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FIRE PROTECTION OF BIOETHANOL STORAGE TANKS: THE PRACTICAL EXPERIENCE OF AN ITALIAN BIOREFINERY

In many countries the ethanol use is significantly increased in order to replace fossil fuels with renewable fuels. This trend has introduced problems, which are referred to fight of ethanol fires. In fact the thermal radiation from an ethanol fire can be significantly higher than that of a gasoline fire. Bioethanol can be also produced by renewable sources in industrial plants, which are called "biorefineries". The paper is focused on the practical experience of an Italian biorefinery and describes the firefighting systems, which have been applied to the ethanol storage area in order to guarantee that an unexpected fire can be controlled and extinguished in short times and limit the fire effects on human health.


Bioethanol storage tanks

In these last years ethanol use is significantly increased both in Europe and in USA. It can be used in vehicles or small engines, which are fed by conventional fuels, and is utilized as a fuel extender and octane improver with blends, that usually are 10% ethanol and 90% unleaded gasoline. Ethanol is sold in two main forms: E10 and E85. However E85 can be only used in "flex-vehicles", which are designed and manufactured to use E85 [1]. As there is the real possibility that ethanol continues to be one of the main alternatives to fossil fuels in the transports field, the volumes of produced and stored ethanol will undergo an increase in coming years. Therefore the firefighting of ethanol storage tanks is a problem of international character. Nowadays there is a significant lack of knowledge and practical experience in the field of bioethanol tanks fires in particular in Europe, though various researches are developing in some countries. Experience in fires, which have involved ethanol or other water miscible fuels, is very limited and the few tanks fires, that have occurred, have resulted in burn out rather than extinguishment. A very important issue is that the burning behavior of a large scale ethanol fire may be significantly different from that of a petroleum fire [2]. Previous tests with similar fuels indicate that the heat flux from an ethanol fire can be significantly higher than that of a gasoline fire [3]. This increases the risks for fire escalation and therefore efficient firefighting systems are required. The reason for this difference is that as the scale increases, gasoline fires increasingly generate larger amounts of smoke, which tends to block the visible parts of the flames, thereby reducing the heat flux. An acetone/ethanol fire is almost free from smoke and therefore the heat flux is not dissipated by smoke. This implies that the heat flux from an ethanol fire will exceed that of a gasoline fire with the difference, that grows as the scale increases. This biofuel can be also generated by renewable sources in industrial plants, which are called "biorefineries". The paper has been focused on the practical experience of an Italian biorefinery and describes the firefighting systems, which have been applied to the ethanol storage area in order to guarantee that an unexpected fire can be controlled and extinguished in short times and limit the fire effects on human health. The goal of this paper is to illustrate a practical experience, which can provide an useful example in order to improve the firefighting of ethanol storage tanks and ensure their safer operation.

Biorefinery: description of the bioethanol production process

The examined biorefinery is located at Crescentino (VC, Italy) and produces about 40,000 t/y of ethanol. Bioethanol production process (Fig. 1) is based on a technology, which has been designed to utilize non-eatable biomasses such as residues from food industry (arundo donax, sugar-cane bagasse, wheat straw, etc.), wastes from agriculture and energetic cultivations. This process is based on five phases:
1) pre-treatment of lignocellulosic biomasses;
2) enzymatic hydrolysis;
3) fermentation;
4) distillation;
5) energy production.

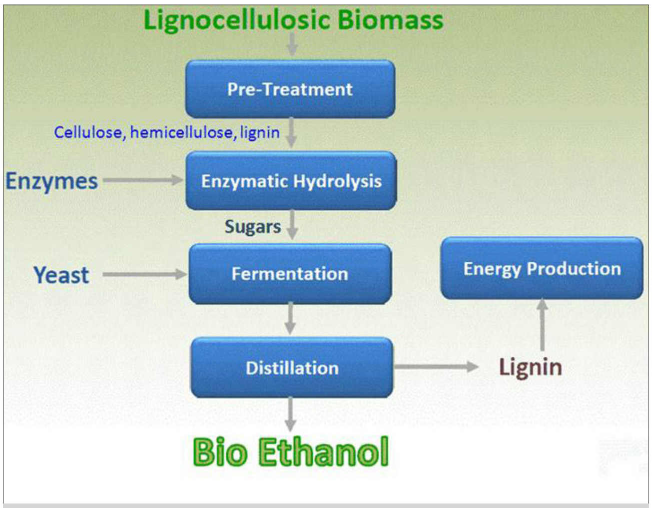

Fig. 1 - Bioethanol production process

This technology encompasses a first innovative pre-treatment step [4], which is necessary to separate the three basic polymeric components of the biomass: lignin, cellulose and hemicellulose. This phase is followed by a process aimed at reducing the viscosity; it prepares the substrate for the subsequent simultaneous saccharification of cellulose and hemicellulose and the co-fermentation of simple sugars (C5 and C6), so obtained, into ethanol. The saccharification of the complex sugars to monomeric fermentable sugars occurs by enzymatic hydrolysis and is performed by a biocatalyst (enzymes cocktail). This process is acid, alkali-free and has minimal by-products. In order to achieve a high separation efficiency, chemical additives are not required and steam and water are used during the pre-treatment step.

Bioethanol storage

The biofuel is stored in outdoor fixed roof tanks, having an internal floating roof. The industrial settlement has three daily tanks ($V_{daily\ tank}$=193 m^3), two weekly tanks ($V_{weekly\ tank}$=1450 m^3) and one denaturant tank ($V_{denaturant\ tank}$=300 m^3 and its diameter is 7 m), which is located in the basin, including the daily tanks. The bioethanol, which must carry out the quality tests, is stored in the daily tanks, while the biofuel, that has passed the tests, is stored in the weekly tanks. The daily and weekly tanks are included in two different basins, which respectively have an area of 896 m^2 and 1248 m^2. Diameter of the daily tank measures 6 m and its height is equal to eight meters. The weekly tank has the following dimensions:
- diameter = 12 m;
- height = 14 m.

Ethanol storage area: firefighting strategy

The firefighting strategy [5] is used to mitigate the outcomes of industrial fires and preserve the mankind health. In the biorefinery this strategy has defined:

1) suppressant agent (this choice mainly depends on the chemical properties of the fuel);
2) fire detection systems;
3) firefighting systems;
4) design criteria of firefighting systems: minimum nozzles number, operating pressures, minimum application rates, minimum application duration, monitors number, monitors jets, etc.;
5) foam inventory;
6) technical solutions aimed at ensuring the supply of suppressant agent in case of pumps failure;
7) passive fire protection methods (safety distances for ethanol storage tanks).

In the following paragraphs the previous points are illustrated and the attention has been focused on the ethanol storage area. In particular firefighting systems have been chosen to decrease the insurgence of domino effects and mitigate the consequences of a pool fire, which could be generated by an accidental release of biofuel in the containment basins. In order to ensure these two goals the following safety devices have been installed in the biorefinery:

1) low-expansion systems and sprinklers (storage tanks protection);
2) foam monitors (basins protection);
3) hydrants.

The choice of the suppressant agent

An alcohol-resistant aqueous film forming foam (AR-AFFF) has been chosen as suppressant agent, because ethanol generates class B fires and belongs to the category of the water miscible fuels. Fires in flammable liquids [6], that readily mix with water, are more difficult to extinguish than hydrocarbon fires. In fact polar solvents and alcohol liquids destroy any foam blanket [7], which is generated using standard AFFF or film forming fluoroprotein foam concentrates (FFFP). Water in the generated foam blanket mixes with alcohol, causing the foam blanket to collapse and disappear until the fuel surface is completely exposed to the air. In the last years many series of fire tests were conducted in the USA in order to provide useful recommendations to the fire brigades about foams, which were able to ensure a rapid and efficient extinguishment of ethanol fires [8]. Tests data, both in large scale and in small scale, showed that the use of high quality alcohol-resistant foam is a crucial factor to obtain successful extinguishment of water miscible fuels (ethanol) [9]. AR-AFFF was developed to overcome this problem. Using AFFF concentrate as a base material, a high molecular weight polymer is added during the manufacturing process. When AR-AFFF is used on a polar solvent fuel fire, the polar solvent fuel tries to absorb water from the foam blanket. A polymer precipitates out, forming a physical barrier between the fuel surface and foam blanket. This barrier protects the foam blanket from destruction by the ethanol. It follows that AR-AFFF meets the stringent requirements of ethanol storage tanks fires. In fact AR-AFFF improves the burnback resistance, allows a fast extinguishment of ethanol fires and has a lower viscosity than conventional AFFF. This typology of foam increases water retention in the foam and resistance to fuel reignition. In this case both hydrocarbon and fluorocarbon surfactants are used in AR-AFFF formulation: the hydrocarbon surfactants produce a low energy of the interface, which is in contact with the fuel, while the fluorocarbon surfactants minimize the energy of the upper surface of the film [10]. These elements influence the film formation and improve the fire control. In this application a 3% AR-AFFF concentrate has been used as suppressant agent.

Ethanol storage area: fire detection systems

The fast fire extinguishment also depends on its quick detection. In order to fulfil this requirement a heat detector cable is located on every ring, which surrounds the ethanol tank. It can be defined as a continuous heat detector and detects heat anywhere along its length. In this way the control of abnormal temperature increases is guaranteed. Every tank is equipped with two heat detector cables, whereas every basin is equipped with one heat detector cable, that is located along the entire perimeter. The cable is composed by two copper wires, which are individually insulated with a heat sensitive polymer. At the rated temperature the polymer insulation melts, permitting the conductors to short-circuit and therefore an alarm signal is generated and transmitted to the control room in order to activate the firefighting systems. Two temperature alarm levels are available: 68 °C and 105 °C. Detector response time is very short (10 seconds for direct flame), because the cable is laid very close

Fig. 2 - Fixed surface system and sprinklers

to the potential fire source and therefore there is not any strict dependence from air convection and temperature variations. These detectors are characterized by easy installation and maintenance, fast substitution of the short-circuited cable, minimum false alarms and simple integration with fire extinguishment systems.

Protection of ethanol storage tanks: low-expansion systems and sprinklers

In the event of a fire in a flammable liquid storage tank, it is vital to suppress the fire in shortest times in order to protect the tank structure as well as workers health. The NFPA 11 has been used to determine design parameters of low-expansion systems and foam monitors. Both daily and weekly tanks are equipped with fixed surface systems (Fig. 2), which apply foam to the fuel surface to create a blanket and suppress the vapors. Minimum foam application rates (Q_{foam}) have been calculated by the following equation in accordance with the mentioned standard [11]:

$$Q_{foam} = (D^2/4)\pi\cdot 4.1 \qquad (1)$$

where:

- Q_{foam} is expressed in liters per minute (l/min.);
- D is the tank diameter (m);
- 4.1 is the minimum application rate per square meter (l/min. x m^2) in accordance with NFPA 11.

The calculated rates are:

Q_{foam} (daily tank) = (36/4)·3.14·4.1 ≈ 116 l/min.
Q_{foam} (weekly tank) = (144/4)·3.14·4.1 ≈ 464 l/min.
Q_{foam} (denaturant tank) = (49/4)·3.14·4.1 ≈ 158 l/min.

Considering these calculated values, a low expansion system has been chosen to protect the ethanol storage tanks. In accordance with NFPA 11, daily and weekly tanks and denaturant tank are equipped with one foam nozzle (their diameters are lower than 24 meters) and sprinklers, which are mounted on two rings, surrounding every tank; in the daily tanks and denaturant tank the nozzle is able to inject up to 400 l/min. at 7 bar (operating pressure), while in the weekly tanks the foam nozzle is able to inject up to 800 l/min. at 5 bar (operating pressure). These flowrates have been increased to make easy and fast the fire extinguishment and improve the safety level of the storage area. The minimum discharge time of fixed foam nozzles, which are used for the ethanol tanks, is equal to 55 min., because ethanol flash-point is below 38 °C. The foam nozzles are made of brass and have a upper chamber in which the speed of the liquid, that flows from the nozzle, aspirates air through two slits in the upper part and this ensures a good spreading of the foam on the surface, which must be protected. The foam nozzles and sprinklers are installed to prevent domino effects, that can often make the fire outcomes worse. The daily tanks are equipped with twenty-two sprinklers (eleven elements for every ring), while the weekly tanks are equipped with fifty sprinklers (twenty-five elements for every ring). The sprinklers are equally spaced around the tanks circumferences. The daily tanks sprinklers are able to inject 35 l/min. at operating pressures, which range between 7.6 and 9.1 bar, while the weekly tanks sprinklers are able to inject 48 l/min. at pressures, that range from 5.2 to 9.6 bar. This depends on the sprinkler position.

Fixed surface systems: foam inventories

An adequate foam inventory is fundamental to face large fires of ethanol tanks. In the biorefinery the minimum foam inventory (MFI) has been calculated in accordance with NFPA 11. The following equa-

Fig. 3 - Fixed foam monitors

tion has been used to achieve this aim:

$$\text{MFI} = \text{tank area} \cdot \text{AR} \cdot \text{FC} \cdot \text{AD} \qquad (2)$$

where:
- AR (application rate) = 0.16 gpm/ft^2 (ethanol);
- FC (foam concentrate) = 3% (AR-AFFF);
- AD (application duration) = 55 min.

The minimum foam inventory is expressed in gallons and subsequently converted in liters. For the examined plant the required MFI are reported:

MFI (Daily tanks) = $3 \cdot 9.84^2 \cdot 3.14 \cdot 0.16 \cdot 0.03 \cdot 55 \cdot 2$ = 1825 l (482 gal)

MFI (Weekly tanks) = $2 \cdot 19.7^2 \cdot 3.14 \cdot 0.16 \cdot 0.03 \cdot 55 \cdot 2$ = 4872 l (1287 gal)

MFI (Denaturant tank) = $11.5^2 \cdot 3.14 \cdot 0.16 \cdot 0.03 \cdot 55 \cdot 2$ = 833 l (220 gal)

Every minimum foam inventory has been doubled to add a considerable reserve in case of emergency. Considering this choice, the overall foam inventory is equal to 7530 liters.

Protection of ethanol storage area: fixed monitors

In the biorefinery foam monitors (Fig. 3) are installed to protect the containment basins. They allow to protect pumps, meters, vehicles and equipment, which are associated with the loading and unloading operations, in the event of a pool fire. Foam monitors are characterized by high jets, which are used to deliver large quantities of foam to the affected area in a shortest time and from a safe distance. Some monitors, that protect the ethanol storage area, are able to inject, in case of a fire, the suppressant agent (AR-AFFF) in the basin, which includes biofuel transfer pumps. These devices can be used to suppress fires in a wide variety of special hazard and high risk applications (refineries, chemical plants, fuels storage, etc.). A heat detector cable is located on the perimetric piping of every basin in order to detect possible fires. Monitor size has been chosen on the ground of design specifications (capacity and jet) and functionality. Monitors application rate is based on the "total area", which is calculated by the difference between basin surface and area of the included tanks. The design criteria for diked areas (basins), which involve flammable or combustible liquids (ethanol), requiring alcohol-resistant foams are reported in Tab. 1.

Type of foam discharge outlet	Minimum application rate (l/min. m^2)	Minimum discharge time (min.)
Monitor	6.5	30

Tab. 1 - Minimum application rate and discharge time for monitors on diked area involving flammable liquids

The minimum required rates for the monitors are shown in Tab. 2. Every side of the basins is equipped with two foam monitors (eight monitors are installed in every basin). In order to satisfy the required rates, the monitor flowrate covers a range from 700 l/min. to 1300 l/min.

Monitors performances in terms of capacity and jet are reported in Fig. 4. Their operating pressure ranges from 5 bar to 10 bar and this choice depends on the monitor position. Both manual operation and remote control operation are available for the monitors in order to ensure their unfailing intervention. Monitors are manufactured from corrosion resistant bronze and perfectly suited to harsh environmen-

	Daily storage	Weekly storage
Basin area (m^2)	896	1248
Tanks number	4	2
Tanks diameter (m)-Ethanol storage	6	12
Tank diameter (m)-Denaturant storage	7	-
Tanks area (m^2)	123.24	226
Total area (m^2)	772.76	1022
Minimum required rate (l/min.)	5023	6643

Tab. 2 - Monitors: minimum required rates

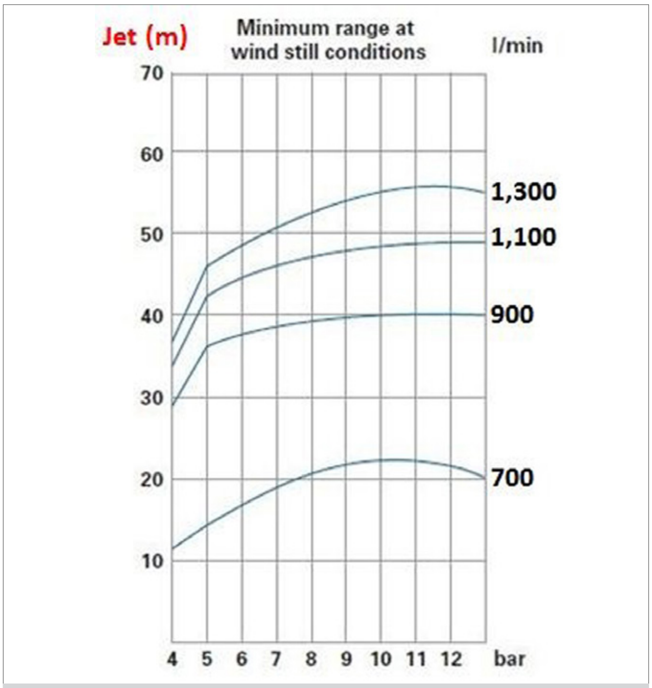

Fig. 4 - Monitor performances

Fig. 5 - The pumping station (water storage and cabins)

tal applications. Foam monitors have grease fittings on the rotation joints to provide easy lubrication and maintenance. The joints are fitted by stainless steel ball bearings. Their horizontal rotation is 360°, while the vertical rotation is about 160°.

Hydrants

The hydrants have been dimensioned in accordance with Italian Legislation (Ministerial Decree 18/05/95). The ethanol depot is outdoor and its capacity is higher than 3000 m^3 (the overall volume is equal to 3779 m^3). These aspects have determined the choice of UNI 70 hydrants, which are able to deliver at least 400 l/min. at 3 bar. The biorefinery is equipped with 74 hydrants.

The pumping station

The pumping station (Fig. 5) has been designed to ensure the required water flow for the protection of the biorefinery. The station is composed by:

- one storage tank (its operating volume is equal to 500 m^3);
- two cabins, which supply hydrants, foam monitors, sprinklers and low-expansion systems;
- a jockey pump and a controller;
- an electric pump with pump controller and remote alarm panel;
- a diesel pump with pump controller and remote alarm panel.

Every cabin includes the three mentioned pumps, which have different operation ranges (their operating pressures are shown in Tab. 3). During the normal operation the jockey pump only works, while the other pumps are in stand-by. This choice allows to guarantee the supply of monitors, low-expansion systems and hydrants in case of pumps failure.

Pumps	Fixed firefighting systems	Hydrants
jockey pump	7<p≤10 (bar)	5<p≤6 (bar)
electric pump	5<p≤7 (bar)	4<p≤5 (bar)
diesel pump	p≤5 (bar)	p≤ 4(bar)

Tab. 3 - Operating pressures (pumps)

Passive fire protection: the safety distances for the ethanol depot

The combined action of the active (low-expansion systems, sprinklers, monitors, etc.) fire protection and passive fire protection systems allows to mitigate the consequences of industrial fires. In this case the safety distances of the bioethanol depot have been established in accordance with Ministerial Decree 18/05/95 and they are:

- the protection distance (>5 meters); it indicates the minimum distance between the bioethanol depot and the boundary, which delimitates the biofuel storage area;

- the internal safety distance (>7 meters); it represents the minimum distance between the depot and the biorefinery components (ethanol transfer pumps, transformer rooms, loading areas of the tank trucks, etc.), which are considered dangerous in consequence of the included fluids and their operating conditions;
- the external safety distance (>15 meters); it indicates the minimum distance between the depot and the nearest building sited outside the biorefinery boundary;
- the distance between adjacent tanks (>0.5 D_{max}); D_{max} indicates the biggest diameter between two adjacent tanks.

Conclusions

In many countries the ethanol use is significantly increased in order to replace fossil fuels with renewable fuels. This trend has introduced problems, which are referred to fight of ethanol fires. In fact the heat flux from an ethanol fire can be significantly higher than that of a gasoline fire. This increases the risks for fire escalation. The reason for this difference is that as the scale increases, gasoline fires generate larger amounts of smoke, which tends to block the visible parts of the flames, thereby reducing the heat flux. On the contrary an ethanol fire is almost free from smoke and therefore the heat flux is not dissipated by smoke. The choice of AR-AFFF (the suppressant agent) is the first step to enhance ethanol tanks fire protection. In fact foam stabilizers are the crucial ingredient of AR-AFFF in the fight against ethanol fires, because they provide the protective membrane, which ensures the alcohol does not destroy the foam. This action allows a fast knock down of the fire. Another very important consideration is that foam application rate must be increased as regards petroleum (water immiscible) products and the direct consequence is a larger foam inventory than liquid hydrocarbons storage. The existing Standards such as NFPA 11 are useful tools to start a valid pathway towards a safer storage of ethanol, but a growing safety level can be only reached by a better knowledge and experience of ethanol fires. The installation of fixed surface systems, sprinklers (tanks protection) and foam monitors (basins protection) notably decreases the probability that domino effects can occur. This aspect is crucial in the industrial safety, because domino effects often increase the outcomes of accidents in the process industry.

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Sistemi antincendio nello stoccaggio di bioetanolo: l'esperienza di una bioraffineria italiana

In molti Paesi è cresciuto significativamente l'utilizzo dell'etanolo al fine di sostituire i combustibili fossili con quelli rinnovabili. Questa tendenza ha introdotto problemi riconducibili all'estinzione di incendi di etanolo. Infatti la radiazione termica generata da un incendio di etanolo può essere decisamente più grande di quella derivante dalla benzina. Il bioetanolo può essere anche prodotto a partire da biomasse in impianti, che prendono il nome di bioraffinerie. L'articolo è focalizzato sull'esperienza pratica di una bioraffineria italiana e descrive i sistemi antincendio, che sono stati applicati all'area di stoccaggio del bioetanolo al fine di garantire che un improvviso incendio possa essere controllato ed estinto in tempi brevi e di limitare i suoi effetti sulla salute delle persone.