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OPERATIONAL RISK ANALYSIS FOR UNDESIRED POLYMERIZATION IN OVERHEAD CONDENSER OF BUTADIENE COLUMN

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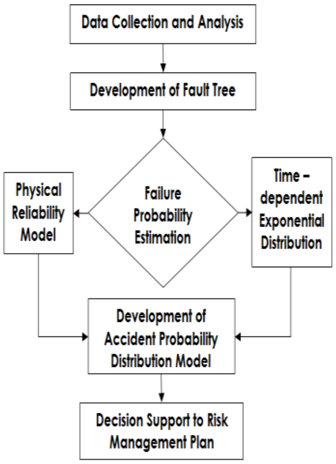
Graphical abstract



Abstract

An accident model based on fault tree analysis was developed and applied to analyze the recurrence of undesired reactions producing popcorn polymers in the overhead condenser of an industrial butadiene distillation column. The modeling framework incorporates reliability data associated with asset integrity and human performance along with data on selected process variables. These variables, i.e., pressure, feed velocity and temperature of the condenser, which were identified from root cause analysis of the incident provided dynamic contributions to the model, and were represented in the form of Weibull distribution functions. The results obtained proved the potentials of the proposed methodology. Based on the case study considered, operating pressure was identified as the most influential process variables that needed closer monitoring. The methodology provides an opportunity for risk management to be implemented dynamically to facilitate maintenance plan and management of change.

Keywords: Operational risk, fault tree, dynamic probability, Weibull distribution, popcorn polymerization

Abstrak

Satu model kemalangan berdasarkan analisis kegagalan pokok telah dibina dan digunakan untuk menganalisis tindak balas tidak diingini yang menghasilkan polimer bertih jagung secara berulang-ulang di bahagian atas pemeluwap pada kolum penyulingan industri butadiene. Rangka kerja pemodelan menggabungkan data kebolehpercayaan integriti aset dan prestasi manusia bersama dengan data pembolehubah proses yang telah dipilih. Pembolehubah ini iaitu tekanan, halaju suapan dan suhu pemeluwap yang telah dikenal pasti daripada analisis punca asas kejadian, telah memberikan sumbangan dinamik kepada model dan disampaikan dalam bentuk fungsi taburan Weibull. Keputusan yang diperolehi membuktikan potensi kaedah yang dicadangkan. Berdasarkan kajian kes, tekanan operasi telah dikenal pasti sebagai pemboleh ubah proses yang paling berpengaruh yang memerlukan pemantauan yang lebih rapi. Kaedah ini memberi peluang bagi pengurusan risiko dilaksanakan secara dinamik untuk memudahkan pelan penyelenggaraan dan pengurusan perubahan.

Kata kunci: Risiko operasi, carta kegagalan, kebarangkalian dinamik, taburan Weibull, pempolimeran bertih jagung

1.0 INTRODUCTION

Butadiene (BD) is a major product from petrochemicals industries that is widely used as a monomer in the manufacturing of synthetic rubbers. It is carcinogenic and has strong tendency to react with large range of chemicals to form polymers, thus requiring special handlings and stringent operating procedures. Several researchers [1–4] have studied the reactivity of butadiene under various conditions and concluded that reactions of butadiene in the presence of peroxide or any free radical initiators may lead to the formation variety of polymers. Since these reactions are not intended by the process design, variety of safety and operability issues may arise.

Some of these unwanted polymers are commonly known as popcorn polymers, which are hard, opaque and porous. Popcorn polymers grow exponentially, particularly in the presence of seeds or oxygen and dust. Their rapid growth generate high pressure and temperature conditions resulting in sudden rupture or plugging in process facilities such as tube rupture in overhead condenser and bulging of condenser shell in a distillation process [1]. In addition to potential damages to process equipment, this condition may also lead to toxic and flammable butadiene release that can potentially cause fire and explosion.

Due to these hazardous risks, special considerations are made in the design and operation of processes involving BD. For example, dead zones are avoided in the structure of storage vessels and piping systems to prevent the accumulation of stagnant highly concentrated BD. Both pressure-discharging and emergency systems are also installed as part of the mitigating measures. However, high boiling points of many of these inhibitors render them effective primarily in the liquid phase leaving the gaseous phase more vulnerable to reaction initiation. Furthermore, since BD reacts readily with oxygen to form polymeric and peroxides that are initiators for polymerization, it is imperative to prevent oxygen contact with BD. Due to these conditions, some practical initiatives are typically implemented in the industrial BD extraction process including:

i. Metal surface passivation and removal of popcorn polymer seeds, which can mitigate the tendency of polymerization
ii. Regular air-tightness test at potential ingress point such as flanges
iii. Addition of antioxidants such as 4-tertiary butyl catechol (TBC) or butyl-lated hydroxy toluene (BHT) which can remove the free radicals that are known to initiate rapid exothermic polymerizations
iv. Scheduled monitoring of oxygen, peroxides and inhibitors contents

Despite all these measures, undesired polymerizations of BD continues to occur in the process industry leading to many incidents [4], and additional measures are therefore needed. One common approach is to periodically revisit the fitness of the plant safety and operability by conducting process hazard analysis techniques such as hazard and operability (HAZOP) study or layer of protection analysis (LOPA). This has also been a standard practice by most process plants as it has been incorporated in the legislation or adopted as best practices in many countries. Another alternative, which is essentially the focus of this paper, is to provide accident modeling and prediction capability so that corrective measures can be planned and implemented ahead of time. These can be incorporated as part of the preventive maintenance schedule or plant upgrades and revamps.

Several risk analysis techniques can be adopted to construct suitable accident model of a process. These include fault tree analysis (FTA), event tree analysis (ETA), bow-tie model and quantitative risk assessment. FTA has been widely used to model accidents in various case studies [5,6]. It is a deductive approach focusing on a top event for calculating the frequency of intermediate and base events. On the contrary, ETA is an inductive approach that identifies and evaluates potential consequences based on the top event to determine the probability of its consequences. Taking the advantage of these models, a bow-tie model was formulated to assimilate an accident scenario to a sequence of events and a sequence of mitigation barriers [7]. However, it is more difficult to be applied for large scale systems and is not widely recognized in the context of dynamic risk analysis.

In this paper, an operational risk analysis approach is proposed to predict the probability of popcorn formation in a condenser of a butadiene column. While this framework is based on FTA technique, it is integrated with covariate models to incorporate process dynamics, thus offering dynamic risk assessment capability that is much needed to address the influence of process operation towards the vulnerability of process equipment and likelihood of accidents.

2.0 CASE STUDY: POPCORN IN BUTADIENE (BD) OVERHEAD CONDENSER

2.1 Overview of BD Extraction Unit

A schematic diagram of the BD extraction process considered as the case study is shown in Figure 1. The unit is designed to separate a C_4 hydrocarbon mixtures containing butanes, butenes, butadiene, C_3 acetylenes and C_4 acetylenes into two product streams; one containing mainly 1,3 butadiene product and the other containing the C_4 raffinates. In this process, the feed is first separated in an extractive distillation unit using N–methyl–2–pyrrolidone (NMP) as the entrainer. The crude butadiene stream leaving the extractive process is then further purified in a two-stage conventional distillation process. In the first stage, propene is removed, while heavier components are removed in the second stage that is known as the BD column.

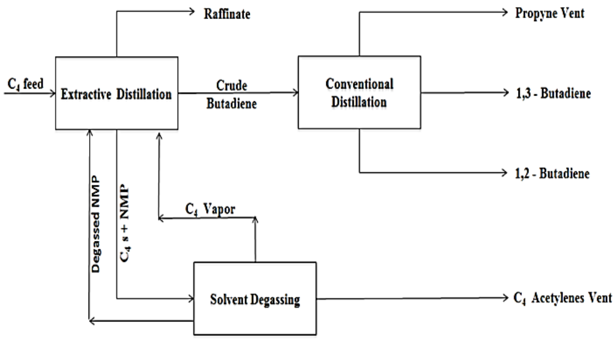


Figure 1 Overall block flow diagram of BD extraction process

The schematic diagram of the BD column is shown in Figure 2. The column receives crude BD as a feed and purify the desired 1,3 Butadiene product to the required product specification. At the top of the column, the overhead vapors are condensed in a vertical condenser, and the liquid is collected in an accumulator. Part of the liquid that leaves the accumulator is refluxed back to the column, while the remainder is drawn as product. This BD product is then cooled to 5°C in a product cooler. To maintain desirable product properties, an inhibitor, i.e., diluted TBC solution is sprayed into the condenser to reduce the propensity for polymer formation. Additional TBC is also added to the product before being sent to the storage.

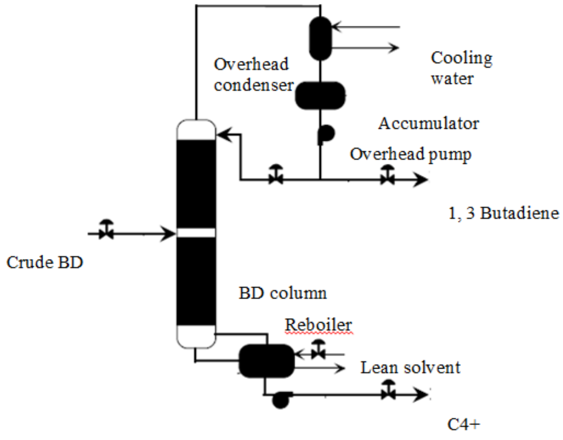


Figure 2 BD column process flow diagram

2.2 Popcorn Accident

In the middle of 2009, bulging was observed for the first time in the BD column overhead condenser in a petrochemical plant, 13 months after the unit was commissioned. This incident was caused by the rapid polymerization reaction to produce popcorn polymers in the shell side of the vertical condenser. It was suspected that the polymerization took place either due to free radical mechanisms with initiator such as oxygen, peroxide, and dust; or due to highly concentrated stagnant BD accumulated in one area. Subsequently, several efforts were taken to improve the cooling water system. These include replacing the manual injection procedure with automatic caustic solution injection to provide better pH control, close monitoring on the tightness of flanges and seals, and replacement of the side stream filter sand.

However, a second failure occurred about a year later in May 2010, causing a total loss of around USD 700,000. More preventive measures were then implemented including the addition of chemical injection system to feed anti–polymerant (radical scavenger) as additional protection against popcorn formation in the condenser. To avoid accumulation of concentrated stagnant BD and/or other initiators in the shell side of the condenser, six flushing lines with individual spray nozzle were installed. In addition, a vent line was also added to periodically vent off oxygen to the flare system.

Unfortunately, despite these measures, in June 2012, minor bulging was again observed in the BD overhead condenser. According to the final investigation report issued by the investigation team, potential root causes of the problems include faults in design and operation of process facilities such as failure in chemical treatment, ingress of impurities or failure related to process operation leading to undesired rapid polymerization. The failure of chemical treatment can be caused by insufficient injection of TBC or anti–polymerant. Deficiencies in side stream sand filter, flanges or seals at piping or equipment or incomplete passivation process during plant startup can lead to ingress of impurities such as polymer seed from upstream process, oxygen and rust into overhead condenser, causing rapid polymerization in the shell side of the overhead condenser. The growth of popcorn polymer then propagates until eventually causing the bulging of the condenser. A number of initiatives have been proposed to tackle the issue with detailed study needed prior to implementation due to high capital cost investment.

3.0 MODELING FRAMEWORK

In the search of more insights on the incidents, an accident modeling approach was proposed. The framework was based of FTA, taking the incident as the top event and logically constructing the relationships between the primary events based available process knowledge and insights. Once the FT has been structured, quantitative analysis was carried out to determine the top event probabilities based the assigned probabilities of the primary events and their logical relationships. Following systematic deduction of plausible causes of the incidents, the incident scenario was constructed and is represented by the FT shown in Figure 3. This FT model consists of three intermediate elements resulting from logical combinations constructed based on 9 primary events (PE) that have been identified as potential causes of the popcorn incident. These PE's are as defined in Table 1.

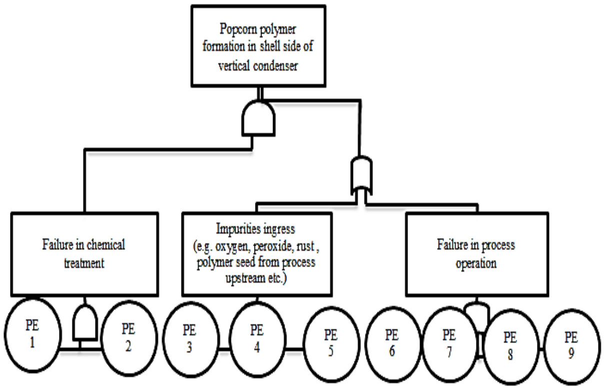


Figure 3 Fault tree of popcorn polymer formation

Table 1 Primary event for popcorn formation

Index	Components
PE 1	Insufficient dosage injection of anti - polymerant (radical scavenger)
PE 2	Insufficient injection of TBC (polymer inhibitor)
PE 3	Failure in side stream sand filter
PE 4	Improper tightness of flanges or seals
PE 5	Insufficient passivation of entire equipment or piping system
PE 6	Inconsistent flushing (Stagnant zone exist)
PE 7	High distillation overhead temperature
PE 8	Low process flow velocity
PE 9	High distillation overhead pressure

In addition to standard FT, the proposed model treated one of the intermediate elements, i.e., failure in process operation as a dynamic node, taking into consideration the changes of operating conditions in determining its failure probability. By using the updated probabilities of primary events occurrence, the estimated failure probability of top event can be revised. Combining the three components, the probability of failures of the top element *Pr(TE)* can thus be estimated using Eq.(1) below:

$$Pr(TE) = Pr(chemical\ ) \ x \ \{Pr(impurity\ ingress\ ) + Pr(process\ operation)\} \tag{1}$$

Note that *Pr(TE)* indicates the likelihood of occurrence of popcorn incident that are to be avoided by the plant.

3.1 Determination of Failure Probability using Database

For the purpose of computation, it was assumed that six of the primary events follow a time – dependent exponential distribution. The remaining three primary events, i.e., high distillation overhead temperature (PE7), low process flow velocity (PE8) and high distillation overhead pressure (PE9) were represented by covariate models, which will be explained in the next section. Failure data needed for the analyses were obtained from various history database including those published by Center for Chemical Process Safety, Offshore Reliability Data Handbook, CSB historical records and expert judgment.

Intermediate failure events in chemical treatment e.g. the insufficient dosage of injection of anti–polymerant (PE1) or TBC (PE2) can be triggered by the failure of instrumentation components (e.g. concentration analyzer, controller & control valve) or mechanical device (e.g. pump seal leaks). The failures rate of PE1 and PE2 were estimated by summing the failures of basic process control system (BPCS) instrument loops and mechanical devices. In this case study, since both injection systems had similar instrument loops and type of pump, PE1 and PE2 were identical. The failure of instrument loops and mechanical device was estimated as 0.1 faults per year, respectively [8]. The failure of the side sand filter (PE3) was estimated based on result as provided by Khakzad *et al.* [6] with the assumption that improper sized filter was the only cause that can lead to failure.

The failure frequency for PE4, PE5 and PE6 were associated with human error caused by an operator, maintenance personnel or vendor in carrying out their tasks. The failure to select of the appropriate gasket for proper tightness or seals for the piping and equipment were unlikely to happen due to stringent work process established for material quality assurance. Correct composition of chemical mixture for equipment and piping passivation were provided by supplier and prechecked by chemist prior to application. Insufficient passivation was also unlikely as a result of incorrect chemical composition used for passivation. Hence, the chances for the failure of PE4 and PE5 are most likely related to maintenance personnel and vendor activities in carrying out tightness check and passivation of piping and equipment. Meanwhile, the BD flushing in the vertical overhead condenser is truly executed manually by operator through an on-off switch in the control room and is therefore subjected to human error.

As industrial common practices, the tightness check of flanges or pump seals and equipment passivation normally will be executed as the opportunity for planned or unplanned process plant shutdown activity is available. The opportunity for planned process plant shutdown is once in every 3 years as part of regulatory requirements for preventive maintenance. The unplanned shutdown opportunity is assumed as zero as the plant is designed to operate for consecutive 3 years. The failure probabilities of PE4 and PE5 were estimated by multiplying the failure of human factor (0.01 faults/year/opportunity) [8] and 1/3 opportunity is available to carry out the flanges or seals tightness check and piping or equipment passivation in a year. The BD flushing executed by the operator to prevent the existence of BD vapor stagnant scenario in vertical overhead condenser was also subjected to human error in executing the routine procedure. In this case, the operator failure was taken as 0.01 faults per year regardless of frequency of task executed by operator in a year. Table 2 tabulates the failure rates λ and probabilities of primary events of fault tree for PE1 to PE6.

Table 2 Prior probabilities of primary events of fault tree

Index	Components	λ (per year)	Probability
PE 1	Insufficient dosage injection of anti - polymerant (radical scavenger)	0.200	0.181
PE 2	Insufficient injection of TBC (polymer inhibitor)	0.200	0.181
PE 3	Failure in side stream sand filter	0.010	0.095
PE 4	Improper tightness of flanges or seals	0.003	0.003
PE 5	Insufficient passivation of entire equipment or piping system	0.003	0.003
PE 6	Inconsistent flushing (Stagnant zone exist)	0.010	0.095

3.2 Determination of Failure Probability Using Physical Reliability Model

The dynamic part of the model, i.e., PE7, PE8, PE9, was represented by a covariate function. This was achieved by treating the variables, i.e. temperature, pressure and flow rate (velocity) of the shell side condenser according to Weibull distribution. The Weibull distribution is widely employed for reliability related problems due to its flexibility. It can be identical or similar to the several others of common distributions [9]. The Weibull cumulative distribution function is defined as [10]:

$$F(t) = 1 - Exp\,\{-(t/\theta)^\wedge\beta\,\} \qquad (2)$$

Where:

β = shape parameter ($0<\beta<\infty$)

θ = scale parameter ($0<\theta<\infty$)

In order to make failure rate of Weibull distribution dependent on covariates, the scale parameter, θ was assumed to be function of covariates:

$$\theta(x) = Exp(\textstyle\sum_{i=0}^{n} a_i x_i) \qquad (3)$$

The time-dependent failure rate of Weibull distribution is given by:

$$\lambda(t) = \beta t^{\beta-1}\theta^{-\beta} \qquad (4)$$

Substituting $\theta(X)$ into Eq. 4 results in:

$$\lambda(t,X) = \beta t^{\beta-1}\{Exp(\textstyle\sum_{i=0}^{n} a_i x_i)\}^{-\beta} \qquad (5)$$

3.3 Maximum Likelihood Estimation (MLE) Method

Given a sample of failure times {t_1, … , t_n} and the set of covariates x_{ij} associated with each failure time (x_{ij} is the value of the *i*th covariate which is associated with the *j*th failure time), MLE can be applied to estimate unknown parameters of the distribution. In this regard, flow velocity, *V* (PE7), overhead temperature, *T* (PE8) and pressure, *P* (PE9) events led to one common process deviation failure and with a Weibull distribution whose scale parameter, θ, is a function of covariates is given as below:

$$\theta(X) = Exp(a_0 + a_1V + a_2P + a_3T) \qquad (5)$$

Using the data in Table 1, the failure distribution parameters of process deviation failure (consists of PE7, PE8 and PE9) were estimated as β = 1.9775, a_0 = 0, a_1 = -0.0108, a_2 = -29.8215 and a_3 = 0.3602 applying maximum likelihood estimation method. Since x_0 = 1 by convention, the covariate model for determining time-dependent failure probability *F(t)* the intermediate failure event that represents the process dynamics takes the following form:

$$F(t) = 1 - Exp\,\{-(t/(Exp(-0.0108V - 29.8215P + 0.3602T)))^\wedge 1.9775\,\} \qquad (6)$$

3.4 Data Collection and Analysis

In this study, only process variables that were thought to be associated with the popcorn formation were considered. The data for these variables, i.e., process temperature, pressure and inlet flow rate of overhead condenser, were extracted from the plant record with one hour interval for the period of 4 years from the time of plant commissioning. Process data during the shutdown period were excluded. The interval of failure time was determined based on the date of plant commissioned and the first time the popcorn was detection, or between the subsequent detections of the popcorn formation. The beginning of the undesired polymerization was assumed to happen when high fluctuation of overhead pressure was noticed, and the corresponding flow rate of BD product, reflux flow rate, overhead temperature and pressure were recorded. Since there was no flow measurement available at overhead column vapor stream, the overhead column vapor process flow rate was estimated by summing the flow rate of the BD product and reflux streams. The process flow velocity entering the vertical condenser was estimated by dividing the total mixture liquid flow rate with the total area of 2 inlet piping (10 inches diameter each). These data were used to estimate the unknown parameters of Weibull distribution as tabulated in Table 3.

Table 3 Data used to estimate the unknown parameters of Weibull distribution for failure of process operation

Failure time, t_i (year)	Flow velocity, m/h	Pressure, kg/cm²	Temperature, °C
1.08	724.10	3.54	41.40
0.92	828.40	3.49	40.80
2.25	1166.03	3.38	39.51

Note that the following assumptions were involved in the work:

i. The overhead column vapor flow rate was equivalent to total flow rate of BD product and reflux flow as the BD vapor condensation rate is assumed to be in steady state.
ii. The mixture of BD liquid density in the product and reflux stream were considered identical and given as 595.9 *kg/m³*.

The starting time of high fluctuation of overhead column vapor pressure was considered as the starting time of polymerization occurred in the shell side of vertical overhead condenser.

4.0 EFFECT OF PROCESS VARIABLE ON PROBABILITY OF POPCORN FORMATION

In this research, the concept of physical reliability model was used to revise the probability of primary events of the FT, which in turn, results in top event updating. By incorporating primary events associated with process operations, i.e., PE 7, PE 8 and PE 9, components of process dynamic that contribute to the incident are illustrated in the following subsections below.

4.1 Effect of Pressure

Figure 4 indicates the effect of overhead pressure on the probability of the popcorn incident at constant temperature and entry flow velocity at 313.95 *K* and 878.66 *m/h* respectively. The probabilities was constant at a lower value of 0.0066 at lower pressure and when the pressure exceeds 3.40 *kg/cm²*, the probability increases to a maximum value of 0.0389 and plateaued as the pressure reached 3.50 *kg/cm²*. Note that at high pressure, the BD vapor phase is less protected by inhibitors because of the low volatility of these inhibitors e.g. TBC, thus making it more prone to polymer popcorn formation.

4.2 Effect of Temperature

The effect of overhead vapor temperature on the probability of top event is as illustrated in Figure 5. With overhead vapor pressure and inlet entry flow velocity were maintained constantly at 3.44 *kg/cm²* and 878.66 *m/h* respectively, the probability of top event decreases in the overhead temperature range of 308.975 to 314.975 *K* and subsequently plateaued at a minimum value of 0.0065 as temperature exceeds 316.975 *K*. This is however inconsistent with the argument by Aldeeb *et al.* [1], which claimed that the BD vapor at higher temperature is more susceptible to polymer popcorn formation. This was probably due to the lower composition of BD in the overhead vapor due to high distillation temperature and low reflux flow rate. Furthermore, inhibited crude butadiene liquid from a slip stream was also sprayed into the vapour inlet of the condenser to prevent the polymerization.

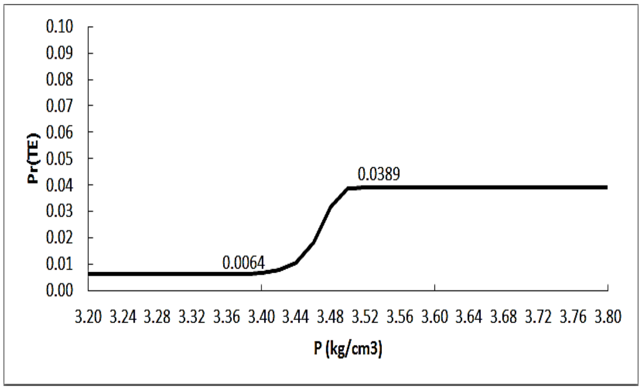


Figure 4 Top event probability updating for different overhead pressure (*P*)

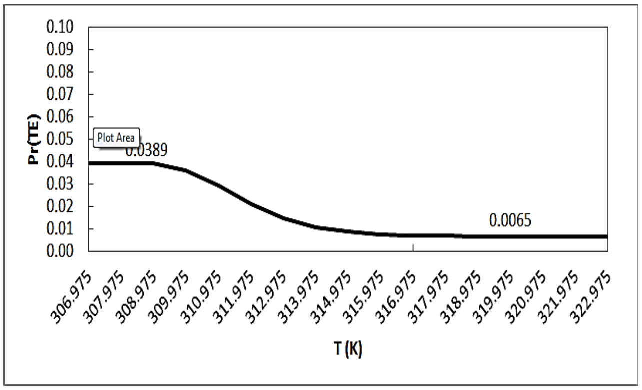


Figure 5 Top event probability updating for different overhead temperature (*T*)

4.3 Effect of Flow Velocity

The probability of the top event also increases with the estimated BD vapor entry velocity at constant temperature and overhead pressure at 313.95 *K* and 3.44 *kg/cm²* respectively. As shown in Figure 6, the increasing trend is suspected to be related to the accumulation of the high concentrated BD vapor at the zone above the feed entry point of the vertical condenser as a result of a layer of barrier formed by high BD vapor entry velocity, making it more vulnerable to reaction initiation.

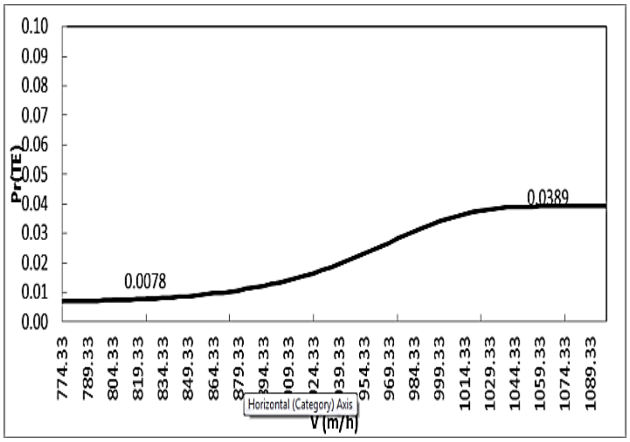


Figure 6 Top event probability updating for different estimated entry velocity (*V*)

4.4 Recommendation for Plant Operation

The results obtained have proven that high boiling points of many of these inhibitors render them effective primarily in the liquid phase leaving the gaseous phase more vulnerable to reaction initiation. The results also indicated the impact of changes in the plant operating conditions can be studied using the proposed failure model. Examples have been given in Figures 4-6. The tabulated results in Table 4 indicated that the overhead pressure was the dominant. At constant temperature and estimated vapor entry velocity, the effect of overhead pressure on risk profile was much larger than that of temperature and estimated vapor entry velocity. Thus, based on the finding of this study, more attention should be given to managing the overhead pressure.

Table 4 The changes in probability of the top event for each unit changes of the physical parameters

Physical Parameter		Probability	$\Delta, \mathrm{Pr}(\boldsymbol{TE})$ $/\boldsymbol{unit}$
Pressure, kg/cm^2	3.5000	0.0389	0.3250/ kg/cm^2
	3.4000	0.0064	
Temperature, K	314.9750	0.0086	-0.0051 /K
	308.9750	0.0389	
Velocity, m/h	1044.3300	0.0389	0.0002/ (m/h)
	894.3300	0.0117	

Figure 7 shows the probability of top events at varying operating pressure at constant temperature and inlet entry flow velocity of 308.975 *K* and 878.66 *m/h*, respectively. The curves clearly demonstrate the dynamic effect of operating pressure to the probability of popcorn formation. The temperature of 308.975 *K* was chosen based on the results shown in Figure 6.

Note that the results indicated that the high probability value is reached within a year when the operating pressure if the operating pressure is fixed at 3.44 *kg/cm*^{2}, and about 2 years for operating pressure of 3.42 *kg/cm*^{2}. This is consistent with the actual incident experienced by the plant considered in this study. The model is therefore considered to be a reasonable representation of the failure case and should therefore be useful to be used as a guide for preventive maintenance planning, risk management efforts or any management of change activities. The optimal interval for major process facilities maintenance program also can be determined based on the estimated probability of top event as illustrated in Figure 7.

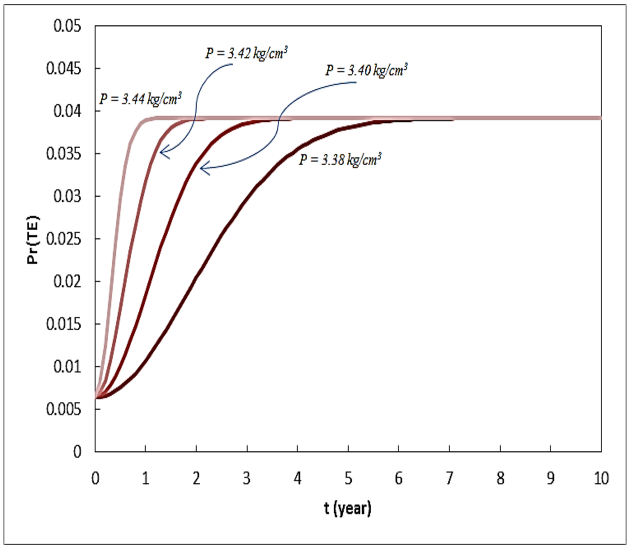


Figure 7 Top event probability updating at different pressure within 10 years

These revised probabilities of the top event directly update the estimated risk associated with safety, health, environment and direct financial impacts to the business operation. However, among the different pairs of covariates (overhead pressure), the optimum condition should be chosen in order to optimize the operating cost without compromising reliability and process safety of the existing process facility.

5.0 CONCLUSION

This work combined FT with dynamic risk analysis concepts to incorporate dynamic process operating condition in failure analysis. Based on the results obtained in this study the following conclusion can be made:

i. The use of Weibull distribution in the FT model has been proven as an effective way of incorporating process dynamics into risk analysis thus making dynamic risk assessment possible in a convenient manner.
ii. In the case study considered, operating pressure was the dominant process variable to the probability of popcorn polymer formation in the case study considered.
iii. The top event probability can be monitored based on the plant operating condition, thus

providing opportunities for dynamically managing the risk of incidents. The information can be used by risk managers to determine the interval of preventive maintenance e.g. cleaning activities in overhead condenser of the BD column based on the estimated probability.

This work has illustrates the importance of dynamic risk assessment in facilitating the operation of process plants in the chemical process industries. Further refinements of the approach by incorporating more accurate probability estimation approaches, and including various other potential sources of failures such as natural disasters or manmade hazards can provide more values to the current works.

Acknowledgement

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