Models for assessing the spread of flammable liquid spills and their burning

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Abstract

An understanding of the manner in which different types of flammable liquids get spread over different types of surfaces when accidentally spilled, is crucial for preventing escalation of accidents involving such spills. Enormous quantities of flammable liquids ─ of which petrol, diesel, kerosene, liquid petroleum gas (LPG), and compressed natural gas (CNG) are among the most common ─ are manufactured, refilled, stored, transported, and utilized round the clock all over the world. This makes the risk of accidental spill of such chemicals alive all the time. The enormity of this risk can be gauged from the fact that majority of industrial disasters, which have killed or injured scores of people and caused loss of property worth hundreds of billions of US dollars, have started with a mere spill. In very many cases spills have triggered larger fires and explosions whereby the initial accidents escalated into horrific disasters. This paper presents an state-of-art survey of the models developed so far on forecasting the spill dynamics of flammable liquids and the heat generated if they catch fire.

Keywords: Flammable liquids, spill forecast models, fire, explosion, burning rate, fuel spread

1. Introduction

A survey of past accidents that have occurred in chemical process industries handling flammable liquids, either within the industrial premises or during transportation from or to the industries, reveals that majority of the accidents had begun with a mere spill of a flammable liquid (Khan and Abbasi 1997a, b, c; 1998 a, b, c, d; 1999a, b; 2001a, b, c, d; 2002; Abbasi *et al.,* 2010; 2013). Before it could be contained, the spill had either caught fire or evaporated to form a highly flammable vapour cloud which then got ignited to either generate flash fire or an explosion accompanied with a fire ball(Abbasi and Abbasi 2005; 2007 a, b, c; 2008; Tauseef *et al.,* 2010; 2011 a, b; Vasanth *et al.,* 2013). These happenings then precipitated other spills, thereby escalating the accident to catastrophic levels(Abdulhamidzadeh*et al.,* 2010; 2011).

An example of how accidental spills snowball to catastrophic accidents is the CAPECO refinery episode of 23 October 2009, which occurred at Bayamon, Puerto Rico. While transferring gasoline from a tanker ship to a storage tank in the refinery, there was a spill. It quickly formed a large vapor cloud, which ignited after reaching an ignition source in the wastewater treatment (WWT) area of the refinery, and exploded. The resulting blast and fire then led to multiple secondary explosions. As a result, there was serious damage to 17 of the 48 petroleum storage tanks and other equipment. The fires (Figure 1) burned for almost 60 hours. The biggest of the blasts created an earthquake-like pressure wave registering 2.9 on the Richter scale and damaged approximately 300 homes and businesses up to 1.25 miles from the site. In particular, the nearby Fort Buchanan military facility suffered worth damages US $5 million. Similarly heavy damage was suffered by the refinery and the other establishments affected by the disaster. Air and vehicle transportation was interrupted; and thousands of gallons of oil, fire suppression foam, and contaminated runoff were released to the environment, causing irreparable damage.

Figure 1: A scene from the CAPECO refinery disaster of 2009
(ejatlas.org/conflict/capeco-caribbean-petroleum-company)

Table 1 provides illustrative examples of a few of the hundreds of major accidents that have occurred all over the world which had begun with an accident spill of one or other type of flammable liquid.

Table 1: Seven illustrative examples form among hundreds of major disaster which began with an accidental spill

Accident identifier	Year	Number of deaths	Number of people injured	Estimated losses, in million US dollars
Pernis	1968	2	85	141
Sao Paulo	1984	508	>1000	Not available
Siberia	1989	462	>96	Not available
Tolouse	2001	29	2500	1000
Bruncefield	2005	-	43	13000
Jaipur (IOC)	2009	12	200	32
Thiland	1999	-	-	22.3

Spills can be classified according to the environment in which they occur (land/water), the activity during which they occur (storage, handling, transport), and the duration and the rate at which they occur. The rate of spillage can be sub-classified as instantaneous, continuous, and quasi continuous (or pulsed). These manners of spillage are influenced by the size of the spill, properties of the spilling liquids and the environmentinto which the spill occurs (Raj et al., 1981).

Cryogenic liquids like LPG and CNG or liquid hydrogen can evaporate rapidly to form vapour clouds before they get ignited while less volatile fuels like petrol and diesel normally catch fire in liquid state. Besides direct harm in terms and injuries and death, and damage to property running into millions of dollars occurring *in each major accident*, fuel spills also cause serious contamination of land and water. The direct and indirect harm to environment caused by them is, in fact, incalculable. This is because fuel oils and their decomposition products ─ of which several are toxic ─ can persist in the environment for hundreds of years, interfering with food chains and biogechemical cycles in so many different ways that are impossible to quantify and remediate. The spill that occurred in the offshore rig of BP reginery in 2010 is considered as the worst ever environmental disasters of its kind (Mukhim, 2016).

Give this backdrop, it is exceedingly important to understand the ways in which fuel spills occur, spread, and burn, and the factors which influence them. Only with this understanding that strategies can be devised to contain the spillsand minimize the harm they cause. The present paper deals with the models that have been developed to understand the contribution of different factors in influencing the dynamics and the burning of the fuel spills.

2. The spill models: general

The spill models deal with the spreading, vaporization and pool formation of liquids over different types of receiving surfaces. The extent of hazard associated with the accident spilling of a flammable and/or toxic substance, according to Raj *et al.,* 1981, "depends on the source strength of vapour, pool size and the temporal behavior of the spilled liquid.

These can be forecast by using the models developed for the spill size, liquid evaporation rates and other aspects of spill behavior" (Raj et al., 1981; Bohl and Jackson., 2006).

A liquid spill is distinguished as confined or unconfined depending upon its boundary region. The spreading of liquid fuel follows three regimes — gravity-inertia, gravity-viscous, and viscous-surface tension. These regimes are named after the forces which tends to spread the liquid and the ones which oppose the flow (Putorti et al., 2001; Benfer, 2010).

A review of the models for liquid the spills of flammable liquids occurring on land is presented below.

3. SPILL (Shaw and Briscoe, 1980)

The SPILL model was developed by the Safety and Reliability Directorate (SRD) of the Health and Safety Executive (HSE), UK. This model is suitable for liquid pools of cryogenic and pressurized liquid releases on both land (concrete and soil) and water. Both catastrophic failure and minor containment failure is considered where the rate of release of the liquid is instantaneous and continuous.

This model predicts the vaporization rates of liquid pool by accounting simultaneous pool spreading and vaporization.

The spreading of liquid is mainly driven by gravity force and is also assisted by net surface tension, which becomes significant in smooth surfaces. Shaw and Briscoe (1990) developed spreading equations for gravity inertia regime of spreading of liquid pool.

The vaporization rate in a unit area is determined by the heat transfer between the liquid and the ground, where it assumes the heat transfer as controlling mechanism. Hence the model overestimates the heat transfer rates, predicting higher vaporization rates.

According to Briscoe and Shaw (1980), the "model is based on the following assumptions:

1. Liquid pool is thin and remains at its boiling point.
2. The pool is in perfect thermal contact with the ground.
3. Heat of conduction in the ground is one dimensional".

The volume release rate of the liquid is calculated as

$$V_c = AC_d \left\{ 2gh + \frac{2}{\rho}(p - p_a) \right\}^{1/2} \qquad \dots 1$$

Where, a is the cross sectional area of the hole, C_d is discharge coefficient, ρ is the density of liquid.
The spreading of pool uses Fay's equation where pool radius is defined as a function of time.
For instantaneous spill,
The radius of the pool is determined by

$$r = \left[r_0^2 + \left(\frac{8g\Delta V_0}{\pi} \right)^{0.5} t \right]^{0.5} \qquad \dots 2$$

Where

R_0 is the initial radius and

V_0 is the initial spill volume

For continuous spills, the radius of pool is given by

$$r = \left(\frac{32g\Delta V_c}{9\pi}\right)^{1/4} t^{3/3} \qquad \ldots 3$$

*Vaporisationrate:*The vaporisation rate from the cryogenic pool per unit area is obtained directly which the heat flux from the surface by

$$m^{"}_{vap} = \frac{Q^{"}_{surf}}{\Delta H_{vap}} \qquad \ldots 4$$

Where,

$\dot{m}^{"}_{vap}$ = pool vaporisation rate per unit area

$Q^{"}_{surf}$ = heat flux from the surface

ΔH_{vap} =heat of vaporisation at the pool temperature

3.1 Inputs required

The inputs required for the model are initial volume of spill, heat flux from the surface, and heat vaporization at pool temperature.

3.2 Strength and weakness

Strength:

1. It is suitable for both refrigerated and pressurized liquids
2. It is simple and conservative.

Weakness:

1. It does not calculate vaporization rates for liquids with boiling point above ambient pressure.
2. The analytical solutions of cryogenic spills on land give erroneous results.

4.DRIVAS (Drivas, 1990)

This model calculates evaporation rates of individual compounds in a multicomponent liquid mixture. It focuses on the evaporation of confined spills. It calculates total evaporation rate, liquid composition and vapour composition.

The individual evaporation rates of a multicomponent spill are calculated based on convective mass transfer theory. This model is applicable only for volatile liquids and not

suitable for liquefied gases. The initial mole fraction is determined from the vapor composition using Raoult's law.

The assumptions made in this model are:

1. The multicomponent pool is an ideal solution and is well mixed.
2. The pool remains at uniform temperature and concentration.

Applying the mass transfer rate equation for each component in the mixture, the resultant equations for total number of moles in a pool (n_T) is

$$n_T = \sum_{i=1}^{n} n_i^0 \, exp\left(-kAP_{vapi}t\right) \qquad \qquad \dots 5$$

Where

$n^i{}_0$is the initial number of moles of component i in the pool, *A* is area of pool, *t* is time and P_{vapi} is partial pressure of compound.
The total mass of the pool is given by

$$\frac{dM_{pool}}{dt} = -k. \, M_{pool}^0 \sum_{i=1}^{N} \frac{P_{vap\,i} \cdot x_{pool\,i}^0 \cdot M_{w\,i} \cdot exp\left(-k.P_{vap\,i}.t\right)}{\sum_{i=1}^{N} x_{pool\,i}^0 \cdot M_{w\,i}} \qquad \dots 6$$

Where
M_{pool} - total mass in the pool
 k-   Mass transfer coefficient
$M^0{}_{pool}$ - total mass in the pool at the previous time step
$M_{w\,i}$ - molecular weight of component i
$X^0{}_{pool\,i}$ - mass fraction of component i in the pool at the previous time step
N- Total number of components in the mixture.

4.1 Inputs required

The inputs are initial mass of spill, initial liquid composition, spill area, ambient air temperature, wind speed and atmospheric stability.

4.2 Strength and Weakness

Strength:
1. It uses relatively simple formulation for calculation of evaporation rates**.**
2. This formulation could be modified according to the compounds, and is applicable in air quality simulation models.

Weakness:
1. It is not suitable for liquefied gases.
2. It is suitable for confined pools.

5. OILSFSM (Hussein et al, 2002)

OILSFSM is a "screening model for predicting the surface flow of oil by considering infiltration and evaporation. Surface flow is simulated by semi analytical model (cfpub.epa.gov) considering viscous forces. Infiltration is simulated by Green-Ampt infiltration model and evaporation is calculated by compositional model which accounts fractional changes of each compound. This model is suitable for permeable surfaces and it can model both continuous and instantaneous spills. The OILSFSM consists of three modules:the surface flow module, the infiltration module and the evaporation module.

The surface flow module:

According to Hussein (2002) the "surface flow of liquids on horizontal and inclined surfaces can be considered as a special case of gravity current that occurs when a fluid of a given density (oil) flows into another fluid of a different density (air), which is driven by gravitational forces. The gravity currents are influenced by three forces such as inertial forces, viscous forces and gravity forces".

The surface flow is predicted in both horizontal and inclined surfaces.
i.   *Horizontal surfaces:*V_{eff} is the volume of spill due to lateral spreading which is given by,

$$V_{eff}(t) = V(t) - (2\pi)^m \int_0^t \int_0^{x_N(t)} \{x^m (q_i(x,t) + q_c(x,t)) dx d\tau\} - (\pi x_N(t))^m x_N(t) h_d$$

…7

Where, "$q_i(x,t)$ and $q_e(x,t)$ are the infiltration and evaporation fluxes per unit area of the spill, and h_d is the ponding depth and v is the volume of spill" (Hussein, 2002).

Extent of spill is given by

$$x_N(t) = \xi_N (RV^3 t)^{1/(5+3m)}$$

…8

Where, ξ_N is a constant that depends on the type of spill and the type of source.

Rate of increase of spill is given by

$$\frac{dx_N}{dt} = \frac{(3\alpha+1)}{(5+3m)} \xi_N \left(RV_{eff}^3\right)^{\frac{1}{5+3m}} t^{\frac{-(4+3m)}{(5+3m)}}$$

…9

Minimum thickness of spill is given by
$$h_{min} = h_s + h_d$$

…10

*Inclined surfaces:*The model considers both line and point sources.

For line source:

$$\int_{x_T(t)}^{x_N(t)} xh(x,t)dx = V(t)…11$$

Where x is the coordinate in the down-slope direction

For point source,

$$\int_{x_T(t)}^{x_N(t)} \int_{-y_P(x,t)}^{y_P(x,t)} x h(x,t)\, dx = V(t) \ldots 12$$

Where "y is the coordinate in the cross-slope direction, and x is the coordinate in the downslope direction; $y_P(t)$ is the extent of the spill along the y-direction at any time, t, which is assumed to be symmetric about the y-axis" (Hussein, 2002).

The extent of the spill is given by

$$x_N(t) = \zeta_N (RV^2 t \sin\theta)^{1/3} \quad \text{for a line source} \qquad \ldots 13$$

$$x_N(t) = \zeta_N \left(\frac{R^3 V^4 t^3 \sin^5\theta}{\cos^2\theta} \right)^{1/9} \quad \text{for a point source} \qquad \ldots 14$$

Effective volume is given by

$$V_{eff}(t) = V(t) - \int_0^t \int_{x_T(t)}^{x_N(t)} \int_{-y_P(x,t)}^{y_P(x,t)} (q_i(x,t) + q_e(x,t))\, dy\, dx\, d\tau$$

$$- \int_{x_T(t)}^{x_N(t)} \int_{y_P(x,t)}^{y_P(x,t)} h_d\, dy\, dx \qquad \ldots 15$$

Infiltration of liquid: Infiltration of oil in land is influenced by the interaction between air, oil and water. The "governing equations for oil infiltration to the vadose zone are nonlinear and coupled with equations describing the flow of water and air" (Cochran, 1981).

As detailed by Hussein (2002), the depth of the infiltration measured from the ground surface, zf (t) at some time, t,

$$t - t_0 = \frac{n S_1}{K_1} \left(Z_f(t) - z(t_0) - (h - H_f) \ln\left(\frac{Z_f(t) + h - H_f}{Z_f(t_0) + h - H_f} \right) \right) \qquad \ldots 16$$

"Where, n is the porosity, K_1 is the oil conductivity of the soil, and S_1 is the oil saturation behind the invading front" (Hussein, 2002).

"The volumetric flux per unit area of the spill, q_i, can then be estimated from" (Hussein, 2002).

$$q_f = K_1(S_1) \left(\frac{h + z_f - H_f}{z_f} \right) \qquad \ldots 17$$

Evaporation: Evaporation of oil depends upon spill conditions and chemical composition. This model is suitable for both pure liquid and mixture of volatile liquids.

For pure liquids,

$$q_e = k_g \, v \, P/RT \qquad \qquad \dots 18$$

"Where, kg is the gas-phase mass transfer coefficient, v is the liquid molar volume, P is the vapor pressure, R is the universal gas law constant, and T is the temperature" (Hussein, 2002).

For mixture of volatile compounds,

$$q_{ej} = k_{gj} \frac{v_c}{V_o} n_j v_j \frac{P_j}{RT} \qquad \qquad \dots 19$$

"Where, v_c is the mean effective oil molar volume, V_o is the oil volume, k_{gj} is the gas phase mass transfer constant, n_j is number of moles, v_j is the molar volume, and P_j is the vapor pressure" (Hussein, 2002).

5.1 Inputs required

The inputs required are infiltration and evaporation fluxes, volume of spill, number of moles.

5.2 Strength and weakness

Strength:

1. It considers both point and line sources.
2. It provides additional information about the spatial variation in the infiltration depth

Weakness:

1. The model cannot predict the redistribution phase in infiltration.

6.REACTPOOL (Kapiasand Griffiths, 2001)

This is one of the pool models which describes the features of pool behavior which is predominantly modeled "for accidental releasesof SO_3 and oleum, but can be applied for other liquids irrespective of volatility and reactivity" (interscience.metapress.com). The model is suitable for instantaneous and continuous releases.

The core of the model consists of the sub models for spill, reaction, and evaporation.

*Spill module:*It describes the spreading behavior of liquid over the land which is based upon the equation of conservation of mass, momentum and energy.

For instantaneous releases,

$$\frac{dR}{dt} = \sqrt{1.08g(h_0 - h)} \qquad \qquad \dots 20$$

Where, $R=R_0$ at $t=t_0$ which is the time taken for the liquid to be spilled, and the pool depths h and h_0 are

$$h = \frac{V}{\pi R^2} \qquad \qquad …21$$

$$h_0 = \frac{V_0}{\pi R_0^2} \qquad \qquad …22$$

According to Kapias (1998), the "pool spreads until it reaches a minimum layer thickness, hmin, depending on the roughness of the substrate; the pool then shrinks as the volume decreases due to evaporation and the depth remains constant at h".

For continuous releases, the spreading is given by

$$\frac{dR}{dt} = \sqrt{2g(h - h_{min})} \qquad \qquad …23$$

The pool depth or height will be

$$h = \frac{V}{\pi R^2} \qquad \qquad …24$$

Where, V is the pool volume.

$$V = \frac{M_P}{\varrho} \qquad \qquad …25$$

Reaction module: This module contains of two aspects, reaction with the receiving surface and availability of water. Availability of water accounts for water present on the ground, in the atmosphere, and in the substrate receiving the spill. The model is particularly suited for water reactive chemicals and formation of compounds has been given importance.

The energy balance is calculated, which is used to predict the temperature of the pool.

Evaporation module: The evaporation module makes use of Brighton model which depends on surface roughness, vapour pressure, and friction velocity on mass transfer process. It employs evaporation model for two cases boiling and solidification.

When the heat balance is equal to boiling point, the pool boils and excess temperature is used for vaporization, whereas if the heat balance is equal to freezing point, the pool solidifies.

The wind driven evaporation rate, M'_e

$$M'_e = C_s j_1 u * \pi R^2 \qquad \qquad …26$$

Where, C_s is the vapour concentration, P is the friction velocity of the airflow and j is the dimensionless local evaporation rate.

6.1 Inputs required

The inputs required for spill module are type of spill, type of liquid spilled and rate and amount of spill. The inputs for reaction module consist of surface type, wind speed,

atmospheric humidity. The inputs for evolution mode are spill duration, air temperature and free ground water film thickness.

6.2 Strength and weakness

Strength:

1. The model can be modified for other liquids irrespective of the liquid's volatility and reactivity

Weakness:

1. Molar flux cannot be modelled satisfactorily

7. LEONELLI (Leonelli, 1994)

This model estimates evaporation rates accounting for both ideal and non-ideal liquid mixtures in boiling or evaporative conditions. It is suitable for both confined and unconfined surface and also handles instantaneous and continuous releases.

The pool is modeled in two ways:

1. It is assumed to be well mixed at uniform temperature.
2. It is formed by well mixed bulk and very thin surface layer, having difference in surface and bulk temperature.

This model consists of two sub-models: for spreading and vaporization.

The spreading model: The spreading model builds upon the work of Shaw and Briscoe (1980) for pools on land. Equations for the pool radius as a function of time are presented for both instantaneous and continuous spills. Heat contributions from the surroundings to the pool include conductive heat transfer from the ground, convective heat transfer from the atmosphere and solar incidence.

The vaporisation model: The vaporization model considers both ideal and non-ideal liquids. Raoult's Law is used for ideal liquids and for non-ideal mixtures, activity coefficients are introduced to the model.

The model treats boiling and evaporation pools separately, where transition from one regime to another is allowed.

For boiling pools, a flash calculation using Rachford-Rice relation combined with an energy balance is performed to determine the amount of vapour generated. Comparative analysis is made between MacKay and Matsugu (1973), and Pasquill (1943), heat-mass transfer analogy for a flat plate in laminar flow for evaporative pools.

For stratified pools heat balances are carried out separately for bulk and surface layers. The heat required by for vaporisation"at the pool surface is provided by solar radiation and

convection from the atmosphere and from the bulk layer. The energy balance for the bulk includes conduction from the soil" Kapias (1998) and heat contributions from new mass added to the pool.

7.1 Inputs required

The inputs are volume of spill, temperature of pool, emissivity values.

7.2 Strength and weakness

Strength:

1.   Stratification of liquid pool is included, predicting accurate evaporative rates.

Weakness:

1.Hypothesis of well mixed liquid proves to be wrong, predicting large discrepancies   in temperature value.

8. GASP (Webber, 1990)

This model was developed by the Safety and Reliability Directorate (SRD) for the Health and Safety Executive (HSE). It accounts for both continuous and instantaneous spill over land and water.

GASP model constitutes three sub-models, dealing with spreading, heat transfer, and vaporization.

 Description

*The spreading sub-model:*The spreading model is based on the analytical solution of the shallow water equations generalised to include turbulent or laminar frictional effects on land surfaces. The spreading model distinguishes between three different types of surfaces: smooth ground, rough ground, and water, where the rough surface could hold liquid in large puddles. On a rough surface, the pool will spread until it reaches a minimum thickness which is dependent on the average surface roughness of the ground.

GASP accounts for non-uniform pool heights by incorporating an effective shape factor, s, defined as the ratio between the height at the pool's edge and the mean pool height (Webber, 1990).

*The heat transfer sub-model:*This model accounts for the heat contribution from the surfaces, mass added to the pool (continuous releases), solar radiation, and heating.

Special consideration is also given for cryogenic spills, where film boiling is incorporated by Klimenko relation and is applicable when the heat flux into the pool exceeds a critical heat flux. For non-boiling pools heat transfer coefficients are considered.

*Vaporisation Model:*The vaporization model is based on the Brighton model for mass transfer coefficients. According to Brighton, the mass transfer from the liquid to the air is only limited by molecular diffusion across a stagnant boundary layer above the pool surface. It also provides unified treatment for boiling and evaporative pools.

8.1 Inputs required

The inputs required are substrate properties (surface roughness), liquid properties, and wind speed, volume of spill and radiation flux.

8.2 Strength and weakness

Strength:

1. The model distinguishes between rough and smooth surface providing better results.

Weakness:

1. The "model does not account for surface waves, or the effects of sloping or porous ground, nor multi-component liquid composition" (Higuera, 2002).

9. LSM 90 (Cavanaugh et al., 1994)

LSM90 was developed by Exxon to model simultaneous spreading and vaporisation of multi-component spills on water and land surfaces. LSM90 only considers continuous releases of ideal mixtures.

LSM 90 consists of two sub models,dealing with spreading and vaporization.

*The spreading sub-model:*LSM90 uses Shaw and Briscoe model for the spreading of unconfined spills on land and water. LSM90 introduces a correction to account for the slightly more complex geometryof spills on land in the presence of bunds.

Heat transfer from the atmosphere, ground, bund, mass spill rate (for continuous releases), and the effect of solar incidence are accounted for in the model.

LSM 90 model treats boiling and evaporating pools independently, allowing transitions.

*The vaporisationsub-model:*The model follows DRIVAS equation for calculating

vaporization rate, assuming the liquid pool to be well mixed. In a boiling pool, a flash calculation allows the calculation of the necessary amount of heat to be removed from the pool in order to maintain its temperature at the mixture's bubble point.

9.1 Inputs required

The inputs required are, partial pressure of component, molecular weight of component, initial volume of spill, heat flux from the surface, heat vaporization at pool temperature.

9.2 Strength and weakness

Strength:
1. Introduction of correction factor in spreading equation gives better predictions

Weakness:

1. The model cannot treat non- ideal liquids.
2. The model does not account temperature variations.

The adaptation of LSM90 in HGSYSTEM is given as LPOOL which is described below.

10. LPOOL (Cavanaugh et al., 1994)

This model is similar to LSM90 which is incorporated in HGSYSTEM pool model. LPOOL is utilizable for simulation of time dependent evaporation of multicomponent pools. It accounts for both boiling and non-boiling pools on land and water. It is similar to LSM90, which models spills in presence of dikes.

LPOOL is similar to LSM 90, where spreading and vaporization modules are based on Shaw and Briscoe and Drivas respectively. The size of the pool depends on the release rate from the tank and the evaporation rate.

The spill rates are calculated using equations for choked flow and Bernoulli's equation.

10.1 Inputs required

The inputs required are ground parameters, spill parameters (duration, rates), ambient atmosphere conditions, flashing and aerosol fraction

10.2 Strength and weakness

Weakness:

1. LPOOL cannot model Hydrogen fluoride spills; its prediction of HF chemistry and thermodynamics is not satisfactory.

11. PVAP (PHAST) (Witlox, 2008)

PVAP of PHAST was developed as commercially available software by Det Norske Veritas (DNV) for the purposes of risk assessment in the process industry. PHAST includes a single-component pool model that accounts for spreading, vaporisation and dissolution, for both continuous (constant or variable rate) and instantaneous releases.

The model consists of two sub-models, for spreading and vaporization.

The spreading sub-model:

PVAP spreading model has expanded the work of Shaw and Briscoe (1980) by implementing a spreading law where the velocity at the leading edge of the pool is proportional to the square root of the pool depth.For spreading on water, Dodge equations are used.

PHAST pool model predicts the variation of the pool temperature over time by performing an energy balance over the control volume of the pool. Phast pool model accounts for heat transfer from the surface, atmosphere and solar radiation incidence.

The vaporisationsub-model:

The vaporisation model distinguishes between two limiting cases; a cryogenic release that boils violently upon release and a volatile pool that evaporates at a temperature lower than its boiling point.

For a boiling pool, the vaporisation is driven by the rate of heat entering the pool that provides the necessary energy for the phase change to occur. In an evaporating pool, the vaporisation rate is controlled by the rate of mass transfer across a boundary layer formed above the pool surface.
For evaporation pools, modified equation of MacKay and Matsugu's model is use to find the mass transfer coefficients and Brighton model is used for calculation of vaporization rate.

11.1 Inputs required

The inputs required are volume of spill, mass vaporization flux and atmospheric conditions.

11.2 Strength and weakness

Strength:

1. The model is user friendly, which is very widely used for spreading, vaporization and dissolution providing accurate results.

Weakness:

1. The model is suitable for only single component mixtures, and multicomponent mixtures are treated as single pure component.

12. MOFAT 2D (Katyal et al.,1991)

This is one of the infiltration models, which is necessary in understanding the spill impact of hazardous substances on land. The model is a 2D finite element model which accounts for both saturated and unsaturated porous media.

The model consists of the flow and the transport modules.

*The flow module:*The flow module of MOFAT deals with two categories. One is the 2 phase flow of water and NAPL in the porous soil with gas at constant pressure and other is the 2 phase flow of water and NAPL liquid at variable pressure.

The governing equations are mass conservation equation and Darcy equations for finding the velocity of infiltrated liquid and are coupled to transport flow due to their dependence of permeability and pressure.

*The transport module:*The basic equations in this are continuity and mass flux equations, which are coupled to the fluid flow by interphase mass transfer, viscosity, and phase density.

Multiphase flow and solute transport are considered for unsaturated media whereas only solute transport is carried for saturated media.
The equations are solving by upstream finite element scheme, by influence coefficient approach.

12.1 Inputs required

The inputs required are NAPL surface tension, NAPL viscosity, density hydraulic conductivity, component densities, and equilibrium partition coefficients.

12.2 Strength and weakness
Strength:

1. Gas phase equation is included in flow equations.

13. HSSM (Hydrocarbon Spill Screening Model; Weaver et al., 1994)

This model is also one of the infiltration models which is particularly suitable for LNAPL. The model is used to estimate the fate and transport of LNAPL in subsurface and ground water. The subsurface is assumed to be homogenous, ignoring the lateral spreading. The transport of LNAPL inside the soil is considered as 1-dimensional.

The model is useful for

1. Tracking the flow of LNAPL.
2. Simulated dissolution of various chemicals in ground water.
3. Transport of contaminants to receptors in aquifers.

The HSSM consists of the KOPT, OILENS, and TSGPLUME modules.

OILENS AND TSGPLUME are basically confined to the flow and transport of DNAPL in aquifer and ground water, whereas KOPT simulates flow and transport of chemical constituents from surface to vicinity of Ground water. The KOPT module also assumes that the soil contains water and ignores lateral spreading.

13.1. Input required

The inputs are magnitude and type of DNAPL release, residual oil content, transport properties and soil water retention characteristics.

13.2 Strength and weakness
Strength:

1. It can predict fate and transport of DNAPL liquids in subsurface, vadose zone and ground water.
2. It can predict redistribution phase.

Weakness:

1. It is suitable for only DNAPL liquids.
2. It does not account for lateral spreading**.**

14. Models for simulation of flame spread over flammable material ─ general

As stated earlier, accidental fires in industries and commercial or residential areas are predominantly caused by the spillage of fuels and their subsequent ignition. The resulting flame spreads enveloping the surrounding areas causing major destruction. How a flame spreads"over liquid fuels (Higuera, 2002) is a classic problem of combustion theory, which is of both fundamental interest and practical importance".

The flame spread is defined as a reaction zone where combustible material and oxygen in air diffuses spreading along the surface of the combustible material (Zanganeh et al., 2013).
Many authors have discussed flame spread over porous surfaces (Ishida.,1986,1988,1992,1996,2005,2011; Takeno 1986) and the mechanism of flame spread over liquid surfaces, (Torrence and Mahjen, 1974;Mackinven*et al.,* 1970; Miller and Ross,1992,1995;Ross 1994; Ross and Miller,1997;Glassman andDryer,1981)but only few authors have dealt with flame spread on inclined surface (Zananeh*et al.,*2014).

Flame spread model describes about the mechanism and the physical process which are responsible for the spread of flame over the surfaces with liquid fuel.

A review of some flame spread models is given below.

15. Model for pulsating flame spread. (Blasi et al., 1990)

The model predicts the "main physical and chemical process of flame spread across laminar liquid pools. It is described by unsteady, two dimensional, elliptic and balance equations"(Di Blasi, *et al.,* 1991a) where the solutions are obtained by semi-infinite difference method.

The model has the following assumptions:

1. The flow is laminar
2. Flame and soot radiation is negligible
3. Depth of fuel layer is constant
4. Liquid density and gas density are constant except for variations due to buoyancy.
5. Gas and liquid properties are constant(heat capacities, viscosities, diffusion coefficient, thermal conductivities)
6. Flame spread is two dimensional
7. Ignition is caused at center.

The "model considers flame spread over liquid fuels in a tray. The liquid fuel temperature is controlled by immersing tray in cold bath. Ignition is caused by external heat source"(Di Blasi, *et al.,* 1991a).

The gas phase model relationship is given by
Stream function:

$$\frac{\partial}{\partial x}\left(\frac{\partial \chi}{\partial x}\right) + \frac{\partial}{\partial y}\left(\frac{\partial \chi}{\partial y}\right) = \zeta \qquad \ldots 27$$

Where $\frac{\partial \chi}{\partial x} = -v, \quad \frac{\partial \chi}{\partial y} = u \ and \ \zeta = \frac{\partial u}{\partial y} - \frac{\partial v}{\partial x}$

Energy function

$$c_p \rho \left(\frac{\partial T}{\partial t} + \frac{u \partial T}{\partial x} + \frac{v \partial T}{\partial y}\right) = q + \frac{k\partial}{\partial x}\left(\frac{\partial T}{\partial x}\right) + \frac{k\partial}{\partial y}\left(\frac{\partial T}{\partial y}\right) \qquad \ldots 28$$

Where u and v are stream wise and cross velocity components, T is the temperature, ρ is density, c_p is the specific heat at constant pressure, and k is thermal conductivity.

For liquid phase,
Energy function is

$$c_1 \rho_1 \left(\frac{\partial T_1}{\partial t} + \frac{u_1 \partial T_1}{\partial x} + \frac{v_1 \partial T_1}{\partial y}\right) = \frac{k_1 \partial}{\partial x}\left(\frac{\partial T_1}{\partial x}\right) + \frac{k_1 \partial}{\partial y}\left(\frac{\partial T_1}{\partial y}\right) \qquad \ldots 29$$

Stream function is

$$\frac{\partial}{\partial x}\left(\partial \chi_e / \partial x\right) + \frac{\partial}{\partial y\left(\partial \chi_e / \partial y\right)} = \zeta_1 \qquad \dots 30$$

Where,

$$\partial \chi_e / \partial x = -v_1, \partial \chi_e / \partial y = u_1 \; and \; \zeta_1 = \frac{\partial u_1}{\partial y} - \frac{\partial v_1}{\partial x} \qquad \dots 31$$

Where u_1 and v_1 are stream wise and cross velocity components, T_1 is the temperature, ρ_1 is density, c_{p1} is the specific heat at constant pressure, k_1 is thermal conductivity, ζ_1 is vorticity, χ_e is stream function.

The empirical equation which describes the vaporization process by relating liquid vapour pressure and temperature are

$$log(p_o) = -\frac{F}{T_r} + B - exp\left(-20(T_r - b)\right) \qquad \dots 32$$

Where T_r is reduced temperature,

$$\mu_1(\partial u_1/\partial y) - \frac{d\sigma}{dT(\partial T_1/\partial x)} = \mu \partial u/\partial y \qquad \dots 33$$

The difference between the viscous stress μ_1 is equated to surface tension variation σ, due to temperature variation.

15.1 Inputs required

The inputs are density, viscosity, diffusion coefficient, temperature, heat of combustion and activation energy.

15.2 Strength and weakness

Strength

1. Flame spread over alcohol fuels at low initial liquid temperature is studied.
2. Critical assumptions are neglected.

Weakness

1. It does not account the buoyancy driven flows
2. It does not consider different fuels and forced convective motions.

16. Model for oscillatory phenomenon of flame spread over liquid fuels (Di Blasi et al., 1991)

The gas phase buoyancy due to higher temperature gradients plays a primarily role inducing "convective flow field which opposes spread of flame he stream velocity at liquid/gas interface is equal to liquid requiring that the gas moves in direction of flame.as a

result of these effects, a circulating eddy may exist ahead the flame. This model investigates the liquid phase convective motions, and gas phase flow field in the type of flame spread" (Raj, 1981).

The model has the following assumptions (Blasi, *et al.,* 1991a):

1. "The flow is laminar
2. Flame and soot radiation is negligible
3. Depth of fuel layer is constant
4. Liquid density and gas density are constant except for variations due to buoyancy
5. Gas and liquid properties are constant(heat capacities, viscosities, diffusion coefficient, thermal conductivities)"

"A semi implicit finite difference is used to compute, numerically, where unsteady terms have been approximated by first order-Euler scheme" (Raj, 1981).

For gas phase,
Stream function

$$\frac{\partial}{\partial x}\left(\frac{\partial \chi}{\partial x}\right) + \frac{\partial}{\partial y}\left(\frac{\partial \chi}{\partial y}\right) = \zeta \qquad \ldots 34$$

Where,

$$\frac{\partial \chi}{\partial y} = u, \frac{\partial \chi}{\partial x} = -v \ and \ \zeta = \frac{\partial u}{\partial y} - \frac{\partial v}{\partial x} \qquad \ldots 35$$

Energy function

$$c_p \rho \left(\frac{\partial T}{\partial t} + \frac{u \partial T}{\partial x} + \frac{v \partial T}{\partial y}\right) = q + \frac{k\partial}{\partial x}\left(\frac{\partial T}{\partial x}\right) + \frac{k\partial}{\partial y}\left(\frac{\partial T}{\partial y}\right) \qquad \ldots 36$$

Where u and v is stream wise and cross velocity components, T is the temperature, ρ is density, c_p is the specific heat at constant pressure, and k is thermal conductivity.

For liquid phase,
Energy function

$$c_1 \rho_1 \left(\frac{\partial T_1}{\partial t} + \frac{u_1 \partial T_1}{\partial x} + \frac{v_1 \partial T_1}{\partial y}\right) = \frac{k_1 \partial}{\partial x}\left(\frac{\partial T_1}{\partial x}\right) + \frac{k_1 \partial}{\partial y}\left(\frac{\partial T_1}{\partial y}\right) \qquad \ldots 37$$

Stream function

$$\frac{\partial}{\partial x}\left(\frac{\partial \chi_1}{\partial x}\right) + \frac{\partial}{\partial y}\left(\frac{\partial \chi_1}{\partial y}\right) = \zeta_1 \qquad \ldots 38$$

Where

$$\frac{\partial \chi_1}{\partial y} = u_1, \frac{\partial \chi_1}{\partial x} = -v_1 \ and \ \zeta_1 = \frac{\partial u_1}{\partial y} - \frac{\partial v_1}{\partial x} \qquad \ldots 39$$

and u_1 and v_1 are stream wise and cross velocity components, T_1 is the temperature, ρ_1 is density, c_{p1} is the specific heat at constant pressure, k_1 is thermal conductivity, ζ_1 is vorticity, χ_e is stream function.

16.1 Inputs required

The inputs are density, viscosity, diffusion coefficient, temperature, heat of combustion and activation energy.

16.2 Strength and weakness

Strength

1. "Complete information on the dynamics of ignition transient and flame spread over liquid fuels at low temperature.
2. Special emphasis is given for interaction between liquid phase flow field and gas phase flow field" (Blasi, *et al.,* 1991b).

Weakness

1. Quantitative predictions cannot be computed.

17. Computational analysis of flame spread over alcohol pools. (Schiller et al., 1996)

This is a 2D numerical model, which addresses "pulsating and uniform flame spread mechanisms and the effects of gravity level, pool depth, fluid properties, and chemical kinetic coefficients on flame spread across liquid fuel pools without forced flow. The numerical model uses SIMPLE algorithm with SIMPLEC modification and hybrid differencing scheme" ((Schiller, *et al.,* 1996).

It has the following assumptions:

1. "The liquid surface does not recede and remains flat and horizontal
2. Solute capillary forces are neglected
3. The binary diffusion coefficient is the same for each species
4. One-step, finite-rate chemical kinetics are assumed, and
5. Gas-phase radiation and radiation from the igniter are neglected" (Kim and Sirignano, 2003).

The general findings, according to Kim*et al.,*(1998) have been:

1. "There is little heat input to the liquid by gas-phase conduction ahead of the flame leading edge for both the uniform spread regime and the pulsating spread regime. Instead, gas-phase conduction inputs energy to the liquid primarily behind the flame leading edge, and the liquid is preheated ahead of the flame by stream wise convection through the liquid.

2. Pulsating flame spread requires a gas-phase recirculation cell just forward of the flame. Without forced flow, this recirculation cell can form due to the combination of countercurrent, buoyancy-driven flow and concurrent, surface-tension-driven flow. Hot gas expansion plays a critical role in the prevention of the formation of the recirculation cell during uniform spread and the destruction of the recirculation cell and acceleration of the flame during pulsating spread.

3. Mixed-mode combustion occurs in the flame leading edge region due to the presence of a premixed region ahead of the flame and the combustion of excess air with the diffusing fuel vapor from the liquid surface below the reaction zone".

18. Opposed-flow flame spread across *n*-propanol pools (Schiller and Sirignano, 1996)

The "computational study examines the effects of forced, opposed, air flow on pulsating and uniform flame spread across liquid fuel pools initially below the flash point temperature at either normal or zero gravity conditions" (hse.gov.uk).

The model is based on the assumptions:

1. "The liquid surface does not recede and remains flat and horizontal,
2. Solute capillary forces are neglected,
3. The binary diffusion coefficient is the same for each species,
4. One-step, finite-rate chemical kinetics are assumed, and
5. Gas-phase radiation and radiation from the igniter are neglected.
6. The effects of concentration gradients on the diffusion of energy are neglected" (Kim and Sirignano, 2003).

The "numerical method uses SIMPLE algorithm with the SIMPLEC modification and hybrid differencing scheme" (Kim and Sirignano, 2003).

The "boundary conditions at the gas/liquid interface follow from a heat balance and balance of the shear stresses with surface tension; a continuity of the temperature and tangential velocity; no dissolution of air or combustion products into the liquid" (fliu.eng.uci.edu).

"Temperature gradients along the liquid surface create thermo capillary stresses that are typically larger than gas-phase shear" (hse.gov.uk) is:

$$(\mu \partial u/\partial y)_l = (\mu \partial u/\partial y)_g + \sigma_T (dT/dx)_{lg} \qquad \text{…40}$$

18.1 Inputs required

The inputs are density, viscosity, specific heat, thermal conductivity, pressure.

18.2 Strength and weakness

Strength

1. Flame spread at forced flow conditions at both zero and normal gravity is computed.

Weakness

1. Gas phase radiation at low velocity of no forced flow is not included.

19. Axisymmetric flame spread across propanol pools in normal and zero gravities(Kim et al.,2007)

"Axisymmetric ignition and flame propagation across propanol pools is investigated numerically with finite-rate one-step chemical kinetics, variable properties, and an adaptive finite-difference gridding scheme without forced gas-phase flow", (Kim*et al.,* 1998).

The following conditions are examined.

1. The "effect of the initial profile of fuel vapor concentration in the gas phase before ignition at both normal gravity and zero gravity" (www.huxley.ic.ac.uk,Cai *et al.,* 2002).
2. The flame "spread is investigated as a function of oxygen concentration
3. Flame propagation as a function of initial pool temperature is compared between the axisymmetric and two-dimensional configurations" (Kim *et al.,*1998).

The following assumptions are made:

1. "The liquid surface does not recede and remains flat and horizontal.
2. Solute capillary forces are neglected.
3. The binary diffusion coefficient is the same for each species.
4. One-step, finite-rate chemical kinetics is assumed.
5. Gas-phase radiation and radiation from the igniter are neglected" (Kim and Sirignano, 2003).

The numerical model uses SIMPLE algorithm with the SIMPLEC modification and hybrid difference scheme.

The dimensional conservation equations of mass, momentum, energy of the gas phase are;

$$\frac{\partial \rho}{\partial t} + \nabla.\rho\vec{V} = 0 \qquad \qquad \dots 41$$

$$\frac{\partial \rho\vec{V}}{\partial t} + \nabla.\rho\vec{V}\vec{V} = -\nabla P_D + \nabla.\bar{\bar{T}} + (\rho - \rho_0)\vec{g} \qquad \qquad \dots 42$$

$$\frac{\partial \rho h_1}{\partial t} + \nabla.\rho\vec{V}h_1 = \nabla.\left(\frac{k}{c_p}\nabla h_1\right) - Q_c r_F^m \qquad \qquad \dots 43$$

Where

T is the temperature, ρ is density, c_p is the specific heat at constant pressure, k is thermal conductivity, P_D is the modified pressure.

For heat input required for liquid preheating in axisymmetric condition,

$$q_{l,axi} = \rho_l \delta \phi C_{pl} \Delta T_l \qquad \qquad …44$$

$$\phi = 1 + \frac{\delta}{2r_{fl}} \qquad \qquad …45$$

The heat required for planar configuration

$$q_{l,planar} = \rho_l \delta C_{pl} \Delta T_l \qquad \qquad …46$$

Where ΔT is average temperature.

19.1 Inputs required

The inputs are physical properties (density, viscosity, specific heat, thermal conductivity) total pressure and thermodynamic pressure.

19.2 Strength and weakness

Strength

1. It computes the flame spread at both normal and zero gravity conditions.
2. They neglect planar conditions thus predicting more accurate results.

Weakness

1. It does not include the mechanisms of axisymmetric flame spread in forced gas flows and different fuels.

20. Computational study of opposed-force-flow flame spread across propanol pools (Kim and Sirignano,2003)

The model investigates "the two-dimensional flame-spread across sub-flash-point propanol pools in opposed-forced airflow numerically for normal and zero gravities with finite-rate, one-step chemical kinetics, variable properties, and an adaptive finite-difference gridding scheme. It examines effects of air speed, liquid depth, and gravity on the characteristics of the flame-spread with correct initial profiles for the gas-phase velocity and the mass-fraction of fuel vapor before ignition" (Kim and Sirignano, 2003).

"The un-steady conservation equations of mass, momentum, energy, and species for the gas phase are" (Kim and Sirignano, 2003):

$$\frac{\partial \rho}{\partial t} + \nabla.(\rho V) = 0 \qquad \qquad …47$$

$$\frac{\partial \rho V}{\partial t} + \nabla.(\rho V V) = -\nabla P_D + \nabla.\tau + (\rho - \rho_0)g \qquad \qquad …48$$

$$\frac{\partial \rho h_1}{\partial t} + \nabla.(\rho V h_1) = \nabla.\left(\frac{k}{c_p} \nabla h_1\right) - Q_c r_F^m \qquad \text{…49}$$

Where

T is the temperature, ρ is density, $c_p$is the specific heat at constant pressure, k is thermal conductivity, P_D is the modified pressure.

The "conditions at the gas-liquid interface are obtained from an energy balance and balance of the Stresses, continuity of the temperature and tangential velocity, conservation of species, and the assumption of negligible recession of the liquid surface" (Kim and Sirignano, 2003).

$$\left(k \frac{\partial T}{\partial y}\right)_l = \left(k \frac{\partial T}{\partial y}\right)_g - \rho_g V_g h_{fg} \qquad \text{…50}$$

$$\left(\mu \frac{\partial u}{\partial y}\right)_l = \left(\mu \frac{\partial u}{\partial y}\right)_g + \frac{d\sigma}{dT}\left(\frac{dT}{dx}\right)_{lg} \qquad \text{…51}$$
$$T_g = T_l$$
$$u_g = u_l$$

20.1 Inputs required

The inputs are density, viscosity, specific heat, thermal conductivity, and pressure.

20.2 Strength and weakness

Strength
1. Different pool depth has been studied.

Weakness
1. Determination of pseudo uniform regime in shallow pools and gravity is not carried.

21. Liquid-fuel thermo capillary flow induced by a spreading flame (Higuera, 2002)

The flame spread is modelled considering, according to Higuera (2002),"flow in a layer of liquid whose surface tension varies under the action of a moving surface heat flux distribution. The surface temperature increases from the ambient temperature of the liquid, far upstream, to its vaporization temperature at a moving vaporization front, and stays constant at this value downstream of the vaporization front. The speed of the front is determined by a condition of regularity of the temperature".

The thermo capillary flow, according to Higuera (2002), "induced in the liquid by the spreading of a flame over its surface, in order to ascertain the role of the liquid-phase in the different regimes of flame spread" is studied.

The flow of liquid is given by

$$\nabla . v = 0$$

$$Re\left(\frac{\partial v}{\partial t} + v.\nabla v\right) = -\nabla p + \nabla^2 v \qquad \dots 52$$

$$RePr\left(\frac{\partial \theta}{\partial t} + v.\nabla \theta\right) = \nabla^2 \theta \qquad \dots 53$$

$$v_c = |\sigma'|(T_v - T_0)/\mu \qquad \dots 54$$

Where, $\sigma' = d\sigma/dT < 0$

The heat flux, $qg(x)$, is modelled by a Gaussian distribution,

$$q_g(x) = q_0 exp\left(-\frac{x^2}{\lambda^2}\right) \qquad \dots 55$$

The total energy released per unit time by the flame in this region is of order

$$k_g \Delta T_g = \left(k_g/c_p\right)Q/(1+s) \qquad \dots 56$$

21.1 Inputs required

The inputs required are density, viscosity, specific heat, thermal conductivity, and pressure.

21.2 Strength and weakness

Strength
1. The "effect of the vaporization mass flux on the dynamics of the liquid around the vaporization front is neglected in comparison with the larger fluxes prevailing in the bulk of the liquid" (Higuera, 2002) minimizing errors.

Weakness
1. It does not account for the shape and strength of the pulsations.

Summary

The paper highlights the fact that a large number of major disasters involving the manufacture, transport, storing, or utilization of flammable liquids start with a mere spillage of those liquids. When not controlled and ameliorated quickly, such spills lead to fires and explosions, converting the simple initial accident to complex and extremely damaging major disasters. The paper then draws attention to the importance of studying spill dynamics and the factors which influence it as a pre-requisite to developing strategies for quickly controlling and containing the spills. In this backdrop all the important models that have been developed so far to study and forecast accidental spills, and the manner in which the spilled liquid would burn upon catching fire, are discussed.

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