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RISK ANALYSIS FOR AN AGROCHEMICALS PRODUCTION UNIT AT BUTIBORI, NAGPUR



For **Crystal Crop Protection Ltd.**

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1.0	24/10/2018	--	Kusuma M	Krishnaprasad
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I. INTRODUCTION

I.1 CONTEXT

This work has been carried out by FLUIDYN in the context of 3D Quantitative Risk Analysis for the Butibori-Nagpur Plant of M/s Crystal Crop Protection Ltd (CCPL), using *fluidyn* tools. The purpose of this study is to identify and quantify the maximum credible accidents due to the handling and storage of hazardous substances in the plant. Location of the plant is shown in *Figure 1*.



Figure 1: Satellite image of the Crystal Crop Protection Limited at Butibori, Nagpur

I.2 PHILOSOPHY OF RISK ASSESSMENT

Industries have a wide variety of process involving consumption, production and storage of chemicals. The condition that contributes to the danger, by these chemicals, are when these chemicals are not kept/stable at normal pressure and temperature. Very often these chemicals are kept at/or high pressure and temperatures; these gases in liquefied state by refrigeration, to facilitate storage in bulk quantities. Under these circumstances, it is essential to achieve and maintain high standards of plant integrity through good design, management and operational controls.

However, accidents do occur and these can cause serious injuries to employees or the public, and damage to property. The public concern at such events invariably leads to call for additional control at national and international levels. It is against this background that the various Section and Rules under the Environment Protection Act, 1986, the Factories Act, 1948 and other Acts specify the

requirements for a safe and reliable working of an industry. They require carrying out various studies and analysis to assess and mitigate hazards prevalent in the factory in line with the above goal of safe and reliable working. These are more commonly known as “Risk Assessment Studies”. This chapter explains the basis of Risk Assessment and its objectives.

Major hazard installations have to be operated to a very high degree of safety; this is the core responsibility of the management. In addition, management holds a key role in the organization in the implementation of a major hazard control systems. In particular, the management has the responsibility to:

- Provide the information required to identify major hazard installations.
- Carry out hazard/risk assessment.
- Report to the authorities on the results of the hazard / risk assessment.
- Conceive Disaster Management plans and carryout “MOCK DRILLS” on the scenarios envisaged.
- Adequately inform the Vulnerability status of the company to district management.
- Undertake measures to in-plant safety assurance systems.

In order to fulfil the above responsibility, the Management must be aware of the nature of the hazard, of the events that cause accidents and of the potential consequences of such accidents. In order to control a major hazard successfully, the Management must have answers to the following questions:

- Do toxic, explosive or flammable substances in our facility constitute a major hazard?
- Which failures or errors can cause abnormal conditions leading to a major accident?
- If a major accident occurs, what are the consequences of a fire, an explosion or a toxic release for the employees, people living outside the factory, the plant or the Environment?
- What can Management do to prevent these accidents from happening?
- What can be done to mitigate the consequences of an accident?

The most appropriate way of answering these questions is to carry out a hazard or risk assessment study, the purpose of which is to understand, why accidents occur and how they can be avoided or at least mitigated. A properly conducted RISK assessment will therefore to

- Analyze the existing safety concept or develop a new one;
- Develop optimum measures for technical and organization protection in event of an abnormal plant operation.

1.3 STUDY OBJECTIVES

The primary objective of this study are:

- Identify major accident scenarios associated with the storage and handling of various hazardous materials in the plant
- Carry out consequence analysis for the significant accident scenarios

- Carry out quantitative risk analysis
- Compare the risk values with specified risk tolerance criteria and
- Identify measures for risk reduction wherever warranted.

II. METHODOLOGY

Risk arises from hazards. Risk is defined as the product of severity of consequence and likelihood of occurrence. Risk may be to people, environment, assets or business reputation. This study is specifically concerned with risk of serious injury or fatality to people due to process hazards related to storage and handling of hazardous materials.

The following steps are involved in Quantitative Risk Assessment:

- Study of the plant facilities and systems
- Identification of the hazards
- Enumeration of the failure incidents
- Estimation of the consequences for the selected failure incidents
- Risk analysis taking into account the failure frequency, extent of consequences and exposure of people to the hazards

Risk assessment to compare the calculated risk level with risk tolerability criteria and review of the risk management system to ensure that the risk is “As Low As Reasonably Practicable” (ALARP).

II.1 CONSEQUENCE ANALYSIS

Consequence analysis for the selected failure scenarios is carried out using 3D consequence modelling tools of FLUIDYN for selected failure scenarios as below:

- Dispersion of toxic /hazardous clouds to define threshold concentration levels
- Heat radiation intensity due to pool fire and jet fire
- Explosion overpressure

II.2 3D TOOLS EMPLOYED FOR CONSEQUENCE MODELLING

II.2.1 *fluidyn*-PANEP: 3D CFD Dispersion Modelling Software

PANEP is a dedicated software for 3D simulation of dispersion from different sources such as industrial sites, stacks, accidental leaks, etc. It analyses the consequences of accidental dispersion of pollutant discharge in process industries due to rupture or leaks and combustion bi-products due to fires.

It can be used to plan anticipatory measures and solve problems in case of industrial accidents. It integrates the 3D modelling characteristics such as wind, turbulence and pollutant transport and takes into account the influence of topography, obstacles, buildings, influence of vegetation and terrain on dispersion, solar radiation effects and ambient atmospheric conditions. It can simulate

transient effects of the following physical phenomena: compressible flow, buoyancy effects, atmospheric release interactions and variable source time.



Figure 2: Wind flow pattern and vapour dispersion for a complex industrial site

It can be applied to different scenarios such as:

- Gas release from a pressurised storage tank or pipe: two-phase (particles or droplets) with variable rate or liquid release
- Dense gas dispersion with
- Multiple pollutant sources such as stacks and storage leaks
- Interaction with structures such as tanks and ground
- Exact simulation of flow between building and chemical units by curvilinear mesh and a second order solver
- Analysis of toxicology risks from threshold database (does calculation for SEI, SEL and SELS thresholds) and determination of plume opacity
- Dispersion of an explosive cloud (UVCE): Cloud volume and mass flammability limits (for UVCE or ATEX calculations)

II.2.2 *fluidyn*-PANFIRE: 3D Fire Radiation Evaluation Software

It is a dedicated software tool for 3D simulation of fire accidents - combustion of solid products and liquid pool. It calculates the heat fluxes generated by the combustion of the products such as hydrocarbon, papers, plastics, cartons, alcohols, etc.) under selected weather conditions. It helps to establish a 3D estimate of the heat radiation generated by fires and combustion thereby allowing comparisons with the statutory thresholds by taking into account the material (nature, combustion rate and proportion), 3D geometry of the warehouses and mitigation measures (firewalls, sprinklers and obstacles).

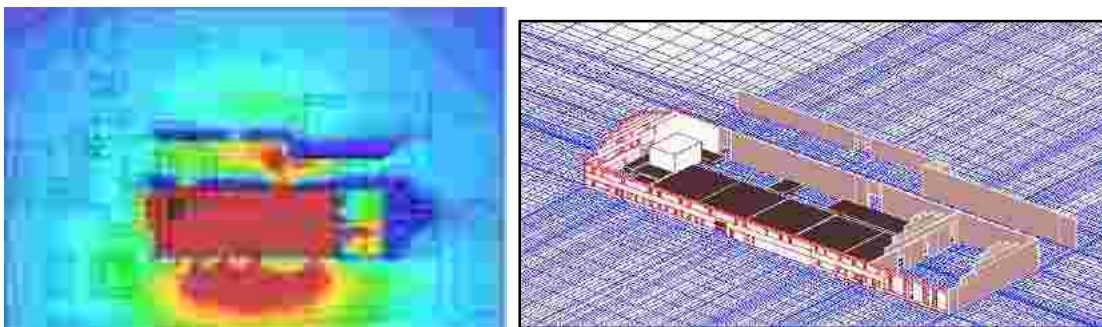


Figure 3: Warehouse fire radiation simulation & results

It has many integrated models to calculate heat flux adaptable to different scenarios:

- Solid, dry bulk or rack fires
- Pool fires in retention bunds
- Fires inside buildings

Some of the salient features of PANFIRE include:

- Simple to complex configuration of the site under consideration
- Multiple fire sources with collapsing / non-collapsing walls
- Mixture of storage materials with individual burning characteristics
- Modules to determine the flame geometry (form and height) using fuel characteristics
- User control of initial flux values
- 3D radiation using advanced view factor methods

PANFIRE finds its application in several contexts:

- Consequence of heat radiation due to fire in storage yards on the occupants
- Occurrence of domino effect due to fire
- Design of fire walls – their strength and position
- Effectiveness of safety measures such as sprinklers or water curtains etc..
- Site layout planning in terms of storage of different combustible materials, their separation etc.
- Identification of safe zones, escape routes etc.. in case of fire accidents

II.3 ELEMENTS OF THE RISK ANALYSIS STUDY

II.3.1 STORAGE AND HANDLING OF HAZARDOUS CHEMICALS.

Identification, analysis and assessment of hazard and risk are very useful in providing information to risk management. It provides basis for what should be the type and capacity of its preparedness, on-site and off-site emergency plans. Risk analysis is carried out considering storage and handling of various hazardous raw materials, manufacturing process and storage of hazardous finished goods.

II.4 CONSEQUENCE CALCULATIONS

In consequence analysis use is made of a number of calculation models to estimate the physical effects of an accident (spill of hazardous material) and to predict the damage (lethality, injury, material destruction) of the effects. Accidental release of flammable liquids can result in severe consequences. Immediate ignition of the pressurized chemical will result in a jet flame. Delayed ignition of flammable vapours can result in blast overpressures covering large areas.

The calculations can roughly be divided in three major groups:

- a. Determination of the source strength parameters;
- b. Determination of the consequential effects;
- c. Determination of the damage or damage distances

II.4.1 SOURCE STRENGTH PARAMETERS

- Calculation of the outflow of liquid vapours out of a vessel/tank or a pipe, in case of rupture. In addition, two-phase outflow can be calculated.
- Calculation, in case of liquid outflow, of the instantaneous flash evaporation and of the dimensions of the remaining liquid pool.
- Calculation of the evaporation rate, as a function of volatility of the material, pool dimensions and wind velocity.
- Source strength equals pump capacities, etc. in some cases.

II.4.2 CONSEQUENTIAL EFFECTS

- Dispersion of gaseous material in the atmosphere as a function of source strength, relative density of the gas, weather conditions and topographical situation of the surrounding area.
- Intensity of heat radiation [in kW/ m²] due to a fire, as a function of the distance to the source.
- Energy of vapour cloud explosions [in bar], as a function of the distance to the distance of the exploding cloud.
- Concentration of gaseous material in the atmosphere, due to the dispersion of evaporated chemical. The latter can be either explosive or toxic.

II.5 SELECTION OF DAMAGE CRITERIA

The damage criteria give the relation between the extents of the physical effects (exposure) and the effect of consequences. For assessing, the effects on human beings consequences are expressed in terms of injuries and the effects on equipment / property in terms of monetary loss. The effect of consequences for explosion or fire can be categorized as:

- Damage caused by heat radiation on material and people
- Damage caused by explosion on structure and people
- In consequence, analysis studies, in principle three types of exposure to hazardous effects are distinguished:
- Heat radiation due to fires - in this study, the concern is that of Jet fires and pool fires
- Explosions

- Toxic effects, from toxic materials.

The knowledge about these relations depends strongly on the nature of the exposure. Following are the criteria selected for damage estimation:

Heat Radiation:

The effect of fire on a human being is in the form of burns. There are three categories of burn such as first degree, second degree and third degree burns. The consequences caused by exposure to heat radiation are a function of:

- The radiation energy onto the human body [kW/m²];
- The exposure duration [sec];
- The protection of the skin tissue (clothed or naked body);

The limits for 1% of the exposed people to be killed due to heat radiation, and for second degree burns are given in the table below:

Table 1: Damages to human life due to heat radiation

Exposure Duration	Radiation Energy (1% Lethality), kW/m ²	Radiation Energy (Second Degree Burns), kW/m ²	Radiation Energy (First Degree Burns), kW/m ²
10 sec	21.2	16.0	12.5
20 sec	9.3	7.0	4.0

Table 2: Effects due to incident radiation intensity

Incident Radiation (kW/m ²)	Type of Damage
0.7	Equivalent to Solar Radiation
4.0	Sufficient to cause pain within 20sec. Blistering of skin (first degree burns are likely)
12.5	Minimum energy required for piloted ignition of wood, melting plastic tubing etc.
37.5	Heavy Damage to process equipments

Reference: CCPS, Guidelines for Chemical Process Quantitative Risk Analysis

The actual results would be less severe due to the various assumptions made in the models arising out of the flame geometry, emissivity, angle of incidence, view factor and others. The radiation output of the flame would be dependent upon the fire size, extent of mixing with air and the flame temperature.

As per the guidelines of CPR 18 E Purple Book:

- The lethality of a jet fire and pool fire is assumed to be 100% for the people who are caught in the flame. Outside the flame area, the lethality depends on the heat radiation distances.
- For the flash fires lethality is taken as 100% for all the people caught outdoors and for 10% who are indoors within the flammable cloud. No fatality has been assumed outside the flash fire area.
- Overpressure more than 0.3 bar corresponds approximately with 50% lethality.
- An overpressure above 0.2 bar would result in 10% fatalities.
- An overpressure less than 0.1 bar would not cause any fatalities to the public.
- 100% lethality is assumed for all people who are present within the cloud proper.

Explosions:

Table 3: Damage due to overpressures

Peak Overpressure	Damage Type	Description
0.3 bar	Heavy Damage	Major damage to plant equipment failure
0.1 bar	Moderate Damage	Repairable damage to plant equipment and structure
0.03 bar	Significant Damage	Shattering of glass

II.6 HAZARDOUS INVENTORIES

Major hazardous inventories handled in the Crystal Crop Protection Limited, Butibori Nagpur Plant are as listed below:

Table 4: Hazardous material inventories in the plant

Material / Equipment	Scenario	Risk Envisaged
HCl Storage Tanks	Spillage	Not significant
NCMA Storage Tank	Spillage	Not significant
SOCI ₂ Storage Tank	Spillage	Not significant
CMAC Storage Tank	Spillage	Toxic Vapors
10% Hypochlorite Storage Tank	NA	NA
DMF Storage Tank	Tank Fire; Pool Fire after spillage while	Fire Radiation Hazard

	unloading	
EDC Storage Tank	Tank Fire; Pool Fire after spillage while unloading	Fire Radiation Hazard
Na2SO3 Storage Tank	NA	NA
Methyl Alcohol (UG)	Pool Fire after spillage while unloading	Fire Radiation Hazard; Possible Explosive Cloud of vapors
Toluene Storage Tank (UG)	Pool Fire after spillage while unloading	Fire Radiation Hazard
Hexane Storage Tank (UG)	Pool Fire after spillage while unloading	Fire Radiation Hazard; Possible Explosive Cloud of vapors

* Only primary scenario have been selected for the consequence modelling.

III. CONSEQUENCE MODELING

III.1 DISPERSION SCENARIO

Worst case scenario of the spillage of hazardous inventories were considered for dispersion. Among the scenario identified, the critical one are found to be the evaporation of highly volatile hydrocarbons to form explosive cloud. The worst case scenario is identified to be the spillage of Methanol to form pool and dispersion of the vapors. Source estimation for the pool formation and evaporation rate was done using *fluidyn*-ASSESSRISK, a tool for scenario quantification and 2D risk estimates. The critical scenario were identified and then subjected to detailed 3D consequence modelling using CFD based tools – PANEP (dispersion), PANFIRE (fire radiation) and VENTEX (explosions).

III.1.1 Numerical Model of Terrain:

Dispersion of gases in the atmosphere is largely influenced by the topography of the site under consideration. The terrain elements such as undulations (hills, valley), land cover (vegetation, water bodies etc.), urban canopy (heat island, roughness) and significantly the obstacles (buildings, process units, ground level tanks etc.). Wind flow over each of such terrain elements shall be disturbed in terms of drag (boundary layer phenomena) and turbulence (mixing). Thus the significant topographical features were digitised to create numerical terrain model. PANEP interface (*Figure 4*) is customized to generate such significant features with ease of use.

The terrain model created for Crystal Crop plant is shown in the *Figure 5*.

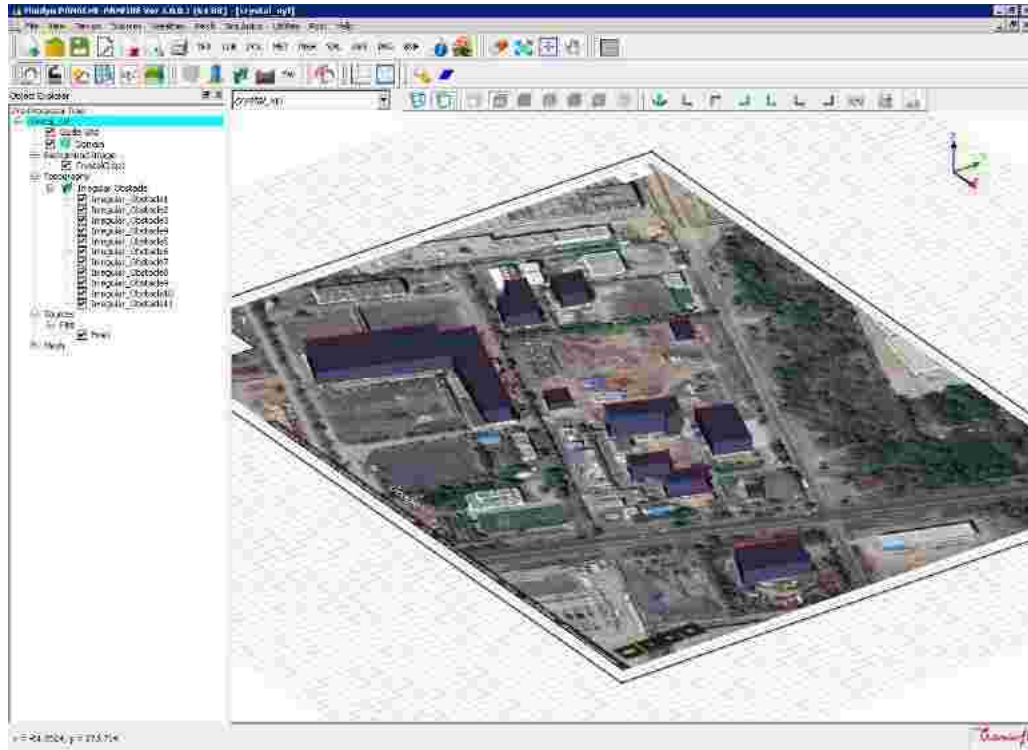


Figure 4: PANEP customized interface for 3D dispersion modeling

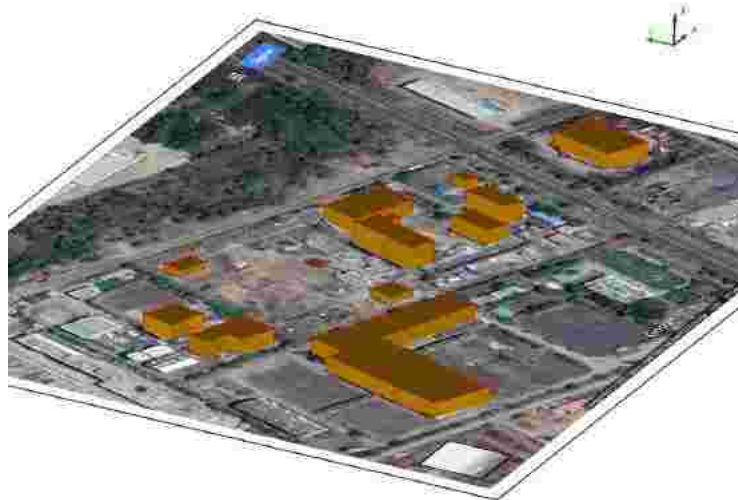


Figure 5: Digital terrain model of the site for 3D simulations

III.1.2 Weather Scenario:

As the wind flow influences both the pool evaporation rate as well as the dispersion of vapours, two worst case weather phenomena were considered in terms of wind speed and atmospheric stability based on European Guidelines – one with high wind speed at neutral stability conditions; another with low wind speed at stable conditions.

Table 5: Weather Scenario considered for dispersion

Scenario	Wind Direction	Wind Speed, m/s	Stability Class
2F- 15	15 ⁰	2.0	F
2F-285	285 ⁰		
5D- 15	15 ⁰	5.0	D
5D-285	285 ⁰		

Two wind directions were chosen for simulation based on the significant target locations:

- towards the administrative building inside the plant (eastwards, 285⁰)
- towards the nearest boundary for offsite impacts (southwards, 15⁰)



Figure 6: Wind directions chosen for the worst case dispersion scenario

III.1.3 Source Terms:

As mentioned earlier, the scenario to estimate vapour cloud (flammable / explosive) for Hexane pool was evaluated using ASSESS_RISK. Table 6 shows the source characteristics in terms of pool size and evaporation rate derived.

Table 6: Pool Evaporation Scenario considered for dispersion (flammable cloud)

Scenario	Evaporation Rate, Kg/s	Pool Radius, m
2F	0.201	8.4
5D	0.405	8.3

III.1.4 Dispersion Simulation Results:

The dispersion of hazardous vapours are largely influenced by the windflow pattern over the complex site features. Hence the simulations to establish windflow patterns in the site were carried out for both the scenario. *Figure 7 & Figure 8* below show the mesh considered and location of pool.



Figure 7: Mesh Considered for the simulations

Figure 9 shows the windflow pattern and the subsequent dispersion of simulated by PANEPR.

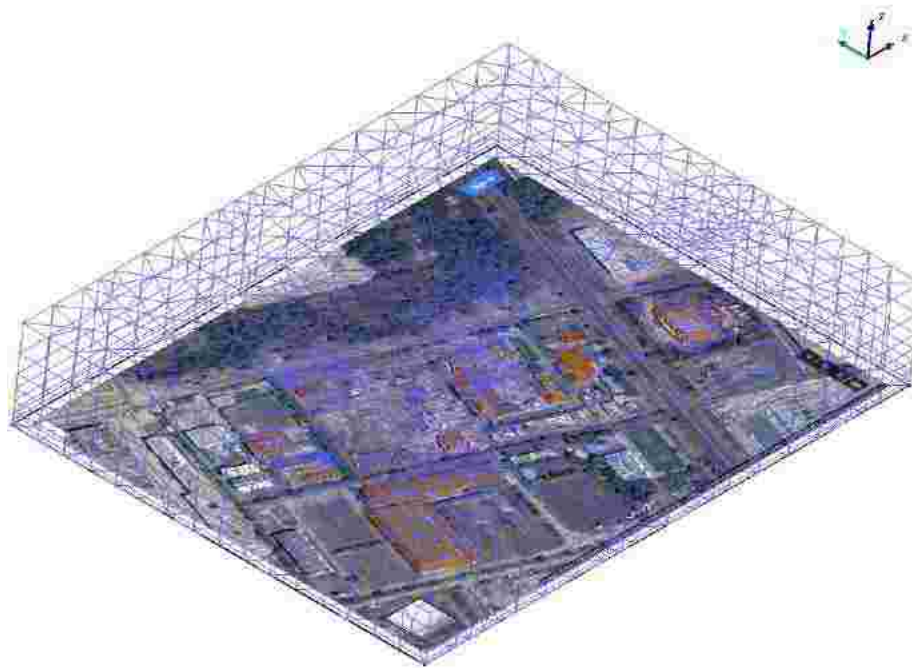


Figure 8: Mesh in 3D

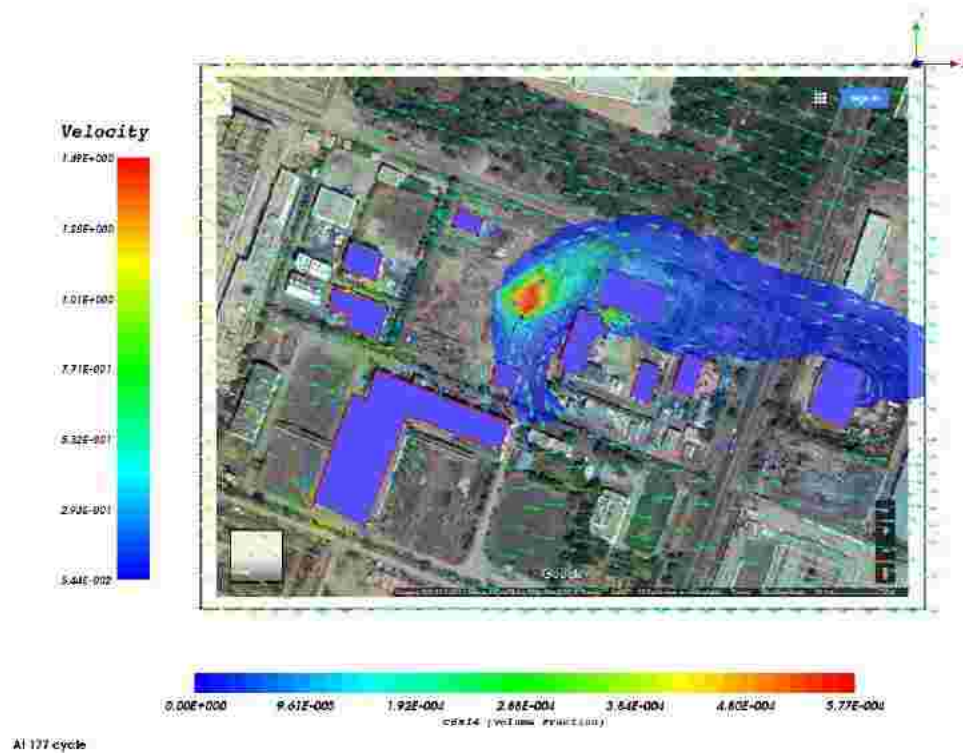


Figure 9: Simulated wind flow and Dispersion pattern over the site, Scenario [2F-285⁰]

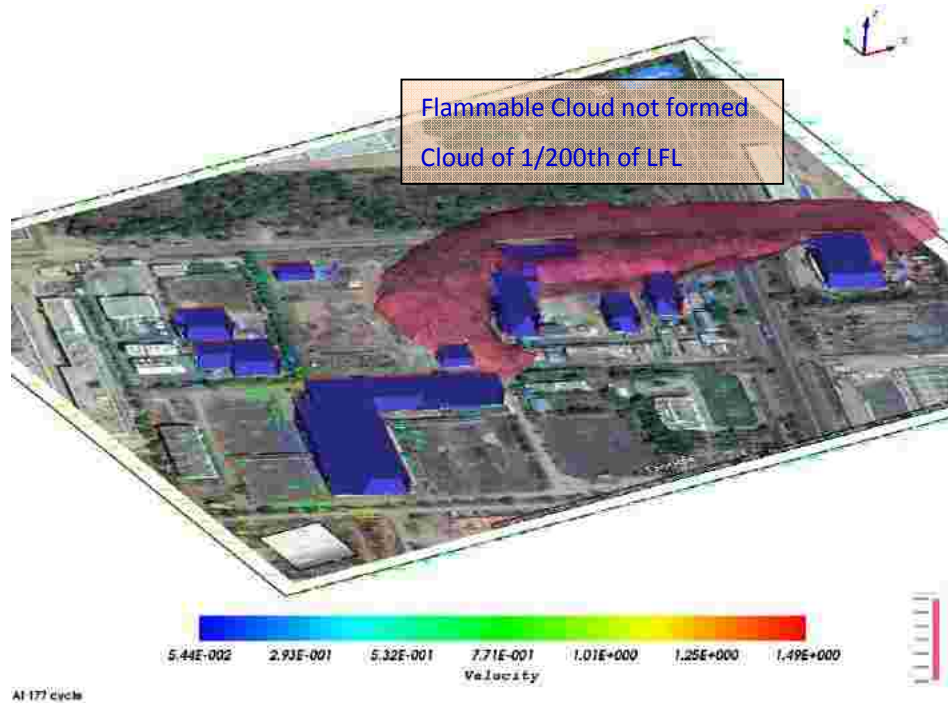


Figure 10: 3D Cloud of 5.0E-05 volume fraction, Scenario [2F-285⁰]

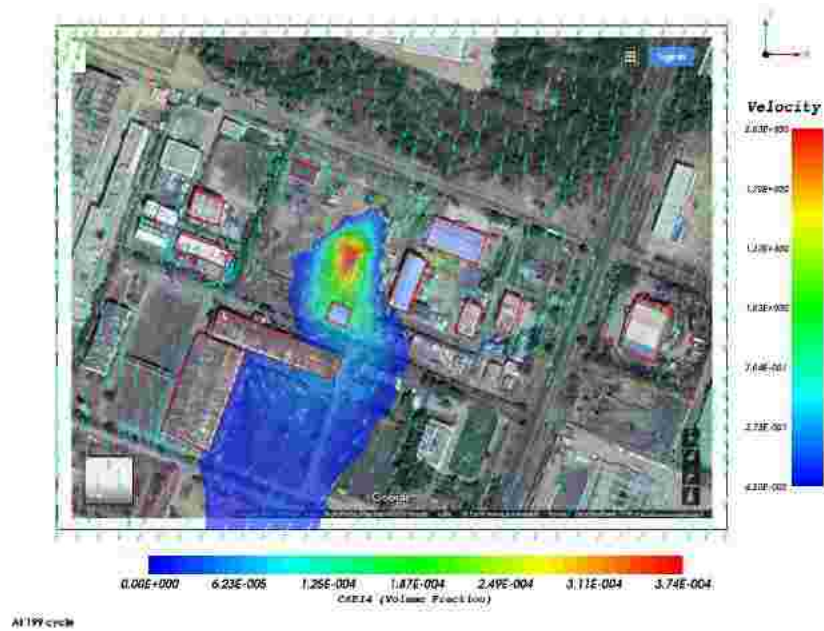


Figure 11: Simulated wind flow and Dispersion pattern over the site, Scenario [2F-15⁰]

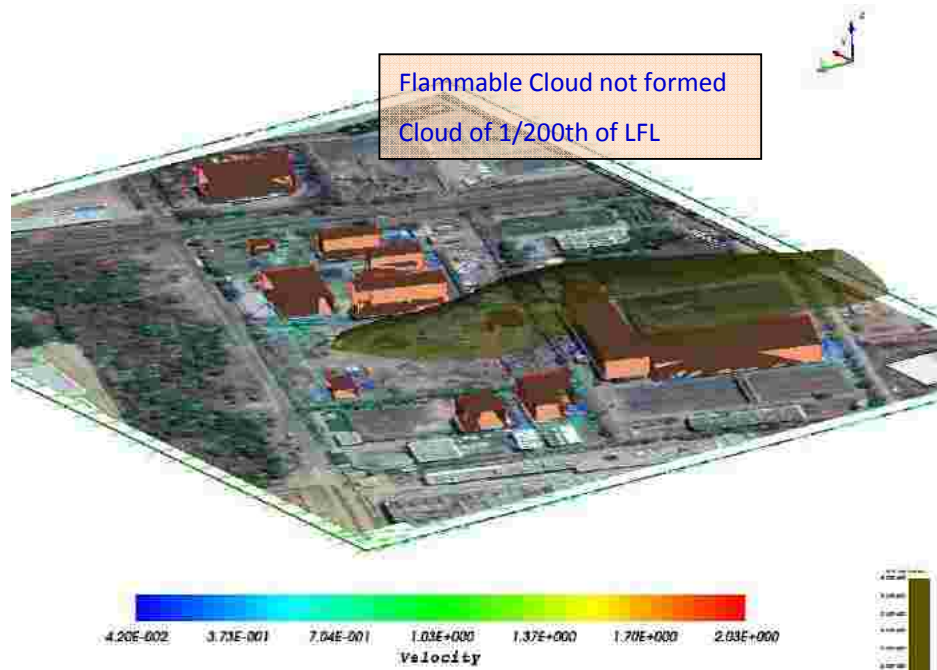


Figure 12: 3D Cloud of 5.0E-05 volume fraction, Scenario [2F-15⁰]

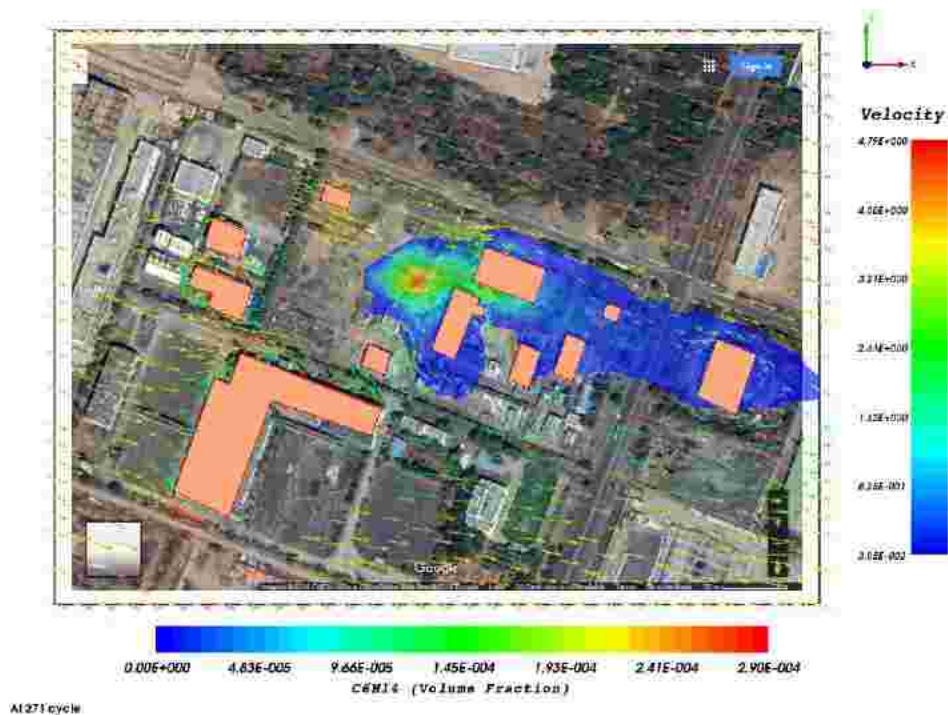


Figure 13: Simulated wind flow and Dispersion pattern over the site, Scenario [5D-285⁰]



Figure 14: 3D Cloud of 5.0E-05 volume fraction, Scenario [5D-285°]

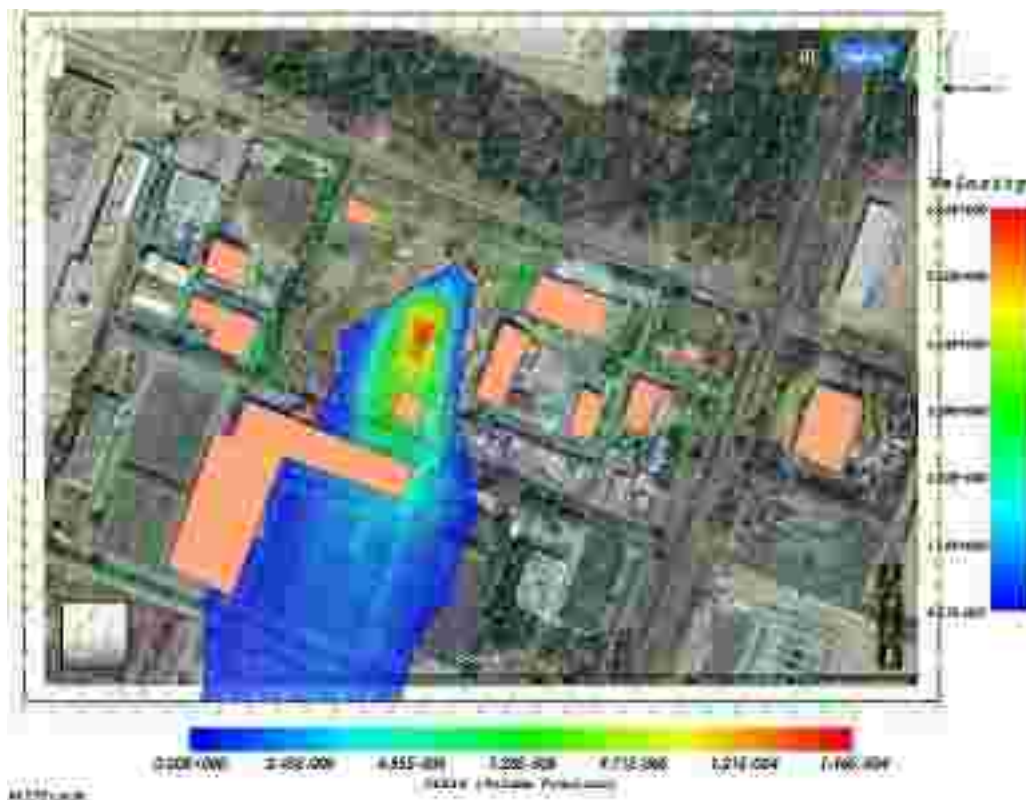


Figure 15: Simulated wind flow and Dispersion pattern over the site, Scenario [5D-15°]

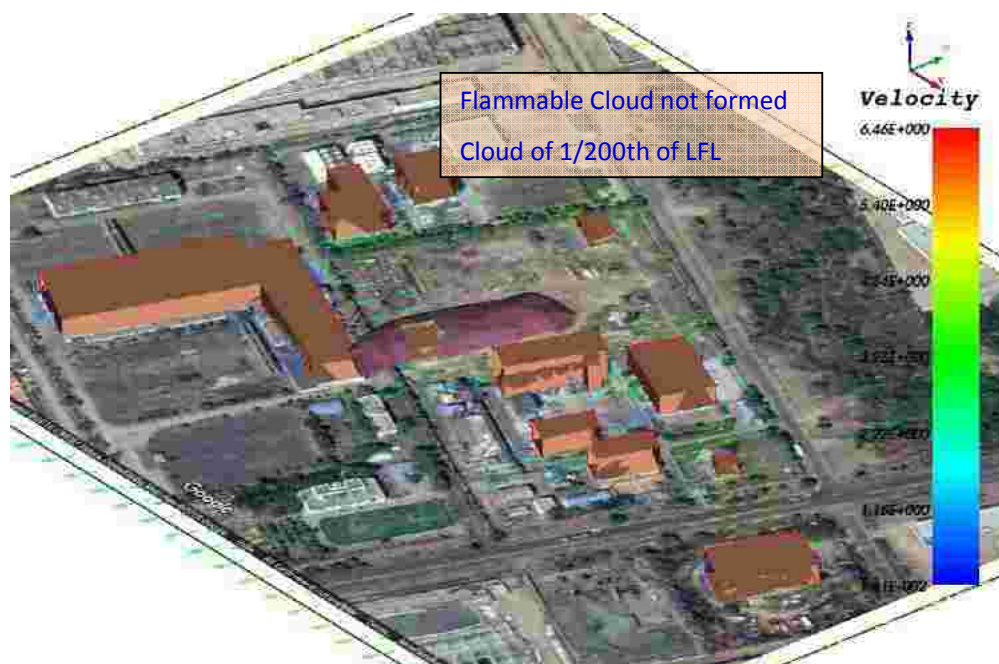


Figure 16: 3D Cloud of 5.0E-05 volume fraction, Scenario [5D-15⁰]

III.2 FIRE RADIATION:

Following scenario are envisaged for fire radiation simulations:

- Tank Fire for above ground storage tanks
- Pool fire due to the spillage of hydrocarbons while unloading or loss of containment

Among the above, the critical ones (materials) are the pool fires both in terms of the source extent and also the heat energy. Thus pool fire scenario for the below hydrocarbons were considered.

III.2.1 Methyl Alcohol:

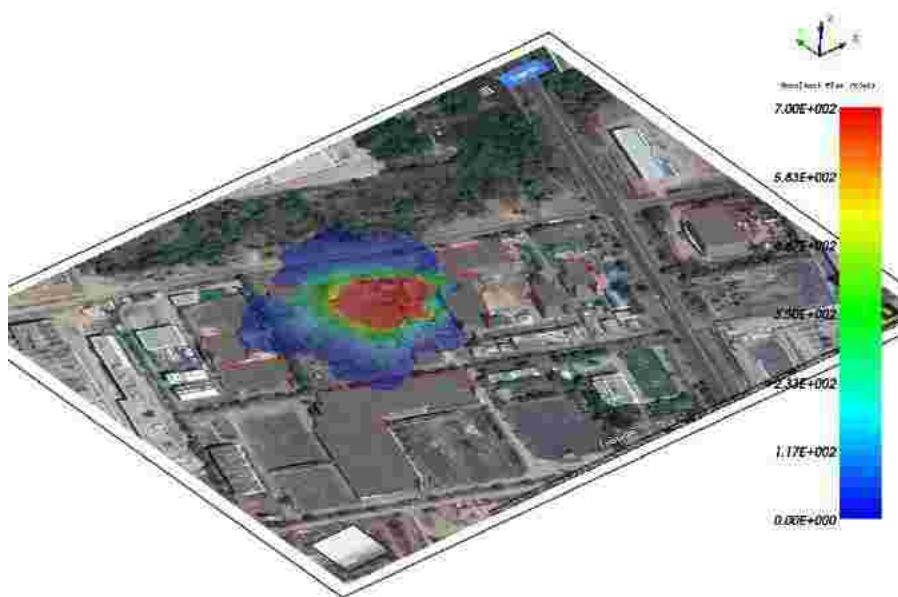


Figure 17: Impact area (in Red) of 0.7KW/m^2 Heat Radiation

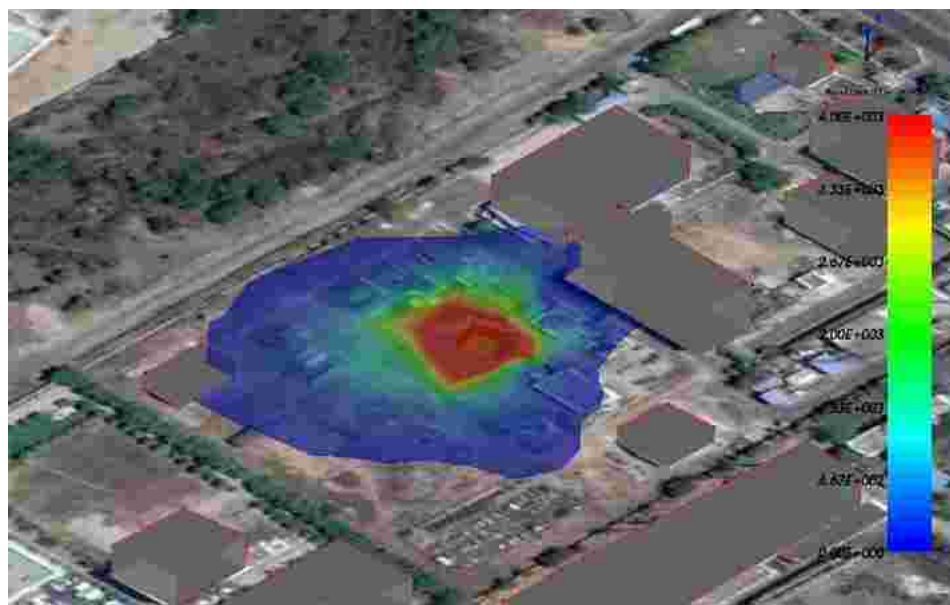


Figure 18: Impact area (in Red) of 4.0KW/m² Heat Radiation

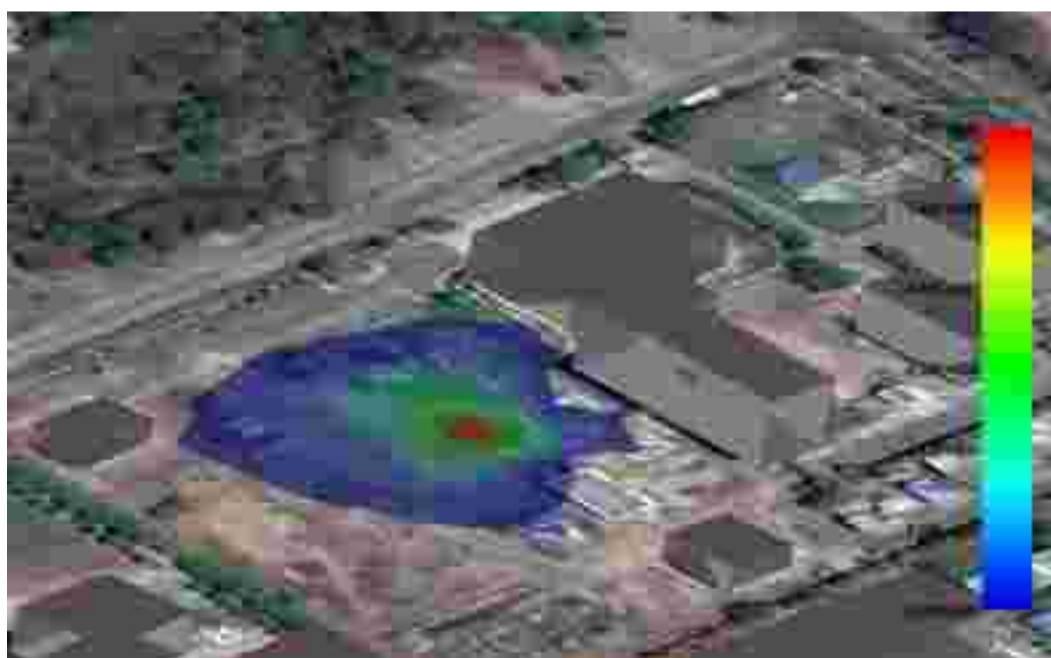


Figure 19: Impact area (no threat zone identified) of 12.5KW/m² Heat Radiation

III.2.2 Toluene:

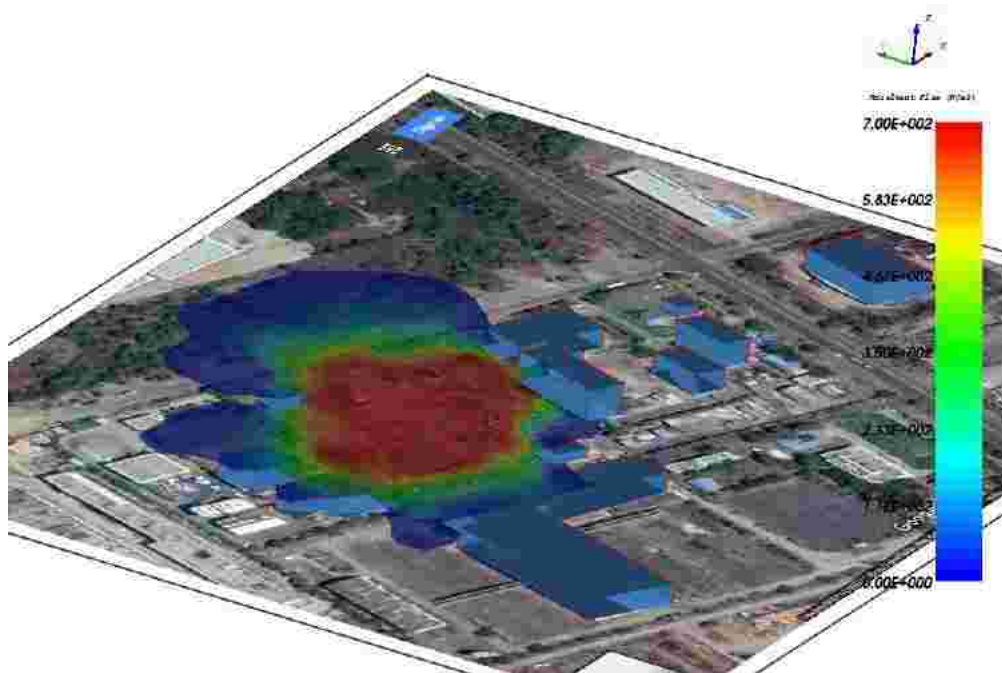


Figure 20: Impact area (in Red) of 0.7KW/m^2 Heat Radiation

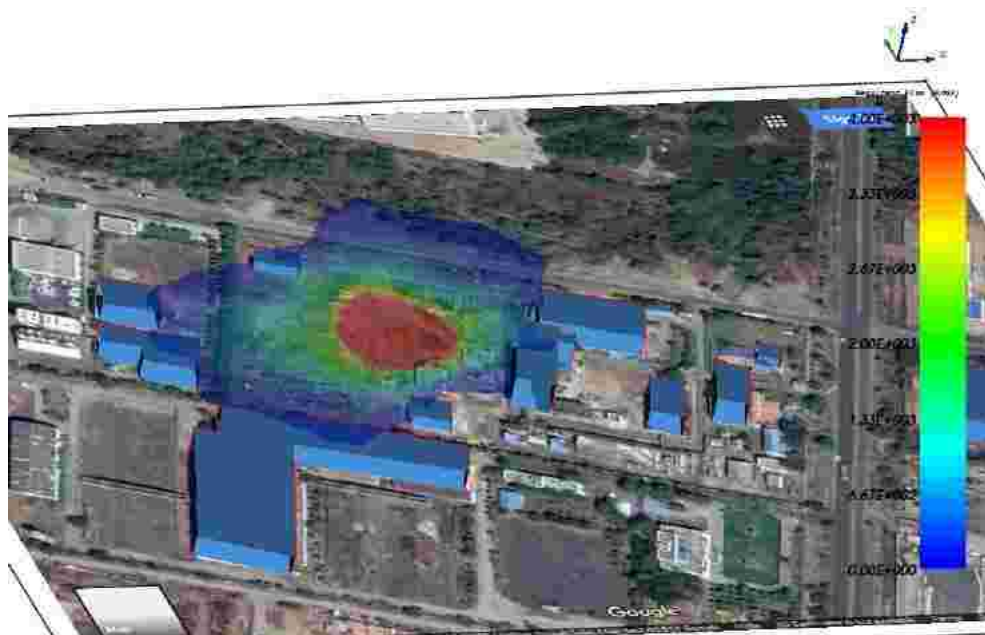


Figure 21: Impact area (in Red) of 4.0KW/m^2 Heat Radiation

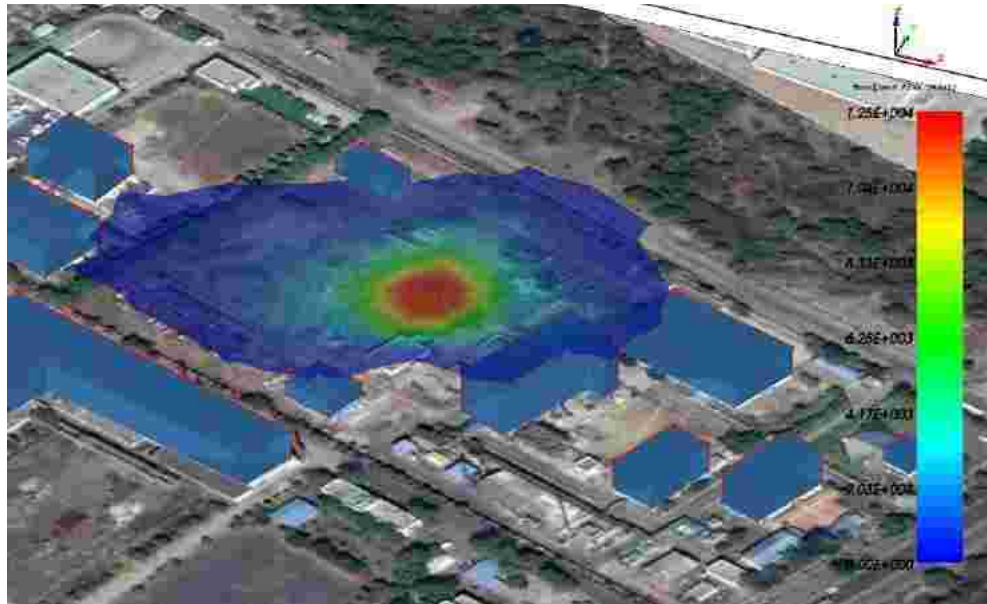


Figure 22: Impact area (in Red) of 12.5KW/m² Heat Radiation



Figure 23: Impact area (no threat zone identified) of 37.5KW/m² Heat Radiation

III.2.3 Hexane:

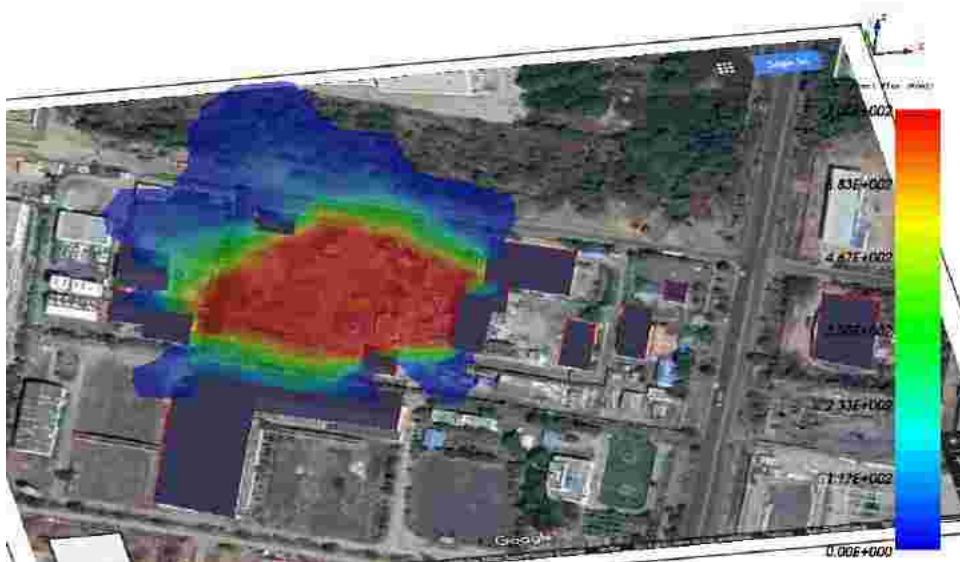


Figure 24: Impact area (in Red) of 0.7KW/m^2 Heat Radiation

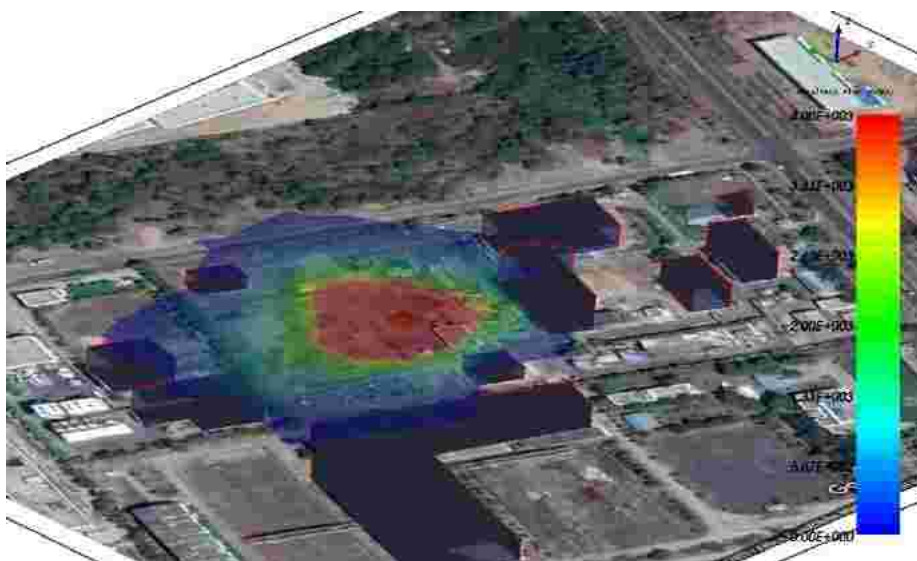


Figure 25: Impact area (in Red) of 4.0KW/m^2 Heat Radiation

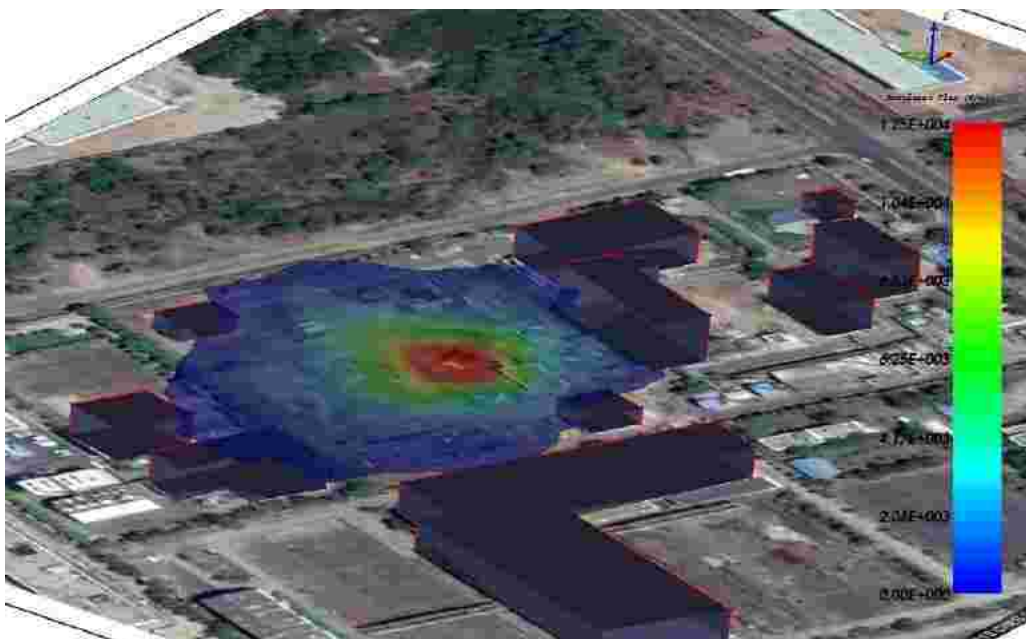


Figure 26: Impact area (in Red) of 12.5KW/m^2 Heat Radiation

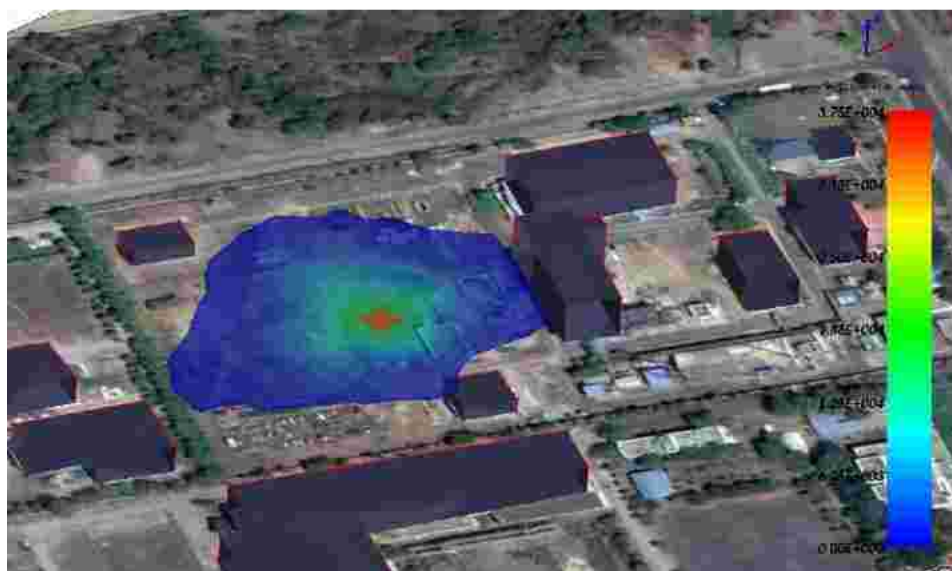


Figure 27: Impact area (no threat zone identified) of 37.5KW/m^2 Heat Radiation

III.3 VAPOUR CLOUD EXPLOSION:

The dispersion simulation of pool evaporation from critical accidental scenario have shown that there is no formation of vapour cloud hence no explosion scenario is envisaged.

III.4 DISCUSSIONS ON THE RESULTS

Table 7 and Table 8 summarises the findings of consequence scenario modelling using 3D tools for flammable cloud dispersion and Fire Radiation. While it is observed that in both the worst case weather scenario considered the pool evaporation failed to form flammable cloud. This is due to the small evaporation rate of the hydrocarbons.

Table 7: Threshold distances for dispersion scenario modelled for Hexane

Weather Scenario	Flammable Cloud Size / extent
2F-285	Nil
2F-15	Nil
5D-285	Nil
5D-15	Nil

Pool fire scenario for the highly flammable hydrocarbons was chosen over the tank fire due to the source size. Fire Radiation simulations carried out using 3D tool PANFIRE using discrete ordinate method and the results are summarised in Table 8. The maximum distance has been found to be 86.9m for Hexane and the impact area is seen within the premises.

Table 8: Threshold distances for Fire Radiation scenario modelled

Threshold Radiation Level	Maximum Impact Distance, m		
	Methanol	Toluene	Hexane
0.7 KW/m ²	36.4	81.5	86.9
4.0 KW/m ²	14.8	30.1	38.0
12.5 KW/m ²	Not Attained	10.5	12.5
37.5 KW/m ²	Not Attained	Not Attained	Not Attained

Only primary fire scenario have been considered presuming that these will not trigger secondary fires (domino effects). This consideration is based on the fact that the industry shall abide by the standard Risk mitigation procedures applicable to storage tanks in terms of isolation such as – water sprinklers, fire fighting measures etc.. It was also seen from the fire radiation results tabulated above that a heat radiation value of 37.5kw/m² which is essential to cause damage to the process equipments, tanks etc.. is not attained in any of the scenario. However, from the results it is recommended that:

1. The unloading operation be carried out at sufficient distance from the tanks as to facilitate leakage isolation / displacement of the truck in case of eventual leakage.

2. Adjacent tanks containing hydrocarbons be provided with water sprinklers to contain temperature build-up within the fire point of storage materials
3. It is also recommended to avoid / isolate the possible ignition sources as much as possible in the tank farm region.

IV. SUMMARY AND CONCLUSIONS

3D Quantitative Risk Analysis of critical scenario for the Greenfield project of M/s Crystal Crop Protection Limited, located at MIDC, Butibori, Nagpur was carried out using *fluidyn* tools and the impact distances determined are presented in this report.

There are no major inventories of toxic gases being handled in the plant.

However, critical scenario were identified for highly flammable liquids viz., Methyl Alcohol, Toluene and Hexane. Spillage events during truck unloading, full guillotine rupture was considered for subsequent consequences. Formation of pool and subsequent ignition was modelled to determine extent of threshold radiation levels during eventual fires. The distances modelled for different hydrocarbons are presented in Table 8. Threshold extent for minimum impact (uncomfortable heat levels without any injury) was found to be within the site boundary. Maximum distance of 12.5m found for a Heat Radiation threshold to cause secondary fire should be considered during operational procedures.

Explosive cloud formation due to delayed ignition of vapour cloud was modelled using 3D dispersion model, PANEP. Critical material considered for dispersion was Hexane and it was found that no flammable cloud is formed, under both the worst case weather scenario.