Microwave Essential Oil Extraction via Alternative Solvent

Abstract

The objectives of this project were to investigate alternative solvents for microwave oil extraction, quantify solvent effectiveness by evaluating oil yield compared to a water standard, and optimize the best solvent for use in the EssenEx™ 100 microwave unit. The team developed a solvent matrix that allowed direct comparison of several solvent characteristics such as molecular weight, polarity, miscibility in oil and water, boiling point, toxicity, and FDA approval. The team chose the top five that met safety, ease of use, and customer accessibility metrics. The solvents under investigation were ethyl acetate, isopropanol, ethanol, limonene, and methyl THF. The team investigated the oil yields of orange peels because they are readily available and have been proven to work in the unit. Blended hops were also investigated because they had not been successfully used in the EssenEx™ 100 unit. The optimal solvent volume for orange oil extraction was determined to be 30 mL. Orange oil yield from Nearly Normal's oranges increased by 18% with ethanol and 54% with isopropanol. Orange oil yield from Safeway oranges increased by 82% with ethanol and 95% with isopropanol. The solvent volume required for hop rehydration and oil extraction was determined to be 50 mL. Hop oil yield decreased with pure ethanol and 70% aqueous isopropanol, but increased by 27% using a 70% aqueous ethanol solution.

Background

<u>The Unit</u>

OilExTech developed the EssenEx™ 100 microwave oil extraction unit for home use in 2012. The EssenEx™ 100 extracts essential oils from botanical material in approximately 6 min and produces a higher quality oil than steam distillation methods, which can take up to 4-6 hrs. The unit works by using microwave energy to vaporize the water and oil contained in botanical material and releasing it into the air. This water and oil mixture is carried to the top of the unit and condensed on the center ice core. The oil and water are collected in a center beaker, forming a hydrosol where ideally a two phase region would form; less dense oil on top and water on the bottom. The user removes the beaker after a complete run in the microwave and transfers the hydrosol to a volumetric flask. The essential oil is easily pipetted off the top. *Figure 1* shows a sketch of the EssenEx™ 100 unit.

Figure 1. *OilExTech's EssenEx™ 100 unit consists of a 2 L glass jar, a 250 mL beaker surrounded by Teflon coated mesh, and a 200 mL ice core. The oils are condensed on the ice core and collected in the beaker. The collection beaker is then poured into a volumetric flask, where the oils are separated from the water. Solvent, oil, and water molecules are included to demonstrate how oil is carried to the ice core.*

The Product

Essential oils can be found in large quantities in the seeds, peels, or fleshy parts of some botanical materials. These oils are extracted for use in food products, but are more commonly used in health and aromatherapy products.

Hops are perennial flowers that are most commonly used in the brewing process for bittering and flavoring beer. Hop flowers or cones resemble small pinecones, but are made of green, papery bracteoles. At the base of the bracteoles are waxy, yellow glands that contain essential oils responsible for giving beer its flavor and aroma, and the alpha acids credited with bittering beer.[1] Several breweries are beginning to extract and use hop oil in place of whole cone hops to improve aroma and decrease bitterness. Hop oil is commercially obtained from solvent extraction with supercritical CO_2 or hexane. Although the majority of brewers still use whole cone hops, many craft breweries or home brewers are interested in using hop oil as a substitute to hop cones. Essential oils in hops are the same regardless of variety, but vary in composition. Dry hop cones contain 1-2 wt% essential oil. Some of the compounds in hop oil are water soluble and utilizing a solvent could increase yield and make separation easier.

Oranges are a citrus fruit and are the most cultivated fruit tree in the world. Orange oil is extracted from the peel of an orange and makes up approximately 1.5 - 3 wt% of the total peel weight.[2] Orange oil is used in the food and beverage industry to flavor drinks and is also used in the perfume and aromatherapy industry. Orange oil is 90% D-limonene which is used as a solvent in various household chemicals such as furniture and wood conditioners, as well as detergents and hand soaps.[3]

Solvent Candidates

An alternative solvent was used in the EssenEx™ 100 by either soaking the plant material in solvent, soaking in a mixture of solvent and water, or adding solvent directly to the unit with no soak time.

The five main criteria for the solvent candidates were:

- low boiling point
- large molecular weight
- low toxicity
- compatibility with oil
- customer accessibility

The boiling temperature of the ideal solvent is lower than 100 °C to ensure it can be vaporized by water. The quantity of solvent required to carry the oil compounds to the collection beaker is minimized with a larger molecular weight solvent. This can be seen in *Figure 1*. The hop oil may be used in food products and needed to be safe enough for typical household use. The toxicity of the solvent should also be low and preferably FDA approved. The solvent needed to be compatible with the hop oil and not alter the essential oil compounds. The solvent should also be unreactive with water and hop oil. Microwave reactivity was explored for all solvents. The taste and aroma of essential oils are critical end use characteristics and should be minimally affected by solvent use. The ideal solvent would be highly

[1] *A Brief History in Beer*. MDA Creative Products. Web. Accessed 14 Mar 2015.
[2] *Percent Yield Guide for Essential Oil Distillation*. The Essential Oil Company. 2015. Web. Date Accessed 6 June 2015.
[3] "D-Limonene". International Programme on Chemical Safety. Apr 2005. Web. Date Accessed 6 June 2015.

accessible to customers and would require no special ordering. The viability of all potential solvents were evaluated in the project. *Table 1* displays information regarding the five potential solvents.[4,5,6]

Table 1. *The table contains the molecular weight, boiling temperature, miscibility, and FDA rating for the five potential solvents. Limonene has an FDA rating of GRAS (generally recognized as safe). THF FDA solvent class is used for methyl THF due to lack of data. Solvents in Class 2 should be in limited amounts in products because of their toxicity. Class 3 solvents are less toxic, have lower risk of harm, and do not cause any health issues at levels accepted in pharmaceuticals.*

Common Name	Chemical Formula	Molecular Weight	Boiling Point	Miscible with Hop Oil	Miscible with Limonene	FDA Approved
		g/mol	*C			
Isopropanol	C3H8O	60.1	82.6	Partial	No	Class 3
Ethyl acetate	C4H8O2	88.11	77.11	Partial	Yes	Class 3
Ethanol	C2H5OH	46.07	78.37	Yes	No	Class 3
Methyl THF	$CH_3C_4H_7O$	86.13	78	Yes	Yes	Class 2 (THF)
Limonene	C10H16	136.23	176	Yes	N/A	GRAS

Methyl THF was recommended by OilExTech. It is a greener alternative to THF, however, the FDA does not have toxicity data on this particular solvent.[7] Limonene was investigated to aid in extraction of the hop oil from the plant, but it is miscible with hop oil making it difficult to quantify yields. Ethanol is a commonly used organic solvent for food and herbal extractions, is easily accessible, and is soluble in water.[8] Isopropanol is also soluble in water and has a higher molecular weight than ethanol. Ethyl acetate is considered a lower toxicity solvent, green, and is recognized as safe for use as an additive for food products.[5,6] Solvents that were miscible with oil would need more steps to extract the oil. At first, a solvent that was immiscible with water was desired because hop oil was slightly miscible with water. Immiscibility with oil became a priority to eliminate the need for an additional separation step.

Methods

Approximately 100 lbs of dried whole cone Columbus hops were obtained from the Food Science and Technology department. The hops were from a single crop harvested in 2013 from Coleman Farms. Dried hops should be coarsely ground before extraction according to the steam distillation standard established by the American Society of Brewing Chemists (ASBC).[9] Grinding increases the interfacial surface area and exposes the oil glands to the extraction solvent. Fifty grams of hops were used to test three grinding/blending techniques. In the first method, the hops' bracteoles were pried apart from the center

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[4] *Evaluation of Selected Medicinal Plants Extracted in Different Ethanol Concentrations for Antibacterial Activity against Human Pathogens.* Wendakoon, Chitra, Peter Calderon, Daniel Gagnon. 2012. Journal of Medicinally Active Plants 1(2):60-68.

[5] *Ethyl Acetate.* Sekab Biofuels & Chemicals. http://www.sekab.com/chemistry/ethyl-acetate

[6] *Ethyl Acetate and Cyclohexane – A Toxicological Review.* Lubrizol.TDS-94. Mar 1995.

[7] A Green Alternative to THF. Dr. Rainer Aul and Dr Bogdan Comanita. Manufacturing Chemist. May 2007.

[8] Evaluation of Selected Medicinal Plants Extracted in Different Ethanol Concentrations for Antibacterial Activity against Human Pathogens. Wendakoon, Chitra, Peter Calderon, Daniel Gagnon. 2012. Journal of Medicinally Active Plants 1(2):60-68.

[9] American Society of Brewing Chemists. Report of Subcommittee on Essential Oil in Hops and Hop Pellets. *Journal* 46:121 (1988).

stem, known as the strig. In the second method, hops were finely ground using a mortar and pestle in 3 g batches. In the third method, hops were processed in Ninja blender (Model Number: QB900B 54. 120 V) using the pulse setting for 5 s in 10 g batches. The three grinding techniques were evaluated based on the time required to process 50 g of hops, ease of use, and quality of grind. The team ultimately decided the Ninja blender would be used for all additional testing due to its rapid blend and material consistency.

Two methods of rehydration for hops were investigated. Three hop samples were prepared using each rehydration method. In the first method, 50 g of blended hops were added to an excess of water (1000 mL) in a 2 L beaker. A 1.5 L beaker was nested in the 2 L beaker to force the hops under the surface of the water. The samples were sealed with saran wrap and allowed to sit undisturbed for 48 hrs. Prior to use, these samples were wrung out using cheesecloth to remove excess water. In the second method, ground hops were rehydrated with water in 50 mL increments to determine the minimal ratio of water to hops required for rehydration. A total of 100 mL of water was added to 50 g of blended hops. The samples were also sealed using saran wrap and allowed to sit undisturbed for 48 hrs.

OilExTech's EssenEx™ 100 unit was used to carry out the extractions. The unit was prepared according to the operating manual provided by OilExTech.[10] The unit and a ceramic mug filled with 200 mL of water were placed in a General Electric 100W microwave (Model Number: DE68-00307A). An average extraction time of 5 min was used. The amount of ice core remaining was qualitatively recorded. The hydrosol was transferred to a 150 mL volumetric flask to allow the oil to separate from the water.

A qualitative solubility test was run on solvent-water-essential oil mixtures. A vial was filled with 10 mL of water, 10 mL of essential oil (hop oil from HopTech and D-limonene from Blubonic Indsutries), and 10 mL of solvent. Methyl THF, ethyl acetate, limonene, and ethanol were all tested. The vials were shaken and left in a dark cupboard to settle for one day.

The team determined that oil yield is highly dependent on freshness of the botanical material. The hops obtained from the Food Science and Technology department were not properly packaged or stored. Hop oil in improperly stored hops volatilizes and oxidizes over time, which could affect oil quality and yield. Hops available at a brewing supply store are vacuum sealed and stored in a refrigerator to preserve freshness. The team purchased 2 lbs of dried, whole cone, Hopunion Citra hops from Corvallis Brewing Supply for use in all quantitative hop oil extraction tests. All hop extraction trials were conducted using 50 g of blended hops. Fifty mL of water or solvent were added to the unit and combined with the hops using a stirring rod. Water extractions were used as a control. All extractions were run for 4.5 min.

Orange peels were obtained from multiple local locations including Nearly Normal's and Safeway. The team removed any excess pulp stuck to the peel and blended them using a Ninja (Model Number: QB900B 54. 120 V) to create a homogenous mixture. Each orange batch was separated by location and all trials documented which of the two locations the orange peels originated from. This allowed the team to identify the quality of the orange peel and explain any discrepancies in overall orange oil yield. The team ran several preliminary tests on all oranges to determine a baseline oil yield. The team followed the SOP provided by OilExTech to perform all baseline tests and did not add any solvent or water to the unit. Multiple trials were performed for each orange location for data and error analysis.

Solvent was added to the blended orange peels in one of two ways: adding solvent to the blended oranges and thoroughly mixing, or adding solvent directly to the bottom of the unit and layering the oranges overtop. The solvent was added to the oranges immediately before extraction and did not require any

[10] *EssenEx100 Operators Manual*. Home/Lab Microwave Essential Oil Extraction. OilExTech. Web. Accessed 15 Mar 2015.

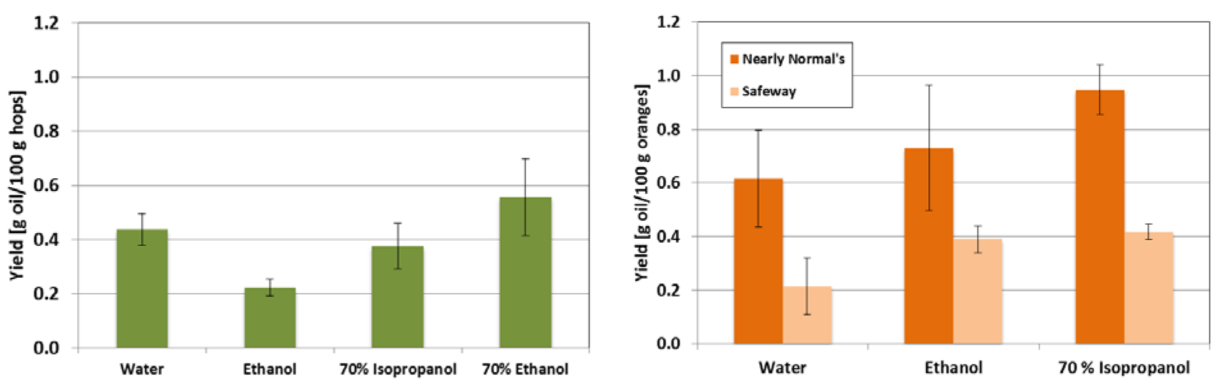
soak time. All trials were done with 100 g of orange peels and the unit was ran in the microwave for 5.5 min. The hydrosol was removed from the unit and poured into a 150 mL volumetric flask and the oil layer was pipetted off the top. Oil yield was determined as a mass percent of the total original botanical material. Unused oranges were placed in the freezer to preserve freshness.

Results

Oil could not be effectively extracted from the Columbus hops provided by the Food Science and Technology Department. Either the oil had evaporated due to poor storage or the oxidation of the oil/acids caused too many changes in the chemical makeup. The hops had to be soaked in order to extract any oil out of the plant material. No soaking was required with the newer Citra hops.

Standard steam distillation was performed with 100g of Columbus hops for 4 hours. Approximately 1 mL of a dark yellow and pungent oil was produced. This proved that the hops did contain oil, but could not be efficiently extracted using the EssenEx™ 100 unit. Oil extracted from the Citra hops had a more pleasant aroma and was clear and tinted yellow. This was closer to the quality of the pure Hopsteiner oil donated to the team.

Figure 2 shows oil yield for oranges and hops using ethanol and isopropanol. Each is compared to a standard of water. The orange peel standard used water already contained in the plant material. Water was added for the hop runs.



(a) (b)

Figure 2. *(a) Extraction results from Citra hops show that 70% ethanol and water had the highest oil yield. Pure ethanol has a lower yield than the water standard. (b) Extraction results from Nearly Normal's and Safeway oranges. Both brands of oranges had increased yields with solvent use. Isopropanol had the greatest increase with an average of 95% for Safeway oranges.*

The Nearly Normal's oranges were fresher which caused them to have a higher oil content than the Safeway oranges. There were large variations in orange oil content between batches, resulting in large error bars. Both isopropanol and ethanol improved the orange oil extraction yield. Orange oil yield from Nearly Normal's oranges increased by 18% with ethanol and 54% with isopropanol. Extraction results from Safeway oranges followed a similar trend as the Nearly Normal's tests, but had a much more significant increase over the control. Orange oil yield from Safeway oranges increased by 82% with ethanol and 95% with isopropanol.

Ethyl acetate and methyl THF were not used for final experiments due to their miscibility with the essential oils. It was difficult to quantify the yields without using a second extraction method to separate the oil and solvent. Ethyl acetate and methyl THF may have also caused damage to the microwave interior.

Soaking experiments led to no definitive results. Some oil was extracted from hops, but could not be separated from the water. No increase in oil production was found after soaking orange peels. The solvents may be too volatile to soak, or better soaking procedures/equipment is needed.

Ethanol and isopropanol were both found to be microwave reactive. Both solvents boiled in 19 sec. The fast volatilization of these compounds can lead to a faster extraction. The ice core melted much faster with the solvents added although this was not quantitatively measured. This indicates the solvents extract more oil in less time. Water does extract most of the oil in the first run, but solvents are more efficient and allow for more oil to be extracted per run.

Conclusions and Recommendations

Variation between batches is mainly attributed to the natural variation of oil content of the botanical. Future teams should acquire and prepare all botanical material at the start of the project to control for natural variation. This homogenous source of extraction material should have a uniform oil composition and should be used for all extraction tests.

Isopropanol increased the oil yield in Nearly Normal's and Safeway oranges by an average of 74%. The team would recommend customers of OilExTech use 30 mL isopropanol for 100 g orange peels to increase orange oil yield. A mixture of 70% ethanol and 30% water, by volume, increased Citra hop yield by an average of 27%. The team currently recommends using 50 mL of this solvent mixture for 50 g blended hops.

Ethanol and 70% isopropanol had different effects on the oil yield of hops and oranges. These two solvents improved orange oil yield but hindered hop oil yield. Curiously, 70% ethanol improved hop oil yield over the water control. The miscibility of essential oil in solvent appeared to have an influence on oil yield. Based on this assumption, an ideal solvent would be immiscible with the essential oil. Solvents that are miscible with the essential oil could be effective if a viable means of separation is developed or if a mixture of solvent and oil is desirable. A homogenous mixture of oil and ethanol may be a desirable characteristic for fermented beverages since the mixture could be added directly and eliminates the need to create an aqueous solution. Gas chromatography (GC) could be used to determine the quantity of oil extracted in homogenous oil and solvent mixtures.

The team recommends testing different plant materials with solvents including lemongrass, thyme, mint, and lavender. The team also recommends experimenting with different soaking techniques by either soaking in an air tight environment or by blending botanical material directly with solvent. Testing different ethanol and water, or isopropanol and water mixtures by varying the ratio of each species is recommended. The team recommends testing different hop varieties to observe the difference in overall oil yield and solvent capability. An investigation is recommended to examine the relationship between botanical mass and solvent required; a linear relationship is expected.

The solvent matrix and the team's research suggests ethyl acetate would be an effective extraction solvent. Its miscibility with essential oils prevented the team from pursuing it further. Dry ice may be a viable means of separating the solvent from the oil by exploiting the difference in freezing points (-83.6°C and -10°C for ethyl acetate and hop oil, respectively)

Essential oil applications may include products that are ingested or come into contact with the skin. The effects of solvent extraction on essential oils should be investigated through the use of a GC or other analytical techniques. This will ensure that a pure, high quality product is extracted. The quantity of residual solvents could be compared to FDA recommendations and other extraction methods to determine the safety of the oil.

Acknowledgements
The team thanks the following people and companies for their guidance throughout the project: Dr. Hackleman and Bill Dean for project sponsorship, guidance, and expertise, Jackie Toftner for assistance with solvent selection, Dr. Shellhammer for the hop donation, project advice, and access to steam distillation equipment, Hopsteiner for hop oil donation, Nearly Normal's and White Wind Superfoods for orange peel donation, and Dr. Harding for feedback and project guidance.

Appendix A. Solvent SOPs

(on attached pages)

SOLVENT STANDARD OPERATING PROCEDURE: ORANGE PEEL

Materials

- EssenEx™ 100 oil distillation unit
- 4-6 fresh large or medium oranges
- Ninja blender

Procedure

1. Peel oranges and ensure all orange peels are free of excess pulp
2. Blend orange peels in Ninja blender to create uniform dime size pieces
3. Weigh out 100 g blended orange peels, set aside
4. Using graduated cylinder, measure out 30 mL of 70% isopropanol and pour into bottom of unit
5. In unit, layer blended oranges over ethanol with as little jostling as possible
6. Insert center beaker (250 mL) inside shield cylinder in unit, gently pushing oranges to the edge as needed
7. Place upper shield in unit and center the beaker, lower and upper shields
8. Remove ice core from mold and attach ice core to lid
9. Place lid on unit to complete the unit assembly
10. Place mug filled with 200 mL cold water in microwave, add assembled unit to microwave
11. Microwave on high power for 5.5 min
12. Let unit sit in microwave for 2 min after complete run
13. Remove unit from microwave using heat gloves, keep unit level to not spill liquid within
14. Carefully remove center beaker and pour hydrosol into 150 mL volumetric flask
15. Pipette oil layer off the top and place into pre-weighed 2 mL vial
16. Yield is calculated as the wt % of oil in 100 g of hops. $Yield = \frac{mass\ of\ oil\ collected * 100}{mass\ of\ hops}$
17. Store in a refrigerated environment to preserve freshness

SOLVENT STANDARD OPERATING PROCEDURE: HOPS

Materials

- EssenEx™ 100 oil distillation unit
- Fresh hop, properly stored
- Ninja blender

Procedure

1. Weigh out 50 g of hops
2. Use a blender to coarsely grind the hops in 10 g batches
3. Add the blended hops to the 2 L glass jar
4. Use a graduated cylinder to measure 15 mL of water and 35 mL of ethanol. (Ideal solvent to hops ratio is 1:1)
5. Add the ethanol solution to the hops and thoroughly combine using a stirring rod
6. Move the hops toward the walls of the unit to create a space for the collection beaker
7. Place the microwave shield and 250 mL collection beaker in the center of the unit
8. Remove the ice core from the mold and affix it to the lid
9. Place the ice core shield on the top of the unit; ensure that it sits flush and the two shields do not touch
10. Cover the unit with the lid-ice core assembly
11. Fill the mug with 200 mL of water
12. Run the unit and mug in the microwave for 4.5 min on high
13. Let the unit cool in the microwave for ~1 min
14. Transfer the contents of the collection beaker to the 150 mL volumetric flask. (Note: Not all of the hydrosol in the collection beaker will fit in the volumetric flask. However, the transfer process should transport the entirety of the oil layer to the volumetric flask
15. Use a pipette to transfer the oil layer to a pre-weighed 2 mL glass vial
16. Yield is calculated as the wt % of oil in 100 g of hops. $Yield = \frac{mass\ of\ oil\ collected * 100}{mass\ of\ hops}$
17. Store in a refrigerated environment to preserve freshness