

THE TROUBLE WITH TERPENES

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ABSTRACT

The expanded use of high vacuum distillation equipment in the cannabis and hemp processing industry has demonstrated the challenges associated with the processing of terpenoid fractions within the complex chemistry of the extracted oils. The terpenoid fraction normally constitutes the lowest boiling point fraction of extracted oils and frequently its separation from the extracted oil is required prior to separating and concentrating the higher boiling cannabinoid fraction at high vacuum levels. Further, the terpenoids can accumulate in vacuum equipment affecting the equipment performance and potentially damaging the equipment.

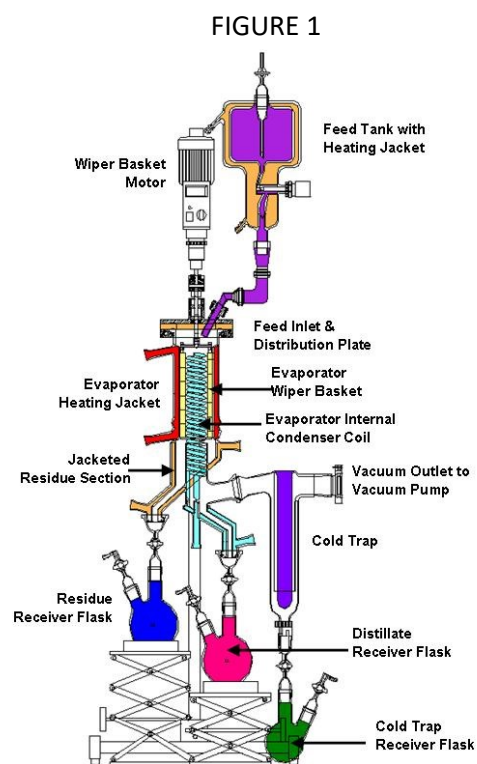
This article discusses the high vacuum distillation of hemp and cannabis oils in short path distillation equipment (also referred to as molecular separation), and the process considerations related to the separation of terpenes from the extracted oil. Recommendations are also presented to implement the best operating practice for distillation equipment to achieve optimal processing results.

SINGLE-STAGE DISTILLATION OF CANNABIS OR HEMP

In a typical single stage short path distillation, a crude oil extract will be distilled into three separate fractions: (a) high molecular weight residue fraction; (b) concentrated CBD or THC distillate fraction; and (c) the terpene fraction which will be captured in the cold trap. Figure 1 depicts where these three fractions will be collected on a Chemtech KDL-6 Evaporator.

Typical operating conditions of the Single Stage KDL-6 evaporator (or other size evaporators manufactured by Chemtech) experienced by clients in the hemp or cannabis fields are indicated in Table 1 below:

Feed Tank Temperature:	80°C
Feed Rate:	2 kg/hour
Evaporator Jacket Temperature:	160°C
Evaporator Residue Temperature:	110°C
Evaporator Condenser Temperature	80°C
Evaporator Cold Trap Temperature	Approx. -40°C
Vacuum (expressed as absolute pressure)	<0.050 mm Hg
Evaporator Atmospheric Equivalent Temperature (or AET) of Operation	>475°C



The primary separation of the high molecular weight waxes in the residue, and the more valuable target molecules in the distillate (THC and/or CBD) is quite easily achieved. Capturing all of the terpene products in the cold trap is however a more difficult endeavor. The challenges associated with capturing

the terpenes can be explained by examining a few scientific principles which govern the transition of molecules from the liquid to vapor phase (e.g., boiling), and the return to the liquid phase (condensation).

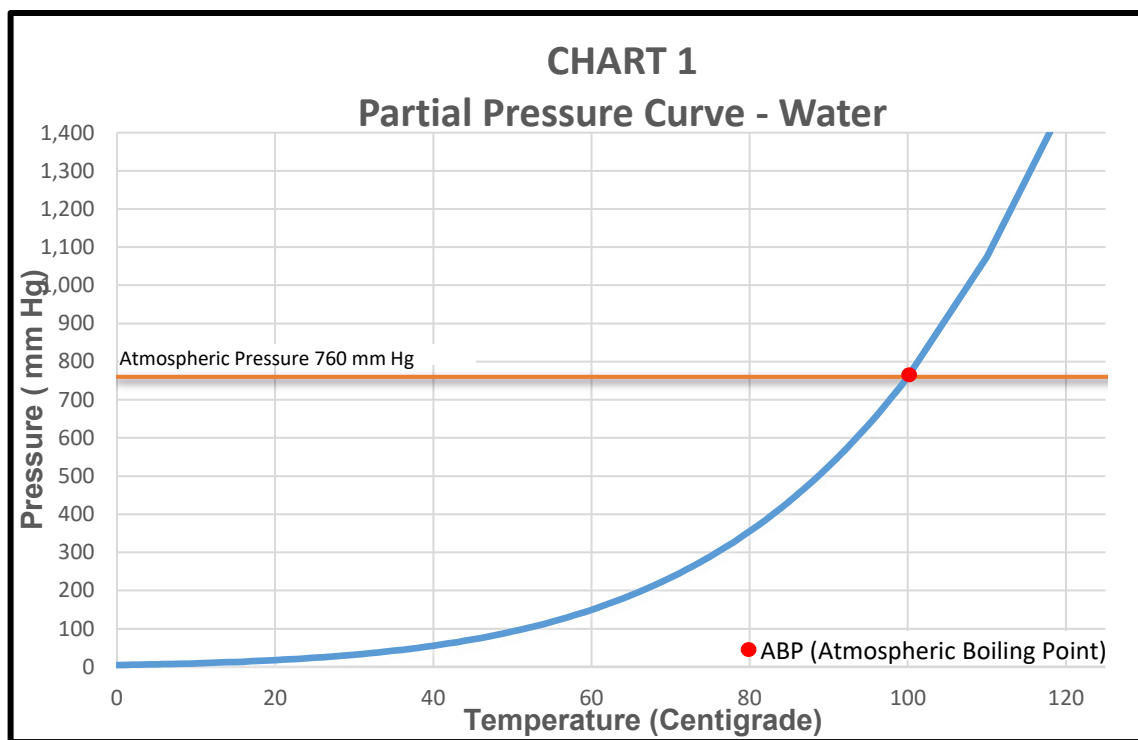
Principles of Distillation

As suggested above, distillation encompasses the phase transformation of a liquid to vapor phase and subsequent condensation of the vapor phase molecules. Frequently the boiling point of a product is used as a reference when considering the temperature at which a liquid prefers to transition to a vapor state. However, the boiling point of a liquid does not tell the entire story, and a more appropriate reference associated with the transition of a liquid to a vapor is the "Partial Pressure Curve." This discussion is most easily understood when we consider a molecule we are all familiar with, water (or H₂O). We are probably also familiar with the two common phase transformation points of water, the melt point (or freeze point if you prefer) of 32°F (or 0°C), and the boiling point of 212°F (or 100°C). However, not a lot of thought is focused upon what is happening to a mass of water between the melting point and the boiling point. In fact, water in a container at any temperature between 32°C and 212°C will exhibit two phases, liquid and vapor. The vapor phase is not very apparent until the temperature of the water approaches the boiling point, but nevertheless there is still vapor. Consider that a puddle of water on a warm day will evaporate relatively quickly (depending on temperature), or in scientific nomenclature it will transition into the vapor phase. So, although boiling never occurs evaporation takes place based upon the partial pressure of the water as a function of the atmospheric temperature (and pressure).

Enter, the "Partial Pressure Curve." In 1888 a French Scientist, Louis Charles Antoine, a French researcher, developed a somewhat complex equation¹ which accurately predicted the relative pressure of water vapor in the air which when summed with the dry air pressure constituted the total "Atmospheric Pressure." The equation included three (3) constants which are unique to any given substance. The equation calculated the partial pressure of a liquid as a function of temperature using the metric scales of pressure and temperature (i.e. mm Hg and °C).

Chart 1, indicated below, illustrates the partial pressure curve of water as defined by the Antoine Equation. As suggested earlier, although water may not be at its boiling point of 212°F, it has vapor pressure which is a function of its temperature. In the curve below, atmospheric pressure is represented as 760 mm Hg (29.92" Hg or 14.7 psi), and the boiling point of water, 100°C (or 212°F) marks the intersection of atmospheric pressure with the partial pressure of water at this temperature.

¹ Antoine, C. (1888), "Tensions des vapeurs; nouvelle relation entre les tensions et les températures" [Vapor Pressure: a new relationship between pressure and temperature], *Comptes Rendus des Séances de l'Académie des Sciences* (in French), 107: 681–684, 778–780, 836–837.



We are vaguely aware of the fact that water exhibits a vapor phase under atmospheric conditions, but below the boiling point, because the weatherman keeps talking about the “relative humidity” of the air, or in other words the amount of water vapor in the air. Saturation of the vapor phase may occur especially when temperatures are falling, and when 100% saturation occurs, we experience (you guessed it) rain, or in scientific terms transition from vapor to liquid phase. This is of course what we hope to achieve in relation to cannabinoids and terpenes when distilling (under high vacuum) the extracted oils from hemp or cannabis.

While we are on the subject of boiling point and vapor pressure as related to pressure and temperature conditions, it is useful to understand a couple of equations which are: (a) the Clausius Clapeyron Equation² and (b) the Maxwell-Bonnell Correlation³, which equation provides a basis for determining the boiling point of a substance under vacuum conditions. For practical purposes, the Maxwell-Bonnell correlation is perhaps the easier method for evaluating boiling points at different pressures, and we will use this methodology in a later example.

² Rudolf Julius Emanuel Clausius and Benoît Paul Émile Clapeyron Equation (independent publications Clapeyron in 1834 and Clausius in 1850). There are many variations of the equation with one indicated below:

$T_2 = 1 / \{ [1/T_1] - [R \times \ln(P_2/P_1)] / [\Delta H_{vap}] \}$ - Where : T_2 is the temperature of interest; P_2 is the corresponding vapor pressure at the temperature of interest T_2 ; T_1 is the temperature at another point; P_1 is the corresponding vapor pressure at the known temperature T_1 ; ΔH_{vap} is the molar enthalpy of vaporization

³ J. B. Maxwell, and L. S. Bonnell, of Esso Research and Engineering Company, introduced the Maxwell-Bonnell Correlation in a technical article titled: Derivation and Precision of a New Vapor Pressure Correlation for Petroleum Hydrocarbons, published in Ind. Eng. Chem., July 1957, 49 (7), pp 1187–1196.

Maxwell-Bonnell Equation: $AET = (748.1 \times A / \{ [1 / (T + 273.1)] + 0.3861 \times A - 0.00051606 \}) - 273.1$

where: AET = Atmospheric Equivalent Temperature, °C

T = Temperature, °C

A = a pressure term, depending on the observed pressure

Before we evaluate distillation conditions, let us consider for a moment some of the chemical characteristics of hemp and cannabis oils. The extracted oils from hemp or cannabis plants likely contain over 300 different molecules all of which have their own distinct partial pressure curves, just like water. Let's also consider the fact that these oils contain varying fractions of low boiling point terpenes (or more broadly, terpenoids) as well as the sought-after cannabinoids. Table 2 below illustrates just a small sample of the terpenes and cannabinoids we might expect in an extracted oil. However, it is apparent that the boiling point of the most frequently encountered terpenes is considerably below that of the cannabinoids, by almost 200°C (note the actual boiling point range of terpenoids is approximately 150°C to 350°C).

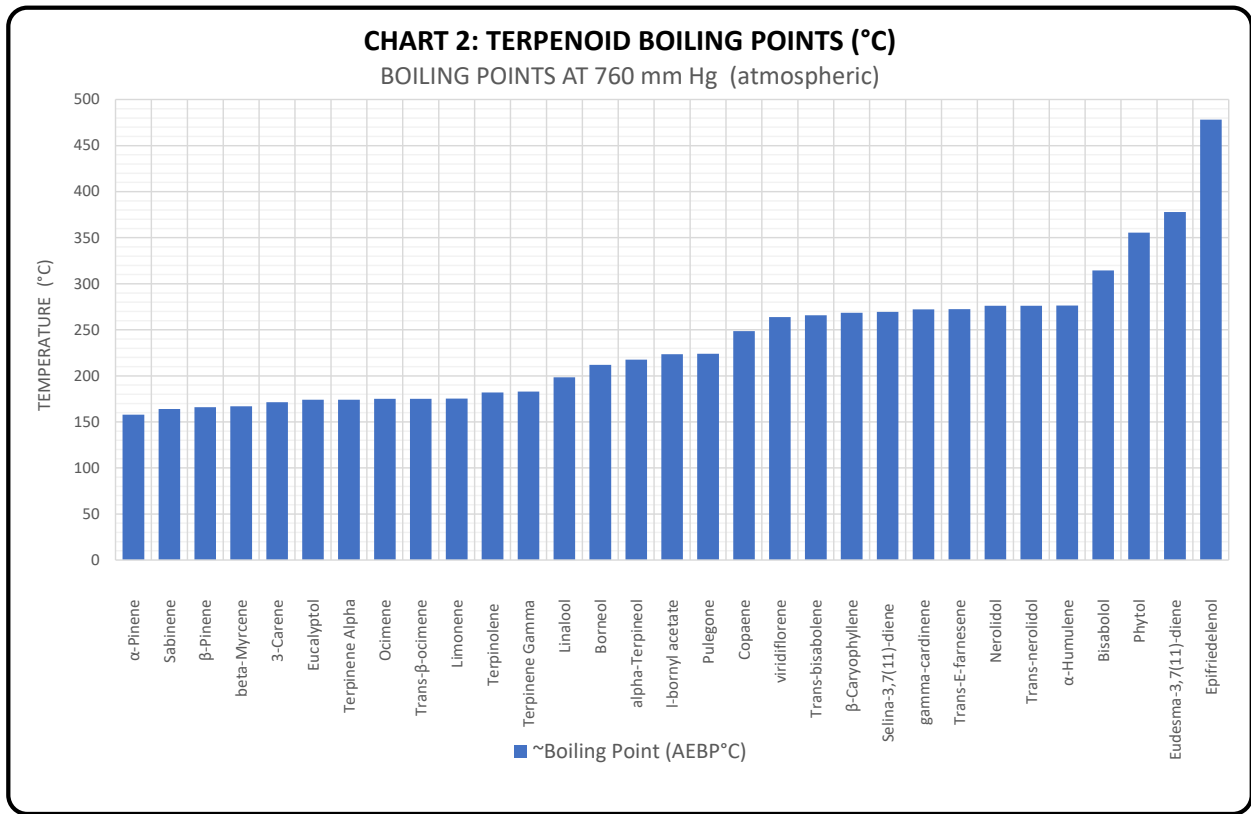
TABLE 2

Product (acronym)	Boiling Point (°C)		Boiling Point (°F)	
	Value	Unit	Value	Unit
α – Pinene (monoterpene)	155	°C	311	°F
β-Caryophyllene (sesquiterpene)	160	°C	320	°F
β-Myrcene (monoterpene)	168	°C	334	°F
D-Limonene (cyclic terpene)	176	°C	349	°F
Linalool (terpene)	198	°C	388	°F
Humulene (sesquiterpene)	198	°C	388	°F
THC-A	339	°C	642	°F
THC	408	°C	766	°F
CBD	438	°C	820	°F
CBN	445	°C	833	°F
CBC	489	°C	912	°F
CBG	NA			°F
CBD-A	NA			°F

In fact, it has been estimated that there are over 100 molecules in cannabis or hemp oils which fall into the chemical category of terpenoids. The terpenoids are most commonly recognized as the flavor and fragrance elements of cannabis and hemp oils, but medical research in recent decades has also recognized the terpenoids may also contribute significantly to the entourage effects of cannabis medical extracts. However, the fact that many of these terpenoids have relatively low boiling points compared to the cannabinoids complicates the distillation process where the concentrating of the cannabinoids, from oil extracts, is the main objective.

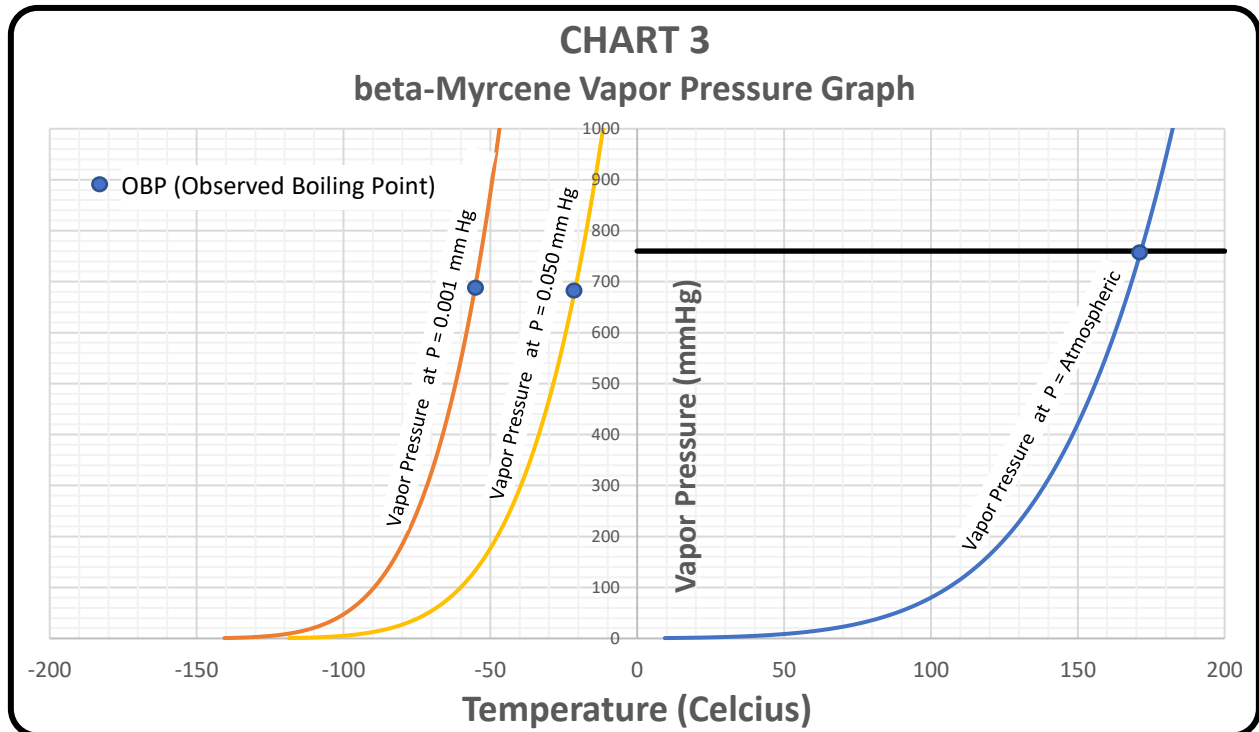
Consider, for a moment, the distillation objective of concentrating the cannabinoids THC and CBD from a crude cannabis or hemp oil extract which contains a multitude of molecules having boiling points both above and below that of THC and CBD (i. e., ~408°C and ~438°C, respectively). If this distillation is

conducted on a single stage short path distillation (SPD) system, the general procedure would be to operate the SPD at a jacket temperature of 160°C and an absolute pressure (or vacuum) of 0.005 mm Hg. These Temperature/Pressure conditions would suggest an Atmospheric Equivalent Temperature (AET) of 475°C which would assure the distillation of the majority of the CBD and THC molecules (i.e., CBD and THC molecules would vaporize in the evaporator and subsequently condense on the lower temperature condensing element operated at ~85°C, or considering AET condition, 365°C). Further, we must consider the operation and effectiveness of the cold trap whose function is to protect the vacuum system by condensing all lightweight molecules, like terpenes. Referring to the chart in Table 2, the light terpenoids have boiling points generally in the range of 155°C to 200°C, however there are some terpenoids which have boiling points as high as 500°C. Chart 2 below provides a more comprehensive listing of the boiling points associated with common terpenoids found in hemp and cannabis oils.



We have discussed briefly some of the characteristics of vapor pressure as a function of temperature, as defined by the Antoine Equation, and a liquids boiling point as a function of pressure, described by the Maxwell-Bonnell correlation, so let's explore a little deeper into these relationships as they related to cannabis and hemp compositions. Let's start this study by examining data associated with Beta Myrcene, a common terpenoid in cannabis or hemp. Chart 3 below illustrates the partial pressure curve for beta-Myrcene at atmospheric conditions (curve calculated using the Antoine equation is on the right) where the AEBP is approximately 168°C. The two curves to the left of the Antoine equation partial pressure curve represent adjusted curves based upon indexing the Antoine equation curve utilizing the Maxwell-Bonnell correlation which suggests the Observed Boiling Points (OBP) for absolute pressures of 0.050 mm Hg and 0.001 mm Hg are -22°C and -55°C, respectively. Of course, the Y-Axis relevant to the Antoine equation curve is not applicable to the Maxwell-Bonnell adjusted curves. However, the consequence of the estimated vapor pressure curves indicated in Chart 3, is that cold trap operating

temperatures should be significantly lower than the Maxwell-Bonnell adjusted boiling point to assure that the majority (if not all) of the vapors are in fact condensed in the cold trap. For example, if a cannabinoid oil containing quantities of beta-Myrcene is distilled at an absolute pressure of 0.001 mm Hg (high vacuum conditions), then the cold trap should be operated at or below -100°C to assure the majority of vapors are condensed in the cold trap. Vapors not condensed in the cold trap may result in contaminated vacuum equipment which may impair its performance. For example, rotary vane pumps utilize a special vacuum pump oil to form the vacuum chamber, and if the oil becomes contaminated the vacuum capability of the pump is impaired, and prolonged exposure to these conditions may result in pump failure.



For reference, it is useful to establish the baseline parameters for the boiling point value at high vacuum conditions, for the same terpenoids defined in Chart 2. Chart 4, indicated below, illustrates the dramatic reduction in boiling point for the referenced terpenoids.

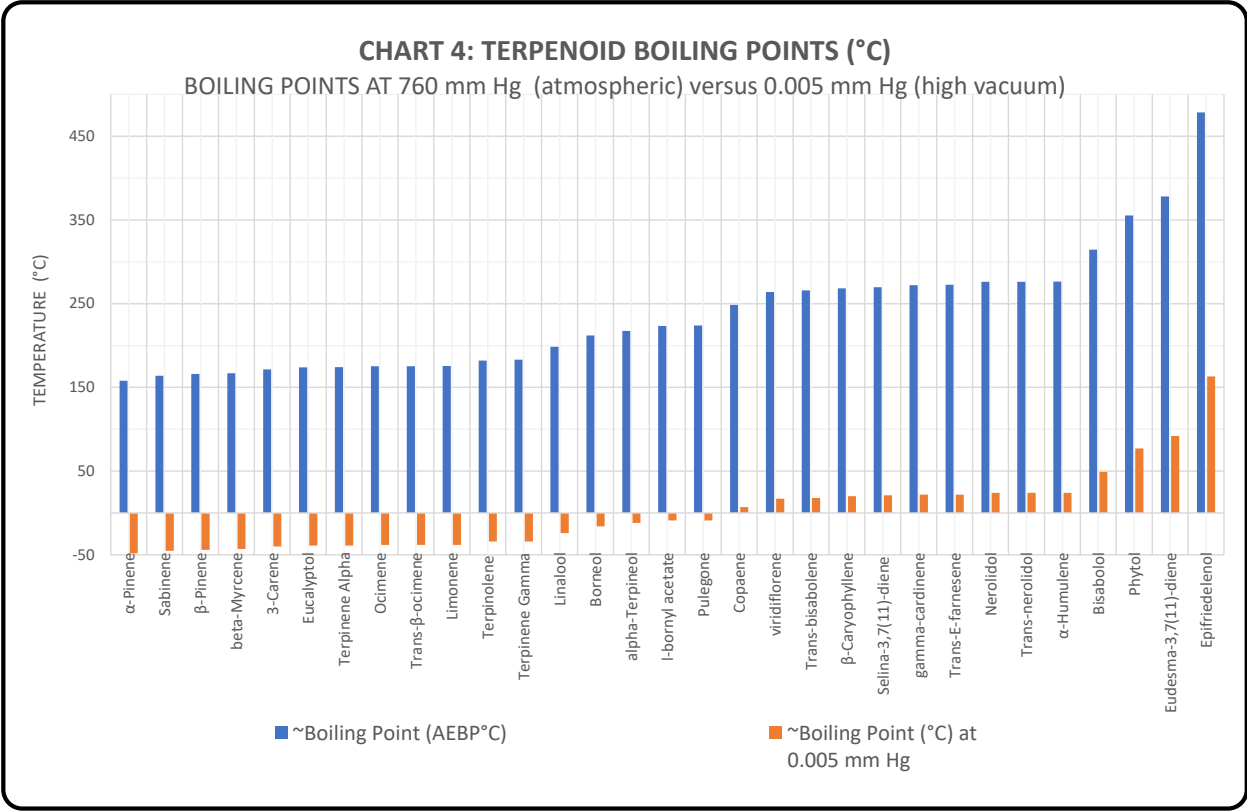
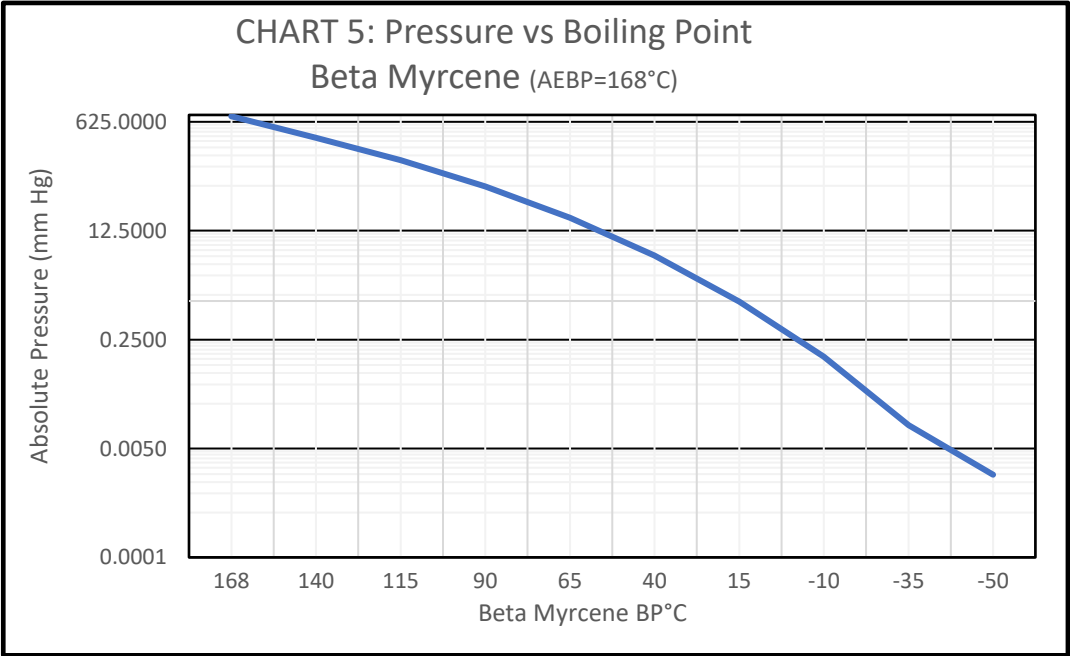
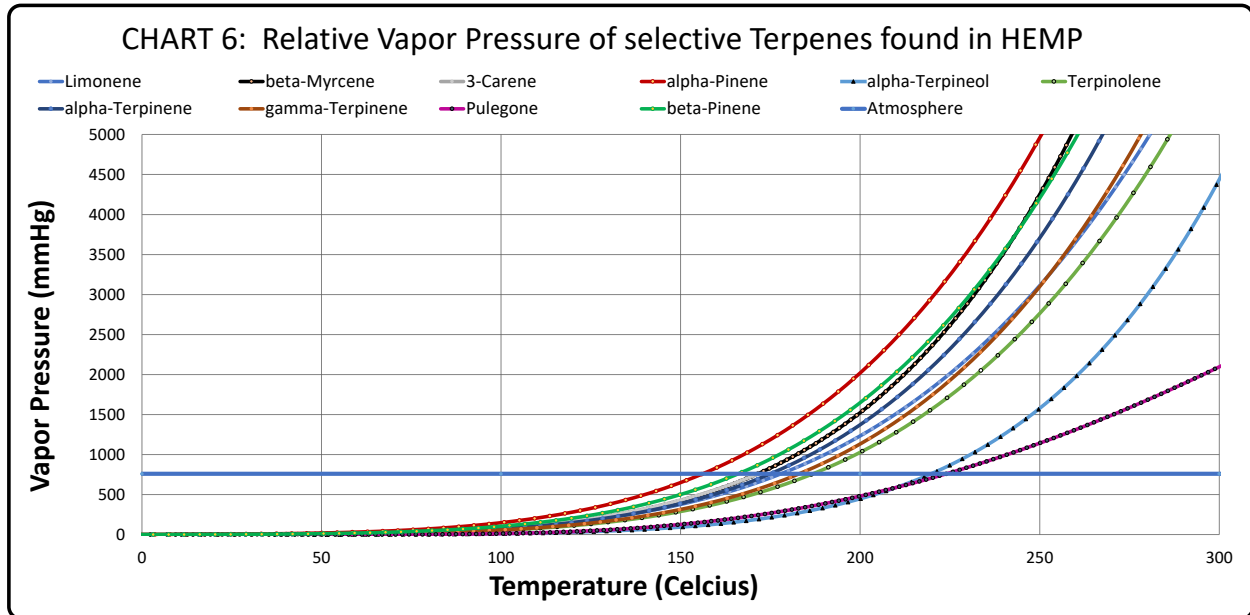


Chart 5 below provides additional prospective related to the effect of pressure conditions on the boiling point of a substance. Beta Myrcene was again used for this example, with the boiling point of beta Myrcene falling from 168°C at atmospheric conditions to -50°C at an absolute pressure (i.e., high vacuum) of 0.001 mm Hg.



As previously indicated, Beta Myrcene is just one of many terpenoids which might be found in cannabis or hemp extracted oils. Chart 6 below illustrates the partial pressure curves, at atmospheric conditions, for a number of the other terpenoids indicated in Chart 4, which suggests that all of the terpenoids exhibit gently sloping curves with the slope value decreasing somewhat in proportion to the increase in boiling point.



The preceding information has focused specifically on chemical parameters related to terpenoids, but the larger scope to be examined is to understand the most effective use of high vacuum, short path distillation equipment in processing crude cannabis or hemp oils for commercial sale. Therefore, in the broader scope, understanding the chemical composition of cannabis oils, and specifically, the terpenoids present in the oils, is a prerequisite to conducting an effective distillation program where the ultimate objective is to concentrate the cannabinoids.

It should also be appreciated that the terpenoids themselves have commercial value, and there are benefits to be derived by planning a distillation campaign which will provide for collection of terpenoids as well as concentrating of cannabinoids. In a single stage distillation system, similar to that depicted in Illustration 1, extracted cannabis or hemp oils which contain terpenoids suggest a cost-effective use of the equipment is to plan a distillation campaign which anticipates multiple stages (or passes) of distillation (using the same single-stage system) with each stage targeted at a different objective. Most operators of single stage systems plan on at least three passes of product from a single lot through the distillation unit. The following objectives are typically defined as optimum for a multiple pass distillation of a crude hemp oil: (i) separate low boiling point terpenoids from feed material, as 1st distillate; (ii) using residue product from 1st pass, separate cannabinoids from waxes and triglycerides (2nd distillate and residue, respectively); and (iii) using 2nd distillate containing cannabinoids, the 3rd pass is a polishing and concentrating pass where the resultant 3rd distillate is a more highly concentrated and purified cannabinoid oil, with optimum color qualities, while any remaining waxes, triglycerides and color bodies are collected as the 3rd residue product. Figure 2 below depicts the multiple pass distillation procedure suggested above.

FIGURE 2

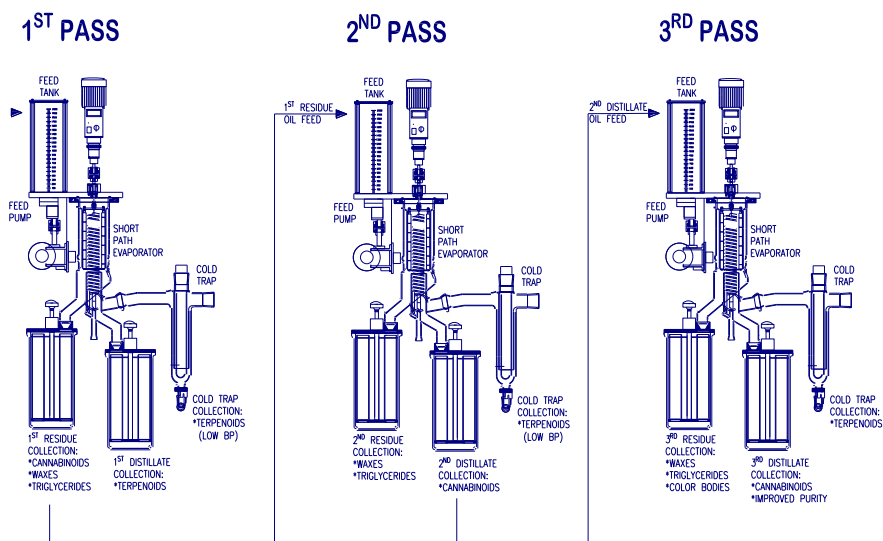


TABLE 3: Possible Operating Parameters for a 3-Pass Hemp Oil Distillation in a Single Stage System

Distillation Variable	1 st Pass	2 nd Pass	3 rd Pass
Evaporator Actual Temperature (°C)	120	180	150
Evaporator Pressure (mm Hg, absolute)	1.5	0.005	0.002
Atmospheric Equivalent Temp. (°C)	300	500	475
Condenser Temperature (°C): (Observed and Atmospheric Equivalent)	+20, +166	+85, +365	+85, +384
Cold Trap Temperature (°C): (Observed and Atmospheric Equivalent)	-35, +90	-35, +180	-35, +160

Notes: 1. The above indicated variables are the most relevant to the separation of CBD from non-CBD molecules.
 2. Evaporator AET of 300°C in 1st Pass is intended to separate all terpenoids with BP's < 300°C as distillate.
 3. Residue from 1st Pass is distilled in 2nd Pass at AET of 500°C to separate cannabinoids as distillate, while heavy triglycerides and waxes are residue.
 4. Cold Trap temperature of -35°C, and 1st Pass pressure of 1.5 mm Hg, is intended to condense terpenoids, and minimize partial pressure concerns.

TABLE 4: Possible Compositional Data for a 3-Pass Hemp Oil Distillation in a Single Stage System

Chemical Compound(s)	Feed Oil	Residue 1		Distillate 1		Residue 2		Distillate 2		Residue 3		Distillate 3	
		%R1	%Feed Oil	%D1	%Feed Oil	%R2	% Feed Oil	%D2	% Feed Oil	%R3	%Feed Oil	%D3	% Feed Oil
Input Product %	100%	100%	90%	100%	10%	100%	49%	100%	41%	100%	50%	100%	40%
Waxes & Triglycerides	50%	56%	50%	trace		92.0%	46%	8%	4%	99%	50%	1%	1%
Terpenoids	10%	0%	0%	100%	10%	trace		trace		trace		trace	
Cannabinoids	40%	44%	40%	trace		8.0%	3.2%	92%	37%	1.0%	0.4%	99%	40%

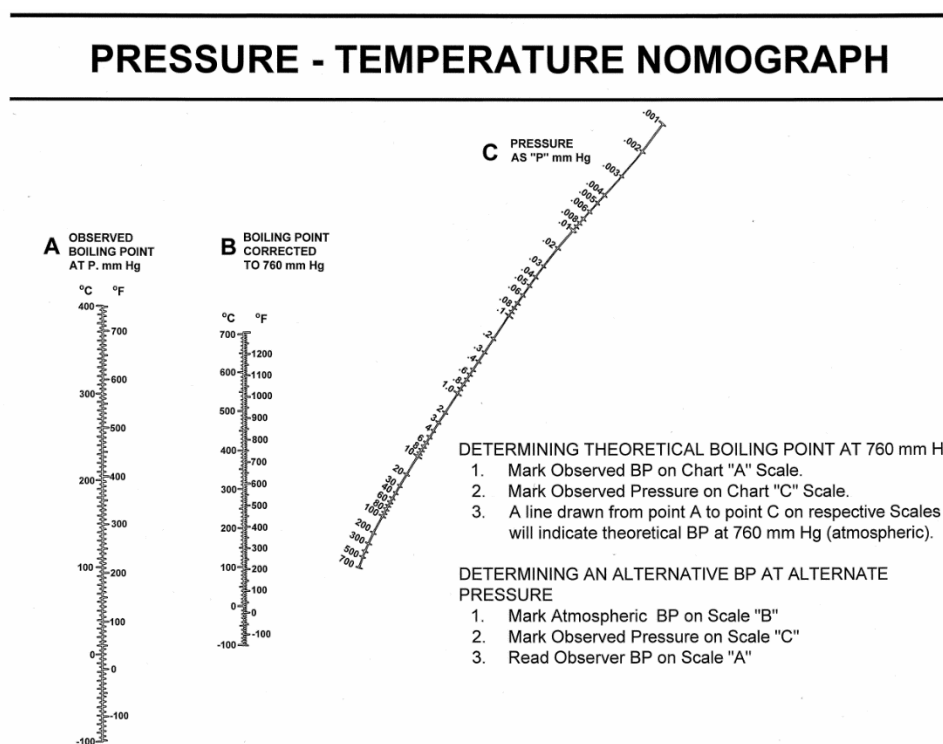
Note: The compositional information indicated above is intended to serve as an example and should not be interpreted as results obtained from a specific distillation. Extracted oils from cannabis plants may contain over 300 molecules and although the molecules typically fall within the chemical compound categories indicated in this table, this is an over simplification of results experienced in actual distillations.

Tables 3 and 4 represent an example of operating parameters and compositional results, respectively, which might be associated with a multiple pass distillation of a cannabinoid oil extract as depicted in Illustration 2. Note that the Atmospheric Equivalent Temperature (AET) is an important calculated variable which provides a benchmark for not only the vaporization of molecules under vacuum conditions but also as an indicator for condenser and cold trap capabilities associated with condensing vapors while still maintaining a liquid state in these vessels. For example, the condenser on the 1st Pass (or Stage #1) is shown in Table 3 to be operated at a temperature of +20°C which at the indicated absolute pressure (vacuum) level of 1.5 mm Hg., would suggest an AET of 166°C which will condense most of the terpenoids, but not all. Therefore, most of the remaining terpenoids will likely condense in the Cold Trap which is being operated at -35°C, or an AET of +90°C. Referring back to Chart 4. We can see that in general, the terpenoids have boiling points above 150°C, so a Cold Trap operated at an AET of +90°C should assure only a trace amount of terpenoids will bypass the 1st Pass Cold Trap. It should be

noted however that even trace terpenoids bypassing the Cold Trap may accumulate in the vacuum system and ultimately cause operating problems. The solution to this potential problem is a colder Cold Trap and frequent oil changes in the vacuum system. For reference, experience has indicated the coldest Cold Trap is a liquid nitrogen cryowell which operates at an observed temperature of approximately -160°C and an AET (at 1.5 mm Hg) of -94°C, at which temperature the vacuum pump has optimum protection.

Figure 3 below represents a Pressure-Temperature Nomograph which is a quick and helpful tool for determining Atmospheric Equivalent Temperature knowing the Observed Temperature and Absolute Pressure.

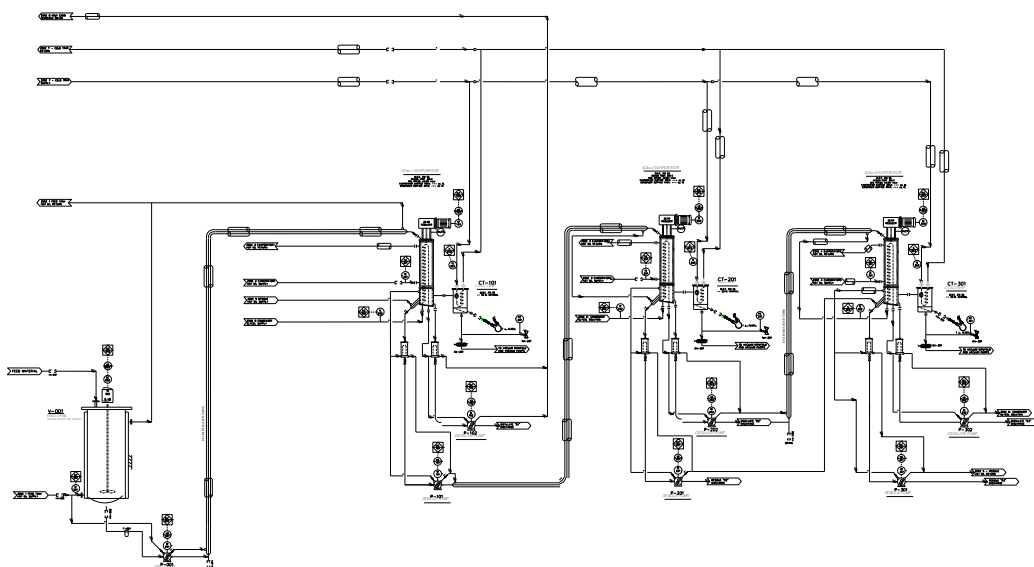
FIGURE 3: Pressure-Temperature Nomograph



The disadvantage to a multiple pass distillation process using a Single Stage System is the fact that it will involve more handling of the oil products before the final, purified cannabinoid oil is obtained. The handling process is further complicated by the fact that cannabinoid oil extracts are normally solid materials at room temperature, and will typically require heating to liquify the products prior to re-charging the feed tank with processed fractions.

More efficient oil processing operations typically prefer a multiple stage distillation system where the specific distillation parameters (e.g., temperature and pressure variables) can be adjusted at each stage to produce the desired separation for that particular stage. Figure 4 below depicts a P&ID (Process and Instrumentation Diagram) for a 3-Stage Distillation System which follows a process flow path similar to that described for a multiple pass use of a Single Stage System. Note that in the case of a multiple stage system 1st, 2nd, and 3rd pass distillation objectives are obtained by using a single pass through the multiple stage system. The specific operating conditions and chemical composition of final distillate and residue streams will be nearly identical to those obtained in the multiple pass use of a single stage system.

FIGURE 4



As noted previously, the primary benefit of a multiple stage distillation system as compared to multiple passes through a single stage distillation system is one of efficiency, but under normal operating conditions it is also cost effective. A multiple stage system precludes the necessity of reheating and recharging products for subsequent passes, and also avoids potential product losses due to transfer methods and chemical losses at the molecular level due to repeated heating cycles. Further, repeated rehandling of products in the single stage, multiple pass example also introduces an added potential for contamination of the product which should be processed in a sanitary environment.

In conclusion, the intent of this discussion is to encourage a process methodology which provides a distinct separation stage or pass where terpenoids, and potentially other low boiling point molecules, are distilled and collected from the feed product prior to processing the higher boiling point cannabinoid products. This methodology also allows the reintroduction of terpenoid products back into the refined cannabinoid distillate at a percentage level controlled by the processor.

In addition, the author wants to emphasize the importance of understanding process issues related to Atmospheric Equivalent Temperature (and boiling point) specifically in order to control condenser and cold trap operating temperatures to assure the capture of vaporized terpenoid molecules, both as a function of the value of these molecules, but also as a means of precluding contamination of downstream vacuum systems and associated maintenance problems contamination may present.