

FUGITIVE EMISSIONS FROM MIXING EQUIPMENT

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ABSTRACT: During process plant development and preliminary design stages emissions resulting from the daily manufacturing operations are identified and measures are taken to control them in order to prevent possible adverse impacts on people and the environment. Process industry experiences not only emissions resulting from the daily manufacturing operations but also emissions which are fugitive or unanticipated. Fugitive emissions during process plant operation stage are often monitored because they are an occupational health concern. However the attention on fugitive emissions during the plant design stage is lacking. During this stage the equipment that involves large fugitive emissions could be identified and avoided. For this, methods to estimate fugitive emissions from various equipment used in the process industry are required. This work proposes a methodology to estimate the amount of potential fugitive emissions resulting from a mixing vessel used in the mixing operation. The distribution of those emissions in the environment which are essential to identify the impacts on the environment and human well-being is also looked at. Two designs of mixing vessels are studied for fugitive emissions. First is a closed design where fugitive emissions are assumed to occur under well controlled conditions. The second is an open design where emission from surface evaporation occurs from an open mixing vessel. The method is applied on a paint mixing vessel in the paint manufacturing industry during early design stage and potential fugitive emission quantities are estimated. The results indicate that the fugitive emission estimates from closed design mixing vessel have lower environmental concentrations compared to that of the open design.

KEYWORDS: fugitive emissions, mixing

1. INTRODUCTION

In early stages of chemical plant development and design the choice of equipment in the process line is one of the key design decisions that has to be made by the designer. This decision is often taken mainly based on the process technological requirements and economic factors. Apart from these factors, environmental friendliness is one other aspect that needs to be looked at during this stage of decision making. Methods are lacking to assess process equipment based on their environmental friendliness. In early stages of chemical process plant design the

chemical process route which is considered as the raw materials and the sequence of reaction steps that convert them to desired product is selected. Once this is done the equipment involved in the process will be decided. The choice of equipment made during early design stages based on environmental friendliness would make any changes needed to be done to the design to incorporate environmentally benign design features easier. Making such changes at this stage is less costly as well. In the process of selecting the most environmentally friendly equipment it is important to identify the environmental releases from the process. These

releases can have adverse impacts on the environment as well as on the economics.

The environmental friendliness of a plant can be assessed by considering the 'worst' possible unplanned environmental impact that could occur during plant operation or by considering the environmental impacts due to day to day plant operation or by considering both these (Cave and Edwards, 1997). Many of the day to day plant operation emissions are the result of the actual process streams. In addition to this during day to day operation unanticipated emissions also occur which are usually referred to as fugitive emissions (Onat, 2006). Fugitive emissions are defined as a chemical or a mixture of chemicals in any physical form which represents an unanticipated or spurious leak in an industrial site (ESA/FSA, 1998). The unanticipated emissions have an impact on the well being of people within the plant as well as people outside the plant. Use of equipment which has low fugitive emission potential in chemical process plants lead to lower fugitive emissions and therefore more environmentally friendly plants.

This paper focuses on the fugacity emissions from a stirred mixing vessel at early design stages of chemical process plant design. The fugitive emission estimation method from a closed and an open mixing vessel is proposed and the 'best' mixing vessel based on predicted environmental concentration and environmental friendliness is chosen. It should be noted that the overall best equipment selection should consider other factors such as economics, safety and environmental impacts of continuous process emissions as well. The emission estimation method is applied on a paint mixing operation using the two types of mixing tanks.

Methodologies to estimate fugitive emissions

have been developed by EPA (1995). Four approaches for estimating equipment leak emissions have been presented. From the four methods 'average emission factor' method is the one that can be used during early design stages of a chemical process plant (EPA, 1996). It indicates a mass emission rate from an individual piece of equipment. This method which is based on emission factors (EPA, 1988) is the most suitable to be used in the absence of detailed process information. One other method proposed by EPA (1995) is the correlation equation approach. This method needs more data and is used in estimating emission rates of different units such as valves, pump, connectors, flanges, and open ended lines in processing facilities. Dadashzadeh *et al.* (2011) have optimized these equations and a new set of equations has been developed to estimate the emission rates of different units in an oil and gas facility. The EPA Emission Inventory Improvement program (EIIP) documents (EPA, 2005) present methods to estimate air emissions from paint, ink, and other coating manufacturing facilities. In order to understand the impact on the occupational health of the worker due to continuous exposure to the fugitive emission, during chemical process design stage, estimation of the chemical concentration of these emissions must be done. Hassim and the others (2010) have developed a methodology to estimate fugitive emission concentrations during chemical process design using the emission factors proposed by EPA (1988). They have used these factors to calculate fugitive emission rates for standards modules such as absorber, stripper, ion exchanger, CSTR, PFR, Distillation column and liquid-liquid extractor. Using an estimated air volumetric flow rate the fugitive emission concentrations are determined.

2. SELECTION OF MIXING TANK

Mixing is one of the unit operations used in the chemical process industry. There are different types of equipments used in this operation depending on the nature of the application. In this work a mixing vessel used for mixing liquid mixtures is studied. The liquid mixing vessel is agitated using an impeller mounted on an overhung shaft and is cylindrical with vertical axis. Batch wise mixing operation is considered. The liquid depth is assumed to be approximately equal to the diameter of the tank. Two types of agitated mixing vessels are considered. One is a vessel where the top of the vessel is open to air and the other is a closed mixing vessel. The vessel is selected based on their potential hazard to the people in the environment and in the work place due to fugitive emissions in the atmospheric environment.

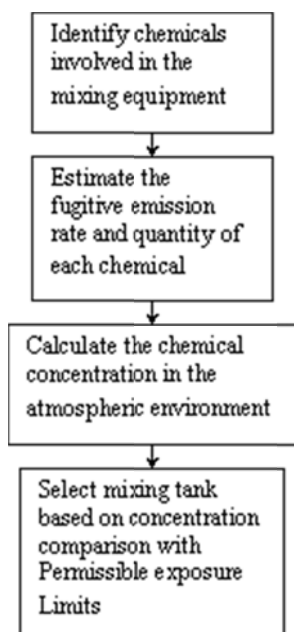


Figure 1. Schematic procedure to compare the two mixing tanks

The total quantity of fugitive emissions and their rates for each chemical from all sub operations in mixing such as loading, mixing and unloading are estimated. Then the concentration of this emitted substance in the environment is determined. A lower

concentration indicates a higher environmental friendliness. Further the predicted environmental concentration should be lower than the permissible exposure levels of the substance. Figure 1 shows a schematic procedure to compare the two mixing tanks based on their environmental friendliness.

During plant development simple process flow diagram (PFD) is drawn. At this stage very little data are available to select the more environmentally friendly equipment to draw the detailed PFD and design equipment. However an estimate can be made for the capacity of the tank and the material balance and then compositions of chemicals involved in the streams in the tank could be determined.

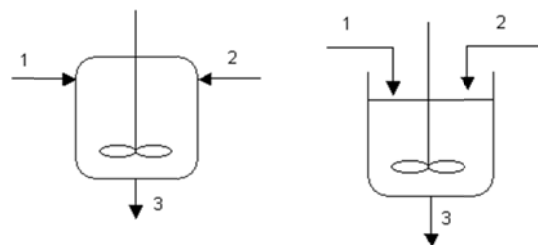


Figure 2. Streams associated with mixing tanks (a) Closed mixing vessel (b) Open mixing vessel.

In this work five streams are considered for possible chemical fugitive leaks. Figure 2 shows three streams involved with the mixing tank. There are two inlet streams and one outlet stream. These are possible points from which chemical fugitive emissions could occur. Stream four considered in this work is the emissions resulting collectively from the pressure relief valve, top flange of the closed vessel, agitator seal and sampling connection. The stream five is taken as the fugitive emissions from surface evaporation. After identifying the chemicals compositions in each stream the emissions rates from each stream can be estimated.

2.1 Stream's Fugitive emission rates

The emission rate associated with each stream is identified by referring to the data shown in Table 1.

The data in streams 1, 3 and 4 in this table are developed by using the average emission factor values given by EPA (1995) for fugitive emissions from different equipment types such as valves, pump seals, compressor seals, pressure relief valves, flanges, sampling connections, open ended lines and agitator seals. In order to use the data in Table 1 the service type of the fluid in the stream must be known. A liquid stream is classified as a light liquid (LL) service if the stream mainly contains highly volatile chemicals where the vapour pressure of the pure chemical is greater than 0.3 kPa at 20 °C. A gas or a vapour stream is considered as a gas service and liquid other than light liquid and gas are considered as Heavy Liquid (HL) services (EPA, 1995; Hassim *et al.*, 2010).

Table 1. Emission rates for streams

Stream	Service	Emission Rate Kg/h	
		Closed Tank	Open Tank
1. inlet 1	LL	0.02576	0.02576
	HL	0.01068	0.01068
2. inlet 2	Powder/solids	Nil	0.0108
3. outlet 3	LL	0.00586	0.00586
	HL	0.00206	0.00206
4. tank	All	0.14073	Nil
5. surface evaporation	N/A	N/A	Equation (1)

N/A - Not Applicable as no fugitive emissions involved

During PFD development stage the exact number of equipments such as valves or flanges involved with the mixing operation is not known. Therefore quantifying the fugitive emissions with this limited data is not very possible. However, considering a mixing equipment in a chemical process industry fugitive emission rates data can be precalculated. Therefore using the average emission factor values given in EPA (1995) the fugitive emissions associated with each stream in the mixing tank were determined for all services. The types of equipment considered for each stream and the emission rates for each stream for the closed and open mixing tank

designs are presented in Table 2. Similar procedure had been adopted by Hassim and Hurme (2010) in their work in estimating fugitive emissions from various equipment in a chemical process plant at early route selection stages of plant development.

Table 2. Components considered in streams and corresponding average emission factors

Stream	Service	Equipment	Average emission factor kg/h/source (EPA, 1995)	
			Closed Tank	Open Tank
1. inlet 1	LL	Pump	0.0199	0.0199
		Flange	0.00183	0.00183
		Valve	0.00403	0.00403
	HL	Pump	0.00862	0.00862
		Flange	0.00183	0.00183
		Valve	0.00023	0.00023
3. outlet 3	LL	Valve	0.00403	0.00403
		flange	0.00183	0.00183
	HL	valve	0.00023	0.00023
		flange	0.00183	0.00183
4. Tank	All	Flange	0.00183	N/A
		Agitator seal	0.0199	
		Sample port	0.015	
		Pressure relief valve	0.104	

N/A - Not Applicable as no fugitive emissions involved

The stream number 2 is an inlet used for feeding powder or solid material into the mixing vessel. In the emission rate estimation of this stream the emission rates for dust from various equipment data available in the work done by Carson and Mumford (1985) are considered. The dust emission from the stream 2 of the open tank is assumed be equivalent to the emission from manual slitting and dumping from bags, 3 mg/s as given in their study. In the closed vessel it is assumed that there are no dust emissions from the stream 2. Further the stream number 5 is considered as the fugitive emissions resulting from surface evaporation. The vaporization rate from the liquid surface from an open vessel is estimated from the simplified equation given in Crowl and Louver (2001). This equation is shown in equation (1). The equation used to estimate the mass transfer coefficient is shown in equation (2) (Crowl and Louver, 2001). In this the partial pressure of the vapour above the bulk stagnant gas above the liquid

is assumed to be negligible compared to the saturation pressure.

$$Q_m = \frac{MKAP^{sat}}{RT} \quad (1)$$

where,

Q_m – evaporation rate

K – mass transfer coefficient for an area A

M – molecular weight of the volatile substance

R – ideal gas constant

T – absolute temperature of the liquid

P^{sat} – saturation vapour pressure

$$K = K_0 \left(\frac{M_0}{M} \right)^{1/3} \quad (2)$$

Where K_0 is the mass transfer coefficient of reference substance and M_0 is the molecular weight of reference substance.

In surface evaporation since vaporization from a liquid surface is considered the determination of the service type of the stream is not required. Further in a closed vessel it is assumed that there are no fugitive emissions resulting from surface evaporation. However, in the stream number 4 where the leaking of substances from the tank is focused the evaporated vapour in the free volume at the top of the closed mixing vessel is considered as the service type.

The emission rate calculated from equation (1) would give the emission from one substance where as the other emission rate data in the Table 1 are for all the volatile substance in the fugitive emission stream together.

2.2 Fugitive emission of each chemical

The mixing operation studied in this work is a batch wise operation where three sub operations are assumed for fugitive emission estimation. They are material loading, mixing and unloading operations.

Vessel cleaning operation is also an important sub-operation involved in the mixing operation. The emission during this is considered as an emission due to the process and not considered under fugitive or unanticipated emissions. The streams that contribute to fugitive emissions in each sub operation in mixing are given in Table 3 and Table 4. In these tables where there are no fugitive emissions are involved it is indicated as not applicable (N/A).

Table 3. Emission rates in closed tank mixing sub operations

Stream	Service	Emission Rate (kg/h) Closed tank		
		loading	mixing	unloading
1. inlet 1	LL	0.02576	N/A	N/A
	HL	0.01068		
2. inlet 2	Powder/ Solids	N/A	N/A	N/A
3. outlet 3	LL	N/A	N/A	0.00586
	HL			0.00206
4. tank	All	0.14073	0.14073	0.14073
5. surface evaporation	N/A	N/A	N/A	N/A

N/A - Not Applicable as no fugitive emissions involved

Table 4. Emission rates in Open tank mixing sub operations

Stream	Service	Emission Rate (kg/h) Open tank		
		loading	mixing	unloading
1. inlet 1	LL	0.02576	N/A	N/A
	HL	0.01068		
2. inlet 2	Powder/ solids	0.0108	N/A	N/A
3. outlet 3	LL	N/A	N/A	0.00586
	HL			0.00206
4. tank	All	N/A	N/A	N/A
5. surface evaporation	N/A	Q_m Eq. (1)	Q_m Eq. (1)	Q_m Eq. (1)

N/A - Not Applicable as no fugitive emissions involved

Similar to the method described in EPA (1996) the fugitive emission rate of each chemical in these streams is determined by multiplying the stream emission rates with the respective weight composition of the volatile substances in the stream. In stream number 5 where surface evaporation is involved, the above determination is not necessary because the surface emission rate calculated using equation (1) is for each chemical individually

present in the stream. In loading it is assumed that the pure chemical is loaded and in the unloading sub operation the mixture is unloaded.

The fugitive emission of a substance from one sub operation is given by equation (3).

$$CFE_s = \sum_{n=1}^5 CFER_{s,n} \times OT_{s,n} \quad (3)$$

where,

n is the number of streams for leaking substance,

s is the sub mixing operation, three in this study,

OT is the operating time associated with the stream n in sub operation s, hrs

$CFER_{s,n}$ chemical fugitive emission rate of the substance in stream n of sub operation s, kg/h

CFE_s chemical fugitive emission of the substance in sub operation s, kg

The fugitive emission rate (kg/h) of a substance from one sub operation ($CFER_s$) is given by equation (4).

$$CFER_s = \sum_{n=1}^5 CFER_{s,n} \quad (4)$$

The total fugitive emission of a chemical substance CFE from all sub operations is given by equation (5).

$$CFE = \sum_{s=1}^3 CFE_s \quad (5)$$

Where CFE_s is the chemical fugitive emission of a substance in sub operation s, in kg.

2.3 Environmental Concentration

In the process of mixing equipment design type selection, before comparison with the reference exposure limit values, the chemical concentration in the environment must be estimated. In this work two model environments are considered in estimating chemical concentrations in the environment. One is the manufacturing plant environment where the working people are exposed to and the other is the environment including outside the plant where general population is exposed to fugitive emissions.

For the environmental concentration calculation above determined amount of fugitive emissions of a chemical (CFE) and emission rate value $CFER_s$ are used.

The chemical concentration inside the plant is estimated using the method proposed by Hassim *et al.* (2010). For this the air volumetric flow rate within the process area is estimated. Volumetric flow rate is determined using the wind speed, plot area of the mixing equipment in the plant and height below which the leak source is located. The same plot area required for a continuous stirred tank reactor which is 95 m² given in Hassim and Hurme (2010) is considered in arriving at the plot area for the mixing tank. Assuming square shape plot plan the edge width of the area is determined. Further the process vertical height of 7 m and a typical average wind speed of 4 m/s are assumed and the air volumetric flow rate is calculated (Hassim *et al.*, 2010). The concentration of the chemical in this plot volume is calculated with the estimated volumetric air flow rate and $CFER_s$ value. It is assumed that the chemical released from the leak source is uniformly distributed in the plot volume considered.

The concentration distribution of the fugitive emission of a chemical in the environment where general population is affected is done using the model environment called a 'unit world' (Mackay and Paterson, 1990). The unit world with a 6 km atmospheric height has a 1 km² cross sectional area and it has six compartments: air, water, biota (aquatic life), soil, sediment and suspended sediment. This environment is assumed to be the place where the chemicals emitted would be most concentrated. The total quantity of the chemical emitted (CFE) is assumed to have been released to this environment. In this work the chemical distribution in the 'unit world' environment is estimated using level I

fugacity model proposed by Mackay (2001). It assumes steady state equilibrium distribution of the chemical in the environment and estimates equilibrium concentration of the chemical in different environmental compartments. This concentration is referred to as the Predicted Environmental Concentration (PEC) in this work. Although the fate of the emitted fugitive dust in the unit world environment is not considered in this work it is recognized that for a complete analysis this aspect also must be considered.

3. EXAMPLE

The method proposed in this work has been applied in mixing operation of paint manufacturing industry. A solvent based paint manufacturing process is selected and it is assumed that volatile organic carbon compounds and pigment dust are the main fugitive emissions in the plant. The volatile raw materials used in the operation are toluene, xylene and isobutyl acetate. Same raw materials have been used in a solvent based paint manufacturing plant where a waste minimization study has been done by Dursun and Sengul (2006). A paint batch volume of 9 m³ with a paint density 1.4 kg/l is studied in this work. The composition of the paint is assumed as 39% volatile substances, 25% powder material and 36% non volatiles in weight percents. In the volatile component composition of xylene, isobutyl acetate and toluene is taken as 24%, 8% and 7% respectively. It is also assumed that the raw material feeding and product unloading are done at a rate of 20l/min and mixing sub operation is done for 4 hours.

The Figure 3 shows the fugitive emission chemical concentration to permissible exposure level (PEL) value ratios of the volatile chemicals involved. The fugitive emissions from the open vessel are higher than that of the closed vessel. Major part of

this emission is from surface evaporation in the open vessel. Fugitive emission chemical concentrations in the plant environment from both vessels are lower than the PEL values taken from HSDB (2011).

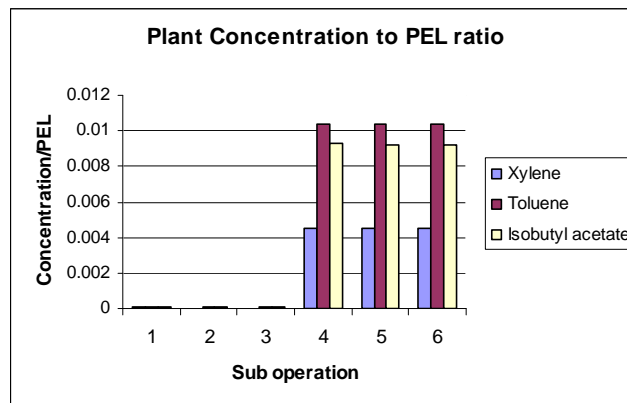


Figure 3. Plant concentration to PEL ratio (1.closed Loading; 2. closed mixing; 3. closed unloading; 4. open loading; 5. open mixing; 6. open unloading)

The ratios of concentration of Xylene in the unit world environment considered (PEC) to PEL are shown in Table 5.

Table 5. Xylene (PEC/PEL) ratios in the environment

Mixing Vessel	PEC/PEL
Closed mixing vessel	1.06E-07
Open mixing vessel	9.69E-06

The estimated chemical concentrations in the atmospheric environment are very low when compared with the PEL values in both designs. In this unit world environment also the closed vessel shows a lower chemical concentration than that of in the open vessel.

The method proposed in this work can be used to select one of the two types of mixing equipment based on assessment of the fugitive emissions and the concentrations in the atmospheric environment at early design stages of plant development. The

method has been applied in paint mixing operation and found to be simple and make effective use of the available data. Although in this work only two design types of the equipment have been considered for the selection process, as the next step this method could be further developed to include more mixing vessel designs.

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