

# QUANTIFICATION OF FUGITIVE EMISSIONS FOR PROPOSED CHEMICAL PLANTS

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## Introduction

Occupational health concerns with the two-way relationship between work and health. Previously, occupational health and safety was treated as a single subject by industries. However, most often higher attention was paid on process safety rather than occupational health aspect. Unlike process safety that primarily deals with major and short-term events, occupational health concerns with continuous and minor events, which remain unnoticed most of the time. The underlying principles of occupational health is further complicated by the fact that upon exposures, it takes some time before the effects to appear. Many did and still do not realize that the impact of occupational health on chemical industries is just as denoting as process safety. Each year, more people die from diseases caused by work than are killed in industrial accidents. Various methods are available for assessing the risk of health hazards in workplaces. However, they are applicable only to operating plants. According to Trevor Kletz (1991), the father of inherent safety concept, inherent hazards of a process should be identified as early as possible; that is when the plant is still under the development phase. The main idea is to improve process safety by eliminating or reducing hazards rather than managing or controlling them. As the project progresses through the lifecycles, the opportunities are decreasing and costs for applying modifications are increasing. Later the ideology was extended to inherent occupational health (Hassim and Hurme, 2008a, b; Hassim and Edwards, 2006; Hassim *et al.*, 2006).

## ***Fugitive Emissions***

When evaluating occupational health aspect of chemical plant, basic factors that need to be addressed are: 1) amount of the airborne contaminants; 2) dilution factor within the workplace; and 3) potential chemical exposures to workers. This paper tends to discuss the first point in the list; the proposed estimation methods are described and the results are presented.

From the context of occupational health, long-term exposure as a result of fugitive emissions is the most important sources of hazards for worker exposure in chemical plants. Fugitive emissions can be defined as 'leaks' or 'releases' that occur wherever there are discontinuities in the solid barrier that maintains containment. These emissions that cannot be caught by a capture system are originated from unanticipated or spurious leak from anywhere in an industrial site. Commonly, fugitive emissions involve leaks that will rapidly evaporate. Thus, they are difficult to be identified. Despite being very small and mostly invisible to the naked eye, fugitive emissions are the main sources of origin of the continuous background exposure to workers. The small but continuous exposures experienced by workers may chronically affect their health in various ways, depending on the type of contaminants they are exposed to.

## Estimating Potential Fugitive Emissions

In operating plants, fugitive emissions are measured as part of the plant-monitoring program. However, direct measurement is not possible for a plant, which is still 'on paper'. Therefore, we propose a set of methodology for estimating fugitive emissions that are potentially emitted from a chemical process. The methods were developed based on the amount of information available in different process design stages; simple process flow diagrams (PFDs), detailed PFDs, and piping & instrumentation diagrams (PIDs).

Since process data is still very much lacking in the design stage, the approach for estimating fugitive emissions was developed based on the Average Emission Factor method, as devised by the U. S. Environmental Protection Agency (EPA, 1988). This is the only method that does not require screening values. Instead, only a straight-forward equipment count and average emission factors are needed. For PFDs, the uncontrolled average emission factors for traditional component types (e.g. pump and valve) are used (EPA, 1995). The phrase 'traditional component types' refers to those that have conventionally been considered and reported as sources of equipment leak fugitive emissions by the U. S. EPA. For PIDs, emission factors for more specific traditional components (e.g. pump shaft with single mechanical seal) as well as non-traditional components (e.g. exchanger head) are utilized. Therefore, a more accurate estimate of emissions is expected.

### ***Simple Process Flow Diagrams (PFDs)***

Simple PFDs comprehend simplified process diagram and process descriptions found in patents or literatures such as encyclopedias. With this limited process data, the task of quantifying fugitive emissions can be tough. Therefore, the fugitive emission evaluation method was developed based on the idea of precalculated modules. Precalculated modules provide the fugitive emission rates which have been precalculated for standard module types in a chemical process. The standard process modules represent typical operations in chemical plants such as distillation, flash, reactor, absorption etc. systems. The precalculated modules were created by evaluating the number of leak sources in these operations by studying typical piping and instrumentation diagrams (PIDs) of the process modules. To ensure comprehensiveness, the emission from each module stream is calculated for all possible types of service; gas/vapor, light liquid, and heavy liquid. The calculation was made based on the average emission factors provided by the U. S. EPA (see Table 1).

The estimation procedure is very simple that first, process drawing is divided into standard modules. Then, based on process descriptions, chemicals present in each module stream are identified before they can be classified into particular service types. For liquid stream, if it mainly contains highly volatile chemicals, the stream is in light liquid service. Otherwise, it is a heavy liquid. The fugitive emissions from the module streams are determined simply by referring to the table of precalculated emissions provided (see Table 2). The total fugitive emissions from a process are a summation of emissions from all module streams. However, for the purpose of occupational health assessment, which is the research interest, it is important to know the

emissions rate of the individual chemicals present in the process. Due to the lack of process data, this is done by determining the most toxic chemical ('worst chemical'), which is the major component with the lowest reference limit value to represent the stream emission rate. For the same 'worst chemical', the stream emission rates in the process are aggregated.

### ***Detailed Process Flow Diagrams (PFDs)***

Detailed PFDs offer additional process data of mass and energy balances. The overall approaches for estimating fugitive emissions are the similar precalculated modules-based method, as used for simple PFDs. The difference is in classifying the service type of module streams. For a liquid stream under operating conditions, the vapor pressure at 20 °C of individual chemicals in the mixture is determined. For those with vapor pressure above 0.3 kPa, their weight compositions are summed up. If the weight composition is  $\geq 20$  wt%, the stream is in a light liquid service; or else, it is a heavy liquid. Besides, the determination of the 'worst chemical' in each process stream is now unnecessary. Instead, the stream emission rate is multiplied with the respective weight composition of that particular stream. Similarly, the stream emission rates are added up for the same chemical substances throughout the process.

### ***Piping and Instrumentation Diagrams (PIDs)***

PIDs offer further process data in greater detail; hence more comprehensive assessment is feasible. Fugitive emission rates can be estimated more accurately by considering piping and equipment details available from PIDs. The rates are determined based on specific type of piping components instead of service types. Likewise in detailed PFDs, the emission rate of each process stream is multiplied with the respective chemical weight composition. With PIDs, it is possible to quantify the fugitive emission rates for both fluids and dusts. The emission factors data are provided for different types of piping components to ease the estimation. For fluids, the database was constructed by referring to various references. Some of the emission factors needed to be recalculated in order to tailor them to the estimation approach.

## **Application to Case Study**

For demonstration, the methods are applied on a case study, which is the first sub process in the ethylene via propionaldehyde (C2/PA) based route for methyl methacrylate (MMA) production (Figure 1). Propionaldehyde is produced from a reaction that takes place at 100 °C and 15 bar; with ethylene, carbon monoxide and hydrogen act as the raw materials (Bakshi, 1985).



**Table 1.** Average emission factors for fugitive emissions (EPA, 1995)

Equipment Type	Service	Emission Factor (kg/hr/source)
Valves	Gas	0.00597
	Light liquid	0.00403
	Heavy liquid	0.00023
Pump seals	Light liquid	0.0199
	Heavy liquid	0.00862
Compressor seals	Gas	0.228
Pressure relief valves	Gas	0.104
Flanges	All	0.00183
Sampling connections	All	0.015
Open-ended lines	All	0.0017
Agitator seals	All	0.0199

**Table 2.** Summary of fugitive emission rates for process module stream

Process Module (Fugitive Emission Rate, kg/h)												
Stream	Service	Absorber	Normal	Vacuum	Flash	LEX	Ion Exch	CSTR	PFR	Normal	Vacuum	Total Comp
			Stripper							Distillation		
Feed 1	G/V	0.024	0.117	0	0.057		0.052	0.102	0.059	0.044	0	0.454
	LL		0.098	0	0.053	0.048	0.044	0.082	0.127	0.036	0	
	HL		0.060	0	0.046	0.025	0.029	0.044	0.082	0.021	0	
Feed 2	G/V							0.110	0.063			
	LL	0.113				0.235		0.088	0.052			
	HL	0.063				0.125		0.046	0.029			
Outlet 2/3	G/V	0.109	0.002	0	0.021		0.123		0.163	0.025	0	
	LL		0.464	0.225		0.055	0.100	0.560	0.271	0.405	0.239	
	HL		0.324	0.127		0.036	0.054	0.378	0.156	0.254	0.137	
	G&LL mix								0.498			
	G&HL mix								0.380			
Outlet 3/4	G/V											
	LL	0.236	0.159	0	0.301	0.097				0.217	0.139	
	HL	0.134	0.094	0	0.165	0.059				0.137	0.082	

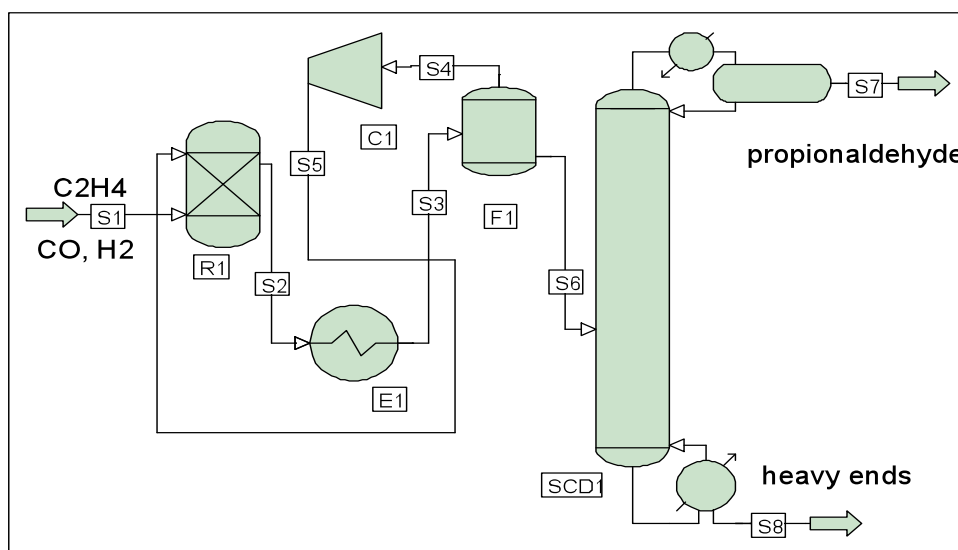
G:gas,V:vapor,LL:light liquid,HL:heavy liquid,LEX:liquid-liquid extractor,Ion Exch:ion exchanger,Comp:compressor

## Results and Discussions

The fugitive emission rates are calculated based on information provided by simple PFD, detailed PFD, and PID of the C2/PA sub process. Drawing and descriptions of the sub process are given by Bakshi (1985). The process is simulated using a flowsheeting program for the mass balance data. The results are summarized in Table 3.

Since the ‘worst chemical’ approach is used for simple PFD, not all chemicals in the process are involved in the assessment. Only chemicals with the lowest reference exposure limit value in each stream are considered. This is a valid basis of work as in practice; some plants measure the emission concentrations of highly toxic chemicals only, particularly carcinogens.

From Table 3, the fugitive emissions appear to be smaller with the availability of more process data. As for PFDs, the EPA ‘average’ emission factors were used (EPA, 1995), contributing to larger emissions. These factors are larger because they are based on unmonitored equipment data. Nowadays, equipment is emission-monitored, resulting to smaller emission factors data (Lipton and Lynch, 1994), which were used for the PID stage. Detail piping and equipment data allows more specific component types to be used, hence resulting to smaller emissions. Fugitive emission estimates based on PID is believed to resemble more the actual emissions compared to those given by simple and detailed PFDs. This is justifiable since more resources are demanded; the information, amount of work and time. As the saying goes, ‘you get what you pay for’. However, bear in mind that the overall aim of the research is not to compare the estimate value between the methods. In fact, it is to demonstrate how fugitive emissions can be estimated earlier with different type of information. The information can be used for comparing process design concepts to enhance the occupational health features of the plant.



**Figure 1.** Flow Diagram of C2/PA Sub Process

**Table 3.** Estimation of fugitive emission rates for the C2/PA sub process

Chemical	Fugitive Emission Rate (kg/h)		
	Simple PFD	Detailed PFD	PID
Ethylene	-	0.149	0.091
Carbon monoxide	0.534	0.152	0.094
Hydrogen	-	0.010	0.006
Propionaldehyde	1.435	1.658	0.899

## Conclusions

Information on fugitive emissions especially from chemical processes is substantial for economic, occupational health, and environmental assessment reasons. It is critical to have this information as early a possible, before the plant progresses to the construction phase. It is easier and cheaper to apply changes using an eraser rather than a hammer.

Three methods are proposed for estimating potential fugitive emissions during the design phase of chemical processes. The methods offer variations in terms of the simplicity, results accuracy, and data requirement. The methods were developed based on information availability in different design stages; simple PFDs, detailed PFDs, and PIDs. With PFDs, a rough and quick estimate is possible. A more refined and accurate estimate is expected from PID.

These methods are very useful for occupational health assessment since the key evaluation step is to quantify worker exposures before risks can be characterized. The estimation methods will not give exact results, but they do provide a swift and simple estimate that can be used as a general indication of emissions in a proposed chemical plant. Hopefully, with the introduction of these methods, the impact of fugitive emissions on occupational health risk will be gradually realized increased and this aspect will be looked into when developing a chemical process.

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