"Its in the Spirit: Distilled Beverage Flavors and Their Evaluation"

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Overview

- The distilled spirits industry includes the production of whisk(e)y, gin, vodka, rum and brandy. [See details - www.epa.gov/ttn]
- This lecture will focus on some of those distilled products still made using pot-stills and using wooden barrels for aging as these features contribute to spirits with much 'character'.
- A commonality of flavor notes will also be seen from this type of spirit production.

Outline

- Types of pot-still derived products (whiskies, rums, gin, vodka's and tequila). Basics of Bourbon production.
- Where do spirit flavors originate? (Raw materials, fermentation, processing, distilling and aging).
- The need for a common flavor language and the Scotch Whisky flavor wheel as an example.
- A few common flavor notes will be illustrated through Aroma bottle samples.

Section 1

Types of pot-still derived products (whiskies, rums, vodka's, gins and tequila).

Spirit Types

- Pot still - Scotch Whiskies and Heavy Rums- beverages retain the color, aroma and taste derived from the raw materials used in the fermenter and the method of their production and maturation.
- Grain whiskies and vodka and gin now typically from continuous distillation. Distillation and rectification removes most of the congeners. The neutral spirits, as purer spirits, derive flavors from infusions or co-distillations with botanicals and from maturation.

What Can You Make?

- You are free to make any type of beverage (legally permitting): Whiskies (incl. Bourbon), Rums, Gins, Vodkas, Brandies. Liqueurs.
- By Internationally accepted laws you cannot make and call a product Scotch, Irish or Canadian Whisk(e)y (as also seen in the Addendum).
- Tequila and Mezcal made in Mexico only.
- See the BATF Beverage Manual (Spirits) and other BATF documents for full definitions (classes and types) and labeling rules.

Spirit Production

- We consider some typical features for Scotch whisky production. These basics can apply to all whiskies and other pot still beverages. [There are Variations - Research the Specifics]
- We then consider Bourbon whiskey production, a unique American beverage, in more detail.
- Details covering Scotch Whisky, Irish Whiskey and Rum (as guides to how they are formulated, and applicable rules for production) are included in the Addendum to this paper.

Spirit Production - Basics

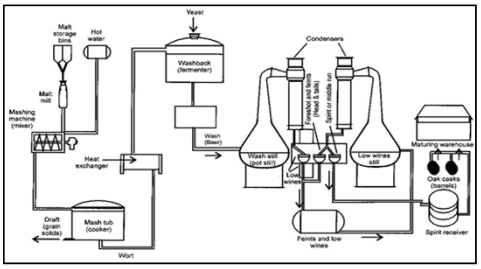
- Typical features for Scotch here can apply to all whiskies.
- Pot still - double or two stage distillation.

  Mashing to Fermentation (wort ca. 15% sugar)

  Wash from Fermenter (ca. 8% v/v alcohol) to the *Wash Still* - boiled 5-6 hrs to produce a "low wines" distillate (20-26% v/v alcohol).

  To the *Spirit Still* - Yields three fractions incl. Spirit at 66 -73% v/v (132-146 Proof) alcohol.

Summary Flow diagram showing the principal operations during production of Scotch malt whisky



Some Flavors of Pot-still Products

- Esters, aldehydes, mercaptans and fusel alcohols* come through from the heads and intermediate fractions of the still. [*Fusels are left over from last tails or "Feints".]
- Organic acids, short and long chain fatty acid esters, sulfur compounds and phenols end in the tails fraction.
- Many flavors derive from the oak wood used in maturation (bourbon, sherry or new wood). Vanillin is a key component along with complex wood components e.g., terpenes.

Bourbon - I

- Originated in Bourbon County, KY.
- Made with at least 51% corn.
- Unmalted Barley, Rye or Wheat (with Barley malt at about 10-15%) makes up the rest, e.g., 70% corn, 15% malt and 15% wheat.
- Backset (stillage) with pH of about 4.6 is used to start the next batch- "sour" OR
- Sour mash culture (*L. delbruecki*) is employed followed by pasteurization and then introduction of the yeast.

Bourbon - II

- Fermentation - Starts at 22-25 ^{0}C and lasts 3-4 days - generally no control of temperature (rises to about 36 ^{0}C). Open wood or SS vessel. Not stirred.
- Yeast used once (it is all distilled!). Hops can be used to control microbial contamination in culturing.
- Usually distilled in a continuous (Coffey) still but can use Pot stills (copper).

Bourbon - III

- First distillation condensate at about 60% v/v (low wine).
- Second still (Doubler) is a short still yielding high wines at 65% v/v. [Must not exceed 80% v/v.]
- High wine diluted to 55% v/v (110 or barreling proof - must not exceed 125 Proof) and is aged in new white oak barrels (charred). Two years minimum (5-6 yrs typical). "Angels' share" lost in aging.

Section 2

Where do spirit flavors originate? (Raw materials, fermentation, processing, distillation and aging).

Where do the Flavors come from? - I

- As for beer production there are multi-faceted operations which lead to flavor production:
- Water and Raw Materials (Bourbon from limestone water. Pure water for dilution.) Types of grains/fermentables. [Barley varieties and seasonal issues.]
- Kilning - Peat smoke and gas contaminants in Scotch. Maillard components in any darker grains, esp. pyrazines, (potential for flavor manipulation here?).

Where do the Flavors come from? - II

- Fermentation (non-sterile mash - microbial flavors, yeast strains).
- Distillation - exceedingly complex. [Operator skill in ensuring low bleed-over of "Feints". Knowing when to make cuts!]
- Maturation (type of maturation vessel, history and warehousing).
- Blending - Sensory Skills (opinion) of the blender (nosing).

Raw Materials - I

- Malt, other grains and sugars and syrups (molasses).
- Mould on grains can pass off-flavors through to final product.
- Smoked malts - peat - smoky flavors (phenols, cresols and guaiacols) and Maillard reaction products - "burnt", "caramel" and furfural (grainy) flavors. [Rum heavy in furfural from the molasses.]

Raw Materials - II

- Peating also gives rise to pyridines, pyrazoles and thiazoles. These may make a significant contribution to whisky flavor.
- Exist at very low concentrations (ppb levels) but have very low flavor threshold values.
- Pyridines:- green, bitter, astringent, roasted and burnt -even fishy! Undesirable! [With pH drop in whisky maturation not a problem after aging!]

Raw Materials - III

- Pyrazines have odors associated with pleasant roasted foods; burnt, roasted, nutty, earthy, fruity and woody have been applied.
- These do come through the aging/maturation process and the recovery of such compounds is more efficient than for the phenols.

Phenols - I

- Peat smoked malts give rise to phenols - make for distinctive whiskies.
- Only about 20 malt phenols end up in distillates.
- Quantitatively important phenols include: phenol, cresols, xylenols, para- and meta-ethylphenol, guaiacol (v. low flavor threshold at only 3 ppb in 10% v/v spirit!) and 4-methyl and 4-ethyl guaiacols.

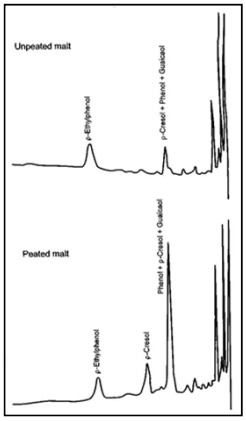
Phenols - II

- Rye is abundant in phenolic acids leading to 4-vinyl guaiacol and 4 ethyl phenols. [Rye is a spicy ingredient.]
- Phenols also arise from ferulic acid in malt (as for beer) leading to clove-like phenolic notes.

Phenols - Samples

- Cresols:- [Mixed forms.] Tarry, medicinal, leathery, phenolic and smoky.
- Guaiacol (2 methoxyphenol) -100 ppb in Scotch. Smoky, burnt, somewhat medicinal - warm sweet taste yet burning.

Gas-liquid chromatograms of extracts of unpeated and peated Scotch barley malts showing the contribution peating makes to the content of phenols in the malt.



Mash - Contamination and Bacterially Derived Flavors - I

- Mash not boiled - if contaminated can get souring - lactic and acetic flavors - affecting yield and promote off-flavors in the finished product. [Controlled pH changes - backset, sour-mashes.]
- Acrolein from bacterial metabolism as one potent example. Occasional problem - very potent. [Peppery/lachrymator.]

Mash - Contamination and Bacterially Derived Flavors - II

- With some rum production bacterial flora e.g., *Clostridium saccharobutyricum* introduced deliberately - many organic acids contribute to final product (butyric, acetic, propionic and caproic).
- Wild yeast infections can give rise to many kinds of unusual/off-flavors.

Butyric acid and Ethyl Butyrate - Samples

- Butyric acid:- Buttery, rancid, cheesy, sweaty, sickly, baby vomit - not pleasant but produced in some rums deliberately.
- Ethyl Butyrate:- Fruity, papaya, butter, sweetish, apple, perfumed.

Fermentation and Yeast Flavors - Introduction

- Yeast give rise to many flavor components. Esters, alcohols and C_4-C_8 + fatty acid ethyl esters.
- GC - Whisky, cognac and rum are similar.
- All pot-distilled beverages contain:
  - Isoamyl alcohol [Predominant fusel oil].
  - Ethyl acetate plus many other esters.
  - Caprate, laurate, myristate, palmitate, palmitoleate.

Fermentation Flavors - I

- FUSELS:- Whisky and brandy - sensory character in part due to fusel alcohols (alcohols higher than ethanol).
- These “impart a sense of body or depth”.
- Higher temperatures of fermentation (and higher amino acid levels) favor fusel oils in grain fermentations.
- Many fusels come off in the feints (tails).

Fusel Oils - Samples

- Iso-Amyl Alcohol:- Alcoholic, pungent, banana, sweetish, aromatic.
- Whisky Fusels:- a natural complex mixture of the higher alcohols and other components making up fusel oils. [Vinous, ethereal and pungent, oily-smelling.]

Fermentation Flavors - II

- Acetaldehyde:- An intermediate in fusel oil formation. Strain-dependent production and also a problem with nutrient deficient media.
- Lower aldehydes (acetaldehyde, isobutyraldehyde, isovaleraldehyde, and 2-methylbutyraldehyde) impart fruity and roast characters to flavor compositions.
- Acetals derived from the aliphatic aldehydes have odor characteristics resembling those of the aldehydes but less pronounced.

Isovaleraldehyde - Sample

- Isovaleraldehyde:- [Isovaleric aldehyde, 3-methyl butanal.] Found in new make whisky at about 2.5 ppm with an odor threshold (OT) of 0.12 ppm. Pungent apple-like odor. [Unripe banana, cherry, cheese.]

Fermentation Flavors - III

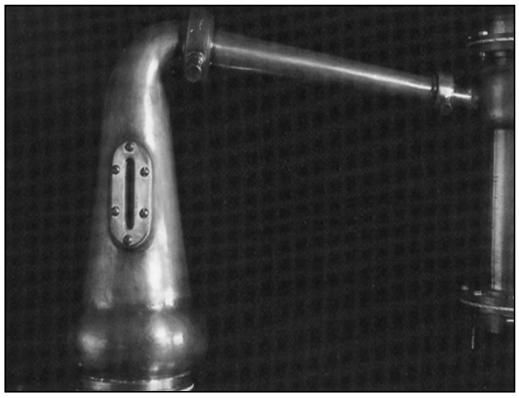
- SULFUR FLAVORS: Distilled Spirits may contain:-
  - DMS [dimethyl sulfide]
  - DMDS [dimethyl disulfide]
  - DMTS [dimethyl trisulfide, a polysulfide]
  - CS_2 [carbon disulfide]
  - Methanethiol
  - H_2S [hydrogen sulfide]

Fermentation Flavors - IV

- The sulfur flavors DMS, DMDS, and DMTS play important roles in whisky aroma. These are present at high concentrations in NEW MAKE SPIRITS.
- DMS arises from malt/grains.
- DMDS and DMTS arise from the heating of grain mashes in distillation (grain whiskies).

Sulfur Compounds - Samples

- DMS:- [dimethyl sulfide, CH_3-S-CH_3] Cooked corn through celery, tomato juice/oysters to garlic.
- DMTS:- [dimethyl trisulfide, CH_3-S-S-S-CH_3] Sulfury, rubbery, gassy or penetrating like fresh onion - detected at about 3 ppm.



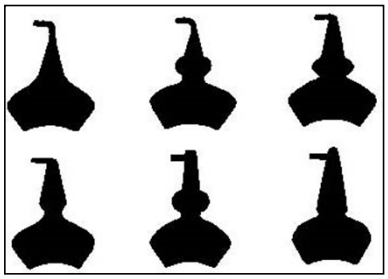
Distillation Introduction - I

- The absolute and the relative amounts of volatiles are altered by distillation. Volatiles flash-off according to boiling points. Low BPt components off first. BUT…
- The Partition Coefficients of volatiles vary with ethanol concentration. So volatiles change from start to the end of distillation.
- Process of distilling is complex and requires a lot of knowledge and skill!

Distillation Introduction - II

- This Leads to the "ART" of Distilling - The expertise of the distiller in knowing how the still works, how to adjust operations and when to make "cuts" and how and when to recycle the various fractions.
- The still type and design (shape, size, connections and angles from still to condensers - Lyne Arms -) influence the composition of the distillate via reflux and condensation.

A selection of different pot still shapes



Whitby, 1992

A Small Pot Still With A Short Column

Jacob Carl

Vendome Copper

Vendome Copper

Spirit Stills: Fractionation - I

- Earliest fraction "Foreshots" (or "Heads") contains the most volatile (lowest boiling point) and undesirable congeners.
- Solventy and fruity notes. Some esters - Et. acetate most abundant. Short chain alcohol esters also.
- Some fusels oils from previous feints, and water insoluble oils - higher fatty acid esters.
- Foreshots are recycled back to the next spirit run to maximize ethanol recovery.

Spirit Stills: Fractionation - II

- "Spirit cut" or Middle fraction. Collected at desired concentration of ethanol and before "feints" come through. [Misting test for spirit cut collection - clears at 45.7% v/v alc.]
- Contains ethyl esters; hexanoate (caproate, C6), octanoate (caprylate, C8), decanoate (caprate, C10), dodecanoate (laurate, C12) and lactate. Important in whisky flavor. Higher chain lengths lead to soapy, oily and sour notes - "immature notes".

Spirit Cut - Samples

- Ethyl caprylate: Apple, sweetish, fruity.
- Ethyl laurate: [Lauric acid ethyl ester] Soapy, warm, waxy, estery, oily, fatty. Petal-like with fruity undertones. [5.50 ppm in whisky, OT at 0.64 ppm]

Spirit Stills: Fractionation - III

- Poor cut from foreshots to spirits leads to heavy contamination of fusels, ethyl acetate, short chain fatty acids and yields a spirit with a characteristic "pear drop" aroma.
- Third fraction- "Feints" (incl. acetal, methanol and fusels - propanols, butanols and the pungent amyl alcohols) distilled over until alcohol conc. reduced to 0.10 - 0.15%. [Feints are said to have a metallic aftertaste.]

Feints (Tails) Cut - Samples

- The mixture known as feints is described as cereal-like, leathery, tobacco, sweaty, stale fish-like.
- Acetal [Acetaldehyde diethyl acetal] Diethyl acetal is formed at concentrations well above its threshold and is said to give a "delicate fragrance" or "pleasing component" to many distilled beverages. Strong, tart, fruity.

Distillation - I

- Chemical Reactions in the hot vapor phase of Distillation:-
- Acids and alcohols react to form esters. Acid catalyzed addition of two alcohols to an aldehyde leads to the acetals.
- Oxidation/reduction reactions occur e.g., aldehydes are converted to acids and some are reduced to alcohols.
- Many of these reactions are catalyzed by copper. Copper also has a profound effect on lipids - altering their profiles.

Distillation - II

- Still shape and size and distillation rate influences the contact time with copper.
- Maillard reactions lead to heterocycles.
- Furfural production occurs in indirect-fired pot stills. (As this is pH dependent earlier control of wash pH can be implemented to control this).

Heterocyclics - Samples

- Furfural:- [2-Furaldehyde -oxygen in ring]. Sweet, woody, almond, baked bread, penetrating. Grainy in whisky at 20-30 ppm.
- Maltol:- [3-hydroxy-2-methyl-(1,4) pyran - a Pyrrole - oxygen in ring] malt, bread crust caramellic, (warm, sweet fruity odor!). [Ethyl maltol more potent-sweet-caramel-like odor.]
- 2,3,5-trimethylpyrazine [nitrogen in ring] nutty, cocoa, green, roasted chocolate.

Distillation - III

- Sulfur compounds undergoing pyrolysis cause generation of thiophenes and polysulfides which are said to give to whisky a "heavy roasted character".
- Copper removes sulfides and mercaptans.
- DMTS is actually formed (aided in the presence of copper) by the heating of grain mashes in distillation.

Distillation - IV

- Coumaric and ferulic acids derived from barley (rye) or grapes can break down to give compounds with spicy or medicinal aromas, such as 4-vinylguaiacol under the heat of distillation.
- Pungent peppery aroma in new spirits (whisky, cognac or rum) is due to acrolein (glycerol derivative) formed during the heat of distillation from a precursor formed by bacteria during fermentation.

Maturation/Aging

- Whiskies (when young are pungent, oily and sour) but become smoother and develop sweet, spicy, vanilla, floral and woody attributes on aging in the barrel. Phenolic, sour, meaty (sulfury) and catty notes decrease.
- The aging process effects three changes to new make spirit: it adds, removes and produces flavors. Subtle reactions occur during aging.

Casks: Thermal Degradation of Wood

- A layer of active carbon is produced which can remove undesirable flavor elements during maturation.
- Oak lignin is anaerobically degraded in the layer immediately under the charcoal and flavor components such as vanilla are released and extracted into the whisky.
- Total wood extract, color and phenols in the maturing spirits are increased and, via oxidative interactions, flavor components are produced.

Oak Aging - I

- Aroma Volatiles Depend on:-
  - ☑ Oak Species and Source of Oakwood.
  - ☑ Time & climate during seasoning of the wood.
  - ☑ Toast or char level of oak.
  - ☑ Cooperage techniques.
  - ☑ Age and size of barrel.
  - ☑ Time and temperature of storage.

Oak Aging - II

- Direct extraction of wood components.
- Decomposition of the macromolecules of wood -lignin, cellulose, hemi-cellulose and elution to spirit.
- Rxns of wood components with unaged spirit components.
- Rxns involving only extracted wood materials.
- Rxns involving only distillate components.
- Evaporation of low-BPt components through the wood.

Oak Aging - III

- Need a minimum of a year for maturation (legally and better maybe more).
- Tannins appear in the spirit.
- Solids increase in the spirit.
- Color added to spirit.
- DMS disappears over a year.
- DMDS and DMTS decrease gradually (less so the DMTS). Oak is indispensable for this.

Casks: Size and Nature - I

- Charring and toasting removes raw woody aroma and astringent taste.
- Characteristic sweet and burnt aroma in bourbon is from maltol and 2-hydroxy-3-methyl-2-cyclopentenone.
- American or European Oak? French - more tannin and color. American - more oak lactone.
- Sherry or Bourbon use? [Port, Other?].

Casks: Size and Nature

- Cask size - smaller casks with high surface to volume ratio produce a higher extract and faster maturation.
- Age of Cask (become spent of volatile acids, esters, tannins, color and furfural etc.) Even with re-charring and re-seasoning the levels are never the same as for first use!
- Monitor - tag casks - know their history (No. of fills, type of fill, cleaning regimes steam/ammonia stripping?).

Casks: Maturation Chemistry - I

- EtOH + O_2 ------ Acetaldehyde
- Acetaldehyde + O_2 ----- Acetic Acid [Acetic also from barrel wood!]
- EtOH + Acetic Acid --- Ethyl acetate
- Lignin in wood combines with EtOH to produce coniferyl and sinapic alcohols.
- Coniferyl and sinapic alcohols are oxidized to coniferaldehyde and sinapaldehyde.
- Coniferaldehyde is further oxidized to vanillin and also possibly ferulic acid. (Precursor to eugenol-like compounds).

Oak Components - I

- Summary of Compounds from Oak:-
- Vanillin and syringaldehyde responsible for vanilla flavor. From lignin.
- Hydroxymethylfurfural and ethyl maltol (derived from the charring reactions).
- Eugenol and other volatile phenolic compounds from new oak.

Oak Components - II

- Oak lactone (β-methyl-γ-octalactone) - or whiskey lactone - Oak wood aroma!
- Tannic constituents - give bitterness and astringency.
- Terpenes and other secondary metabolites - complexity! [Resinous, piney, woody aromas.]
- Heating and charring (Maillard rxns) gives us:- furans, pyrazines, pyridines and pyrans - with smoky, burnt and nutty flavors.

Oak flavors - Samples - I

- Eugenol:- [2-methoxy-4-allylphenol] Spicy, clove-like odor. About 50 ppb. in Scotch malt and Irish whiskies and 195 ppb in Bourbon.
- Whisky or oak lactone:- [β–methyl-γ-octalactone - a Key lactone - cis and trans isomers] Found in all beverages that have undergone maturation in oak. Woody, warm, sweet, coconut notes.

Oak flavors - Samples - II

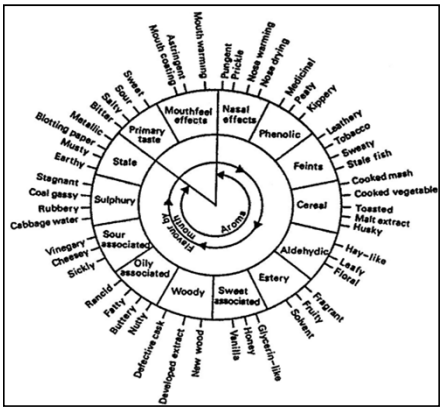
- Vanillin:- [4-hydroxy-3-methoxy benzaldehyde, or vanillic aldehyde] Creamy, vanilla-like odor.
- Ultimately from breakdown and oxidation of lignin. Vanillin and acetaldehyde are co-byproducts of breakdown of these wood derived intermediates.

Section 3

Flavor Terminology and Flavor Wheels
(the Whisky Wheel)

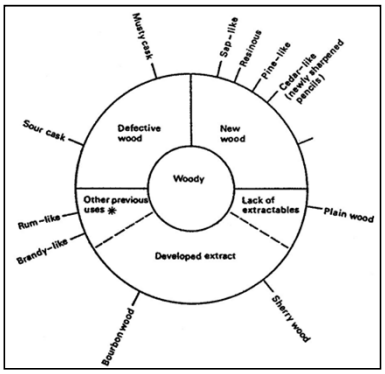
Flavor Wheels

- Like the Beer Flavor Wheel there are some Spirit flavor wheels available as a tool for the sensory evaluation of spirits.
- Most famous and detailed is the Scotch Whisky Wheel.



Cask Flavor Wheel

- Another ("sub-division") wheel is available for whisky and deals with the aspects of "Woody" from cask (barrel) maturation.
- Sensory characteristics of the maturation process - the most important for whisky evaluation - were the least well developed.
- Woody- Ambiguous (Wine and Whisky) so 2nd and 3rd tier terms used to "hone-in" on "woody" or to qualify it as a common descriptor.
- Needed an understanding of the chemistry of maturation (more of this later).



Specific Standards

- The Scottish whisky industry (and SWRI) are now working on defined standards and attempting to define the common language for a full and communicable sensory understanding of malt and grain whisky.
- So far limited success (about 16 chemicals have been assessed as standards with less than ideal results).

Conclusion - I

- Major products of yeast fermentation contribute a generic background flavor to all fermented beverages (esters and alcohols).
- Subtle nuances impacting the total flavor originate from all aspects of the overall production process.
- These subtle combinations of trace components usually elicit the characteristic aromas of these complex beverages.

Conclusion - II

- Flavor chemistry is complex and has a profound effect on the flavor of distilled spirits.
- We now understand a good deal about flavor production and development but we still need to build up and understand the flavor-terminology data base.

Spedding and Bird - AIBD - 2002.

Addendum

The addendum contains material pertaining to Scotch and Irish Whisky Production and to the Production of Rum. Rules for Scotch and Irish whisk(e)y production are also presented. In addition, Canadian whiskey can only be made in Canada. The BATF web sites can be consulted for full information on all spirit classes, types and styles.

Scotch Malt Whisky - I

- **According to statutes, to be called Scotch (malt) whisky, spirits must:-**
- **Be produced at a distillery in Scotland.**
- **Made from water and 100% malted barley (peated or unpeated).**
- **Processed at that distillery into a mash. Mash infusion and separation.**
- **Converted to fermentable carbohydrate only by endogenous enzymes.**

Scotch Malt Whisky - II

- **Fermented only by the addition of yeast (a mix of brewers and distillers strains).**
- **Be distilled to an alcohol strength less than 94.8%, so that the distillate has the aroma and taste derived from the raw materials.**
- **Be matured in Scotland in used oak casks (less than 700 L) for a minimum of three years.**

Scotch Malt Whisky - III

- **Must retain the color, aroma, and taste derived from the raw materials.**
- **AND Nothing must be added except water and spirit caramel!!**

Irish Malt Whiskey - I

- **Irish pot still whiskies are distinguished from blends and are those spirits distilled in pot stills in the Republic or Northern Ireland from a mash of cereal grains normally grown in that country.**
- **Saccharified by the diastase of malt contained therein, with or without other natural diastase (can use microbial enzymes). Made with unmalted barley (upto 60%) and unpeated malted barley. Infusion mash and wort separation.**

Irish Malt Whiskey - II

- **Aged for at least three years in Ireland in wooden barrels.**
- **Does not possess the "smoky" taste and aroma of Scotch but is more flavorful and and is heavier bodied than its Scottish rival.**
- **It is (OFTEN!) distilled three times to produce a very strong spirit of 86% v/v [GL] (172 Proof).**

Rum - I

- The BATF states that Rum is "An alcoholic distillate from the fermented juice of sugar cane, sugar-cane syrup, sugar in molasses or other sugar-cane by-products, produced at less than 190^0 proof (95% v/v) in such a manner that the distillate possesses the taste, aroma and characteristics generally attributed to rum, and bottled at not less than 80^0 proof (40% v/v)".

Rum - II

- Light Rum:- nearly neutral made as continuous still products.
- Heavy Rum:- dark, Navy-type are pot still products.
- If made from molasses the source has a strong influence on the aromatic quality of the rum.
- Beet molasses do not possess the same characteristics as cane molasses. Blackstrap molasses are considered the best.

Rum - III

- Bacterial contaminations and even introduced bacteria produce acids and esters for flavor.
- E.g., *Clostridium saccharobutyricum*:-

  Butyric acid

  Acetic acid

  Propionic acid

  Caproic acid

  These react with Ethanol to produce desirable esters.

Rum - IV

- Rum is often matured in Oak Barrels. Some are not aged (white rums).
- Light rums (Amber - with low levels of congeners) are aged a short time.
- Heavy (Dark) rums have longer aging (for palatability), e.g., 5 years or more.
- Bourbon barrels are used with or without the char removed. Some light types aged in new or once used barrels end up with bourbon character, odor and taste. (Bourbon character is derived from oak wood.)

Rum - V

- In the second still run, the heads may again be discarded along with the tails. The "center cut" - the bulk of the distillate contains the more pleasant aromas of fruity esters "characteristic of rum".
- Rums are very ester rich! [100 + With up to 640 ppm total ester concentration.]
- Diacetyl (VDK's) 460-4400 ppb in Rum!! Dark rums can be very buttery.
- Normally two pot distillations but sometimes three!