

## DISTILLATION - HOW IT WORKS

There is a growing interest in distillation by amateurs, particularly in New Zealand where happily it has been legal since October 1996 - for home consumption only though - not, repeat **NOT** for sale!!! The purpose of this article is to describe the principles of distillation in the hope that those interested in the subject may achieve better understanding in what they are trying to do. It is a basic description only, and those with rigorous scientific leanings should feel free to contact me if they find any alarming errors of fact. However, I ask that criticism be tempered with the intent of the article in mind.

### Vapour pressure.

Every substance is a collection of molecules held together by mutual attraction. The temperature of that substance is a measure of the kinetic energy these molecules have - the faster they vibrate about their mean position, the higher the temperature. Depending on the temperature and the pressure under which the substance exists, the molecules may pack together tightly as a solid, may pack together loosely as a liquid, or may freely move around as a vapour. These states of matter are termed phases, and the transition from one phase to another is almost invariably sharply defined by temperature and pressure. It may be noted in passing that some substances pass directly from the solid to the vapour phase - they sublime - but I don't think that many reading this will be interested in the behaviour of mothballs!

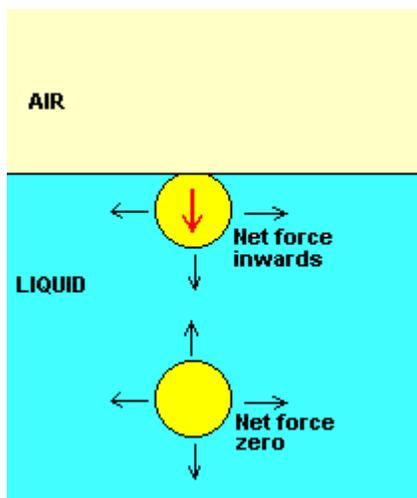


Figure 1

Having established that there is an orderly transition from one phase to another, the spanner in the works is that both solids and liquids lose molecules to the vapour phase directly - so perhaps we **should** be interested in mothballs! They do this by having enough energy to escape a barrier at the surface caused by the fact that when inside the solid or liquid the attraction of other molecules is evenly distributed in all directions, but at the surface is directed solely towards the body of the substance. This is a potent force manifesting itself in liquids by what we call Surface Tension. It is this which causes the surface of a liquid to form a meniscus against the side of a beaker, or to make globules of mercury scoot around like ball bearings. Many insects depend on it to walk on water!

It takes a lot of energy to vaporize a liquid, far more than to just heat it up, this being the energy needed to overcome the surface tension. Just bear in mind that the ease with which a liquid vaporizes is directly related to its surface tension and that the lower the surface tension the more molecules will be in the vapour phase to contribute to the vapour pressure. Please do not confuse vapour pressure with smell. It is of course true that scents and smells come to us by way of airborne molecules, but a strong smell does **not** imply a high vapour pressure. The strongest smells are those triggered by a class of chemicals called mercaptans. Do not even **think** about accepting an offer to let you smell one of these as the word 'vile' doesn't even come close to describing them! However, it takes very, very few of these molecules to create an incredible stink. On the distilling side, almost odourless ethanol has a higher vapour pressure than the heavier fusel oils that come off in the tails and which smell so awful.

### **An Illustration of Vapour Pressure.**

The vapour pressure of a substance is the contribution these freed molecules make to the pressure of the area surrounding the substance. This may be illustrated in a simple experiment most have seen at school. Take a long glass tube and fill it with mercury. Upend it in a beaker of mercury and if the tube is long enough then it will be seen that the mercury will be held up in the tube as far as the surrounding atmospheric pressure enables it to do - a vacuum being left in the top of the tube (purists - please ignore the vapour pressure of mercury and glass!). Now introduce a few drops of water into the bottom of the tube. These droplets will float to the top of the mercury column and will be seen to boil rapidly. Eventually, you will be left with a few drops of water floating on top of the mercury column and the mercury column will have lowered by about an inch or two. The lowering of the mercury column is a measure of the vapour pressure of the water at that temperature. Increase the temperature and you will need more water and the mercury column will reduce even more. At around 100 °C the tube will finally be empty of mercury and contain just water vapour. **The vapour pressure of water, or any liquid, equals atmospheric pressure at its boiling point for that pressure.** Lower the surrounding pressure and you lower the boiling point. Increase the surrounding pressure, as in a pressure cooker, and you raise the boiling point. This may seem to be an awfully long-winded way of going about describing what happens in distillation but believe me, it's necessary to have that picture in your mind.

### **Mixtures.**

Take pure water and you will have a liquid that boils at 100 °C (all pressures from now on being taken to be standard one atmosphere) and has a surface tension of 54.9 dynes/cm<sup>2</sup> (1 dyne = force to accelerate 1 gm at 1 cm/sec/sec). Take pure ethanol and you have a liquid which boils at 78.5 °C and has a surface tension of 21.38 dynes/cm<sup>2</sup>. You may therefore have guessed that the ethanol has a **higher** vapour pressure than the water, needing as it does less energy to release molecules to the vapour. Put some on your hand and feel the cold as it evaporates quickly - now compare that with water.

Now mix the two. Whatever ratio you have chosen, the boiling point of the resulting mixture will be somewhere above 78.15 °C (adding less than 5% water to ethanol actually depresses the boiling point below 78.5 °C rather than increasing it) and somewhere below 100 °C.

Now, to dispel a myth. Do not think that because your mixture contains ethanol that boils in its pure state at a lower temperature than water you can just keep the temperature of the mixture below 100 °C and you will be the delighted recipient of pure ethanol that boils off at a lower temperature! Believe me - I have seen that seriously advanced as the gospel truth!!!

What happens, and this is the crux of the distillation process, is that the mixture boils at some temperature depending on the relative concentrations and produces a vapour that is a mixture of the two substances. However, not just any old mixture. Remember that bit about vapour pressure and the energy to release molecules from a liquid? The substance with the highest vapour pressure will contribute more molecules to the resulting vapour than will the substance with the lower vapour pressure. So, whatever mixture you started out with, you end up with a vapour that will be richer in ethanol molecules than water molecules. Excellent! You can now condense this vapour and enjoy a good drink, which is exactly what they did in the Good Old Days. Of course, it didn't take long for cunning processors in those same Good Old Days to work out that if you went through the same process again then you would end up with something even richer in ethanol, and so on...

However, and there's always a 'however', what has been described with water and ethanol also applies to other substances, many of which supplied the flavour to the resulting drink but which had lower vapour pressures than ethanol. The result of repeated distillations was therefore more of the intoxicating stuff, but less and less of the tasty stuff. The end result was, as usual, a happy compromise. Booze produced in bulk was distilled two, three, or even four times, but then either 'treated' or left to mature (more on this another moment) before being consumed. This was fine for bulk as there was enough 'float' to tide you over until the good stuff matured. In other cases, where bulk wasn't the prime mover, another approach was taken. The ethanol was distilled and distilled to make it as pure as possible. At the same time, flavours were seeped or distilled from botanicals to form the basis for flavourings. The two were then 'married' as you would a perfume and other substances added to produce the exact flavour and palate you were seeking. In general, the results required less maturation than their bulk cousins, but often benefited from this as well as many subtle flavours couldn't be manufactured in any other way. This approach fitted in well with the monastic life of the church as a) they had extensive knowledge of herbs and the patience to experiment with different combinations, and b) the resulting product was clearly not in the same class as the Demon Drink of the masses. It could even be said to be Spiritual!

### **Cleaning and Maturation.**

A few more myths to be dispelled here!

Carbon treatment of raw spirit is said to be as old as the hills. No doubt others who have researched ancient matters will be able to fill in the blanks, but it would not be far from the truth to say that after pottery vessels such as amphorae, wooden barrels were used for bulk storage as they were less fragile than previously used vessels. Steel containers are now the thing. Old wine barrels were, and still are in many places in the world, favoured for ageing spirits as they impart a nice colour and subtle flavour both from their previous contents and the wood. However, before using old wine barrels, it would have been prudent to sterilise them as best you could to get rid of all the old moulds that grow apace when the barrels are empty. Fire was (and still is) the quickest and best way of accomplishing this without a lot of work and introduction of strange flavours, and if the resulting carbon had anything to do with the cleaning the stored spirit as well - although not very likely - so much the better. However, we now know a bit more about the action of activated carbon in adsorbing chemicals, both from the spirits trade and from the manufacture of respiration masks. Activated carbons are 'custom built' for their end purpose, generally involving careful selection of ingredients and very high temperature and gas treatment. They work by physical adsorption on the enormous internal surface area of the carbon, typically 1,000 square metres per gram (hard to believe, but true!). Note that it is a physical and not a chemical effect that makes them work. It therefore pays to be very careful about choosing the source and type of activated carbon you use to clean a spirit. Aquarium carbon will **not** do! It is a cheap and nasty mixture of all sorts of quickly charcoaled substances containing bits that may well remove a small fraction of the congeners from the spirit, but also containing bits that will introduce rather nasty trace elements and flavours to your hard won product. Fish won't mind, but you will! Properly sourced activated carbon is on the market now, specifically designed for the purpose of cleaning and polishing spirits.

As for maturing, this has nothing to do with some strange ability of fusel oils to 'seep' through the wood and disappear from their confinement (I've heard it seriously said that fusels can do this as they are 'slippery oils'). If this was the mechanism of maturation then uncounted vintners around the world are wasting their time laying down cellars of wine, carefully bottled in glass. Such a Houdini act would be remarkable enough, but maturation is in fact rather more complicated - it's a number of very slow chemical reactions whereby the large organic molecules comprising the 'nasties' are broken down into esters and other flavour enhancing chemicals. It may be that cunning chemists have come up with commercial ways of hastening this process, but in general it remains the most practical and cost effective way of making wines and spirits more palatable. Unless - and there is always an 'unless' - you follow the route of the monasteries.

## Pot Stills.



Figure 2

Starting from the beginning, many simple stills were devised - and some from China not so simple - but all sharing the same basic principle: if you boil up a liquid containing ethanol in a pot and condense the vapour then the resulting liquid will contain a higher percentage of ethanol than when you first started. If you repeat this several times then you will end up with more and more ethanol.



Figure 3

The first type of still was called an Alembic, although this properly referred to the cap with a spout that sat on top of the boiling vessel. It worked well, and with variations to make use of modern materials is just what you need to distill botanicals. The second is reminiscent of the moonshine contraptions still used (and raided) in America, but without the cooling 'worm' so characteristic of them.

The problem with both is that if used to distill ethanol then you also end up with all the other undesirable products - the congeners. Congeners is a term used to indicate a 'family', in this case the family of alcohols that are produced when you ferment sugars to produce ethanol. The lightest of these is Methanol, which because it has the lowest vapour pressure comes through almost in its entirety (also known as the 'heads') and the heaviest include goodies such as propyl, butyl, and amyl alcohols. In addition to the congeners, you may also get acetone (ever tried drinking dry-cleaning fluid?) and ethyl acetate which come off with the heads.

So how do you get rid of them? You can use one of the commercial stills around that are marketed as fractionating stills (and sometimes even as refluxing stills - but you'll be able to judge that claim for yourself better later on) and chuck away the first lot of distillate that comes across. You are fairly sure to get rid of most of the heads that way. You can then continue to distill until you are fairly sure that the nasty 'tails' are coming through in strength, then stop and run all your product through carbon cleaning and polishing. This has the advantages that the equipment is relatively cheap and the process fairly quick. Unfortunately, as we learned earlier in the discussion of mixtures, your middle product is going to be laced fairly heavily with congeners. The carbon will get rid of a lot of these, but it's messy process and it doesn't get rid of them entirely. Let me hasten to stress here that I have nothing whatsoever against these stills - they are a rapid and economic way of distilling if you take the trouble to go through all the cleaning etc afterwards. I would hate to have some of my supplier friends accusing me of taking away their business! However, they are **not** columns, even if they have a little tower on top, and most especially **not** reflux columns.

## The Distillation Column.

And now to the crux of this whole thing. How does a distillation column work, and how does it differ from a pot still? This short article will not go into the nuts and bolts of an actual design - for that you need to get John Stone's excellent book, "Making Gin & Vodka - A Professional Guide for Amateur Distillers" via his website <http://www.gin-vodka.com> (but hurry - there are less than 150 left!).

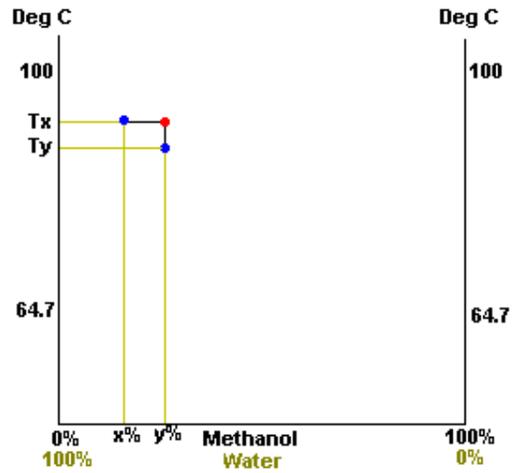


Figure 4

For a start, let's go back to basic principles and think about what would happen if you heated a mixture of liquids in a boiler and let the vapour rise in a long column. The first vapour would be richest in those constituents which have the highest vapour pressures - the acetone, ethyl acetate and the methanol. Then would come ethanol, followed by propyl alcohol and water, and with a trace of the heaviest congeners that follow propyl alcohol. This vapour would rise up the column until its temperature dropped to that point when this mixture liquefies. Running down the sides of the column you would now have this richer liquid meeting the hot vapours that are still rising, and they would boil off again, this time with even richer proportions of the first molecules mentioned above, but with a lesser proportion of the last ones. This would continue the higher you rise in the column and what you have is essentially what they have with the big pot stills used to distill whisky.

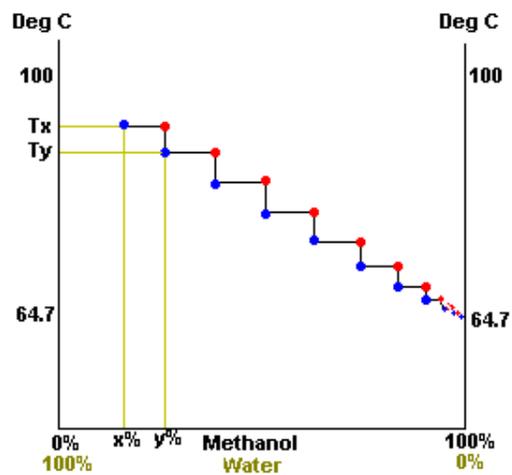
Now introduce packing into the column. The whole idea is to provide a much bigger surface area onto which the vapour can condense than just the walls themselves, but without interrupting the flow of vapour upwards and the flow of liquid downwards. Much more efficient as the surface area of the liquid is greater and the interchange between liquid and vapour will be faster. It is obvious that the bigger the surface area we can provide then the more efficient the column will be. So what should the packing be? We are looking for something that occupies the least volume yet provides the greatest surface area. Spheres? Well, they have a nice shape and marbles are readily available, but spheres have the least surface area of any shape. Cylinders? A little better, but not far off spheres - unless you drill through the middle and make them hollow cylinders. We now have Raschig rings which are tiny ceramic hollow cylinders that have a much greater surface area than spheres. However, it's not the direct ratio of surface areas that matters so much as the fact that they pack together more compactly than spheres and offer even greater surface area volume for volume. There are other esoteric geometric shapes that have been designed, but in the end it comes down to cost as well. Raschig rings, even if you can get them, are very expensive. However, not to worry - ordinary domestic metal mesh scouring pads or turnings from a lathe all perform appreciably better than even Raschig rings! They offer an enormously greater surface area volume for volume, and provide innumerable paths for both vapour and liquid transit. Just make sure that you don't pack them into the column so tightly that these paths are closed up, and for the same reason do not use the fine 'wire-wool' type of scouring pad (the metal mesh pads are quite distinctive as the strands look like miniature coils).

So now we have a long, very long perfectly insulated open-ended column packed with suitable surfaces onto which vapour can condense, and then evaporate from again. Make it long enough, and leave it alone to do its thing. What do we end up with? The first thing to note is that the main difference between a pot still and this column is that gravity plays an essential part. The process of condensing out and running back down the column is termed reflux. The process of constituents separating out, the lightest (and highest vapour pressure) at the top and the heaviest at the bottom is termed fractionating. Lets leave it like this for a moment and look at a little bit of theory to see what we should be aiming at.



Let's start with a methanol/water mixture with X% methanol by volume. The top left blue dot charts the boiling point of the liquid mixture as being  $T_x$  °C. The vapour from this mixture contains a higher percentage Y% of methanol as it has a higher vapour pressure than water (shown by the red dot at  $T_x$  °C) and this condenses at  $T_y$  °C.

Figure 5



Subsequent vaporizations and condensations are plotted in this chart. As the concentration of the condensed liquid approaches 100% methanol the boiling point, as might be expected, approaches the boiling point of pure methanol: 64.7 °C.

Figure 6

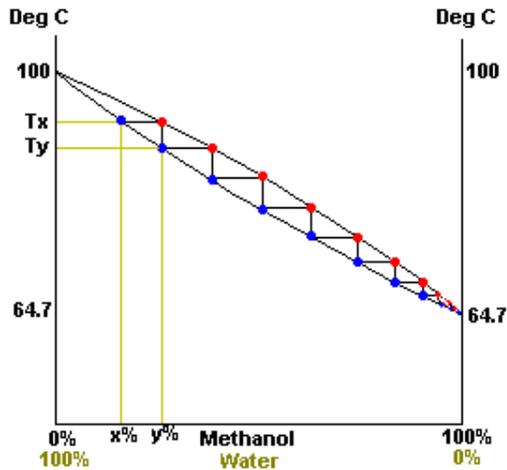


Figure 7

Joining up these dots gives us two curves. The upper one may be called the vapour line. Anything above it is vapour above the boiling point for that mixture, and anything below the lower liquid line is liquid below the boiling point for that mixture.

It is sometimes said that any point lying in between the lines represents a transition phase between liquid and vapour, but a little reflection will show the fallacy of this view. We chose to start at a certain concentration of methanol, but another concentration would have resulted in a similar set of points offset either to the left or right of those shown.

An area where vapour condenses, hangs around and then vaporizes again is termed a 'plate'. It may be likened to an actual plate or tray fitted in the tower. Fractionating towers for oils and fuels are actually built this way.

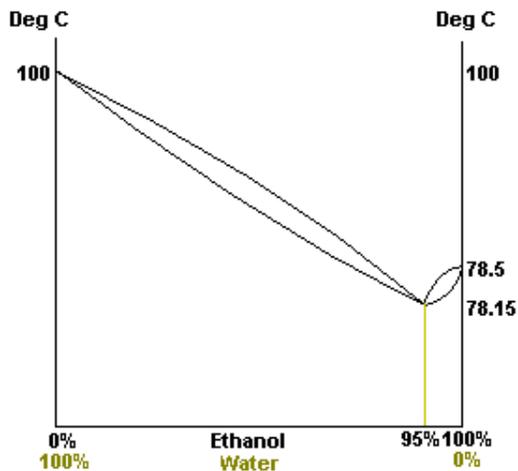


Figure 8

The figures above relate to a methanol/water mixture, and are quite simple. In the case of an ethanol/water mixture we would find that there is a kink in the bottom of the curves. This results from the fact that ethanol and water form an azeotropic mixture when the concentration of ethanol is around 95%. Subsequent vapourization of liquid at this concentration will not yield vapour with a higher concentration of ethanol but one of the same concentration as the liquid. If we started with a mixture that had more than 95% ethanol, then the concentration of ethanol in the vapour would be less and, once again, the system would tend to settle at the azeotropic point

Distillation alone cannot give a concentration of ethanol higher than 95%.

Clever Gnomes have worked out a set of equations which enable you to calculate the number of plates you need in order to achieve such and such a separation between substances, and it turns out that to achieve 95% separation of a water ethanol mixture you need at least 12 plates under full reflux conditions (nothing being taken from the tower, but all falling back on itself). I won't bore you with the calculations here, but those who may be interested may contact me for a full run-down, or search themselves for information on Clausius-Clapeyron and Raoult equations. Start taking stuff from the head of the column and you will need even more plates as you would be disturbing the reflux ratio.

I've described what happens with a mixture of two substances in order to keep the graphs simple. However, the principles that apply to such a mixture apply equally to mixtures of three or more substances. The basic point to keep in mind is that the higher the vapour pressure of a substance the greater its proportion in vapour resulting from boiling the mixture.

## Reflux and Balance.

It would be impractical to have an enormously long tower to achieve the separation we require. Fortunately, there is a little trick that may be used to keep the tower to manageable proportions, yet provide excellent separation. Left to its own devices, the tower works by condensing out richer and richer mixtures the higher you go, the condensate running down again until it re-vaporizes and improves the separation. You can hurry this along by making the column shorter and putting a condenser on top. All the vapour that reaches the top if the column is condensed and the enriched liquid is returned to the column. In washing down the packing this liquid, which evaporates and rises again, causes the top of the column to become very enriched with the lightest fraction. The column compensates for this rude interference by compressing the separation between fractions lower down in the column, but this doesn't matter so long as we confine ourselves to extracting from the top.

Tried and true practice shows that you can achieve almost perfect separation between fractions by using a tower of about 3.5 cm diameter and around 1 metre long. The secret is to allow time for the process of wash-down and separation to settle to a stable condition by imposing 100% reflux for about 4 hours. After this time, at least the top half of the tower will be filled with almost pure methanol (at the start), as indicated by the temperatures up the tower having settled down to a stable condition - ie the tower is **balanced**. By bleeding off methanol slowly, maintaining a reflux ratio of at least 10 to 1 (return 9 parts for every 1 drawn off, the ratio being that drawn off versus that supplied by the column) you can maintain this balance and remove all the methanol with only a small 'blur' when ethanol begins to follow the exhausted methanol up the column. The point at which pure ethanol starts being drawn off is obvious from both the increased temperature at the head of the column and the clean smell of the product. This will be 95% ethanol - remember it forms an azeotropic mixture with water and you can't get better than that. Finally, after about 20 to 24 hours (the price you pay for purity), the pungent tails with all the nasty congeners will start to make themselves known.

## Conclusion.

So there we are. I hope this article has been useful and not bruised too many firmly held opinions. For those who hold the latter, all I can say is go and check it out for yourselves. As I have stated before, I believe there is a place for all types of still, from the simplest alembic to the full reflux fractionating column. My personal preference is for the latter as I find, despite first appearances, it is cheaper and less time consuming in the long run. I also have this funny notion that I should know exactly what's in a drink that I guzzle, and by adding known ingredients to a pure product I feel more in control of my destiny. Incidentally, it's not only booze that I use this product for - as a keen cook I enjoy the opportunity to make my own food essences.

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