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Distillation technology and modelling techniques

Part 3: Walkthrough and analysis of a continuous brandy distillery

In this third and final part of the series, Konrad Miller presents an overview of a continuous distillery, with analysis of fermentation, distillation, and congener removal. As discussed in a prior article, distillation is a science with many applications; petroleum, commodity chemicals, and biofuels among them. However, the genesis of distillation was in the production of alcoholic beverages.

Up until the late 19th century, both spirits and petroleum were produced via batch distillation, with multiple distillations taking place to achieve higher purity as needed. As distillation technology has evolved, so has spirits production. This article walks through the production process of a modern brandy distillery, with concepts directly applicable to whiskey, rum, and vodka production.

Brandy is wine distillate, typically produced at approximately 150 proof (0.6 mass fraction ethanol) off the still. Like all distilled spirits, brandy is colourless when produced; it gains colour from oak maturation (tannin, colour, and flavour extraction). All brandy begins its life as grapes. From September to November, California grapes are harvested for wine production. Just as there are different classes of crude oil and coal, grapes are divided into different varietals, each with their own characteristics. Key California brandy grape varietals are French Columbard (sweet, tropical fruit), Muscat (floral, 'fruit loops'), and Barbera (red fruit). This fruit is crushed to extract the juice, treated to remove solids, and then fermented to produce wine.

Figure 1: A screw conveyer for handling grapes

Ethanol modelling

Ethanol fermentations by *Saccharomyces cerevisiae* are well modelled by nutrient (sugar) limited, product (ethanol) inhibited Monod kinetics. Equation 1 delineates the governing fermentation equations, where 'C' is concentration, subscript 'c' is cells, subscript 's' is sugar, subscript 'p' is product (ethanol), 'k' refers to a kinetic rate parameter, 'μ' is the specific growth rate, 'C*p' is the maximum ethanol level yeast can grow in, and 'Y' refers to a yield coefficient:

Equation 1a: Cellular Concentration

$$\frac{dC_c}{dt} = (r_g - r_d)$$

Equation 1b: Sugar Depletion

$$\frac{dC_s}{dt} = Y_{s/c}\,(-r_g) - r_{sm}$$

Equation 1c: Ethanol Production

$$\frac{dC_p}{dt} = Y_{p/c}\,(r_g)$$

Equation 1d: Cell Growth Rate

$$r_g = \mu_{max} * \left(1 - \frac{C_p}{C_p^*}\right)^{0.52} * \frac{C_c C_s}{K_s + C_s}$$

Equation 1e: Cell Death Rate

$$r_d = K_d C_c$$

Equation 1f: Cellular Maintenance Sugar Depletion

$$r_{sm} = mC_c$$

Fermentable sugars are expressed as Residual Sugar (RS), or grams fermentable sugars per 100 mL. When the above coupled differential equations are fed into MATLAB, the sugar and alcohol concentration can be generated and plotted:

Care must be taken during fermentation as the process is highly exothermic. Uncontrolled fermentations can peak at temperatures in excess of 45°C. This can lead to a kind of 'auto-pasteurisation' and arrest fermentation. Smaller fermentation tanks (<200,000 litres) are typically jacketed with glycol to control the temperature. Larger tanks (>400,000 litres) lack sufficient surface area for jacketing to be effective, so external shell-and-tube heat exchangers are employed to control fermentation temperature.

Prior to distillation, fermented wine is passed through a centrifuge to remove residual grape solids and residual yeast hulls, as these can foul the plate and frame exchangers used in the distillery pre-heat train. Red wines require additional processing to remove the grape skins and seeds, which are the source of the eponymous red colour and associated tannins. White wines typically have their skins and seeds removed prior to fermentation.

Distillation column

A typical spirits distillation column might contain 70-100 trays, a column diameter of 0.5 to 2.5m and employ copper bubble cap trays above the feed point and stainless-steel sieve trays below the feed point. The high number of stages allows for a powerful fractionation of dilute components and minimises the required steam demand (as seen in the prior article, there is an inverse relationship between tray count and the required steam and condenser duties for a given separation). Figure 3 shows the ethanol-water profile along the column height. Copper bubble cap trays are used for their high efficiency, excellent turn down, and ability to react away volatile sulphur compounds, which are offensive to the nose and palate. Figure 4 is a simplified process flow diagram for a brandy distillation, and precedes a description of the column operation.

Before being fed to the column, incoming feed is run through a heat-exchanger with the outgoing bottoms to recover waste heat. This process decreases the total steam demand on the column and allows the hot bottoms, which are rich in organic material, to be sent to an anaerobic digester to produce environmentally friendly methane to feed the steam boilers. Spiral heat-exchangers are selected for this service, due to their high fouling resistance and excellent countercurrent flow patterns (Figure 5).

While spirits distillations can be approximated as a binary system (LK=ethanol, HK=water) for most purposes, it is in fact a complex multi-component mixture. Non-key species are typically divided into two categories- 'Fusel Oils' (alcohols with three or more carbons, such as propanol, butanol, amyl alcohol, etc.) and 'Heads' (highly volatile impurities), both of which are called 'congeners' by the fermented beverage industry. The distillation column must be tuned to permit some of these impurities into the product spirit, as they impart character, but care must be taken as they are unpleasant in excess.

Side draw fusel oil

Fusel oils are more viscous than ethanol or water, and impart a full mouthfeel to the spirit. Fusel oils are 'Intermediate Keys', meaning they accumulate between the Light Key (ethanol) and Heavy Key (water). This dynamic can lead to unsteady-state accretion of fusel oils in the column – as the fusel oils accumulate they migrate up towards the product line, dropping the product draw tray temperature. The operator responds

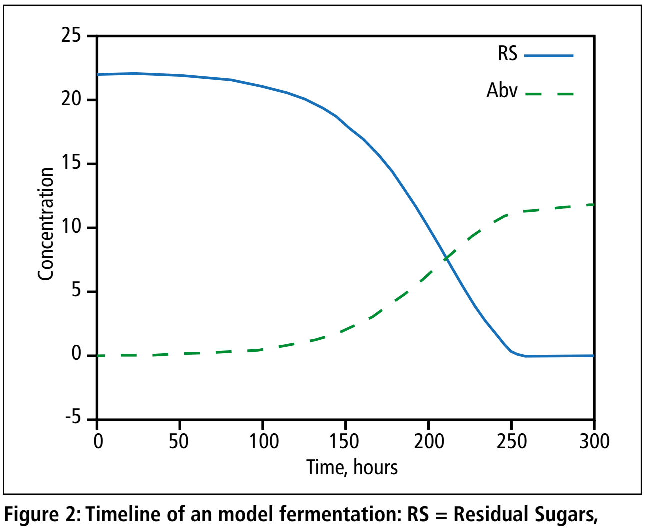

Figure 2: Timeline of an model fermentation: RS = Residual Sugars, g/100mL; Abv = Alcohol by volume, %

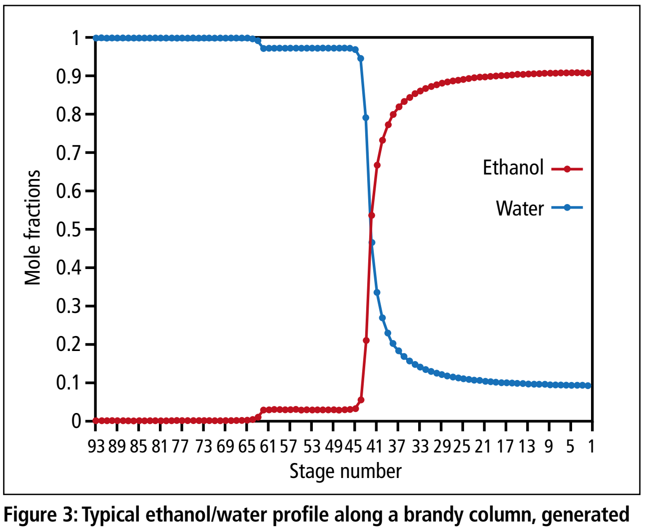

Figure 3: Typical ethanol/water profile along a brandy column, generated via ChemCAD SCDS model

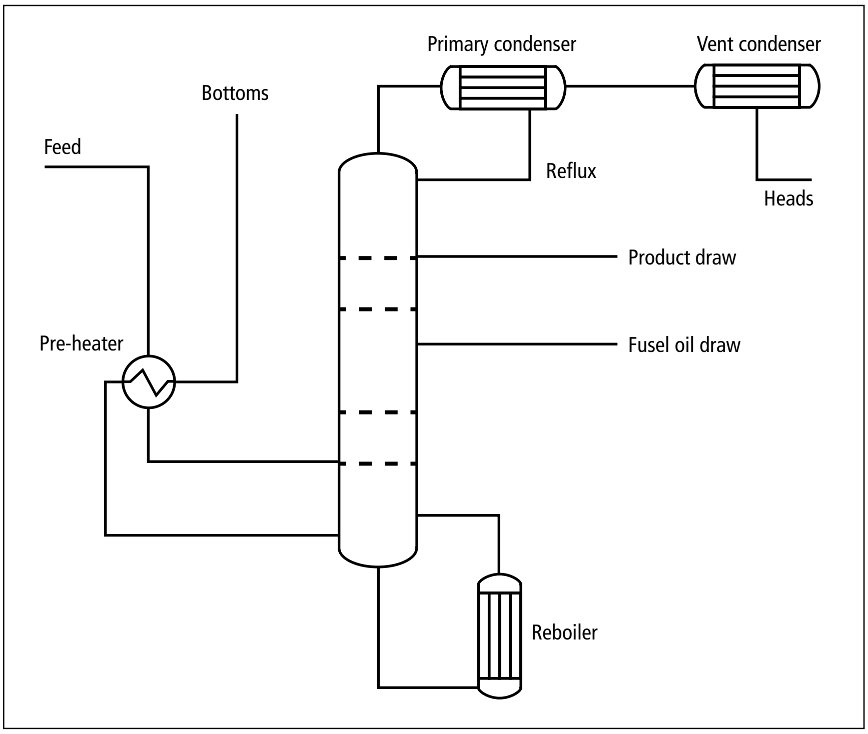

Figure 4: Simplified process flow diagram of a spirits distillation column

by increasing the reflux ratio, driving the fusel oils back down the column. This results in a cooling of the bottom trays, which is indicative of product loss (ethanol) out the bottoms. The operator responds by increasing the steam to the column, thereby increasing the boilup ratio. This pushes the fusel oils back up the column. This increases until sufficient fusel oils accumulate to form second liquid layer on the distillation trays (Figure 6). This two-phase liquid system significantly impedes mass transfer in the column and can lead to column flooding or 'crashing'. It also leads to excess fusel oils in the product, which results in an unpleasant 'wet cardboard' odour in the spirit.

To combat this, a slight side draw (called a fusel oil draw) is taken off of a stage between the feed and the product draw. Operators analyse different trays on the column for fusel oil content, and adjust the fusel oil draw accordingly.

The fusel oil draw is shunted off to a single-stage liquid-liquid extractor known as a fusel oil decanter. In-line to the extractor, it is mixed with water (typically in a volumetric ratio of one part fusel oil draw to three parts water), which functions as a fusel oil antisolvent due to unfavourable van der Waals interactions (water is dominated by hydrogen bonds, while the large carbon backbone in fusel oils promotes London dispersion forces). This pushes the composition into the two-phase envelope shown in Figure 6. The less-dense organic phase is decanted off to remove fusel oils, while the aqueous phase is returned to the column to conserve ethanol.

Final product heads

The level of heads in the final product must also be carefully titrated – too low, and the spirit lacks a certain sweet, fruity character; too much, and the spirit becomes harsh and biting. Heads are comprised of lighter-than-light key (LLK) components, such as methanol, acetaldehyde, and ethyl acetate. These components are removed by means of a dual condenser train. The first (primary) condenser is maintained around 77°C, just below the condensation point for ethanol at 1 atmosphere. The second (vent) condenser is maintained at 16°C. This is designed such that ethanol condenses in the primary condenser, while the majority of the heads are condensed in the vent condenser. All material condensed in the primary condenser (about 95% of the vapour leaving the

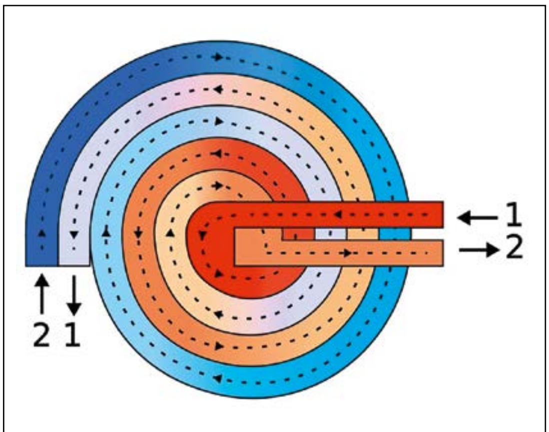

Figure 5: Flow patterns in spiral heat exchangers promote good heat transfer (due to counter-current operation) and resist fouling well

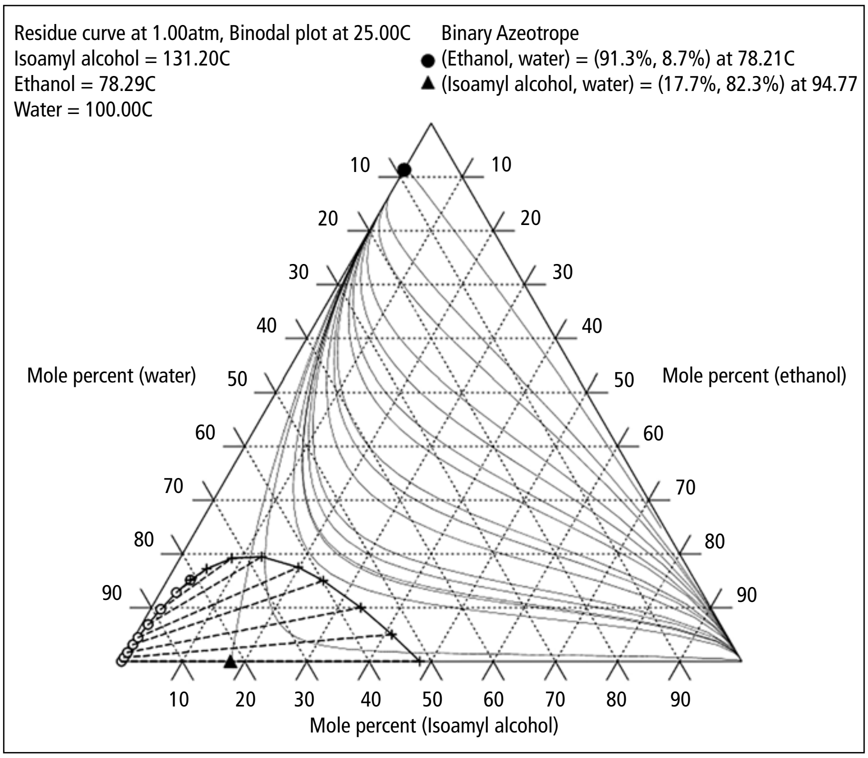

Figure 6: Residue curve between water, ethanol, and isoamyl alcohol via NRTL model on ChemCAD. Note the existence of two liquid phases in the absence of ethanol. This phenomenon can cause two-phase formation on column, and is exploited in the fusel oil decanter

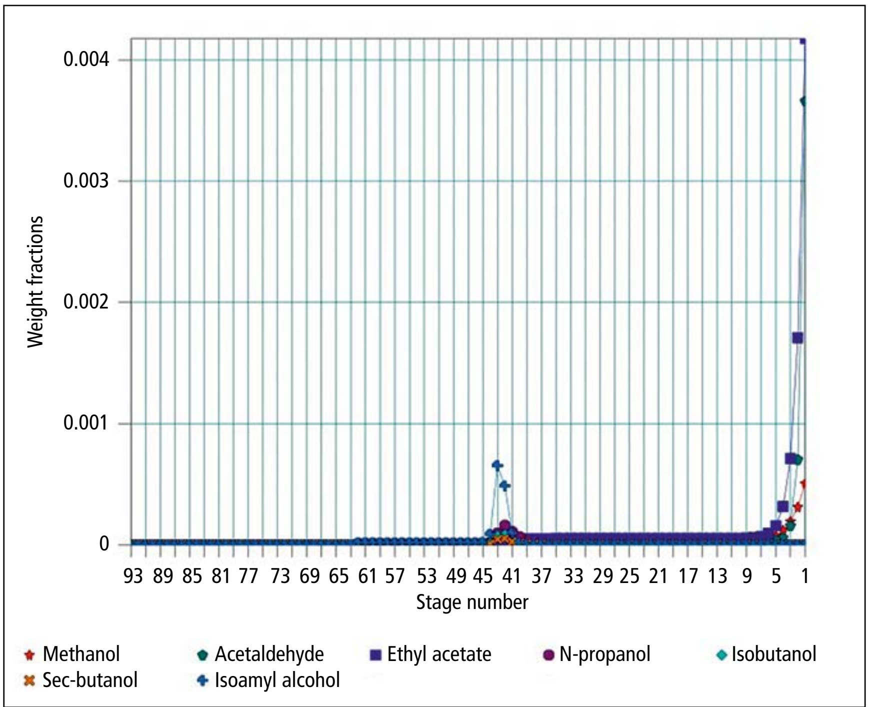

Figure 7: Congener profile in a column. Fusel oils accumulate in the middle, while heads partition to the top of the column. Generated via SCDS model with ChemCAD

column) is returned to the top tray as reflux, for an effective reflux ratio of around 20. Figure 7 shows a typical column profile of the various congeners in a spirits column.

Finally, product is taken near the top of the column. A distiller is typically on site to analyse the spirit, both for taste and chemical markers. The distiller adjusts the product proof, steam duty, reflux ratio, fusel oil draw, heads draw, and product draw plate until the desired sensory characters are achieved. This spirit is known as 'GBD', or grape brandy distillate. It becomes brandy after being aged in oak for at least two years. David Warter, a chemical engineer and spirits production expert, describes the sensory characteristics of GBD and brandy thusly:

"GBD normally has prominent fresh fruit notes (normally apple/pear for white grapes and cherry/raspberry for red grapes). Sometimes the GBD will have floral notes depending on the varietal distilled. GBD will have variable mouthfeel depending on the distillation technique and the varietal.

Brandy will have a brown sweet note from the oak. It will have less burn and a more round mouthfeel. The floral and red notes will generally decrease, but the apple note complements the oak well."

Prior to the installation of new distillation columns, ChemCAD computer modelling is applied to optimise the columns with respect to flavour profile and operational efficiency. Table 1 shows the material balance around a typical spirits column.

And finally

From the distillery, brandy is transported to a barrelling facility, where the GBD is cut to ~120 proof, 60% ABV and aged for several years to smooth out harsh notes and gain the more familiar brown colour of aged spirits. Once the distillers determine how to blend the aged brandy (VS, VSOP, or XO, depending on sensory characteristics and target styles), it is decanted out, charcoal filtered for smoothness, cut to 80 proof, and bottled.

Thus concludes our review of distillation technology. We have reviewed the fundamental concepts around distillation, how to apply shortcut methods to understand the inner workings of a column – and finally seen the technology in action during our walkthrough of a brandy distillery. From its medieval roots in spirits production to state of the art petroleum column, distillation has evolved with our society, and no doubt will continue to be the 'top shelf' choice in chemical separations for years to come.

Component	Feed	Product	Bottoms	Fusel Oils	Heads
Ethanol	133	125	0	2	6
Water	1381	110	1264	6	1
Methanol	0.02	0.01	0	0	0.01
Acetaldehyde	0.1	0.01	0	0	0.09
Ethyl Acetate	0.04	0.01	0	0	0.03
N-Propanol	0.04	0.03	0	0.01	0
Isobutanol	0.02	0.02	0	0	0
Sec-Butanol	0.02	0.1	0	0.01	0
Isoamyl Alcohol	0.09	0.07	0	0.02	0

Table 1: Typical column material balance. Generated via SCDS model with ChemCAD. All units in kg-mole/hr

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