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**Potential Explosion Hazards due to
Evaporating Ethanol In Whisky Distilleries**

HSL/2003/08

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EXECUTIVE SUMMARY

Ethanol is a highly flammable liquid with a relatively low flash point, ≈ 21 °C – the flash point is dependent on the alcohol concentration. There is a concern that evaporating ethanol could pose an explosion hazard in bonded warehouses and in stills rooms. A literature search was carried out to ascertain the incident rate of explosions in distilleries. It appears that explosions occur only very rarely. A report from the mid-1960's suggested that explosions leading to fatalities and casualties as well as substantial destruction of buildings happen, apparently as a result of a preceding fire in many cases, but that very severe incidents occur fairly rarely.

Whisky is produced through a multi-stage process, of which distillation of the wash is the penultimate stage, by which the alcohol level in the whisky is raised to 70-80 %, by volume. The distillation takes place in copper distillers located in a stills room. Ethanol boils at a temperature of 78.4 °C. The surface of the copper vessel is at a temperature at or in excess of the boiling point of ethanol. The surface temperature is, however, well below the auto-ignition temperature of ethanol, which is around 426 °C, which precludes auto-ignition by the stills vessel surface. The whisky is then stored in casks, made of oak, in bonded warehouses for a minimum period of three years, used for blends, some single malts are exported after five to seven years, while other single malts are stored for eight to 40 years. A considerable amount of whisky is stored in these warehouses. The warehouses are often old, possibly of Victorian origin, and built with stone. The natural ventilation is an integral part in the maturing process of the whisky, lending it a particular quality, which will be different from region to region. It has been assumed that a typical air change rate is of the order of ten air changes per hour.

It is not within the remit of the present study to delve deeper into the potential sources of ignition. Possible sources of ignition are however likely to fall into one of the following categories - a lightning strike, open fire, discarded and still lit cigarettes, static electricity, sparks generated due to electrical faults, etc.

There appears to be a low probability of an explosion due to the ignition of an ethanol/air mixture. The evaporation rate of ethanol at 25 °C is too low; the natural ventilation would almost certainly be able to dilute the gas cloud ethanol concentration down to well below its lower flammability limit. However, the present study does not take into account the possibility of recirculation zones or stagnant regions, where the gas cloud could, potentially, become enriched so as to fall between the lower and upper flammability limit. It would be necessary to use more sophisticated tools, e.g. Computational Fluid Dynamics, to investigate gas build up in these regions.

OBJECTIVES

1. To investigate the likelihood of an explosion due to evaporating alcohol in a whisky distillery storage room
2. To investigate the likelihood of an explosion due to evaporating alcohol in a whisky stills room
3. To compile information about explosions in whisky and other spirits producing distilleries

MAIN FINDINGS

1. Explosions in distilleries appear to occur infrequently. There are only a few incidents reported in the literature, as a search through various databases, including HSE's major accidents database, revealed.
2. The results from the calculations suggest that there is not a problem with the formation of an explosive/flammable ethanol/air mixture, at the conditions assumed in the present study, e.g. ambient temperature. It is worth noting that possible build up of a flammable gas cloud in recirculation or stagnant regions, caused by the natural ventilation flow, have been ignored.

MAIN RECOMMENDATION

1. There are no recommendations.

1 INTRODUCTION

The present project was initiated to investigate the likelihood of an explosion due to evaporation of ethanol from pools caused by accidental spillage of whisky in distilleries.

Fleischman, Parris, Daley and Looby (1995) estimated the spillage at the cask filling stage to be just under 500 kg year⁻¹ for a medium size bourbon distillery, which represents roughly a loss of the order of 0.005 % of the annual production. Carter and Linsky (1974) studied the emission of ethanol from whiskey fermentation vats. Carter and Linsky quoted average ethanol emission figures of 182 g m⁻³ of grain input. UDV, the spirits and wine division of Diageo (with labels such as Guinness, classic single malts, Johnny Walker, etc.), produced an environmental report, Anon (2001), where it was suggested that an estimated 15,000 tonnes of ethanol was released into the atmosphere from maturing whisky in Scottish distilleries. Mascone (1978) investigated the ethanol losses in the American whiskey industry. Mascone estimated the loss of ethanol to be 3.2 kg barrel⁻¹ year⁻¹ during the ageing phase of whiskey production. However, of more concern is spillage in the stills room or in the warehouse. The loss of ethanol due to the evaporation from the casks, known as the angels' share, is not considered in the present study. The concern with evaporating ethanol is equally valid in distilleries producing other spirits, such as gin, vodka, etc.

Rasbash (1966) examined a number of incidents involving fire and explosion in spirits warehouses. Rasbash found that the incidents were rare occurrences. In one case, a fire started in the warehouse, which after several hours build up led to an explosion, which tore the building apart. The common theme in the incidents was that a fire would precede an explosion - radiation and convection enhancing the vaporisation of ethanol, destroying casks and/or structures leading to further spillage and subsequent ignition of the explosive mixture. Rasbash identified five mechanisms for the production of a flammable mixture:

- Evaporation of ethanol following a leak under normal temperature and pressure
- Evaporation of ethanol from a spillage into a hot ambient atmosphere, due to a fire
- Evaporation of ethanol onto a hot surface, heated by radiation from a fire
- Production of explosive mixture in a tank or cask
- Evaporation of ethanol into a oxygen deficient atmosphere, with a subsequent introduction of air

The current FOD/HSE PM84 Guidance Note, Anon (2000), which is concerned with explosive gas mixtures in gas turbine acoustic enclosures, sets an upper limit for the maximum acceptable gas cloud size (at 50 % LFL). The maximum acceptable gas cloud size is 0.1 % of the total enclosure volume. Experiments have shown that explosions involving gas clouds of that size give rise to negligible over-pressures. The PM84 recommendation has been adopted in the present study – though the layout of a stills room differs significantly from that of an acoustic enclosure.

There was some confusion over how the unit proof is defined. The British definition, Anon (2002a) and Anon (2002b) did not give any explanation of how the proof was calculated, while Anon (2002c) did – the whisky is mixed with gunpowder in some proportion. The mixture is then exposed to a naked flame to see if the flame would ignite the mixture. Table 4 shows the conversion between proof and volume fraction of ethanol. The American definition of proof is that proof is twice the volume fraction of ethanol. The British definition has been used in the calculations throughout the present report.

2 REPORTED EXPLOSIONS

A literature search was carried out to find references to explosions in distilleries. Only a few accidents could be found. In a couple of cases, there appears to be some confusion over the sequence of events, e.g. whether an initial fire caused the explosion or the explosion preceded a fire. The information obtained is scant.

2.1 PEORIA, ILLINOIS - 1935

A bonded warehouse, owned by Hiram Walker & Sons, in Peoria, Illinois, had started listing, Rasbash (1966). Remedial work had been undertaken in order to secure the building. However, the work was not finished and the building was still not in plumb. The lift was not working and the whiskey casks were therefore still stored in the building. Eyewitnesses claimed that they had heard an explosion. It was conjectured that a few whiskey casks might have been dislodged, but how and why they were dislodged is not known. It was never established what had acted as the ignition source.

2.2 PEKIN, ILLINOIS - 1954

A fire had started in American Distilling Company's distillery in Pekin, Illinois, in 1954. The fire built up over several hours. Two warehouses had been burned out. The radiation from the fire in an adjacent building led to the roof of one of the remaining warehouses getting very hot. The increased roof temperature in turn led to the ignition of an ethanol/air mixture. It was not known how the gas cloud had formed, but it is conceivable that an increased evaporation of ethanol due to the radiation from the fire had occurred.

2.3 AHMADNAGAR, INDIA

An explosion occurred in an industrial alcohol distillery in Ahmadnagar, India, on 20 December 1985, Anon (1985). It was an explosion in an acetic acid tank; the cause is not the ignition of evaporating alcohol so the incident is not directly relevant to this study. Nevertheless, there were five fatalities and 45 casualties because of the explosion.

2.4 PUERTO DE SANTA MARIA, SPAIN

An explosion and subsequent fire occurred at the Alcoholes del Puerto factory on 24 August 1988, Anon (1988). The explosion affected six tanks containing ethanol, the distillation plant and offices and personnel buildings. Seven people were killed in the accident, while four persons suffered burns and one person was reported missing. Unfortunately, there was no additional information with regards to the cause of the explosion, or what killed the seven people.

2.5 THONBURI, THAILAND

A series of explosions ripped through a whiskey distillery in Thonburi, Thailand on 14 June 1993, Anon (1993). There were four fatalities and at least 10 injured. The explosions were caused by a fire. The report suggested that the source of ignition were sparks from welding equipment. There were also environmental effects as dangerous chemicals were leaked into a river, Anon (1993).

2.6 LAWRENCEBURG, KENTUCKY, USA

A fire broke out in a warehouse at the Wild Turkey Bourbon distillery in Lawrenceburg, USA on 9th May 2000, Chellgren (2000) and Mazza (2000). A significant amount of bourbon,

between 15000 and 20000 casks, each of which held 53 gallons of whiskey (3000 - 4000 m³), was stored in the seven-story building. The warehouse was reduced to a pile of rubble by the fire. It was reported that workers at a nearby water treatment plant had heard a loud bang, as would be produced by an explosion. They went out to investigate what had happened and they then saw that one end wall and part of one of the sidewalls of the warehouse had been blown out - the warehouse then collapsed after about three minutes. The fire brigade concentrated their efforts on ensuring that the fire would not spread to any of the other eleven warehouses on site. There were no fatalities - though two firemen had to be taken to hospital suffering from heat exhaustion. A water treatment plant, which serves Lawrenceburg and surroundings with drinking water, had to be shut down as bourbon escaped into a nearby river and was about to be drawn into the water treatment plant intake.

2.7 ATCHISON, KANSAS, USA

An explosion took place in the Midwest Grain Inc. ethanol distillery in Atchison, Kansas on 13th September 2002. Four people were injured in the explosion. Eyewitness accounts reported that flames shot out of the windows of the factory, after which the fireball lifted into the air. The roof and one side of the building were completely destroyed by the blast. The strength of the blast was such that ceiling tiles and light lenses fell to the floor in a bowling alley some two blocks west of the distillery. The cause of the explosion is not known.

3 Calculations

3.1 ASSUMPTIONS AND SIMPLIFICATIONS

- The ethanol vapour pressure is not altered by the “active ingredients” in the whisky, which are not well characterised
- The age of the whisky does not affect the vapour pressure
- Equilibrium between the gas and the liquid phase is established
- Raoult’s Law is applicable to the ethanol/water mixture
- The conditions in the warehouse are fully mixed
- The emission rate does not change with time and corresponds to the maximum rate - e.g. after the soakage phase is completed (after 6-18 months) - not needed since it is assumed that equilibrium between the liquid and the vapour phase is established, see above
- Equipment in the stills and storage rooms does not affect the effectiveness of the natural ventilation - nor does it affect the fluid flow in the rooms
- Equilibrium between the gas and the liquid phase is established
- The storage room is 10 m wide, 10 m long and 5 m high
- The air change rate is 10 h^{-1}
- The temperature in the stills room and the storage room is 298.15 K, the humidity is 50 % and the pressure 101,325 Pa (1 atm)
- The temperature and pressure does not change appreciably
- The ambient air is initially made up of oxygen (20.9 % v/v) and nitrogen (71.1 % v/v)
- The concentrations of oxygen and nitrogen in the liquid phase is negligible
- The British definition of whisky strength has been used in the present report – the measurement of strength involved mixing the whisky with gunpowder and thereafter investigate whether a naked flame would ignite the mixture, Anon (2002C)

3.2 PHYSICAL PROPERTIES

3.2.1 Ethanol

TABLE 1: Physical properties of ethanol, at $P = 101,325 \text{ Pa}$ and $T = 298.15 \text{ K}$

Physical property	Value
Lower Flammability Limit (LFL)	3.5 % v/v
Upper Flammability Limit (UFL)	19.0 % v/v
Molecular weight	46.07 kg kmol ⁻¹
Flash point	285.15 K
Boiling point	351.45 K
Vapour pressure	7.9 kPa

The data was obtained from SAX, Anon (1999), except the vapour pressure, which was calculated from Equation 3. Olbrich (1980) quoted slightly different LFL and UFL values, but the SAX data has been used.

3.2.2 Water

TABLE 2: Physical properties of water, at $P = 101,325 \text{ Pa}$ and $T = 298.15 \text{ K}$

Physical property	Value
Molecular weight	18.04 kg kmol ⁻¹
Boiling point	373.15 K
Vapour pressure	3.2 kPa

The vapor pressure for water was calculated from Equation 3.

3.3 RESULTS

Dalton's law relates the partial pressure of a species to the mole fraction of said species in the gas phase and the total pressure:

$$P_i = y_i P_{tot}, \quad (1)$$

where y_i is the mole fraction of species 'i' in the gas phase and P_{tot} is the total pressure.

It has been assumed that Raoult's law applies to the binary mixture. Raoult's law relates the partial pressure of a species to the mole fraction of said species in the liquid phase and the partial pressure the species would exert if it were a pure liquid:

$$P_i = x_i P_i^0, \quad (2)$$

where x_i is the mole fraction of species 'i' in the liquid phase and P_i^0 is the partial pressure of the pure species 'i'.

The vapour pressure of species 'i' varies with temperature and can be calculated using

$$\ln P_i^0 = a_i - \frac{b_i}{T - c_i} \quad [kPa], \quad (3)$$

where a_i , b_i and c_i are species dependent constants, T is the ambient temperature, in K. Table 3 shows the values of the constants used in equation 3.

TABLE 3: Species dependent constants in the vapour pressure equation

Species	a_i	b_i	c_i
Ethanol	16.19	3424.0	-55.72
Water	16.54	3985.0	-39.0

The mole fraction of species 'i' can be readily calculated using the following expression, a combination of equations 1 to 3:

$$y_i = 1000 \frac{x_i}{P_{tot}} \exp \left\{ a_i - \frac{b_i}{T + c_i} \right\}, \quad (4)$$

where the factor 1000 is used to convert the partial pressure to Pa.

TABLE 4: Conversion from proof to volume fraction of ethanol

Proof	Volume fraction of ethanol
70	40
75	43
80	46
90	52
100	56
105	60

It was necessary to carry out an iterative procedure in order to calculate the correct molecular volume, which unfortunately varies quite considerably for the ethanol/air mixture. A diagram in Atkins (1983), Figure 8.1 on page 216, proved to very useful.

3.3.1 70 proof whisky

The number of moles of species ‘i’ in the liquid mixture can be calculated with the following formula:

$$n_i = \frac{V_i}{V_{m,i}}, \quad (5)$$

where V_i is the volume fraction of species ‘i’ in the mixture and $V_{m,i}$ is the molecular volume, interpolated from Figure 8.1 in Atkins (1983). A mole fraction of ethanol was chosen, the corresponding molecular volumes were read from the graph, and a new mole fraction of ethanol could be calculated using Equation 4. A new set of molecular volumes can be read from the graph. This procedure is continued until the mole fractions have converged. There is some uncertainty in the results given the interpolation from a graph. Three iterations were required before the mole fractions could be considered to have converged. The calculations gave the following result; $n_A = 0.85$ and $n_B = 0.15$. The mole fraction of ethanol in the gas phase was 0.0125, which is below LFL for the ethanol/air mixture. Hence, there is no risk of an explosion or fire.

3.3.2 90 proof whisky

The procedure outlined in Section 3.4.1 was followed in the 90 proof case. The calculations of the mole fractions of the two species in the liquid phase yielded the following result; $n_A = 0.774$ and $n_B = 0.226$. The mole fraction of ethanol in the gas phase was 0.0176, which is below LFL for the ethanol/air mixture. Hence, there is no risk of an explosion or fire.

4 DISCUSSION AND CONCLUSIONS

4.1 DISCUSSION

A search through the HSE incident database as well as other databases did not yield a large number of reported incidents. The best source was a report by Rasbash (1966), which contained details of a few incidents involving explosions in whisky bonded warehouses. The information in the report is old – it relates to incidents, which took place between 1935 and 1966. There appears not to have been an update of the report or any other study undertaken since Rasbash's report was published, some 35 years ago. Most of the recent incidents, which were reported in Lloyds Casualty Reports, were described in such brief details as to make it difficult to assess the exact nature of the incidents. However, it would appear that the reported incidents involving explosions were not due to the ignition of an ethanol/air mixture, formed from natural evaporation or spillage.

The ethanol evaporation rate is low in a room at 25 °C, which could represent a typical maximum room temperature in a bonded warehouse. The calculations, carried out in the present study, indicate that the formation of a gas cloud with an ethanol concentration between the lower and upper flammability limits is unlikely. A number of assumptions have been made, though it is unlikely that these would significantly alter the conclusions of the present study. However, it must also be remembered that although the bonded warehouses are naturally ventilated, assuming a typical figure of ten air changes per hour, there could be regions of recirculating flow. The ethanol vapour could find its way into these regions of recirculation, thus giving rise to gas clouds with an ethanol concentration within the flammability limits. The present study does not consider fluid flow effects. A more sophisticated tool, e.g. Computational Fluid Dynamics, would have to be employed if it is desirable to investigate gas cloud build-up in stagnant regions of the warehouse.

Rasbash (1966) suggests that a fire in an adjacent building, if unsuccessfully checked, could lead to a temperature rise in the warehouse. The higher temperature could then result in an increased ethanol evaporation rate and, thus, to the formation of a gas cloud.

The scenario of spillage or leakage in the stills room is more complex. The temperature in the copper distillers is well above 25 °C, so that the surface temperature will also be relatively high, but well below the auto-ignition temperature of ethanol, which is around 430 °C. It is therefore not possible for the hot surface to auto-ignite the ethanol/air mixture. Rasbash (1966) correctly states that a hot surface would lead to an increased evaporation rate of ethanol. Moreover, Rasbash suggested that a hot surface would not necessarily lead to an explosion, if the fire were in the vicinity of the hot surface, as a relatively small fire would ensue. Rasbash (1966) did recognise that a flammable gas cloud could form if the fire was located a substantial distance away from the hot surface. The air change rate and the airflow pattern in the room would be two important factors in deciding whether an explosive mixture would form and where it would be located.

The production of an explosive mixture due to the heating up of a storage tank or cask is not considered explicitly in the present study. It is noted, however, that this scenario is a likely one. It is not known whether any experimental studies into the effects of flame engulfment of oak casks have been undertaken. It is therefore not possible to comment on how long a cask would stand up to a fire. The oak used to manufacture casks is a good insulator, see Table 5, so the temperature rise in the whisky would be relatively slow. A possible outcome of the flame engulfment of a cask is that the metal hoops, with high thermal conductivity, see Table 5, which hold the oak staves together, would heat up first. The transfer of heat to the contents of the cask is of course governed by the heat conductivity of the oak and not the steel. However, it is not clear what is the most likely failure mechanism. It is interesting to note

that the oak has nearly four times higher thermal expansion coefficient than the carbon steel used for the hoops, which means that the staves and the cask ends would expand more than the metal hoops for a given temperature difference. The temperature in a flame could be of the order of 500 °C to 1000 °C, at which steel would begin to soften. One possible failure mechanism would be that the steel hoops snap or get dislodged due to the large difference in thermal expansion between the wood and the steel, thus relieving the pressure in the cask. The ethanol vapour would then ignite. Further study would be required to establish the failure mechanism of flame-engulfed whisky containing oak casks.

Table 5: Physical Properties of oak and carbon steel, Kaye and Laby (1989)

Material	α K ⁻¹	λ W m ⁻¹ K ⁻¹
Oak	35·10 ⁻⁶ - 60·10 ⁻⁶	0.14-0.17
Carbon steel	≈ 16·10 ⁻⁶	≈ 45

4.2 CONCLUSIONS

The calculations performed in the present study seem to indicate that there is very low probability of an explosion of ethanol/air mixture, formed either by a spillage or by natural evaporation. The assumed temperature, pressure and alcohol content of the whisky would be very unlikely to yield a gas cloud with an ethanol concentration in the flammable range.

The failure mechanism of an oak cask is not known. There is a large difference between the thermal expansion coefficients of the oak and the steel hoops.

The accumulation of ethanol vapours at higher concentrations in a slow moving, recirculating flow, due to natural ventilation, cannot be ruled out. However, the effects of the natural ventilation have not been taken into account in the present study. A more sophisticated mathematical tool, e.g. CFD, would need to be employed in order to study the possible accumulation of ethanol in almost stagnant regions within the bonded warehouse.

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