composition Variation with respect to the Standard (2H-xM)

	Extraction Time [min]				
Component	**2**	**2.5**	**3**	**3.25**	Average
Limonene	33%	35%	8%	17%	23%
Cineol	23%	18%	-1%	3%	11%
t-Sabine Hydrate	202%	191%	171%	172%	184%
Menthone	2%	5%	-1%	-26%	-5%
Furan	260%	280%	220%	243%	251%
Isomenthone	-8%	-8%	-10%	-10%	-9%
Esters	-26%	-29%	-26%	-25%	-26%
Neomenthol	-7%	-9%	-6%	-7%	-7%
Terpenen-4-ol	-25%	-25%	-19%	-21%	-22%
Menthol	-13%	-14%	-6%	-8%	-10%
Pulegone	33%	57%	56%	61%	51%
Germacrene-d	9%	10%	26%	21%	17%
Total	1%	1%	2%	-5%	0%

6.10 Two Extraction Step (2 minutes at 1120 Watts- MediumLow)

The effect of the combination of two power levels, starting with 2 minutes at 1120 W (High Level) and followed by 0.5, 1, 1.25, 1.5 and 1.75 minutes on at 518 W (Medium Low).

Is it proven that the breakthrough time occurs on average at 1.2 minutes, which proves that the first step of this combination helps to pass the breakthrough (Figure 6.55). Figure 6.56 proves that the boiling temperature of water has been reached at each extraction time.

The percentage of oil extracted approaches to equilibrium starting at the minute 3.25 and reaching its maximum (68% of oil extracted) at the minute 3.75 (figure 6.57) The percentage of water collected also reaches its maximum at 3.5 minutes (51.8%) and at 3.75 minutes the average is 52% (figure 6.58)

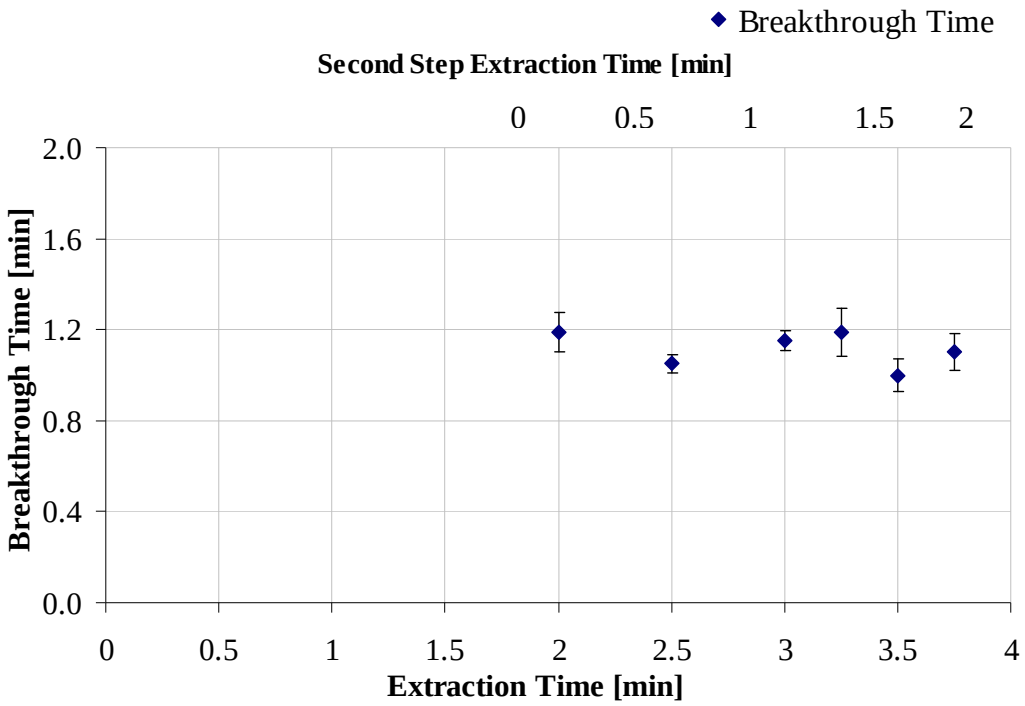


Figure 6. 55 Breakthrough Time vs. Extraction Time relationship (2H-xML)

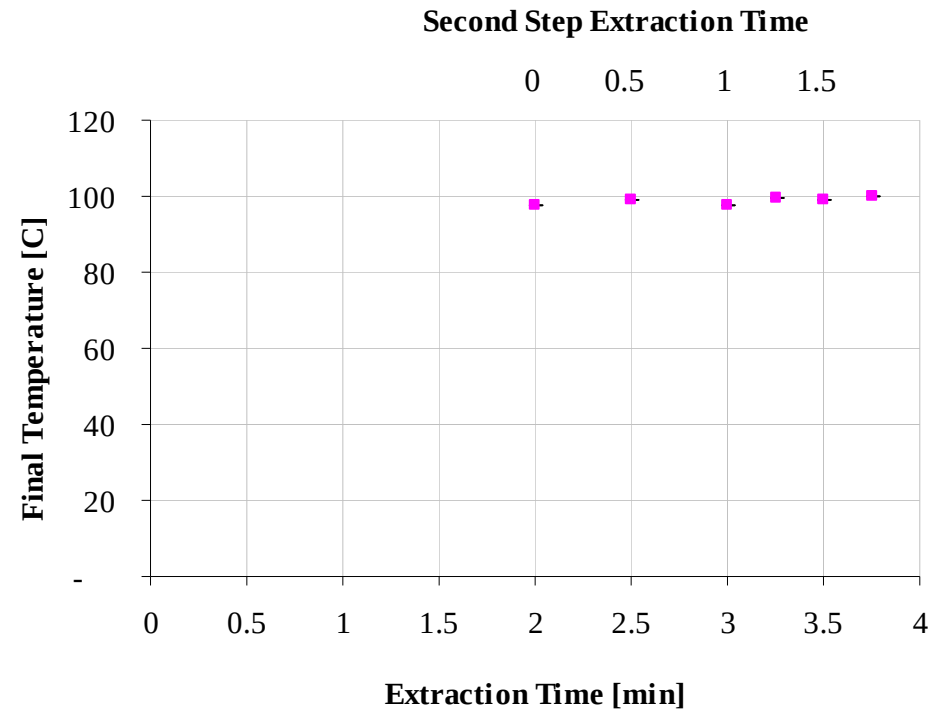


Figure 6. 56 Final Temperature 2H-xML process

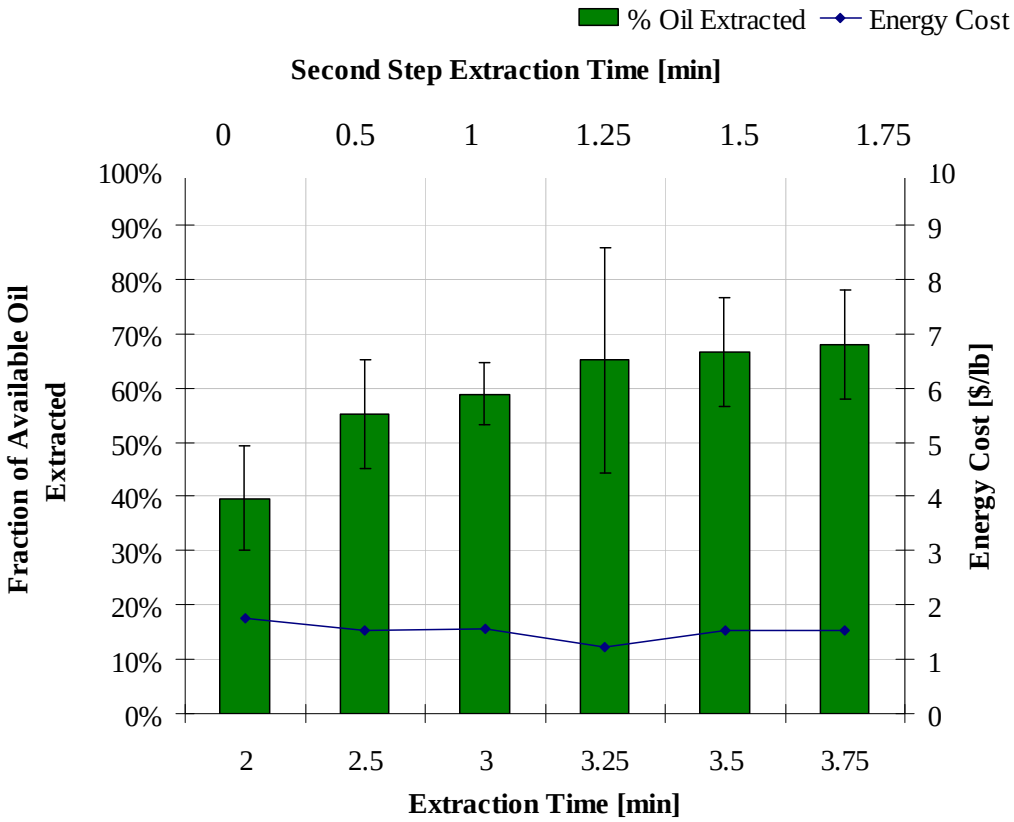


Figure 6. 57 Percentage of Oil Extracted (2H-xML)

Figure 6.58 shows the mass balance on the liquid phase, and figures 6.59 through 6.62 show the composition of the extracted as a function of the extraction time.

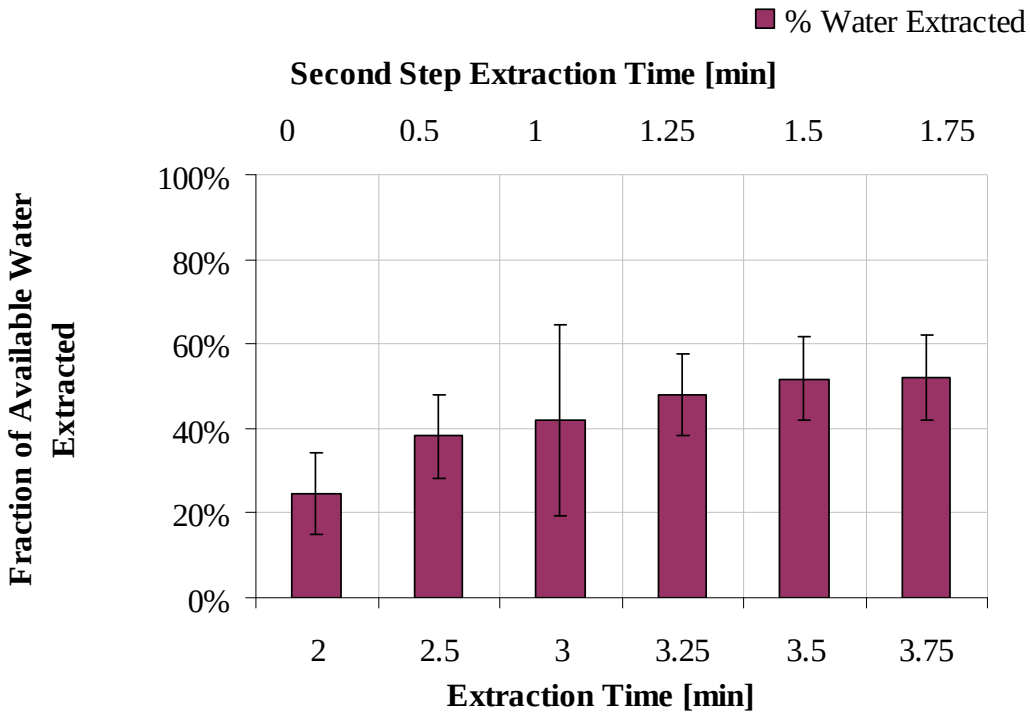


Figure 6. 58 Percentage of Water Extracted (2H-xML)

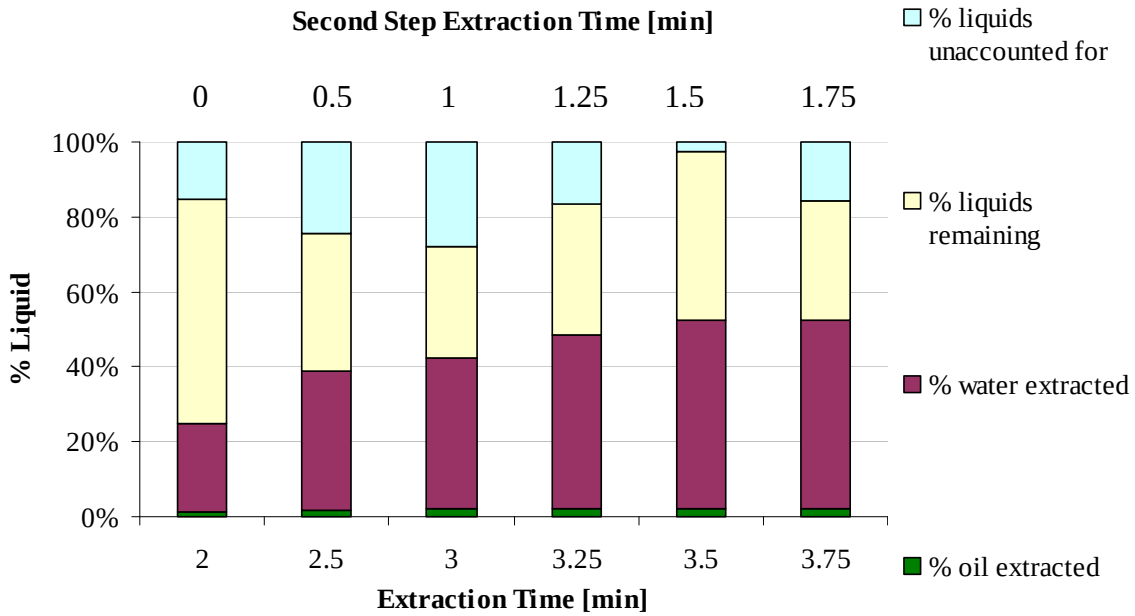


Figure 6. 59 Mass Balance on the Liquid Phase (2H-xML)

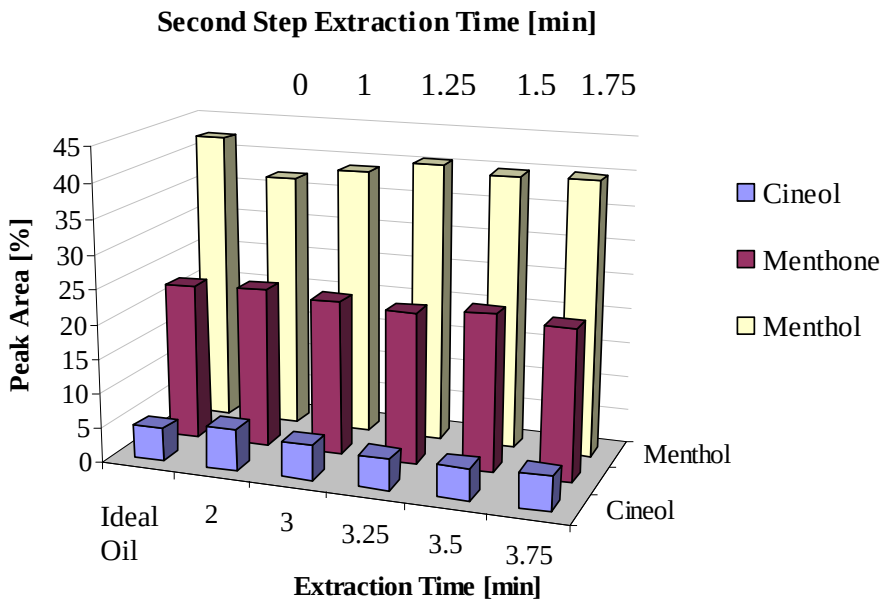


Figure 6. 60 Cineol, Menthol and Menthone Composition (2H-xML)

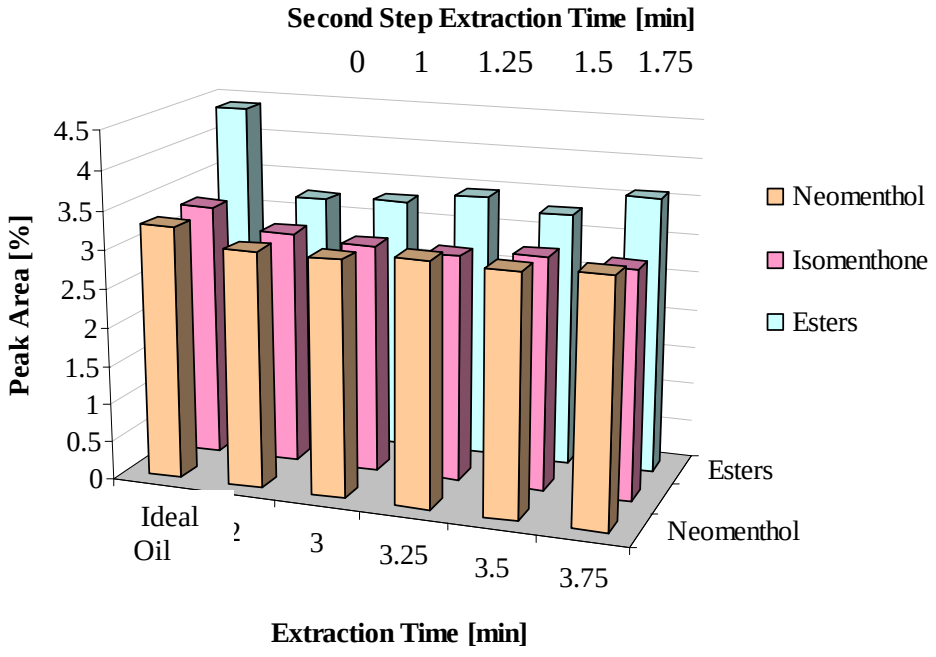


Figure 6. 61 Neomenthol, Isomenthol and Esters Composition (2H-xML)

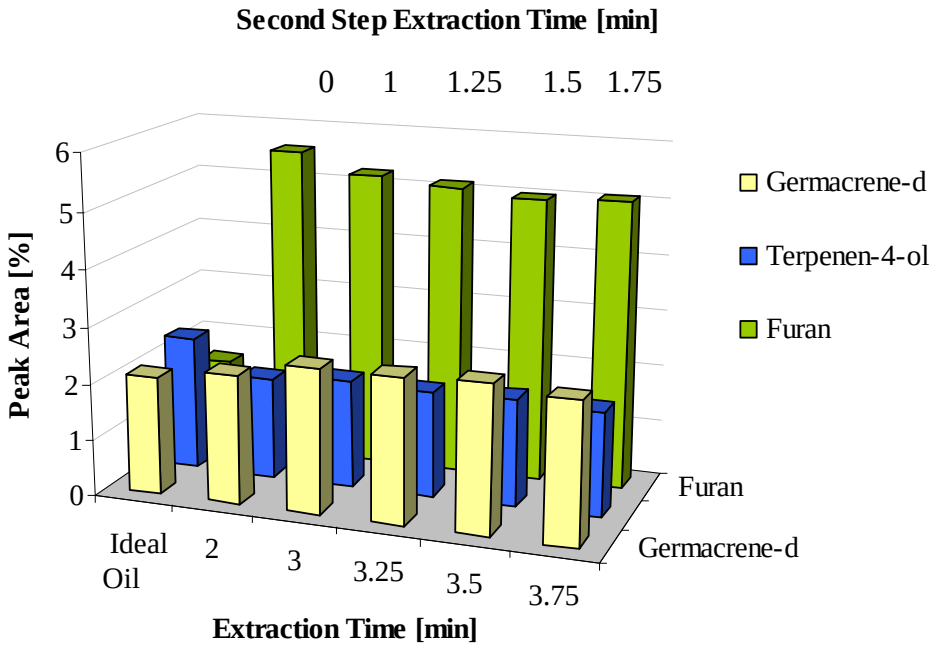


Figure 6. 62 Germacrene-d, Terpenen-4-ol and Furan Composition (2H-xML)

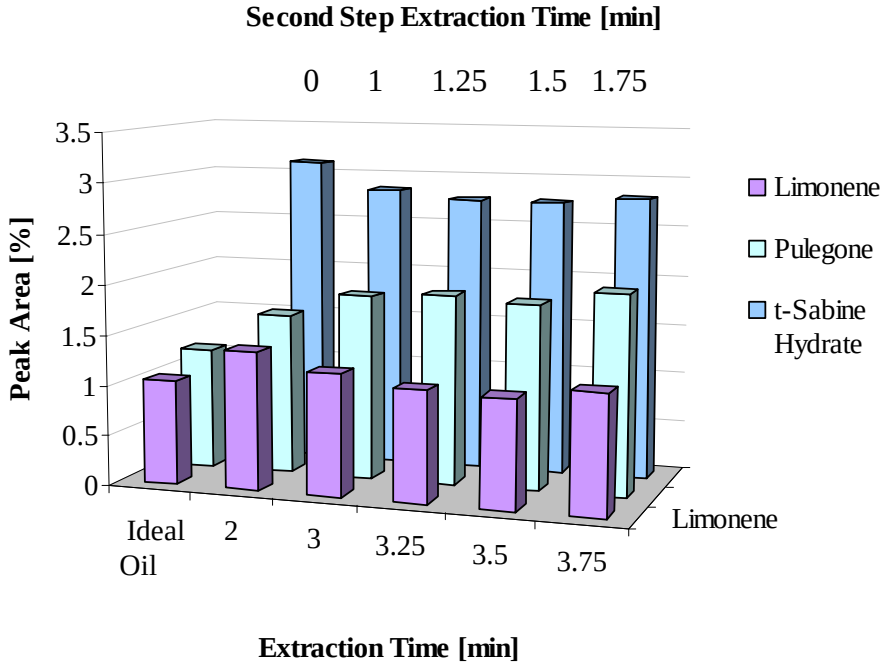


Figure 6. 63 Limonene, Pulegone and t-Sabine Hydrate Composition (2H-xML)

Table 6.8 is the variation of each component with respect to the standard.

Table 6. 8 Composition Variation with respect to the Standard (2H-xML)

	Extraction Time [min]				
Component	**2**	**3**	**3.25**	**3.5**	**3.75**
Limonene	33%	17%	6%	4%	15%
Cineol	23%	5%	-5%	-3%	2%
t-Sabine Hydrate	202%	176%	169%	168%	174%
Menthone	2%	-1%	-4%	1%	-3%
Furan	260%	238%	230%	223%	228%
Isomenthone	-8%	-10%	-11%	-9%	-10%
Esters	-26%	-25%	-22%	-25%	-18%
Neomenthol	-7%	-7%	-4%	-5%	-4%
Terpenen-4-ol	-25%	-20%	-22%	-20%	-23%
Menthol	-13%	-8%	-4%	-6%	-6%
Pulegone	33%	52%	56%	52%	64%
Germacrene-d	9%	23%	23%	25%	19%
Total	1%	1%	2%	2%	2%

6.11 Comparison of best extraction times at different power settings

In this section, the best results from each set of experiments are compared to determine which could be the most recommendable extraction time and power. Figure 6.64 compares maximum percentage of oil extracted by the steam distillation system and the microwave systems. This figure also shows graphically the energy cost of the oil extracted (secondary y axis) and the total extraction time (secondary x axis). The amount of oil obtained from the microwave extraction varies from 54% to 70%.

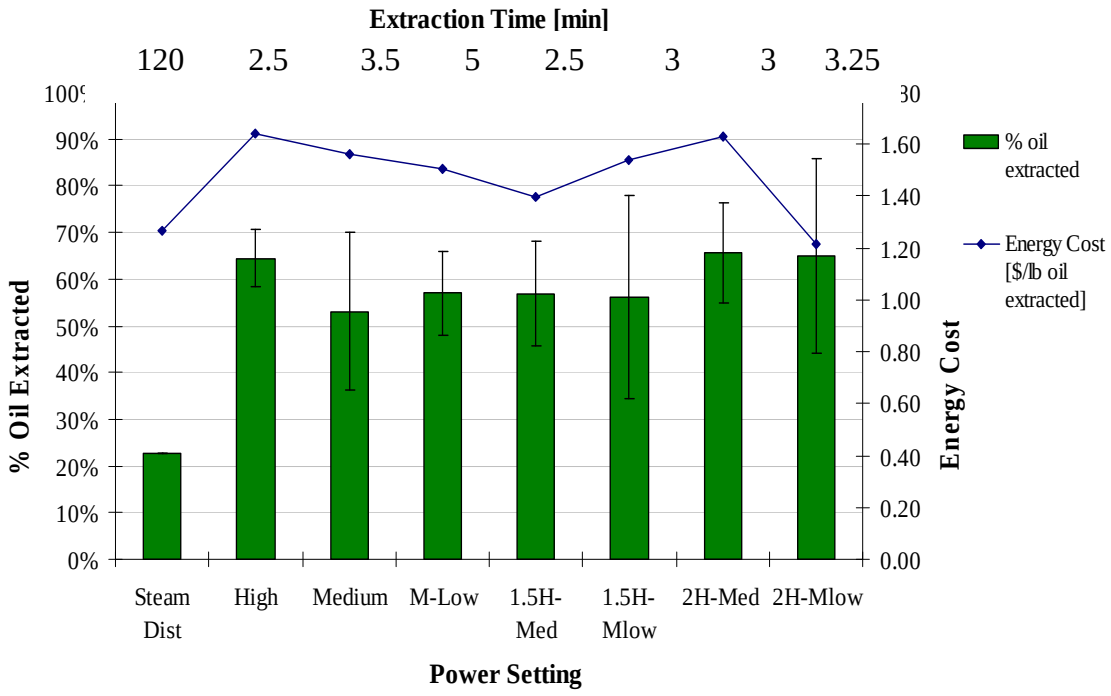


Figure 6. 64 Percentage of Oil Extracted (Best Extraction Settings)

Figure 6.65 shows the fraction of water extracted at each power setting; the amount of water extracted from the steam distillation system was not possible to quantify hence it is not included in this plot. The fraction of water extracted varies from 44% at the two step process 1.5H1.5ML to 59% at also the combination process 2H1Med. The higher percentage of water extracted is the reason why at 2H1Med the energy cost is higher than the other two step extraction costs.

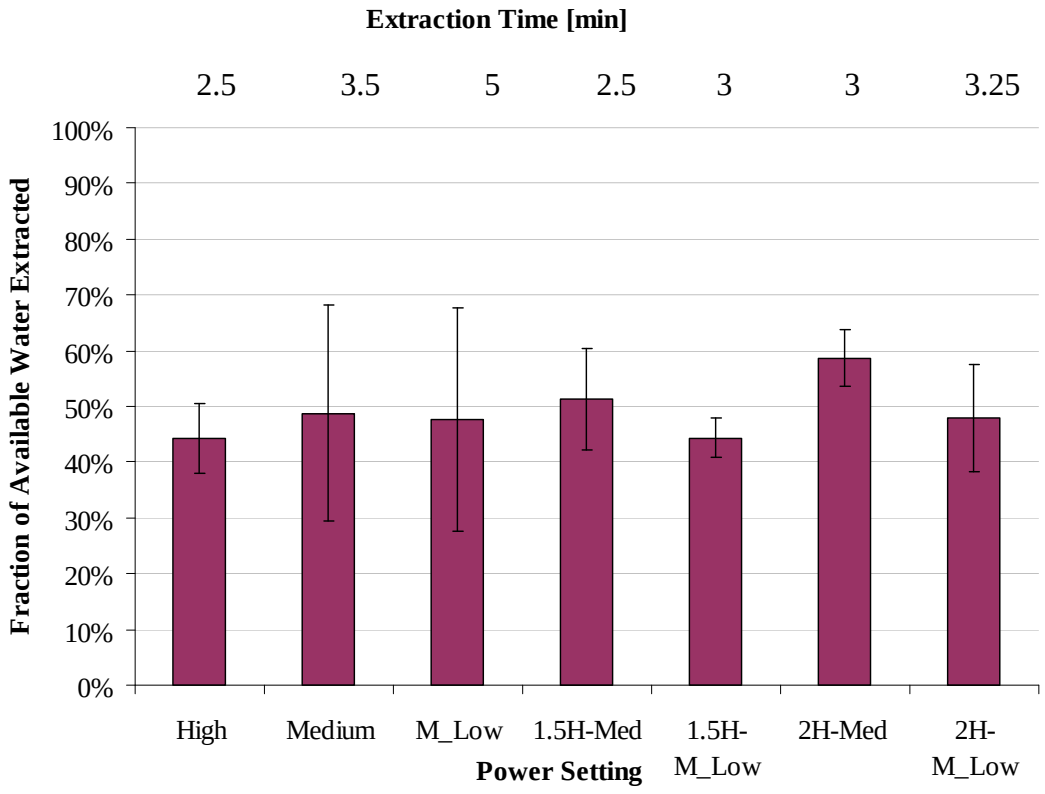


Figure 6. 65 Percentage of Water Extracted (Best Extraction Settings)

Figure 6.66 shows the mass balance at each power setting optimal stage. Figures 6.67 to 6.70 show the average composition of the oil extracted at optimal specific power setting and time.

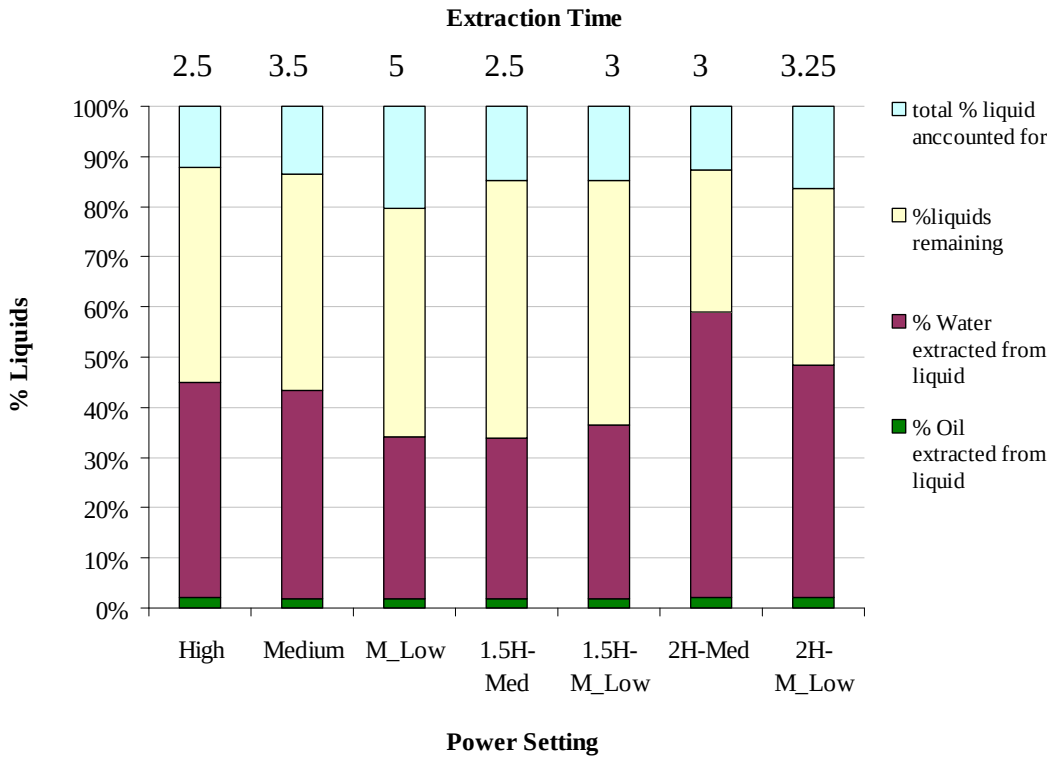


Figure 6. 66 Mass Balance on the Liquid Phase (Best Extraction Settings)

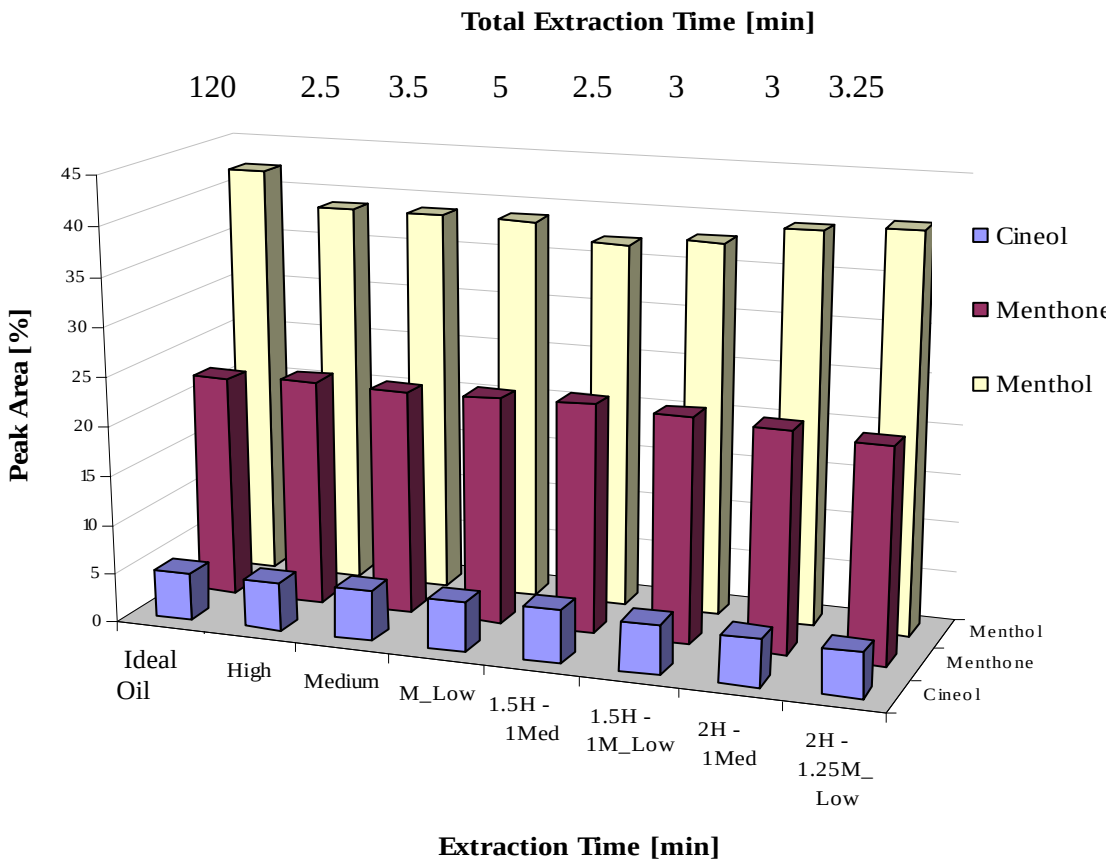


Figure 6. 67 Cineol, Menthol and Menthone Composition (Best Extraction Settings)

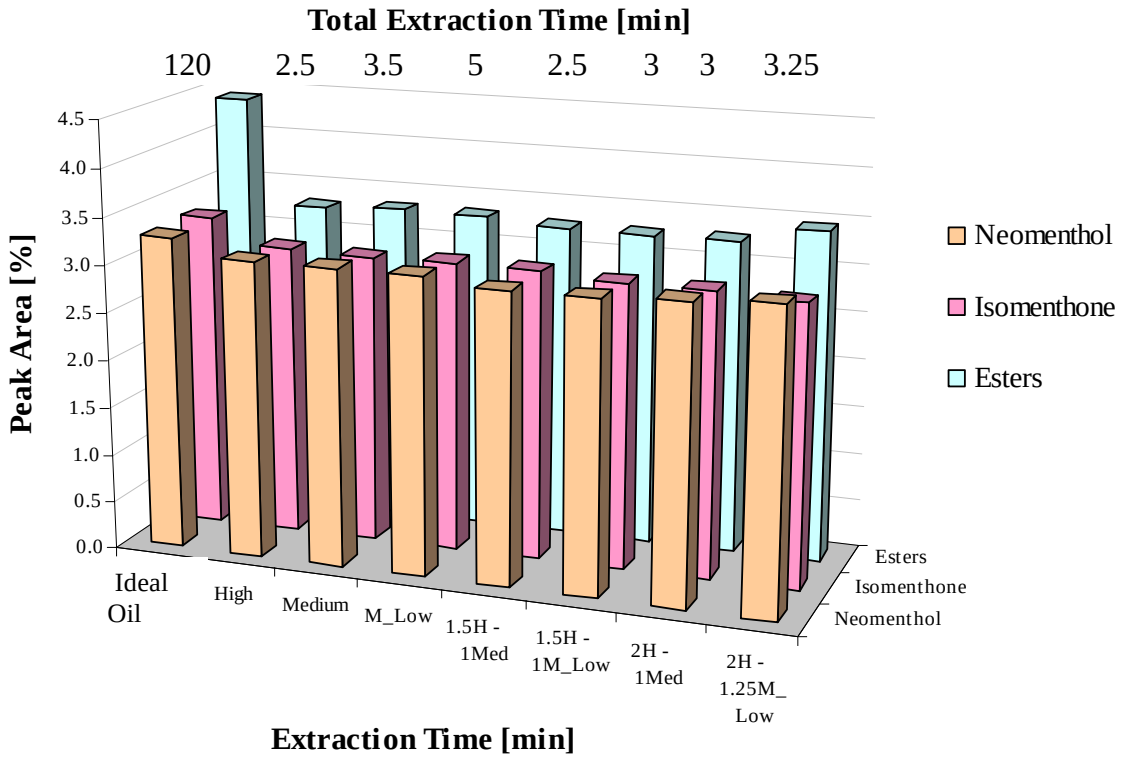


Figure 6. 68 Neomenthol, Isomenthol and Esters Composition (Best Extraction Settings)

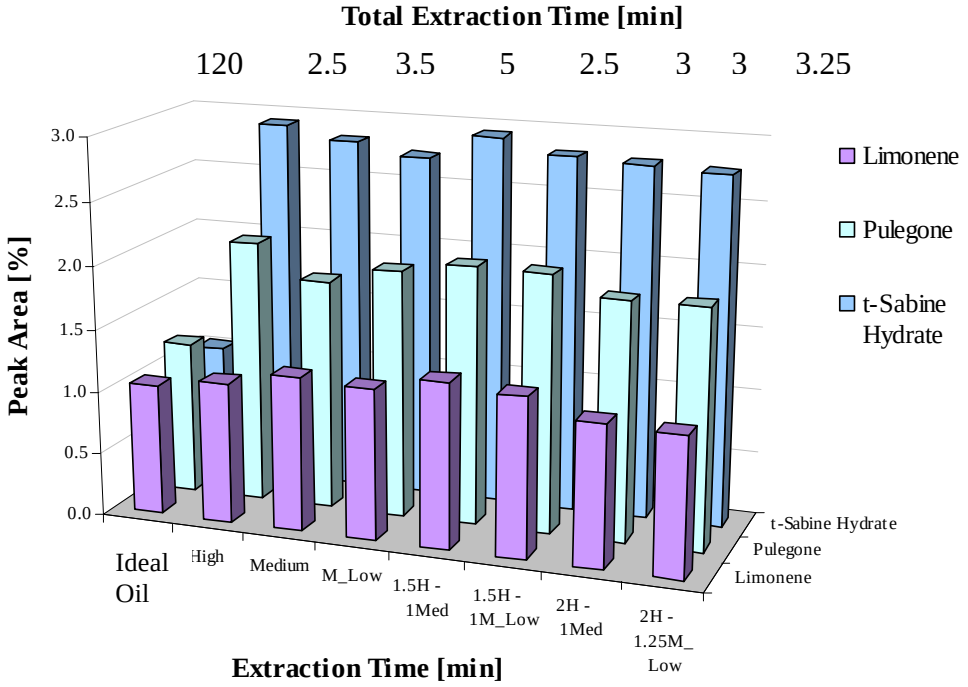


Figure 6. 69 Limonene, Pulegone and t-Sabine Hydrate Composition (Best Extraction Settings)

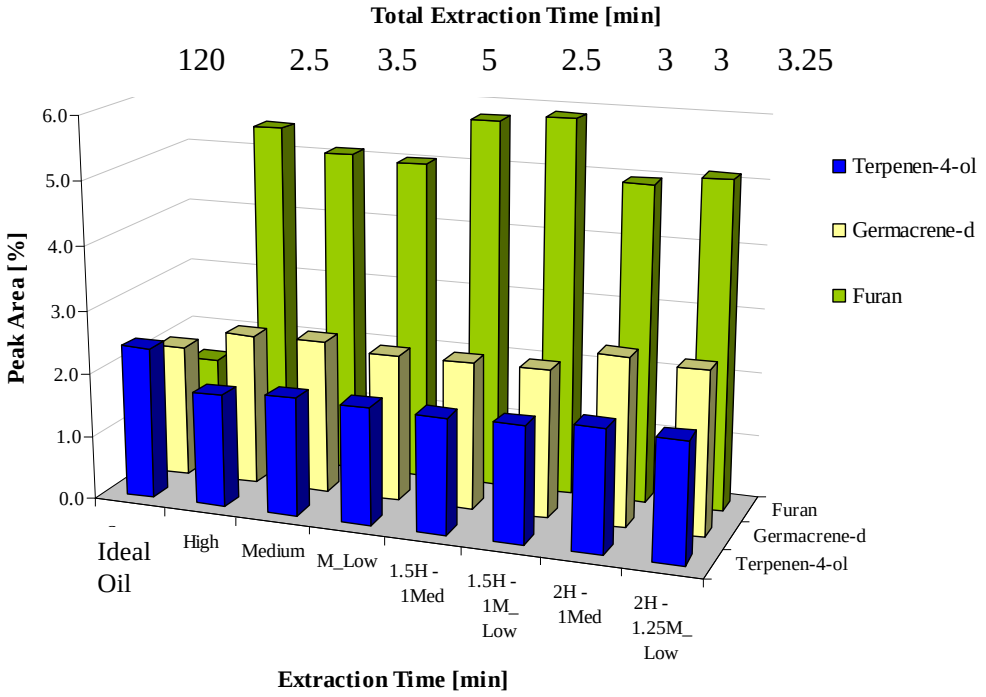


Figure 6. 70 Germacrene-d, Terpenen-4-ol and Furan Composition (Best Extraction Settings)

Table 6. 9 Composition Variation with respect to the Standard (Best Extraction Settings)

	Power Level (Extraction Time [min])						
	High	Medium	M_Low	1.5H-Med	1.5H-M_Low	2H-Med	2H-M_Low
Component	2.5	3.5	5	2.5	3	3	3.25
Limonene	8%	18%	16%	27%	22%	8%	6%
Cineol	3%	7%	4%	12%	4%	-1%	-5%
t-Sabine Hydrate	184%	175%	166%	185%	174%	171%	169%
Menthone	2%	1%	2%	3%	1%	-1%	-4%
Furan	250%	228%	224%	272%	279%	220%	230%
Isomenthone	-8%	-9%	-8%	-8%	-10%	-10%	-11%
Esters	-25%	-24%	-24%	-26%	-26%	-26%	-22%
Neomenthol	-5%	-5%	-5%	-8%	-8%	-6%	-4%
Terpenen-4-ol	-26%	-23%	-23%	-24%	-24%	-19%	-22%
Menthol	-8%	-8%	-8%	-12%	-10%	-6%	-4%
Pulegone	72%	51%	62%	69%	68%	56%	56%
Germacrene-d	14%	15%	10%	10%	11%	26%	23%
Total	2%	2%	1%	1%	1%	2%	2%

The efficiency of optimal extraction settings by the solvent free microwave system was determined by the energy balance (Section 6.2). Figure 6.71 shows the power needed based on energy balance and the power actually consumed by the microwave. As figure 6.72 shows the percentage of energy used to extract the essential oils varies from 40% to 60% of the total energy consumed. This suggests that the lab scale microwave unit is roughly 50% efficient.

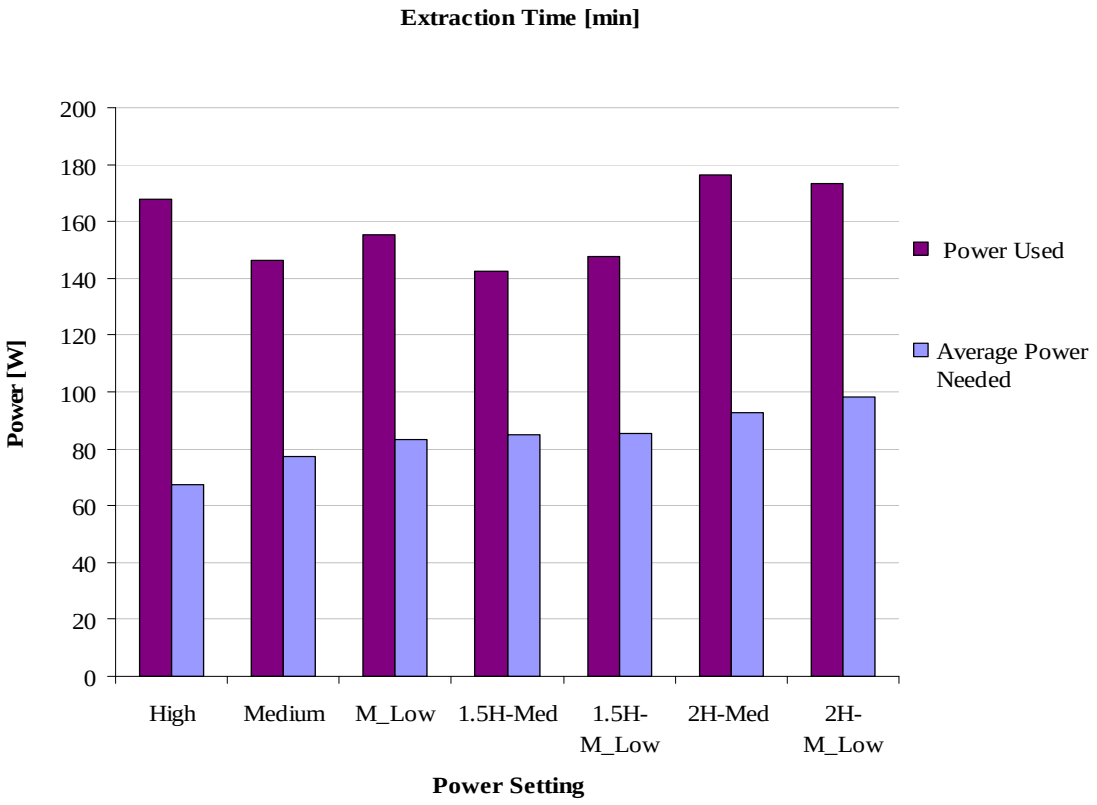


Figure 6. 71 Comparison of Power Used and Needed by the Microwave System

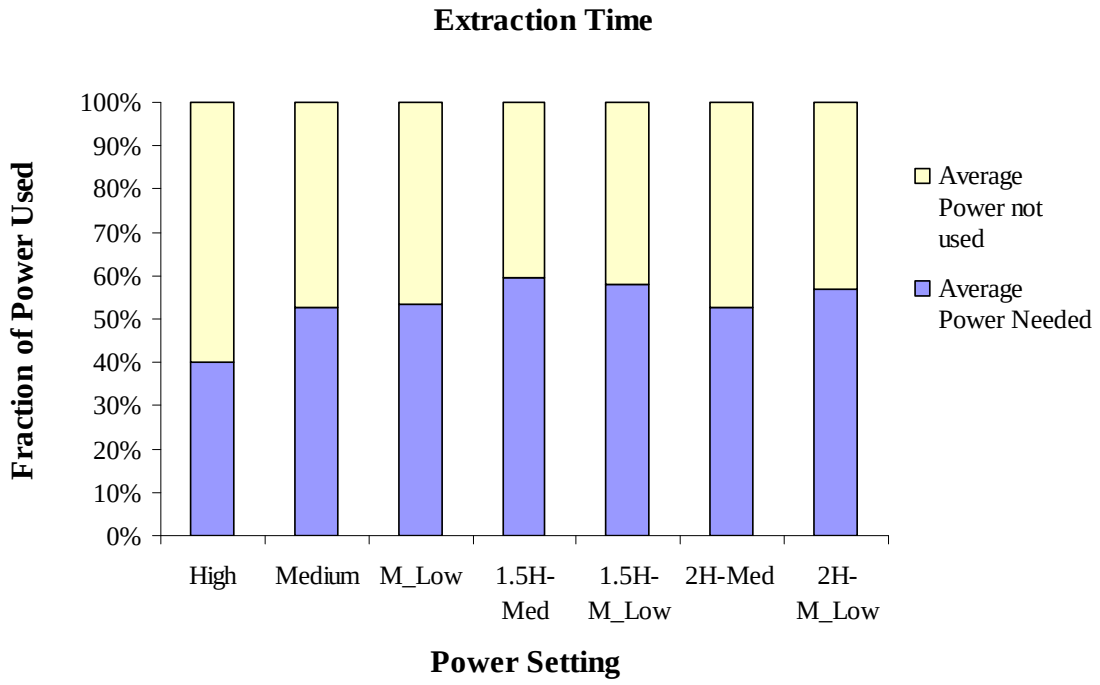


Figure 6. 72 Percentage of Power Needed

As it was mentioned on the literature review (Chapter 1) the composition of any essential oil is a strong function of the weather, altitude, humidity, diseases that attack the plant on growing stages, etc. The standard oil used to compare the results from the microwave extraction is considered an ideal composition.

6.12 Comparison of extraction efficiency using different peppermint hay

With the purpose to validate this efficiency of this method and to explore future opportunities for this field seventeen experiments were run at IP Callison & Sons in Lacey- Washington. The same apparatus used for the main group of experiments was used, however; the peppermint hay utilized was from a different farm. All extractions were done for 3 minutes at 1120 W. Figures 6.73 and 6.74 compares on average the percentage of oil and water recovered from the different samples of peppermint hay.

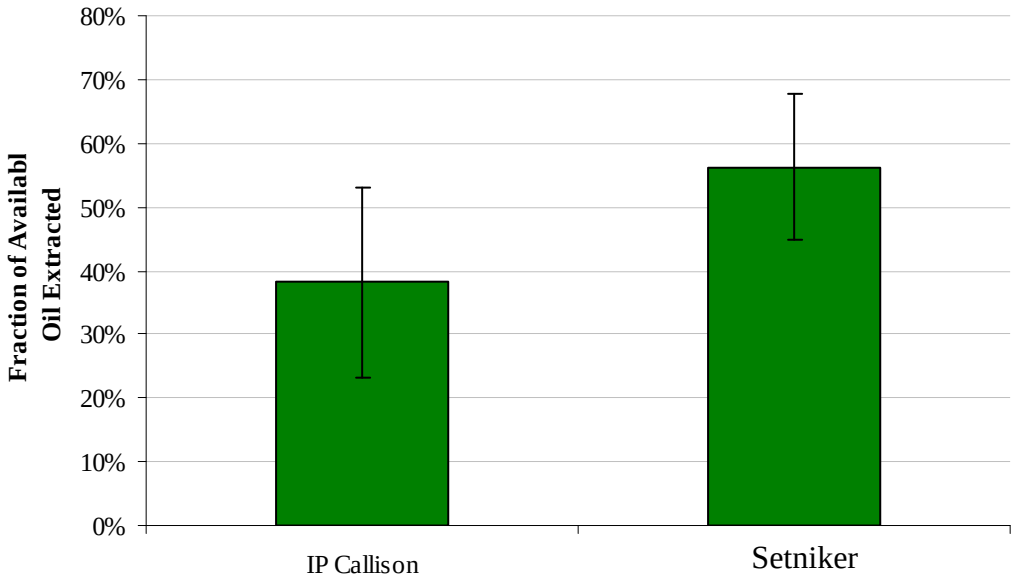


Figure 6. 73 Comparison of percentage of oil extracted from different peppermint hay (3min- 1120W)

The comparison of the oil extracted composition from the steam distillation processs (after blending), the extractions done at the IP Callison facility and the extraction done at Oregon State using the mint hay from the Setniker farm is presented on figures 6.75 to 6.78.

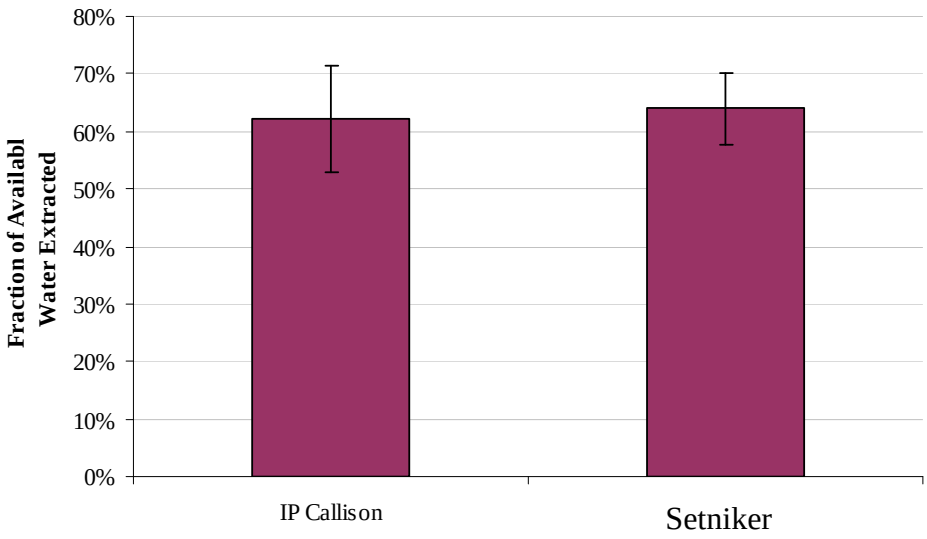


Figure 6. 74 Comparison of percentage of water extracted from different peppermint hay (3min- 1120W)

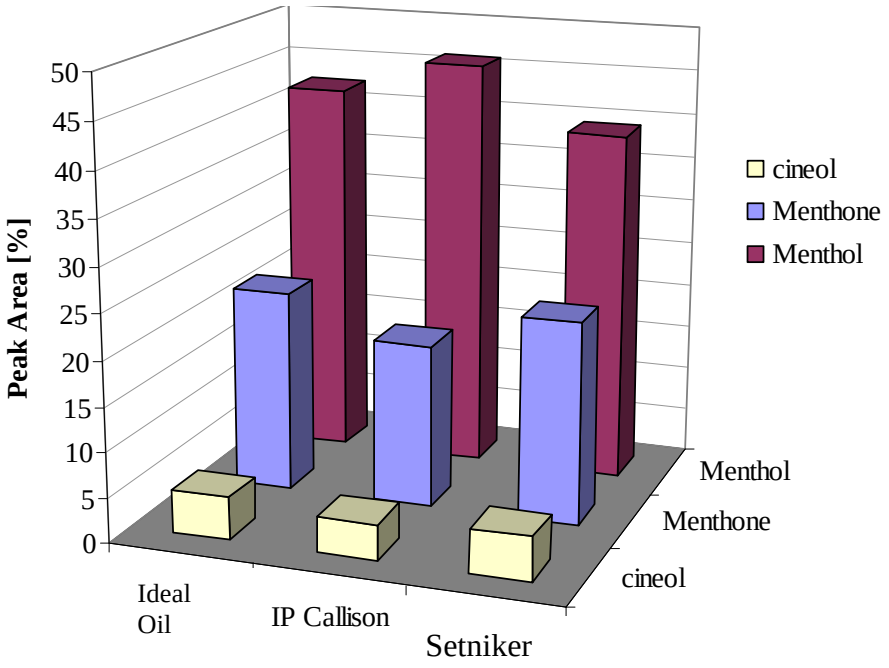


Figure 6. 75 Cineol, Menthol and Menthone Composition (Comparison different hay)

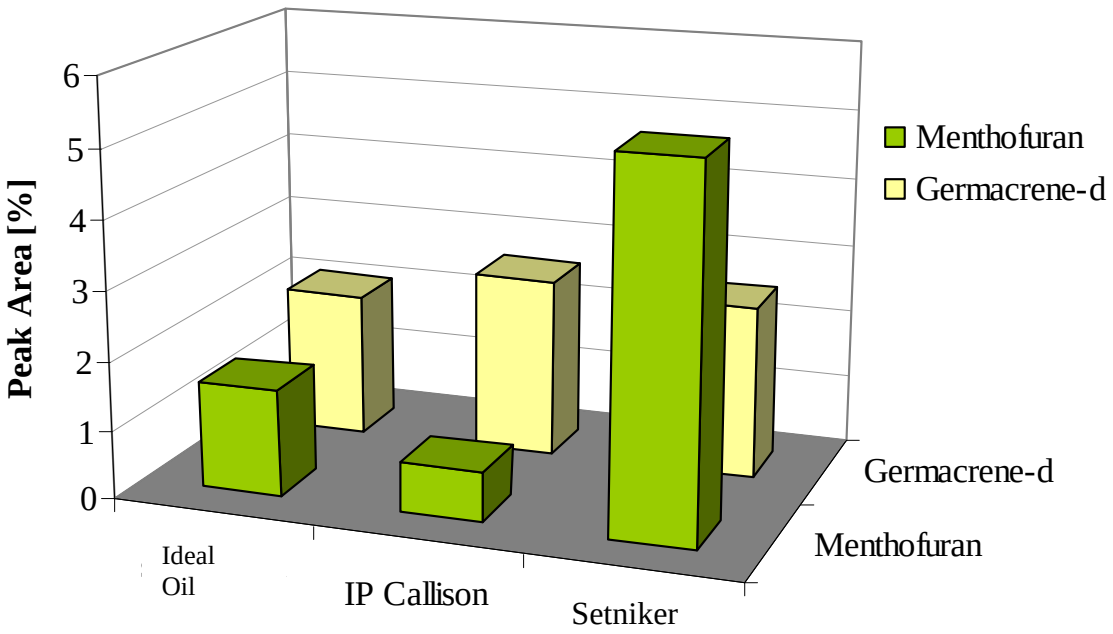


Figure 6. 76 Germacrene-d and Furan Composition Composition (Comparison different hay)

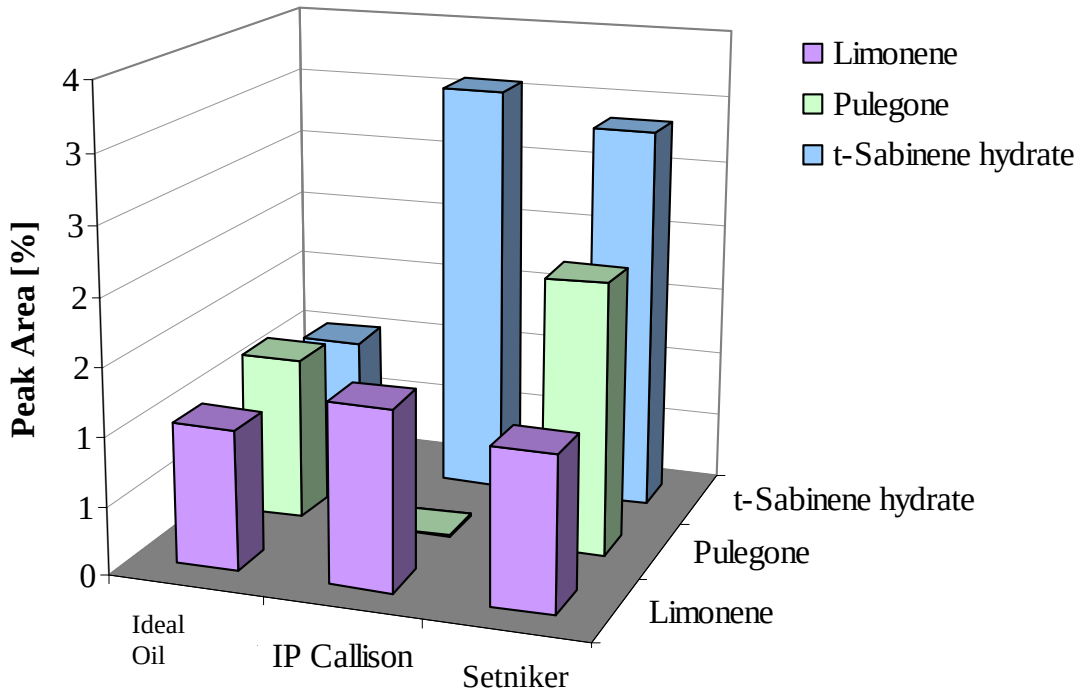


Figure 6. 77 Limonene, Pulegone and t-Sabine Hydrate Composition Composition (Comparison different hay)

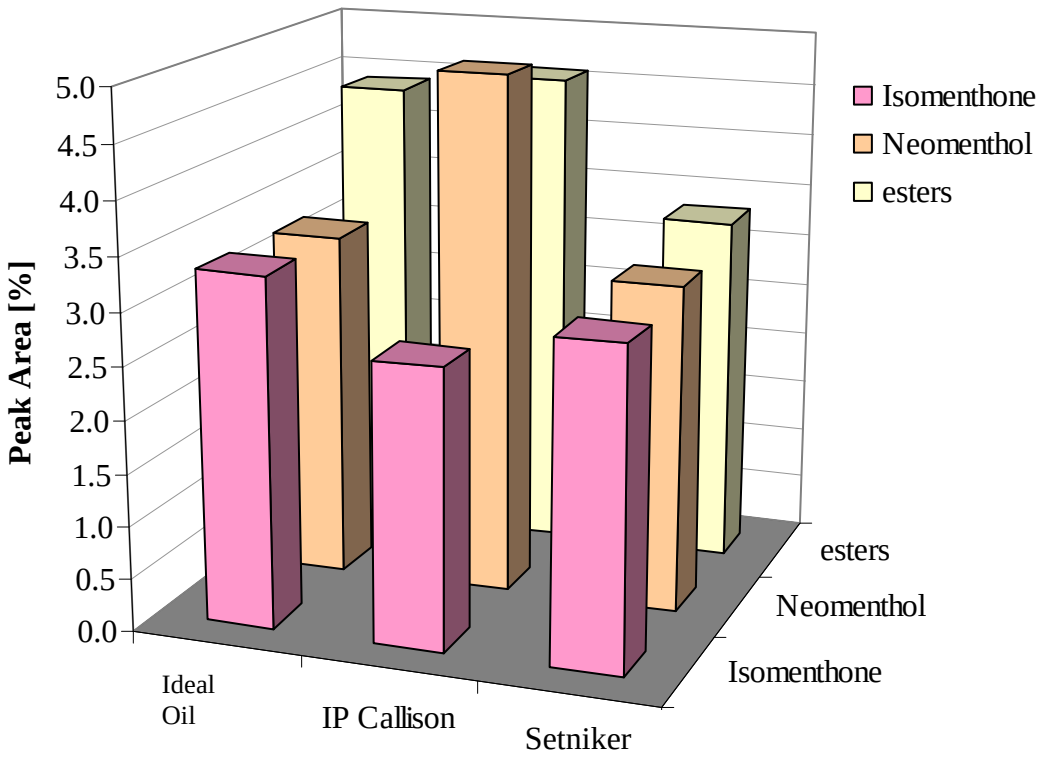


Figure 6. 78 Neomenthol, Isomenthol and Esters Composition Composition (Comparison different hay)

Table 6.10 shows the variation on the composition of oil extracted by using two different samples of peppermint hay.

Table 6. 10 Comparison to the ideal mint oil sample of the extractions done at 3 minutes and 1120 Watts using hay from different farms

Component	IP Callison	Setniker
Limonene	27%	9%
Cineol	-17%	2%
t-Sabine Hydrate	200%	174%
Menthone	-19%	-1%
Furan	-54%	221%
Isomenthone	-20%	-9%
Esters	4%	-24%
Neomenthol	50%	-5%
Menthol	9%	-6%
Pulegone	-100%	61%
Germacrene-d	25%	23%

7. Conclusions

Traditionally peppermint oil is extracted by steam distillation; 20% of the oil available in the plant is extracted. Solvent free microwave extraction is an alternative extraction method that was proposed on this study. The power applied to the plant material and the extraction time were the variables studied in this research. Three power level settings were chosen: 1120 W, 697W and 518 W; two combinations of power were also explored: 1120 W-697W and 1120 W-518 W. The minimum and maximum extraction times varied for the different power settings. The extracted samples were collected and analyzed in the GC to determine its composition. Twelve components which represent 90% of the total concentration were chosen to compare the quality of the oil with ideal peppermint oil.

In all the experiments performed a variation from 10% to 30% on the oil extracted was observed. The variation is in part due to the small amount of material that is being obtained as a small droplet is easily lost in the condenser or the still pot and causes a considerable increase in the experimental error. Also the leaf/stem ratio in the samples used causes more variability than would be seen in a larger sample. The variation on the amount of water extracted (2% -20%) was observed to be less than the variation on the oil extracted because the amount of water in the plant is higher than the oil; in fact water is present in leaves and stems; while the oil is only available from the plant leaves.

Because only 1% of the liquid available for extraction is oil, the boiling point of the mixture could be assumed to be that of water. The final temperature of the sample after extraction shows that the maximum temperature achieved is 100 °C once the breakthrough time was passed. This is why the two step processes are more efficient than the single step processes. More energy is needed at the beginning of the extraction until the water starts vaporizing, then less energy is needed only to keep the temperature high enough to help the vapors transport. This is the reason why applying low energy at the beginning of the process only retarded the breakthrough time which

increases the energy cost. The time needed to achieve 100 °C is 1.5 minutes using 1120 Watts which is similar to the results reported by Lucchesi (Lucchesi, Chemat et al. 2004).

Microwave extraction with no solvent addition was successfully investigated and shown to extract roughly three times more oil from the plant than from the steam process. Results show that the most effective power setting is in fact the combination of 2 minutes at 1120 W and 1.25 minutes at 518W (2H1.25ML). This combination allows extracting 65% of the total oil available in the plant with a variation coefficient of 21%; 48% of the water available with a variation coefficient of 9.25%. The percentage of liquids left in the hay after extraction is 35% and the percentage of liquids unaccounted for is 16%. Figures 7.1 and 7.2 are SEM images from the top of the peppermint leaves before and after extraction. These images show how the oil glands are destroyed after the microwave irradiation was applied to the plant; these images are similar to the ones obtained by Chan who performed microwave extraction of rosemary leafs in hexane (Chen and Spiro 1994).

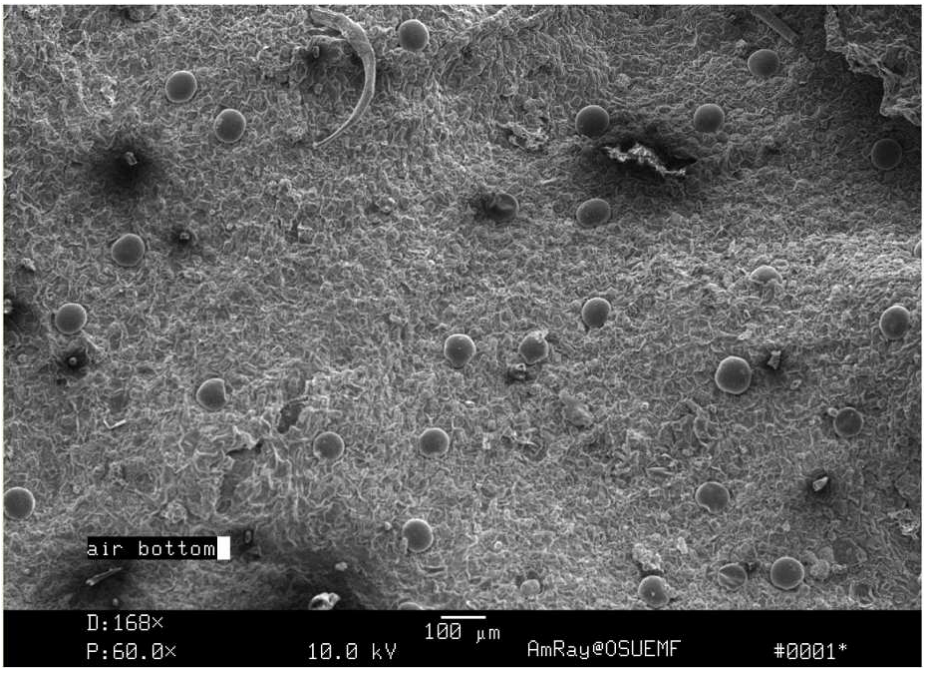


Figure 7. 1 SEM Peppermint leaf prior to extraction

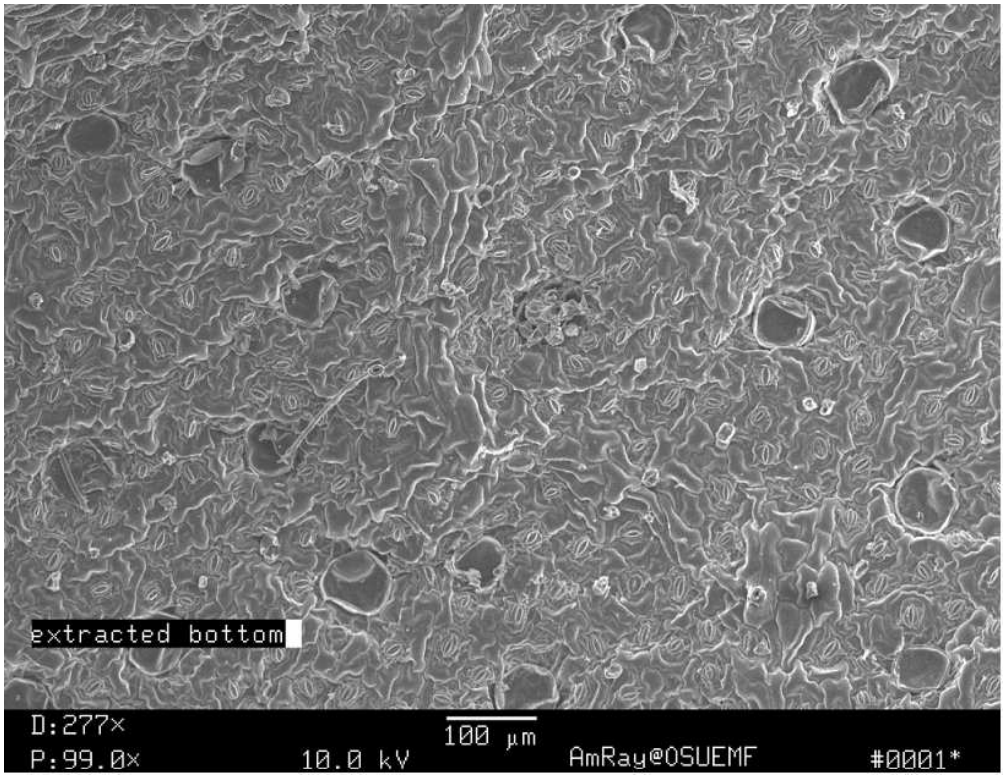


Figure 7. 2 SEM Peppermint leaf image after microwave extraction

The energy cost of the optimal condition extraction is 1.22 $/lb of oil extracted which is 3% lower than steam distillation cost which on average is 1.26 $/lb. This was the only power setting combination that reported a lower energy cost than the steam distillation. On average the energy used by this power combination was 173 KJ (0.048 KWh) to extract the essential oils from 100 grams of peppermint hay. Previous work done by Lucchesi found that 0.25 KWh was used to extract essential oils from 500 g of plant material. This information is comparable to the energy usage reported on this work since 0.24 KWh will be used if 500 grams of hay are used if the optimal settings were used.

The other settings give an energy cost between 1.64 and 1.39 $/ lb of oil extracted which is 23% and 9% higher than the steam distillation energy cost. The microwave efficiency was proved to vary from 40% to 60%; the energy cost can be diminished by using a higher efficiency microwave.

The composition of the oil extracted varies in certain components more than in others. In all runs the concentration of menthol, neomenthol, esters, terpenen-4-ol, pulegone and germacre-d are proportional to the extraction time. Their maximum concentration is reached at the longer extraction until a plateau is reached at usually the last two longer extraction times. In all cases the concentration of menthone, cineol, isomenthone, furan, limonene and t-sabine hydrate decrease as extraction time increases. Because the main component of peppermint oil is menthol the extraction time and the power setting which allow the maximum concentration is desired. The highest concentration of menthol was observed to be 40% at (2H1.25ML) which is 4% less than the concentration of the ideal peppermint oil sample. Under the same conditions the menthone concentration is 4% lower than the standard while the concentration of furan is 230% higher. The furan component in this hay sample did not show a lower concentration than 200% with respect to the steam distillation ideal standard. The sets of extractions done at the IP Callison facility using the OSU microwave and process show that there is a dramatic variation of the oil composition compared to the standard composition as a function of the hay used. Low levels of furan and high levels of menthol were reported from this set of data. The results from these trials infer that the composition of the oil varies significantly with the plant material and maturity. This is why it is necessary to blend the oil from extractions to achieve the desired composition. This does not represent an inconvenience since it is an existing standard practice all the oil extracted by steam distillation is currently blended before it is distributed.

This study proves that far more oil can be extracted from the plant using less energy compared to the traditional steam extraction because as this technique reduces the extraction time to 3.25 minutes from the traditional steam distillation 120 minute extraction time. The extraction time reduction and the percentage of oil extracted are opportunities for the mint industry. Because the solvent free microwave extraction uses only the in-situ water of the plant to extract its essential oils the product obtained is more natural than the product obtained from the steam distillation process. Anti scaling agents and softening chemicals are products used to prevent the hard water

formation the boilers which produce steam to extract the essential oils. These chemicals can end up in the essential oil and they could reduce the quality of the final product.

The true extraction cost of Microwave systems would require analysis of a “pilot scale” or full scale unit. This work offers the foundation for development of a pilot scale microwave system and an associated overall plant operations cost assessment. With no further work, this technology can be used at the lab scale to perform extractions in the field to determine the optimal harvest time, humidity stage and other parameters. Studying other plants from the labiate family can be useful to compare the results from this research. This technique can also be used to study the nature of peppermint from different regions and at different growing stages. Another application is to enable the studying of the extraction time and yield as a function of hay packing in the still flask, useful to determine the optimal conditions.

8. Future Work

The peppermint hay that was used was chopped and dried for approximately 5 days. It was challenging to use a homogeneous sample for each run since the leaves fell to the bottom of the bags and then the still pot. It is recommended to study the extraction efficiency as a function of the dryness of the hay. Even though literature shows that only a small quantity of oil is lost due to simple evaporation it could be useful to study the optimal dry state of the hay.

Implementation of a vertical condenser would facilitate the liquids collection and reduce the percentage of liquids unaccounted due to loss in the inner walls of the condenser.

A better temperature recorder could be useful to determine the temperature profile as a function of time. Implementing a temperature feedback controller will provide the ability to study different combinations of power settings and it can be helpful for easier extraction time control.

A preliminary model to predict the results from this new extraction method has been developed. Equation (12) shows the mass of liquids vaporized calculated from the energy balance:

$$M_{liq} = \frac{P \cdot \eta \cdot (t - t_b)}{\Delta H_{vap}} \quad (12)$$

P is the power applied to the sample, η is the microwave efficiency, t is the overall extraction time, t_b is the breakthrough time and is the ΔH_{vap} heat of vaporization of water.

Figure 8.1 is comparison of the actual data at 1120 Watts to the data obtain from equation 12. This model predicts the first 5 data points; a new model needs to be

developed to have a better approximation when more than 60% of the total oil available has been extracted.

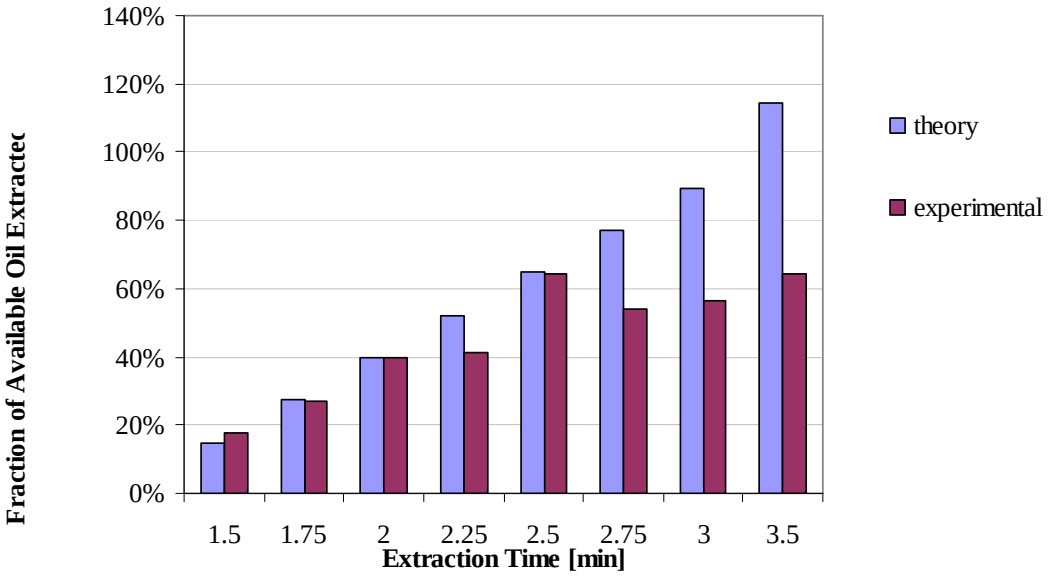


Figure 8. 1 Comparison of experimental data to theoretical model

9. Bibliography

A. Brachet, P. C. J. L. V. (2002). Focused microwave-assisted extraction of cocaine and benzoylecgonine from coca leaves. 13: 162-169.

Adams, J., Wilcox (1963). "Laboratory Experiments in Organic Chemistry." 6.

Bruni, A. and P. Modenesi (1983). "Development, oil storage and dehiscence of peltate trichomes in Thymus vulgaris (Lamiaceae) Fluorescence and electron scanning microscope studies, structure." Nordic journal of botany 3(2): 245-251.

Buffler, C. R. (1993). "Microwave cooking and processing: engineering fundamentals for the food scientist ".

Burbott, A. J. and W. D. Loomis (1969). "Evidence of Metabolic Turnover of Monoterpenes." Plant Physiology 42: 75.

Chen, S. S. and M. Spiro (1994). "Study of microwave extraction of essential oil constituents from plant materials." Journal of Microwave Power and Electromagnetic Energy 29(4): 231-241.

Company, C. R. (1970-1971). "Handbook of Chemistry and Physics." Chemical Rubber Company handbook of chemistry and physics: 20.

Croteau, R., E. Davis, et al. (2005). "(−)-Menthol biosynthesis and molecular genetics." Naturwissenschaften 92(12): 562-577.

Croteau, R. and C. L. Hooper (1978). Metabolism of Monoterpenes: Acetylation of (--)-Menthol by a Soluble Enzyme Preparation from Peppermint (Mentha piperita) Leaves. Plant Physiology. 61: 737-742.

Croteau, R. and J. N. Winters (1982). Demonstration of the Intercellular Compartmentation of l-Menthone Metabolism in Peppermint (Mentha piperita) Leaves. Plant Physiology. 69: 975-977.

Croteau, R. B. and M. R. Wildung (2005). "Genetic engineering of peppermint for improved essential oil composition and yield." Transgenic Research 14(4): 14.

Denny, E. F. K. (1991). "Field Distillation for Herbaceous Oils." Denny, McKenzie Associates.

E. Reverchon, A. A. F. S. (1994). Isolation of peppermint oil using supercritical CO2 extraction. Flavour and Fragrance Journal. 9: 19-23.

Eikani, M. H. and S. Rowshanzamir (2004). Modeling and simulation of superheated water extraction of essential oils, Prague, Czech Republic, Czech Society of Chemical Engineering, Prague 1, 116 68, Czech Republic.

Gershenzon, J., M. E. McConkey, et al. (2000). Regulation of Monoterpene Accumulation in Leaves of Peppermint. 122: 205-214.

Guenther, E. (1949). "The Essential Oils." Flavour and fragrance journal IV.

Hackleman, Velasco. (2007). "Thacker Mint Distillation visit. Bow Island - Canada."

Hay, -. R. K. M. and P. G. Waterman (1993). "Valatile oil crops: their biology, biochemistry and production."

Hughes (1952). "Improvements in The Field Distillation of Peppermint Oil." Agricultural Experiment Station, Oregon State College: 60.

Buckingham, S. T. (2004). "Dictionary of Natural Products ": Chapman and Hall, London, UK.

Jean, H. L. (1994). "Higher plant terpenoids: A phytocentric overview of their ecological roles." Journal of Chemical Ecology 20(6): 1223-1280.

Kwon, J.-H., J. M. R. Belanger, et al. (2003). "Application of the microwave-assisted process to the fast extraction of ginseng saponins." Food Research International 36(5): 491-498.

Loomis, W. D. (1967). "Biosynthesis and metabolism of monoterpenes " Academic Press In Pridham, J.B. (ed.): 22.

Lucchesi, M. E., F. Chemat, et al. (2004). "Solvent-free microwave extraction of essential oil from aromatic herbs: comparison with conventional hydro-distillation." Journal of Chromatography A 1043(2): 323-327.

Lucchesi, M. E., J. Smadja, et al. (2007). "Solvent free microwave extraction of Elletaria cardamomum L.: A multivariate study of a new technique for the extraction of essential oil." Journal of Food Engineering 79(3): 1079-1086.

Maffei, M., F. Chialva, et al. (1989). "Glandular Trichomes and Essential Oils in Developing Peppermint Leaves. I. Variation of Peltate Trichome Number and Terpene Distribution Within Leaves " New phytologist 111(4): 10.

Martinkus, C. and R. Croteau (1981). Metabolism of Monoterpenes : Evidence For Compartmentation Of L-Menthone Metabolism In Peppermint (Mentha Piperita) Leaves. 68: 99-106.

Michael Spiro, S. S. C. (1995). Kinetics of isothermal and microwave extraction of essential oil constituents of peppermint leaves into several solvent systems. Flavour and fragrance journal 10: 259-272.

Mohammad H. Eikani a, Fereshteh Golmohammad a, et al. (2003). "Subcritical water extraction of essential oils from coriander seeds (Coriandrum sativum L.)." Institute of Chemical Technologies, Iranian Research Organization for Science and Technology.

O. GASIC, N. M.-D., D. ADAMOVIC, K. BOROJEVIC (1987). "Variability of content and composition of essential oil in different genotypes

of peppermint." Biochemical systematics and ecology, 1987 15(3): 6.

Pare; J. R. Jocelyn , S. M., Lapointe; Jacques (1991). "Microwave-assisted natural products extraction ".

Ramanadhan, B. (2005). "MICROWAVE EXTRACTION OF ESSENTIAL OILS (FROM BLACK PEPPER AND CORIANDER) AT 2.46 GHz." 169.

Sangwan, N. S., A. H. A. Farooqi, et al. (2001). "Regulation of essential oil production in plants." Plant Growth Regulation 34(1): 3-21.

Sau Soon Chen, M. S. (1995). Kinetics of microwave extraction of rosemary leaves in hexane, ethanol and a hexane + ethanol mixture. Flavour and Fragrance Journal. 10: 101-112.

Smith, P. M. (1976). "The Chemotaxonomy of Plants." 20.

Turner, G. W., J. Gershenzon, et al. (2000). "Development of Peltate Glandular Trichomes of Peppermint." American Society of Plant Physiologists 124(2): 15.

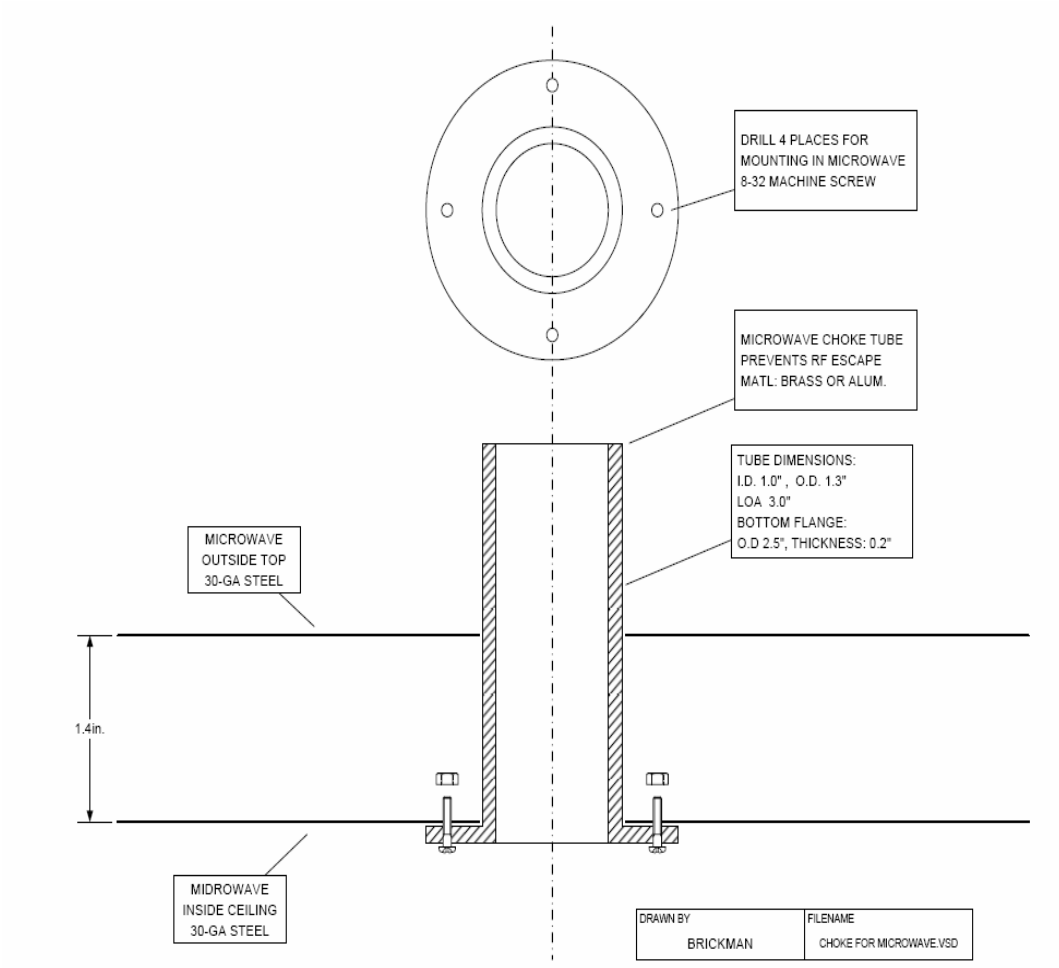
Walter C. McCarthy, K. V. B. C. W. R. L. F. (1963). Some low boiling constituents of peppermint oil. 52: 1005.

Wang, Z., L. Ding, et al. (2006). "Improved solvent-free microwave extraction of essential oil from dried Cuminum cyminum L. and Zanthoxylum bungeanum Maxim." Journal of Chromatography A 1102(1-2): 11-17.

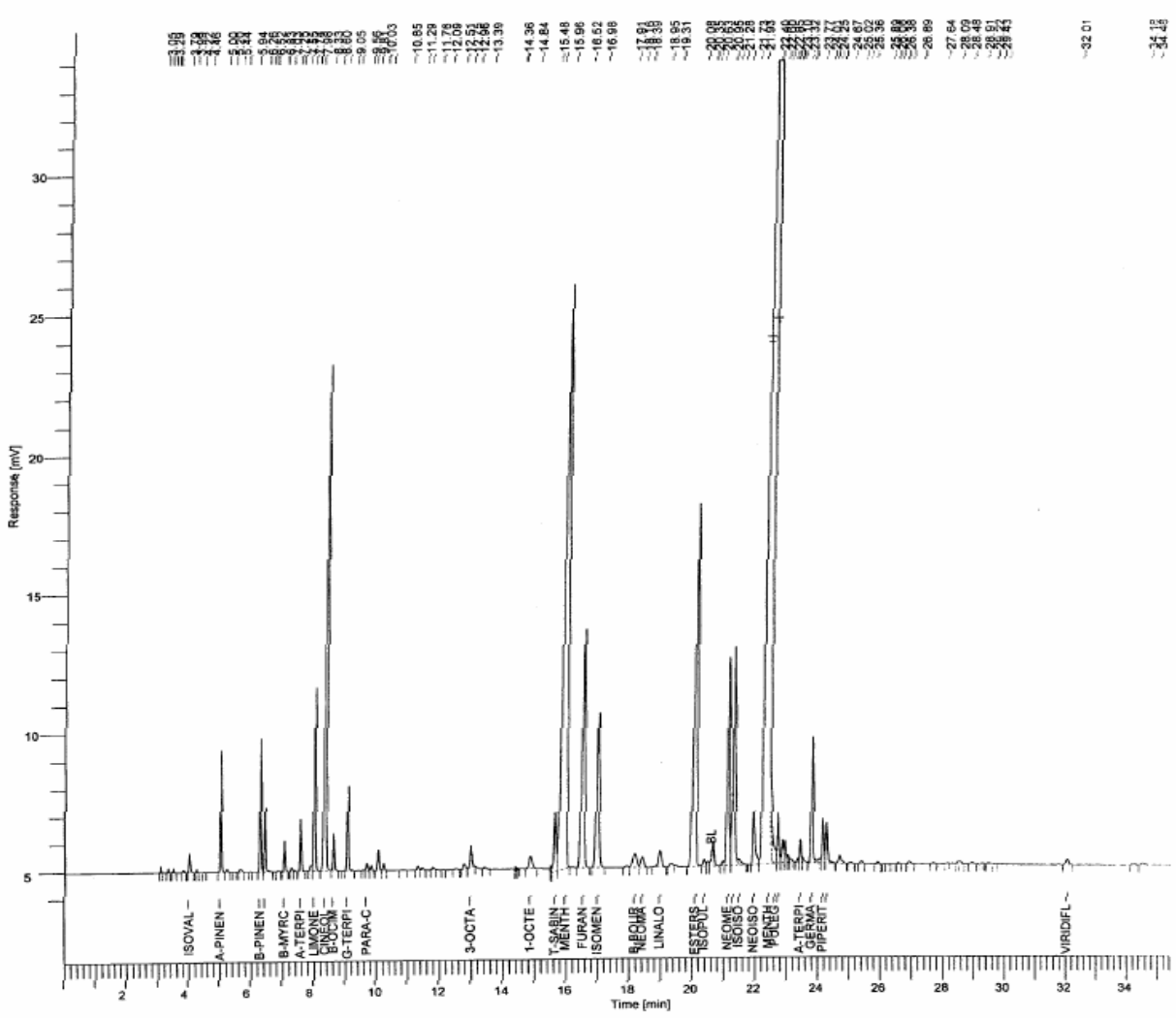
Weiss, E. A. (1997). "Essential Oil crops."

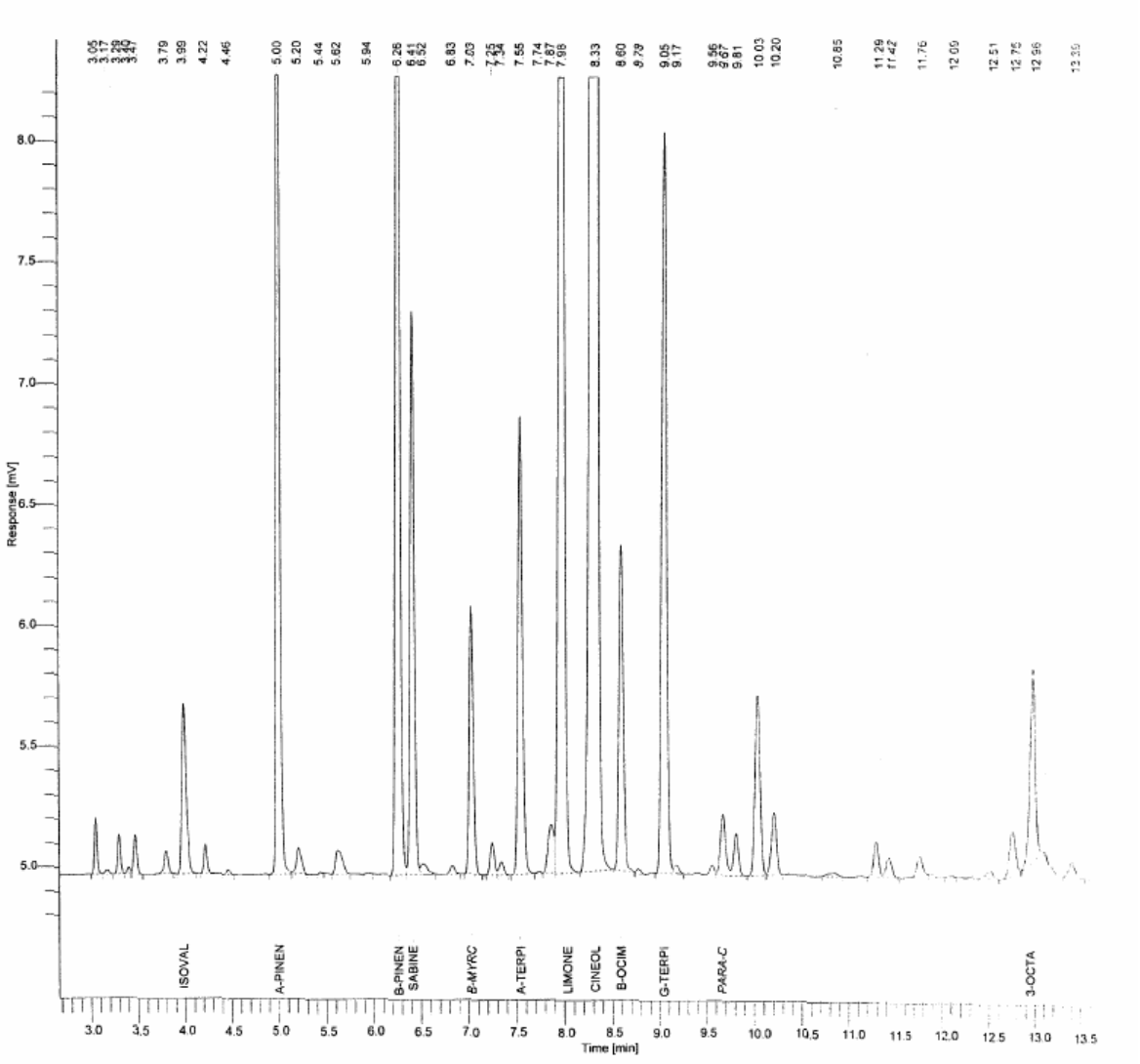
APPENDICES

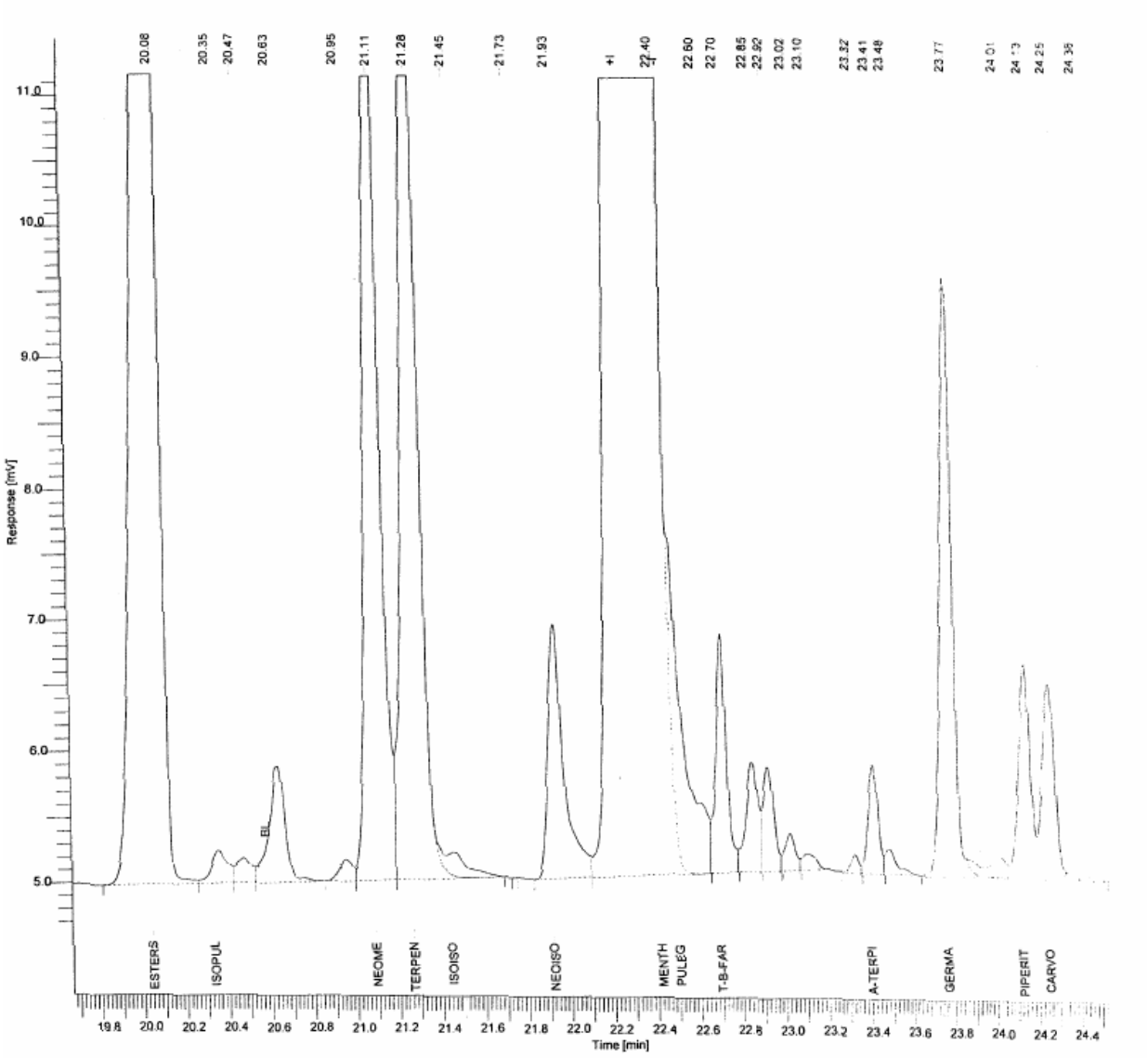
APPENDIX A. Microwave Choke Design



APPENDIX B. Typical Chromatogram Of Willamette Valley Peppermint Oil




Response [mV]
8.0
7.5
7.0
6.5
6.0
5.5
5.0
ISOVAL
A-PINEN
B-PINEN
SABINE
B-MYRC
A-TERPI
LIMONE
CINEOL
B-OCIM
G-TERPI
PARA-C
3-OCTA
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
10.0
10.5
11.0
11.5
12.0
12.5
13.0
13.5
Time [min]


20.08
20.35
20.47
20.63
20.85
21.11
21.28
21.45
21.73
21.93
22.40
22.60
22.70
22.85
22.92
23.02
23.10
23.32
23.41
23.48
23.77
24.01
24.13
24.25
24.38
Response [mV]
11.0
10.0
9.0
8.0
7.0
6.0
5.0
ESTERS
ISOPUL
NEOME
TERPEN
ISOISO
NEOISO
MENTH
PULEG
T-B-FAR
A-TERPI
GERMA
PIPERIT
CARVO
19.8
20.0
20.2
20.4
20.6
20.8
21.0
21.2
21.4
21.6
21.8
22.0
22.2
22.4
22.6
22.8
23.0
23.2
23.4
23.6
23.8
24.0
24.2
24.4
Time [min]

APPENDIX C. Total Organic Carbon Method

ORGANIC CARBON, TOTAL, Mid Range, continued

REQUIRED REAGENTS

Total Organic Carbon Direct Method Mid Range

Test 'N Tube Reagent Set ..... 50 vials 28159-45

Includes:

Description	Quantity Required Per Test	Unit	Cat. No.
Acid Digestion Solution Vials, Mid Range TOC	1	50/pkg	*
Buffer Solution, Sulfate	0.4 mL	25 mL	452-33
Funnel, micro	1	each	25843-35
Indicator Ampules, Mid/High Range TOC	1	50/pkg	*
TOC Persulfate Powder Pillows	1	50/pkg	*
Water, organic-free**	1.0 mL	500 mL	26415-49

REQUIRED APPARATUS

DRB 200 Reactor, 110 V, 15 x 16 mm tubes			LTV082.53.40001
DRB 200 Reactor, 220 V, 15 x 16 mm tubes			LTV082.52.40001
Cylinder, graduated, 10-mL	1	each	508-38
Flask, Erlenmeyer, 50-mL	1	each	505-41
Magnetic Stirrer, 115 V, 4" x 4"	1	each	28812-00
Test Tube Rack	1–3	each	18641-00
Pipet, TenSette®, 0.1 to 1.0 mL	1	each	19700-01
Pipet Tips, for 19700-01 TenSette® Pipet	2	50/pkg	21856-96
Stir Bar, Magnetic	1	each	45315-00
Wipes, Disposable, Kimwipes	1	280/pkg	20970-00

OPTIONAL REAGENTS

Description	Per Test	Unit	Cat. No.
TOC Standard Solution (KHP Standard, 1000 mg/L C)		5/pkg	27915-05
Potassium Acid Phthalate		500 g	315-34
Sulfuric Acid Reagent Solution, 5.25 N		100 mL MDB	2449-32

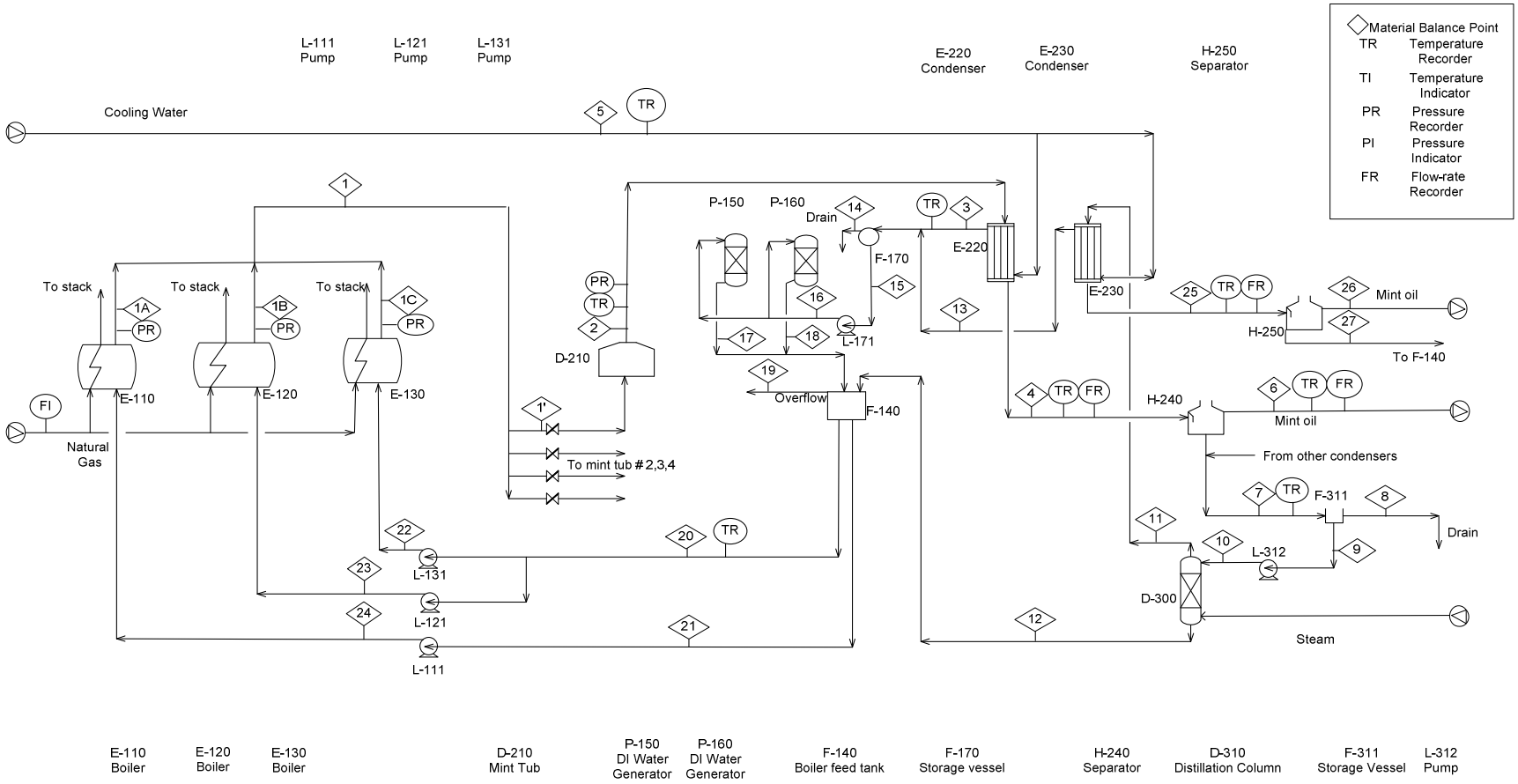
OPTIONAL APPARATUS

Analytical Balance		each	28014-01
DRB 200 Reactor, 110 V, 21 x 16 mm and 4 x 20 mm			LTV082.53.42001
DRB 200 Reactor, 220 V, 21 x 16 mm and 4 x 20 mm			LTV082.52.42001
DRB 200 Reactor, 110 V, 9 x 16 mm and 2 x 20 mm			LTV082.53.30001
DRB 200 Reactor, 220 V, 9 x 16 mm and 2 x 20 mm			LTV082.52.30001
Flask, volumetric, 100-mL		each	14574-42
Pipet, Class A, 10.00-mL		each	14515-38
Pipet, Class A, 15.00-mL		each	14515-39
Pipet Tips, for 19700-01 TenSette Pipet		1000/pkg	21856-28

* These items are not sold separately.

** This item must be purchased separately.

APPENDIX D. Setniker Facility Flow Sheet



APPENDIX E. Mint Tub Heat Loss Calculations

Parameters			
Dimensions	**Ft**		**m**
Width	10		3.048
Length	25		7.62
Hieght	8		2.4384
wall thickness	0.25"		0.006
NG Cost		0.5	$/ therm
Operating Time		120	min
1 Therm =		105506	KJ
Running Tubs		12	
	°C		**K**
Internal Temp	105		378.15
External Temp	29.5		302.65

Heat Loss No Insulation			Thermal Conductivity of Stainless Steel	17	W/mK
			Convective Heat Transfer Coefficient for Air	100	W/m^2 .K
Q1	54.20	kW	**Cost ($) / running tub**	**24.50**	
Q2	169.38	kW	**Therms**	49.01	
Q3	135.50	kW	**Total Cost ($)**	**294.05**	
Total	718.16	kW			
Heat Loss With Insulation Foam			Thermal Conductivity of Foam	0.03	W/mK
			Thickness	0.02	m
				0.79	in
Q1	0.83	kW	**Cost ($) / running tub**	**0.37**	
Q2	2.07	kW	**Therms**	0.75	
Q3	2.59	kW	**Total Cost ($)**	**4.50**	
Total	10.98	kW			

Heat Loss With Rain No Insulation			Convective Heat Transfer Coefficient for H2O	500.00	W/m^2 .K
			Rain Temperature (10 C)	283.15	K
Q1	300.08	kW	**Cost ($) / running tub**	**103.67**	
Q2	937.74	kW	**Therms**	207.34	
Q3	750.19	kW	**Total Cost ($)**	**1244.04**	
Total	3038.28	kW			

Heat Loss With Rain With Foam Insulation			Thermal Conductivity of Foam	0.03	W/mK
			Thickness	0.02	m
				0.79	in
Q1	0.84	kW			
Q2	2.10	kW			
Q3	2.62	kW			
Total	11.11	kW	**Cost ($) / running tub**	**0.38**	
			Therms	0.76	
			Total Cost ($)	**4.55**	

APPENDIX F. Pipes Heat Loss Calculations

Heat Loss in Stream Pipes					
Thermal Conductivitys					
Air	0.0313	W/m2k			
Steel	17	W/m2k			
Foam	0.03	W/m2k			
Tubs running	12				
Diameter	**in**		**m**	**Radious [m]**	
Outside	2		0.0508	0.03	
Inside	1.5		0.0381	0.02	
Wall Thickness	0.25		0.00635		
Foam Thickness	0.5		0.0127		
Outside with foam	3		0.0762	0.04	
Length	**ft**		**m**		
Total	60		18.288		
Temperatures	**C**		**K**		
Air	27		301.15		
Steam in	155		429.15		
Steam out	130		429.15		
Wall pipe	153		429.15		
D Tmean	140.5				
Steam flowrate [kg/sec]	0.0809568		**Convetion Coeffient W/m2.K**		
Heat Capacity [J/kg.K]	4178		**h1**	27.49	
			hair	100.00	
Heat Loss					
Q no insulation kW	6.34	KW			
Cost $	**0.189**		**NG Cost**	0.44	$/kJ
Therms	3.786		**Operating Time**	105	min
Total Cost ($)	**2.271476354**				
Q with insulation kW	0.93	W			
Cost $	**0.028**				
Therms	0.555				
Total Cost ($)	**0.332768762**				

APPENDIX G. Experimental Data and Calculations

Experimental Data and Calculations at 1120 Watts

EXPERIMENTAL DATA	Units	1.5 min			1.75 min			2 min					2.25 min		
Extraction Time	[min]														
Breakthrough Time	[min]	1.20	1.24	1.27	1.10	1.09	1.27	1.14	1.25	1.10	1.30	1.10	1.23	1.25	1.20
Mass Empty Pot	[g]	280.4	251.3	249.2	280.45	280.4	280.4	249.2	280.4	280.4	249.2	280.4	280.4	280.5	280.6
Mass Grass + Pot Before	[g]	382	353.3	352.7	380.4	380.4	380.7	349.2	378.6	380.4	354.4	380.4	370.5	380.5	380.6
Mass Grass + Pot After	[g]	377.1	347.6	347.8	373.5	373.4	372.9	336.4	367.5	371	344.3	370	358.8	367.7	367.6
Mass Grass Before	[g]	101.6	102	103.5	99.95	100	100.3	100	98.2	100	105.2	100	90.1	100	100
Mass Grass After	[g]	96.7	96.3	98.6	93.05	93	92.5	87.2	87.1	90.6	95.1	89.6	78.4	87.2	87
Mass of Beaker	[g]	8.2	8.2	8.2	29.7	29.7	8.2	69	29.8	29.65	8.2	29.7	29.7	29.7	29.7
Mass of Beaker + Water	[g]	10.8	11.4	10.6	33.8	34	13.2	77.2	37.8	36.7	15	37.1	38.8	39.9	39.7
Mass of Water extracted	[g]	2.6	3.2	2.4	4.1	4.3	5	8.2	8	7.05	6.8	7.4	9.1	10.2	10
Mass of Vial	[g]	2.334	2.2879	2.3553	2.53	2.4973	2.3133	2.53	2.5504	2.4584	2.3499	2.4618	2.4642	2.5338	2.531
Mass of Oil + Vial	[g]	2.471	2.5094	2.5402	2.7885	2.7783	2.6881	3.1122	2.8863	2.8601	2.785	2.8908	2.8198	2.9988	2.9038
Mass of Oil extracted	[g]	0.137	0.2215	0.1849	0.2585	0.281	0.3748	0.5822	0.3359	0.4017	0.4351	0.429	0.3556	0.465	0.3728
To	[°C]	20	18	12.8	26.6	24.4	18.6	15.8	20	27.1	8.4	25.1	20		24.4
Tf	[°C]	91	98.3	94.4	99.9	97.5	97.5	96.2	91.3	100.7	100.5	98.2	91.3	103.4	97.5
Tcondensate	[°C]	27.7	30.5	28	27.4	90.6	32.2	27.2	27.7	26.9	26.2	28.5	27.7	26.1	30.6
Moisture Cont. after ext	%	19.3%	19.0%	21.5%	19.5%	19.5%	18.4%	16.5%	17.6%	18.5%	18.7%	16.7%	17.1%	16.7%	16.9%
MASS BALANCE															
oil extracted	%	13%	22%	18%	26%	28%	37%	58%	34%	40%	41%	43%	39%	47%	37%
average % oil extracted	%	18%			27%			40%					41%		
variance	%	23%			6%			10%					12%		
oil non extracted	%	87%	78%	82%	74%	72%	63%	42%	66%	60%	59%	57%	61%	54%	63%
average % oil non ext	%	82%			70%			59%					59%		
H2O extracted	%	9%	11%	8%	14%	14%	17%	28%	27%	24%	22%	25%	34%	34%	34%
average % H2O extracted	%	9%			15%			24%					34%		
variance		15%			10%			10%					1%		
average MASS BALANCE ON LIQUID															
% oil extracted from liquid	%	0.59%			0.91%			1.33%					1.38%		
%H2O extracted from liquid	%	8.8%			14.49%			23.59%					32.79%		
%liquid left	%	67.0%			64.18%			60.00%					56.72%		
total liquid accounted for	%	76.38%			79.57%			84.92%					90.89%		
total % liquid anccounted for	%	23.62%			20.43%			15.08%					9.11%		
total	%	100.0%			100%			100%					100%		
ENERGY BALANCE															
Energy used	[KJ]	100.80	100.80	100.80	117.60	117.60	117.60	134.40	134.40	134.40	134.40	134.40	151.20	151.20	151.20
Energy needed	[KJ]	67.16	74.16	69.62	70.40	70.35	76.45	81.04	73.95	73.69	85.17	77.46	70.50	95.70	78.17
Energy needed average	[KJ]	70.31			72.40			78.26					81.46		
variance	[KJ]	5.1%			4.8%			6.2%					15.9%		
efficiency	%	67%	74%	69%	60%	60%	65%	60%	55%	55%	63%	58%	47%	63%	52%
$$/run	$	0.0012	0.0012	0.0012	0.0014	0.0014	0.0014	0.0016	0.0016	0.0016	0.0016	0.0016	0.0018	0.0018	0.0018
$$/gr of oil extracted	$/g	0.0090	0.0056	0.0067	0.0056	0.0051	0.0038	0.0028	0.0049	0.0041	0.0038	0.0038	0.0052	0.0040	0.0050
$$/lbof oil extracted		4.08	2.52	3.02	2.52	2.32	1.74	1.28	2.22	1.85	1.71	1.74	2.36	1.80	2.25
average	$$/lb of oil ext	3.21			2.19			1.76					2.14		
variance	%	25%			19%			19%					14%		

Experimental Data and Calculations at 1120 Watts (Continuation)

EXPERIMENTAL DATA	Units	2.5 min								2.75 min					3 min			3.5 min	
Extraction Time	[min]																		
Breakthrough Time	[min]	1.13	1.09	1.25	1.27	1.27	1.25	1.3	1.25	1.1	1.2	1.1	1.27	1.2	1.14	1.14	1.13	1.28	1.24
Mass Empty Pot	[g]	249.4	249.2	251.3	249.2	249.2	280.4	249.4	251.3	280.4	280.5	251.4	280.4	251.3	249.2	251.3	249.2	249.2	249.2
Mass Grass + Pot Before	[g]	349.4	371.9	351.8	352.2	350.3	385.7	349.7	351	373.7	380.5	356.2	384.6	350.6	349.2	351.7	380.2	409.8	371.3
Mass Grass + Pot After	[g]	332	354.5	335	335.7	334.2	372.6	332.4	339.5	354.5	361.2	339.2	367.3	331.5	326.5	329.3	350	384.5	347.1
Mass Grass Before	[g]	100	122.7	100.5	103	101.1	105.3	100.3	99.7	93.3	100	104.8	104.2	99.3	100	100.4	131	160.6	122.1
Mass Grass After	[g]	82.6	105.3	83.7	86.5	85	92.2	83	88.2	74.1	80.7	87.8	86.9	80.2	77.3	78	100.8	135.3	97.9
Mass of Beaker	[g]	69.1	29.7	11.1	8.2	8.3	29.7	8.2	8.3	29.7	29.7	52	11.1	11.1	29.6	11.1	69	69.1	29.7
Mass of Beaker + Water	[g]	82.7	43.7	24.9	21.6	21.6	40.8	21.9	21.8	43.5	46.6	64.7	24.9	27.5	47.9	29.6	95.7	90.4	49.9
Mass of Water extracted	[g]	13.6	14	13.8	13.4	13.3	11.1	13.7	13.5	13.8	16.9	12.7	13.8	16.4	18.3	18.5	26.7	21.3	20.2
Mass of Vial	[g]	2.2734	2.5396	3.3923	2.308	3.4524	2.4574	2.3506	2.3024	2.5359	2.4917	2.5138	3.3844	3.3519	2.5144	3.3403	2.573	2.5133	2.563
Mass of Oil + Vial	[g]	2.972	3.2254	4.1085	2.976	4.162	2.8711	2.815	3.0255	2.95	3.0453	3.0234	4.0985	3.9327	3.1279	3.8322	3.338	3.9485	3.3989
Mass of Oil extracted	[g]	0.6986	0.6858	0.7162	0.668	0.7096	0.4137	0.4644	0.7231	0.4141	0.5536	0.5096	0.7141	0.5808	0.6135	0.4919	0.765	1.4352	0.8359
To	[°C]	17.2	17.2	16.9	12.5	10	10	20	15	17.2	29.8	3	10	10	20	21	14	16	10
Tf	[°C]	97.1	97.1	99.2	101.6	100.6	98	99.7	99.6	97.1	101.6	98	100.4	99.5	99	97	97.7	97.6	99
Tcondensate	[°C]	22.1	22.1	23.1	23.4	22.1	30	30		22.1	28.7	27	20.4	20.4			31.1	30	26
Moisture Cont. after ext	%	9.2%	15.1%	8.9%	11.4%	10.6%	12.7%		8.7%	14.2%	7.7%	11.5%	10.9%	5.4%	5.6%	10.3%	8.2%	10.8%	8.2%
MASS BALANCE																			
oil extracted	%	70%	56%	71%	65%	70%	39%	46%	73%	44%	55%	49%	69%	58%	61%	49%	58%	89%	68%
average % oil extracted	%	64%								54%					56%			68%	
variance	%	15%								9%					11%				
oil non extracted	%	30%	44%	29%	35%	30%	61%	54%	27%	56%	45%	51%	31%	42%	39%	51%	42%	11%	32%
average % oil non ext	%	43%								45%					44%				
H2O extracted	%	46%	38%	46%	44%	44%	35%	46%	45%	50%	57%	41%	44%	55%	61%	62%	68%	45%	56%
average % H2O extracted	%	44%								51%					64%			56%	
variance		6%								18%					6%			14%	
average MASS BALANCE ON LIQUID																			
% oil extracted from liquid	%	2.16%								1.82%					1.89%			2.30%	
%H2O extracted from liquid	%	42.72%								49.28%					61.80%			53.71%	
%liquid left	%	42.83%								37.27%					26.97%			31.94%	
total liquid accounted for	%	87.71%								88.36%					90.66%			87.95%	
total % liquid anccounted for	%	12.29%								11.64%					9.34%			12.05%	
total	%	100%								100%					100%			100%	
ENERGY BALANCE																			
Energy used	[KJ]	168.00	168.00	168.00	168.00	168.00	168.00	168.00	168.00	184.80	184.80	184.80	184.80	184.80	201.60	201.60	201.60	235.20	235.20
Energy needed	[KJ]	96.20	99.67	98.54	99.12	99.91	98.69	113.64	98.50	84.78	96.56	103.95	104.01	98.19	103.20	93.62	127.59	141.24	122.61
Energy needed average	[KJ]	103.32								97.50					98.41			131.92	
variance	[KJ]	9.5%								8.1%					6.9%			10.0%	
efficiency	%	57%	59%	59%	59%	59%	59%	68%	59%	46%	52%	56%	56%	53%	51%	46%	63%	60%	52%
$$/run	$	0.0021	0.0021	0.0021	0.0021	0.0021	0.0021	0.0021	0.0021	0.0023	0.0023	0.0023	0.0023	0.0023	0.0025	0.0025	0.0025	0.0029	0.0029
$$/gr of oil extracted	$/g	0.0029	0.0030	0.0029	0.0031	0.0029	0.0050	0.0044	0.0028	0.0055	0.0041	0.0044	0.0032	0.0039	0.0040	0.0050	0.0032	0.0020	0.0034
$$/lbof oil extracted		1.33	1.36	1.30	1.39	1.31	2.25	2.01	1.29	2.47	1.85	2.01	1.43	1.76	1.82	2.27	1.46	0.91	1.56
average $$/lb of oil ext		1.64								1.91					2.05			1.23	
variance	%	29%								20%					16%			37%	

Experimental Data and Calculations at 697 Watts

EXPERIMENTAL DATA	Units	2min	2.5 min			3 min			3.5min			
Extraction Time	[min]	2.00	2.00	1.70	1.90	2.10	1.95	1.98	2	1.7	2.02	2
Breakthrough Time	[min]	280.4	218.9	251.3	280.4	280.45	249.2	249.2	280.4	280.4	251.3	251.3
Mass Empty Pot	[g]	380.4	322.5	352.7	381.2	380.3	348.8	347	380.4	381.5	347.7	350
Mass Grass + Pot Before	[g]	378.1	315.5	345.5	373.9	370	338.4	336.1	366.9	366.2	332.6	331.8
Mass Grass + Pot After	[g]	100	103.6	101.4	100.8	99.85	99.6	97.8	100	101.1	96.4	98.7
Mass Grass Before	[g]	97.7	96.6	94.2	93.5	89.55	89.2	86.9	86.5	85.8	81.3	80.5
Mass Grass After	[g]	8.2	11	8.2	8.2	29.7	8.2	8.2	29.7	8.3	11.1	8.3
Mass of Beaker	[g]	9.1	15.9	13	12.9	36.4	14.8	17.1	40.3	20.7	23	23.6
Mass of Beaker + Water	[g]	0.9	4.9	4.8	4.7	6.7	6.6	8.9	10.6	12.4	11.9	15.3
Mass of Water extracted	[g]	3.3712	2.2084	2.2976	2.3352	2.5266	3.374	3.3608	2.5099	3.4822	3.3816	3.3508
Mass of Vial	[g]	3.4717	2.6059	2.6487	2.6375	2.966	3.8279	3.8345	3.0857	3.9156	4.0498	3.9322
Mass of Oil + Vial	[g]	0.1005	0.3975	0.3511	0.3023	0.4394	0.4539	0.4737	0.5758	0.4334	0.6682	0.5814
Mass of Oil extracted	[g]	19.1	20	16.8	22	24.3	12.2	20.4	21	12.2	19	12.7
To	[°C]	97.4	97	94	94.7	99.3	99.7	100.8		102.6	99.4	98.8
Tf	[°C]	33	33	25.2		30.4	20.3	22		23.9	20.7	
Tcondensate	[°C]	22.0%	21.3%	22.4%	19.6%	22.4%	19.1%	17.8%	16.2%	12.0%	12.0%	11.1%
Moisture Cont. after ext	%											
MASS BALANCE												
oil extracted	%	10%	38%	35%	30%	44%	46%	48%	58%	43%	69%	59%
average % oil extracted	%	28%	34%			46%			53%			
variance	%		12%			5%			17%			
oil non extracted	%	90%	62%	65%	70%	56%	54%	52%	42%	57%	31%	41%
average % oil non ext	%	90%	66%			54%			43%			
H2O extracted	%	3%	16%	16%	16%	23%	22%	31%	36%	41%	41%	52%
average % H2O extracted	%	12%	16%			25%			43%			
variance			1%			19%			19%			
average MASS BALANCE ON LIQUID												
% oil extracted from liquid	%	1%	1%			2%			2%			
%H2O extracted from liquid	%	11%	15%			24%			42%			
%liquid left	%	74%	71%			66%			43%			
total liquid accounted for	%	86%	87%			92%			86%			
total % liquid anccounted for	%	14%	13%			8%			14%			
total	%	100%	100%			100%			100%			
ENERGY BALANCE												
Energy used	[KJ]	83.65	104.57	104.57	104.57	125.48	125.48	125.48	146.39	146.39	146.39	146.39
Energy needed	[KJ]	65.53	66.84	65.58	70.31	66.76	78.54	76.35	26.02	99.02	88.14	95.41
Energy needed average	[KJ]	65.99	67.58			73.88			77.15			
variance	[KJ]	1.1%	3.6%			8.5%			44.6%			
efficiency	%	78%	64%	63%	67%	53%	63%	61%	18%	68%	60%	65%
$$/run	$	0.0010	0.0013	0.0013	0.0013	0.0015	0.0015	0.0015	0.0018	0.0018	0.0018	0.0018
$$/gr of oil extracted	$/g	0.0102	0.0032	0.0036	0.0042	0.0035	0.0034	0.0032	0.0031	0.0041	0.0027	0.0031
$$/lbof oil extracted	$/lb	4.61	1.46	1.65	1.92	1.58	1.53	1.47	1.41	1.87	1.21	1.40
average $$/lb of oil ext		4.61	1.68			1.53			1.56			
variance	%	-	14%			4%			27%			

Experimental Data and Calculations at 697 Watts (Continuation)

EXPERIMENTAL DATA	Units			4 min				4.5 min		5.5 min
Extraction Time	[min]									
Breakthrough Time	[min]	1.8	2	2	2.1	1.7	2	2	1.8	2.05
Mass Empty Pot	[g]	251.3	249.2	249.2	251.3	280.4	251.3	251.3	280.4	280.5
Mass Grass + Pot Before	[g]	351.7	351	351.9	350.6	381	350.3	352	385.1	381.5
Mass Grass + Pot After	[g]	335.3	334.2	333.8	331.8	361.5	335.5	329.8	363.6	352.2
Mass Grass Before	[g]	100.4	101.8	102.7	99.3	100.6	99	100.7	104.7	101
Mass Grass After	[g]	84	85	84.6	80.5	81.1	84.2	78.5	83.2	71.7
Mass of Beaker	[g]	51.9	11	8.3	11	11.1	8.2	8.2	8.2	69.1
Mass of Beaker + Water	[g]	64.9	24.9	23.3	27.3	28.1	22.2	27.3	25.5	94.4
Mass of Water extracted	[g]	13	13.9	15	16.3	17	14	19.1	17.3	25.3
Mass of Vial	[g]	2.5159	2.3483	3.4856	3.42	3.3627	3.3954	2.3275	2.3275	2.5062
Mass of Oil + Vial	[g]	2.8822	2.8332	3.9006	4.0763	3.7065	4.1036	2.8828	2.8828	2.8086
Mass of Oil extracted	[g]	0.3663	0.4849	0.415	0.6563	0.3438	0.7082	0.5553	0.5553	0.3024
To	[°C]	5	10	10	12.2	20	12.2	20	2	12
Tf	[°C]	97	98	107.7	100.8	100.9	100.8	99.3	96	97
Tcondensate	[°C]	28.6	24	24.5	21.3	23.7	21.3			30
Moisture Cont. after ext	%	15.0%	10.8%	9.7%	6.2%	8.8%	11.6%	12.0%	9.7%	8.5%
MASS BALANCE										
oil extracted	%	36%	48%	40%	66%	34%	72%	55%	53%	30%
average % oil extracted	%	40%						54%		30%
variance	%	15%						3%		
oil non extracted	%	64%	52%	60%	34%	66%	28%	45%	47%	70%
average % oil non ext	%	51%						46%		70%
H2O extracted	%	43%	46%	49%	55%	57%	48%	64%	56%	84%
average % H2O extracted	%	49%						60%		84%
variance		12%						10%		
average MASS BALANCE ON LIQUID										
% oil extracted from liquid	%	1%						2%		1%
%H2O extracted from liquid	%	47%						58%		81%
%liquid left	%	35%						36%		29%
total liquid accounted for	%	83%						96%		111%
total % liquid anccounted for	%	17%						4%		-11%
total	%	100%						100%		100%
ENERGY BALANCE										
Energy used	[KJ]	167.31	167.31	167.31	167.31	167.31	167.31	188.22	188.22	230.04
Energy needed	[KJ]	91.94	98.88	107.41	106.34	100.35	95.07	92.56	109.91	105.33
Energy needed average	[KJ]	100.00						101.23		105.33
variance	[KJ]	6.1%						12.1%		-
efficiency	%	55%	59%	64%	64%	60%	57%	49%	58%	46%
$$/run	$	0.0020	0.0020	0.0020	0.0020	0.0020	0.0020	0.0023	0.0023	0.0028
$$/gr of oil extracted	$/g	0.0056	0.0042	0.0049	0.0031	0.0059	0.0029	0.0041	0.0041	0.0093
$$/lbof oil extracted	$/lb	2.53	1.91	2.23	1.41	2.70	1.31	1.879	1.879	4.217
average	$$/lb of oil ext	2.34						1.88		4.22
variance	%	35%						0%		-

Experimental Data and Calculations at 518 Watts

EXPERIMENTAL DATA	Units									
Extraction Time	[min]	3 min	3.25 min		4 min		4.5 min			
Breakthrough Time	[min]	3	2.70	3.00	2.70	3.00	3.10	3.20	2.85	2.50
Mass Empty Pot	[g]	249.2	280.4	251.3	280.5	251.3	251.3	249.3	280.4	249.2
Mass Grass + Pot Before	[g]	350.6	382.4	344.2	380.5	352.4	350.6	349.6	378.3	347.7
Mass Grass + Pot After	[g]	346.5	375.8	338.7	372	341.9	331.8	336.1	365.2	334.5
Mass Grass Before	[g]	101.4	102	92.9	100	101.1	99.3	100.3	97.9	98.5
Mass Grass After	[g]	97.3	95.4	87.4	91.5	90.6	80.5	86.8	84.8	85.3
Mass of Beaker	[g]	8.2	11	8.4	29.7	11	11	8.3	8.2	11
Mass of Beaker + Water	[g]	9.9	14.9	11.4	36.1	18.3	27.3	18.5	17.9	20.7
Mass of Water extracted	[g]	1.7	3.9	3	6.4	7.3	16.3	10.2	9.7	9.7
Mass of Vial	[g]	3.3785	2.5127	3.3679	2.4549	2.2956	3.4284	3.3227	3.3845	3.3528
Mass of Oil + Vial	[g]	3.5688	2.8405	3.6731	2.8987	2.7107	4.1963	3.7571	3.9435	3.9231
Mass of Oil extracted	[g]	0.1903	0.3278	0.3052	0.4438	0.4151	0.7679	0.4344	0.559	0.5703
To	[°C]	20	20	20	23.2	20	20	21.4	22.4	20
Tf	[°C]	93	93	97.7	100.1	96	96	99.4	100.4	99.3
Tcondensate	[°C]	23.9	23.9	24	28.8	28	28	23.3	24.6	28
Moisture Cont. after ext	%	21.4%	19.2%	16.8%	20.8%	16.8%	15.9%	13.4%	12.0%	13.0%
MASS BALANCE										
oil extracted	%	19%	32%	33%	44%	41%	77%	43%	57%	58%
average % oil extracted	%	19%	32%		43%		53%			
variance	%		2%		5%		16%			
oil non extracted	%	81%	68%	67%	56%	59%	23%	57%	43%	42%
average % oil non ext	%	81%	68%		57%		41%			
H2O extracted	%	6%	13%	11%	21%	24%	55%	34%	33%	33%
average % H2O extracted	%	6%	12%		23%		34%			
variance			12%		9%		2%			
average MASS BALANCE ON LIQUID										
% oil extracted from liquid	%	1%	1%		1%		2%			
%H2O extracted from liquid	%	5%	11%		22%		32%			
%liquid left	%	72%	60%		63%		46%			
total liquid accounted for	%	78%	73%		87%		80%			
total % liquid anccounted for	%	22%	27%		13%		20%			
total	%	100%	100%		100%		100%			
ENERGY BALANCE										
Energy used	[KJ]	93.28	101.05	101.05	124.37	124.37	139.91	139.91	139.91	139.91
Energy needed	[KJ]	63.81	71.83	72.12	70.41	77.93	81.77	86.34	89.04	86.52
Energy needed average	[KJ]	63.81	71.97		74.17		85.92			
variance	[KJ]	-	0.3%		7.2%		3.5%			
efficiency	%	68%	71%	71%	57%	63%	58%	62%	64%	62%
$$/run	$	0.0011	0.0012	0.0012	0.0015	0.0015	0.0017	0.0017	0.0017	0.0017
$$/gr of oil extracted	$/g	0.0060	0.0038	0.0040	0.0034	0.0037	0.0022	0.0039	0.0031	0.0030
$$/lbof oil extracted	$/lb	2.717	1.709	1.836	1.554	1.661	1.010	1.786	1.388	1.360
average	$$/lb of oil ext	2.717	1.772		1.607		1.51			
variance	%	-	5%		5%		24%			

Experimental Data and Calculations at 518 Watts (Continuation)

EXPERIMENTAL DATA	Units				5 min						6 min			7.75
Extraction Time	[min]													
Breakthrough Time	[min]	2.80	2.6	3	3.1	2.4	2.8	2.7	2.60	3.00	2.40	3.00	1.43 (3.10)	
Mass Empty Pot	[g]	251.4	249.2	251.2	280.5	280.4	251.3	249.2	280.4	280.4	249.2	249.3	249.3	
Mass Grass + Pot Before	[g]	355.3	353.4	349	381	383	350.9	342.1	391.4	380.3	350.2	352	349.5	
Mass Grass + Pot After	[g]	341.5	338.1	333.8	368.6	370.6	335.9	327.6	377.2	359.7	330.2	334.4	324.3	
Mass Grass Before	[g]	103.9	104.2	97.8	100.5	102.6	99.6	92.9	111	99.9	101	102.7	100.2	
Mass Grass After	[g]	90.1	88.9	82.6	88.1	90.2	84.6	78.4	96.8	79.3	81	85.1	75	
Mass of Beaker	[g]	29.7	11	8.2	8.2	8.3	8.3	8.2	29.5	8.3	8.3	8.2	51.9	
Mass of Beaker + Water	[g]	40.6	19.9	20.8	17.2	17.9	20.9	21.1	40.9	25.1	24.4	22.3	73.9	
Mass of Water extracted	[g]	10.9	8.9	12.6	9	9.6	12.6	12.9	11.4	16.8	16.1	14.1	22	
Mass of Vial	[g]	2.4678	2.5326	2.3327	3.4079	2.3258	3.3781	3.4267	2.4718	2.3228	3.4525	2.3128	2.4647	
Mass of Oil + Vial	[g]	2.8402	3.1582	2.9392	3.9662	2.8425	4.0901	3.7962	3.0748	2.8192	3.9792	2.9208	2.8687	
Mass of Oil extracted	[g]	0.3724	0.6256	0.6065	0.5583	0.5167	0.712	0.3695	0.603	0.4964	0.5267	0.608	0.404	
To	[°C]	10	20	18.3	18.3	20	22.2	18.4		20	11.6	11.6	10	
Tf	[°C]	30	99	99.4	99.4	99	103.5	100.7		98	100.6	100.6	96.9	
Tcondensate	[°C]	99	23.5	21	21	23.5	21.7	20		30	28.2	28.2	24.6	
Moisture Cont. after ext	%	19.6%	12.3%	12.0%	13.6%	16.6%	5.5%	15.0%	12.8%	10.0%		10.3%	8.3%	
MASS BALANCE														
oil extracted	%	36%	60%	62%	56%	50%	71%	40%	54%	50%	52%	59%	40%	
average % oil extracted	%	57%							54%				40%	
variance	%	9%							8%					
oil non extracted	%	64%	40%	38%	44%	50%	29%	60%	46%	50%	48%	41%	60%	
average % oil non ext	%	46%							46%				60%	
H2O extracted	%	35%	29%	43%	30%	31%	42%	47%	35%	56%	54%	46%	74%	
average % H2O extracted	%	33%							48%				74%	
variance		20%							21%					
average MASS BALANCE ON LIQUID														
% oil extracted from liquid	%	2%							2%				1%	
%H2O extracted from liquid	%	32%							46%				71%	
%liquid left	%	45%							37%				28%	
total liquid accounted for	%	80%							85%				100%	
total % liquid anccounted for	%	20%							15%				0%	
total	%	100%							100%				100%	
ENERGY BALANCE														
Energy used	[KJ]	155.46	155.46	155.46	155.46	155.46	155.46	155.46	186.55	186.55	186.55	186.55	240.96	
Energy needed	[KJ]	43.75	92.28	89.49	89.33	83.43	103.32	80.92	49.33	96.21	119.42	101.21	103.40	
Energy needed average	[KJ]	83.22							91.54				240.96	
variance	[KJ]	22.6%							32.6%				-	
efficiency	%	28%	59%	58%	57%	54%	66%	52%	26%	52%	64%	54%	43%	
$$/run	$	0.0019	0.0019	0.0019	0.0019	0.0019	0.0019	0.0019	0.0023	0.0023	0.0023	0.0023	0.0029	
$$/gr of oil extracted	$/g	0.0051	0.0030	0.0031	0.0034	0.0037	0.0027	0.0051	0.0038	0.0046	0.0043	0.0038	0.0073	
$$/lbof oil extracted	$/lb	2.314	1.378	1.421	1.544	1.668	1.210	2.332	1.715	2.083	1.964	1.701	3.307	
average	$$/lb of oil ext	1.50							1.866				3.307	
variance	%	13%							10%				-	

Experimental Data and Calculations 2 Step Process: 1.5 minutes at 1120 W- x minutes at 697W (1.5H-xM)

EXPERIMENTAL DATA	Units	1.5H-0.5M	1.5H-1M			1.5 H-1.5 M			1.5 H-2M			
Extraction Time	[min]	1.1	1.20	1.30	1.05	1.03	1.25	1.26	1.50	1.20	1.50	1.60
Breakthrough Time	[min]	251.3	249.2	251.3	249.3	249.2	280.4	249.3	280.5	280.3	249.3	249.4
Mass Empty Pot	[g]	350.6	351.4	351.1	349.3	349.6	382	349.5	385.7	381.7	349.3	349.4
Mass Grass + Pot Before	[g]	340.3	338.1	338.3	337.8	329.1	365.3	334	366	362.1	331.5	330.5
Mass Grass + Pot After	[g]	99.3	102.2	99.8	100	100.4	101.6	100.2	105.2	101.4	100	100
Mass Grass Before	[g]	89	88.9	87	88.5	79.9	84.9	84.7	85.5	81.8	82.2	81.1
Mass Grass After	[g]	8.3	11.1	8.2	8.3	11	8.2	11	52	11	29.7	8.4
Mass of Beaker	[g]	15.5	21.8	18.4	17.1	27.9	22.1	23.3	68.1	26.6	43.55	24.8
Mass of Beaker + Water	[g]	7.2	10.7	10.2	8.8	16.9	13.9	12.3	16.1	15.6	13.85	16.4
Mass of Water extracted	[g]	3.331	2.3536	3.4906	2.3214	2.3536	2.3454	3.3478	2.4798	2.5087	2.4894	2.3636
Mass of Vial	[g]	3.5861	2.9927	4.0693	2.8215	2.9927	2.9466	3.905	3.1579	3.2422	3.0465	2.949
Mass of Oil + Vial	[g]	0.2551	0.6391	0.5787	0.5001	0.6391	0.6012	0.5572	0.6781	0.7335	0.5571	0.5854
Mass of Oil extracted	[g]	19.4	5.8	19.4	26	22	18.6	16.8	10	2.6	22.7	23.1
To	[°C]	100	98.3	100	99.8	98	100.1	100	97.8	97	93	101.2
Tf	[°C]	22.7		22.7	22.7	27	28	22	27.7	24	26.8	21.4
Tcondensate	[°C]	19.9%	12.9%	16.4%	16.6%	14.0%	12.9%	9.7%	10.6%	12.9%	13.0%	12.3%
Moisture Cont. after ext	%											
MASS BALANCE												
oil extracted	%	26%	63%	58%	50%	64%	59%	56%	64%	72%	56%	59%
average % oil extracted	%	26%	57%			59%			63%			
variance	%	-	11%			7%			12%			
oil non extracted	%	74%	37%	42%	50%	36%	41%	44%	36%	28%	44%	41%
average % oil non ext	%	74%	43%			41%			37%			
H2O extracted	%	24%	35%	34%	30%	57%	46%	41%	51%	52%	47%	55%
average % H2O extracted	%	24%	33%			51%			51%			
variance			9%			15%			7%			
average MASS BALANCE ON LIQUID												
% oil extracted from liquid	%	1%	2%			2%			2%			
%H2O extracted from liquid	%	24%	32%			50%			49%			
%liquid left	%	48%	51%			41%			41%			
total liquid accounted for	%	72%	85%			93%			93%			
total % liquid anccounted for	%	28%	15%			7%			7%			
total	%	100%	100%			100%			100%			
ENERGY BALANCE												
Energy used	[KJ]	121.71	142.63	142.63	142.63	163.54	163.54	163.54	184.45	184.45	184.45	184.45
Energy needed	[KJ]	72.96	96.61	81.28	76.82	86.26	92.88	96.81	104.53	101.07	83.99	89.81
Energy needed average	[KJ]	72.96	84.90			91.99			94.85			
variance	[KJ]	-	12.2%			5.8%			10.1%			
efficiency	%	60%	68%	57%	54%	53%	57%	59%	57%	55%	46%	49%
$$/run	$	0.0012	0.0017	0.0017	0.0017	0.0020	0.0020	0.0020	0.0023	0.0023	0.0023	0.0023
$$/gr of oil extracted	$/g	0.0056	0.0027	0.0030	0.0035	0.0031	0.0033	0.0036	0.0033	0.0031	0.0040	0.0039
$$/lbof oil extracted	$/lb	2.523	1.237	1.366	1.581	1.419	1.508	1.627	1.508	1.394	1.836	1.747
average $$/lb of oil ext		2.52	1.39			1.52			1.62			
variance	%	-	12%			7%			13%			

Experimental Data and Calculations 2 Step Process: 1.5 minutes at 1120 W- x minutes at 518W (1.5H-xML)

EXPERIMENTAL DATA	Units													
Extraction Time	[min]	1.5 H-1.0 ML			1.5 H-1.5 ML			1.5H-2.0 ML			1.5 H-2.5ML			
Breakthrough Time	[min]	1.13	1.25	1.18	1.13	1.25	1.3	1.20	1.10	1.05	1.20	1.50	1.10	1.10	1.25
Mass Empty Pot	[g]	251.3	249.1	280.4	249.2	249.2	280.4	280.4	249	251.3	249.2	280.4	249.3	280.4	280.4
Mass Grass + Pot Before	[g]	352.5	347.3	374.6	341.9	352	381.4	384.2	349	351.4	351.5	381.4	349.3	381.3	374.9
Mass Grass + Pot After	[g]	341.8	337.1	363.7	328.9	338.6	367.8	396.2	331	335.7	330.9	366.8	333.4	363.4	359.2
Mass Grass Before	[g]	101.2	98.2	94.2	92.7	102.8	101	103.8	100	100.1	102.3	101	100	100.9	94.5
Mass Grass After	[g]	90.5	88	83.3	79.7	89.4	87.4	115.8	82	84.4	81.7	86.4	84.1	83	78.8
Mass of Beaker	[g]	8.3	8.2	8.3	8.3	8.4	8.2	8.3	8.3	11.1	11	8.4	8.3	11.1	8.2
Mass of Beaker + Water	[g]	16	16	16.5	18.6	19.1	18.9	20.3	22.9	24.6	28.7	20.3	21	25.8	20.8
Mass of Water extracted	[g]	7.7	7.8	8.2	10.3	10.7	10.7	12	14.6	13.5	17.7	11.9	12.7	14.7	12.6
Mass of Vial	[g]	2.3676	3.472	3.4396	2.382	2.3553	3.3373	2.3312	3.4225	3.4162	2.3203	2.3218	2.3831	3.4078	3.412
Mass of Oil + Vial	[g]	2.786	3.9604	3.9386	2.7867	2.9375	4.0248	2.7926	4.0847	3.9345	2.9985	2.787	2.9196	4.0819	4.0823
Mass of Oil extracted	[g]	0.4184	0.4884	0.499	0.4047	0.5822	0.6875	0.4614	0.6622	0.5183	0.6782	0.4652	0.5365	0.6741	0.6703
To	[°C]	18.5	20	18.5	18.4	17.7	17.5	18.2	16.6	16.6	12.8	14	20.2	20.2	21
Tf	[°C]	97.7	101.6	100	98.3	100.6	96.4	96	100.3	99.8	99	99.7	99.8	108.7	101.4
Tcondensate	[°C]		23.5			23.8	21.7	26.7		22	26.7	30	21.1	21.1	19.6
Moisture Cont. after ext	%	17.2%	15.7%	15.3%	16.5%	16.7%	10.2%	11.4%	7.4%	11.9%	7.8%	15.5%	11.4%		10.9%
MASS BALANCE															
oil extracted	%	41%	50%	53%	44%	57%	68%	44%	66%	52%	66%	46%	54%	67%	71%
average % oil extracted	%	48%			56%			54%			61%				
variance	%	12%			22%			20%			17%				
oil non extracted	%	59%	50%	47%	56%	43%	32%	56%	34%	48%	34%	54%	46%	33%	29%
average % oil non ext	%	52%			44%			46%			39%				
H2O extracted	%	26%	27%	29%	37%	35%	36%	39%	49%	45%	58%	40%	43%	49%	45%
average % H2O extracted	%	27%			36%			44%			47%				
variance		7%			3%			12%			15%				
average MASS BALANCE ON LIQUID															
% oil extracted from liquid	%	2%			2%			2%			2%				
%H2O extracted from liquid	%	26%			35%			43%			45%				
%liquid left	%	54%			49%			34%			38%				
total liquid accounted for	%	82%			85%			79%			86%				
total % liquid anccounted for	%	18%			15%			21%			14%				
total	%	100%			100%			100%			100%				
ENERGY BALANCE															
Energy used	[KJ]	131.89	131.89	131.89	147.44	147.44	147.44	162.98	162.98	162.98	178.53	178.53	178.53	178.53	178.53
Energy needed	[KJ]	79.00	81.30	81.61	76.45	84.06	95.48	87.84	101.76	92.59	104.74	89.21	91.54	121.13	90.62
Energy needed average	[KJ]	80.63			85.33			94.06			99.45				
variance	[KJ]	1.8%			11.2%			7.5%			13.7%				
efficiency	%	60%	62%	62%	52%	57%	65%	54%	62%	57%	59%	50%	51%	68%	51%
$$/run	$	0.0016	0.0016	0.0016	0.0018	0.0018	0.0018	0.0020	0.0020	0.0020	0.0022	0.0022	0.0022	0.0022	0.0022
$$/gr of oil extracted	$/g	0.0039	0.0033	0.0032	0.0045	0.0031	0.0026	0.0043	0.0030	0.0038	0.0032	0.0047	0.0041	0.0032	0.0033
$$/lbof oil extracted	$/lb	1.748	1.497	1.465	2.020	1.404	1.189	1.958	1.364	1.743	1.459	2.128	1.845	1.468	1.477
average	$$/lb of oil ext	1.57			1.54			1.69			1.68				
variance	%	10%			28%			18%			18%				

Experimental Data and Calculations 2 Step Process: 2.0 minutes at 1120 W- x minutes at 697W (2H-xM)

EXPERIMENTAL DATA	Units	2H-0.5 M			2H-1.0 M		2H-1.25 M				
Extraction Time	[min]	1.03	1.25	1.30	1.19	1.25	1.11	1.15	1.20	1.25	1.25
Breakthrough Time	[min]	249.2	280.4	280.4	251.3	251.3	280.4	249.1	280.4	280.4	251.3
Mass Empty Pot	[g]	350.7	380.7	383	348	338.5	380.4	349.6	375.8	382	352.5
Mass Grass + Pot Before	[g]	334.7	366.7	368.3	327.3	321	362.7	331.2	354.5	363.9	335.5
Mass Grass + Pot After	[g]	101.5	100.3	102.6	96.7	87.2	100	100.5	95.4	101.6	101.2
Mass Grass Before	[g]	85.5	86.3	87.9	76	69.7	82.3	82.1	74.1	83.5	84.2
Mass Grass After	[g]	10.9	8.3	8.2	8.3	8.2	29.7	8.2	8.2	8.3	11.1
Mass of Beaker	[g]	24.3	19.8	20.1	25.8	22.9	43.3	23.5	25.2	23.6	25.2
Mass of Beaker + Water	[g]	13.4	11.5	11.9	17.5	14.7	13.6	15.3	17	15.3	14.1
Mass of Water extracted	[g]	2.3306	3.4175	2.3719	2.3483	3.4178	2.464	3.3866	2.3784	3.4033	3.4207
Mass of Vial	[g]	2.6911	3.9787	2.8801	2.9345	4.0329	2.8947	3.9625	2.962	4.0093	4.157
Mass of Oil + Vial	[g]	0.3605	0.5612	0.5082	0.5862	0.6151	0.4307	0.5759	0.5836	0.606	0.7363
Mass of Oil extracted	[g]	20	17	20	18.1	18.1	20.4	19.9	20.4	19.1	19.6
To	[°C]	95	100.7	95	100	99.3	97.5	101.8	97	100.1	100.6
Tf	[°C]	26	22.7	26	20.7	20.7	28.8	22.6	28.8	23.6	21.1
Tcondensate	[°C]	15.0%	10.9%	14.3%	6.8%	10.1%	26.0%	6.1%	7.3%	9.2%	8.0%
Moisture Cont. after ext	%										
MASS BALANCE											
oil extracted	%	36%	56%	50%	61%	71%	43%	57%	61%	60%	73%
average % oil extracted	%	47%			66%	57%	59%				
variance	%	22%			11%		3%				
oil non extracted	%	64%	44%	50%	39%	29%	57%	43%	39%	40%	27%
average % oil non ext	%	53%			34%		41%				
H2O extracted	%	44%	39%	39%	61%	57%	46%	51%	60%	51%	47%
average % H2O extracted	%	41%			59%	57%	54%				
variance		8%			5%		10%				
average MASS BALANCE ON LIQUID											
% oil extracted from liquid	%	2%			2%		2%				
%H2O extracted from liquid	%	39%			57%		52%				
%liquid left	%	45%			28%		25%				
total liquid accounted for	%	86%			87%		79%				
total % liquid anccounted for	%	14%			13%		21%				
total	%	100%			100%		100%				
ENERGY BALANCE											
Energy used	[KJ]	155.31	155.31	155.31	176.23	176.23	186.68	186.68	186.68	186.68	186.68
Energy needed	[KJ]	83.07	96.47	86.41	99.65	85.66	65.09	103.68	96.73	100.01	100.03
Energy needed average	[KJ]	88.65			92.66		93.11				
variance	[KJ]	7.9%			10.7%		17.0%				
efficiency	%	53%	62%	56%	57%	49%	35%	56%	52%	54%	54%
$$/run	$	0.0019	0.0019	0.0019	0.0022	0.0022	0.0023	0.0023	0.0023	0.0023	0.0023
$$/gr of oil extracted	$/g	0.0053	0.0034	0.0037	0.0037	0.0035	0.0053	0.0040	0.0039	0.0038	0.0031
$$/lbof oil extracted	$/lb	2.388	1.534	1.694	1.667	1.588	2.403	1.797	1.773	1.708	1.406
average $$/lb of oil ext		1.87			1.63		1.76				
variance	%	24%			3%		5%				

Experimental Data and Calculations 2 Step Process: 2.0 minutes at 1120 W- x minutes at 518W (2H-xML)

EXPERIMENTAL DATA	Units										
Extraction Time	[min]	2 H- 0.5 ML	2min High/1min Mlow			2H-1.25 ML				2 H-1.5 ML	2 H-1.75 ML
Breakthrough Time	[min]	1.05	1.10	1.20	1.15	1	1.25	1.25	1.25	1	1.10
Mass Empty Pot	[g]	280.4	280.4	280.4	251.3	249.2	251.3	249.2	251.3	249.2	249.3
Mass Grass + Pot Before	[g]	377.9	385.7	379.6	349	349.2	349.7	352	352.5	347	349.3
Mass Grass + Pot After	[g]	363.5	373	362.9	331	331.9	334.8	333.5	335.5	329.7	331.4
Mass Grass Before	[g]	97.5	105.3	99.2	97.7	100	98.4	102.8	101.2	97.8	100
Mass Grass After	[g]	83.1	92.6	82.5	79.7	82.7	83.5	84.3	84.2	80.5	82.1
Mass of Beaker	[g]	8.2	11	8.2	11	8.3	8.5	11.1	11.1	8.2	29.6
Mass of Beaker + Water	[g]	19.4	20.8	21.4	25.4	22.9	20.6	27.1	25.2	23.2	45.1
Mass of Water extracted	[g]	11.2	9.8	13.2	14.4	14.6	12.1	16	14.1	15	15.5
Mass of Vial	[g]	3.3869	2.5307	2.3494	2.379	2.3217	3.4339	3.3916	3.4207	3.4184	2.5269
Mass of Oil + Vial	[g]	3.9248	3.1316	2.9123	2.9914	2.8952	3.8416	3.8908	4.157	4.0695	3.2058
Mass of Oil extracted	[g]	0.5379	0.6009	0.5629	0.6124	0.5735	0.4077	0.4992	0.7363	0.6511	0.6789
To	[°C]	21.7	3	18.1	20.4	26.8	19.3	19.3	19.6	21.7	22.7
Tf	[°C]	99.1	94	101.2	98	100.8	97.9	98.3	100.6	99.1	100.2
Tcondensate	[°C]	24.9	27	20.4	26	22.8	21.1	21.1	21.1	24.9	34.1
Moisture Cont. after ext	%	11.0%	6.8%	12.9%	6.5%	10.6%	11.0%	9.8%		13.4%	9.4%
MASS BALANCE											
oil extracted	%	55%	57%	57%	63%	57%	41%	49%	73%	67%	68%
average % oil extracted	%	55%	59%			65%				67%	68%
variance	%		6%			21%					
oil non extracted	%	45%	43%	43%	37%	43%	59%	51%	27%	33%	32%
average % oil non ext	%	45%	41%			45%				33%	32%
H2O extracted	%	39%	31%	45%	50%	49%	41%	52%	47%	52%	52%
average % H2O extracted	%	38%	42%			48%				52%	52%
variance			23%			10%					
average MASS BALANCE ON LIQUID											
% oil extracted from liquid	%	2%	2%			2%				2%	2%
%H2O extracted from liquid	%	37%	40%			46%				50%	50%
%liquid left	%	37%	29%			35%				45%	32%
total liquid accounted for	%	76%	72%			84%				97%	84%
total % liquid anccounted for	%	24%	28%			16%				3%	16%
total	%	100%	100%			100%				100%	100%
ENERGY BALANCE											
Energy used	[KJ]	149.95	165.49	165.49	165.49	173.27	101.05	101.05	101.05	181.04	188.81
Energy needed	[KJ]	90.70	112.70	92.09	98.24	90.40	90.46	97.03	115.35	85.48	94.61
Energy needed average	[KJ]	90.70	101.01			98.31				85.48	94.61
variance	[KJ]		10.5%			12.0%					
efficiency	%	60%	68%	56%	59%	52%	90%	96%	114%	47%	50%
$$/run	$	0.0018	0.0020	0.0020	0.0020	0.0021	0.0012	0.0012	0.0012	0.0022	0.0023
$$/gr of oil extracted	$/g	0.0034	0.0034	0.0036	0.0033	0.0037	0.0030	0.0025	0.0017	0.0034	0.0034
$$/lbof oil extracted	$/lb	1.545	1.527	1.630	1.498	1.675	1.374	1.122	0.761	1.541	1.542
average $$/lb of oil ext		1.55	1.55			1.22				1.54	1.54
variance	%		4%			39%					