Maple Digest 21A:11-18.

METABOLISM OFF-FLAVOR IN MAPLE SYRUP

Part II: Remediation of metabolism off-flavor in maple syrup

Abby K. van den Berg[1], Timothy D. Perkins[1], Mark L. Isselhardt[1], Mary An Godshall[2] and Steven W. Lloyd[3]

INTRODUCTION

'Metabolism' is an off-flavor described as 'earthy to bitter' which significantly reduces the economic value of maple syrup (Perkins et al. 2006). It periodically occurs in syrup simultaneously over a wide geographic range, and in some years can affect up to 25% of the total annual maple syrup crop (Perkins and van den Berg in press). Research on metabolism at the University of Vermont Proctor Maple Research Center (PMRC) had two main objectives: 1) to identify the primary compound or compounds responsible for metabolism off-flavor in maple syrup, and 2) to develop a technique maple producers and packers could use to effectively remediate the flavor of metabolized maple syrup.

The primary compound associated with metabolism off-flavor was identified as 2,5-dimethylpyrazine (2,5-DMP) (van den Berg et al. 2009a). 2,5-dimethylpyrazine is a naturally-occurring volatile flavor compound found in a variety of heat-processed foods, including roasted beef, cocoa, bacon, and coffee (Maga 1992), as well as maple syrup (Alli et al. 1992, Akochi-K. et al. 1997). In maple syrup with metabolism off-flavor, however, 2,5-DMP occurs in much greater concentrations (up to 40 times greater) than in syrup without the off-flavor (van den Berg et al. 2009a).

In practice, producers and packers attempt to blend out the off-flavor by mixing metabolized syrup in with good-tasting syrup. Unfortunately, it takes a large quantity of non-metabolized syrup to remove or reduce the metabolism off-flavor to a point where the taste is acceptable. This limits the effectiveness of blending as a strategy to reduce the off-flavor.

With the responsible compound identified, the objective of the current study was to examine several possible remediation techniques to determine which, if any, was most effective in reducing or removing metabolism off-flavor from maple syrup.

Materials and Methods

Remediation Treatment Selection and Rationales

An ideal metabolism remediation treatment should maximize the reduction in undesirable metabolism off-flavor while minimizing other negative impacts on syrup quality, such as reductions in color grade or formation of other undesirable off-flavors. In addition, any remediation treatment developed must not violate federal, state or provincial maple purity laws and regulations. Finally, the technique should be relatively easy to employ by maple producers and/or packers. The treatments examined in this study were chosen based on those criteria.

[1]Proctor Maple Research Center, The University of Vermont, P.O. Box 233, Underhill Ctr., VT 05490

[2]Sugar Processing Research Institute, Inc., 1100 Robert E. Lee Blvd., New Orleans, LA 70124

[3]United States Department of Agriculture Agricultural Research Service Southern Regional Research Center, 1100 Robert E. Lee Blvd., New Orleans, LA 70124

In general, four remediation treatments were investigated: heating syrup in an open pan (H), applying air injection to syrup while heating in an open pan (AH), applying air injection to room temperature syrup (ANH), and heating syrup while vacuum was applied (VH).

The predominant compound responsible for metabolism off-flavor, 2,5-dimethylpyrazine, is a volatile compound with a boiling point of 311°F. Akochi-K. et al. (1997) found that the quantity of 2,5-DMP decreased in syrup after reheating a small quantity for 30 min at 211°F. We hypothesized that heating metabolized syrup sufficiently could cause the 2,5-DMP in syrup to either volatilize (to evaporate out of the syrup) or react to form other compounds to a degree great enough to achieve a reduction in the metabolism off-flavor of the syrup. However, while heating syrup in this way could achieve the desired reduction in off-flavor, it would also likely cause syrup to darken substantially. Thus, alternative remediation treatments in which syrup heating could be accomplished with less impact on syrup color were also investigated.

In general, the amount of syrup darkening is proportional to the amount and duration of heat applied to the syrup. Thus, we examined two remediation treatment methods which would potentially allow heating of syrup to occur at lower temperatures than with heating only. First, previous work at the UVM PMRC has shown that air injection systems substantially reduce the temperature of the liquid boiling in the evaporator (an average of 13.5°F lower) (van den Berg et al. 2009b). We hypothesized that applying air injection while heating metabolized syrup could reduce the extent of syrup darkening by maintaining lower temperatures than those obtained when applying heat only, while still promoting the reduction of 2,5-DMP and thus the remediation of metabolism off-flavor.

Second, the temperature at which liquids boil is affected by atmospheric pressure; liquids boil at lower temperatures at reduced pressures (under partial vacuum). We hypothesized that applying vacuum while heating syrup to reduce pressure and thus the temperature at which the syrup boiled could be another way to minimize the extent of syrup darkening, while still achieving clearing of 2,5-DMP and, consequently, reductions in metabolism off-flavor.

Finally, experiments with beet sugar have shown that some off-flavors can be reduced by circulating air through the material at ambient temperature (Duffaut et al. 2004). We hypothesized that applying air injection to syrup without heat application could be an effective way to reduce metabolism off-flavor with very minimal impact on syrup color.

Remediation Eeperiment and Treatment Details

All experiments were conducted at the University of Vermont Proctor Maple Research Center in Underhill Center, Vermont. Pure maple syrup with a pronounced metabolism off-flavor was acquired in 2005 and used for all metabolism remediation experiments.

All experiments began with approximately 8.5 gallons of the original metabolized syrup. All treatments except the vacuum treatment were conducted in a 12" × 20" stainless steel canning unit with a propane burner (Leader Evaporator, St. Albans, VT). Each treatment was applied to syrup for 180 minutes and each of the four treatments was run in duplicate. The specific details of each of the four treatments are described below.

Heating Only

For this treatment, syrup was heated continuously and maintained at boiling throughout the duration of the experiment.

Air Injection with Heating

For this treatment, an air injection system modified to fit the dimensions of the canning unit (D&G USA, Fairfax, VT) was operated while syrup was heated continuously throughout the duration of the experiment.

Air Injection without Heating

For this treatment the air injection system was run continuously with syrup at room temperature throughout the duration of the treatment.

Heating Under Vacuum

Syrup was placed in a large stainless steel container fitted with a hard plastic cover. Vacuum was applied to the inside of the container with a vacuum pump (Model E2M-1, Edwards High Vacuum Pump Co., Crawley, Sussex, England) through tubing connected to a fitting in the plastic cover. Vacuum was maintained at approximately 15"Hg. Vacuum was applied while syrup was heated continuously and maintained at boiling on a propane stove throughout the duration of the experiment. Vacuum was interrupted to collect intermediate syrup samples.

Syrup temperature was monitored and recorded throughout the duration of each experiment with a Type-K thermocouple and Cole-Parmer Digi-sense Model 92801-10 Thermocouple Scanner. Syrup samples were collected at the beginning of each experiment and at 30-minute intervals until its conclusion. At the conclusion of each experiment, each syrup sample collected was adjusted, if necessary, to syrup density (66.9°

Brix minimum) with deionized water. The color of each sample was determined as the percent light transmittance at 560 nm with a Spectronic Genesys 8 spectrophotometer (Thermo Electron Corp., Waltham, MA) using glycerol as a 100% transmittance standard. The quantity of 2,5-dimethylpyrazine and other volatile flavor compounds in each syrup sample was determined by solid-phase microextraction (SPME) and gas chromatography time-of-flight mass spectrometry (GC-TOF-MS) at the Sugar Processing Research Institute, Inc. (New Orleans, LA). The relative quantities of each compound were expressed as peak area counts. The mean and standard error of the color, temperature and 2,5-DMP composition of syrup at each time-point of each treatment were calculated.

Results and Discussion

Figure 1 shows the average temperature of syrup during the three treatments in which heat was applied, and indicates that both air injection during heating and heating under vacuum were effective in maintaining lower temperatures over the course of treatment than applying heat only.

Heating syrup under vacuum resulted in the lowest temperatures. Applying vacuum allowed boiling to occur at approximately 160-170°F throughout the course of treatment, approximately 40-50°F lower than with heating only (Figure 1). Air injection during heating was also effective in maintaining lower temperatures than with heating only. The temperature of syrup heated with air injection was consistently about 20°F lower than syrup that was heated only (Figure 1). A gradual increase in temperature similar to that observed in syrup treated with heating only was observed in this treatment, consistent with the increase in boiling point associated with increasing syrup density.

Figure 2 shows the average quantity of 2,5-DMP present in syrup samples collected over the course of each treatment. All experiments began with the same metabolized syrup, so all syrup contained very similar amounts of 2,5-DMP at the beginning of each experiment. The amount of 2,5-DMP remained essentially unchanged in syrup treated with air injection only (Figure 2), indicating this is not an effective method for remediating metabolism off-flavor. However, the quantity of 2,5-DMP did decrease progres-

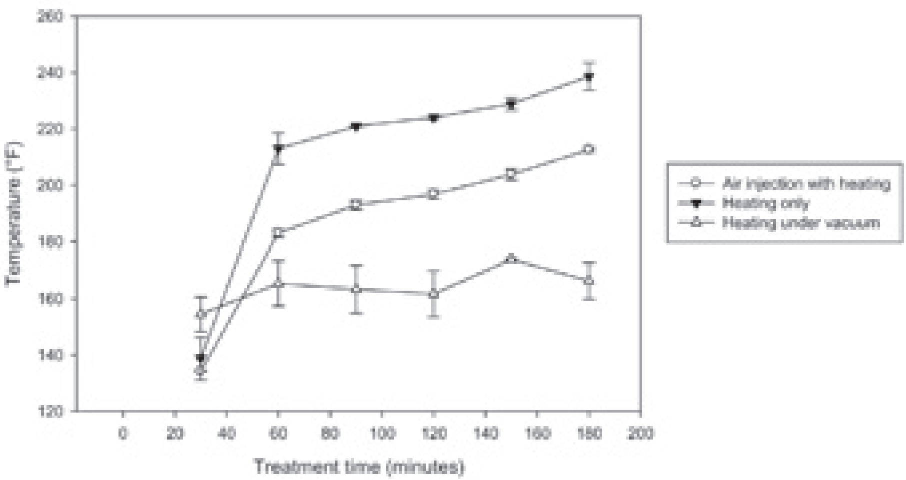

Figure 1. Mean temperature (± standard error) of maple syrup at 30-minute intervals during the application of three treatments investigated for efficacy in remediating metabolism off-flavor: air injection of syrup during syrup heating, heating syrup in an open pan, and heating syrup while vacuum was applied. n=2 at each timepoint.

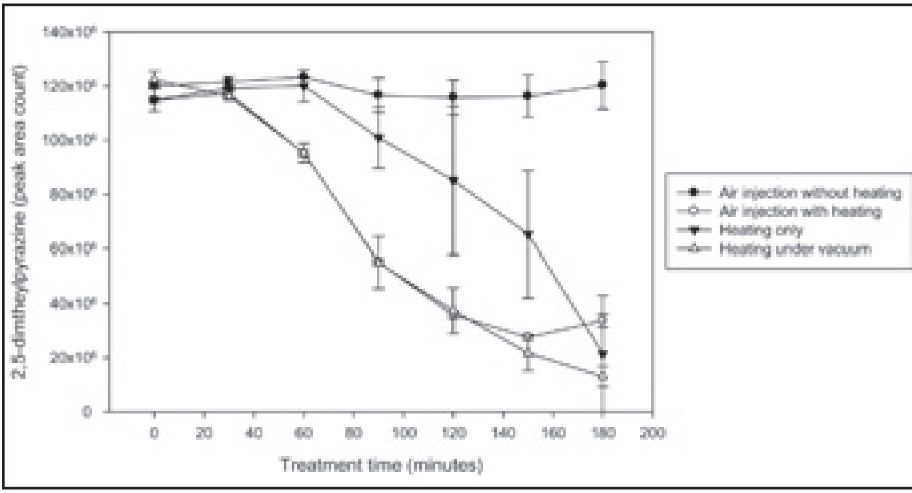

Figure 2. Mean (± standard error) quantity of 2,5-dimethylpyrazine (2,5-DMP) in maple syrup collected at 30-minute intervals during the application of four treatments investigated for efficacy in remediating metabolism off-flavor: air injection of syrup at ambient temperature, air injection of syrup during syrup heating, heating syrup in an open pan, and heating syrup while vacuum was applied. n=2 at each timepoint.

sively over the course of treatment in syrup treated with the other three remediation treatments examined. Syrup treated with air injection during heating and heating under vacuum initially showed the largest reductions in the quantity of 2,5-DMP (Figure 2). Reductions began after 60 min of treatment and continued at similar rates in the two treatments until the conclusion of treatment (except in syrup treated with AH, which showed a slight increase in 2,5-DMP at the very end of treatment). Syrup treated with heating only also showed progressive reductions in the quantity of 2,5-DMP over the course of treatment (Figure 2). Although the initial reductions in 2,5-DMP were smaller than those observed in syrup treated with AH or VH, reductions in the quantity of 2,5-DMP began after 90 min of treatment and continued progressively throughout the duration of treatment. Interestingly, although the initial rates of 2,5-DMP reduction differed between the treatments, by the end of treatment syrup treated with all three treatments contained similar amounts of 2,5-DMP (Figure 2). Thus, after 180 minutes, all three treatments were equally effective in reducing the quantity of 2,5-DMP present in metabolized syrup.

Though the three different heating treatments were equally effective in clearing 2,5-DMP from metabolized syrup, the optimum remediation treatment should result in the least syrup darkening. Figure 3 shows the average color (as % light transmittance) of syrup samples collected over the course of each treatment. Syrup treated with air injection at room temperature darkened slightly over the course of treatment. The greatest darkening by the end of treatment was observed in syrup treated with air injection during heating (Figure 3), which is surprising given the lower syrup temperatures maintained during application of this treatment. Syrup treated with heating under vacuum showed the least amount of darkening, while syrup treated with heating only darkened to levels intermediate of the other two heating treatments (Figure 3). Thus, although air injection with heating yielded large reductions in the quantity of 2,5-DMP in syrup, it also resulted in extensive syrup darkening and is thus not an ideal method for remediating

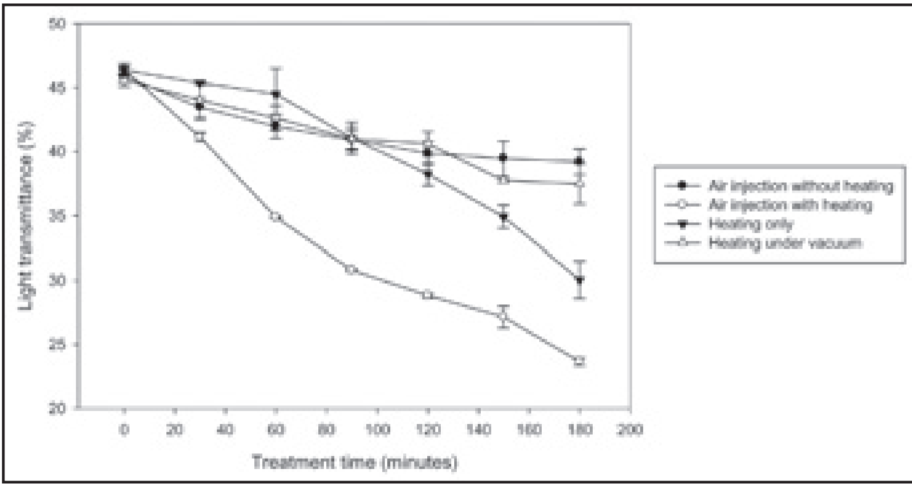

Figure 3. Mean (± standard error) percent light transmittance at 560nm of maple syrup collected at 30-minute intervals during the application of four treatments investigated for efficacy in remediating metabolism off-flavor: air injection of syrup at ambient temperature, air injection of syrup during syrup heating, heating syrup in an open pan, and heating syrup while vacuum was applied. n=2 at each timepoint.

metabolized syrup. The treatment which produced the greatest reductions in 2,5-DMP with the least impact on syrup color was heating syrup under partial vacuum.

As a final step, informal sensory evaluations were conducted to confirm reductions in 2,5-DMP quantity corresponded to reductions in the metabolism off-flavor of syrup. In blind tasting of syrup treated with the four remediation treatments tested, syrup treated with heating only was identified as having the best overall flavor and also the least detectable metabolism off-flavor. This clear preference for the flavor of syrup treated with heating only may be at least partly explained by examining the composition of a class of flavor compounds often associated with maple flavor, the cyclopentenones (CPs), in the treated syrup. Figure 4 shows the average quantity of total CPs in syrup samples collected over the course of each treatment. As with 2,5-DMP, there was no apparent change in the quantity of cyclopentenones over the course of treatment in syrup treated with air injection only. The quantity of CPs decreased progressively in syrup treated with heating under vacuum (Figure 4). Likewise, in syrup treated with air injection during heating, the quantity of CPs decreased during the initial treatment period, though it increased slightly toward the end of treatment. In contrast, the quantity of CPs increased progressively over the course of treatment in syrup treated with heating only (Figure 4). In addition, this syrup contained much greater quantities of CPs at the later stages of treatment than syrup treated with either AH or VH. Thus, in syrup treated with heating only, the quantity of off-flavor compounds (2,5-DMP) was reduced, while the quantity of compounds with more positive flavor attributes (CPs) simultaneously increased.

In conclusion, the results of this study suggest that of the treatments tested, heating syrup in an open pan was the most effective treatment for the remediation of syrup with metabolism off-flavor. This treatment yielded similar reductions in the quantity of 2,5-DMP in syrup as heating syrup under vacuum and applying air injection during heating. Though it resulted in greater syrup darkening than heating syrup under vacuum, heating syrup in an open pan yielded the clearest overall improvements in syrup fla-

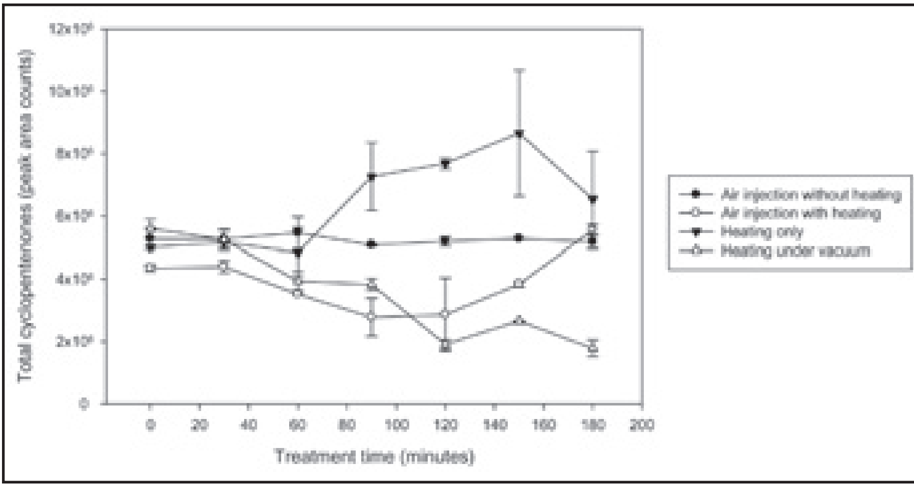

Figure 4. Mean (± standard error) quantity of total cyclopentenones (CPs) in maple syrup collected at 30-minute intervals during the application of four treatments investigated for efficacy in remediating metabolism off-flavor: air injection of syrup at ambient temperature, air injection of syrup during syrup heating, heating syrup in an open pan, and heating syrup while vacuum was applied. n=2 at each timepoint.

vor, both on the basis of improvements in perceived syrup flavor and an increased composition of some more desirable flavor compounds in the syrup. In addition, heating syrup in an open pan is the most practical treatment and could be relatively easily employed by most maple producers. Although not part of this research, this remediation technique might also prove to be useful in removing or reducing other volatile off-flavors in maple syrup. More investigation will be necessary to determine the effectiveness of this approach in remediating other types of off-flavors.

Recommendations for Remediation Treatment Application

The following are basic guidelines for applying the remediation treatment. All equipment should be approved for food use and suitable for the intended purpose. Always use extreme caution and appropriate safety and personal protective equipment when heating syrup to high temperatures. There is an increased danger of burning syrup, scorching pans and personal injury from contact with the hot syrup. Heating syrup to high temperatures results in syrup with very high density, which can behave unpredictably and has an increased propensity to produce large splashes of scalding hot syrup. Syrup treated in this manner may darken appreciably. In severely metabolized syrup, the process can be repeated. Some blending of treated syrup with appropriate (good) tasting syrup may be necessary to achieve the final desired color grade and flavor.

1. Place the syrup to be remediated in equipment designed for heating syrup, such as a finishing pan or canning unit.

2. Heat the syrup until it reaches a temperature between 235 and 240°F. As the syrup boils and concentrates, the likelihood of foaming increases. The syrup batch must be monitored constantly. Small amounts of defoamer should be added when necessary. Excessive stirring of the hot syrup can lead to crystallization and should be avoided.

3. Remove the syrup from the heat and allow it to cool sufficiently enough to allow the safe addition of water. Carefully and slowly add clean, potable water to adjust the

syrup back to standard syrup density. Adding water to the hot syrup can cause the water to boil spontaneously, causing the syrup to splash unpredictably. Therefore extreme caution must be used during this step.

4. Reheating syrup may cause nitre to develop, and filtering with an appropriate filter may be necessary prior to grading and packing.

5. The finished syrup should be graded and packed in accordance with the appropriate federal, state or provincial regulations.

Acknowledgements

This work was supported by U.S. Department of Agriculture CSREES Grant 2005-34430-16529. We thank Henry Marckres (Vermont Agency of Agriculture), Roger Gross and Haven King (Maple Grove Farms of Vermont), David Marvin (Butternut Mountain Farm), and Jerry Kless (Citadelle) for helpful discussions on metabolism off-flavor and for help in acquiring maple syrup with metabolism off-flavor.

References

Akochi-K., E., Alli, I. and Kermasha, S. 1997. Characterization of the pyrazines formed during the processing of maple syrup. Journal of Agricultural and Food Chemistry 45: 3368-3373.

Alli, I., Akochi-K., E. and Kermasha, S. 1992. Flavor compounds in maple syrup. Food Science and Human Nutrition (Ed. G. Charalambous). Elsevier Science Publishers, Amsterdam, The Netherlands. pp 131-140.

Duffaut E., Godshall, M.A. and Grimm, C. 2004. The effect of ozone and air on off-odors in beet sugar. Proceedings of the 2004 Conference on Sugar Processing Research, "New Developments in the Sugar Processing", Atlanta, GA, USA, April 4-7, 2004. pp 193-208.

Maga. J.A. 1992. Pyrazine update. Food Reviews International 8(4): 479-558.

Perkins, T.D., Morselli, M., van den Berg, A.K. and Wilmot, T.R. 2006. Maple chemistry and quality. North American Maple Syrup Producers Manual, 2nd ed. (Eds. Heiligmann, R.B., Koelling, M.R. and Perkins, T.D.). The Ohio State University, Ohio, USA. pp 294-300.

Perkins, T.D. and van den Berg, A.K. (in press) Maple syrup - production, composition, chemistry, and sensory characteristics. Advances in Food and Nutrition Research (Ed. S.L. Taylor). Academic Press, San Diego, CA, USA.

van den Berg, A.K., Perkins, T.D., Godshall, M.A., Lloyd, S.W. and Isselhardt, M.L. 2009a. Metabolism off-flavor in maple syrup Part I: Identification of the compound responsible for metabolism off-flavor. Maple Syrup Digest 21A(1): 15-80.

van den Berg, A.K., Perkins, T.D., Isselhardt, M.L., Godshall, M.A. and Lloyd, S.W. 2009b. Effects of air injection during sap processing on maple syrup color, chemical composition and flavor volatiles. International Sugar Journal 111(1321):37-42.