Final Report: Distillation of Flash Détente Condensate for Recovery of Ethyl Acetate and Other Aromas

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1. Original goals and objectives of the overall project.

Thermovinification (Flash Détente) is more efficient at extracting pigments, fermentable sugars and destroying enzymatic activity in crushed fruits. This allows greater color in the product, but can also remove compounds responsible for aroma profiles in products. In order to determine if this process would work for fruit wines, and if it were possible to recover the aroma producing compounds, a pilot scale version needed to be developed and tested. Therefore, the funded work included the following proposed goals:

I. Development of laboratory scale experimental procedures and analyses to predict successful scale-up of the process.
II. Use of analytical procedures to compare small- and large-scale operations.

2. Abstract.

Profitability in the wine industry is contingent on grape quality, which can be affected by many environmental factors. During some production cycles, grapes become unusable due to these impacts. However, technologies are being developed to remove undesirable attributes of these grapes and to enhance extraction of desirable components. One of these technologies is Flash Détente, or thermovinification. This process allows greater extraction of pigments and fermentable sugars, and the heating process allows enzyme inactivation. In addition to extraction and elimination of undesirable aromas, the process may remove compounds contributing to desirable aromas. Therefore, the proposed work was designed to determine which of the desirable aroma generating compounds were extracted and if it were possible to recover them. Desirable compounds and aroma producing compounds with lower boiling points, such as ethyl acetate, tended to be collected in the first 10% of the distillation fractions. Therefore, future work in this area could focus its attention on recovery of desirable compounds on the earliest fractions produced by the process.

3. Literature review.

Vineyard yields and grape chemistry depend greatly on the environmental factors surrounding the vineyard. U.S. production of wine has steadily increased over the past decade reaching over 3.5 billion liters in 2017.[1] In attempts to keep up with growing production, winemakers have begun to employ a new technique called Flash Détente or thermovinification. Flash Détente uses elevated temperature and reduced pressure to release water contained in grape skins. With this technology winemakers can remove undesirable character such as methoxypyrazines (grassy, bell pepper flavor), denature laccase proteins (a byproduct of mold in grapes), and even eliminate vehicle exhausts or pollutants absorbed in grape skins. They are also able to increase sugar by 1-3 Brix, increase anthocyanins by 30%, and enhance tannin extraction.

Thermovinification effectively increases crop yields by making grapes that were once unusable viable for production.

4. Results and Discussion.

Flash Détente

Typically, red grapes are crushed and the fresh must is immediately fermented. Upon completion of the fermentation the grapes are pressed, settled, aged, filtered, bottled, and sold for consumption. Flash Détente processes are placed between the crushing and fermentation steps. **Fig. 1** is a schematic flow diagram of a generic Détente process. Crushed red grapes are rapidly heated in a furnace to 185 °F over 2 to 5 minutes. The effluent is introduced to a low-pressure chamber from which the liquid phase is directed to a fermenter. Optimum temperatures for red wine fermentations range between 70 °F and 85 °F. The vapor phase was tested on a bench scale to see what desirable aromas that might have been removed during the flashing process could be recovered.

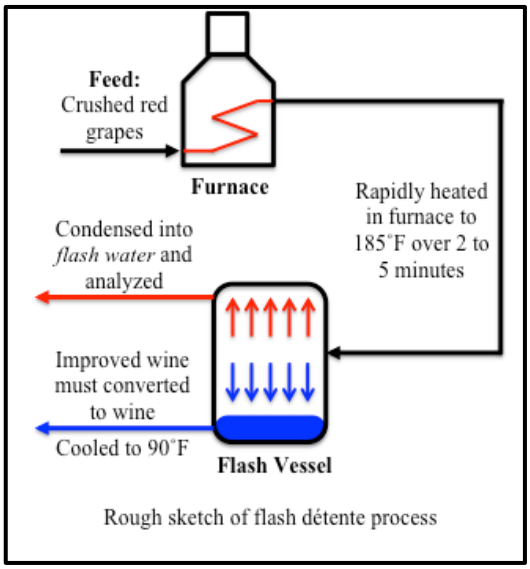

Figure 1. Rough sketch of Flash Détente process

Mass Spectrometry

There was concern that the vapor phase of the Flash Détente process might have included compounds that produce desirable aromas. The vapor was condensed into flash water samples and analyzed. As the name implies, flash water consisted of >99% water by mass. Mass spectrometry was used to identify the character of aroma compounds that existed in the flash water samples of five different grape varieties: Cabernet Franc, Dornfelder, Front Gris, Brown Marquette, and Merlot. **Table 1** shows the compounds that were identified using *GC/MS* with a quadrupole mass analyzer. Ethyl acetate was found to exist in the highest concentration of the 12 most significant compounds measured in the mass spectra. Ethyl acetate was also measured consistently regardless of the grape variety. Compounds and aromas weren't measured in concentrations above a tenth of a percent concentration by mass. Of those, 2, 4-Di-tert-butyl phenol was also consistently measured in all grape varieties. 2, 4-Di-tert-butyl phenol is a common compound in plastics that tends to leach into aqueous solutions. It is believed this compound must have leached into the samples while they were stored in the plastic jugs used to collect and transport the samples.

Table 1. Notable compounds in flash water samples of five different varieties determined using *GC/MS*

	Grape Variety				
	Cabernet Franc (wt. %)	*Dornfelder (wt. %)*	*Front Gris (wt. %)*	*Brown Marquette (wt. %)*	*Merlot (wt. %)*
Ethyl Acetate	>0.01	>0.01	>0.01	>0.01	>0.01
1-Tetradecanol	<0.01	-	-	-	-
2-Octanol	<0.01	-	-	-	-
Hexanoic acid	<0.01	<0.01	<0.01	-	<0.01
Pentanoic acid	<0.01	-	-	-	-
Phenylethyl alcohol	-	<0.01	<0.01	-	<0.01
1-Hexanol	-	-	-	-	<0.01
2-Methyl propanoic acid	<0.01	-	-	-	-
3-Methyl-1-butanol	-	<0.01	-	-	<0.01
2, 4-Di-tert-butyl phenol	<0.01	<0.01	<0.01	<0.01	<0.01
Unknown acids	-	<0.01	-	-	-
Unknown esters	-	<0.01	-	-	-

Fractional Distillation

The Berglund group was intrigued by the possibility of recovering desirable compounds in wine such as ethyl acetate via distillation. Chemical recovery using solvent extraction was also a possibility, but solvents tend not to be very "wine-friendly" and they can be costly to remove. Distillation is a more elegant technique that is more familiar in the beverage processing industry.

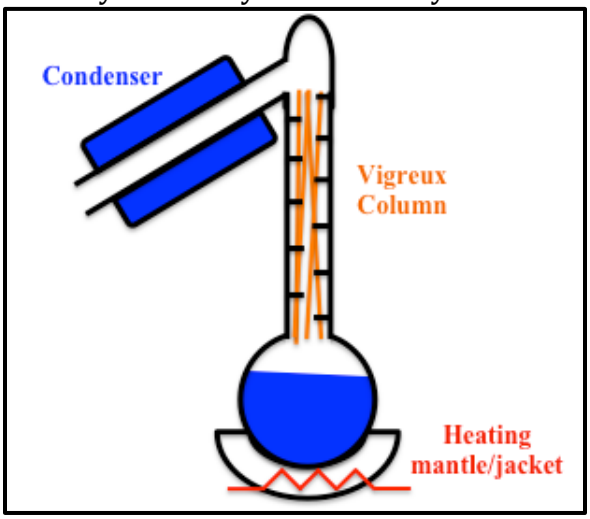

Figure 2. Picture diagram of fractional

Fig. 2 is a graphic illustration of the distillation setup used to analyze samples. Flash water (100 *mL*) was placed in a round bottom flask with boiling chips over a heating mantle. The sample was boiled through a vigreux copper column into a condenser fitted with a cooling water jacket. Distillation fractions were collected in a clean graduated cylinder then placed in 20 *mL* scintillation vials. Five fractions of 10 *mL* were collected followed by two 15 *mL* fractions. The remaining 20 *mL* was removed from the end pot and also analyzed. The ethyl acetate contents of distillation fractions from the cabernet franc grape flash water are presented in **Fig. 3**. Ethyl acetate was concentrated to approximately 0.04 *wt. %* by mass in first 10 *mL* fraction. The concentration of ethyl acetate in subsequent fractions remained at about 0.01 *wt. %*. Heavier compounds tended to elute in later fractions of the distillations.

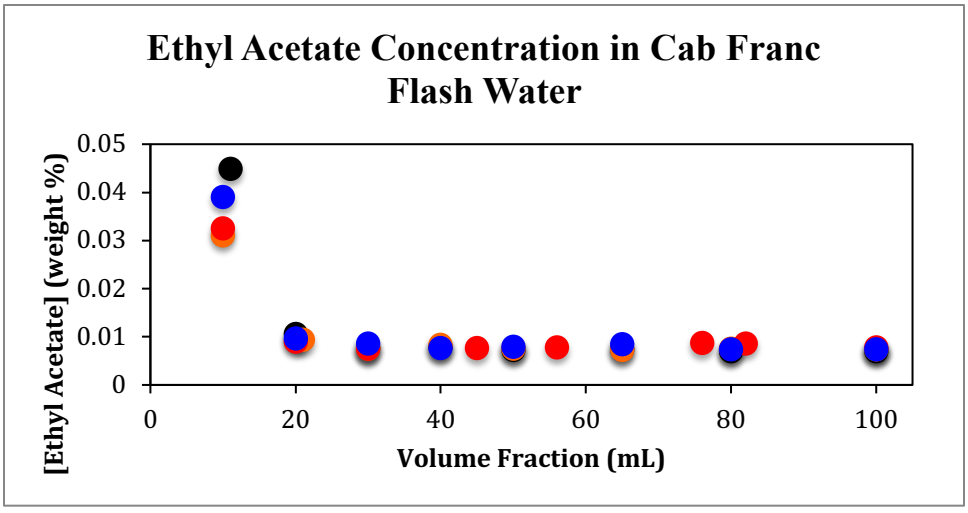

Figure 3. Distillation fractions from four replicates of Cabernet Franc samples analyzed using gas chromatography. Ethyl acetate has a boiling point of 77.1°C. Each color represents a replicate of the analysis.

Summary and Future Recommendations

Flash Détente allows winemakers to produce enhanced wines and to improve yields of their viticulture. Condensates from running Flash Détente on crushed grapes were analyzed using *GC/MS*. Ethyl acetate was measured at the most relevant concentrations. Desirable compounds and aromas with lower boiling points, such as ethyl acetate, tended to be collected in the first 10 *mL* of distillation fractions. Heavier and acidic compounds, such as hexanoic acid, tended to elute in later distillation fractions. Unfortunately, the primary investigator of this project passed away before it could undergo further testing on a large distillation system. It was desired to run the distillation experiments on a larger scale using a copper trayed column. It was also desired to perform a secondary distillation on the first 10 *mL* fractions of each grape variety to see if it was possible to further concentrate the recovered ethyl acetate.

5. The period of time during which the research was conducted.
   January 1, 2017 – December 13, 2018

6. Work accomplished during the period, including methods.
   The methodologies used for this project were not significantly modified from the original proposal, so the techniques used for each step of the work is described there, and in the results and discussion section of the report. The only part of the work that was not possible was a comparison between the laboratory scale work and a larger unit.

7. Communications Activities, Accomplishments, and Impacts.
   This project developed possible intellectual property and as a result none of the results have been published or discussed in a public setting.

8. Funding Partnerships.
   Dr. Berglund died in December and no further work is planned in this area.

References

[1] BW166/Gomberg, Fredrikson & Associates. "California Wine Sales in U.S. Market Hit $35.2 Billion in 2017" Wine Institute. *U.S. Department of Commerce* **May 23, 2018**.